NATIONAL OPEN UNIVERSITY OF NIGERIA

DEPARTMENT OF PURE AND APPLIED SCIENCE
FACULTY OF SCIENCE

COURSE CODE: CHM424

COURSE TITLE: NON AQUEOUS SOLVENT

CHM424

CHEMISTRY OF NON AQUEOUS SOLVENTS

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COURSE GUIDE

INTRODUCTION

This course is titled, non-aqueous solvent and is designed to acquaint the students with detail information about solvents, other than water, which is the most familiar and known solvent. The course reviewed basic information on the general physical properties of solvents and the significance of each of them. Various principles for classifying solvents have been considered and satisfactory examples have been provided. The course also considers the principles that enable solvent and solute molecules to approach each other (i.e solvation) and the four major types of interactions that exist between solvent and solute. The course is also designed to refresh students' knowledge on basic concepts of acid and base since these are essential in understanding the chemistry of solvents. Solvents singled out for detail discussion were protonic (liquid ammonia, an anhydrous sulphuric acid) and non-protonic solvents (liquid SO_2, oxyhalides, which included nitrosyl oxychloride and phosphoryl chloride, dinitrogen tetroxide). Chemical equations related to each discussion have been provided and applications of some of the non-aqueous solvent in titration have also been examined.

COURSE DESCRIPTION

Classification and General Characteristics, solute-solvent interactions. Protonic solvents. Oxyhalide solvents. Liquid halides. Dinitrogen tetroxide, sulphur dioxide. Leveling effects, non-aqueous titrations.

COURSE AIMS

The aim of the course is to bring the students to the knowledge of the basic chemistry of non-aqueous solvents and their properties including physical properties, autoionization, solvolysis, complex ion formation and reactivity.

COURSE OBJECTIVES

- To introduce the students to the existence of solvents other than water for analytical, preparatory, industrial purposes and special purposes
- To explain the various behaviour of non-aqueous solvents and compare them with aqueous medium.
- To encourage the students to present basic equations associated with non-aqueous solvents
- To introduce the students to the various terms relevant for the discussion of the chemistry on non-aqueous solvents
- To classify non-aqueous solvents based on various principles, their properties, reactivity and composition
- To understand what is leveling effect of solvents
- To discuss the chemistry of selected nonaqueous solvents and compare them with aqueous media

WORKING THROUGH THIS COURSE

The course is structured into four modules. All the Modules consist of three units each. It is necessary for the students to study and understand the content of all the units in the respective modules.

COURSE MATERIALS

You will be provided with the following materials:

1. Course Guide

2. Study Units

STUDY UNIT

Module 1 consists of two units. Unit 1 introduces nonaqueous solvents and provided physical parameters that are useful in identifying solvents and their effectiveness. These properties included viscosity, melting and boiling point, heat of vapourization, relative permittivity and refractive index.

Unit 2 deals with acid base properties as they relates to solvents. The concepts consider are Arrhenius concept, Bronstead-Lowry concept, solvent system concept, aprotic acid base concept, Lux flood concept, Lewis concept and autoionization

Module 2 deals with acid base properties as they relates to solvents. The concepts consider are Arrhenius concept, Bronstead-Lowry concept, solvent system concept, aprotic acid base concept, Lux flood concept, Lewis concept and autoionization

Unit 1 covers various classification principles and methods for solvent while Unit 2 deals with solvent-solute interactions. In unit 2 other concepts such as solvation, electronegativity, dipole moment, and permittivity as they affect solvent-solute interactions are closely considered in details. The unit is concluded by detail discussion on the four major forces of interactions between solvent and solute. Worked examples have been provided.

Module 3 consists of three units. Unit 1 deal with solvent properties of nitrosyl chloride and phosphoryl chloride as examples of oxyhalides

Unit 2 considers the non-aqueous chemistry of liquid dinitrogen tetroxide, liquid sulphur (IV) oxide and liquid halides including BrF_3 , ArF_3 and other.

Unit 3 considers protic solvents which included liquid ammonia, acetic acid, anhydrous sulphuric acid, super acids and hydrogen fluoride. Treatments of the non-aqueous chemistry of these solvent considers their physical properties, self-ionization equations and possible chemical reactions

. TEXTBOOKS AND REFERENCES

Textbooks referred to in the development of each unit are presented at the end of the units. However, a list of some General references is presented below:

Emeleus, S. J. and Sharpe, A. J. (1964). Advances in inorganic chemistry and radiochemistry. Academic Press. New York

Grüttner, B., Dove, M. F. A and Clifford , A. F. (2002). Chemistry in Anhydrous, Prototropic Solvents : Inorganic Chemistry in Liquid Hydrogen Cyanide and Liquid Hydrogen Fluoride. Ist Edition. Edited by Gerhart Jander Hans Spandau. Elsevier, Germany

Lee, J. D. (2013). Concise Inorganic Chemistry. 5th edition. Learning solution. Blackwell Science Ltd. UK.

Wong, Y. C., Wong, C. T., Onyinuka, S. O. and Akpamisi, L. E. (1998). University General Chemistry (Physical and Inorganic). African Feb Publishers. Nigeria

ASSESSMENT

There are two aspects of assessment for this course: the tutor-marked assignment (TMA) and end of course examination. The TMAs shall constitute the continuous assessment component of the course. They will be marked by the tutor and equally account for 30 % of the total course score. Each learner shall be examined in four TMAs before the end of course examination. The end of course examination shall constitute 70% of the total course score.

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MODULE 1

UNIT 1: Properties of solvents

MODULE 1

UNIT 2: Acids, Basesand solvent properties

MODULE 3

UNIT 3: Protic solvents

MODULE 1

UNIT 1: Properties of solvents

1.0 Introduction

Solvents are basically liquids that dissolves solid, liquid or gas to form solution. The three types of liquid that can serves as solvents are molecular liquids, ionic liquids and atomic liquids. Among the three, molecular liquids are widely used and include water, many organic liquids and some inorganic liquids such as liquid ammonia and liquid sulphur (IV) oxide. Ionic liquids solvents are mostly molten salts and are suitable for very high temperature reactions. However, there are some ionic liquids called green solvents that are suitable for low temperature reactions. Atomic liquids are rarely available at room temperature (for example mercury).Supercritical fluids are example of atomic liquid that are often used as media for chemical reactions and separation.

Water is the best solvent in inorganic chemistry because it possesses unique properties. Therefore, if water is suitable for a given reaction, it should be used without any recourse to alternative solvents. The choice of water as a solvent is based on the following,

i. Water is cheap and readily available in pure form

ii. Water has a convenient liquid range and is non toxic

iii. It is not very viscous and thus flow freely

iv. Ease of analytical utilization in reactions such as crystallization, precipitation, filtration, etc.

v. Water is a the best solvent (universal solvent) for a large number of solutes

However, some of the factors that give water a disadvantage as a solvent for some reactions are,

i. Water does not allow some substances to be isolated in aqueous form because they are hydrolysed in water.

ii. Reactions involving strong reducing agents cannot be carried out in water because there will be evolution of hydrogen through the reduction of the water.

iii. Reactions cannot be carried out with water as a solvent below its freezing point and above its boiling point, unless under special conditions

Generally, solvent can be classified based on the possession of carbon atom, as organic and the absence of carbon atom as inorganic. Solvents other than water are used in chemical analysis, chemical manufacturing, and in specialized syntheses. Water is an inorganic solvent while the main types of organic solvents are,

i. Hydrocarbon solvents including aliphatic and aromatic hydrocarbons

ii. Oxygenated solvents such as alcohol, ketones, aldehydes, glycol, ether, esters, etc.

iii. Halogenated solvents such as brominated and chlorinated hydrocarbons

Based on polarity, solvents can be classified as polar and non-polar. As a rule, polar solvent (such as water) are those that dissolve polar compounds while nonpolar compounds are dissolved by non-polar solvents.

Water is said to be a universal solvent because it can dissolve most substances on earth. Reactions carried out with water as a solvent is termed reactions in aqueous solvent. Molecular liquid solvents other than water are called nonaqueous solvents. In order to obtaineddesirable solvent properties, non-aqueous solvents maybe mixed with aqueous solvent to give mixed solvent. Examples include, liquid sulphur (IV) oxide, liquid ammonia, sulphur chloride, sulphur chloride fluoride, hydrogen fluoride, pure tetraoxosulphate (VI) acid, bromine pentachloride, antimony trichloride, dinitrogen tetraoxide, etc. Nonaqueous solvents are useful in conducting reactions that cannot occur in aqueous solutions or for reactions that needs special environments.

2.0 Objectives

The objectives of this unit shall among others include the following,

i. To identify basic physical properties of solvents including viscosity, melting and boiling points, density, dielectric constant, polarity, dipole moment, polarizability etc.
ii. To identify the effect of all the identified physical properties on the expected behaviour of non-aqueous solvents
iii. To provide suitable equations that relate solvent properties with their behaviour
iv.

3.0 Main document

3.1 Properties of solvents

3.2. Physical properties of solvents

Water is an excellent solvent because it is non-toxic, non-poisonous, neutral, and colourless. It also has high dielectric constant, long range of melting –boiling point, high specific heat capacity, high dipole moment and high dipole moment. However, other solvents that can compete with water to some extent are non-aqueous. For example, benzene, carbon tetrachloride, acetone, ether etc, which are organic solvents. Also liquid ammonia, sulphuric acid, liquid HF, liquid sulphur dioxide etc. are inorganic solvents.

Desirable properties of solvents may be physical or chemical properties. A good solvent must possess properties that are useful for the intended application. Some of the desirable physical properties of solvents are,

3.2.1 Viscosity

Viscosity affects behavior of solvents due to its interference in processes such as crystallization, precipitation, filtration, solubility, etc. The viscosity (η) influences the rate of mass transfer in the solvent and therefore the conductivity of electrolyte solutions. The lower the viscosity, the better is the tendency of the solvents to fit into various reactions. Viscosity data of some common organic and inorganic solvents are presented in Table 1.

3.2.2 Dielectric constant

Dielectric constant is another factor that affects the efficiency of a solvent. Increase in dielectric constant indicates increase in the tendency of the solvent to dissolve ionic compounds. For example, the dielectric constant of water is (76.5) higher than those of liquid ammonia and sulphur (IV) oxide, which explains why water is the best solvent for ionic compounds than liquid ammonia and sulphur (IV) oxide. Dielectric constants of some solvents are presented in Tables 1 to 3 below. In the Table, protic solvent are those that contain hydrogen while aprotic solvent are those the do not contain hydrogen.

Table 1: Physical properties of some organic solvents

Solvent	**Chemical formula**	**Boiling point (°C)**	**Dielectric constant**	**Density (g/mL)**	**Dipole moment (Debye)**
Hexane	CH_3-CH_2-CH_2-CH_2-CH_2-CH_3	69	2.0	0.655	0.00
benzene	C_6H_6	80	2.3	0.879	0.00
toluene	$C_6H_5CH_3$	111	2.4	0.867	0.36
1,4-dioxane	$(CH_2CH_2O)_2$	101	2.3	1.033	0.45
chloroform	$CHCl_3$	61	4.8	1.498	1.04
diethyl ether	$(CH_3CH_2)_2O$	35	4.3	0.713	1.15
dichloromethane (DCM)	CH_2Cl_2	40	9.1	1.3266	1.60

Table 2: **Physical properties of some polar aprotic solvents**

Solvent	**Chemical formula**	**Boiling point(°C)**	**Dielectric constant**	**Density (g/mL)**	**Dipole moment(Debye)**
N-methyl-pyrrolidone	$CH_3NC(O)C_3H_6$	202	32.2	1.028	4.1
tetrahydrofuran (THF)	C_4H_8O	66	7.5	0.886	1.75
ethyl acetate (EtOAc)	$CH_3CO_2CH_2CH_3$	77	6.0	0.894	1.78
acetone	$CH_3C(O)CH_3$	56	21	0.786	2.88
dimethylformamide (DMF)	$HC(O)N(CH_3)_2$	153	38	0.944	3.82
acetonitrile (MeCN)	CH_3CN	82	37	0.786	3.92
dimethyl sulfoxide (DMSO)	$CH_3S(O)CH_3$	189	47	1.092	3.96

propylene carbonate (PC)	$C_4H_6O_3$	242	64	1.205	4.90

Table 3: Physical properties for some polar protic solvent

Solvent	Chemical formula	Boiling point(°C)	Dielectric constant	Density (g/mL)	Dipole moment (Debye)
Formic acid	HCO_2H	101	58	1.21	1.41
n-butanol	$CH_3CH_2CH_2CH_2OH$	118	18	0.810	1.63
Isopropenol (IPA)	$(CH_3)_2CH(OH)$	82	18	0.785	1.66
Nitromethane	CH_3NO_2	100–103	35.87	1.1371	3.56
Ethanol (EtOH)	CH_3CH_2OH	79	24.55	0.789	1.69
Methanol (MeOH)	CH_3OH	65	33	0.791	1.70
Acetic acid(AcOH)	CH_3-CO_2H	118	6.2	1.049	1.74
Water	H_2O	100	80	1.000	1.85

3.2.3 Melting and boiling points

Melting and boiling point of a solvent is a factor that can affect is application because it affect the liquid range of a solvent. For example, water has a liquid temperature range of 0 to 100 °C, liquid ammonia has -77.7 °C while liquid SO_2 has -75.5 to 10.2 °C (Tables 1 to 3). Therefore, water is a better solvent at high temperature while liquid ammonia and sulphur (IV) oxide can only act as solvent at low temperature.

3.2.4 Heat of vapourization : This is a property that indicates the nature and strength of intermolecular forces holding the solvents together. A solvent that is characterized by high value of heat of vapourization suggest strong intermolecular forces and vice versa. The ratio of heat of vapourization to the boiling point of a solvent is called Trouton constant and it is an index that reflects the degree of association of solvent molecules. Higher value of the constant corresponds to higher molecular association.

The Trouton constant, is also related to entropy of vapourization according to the following equations, When   is less than or equal to 11.6, the solvent is said to be non-structured. For example, values of $_{Tc}$ acetic acid, benzene and acetone are are 10.2, 10.5 and 10.9, respectively. When   is greater than or equal to 12 points to structured solvents. For example values for methanol and water are 12.5 and 13.1 respectively.

The heat of vapourization of a solvent is also related to the cohesive energydensity defined as,

2

where R is the gas constant, T is the temperature and V_m is the molar volume. The solubility parameter, is related to the cohesive energy density according to equation 3

3

c is an index that measures the stickiness of a solvent and is related to the work necessary to create cavities needed to accommodate solute particles in the solvent. The square route of the cohesive pressure is termed Hildebrand's solubility parameter *(δ)*. According to Hilderbrand, the solubility parameter (δ) enables one to predict the solubility of non electrolyte solutes. Hildebrand observed that two liquids are miscible if the differencein δ is less than 3.4 units. Thus is useful in predicting the solubilities of non-electrolyte solutes in low-polarity solvents. Thus two liquids with similar value are miscible while two liquid with different values are immiscible.

Values of c, and for some common solvents are presented in Table 4. From the results, it can be seen that water being the most universal solvent has the highest value of c and .

3.2.5 Relative permittivity

Relative permittivity of a solvents influences the electrostatic forces of interaction that exist between electric charges. If two charged bodies, q_1 and q_2 are separated by a distance, r, the relative permittivity is defined as,

4

where $_0$ is the permittivity of a vacuum which is numerically equal to 8.854 × 10^{12} Fm^{-1}. F_{vac} is a repulsive force if the sign of q_1 and q_2 are the same but attractive force for opposite sign. If the permittivity of a solvent is $_r$, the electrostatic force between them is given as,

5

Values of for most solvent is always higher than 1.8. Least values are obtained for n-pentane (1.84) and n-hexane (1.88). Consequently, dissolution of a solute in a solvent will always weakened the electrostatic interaction between charges. The relative permittivity of a solvent has a significant influence on electrostatic interactions between solute and solvents, solute-solute and dissolution or dissociation of a solute. Therefore, the range for values of is an index for classifying a solvent as polar or non polar. A solvent is regarded as polar when and apolar or non polar when .

Table 4: Trouton and Hildebrand's solubility parameter of some solvents at various internal pressure (▯)

Solvent	c (Mpa)	**▯$^{0.5}$ (MPa$^{0.5}$)**	▯(MPa)
Water	2302	47.9	151
Methanol	887	29.6	285
Ethanol	703	26.0	291
Acetonitrile	590	24.3	379
Dichloromethane	414	20.3	408
Acetone	398	20.2	337
Chloroform	362	19.0	370
Benzene	357	18.8	379
Ethyl acetate	347	18.6	354
Toulene	337	18.4	379
Cyclohexane	285	17.6	326
Diethyl ether	251	15.8	264
n- Hexane	225	14.9	239
Perfluooheptane	136	11.9	220

(**Source**: Abboud J.-L. M., Notario R. (1999) Critical compilation of scales of solvent parameters. part I. pure, non-hydrogen bond donor solvents – technical report. Pure Appl. Chem. 71(4), 645-718 (IUPAC document with large table (1b) of Hildebrand solubility parameter)

Solved question 1

(a) The relative permittivities of four solvents (A, B, C and D) were found to be 23, 12, 44 and 39 respectively. Which of the solvents will be polar or non-polar.

(b) State two major influences or effect of relative permittivity of a solvent on solution properties.

(c) If two charged bodies, q_1 and q_2 are separated by a distance, r. Define the term, relative permittivity using a suitable mathematical equation. Hence, If the permittivity of a solvent is ▯$_r$, write and expression for the electrostatic force between them.

Solution

(a) A solvent is regarded as polar when and apolar or nonpolar when . Therefore, all the solvents except B are polar since their relative permittivitiesvalues are greater than 15.

(b) The relative permittivity of a solvent has a significant influence on electrostatic interactions between solute and solvents, solute-solute and dissolution or dissociation of a solute.

(c) The relative permittivity is definedas , where □$_0$ is the permittivity of a vacuum which is numerically equal to 8.854 × 10^{12} Fm^{-1}. F_{vac} is a repulsive force if the sign of q_1 and q_2 are the same but attractive force for dissimilar sign. If the permittivity of a solvent is □$_r$, the electrostatic force between them is given as,

Solved question 2

(a) Define the term Trouton constant and state its significant in non-aqueous chemistry

(b) Explain the relationship between Trouton's constant and heat of vapourisation of a solvent.

(c) Based on the numerical value of Trouton;s constant of a solvent, what are the characteristics of a solvent that qualify them as structured and non-structured solvents.

Solution

(a) The ratio of heat of vapourisation to the boiling point of a solvent is called Trouton constant and it is an index that reflects the degree of association of solvent molecules. Higher value of the constant corresponds to higher molecular association.

(b) The Trouton constant, is also related to entropy of vapourisation according to the following equations,

(c) Values of less than or equal to 11.6 indicate that the solvent is nonstructured. On the other hand, values greater than or equal to 12 points to structured solvents.

Solved question 3

(a) Write an equation that relates the heat of vapourisation of a solvent with its cohesive density and solubility parameters. Hence explain the significant of these parameters on non-aqueous solvents,

(b) What is the significant of viscosity on the behaviour of solvent

(a) The heat of vapourisation of a solvent is also related to the cohesiveenergy density defined as,

2

where R is the gas constant, T is the temperature and V_m is the molar volume. The solubility parameter, δ is related to the cohesive energy density according to equation 3

3

c is an index that measures the stickiness of a solvent and is related to the work necessary to create cavities needed to accommodate solute particles in the solvent. The square route of the cohesive pressure is termed Hildebrand's solubility parameter *(δ)*. Hildebrand observed that two liquids are miscible if the differencein δ is less than 3.4 units. Thus δ is useful in predicting the solubilities of non-electrolyte solutes in low-polarity solvents. Thus two liquids with similar δ value are miscible while two liquid with different δ values are immiscible.

(b) Viscosity affects behavior of solvents due to its interferences in processes such as crystallization, precipitation, filtration, solubility, etc. Viscosity defines the fluidity of a solvent. The lower the viscosity, the better is the tendency of the solvents to fit into various reactions.

Table 5: Values of permittivities and relaxation time for some Debye and non-Debye solvents

Solvents	(					
Debye solvents						
AN	37.5	1.80	2	0.528	3.3	0.2
Ac	21	1.84	2	0.495	3.3	0.3
DMSO	46.7	2.18	5.7	0.438	19.5	2.4
HMPA	29.6	2.12	3.3	0.438	80	8.9
NB	35.7	2.40	4.1	0.389	45.6	5.2
Py	13.3	2.27	2.3	0.365	6.9	1.2

THF	7.58	1.97	2.3	0.376	3.3	1.0
Non-Debye solvents						
EtOH	24.5	1.85	4.2	0.499	130	22
FA	110	2.09	7.0	0.469	37	2.35
MeOH	32.7	1.76	5.6	0.628	48	8.2
NMF	182	2.04	5.4	0.485	123	3.7
1-PrOH	20.4	1.92	2.2	0.472	390	42
Debye or non-Debye solvents(different viewpoints exist)						
DMF	36.7	2.04	4.5	0.472	11.0	1.3
PC	65	2.02	4.1	0.480	43.0	2.7

Sources

McManis, G.E., Golovin, M.N. and Weaver, M.J. (1986) J. Phys. Chem., 90, 6563; Barthel, J., Bachhuber, K., Buchner, R., Gill, J.B. and Kleebauer, M. (1990) Chem. Phys. Lett., 167, 62; Galus, Z. (1995) Advances in Electrochemical Science and Engineering, vol. 4 (eds H. Gerischer and C.W. Tobias),Wiley-VCH Verlag GmbH, Weinheim, p. 222.

(where is the static permittivity; is the optical permittivity and is the infinite frequency permittivity. represent the solvent Pekar factor, is the Debye relaxation time and is the longitudinal relaxation time)

3.2.6 Dipole moment.

Dipole moment increases with increase in polarity of the molecule. The higher the dipole moment of a solvent, the easier is the tendency of the solvent to dissolve ionic compounds. Most solvents consist of molecules that are intrinsic dipoles and they have permanent dipole moments (▯). Placement of such molecules between two charged plate of a capacitor as a vapour (or a dilute solution in a non-polar liquid), the molecules will be oriented by the electric field such that the orientational and induce polarization will occur simultaneously. Consequently, the relative permittivity of the vapour () will be related to the dipole moment (▯) according to equation 6,

6

where K_B is the Boltzmann constant. From equation6, a plot of versus 1/T will be informative in estimating the values of and through the intercept and slope respectively.

Dipole moment is also informative in the estimation of polarity of a solvent, hence its classification. Solvents with dipole moment greater than or equal to 2.5D (1D = 3.3564 × 10^{30} Cm) are called dipolar solvents, while those with dipole moment less than 2.5 D are called apolar or non-polar solvents.

3.2.7 Refractive index

Refractive index is defined as the ratio of refraction of light in the sodium D-line in a vacuum to that in the medium is a significant solvent parameter that is related to polarizability, α of the solvent molecule according to equation 7,

7

where N_A is the Avogadro's number. The higher the value of , the better the interaction between the solvent molecules or other polarizable molecule by dispersion force.

4.0 Summary

Solvents are known for the roles they play in chemistry. It is convenient to classify solvents into two categories: protic solvents and aprotic solvents. The solvents which contain hydrogen and from which proton can be derived are known as protic solvents, e.g. water, liquid ammonia and hydrogen fluoride. Solvents which have no tendency to accept or release protons are known as aprotic solvents, e.g. benzene, chloroform, CCl_4, etc.

Non- aqueous solvent may be classified into organic or inorganic non aqueous solvents. As a general role, polar solvent dissolve polar compound and vice versa. Solvents are unique in their physical properties. This implies that one solvent differs from another in terms of their physical properties. These properties include boiling and melting point, dipole moment, relative permittivity, density, electrical conductivity, refractive index, etc. The range of values obtained for each of these solvents determines their applications.

5.0 Conclusion

Solvents are essential in the study of chemistry because of the roles they play in dissolution and chemical reactions. Water is well known solvent in most chemical processes but they are essential laboratory or industrial processes that cannot be carried out using water as a solvent. Such limitation to the use of water maybe operational temperature and pressure, degree of solubility, expected level of solubility and other interaction parameters. Therefore, the choice of solvent for chemical processes should be selected based on the nature and the expectation

6.0 Tutor marked assignment

1. What is the significance of melting and boiling point of a solvent?
2. If two charges are separated from each other by a distance of 0.002 m,calculate the electrostatic attraction between the charges if the product of their charges is 0.16 C^2

3. Write an equation that relates the relative permittivity of the vapour () within a solvent with the dipole moment (□). Explain all the terms in the equation.

4. Define the term, refractive index and provide an equation that relates refractive index with polarizability.

5. What are the different interactions involved in the dissolution of a solute in a given solvent?

6. Enumerate the various factors that account for the excellent solvent properties of water

7. Why are nonaqueous solvents of interest to Chemists

8. Enumerate the important physical properties of solvents and their properties

9. Explain the role of dielectric constant of the solvent in the behaviour of solute in solution

7.0 References

Emeleus, S. J. and Sharpe, A. J. (1964). Advance in inorganic chemistry and radiochemistry. Academic Press. New York

Grüttner, B., Dove, M. F. A and Clifford , A. F. (2002). Chemistry in Anhydrous, Prototropic Solvents : Inorganic Chemistry in Liquid Hydrogen Cyanide and Liquid Hydrogen Fluoride. Ist Edition. Edited by Gerhart Jander Hans Spandau. Elsevier, Germany

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Wong, Y. C., Wong, C. T., Onyinuka, S. O. and Akpamisi, L. E. (1998). University General Chemistry (Physical and Inorganic). African Feb Publishers. Nigeria

MODULE 1

UNIT 2: Acids, bases and Nonaqueous solvents

1.0 Introduction

Understanding of the concept of acid and base is significant in the study of nonaqueous solvent because most of the nonaqueous solvents behaves like acid or base, indicating that some processes such as autoionization, solvent leveling effect and others, can best be understood if the concepts of acid and base are comprehended.

There are several concepts or approaches that define acid and base. Arrhenius conceptconsider acid as a source of proton (H^+) and base as a source of hydroxyl ((OH^-) ions. This definition limits acids to hydrides and other replaceable hydrogen-ion containing chemicals. The concept also limit bases to mostly metallic hydroxides. However, there are compounds that neither contain hydrogen ion nor hydroxyl ion but behave like acid or base. Therefore, Arrhenius definition was modified by Bronsted-Lowry concept which defines acid as a proton donor and a base as a proton acceptor. Thus according to Bronsted-Lowry concept, an acid ionizes to increase the concentration of hydroxonium ion (H_3O^+) while bases ionize to decrease the concentration of the hydroxonium ion or increase the concentration of hydroxyl ion. Other concepts include solvent-solvent concept, the Lux and flood definition and Lewis and Pearson concepts, which are among the most useful definitions of acid. The Lewis concept defines acid-base in terms of electron donor-acceptor potential while Pearson defines acid in terms of hard-soft concept in the formation of complex

1.0 Objectives

The objectives of this unit shall include the following,

i. To understand Arrhenius concept of acid and base

ii. To understand Bronsted-Lowry concept of acid and base

iii. To understand the solvent system concept of acid and base

iv. To understand Lux-flood concept of acid and base

v. To understand Aprotic acid base theory

vi. To understand Lewis theory of acid and base

vii. To understand the concept of autoionization with respect to acid and base

viii. To provide useful chemical equations to explain each of the above listed concept

2.0 Main content

2.1 Arrhenius concept of acid

In 1878, a Swedish Chemist, Svante Arrhenius developed an acid-base concept which defines acid as a compound that gives hydrogen ion in water and a base as a compound that yields hydroxyl ion. For example, HCl, H_2SO_4 and HNO_3 are acid which ionizes to give hydrogen ion according to the following equations

$$HCl(aq) \rightarrow H^+ + Cl^-$$

$$H_2SO_{4(aq)} \rightarrow 2H^+ + SO_4^{2-}$$

$$HNO_{3(aq)} \rightarrow H^+ + NO_3^-$$

Similarly, NaOH, $Ca(OH)_2$ and $Mg(OH)_2$ are bases because they contain hydroxyl ion.

$$NaOH(aq) \rightarrow Na^+ + OH^-$$

$$Ca(OH)_{2(aq)} \rightarrow Ca^{2+} + 2OH^-$$

$$Mg(OH)_{2(aq)} \quad \rightarrow \quad Mg^{2+} \quad + \quad 2OH^-$$

The Arrhenius concept is unsatisfactory in defining acid because of the following reasons,

i. It is impossible for a bare proton to exist in solution

ii. It cannot account for acidic and basic properties of compounds such as NH_4NO_3 $AlCl_3$ which behaves as an acid

iii. It is unable to explain reactions in non-aqueous solvents

iv. The theory defines acid and base in terms of hydrogen and hydroxyl compounds only, without consideration of electron distribution and other factors that are relevant in chemical reaction

v. There are compounds that are not acid (by Arrhenius definition) but release hydrogen ion in water (for example N_2O_5 and SO_3). Similarly, there are compounds that are not consider as bases by Arrhenius but are capable of releasing hydroxyl ion in water. Examples of such compounds are Na_2O and K_2O.

In view of the shortcomings that surrounded the Arrhenius concept of acid and base, the definition was ammended. However, this concept still offers elementary information in the definition of acid and base.

3.2 Bronsted-Lowry concept

In 1923, Bronsted and Lowry gave a more plausible definition for acid and base.According to Bronsted-Lowry definition, an acid is a compound or ion which gives proton and a base a compound or ion which accept a proton from an acid. This definition provided the idea of conjugate acid base theory, implying that proton released by acid is accepted by a base. By this definition, if AH is an acid and B is a base, then the equation supporting this concept can be written as,

where AH is a general acid which is dissociable and gives out proton while B is a general base which

accepts a proton. From the above equation, it is seen that an acid, AH releases hydrogen ion, which is accepted by the base, B. The reverse reaction suggest that BH^+ is an acid because it can donate H^+ to a base, A^-. Consequently, an acid and its corresponding base forms a conjugate acidbase pair. For example A^- is a conjugate base 1to the acid, AH (Conjucate Acid 1) and B

(Conjucate Base 2) is a conjugate base to the acid, BH^+(Conjucate. Acid 2). Practical examples are shown below, (Note the equations are written in the form, , which shows conjugate acid and corresponding base)

Generally, the stronger the acid, the weaker the conjugate base and vice versa. That is, the stronger the base, the weaker is its conjugate acid. Before an acid can release its proton, it must come in contact with another substance, which maybe a solvent that has high affinity for proton (i.e. a base). Thus a base accept proton from water molecule to release hydroxyl ion. For example,

Most ions are base because they accept proton to form a neutral solution. A base decreases the concentration of hydroxonium ion in solution while an acid decrease the concentration of hydroxide in a solution. Metal oxides that dissolve in water to form hydroxides are also classified as base. Some substances can be either base or acid depending on their behavior during the reaction. For examples,

Water behave as a base in the first equation but as an acid in the second equation. Substances that display this type of behavior are said to be amphoteric or amphiprotic. Another example is behaving as a base in the first equation but as an acid in the second equation.

Solved problem 1

(a) Write all possible equations to represent ionization of tetraoxosulphate (IV) acid according to Bronsted-Lowry concept of acid. State the conjugate acid and base in all the equations.

(b) Is there any relationship between the strength of a conjugate acid and its corresponding conjugate base?

Solution

(a) The equations are

In the first equation, is the conjugate base of the acid, H_2SO_4 while is the conjugate acid of the base, H_2O. In the second equation, is the conjugate acid of the base, while is the conjugate acid of the base, H_2O.

(b) Generally, the stronger the acid, the weaker the conjugate base and vice versa. That is, the stronger the base, the weaker is its conjugate acid.

3.3 Solvent-System concept

One of the merit of the Bronsted- Lowry concept of acid and base is that it is not restricted nor dependent on any particular solvent. Thus it is applicable to both aqueous and non-aqueous solvents. A non-aqueous solvent such as ammonia contain hydrogen and produces charges as shown below:

Acid Base Acid Base

Acid Base Acid Base

Reaction between water and ammonia can also be represented as

In the above equation, water behaves as an acid while ammonia behaves as a base. On the other hand, the acid property of ammonia is less significant when chlorine is dissolve in ammonia according to the following equation, In the above equation, ammonia acts as an acid and the chlorine as a base. The conjugate base of ammonia is NH_2Cl while the conjugate acid of chlorine is NH_4Cl.

From the above, it is clearly evident that when a substance acts as an acid or a base it acts to furnish a particular type of ion characteristic of the solvent. In 1935, Franklin introduces the solvent-system concept which defines an acid as a *species that increases the concentration of the characteristic cation of the solvent and a base as a species that increases the concentration of the characteristic anion.* This definition of an acid provides a baseline for the treatment of non-aqueous solvent, just like aqueous solvent. For example, at 25 C, the ionization of water (aqueous solvent) and ammonia (non-aqueous solvent) leads to the following equations,

Furthermore, for water, the neutral pH correspond to $-0.5\log K_w$ ($K_w = 10^{-14}$) hence for ammonia, the neutral point will correspond to $-0.5\log K_{am}$. The concept of leveling effect arises from this trend. The effect states that all acids and bases stronger than the characteristic cation and anion of the solvent respectivelywill be “levelled” to the latter; acids and bases weaker than those of the solvent system willremain in equilibrium with them. For example,

However,

This solvent system concept is widely applied in the classification of solvolysis reactions.
For example, in comparing the hydrolysis of non-metal halides with their solvolysis by non-aqueous solvents as the following examples express,

Some solvents are reagents in many reactions behaving sometimes as an acid and sometimesas a base.A solvents which contain hydrogen and from which proton can be derived are known as protic solvents, e.g. water, liquid ammonia and hydrogen fluoride. Solvents which have no tendency to accept or release protons are known as aprotic solvents, e.g. benzene, chloroform, CCl_4, etc.

Solved problem 1

The ionization of water (aqueous solvent) and ammonia (nonaqueous solvent) leads to the following equations,

Calculate the neutral pH range for water and ammonia.

Solution

For water, the neutral pH correspond to $-0.5\log(10^{-14})$ ($K_w = 10^{-14}$) = 7, while for ammonia, the neutral point will correspond to $-0.5\log(10^{-33})$($K_{am} = 10^{-33}$) = 16.5.

Solved problem 2

(a) State the solvent system concept of acid and base

(b) State the concept of leveling effect. Write at least four suitable equations (two for bases and two for acids to support your statement.

(c) With suitable examples, differentiate between aprotic and protic solvents

Solution

(a) The solvent-system concept state that an acid is a species that increases the concentration of the characteristic cation of the solvent and a base a species that increases the concentration of the characteristic anion.

(b) The concept of leveling effect states that all acids and bases stronger than the characteristic cation and anion of the solvent respectively will be “levelled” to the latter; acids and bases weaker than those of the solvent system will remain in equilibrium with them

The equations are

However,

(c) A solvents which contain hydrogen and from which proton can be derived are known as protic solvents, e.g. water, liquid ammonia and hydrogen fluoride. Solvents which have no tendency to accept or release protons are known as aprotic solvents, e.g. benzene, chloroform, CCl_4, etc.

3.4 Aprotic acid and base

Liquid BF_3, liquid SO_4 liquid N_2O_4 and some other non-aqueous solvents do not contain bound hydrogen indicating that Bronsted-Lowry theory may not be applicable to explain their acid base behavior. Fortunately, each of these non-aqueous solvent are good conductor of electricity due to ions arising from autoionization, which can be represented as follows,

The above equations reveal that the cation behaves as acid while the anion behaves like base. In the presence of strong acid or base, the order may change. For example in liquid BF_3, AgF acts as a strong base while SbF_5 acts as a strong acid:

It can be deduced from the above that substances which generate in liquid BrF_3 behave as acids while those that generate in liquid BrF_3 act as bases.

3.5 Lux-Flood acid base concept

H. Lux acid-base concept which was extended by H. Flood, describesthe acid-base behaviour in terms of oxide ion. Their concept form a strong background for analyzingnon-protonic systems which cannot be handled by the Bronsted- Lowry definition. According to Lux-Flood concept, a base is an oxide donor and the acid is an oxide acceptor. For example, in the reaction between MgO and silicon (IV) oxide (shown below), MgO acts as a base while SiO_2 acts as an acid

The Lux-Flood theory is mostly applicable to molten oxides and anhydrides. By definition, Lux-Flood acid is an acid anhydride while Lux-Flood base is a basic anhydride as the following examples display,

3.6 Lewis acid theory

G. N. Lewis in 1923 developed a concept that regards a base as electron donor and acid as electron acceptor. Thus acid and base are defined in terms of electron pair acceptor donor. Thus a Lewis acid is a substance that acts as electron pair acceptor and a Lewis base is a substance that acts as an electron pair donor. If a Lewis acid, A, interact with a Lewis base, B, often omitting any other lone pairs that may be present, the fundamental reaction of Lewis acids and bases is the formation of a complex. A-B, in which A and :B bond together by sharing the electron pair supplied by the base.

3.7 Solvent Leveling and Discrimination in Water

The formation of hydroxonium ion arise from the donation of proton to water according to the following equation

is also an acid indicating that only acids that are stronger than will donate proton to water to form hydroxonium ion. Also acid stronger than cannot survive in water because they will give out their proton completely to water to form. Thus water is said to exhibit a leveling effect. The effective proton affinity of H_2Oin water is estimated at 1130 kJ/mol, therefore all acid with conjugate base having effective proton affinity lower than 1130kJ/mol are level in water. It also follows that a base strong enough to react completely with water to give hydroxyl ion, will be levelled in water (hence OH^- is the strongest base that can exist in water). The proton affinity of OH^- in water is 1188 kJ/mol. Therefore, any base with an effective proton affinity greater than 1188 kJ/mol will be converted into the conjugate acid, producing OH^-. The implication is that it is difficult to study or in water by dissolving their salts since they will undergo complete protonation to NH_3 and CH_4

.The range of acidity that can bestudied in water lies approximately between the effective proton affinities of 1130 kJ/moland 1188 kJ/mol which gives a difference of 58 kJ/mol. If the proton affinity A^- is less than 1130 kJ/mol, an acid HA will be converted to A^- and all the protons will be present as . However, If the proton affinity is greater than 1188 kJ/mol the solute will exist only as HA at the expense of forming OH^- from water. The range within which water can displays its leveling effect can be expressed as equilibrium constant which is related to the free energy change according to the following equation, The value of that takes account of the contribution of reaction entropy is 81000 J instead of 58000 J. By substitution, calculated value of pK is 14

For any solvent, the range over which acid and base strength can be discriminated is given by its antroprotolyis constant. Water has a range of 14 while liquid ammonia has 33, indicating that the proton affinity of NH_2^- is considerably higher than that of OH^-. Hence strong base that are levelled in water will not be levelled in liquid ammonia and the acids that are weak in water may be levelled in ammonia. Anothernon-aqueous solvent of interest is dimethyl sulphoxide (DMSO) solvent which has a pK value of 37. Hence it can be used to study a wide range of acids including H_2SO_4 and phosphine (PH_3)).

Solved problem 3

Under what condition is the solvent leveling effect of ammonia better than that of water? Give reason for your answer

Solution

For any solvent, the range over which acid and base strength can be discriminated is given by its antroprotolyis constant. Water has a range of 14 while liquid ammonia has 33, indicating that the proton affinity of NH_2^- is considerably higher than that of OH^-. Hence strong base that are levelled in water will not be levelled in liquid ammonia and the acids that are weak in water may be levelled in ammonia.

Solved problem 5

Among water, ammonia and DMSO solvents, which of them will be most suitable for studying strong acids and phosphine? Give reason for your answer

Solution

Water has a liquid range of 14, ammonia, 37 and dimethyl sulphoxide (DMSO) has 37. Therefore dimethyl sulphoxide (DMSO) will be more suitable solvent for studying strong acid and phosphine.

Solved problem 6

At what value of standard Gibb free energy change of water will the ionization constant remains at 10^{-14} and at a temperature of 303 K. Hence what is responsible for the difference between the calculated free energy change and the standard heat of neutralization of strong acid by strong base (i.e 58 kJ/mol)

Solution

Standard Gibb free energy change can be estimated using the equation,

Since the ionization constant is 10^{-14}, then the free energy change is

= 81.22 kJ/mol

The value of that takes account of the contribution of reaction entropy is 81.22 kJ instead of 58 kJ.

Solved problem 7

The range of acidity that can bestudied in water lies approximately between the effective proton affinities of 1130 kJ/moland 1188 kJ/mol which gives a difference of 58 kJ/mol. Comment on the expected behaviour of a solute in water having proton affinity outside this range

Solution

If the proton affinity A^- is less than 1130 kJ/mol, an acid HA will be converted to A^- and all the protons will be present as . However, If the proton affinity is greater than 1188 kJ/mol the solute will exist only as HA at the expense of forming OH^- from water.

3.8 Autoionization of Solvents

Self-ionization is a unique properties that is common to few solvents. The concept gives an insight into a detail understanding of reactions in different solvents. Water, ammonia and sulphuricacid (pure liquid) are examples of liquids in which autoionization occurs according to the following equations,

Autoionization is a process that involves proton transfer between two molecules in a liquid. In the above examples, the positive ion is solvated proton (or H^+) while the negative ion is the solvated molecule minus hydrogen ion. The autoprotolysis constants (the equilibrium constants for the above reactions differs. There are 10^{-14}(298K), 10^{-30}(223K) and 1.7 × 10^{-4}(283K).

for water, ammonia and sulphuric acid, respectively. The magnitude of autoprotolysis constant is related to the dielectric constant (i.e. thepermittivity) of the liquid. The permittivity of sulphuric acid, water and ammonia are101(298K), 78.5(298K) and 22 (240K), respectively. The greater the permittivity of the solvent, the larger will be the value of the solvation energy of the ionsproduced in that solvent by autoionization. Also, higher values of solvation energy of an ion points toward better stabilization of the ion and higher concentration in the solvent.

Hydrogenfluoride also undergoes autoionization according to the following equation,

The other possibility for autoionization of HF is

Therefore, acid base reaction can occurs in HF solvent but the solvent has a very strong tendency to donate proton indicating that its solvent interaction with strong acids (such as HCl, H_2SO_4 and HNO_3) makes the strong acid to behave as a base and HF as acid due to its high proton donating affinity, which makes very few substances to act as a base in this solvent. Exceptional examples have been found in perchloric acid and among the fluoride acceptors such as SbF_5, NbF_5, $AsF_5$and BF_3 (as shown in the under listed equations)

Since many substances react with HF, its usefulness as a non-aqueous solvent is limited and is mostly used as a medium for preparing fluoro complexes and chlorides. Solvolysis also occurs with sulphuric acid which produces fluorosulphuric acid

Solved problem 8

Write autoionization equations for water and any three non-aqueous solvents of your choice

Solution

The autoionization equation for water, ammonia, sulphuric acid and hydrogen fluoride are as follows

Solved problem 9

(a) What is autoionization? Write equation for the autoionization reaction of methanol.

(b) Given that the equilibrium constant for the autoionization reaction of methanol is 2 x 10^{17}. Which is the stronger acid? Hence calculate the standard free energy change associated with the autoionization reactionat 303 K. Is the reaction spontaneous or not? Give reasons for your answer.

(c) Give the formula of the strongest base present in appreciable concentrations in methanol.

Solution

(a) Autoionization involves interaction between the same solvent, leading tothe transfer of proton from one molecule to another within the same solvent. The autoionization equation for methanol is

(b) The autoionization equilibrium constant, e.g. K_w for water, is the K_a for the solvent. The constant is larger for water so water is the stronger acid.

The free energy involves in autoionization reaction can be calculated using the following equation,

For water, the value is

= 81222.18 J = 81.22 kJ/mol

For methanol, the value is

= - 82968.63 J = -82.97 kJ/mol

Since the standard free energy change in both cases is negative, the autoionization is spontaneous.

(c) The species is identified by the autoionization reactions: OH^- for water and CH_3O^- for methanol.

Solved problem 10

The sedative barbital (molecular weight 184.19 g/mole) is a weak monoprotic acid whose K_a equals 3.7×10^{-8} at 25ºC.

A chemist prepares a solution at 25.0ºC containing 0.77 g of barbital in 100.0 ml of water. Calculate the pH of the solution.

Solution

The acid is weak and very little dissociates. [HA] = 0.77 g/0.100 = 7.7 g/l. Dividing 7.7 g/l by the molecular weight, 184.19 g/mole, yields the molar concentration of HA, 0.042 M. This will be very close to the equilibrium concentration as very little dissociates. When a HA molecule dissociates, it yields one hydronium and one A^- anion so $[H^+] = [A^-]$. With these results, the problem is now solved by insertion.

$3.7 \times 10^{-8} = [H^+][A^-]/[HA] = [H^+]^2/0.042$. Solving for $[H^+]$, one obtains $[H^+] = 3.9 \times 10^{-5}$ and pH = $-\log_{10}[H^+] = 4.41$

Solved problem 11

(a) Under what condition can the HF solvent act as a base or acid during chemical reactions with H_2SO_4 and $HClO_4$. Write equations to support your answer

(b) What is the limitation in using HF as a solvent and of what advantage is its solvent property?

Solution

(a) HF has a very high affinity to donate proton indicating that it is a very strong acid and other strong acids will act as a base when dissolve in HF solvent. Exception is perchloric acid in which the acid acts as a base while perchloric acid acts as an acid.

(b) Since many substances react with HF, its usefulness as a non-aqueous solvent is limited and is mostly used as a medium for preparing fluoro complexes and chlorides

3.0 Summary

4.0 Conclusion

6.0 Tutor marked assignment

1. Liquid ammonia, $NH_3(l)$, is an ionizing solvent like water. This means that $NH_3(l)$ can dissolve many different ionic compounds and can undergo autoionization. Therefore, there can be acidic, neutral, or basic species in solutions of liquid ammonia.

(a) Write the chemical equation, using the Brønsted-Lowry perspective, that describes the autoionization of $NH_3(l)$.

(b) Identify the species in pure $NH_3(l)$ that can act as Brønsted acids and as Brønsted bases. (There are more than one for each case.)

(c) Write the mass-action expression for the autoionization constant of liquid ammonia.

(d) At -50°C, the autoionization constant of ammonia is 10^{-30}. What are the conditions for “neutral”, “acidic”, and “basic” liquid ammonia solutions at -50°C?

(e) Identify two different compounds so that, when each is dissolved in liquid ammonia, one gives rise to an "acidic" solution and the other to a "basic" solution. Write out the chemical equilibrium that shows how one behaves as an acid, and the other behaves as a base in $NH_3(l)$.

2. Given the following information, $K_w = 1.0 \times 10^{-14}$ and $Ka(HF) = 7.2 \times 10^{-4}$.

   (a) Which of the sovent will behave as acid when reacted with $H_2SO_{4?}$. Give reason for your answer.

   (b) Write equations for autoionization of each of the solvent

   (c) Hence calculate the free energy change associated with the autoionization of each of the solvent.

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MODULE 2

UNIT 1: General classification of solvent

1.0 Introduction

Several bases exist for classifying solvents. For example, based on their content of hydrogen, solvents can be grouped into protic and aprotic solvents. Solvents may be classified based on their ability to accept or donate proton, according to their tendency to coordinate or based on their polarity. Which ever classification method is adopted is not conclusive because solvent classification method is done for convenience and several classification approach interwoven with each other. In this section, the various classifications are briefly considered.

2.0 Objectives of the study

i. To understand what is acidic solvent
ii. To understand what is basic or protophillic solvent
iii. To understand what is amphiprotic solvent
iv. To understand what is protonic/protic solvent

v. To understand what is aprotic solvent
vi. To understand what is coordinating solvent
vii. To understand what is inert solvent

3.1.1 Acidic solvents

Solvents that have strong tendency to donate protons are called acidic solvent because they are acidic in nature Example are H_2SO_4,HF and CH_3COOH.

3.1.2 **Basic or protophillic** solvents

Basic or protophillic solvents have strong tendency to accept protons and are basic in nature Examples are ammonia, hydrazine, ethylenediamine, etc

3.1.3 Amphiprotic solvents

Solvents which neither have a strong tendency to gain nor lose protons are called Amphiprotic solvents. Example: H_2O ,CH_3CH_2OH ,CH_3OH.The most important nonaqueous solvents of this class are the lower alcohols methanol and ethanol. They resemble water in their acid–base properties.But because of their lower dielectric constants, facilitate processes producing ions to a much smaller extent. In particular, the ion products of these solvents are much smaller ($K_s = 10^{-17}$ for CH_3OH and 10^{-19} for C_2H_5OH, compared with 10^{-14} for water), and the dissociation constants of molecular acids and bases are uniformly lower than in water by four to five powers of 10. Nitric acid, for example, which is almost completely dissociated in water (K_a about 20), has $K_a = 2.5 \times 10^{-4}$ in methanol. On the other hand, the equilibrium constants of processes such as $NH_4^+ + ROH \rightleftharpoons NH_3 + ROH_2^+$ and $CH_3CO_2^- + ROH \rightleftharpoons CH_3CO_2H + RO^-$ are similar in all three solvents, since they do not involve any change in the number of ions.

3.1.4 Protonic/protic solvents

Solvents that could be a source of protons (H^+ ions) are called protonic or protic solvents. Some examples of protonic/protic solvents are water, hydrogen flouride, tetraoxosulphate (VI) acid and hydrochloric acid. Protic solvents often have hydrogen bound to oxygen (such as OH^-) or a nitrogen (as in amine). Consequently, any solvent that contains H^+ is called protic solvent.

3.1.5 Aprotic/non protonic solventsdo not contains ionizable hydrogen atom are called non-Protonic Solvents. Example include SO_2, N_2O_4, C_6H_6,$CHCl_3$, CCl_4

Most protic and aprotic solvents that are commonly used are polar. Polar protic solvent are useful in dissolving salts because they have high dielectric constant and high polarity as shown in Table 1. General characteristics of polar protic solvents are:

i. Display of hydrogen bonding
ii. Possession of acidic hydrogen
iii. Ability to dissolve salts which may be cation by unshared free electron pair or anions by hydrogen bonding

Example of polar protic solvents are water, alcohol, hydrogen fluoride and ammonia. They are recommendable solvent for SN1 reactions while polar aprotic solvents are favourable to SN2 reactions.

Polar aprotic solvent do not contain acidic hydrogen indicating that they are hydrogen bond acceptor, which normally have intermediate constants and polarity. According to IUPAC, polar aprotic solvents are those solvents that have high dielectric constant and high dipole moments. For example, acetronitrile. Other examples are contained in Table 1. Consequently, characteristics of polar aprotic solvents are,

i. They accept hydrogen bonds
ii. They do not have acidic hydrogen
iii. They dissolve salts

Generally, polar aprotic solvents are incompatible with strong bases including Grinard reagents and n-butyllitium (which requires ethers and not nitriles, amides or sulfoxides).

i. Ionizable solvents: Solvents that can undergo self-ionization (i.e autoionization) are called ionisablesolvents. Examples are NH_3, HF ,SO_2 ,N_2O_4 ,ClF_3,BrF_3 and $POCl_3$.
ii. Nonionizable solvents: Solvents such as benzene, which do not ionize at all are called non-ionizing solvents. Most hydrocarbon and carbon tetrachloride are other examples of non-ionizing solvents.

3.1.6 Coordinating solvent

Based on the ability to coordinate with cation or anion, non-aqueous solvents can be classified into the following two groups,

iii. **Coordinating solvents**: Coordinating solvents are those solvents that have the ability to coordinate with the metal ion or anions of the solute . Common example of coordinating solvents are ammonia, sulphur (IV) oxide, nitro methane etc.

iv. **Non coordinating solvents**: Solvents such are carbon tetrachloride and saturated hydrocarbons cannot coordinate with metal ion or anion and are referred to as non-coordinating solvents.

3.1.7 Inert solvents

Solvents with low relative permittivities (or dipole moments) and very weak acidic and basic properties are called inert solvents. Examples of inert solvents are CH_2Cl_2, $CHCl_3$ and benzene; inert solvents such as n-hexane andcyclohexane). Inert solvent usually have low polarity and high permittivity. There are useful as solvents where solvent interaction must be check. This is because their low permittivity, electrical conductivity and dipole moment makes them to be less reactive.

Solved problem 1

(a) What are the general characteristics of polar aprotic solvent

(b) What are the general characteristics of polar protic solvents

(c) Differentiate between ionizable and non ionizable solvents. Give at least two examples for each

Solution

(a) Characteristics of polar aprotic solvents are,

i. They accept hydrogen bonds

ii. They do not have acidic hydrogen

iii. They dissolve salts

(b) Characteristics of polar protic solvent are

i. Display of hydrogen bonding

ii. Possession of acidic hydrogen

iii. Ability to dissolve salts which may be cation by unshared free electron pair or anions by hydrogen bonding

(c) Ionizable solvents: Solvents that can undergo self ionization (i.e auto ionization) are called ionisablesolvents. Examples are NH_3, HF ,SO_2 ,N_2O_4 ,ClF_3,BrF_3 and $POCl_3$. On the other hand, non ionizable solventsare solvents such as benzene, which do not ionize. Most hydrocarbon and carbon tetrachloride are other examples of non-ionizing solvents.

4.0 Summary and conclusion

Solvent are classified based on their behaviour. These include, polarity, ionization potential, content of hydrogen/proton, ability to coordinate with metal, acidic or basic properties and inertness. In spite of the various ways of classification, it can be concluded that some classification are more general than others for example, polar solvent refers to all solvents that are polar including protic and aprotic polar solvent.

5.0 Tutored marked assignment

1. What is the unique property of amphiprotic solvents ? Use suitable examples and equations to support your answer.
2. Differentiate between acidic and basic solvents.
3. Differentiate between coordinating and non-coordinating solvents
4. Classify the following solvents into (a) Protic or non protic and (b) polar and non-polar liquid ammonia, anhydrous sulphuric acid, DMSO, nitrosyl tetroxide, phoryl oxide, hydrogen fluoride, liquid sulphur (IV) oxide and oxyhalides. Give reasons for your classification

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MODULE 2

UNIT 2: Solvent solute interaction

1.0 Introduction

In order to understand the concept of solvent interaction properly, some terms must be defined or explained. These include electronegativity, dipole moment, permittivity, dielectric constant, partial charge, etc. Some of these terms have been defined in the previous units of this course. These parameters are essential in controlling the dynamic of solvent-solute interaction which is the required interaction that must overcome all other interactions (including solute- solute and solvent-solvent interactions) before a solution can be formed between solute and solvent.

2.0 Objectives

i. To understand the effect of electronegativity on solvent- solute interaction

ii. To understand the effect of partial charges on solution formation

iii. To understand the effect of dipole moment on solution formation

iv. To understand the mechanism and thermodynamic of solvation

v. To understand the four major forces of interactions between solvent and solute

vi. To be able to solve mathematical problems related to the treated content

3.0 Main content

3.1 Electronegativity.

Electrons are not shared equally in a molecule with unlike atoms. The tendency of any atom to pull electrons towards itself, and away from other atoms, is characterized by a quantity called electronegativity. Fluorine is the most electronegative atom (4.0) and cesium is the least electronegative (0.7). In general, electronegativity increases with nuclear charge while holding number of core electrons constant (i.e. from left to right in a row of the periodic table). Electronegativity increases as nuclear shielding decreases (from bottom to top in a column of the periodic table). For example, in water, electronegative oxygen atom pulls electron density away from the hydrogen atoms. The oxygen carries a partial negative charge and the hydrogen atoms carry partial positive charges. This phenomenon of charge separation is called polarity.

In methanol (CH_3OH), the electronegative oxygen atom pulls electron density away from the carbon and hydrogen atoms. In water (H_2O), the electronegative oxygen atom pulls electron density away from both hydrogen atoms. Methanol and water are polar molecules. N_2 is a non-polar molecule because the two nitrogen atoms have equal electronegativities and so they share electrons equally. Hydrocarbon ($CH_3CH_2...CH_2CH_3$) is non-polar because the electronegativies of carbon and hydrogen are similar.

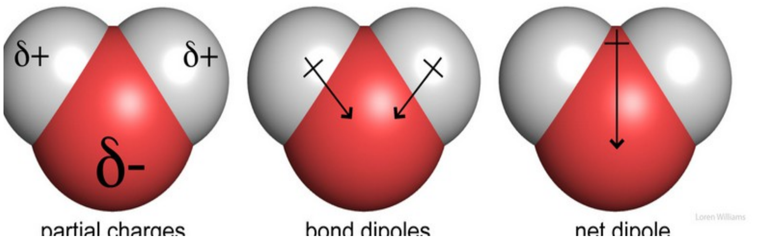


Fig. 1: Pictorial representation of partial charges and dipole moment of water

Fig.1 shows the partial charges and dipole moment of water. Bond dipoles (center) and molecular dipoles (right) can be represented as vectors. The arrows point from positive charge to negative charge.

3.2 Partial Charges

In a molecule composed of atoms of various electronegativities, the atoms with lowest (smallest) electronegativities hold partial positive charges (δ+) and the atoms with the greatest electronegativities hold partial negative charges (δ-). A greater difference in the electronegativities of two bonded atoms causes the bond between them to be more polar, and the partial charges on the atoms to be larger in magnitude. In biological systems, oxygen is generally the most electronegative atom, carrying the largest partial negative charge.

3.3 Dipole moments

The extent of charge separation within a molecule is characterized by the dipole moment μ. A dipole moment is determined by the magnitudes of the partial charges and by the distances between them. In order to estimate dipole moments, charges are expressed in esu's and distances in centimeters. The dipole moment of an electron and a proton separated by 1 Å equals: (4.8 x 10^{-10} esu) (10^{-8}cm) = 4.8 x 10^{-18} esu cm = 4.8 Debye. The dipole moment of water is 1.85 Debye (HCl = 1.1 D; CH_3Cl = 1.9 D; HCN = 2.9 D; NH_3 = 1.47 D).

The orientation of the dipole moment of a peptide is approximately parallel to the N-H bond and is around 3.7 Debye in magnitude.A dipole is surrounded by an electric field, which causes force-at-a-distance on nearby charged and partially charged species. Interactions between dipoles and ions are called Charge-Dipole Interactions (or Ion-Dipole Interactions). Dipoles also interact with other dipoles (Dipole-Dipole Interactions), and induce charge redistribution (polarization) in surrounding molecules (Dipole-Induced Dipole Interactions).

Another example is in CO_2 and HF as shown Fig. 2.

Fig. 2: Representation of dipole moment in HF and CO_2

In CO_2, the more electronegative oxygen atoms pull electron density towards themselves as indicated by the arrows. Carbon dioxide is not polar however because of its linear geometry. A molecule's overall dipole is directional, and is given by the vector sum of the dipoles between the atoms. If the Carbon dioxide molecule is assumed to be centered at 0 in the XY coordinate plane, the molecule's overall dipole would be given by,

$$\mu\cos(0) + \left(-\mu\cos(0)\right) = 0$$

where μ is the dipole moment of the bond (given by μ=Q x r where Q is the charge and r is the distance of separation). Therefore, the two dipoles cancel each other out to yield a molecule with no net dipole. On the other hand, in HF molecule, a molecular dipole exists because there is no opposing dipole moment to cancel as shown by a single arrow in FIG.?. Similarly, if the hydrogen is at the origin of the XY coordinate plane, the dipole would be given by $\mu \cos(0)=\mu$

.

Solved problem 1

The dipole moment of HCl is 1.11D and the distance between atoms is 127 pm. What is the percent ionic character of the HCl bond ?

Solution

If HCl molecules were ionic, a negativecharge chloride ion would be separated from a positive charge hydrogen ion by 127 pm. Therefore the expected dipole moment should be calculated and compared with the actual value.

The observed dipole moment of HCl (1.11) implies that H-Cl bondis

(**Note 1 Debye = 3.3356 x 10^{-30} Ams (ampere meter second) = 3.3356 x 10^{-30} Cm. Therefore, to convert from Debye to Ams or Cm, we multiply by 3.3356 x 10^{-30} but to convert from Cm to Debye, we divide by 3.3356 x 10^{-30}. Also the charge of electron is**)

3.4 Solvent- solute interaction

Solvent-solute interactions play a key role in solution-phase chemistry. These interactions not only stabilize intermediate states by solvation of the corresponding valence charge distributions, but modify energy barriers thereby altering transition states, and allow for ultrafast solvent dynamics in response to solute perturbations (e.g < 100 fs inertial responses of common solvents). Solvent-solute interactions are thus often essential in determining ground-states and steering chemical reactions in solution-phase chemistry.

Solvent effect influences reactivity and physical properties of a solute and hence the rate of reaction and the shift in equilibrium. According to implicit solvation model, Solvent is a uniform, polarizable medium with fixed dielectric constant while the solute is placed inside the cavity in the medium Free energy of solvation is given by where is the free energy required to form the solute cavity (due to the entropic penalty of reorganization of the solvent molecules around the solute and the work done in creating the cavity). is the Van der Waals interaction between solute and solvent, is the electrostatic component(polarization between solute and solvent induces charge redistribution and is the hydrogen bonding term

Handbook of solution chemistry also provide a partition scheme equation for analyzing solvent-solute interaction as follows,

where i stands for the solute and j for the solvent. This approach can be maintained while the identities of the solute and solvent molecules are preserved. In some special cases, it will be necessary to include some solvent molecules in the solute definition. The first term in the above expression is the energy change of the solute due to the electronic and nuclear distortion induced by the solvent molecule and is usually given the name solute polarization. -is the interaction energy between the solute and solvent molecules. The last term is the energy difference between the solvent after and before the introduction of the solute. This term reflects the changes induced by the solute on the solvent structure. It is called cavitation energy in the framework of continuum solvent models and hydrophobic interaction when analyzing the solvation of non-polar molecules.

3.5 Solvation

IUPAC (1997) defines solvation is an interaction of a solute with thesolvent, which leads to stabilization of thesolute species in the solution. During solvation, the solute particles (ions) are surrounded by solvent molecules. It also defines dissolution, which is the process by which a solute dissolves into a solvent. Solvation can be considered to occur in three steps (as depicted by Fig. 3),

- Separate particles of the solute from each other
- Separate particles of the solvent from each other
- Combine separated solute and solvent particles to make solution

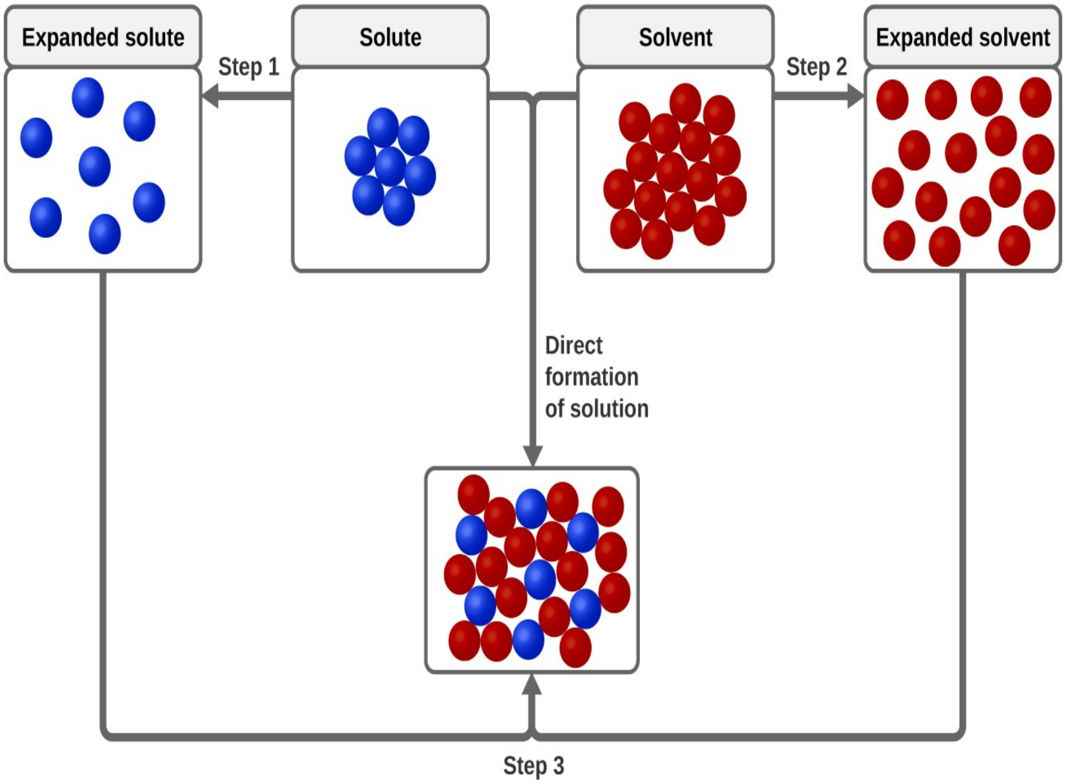


Fig. 3: **: Representation of solvation process as taking place in 3 distinct steps.**

The first two steps require breaking apart the pure solute and the pure solvent, while the third step requires forming the solution.

Since enthalpy is a state function, it is path independent. Therefore the energetics requires breaking apart the solute (step 1) and the solvent (step 2) and then forming the solution (step 3). The breaking process is endothermic (i.e steps 1 and 2) while the formation process is exothermic (step 3. Solvation model can be exothermic (Fig. 4) or endothermic (Fig.5). Figure 4 illustrate exothermic solvation model. From the Figure, it can be seen that the enthalpy change due to solvation is given as,

Since releases more energy than the overall process is exothermic and

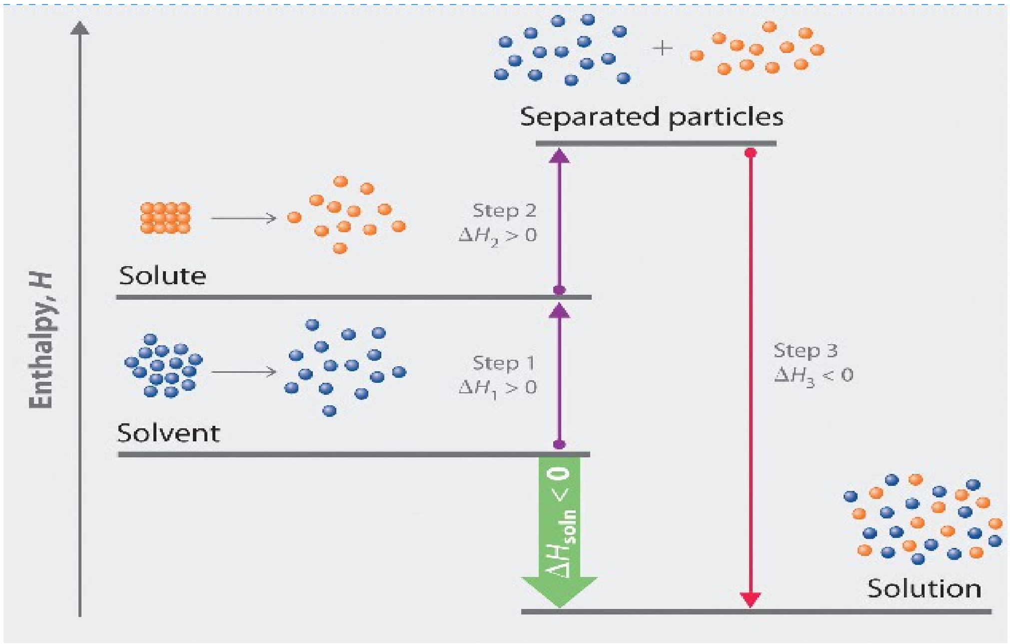


Fig. 4: Exothermic solvationmodel.

In endothermic solvation process, the entropy change is still the same, i.e.

However, endothermic salvation model arises when the energy released by is greater than hence the overall process becomes endothermic and

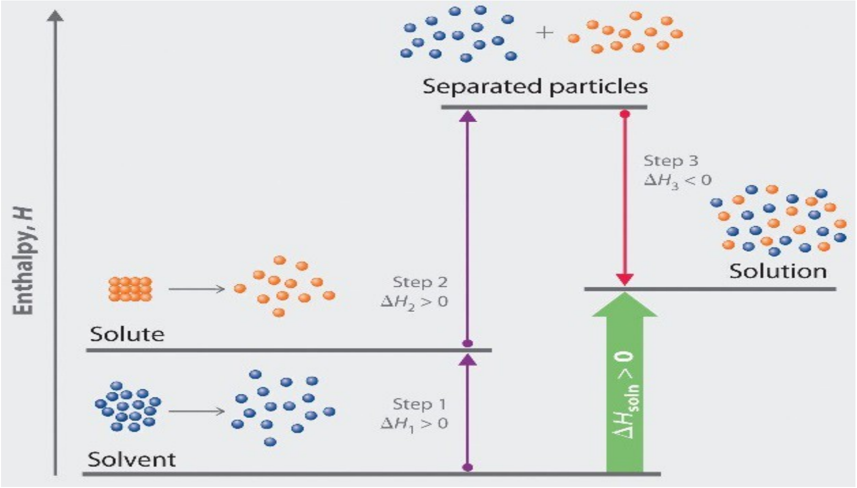


Fig. 5: Scheme for endothermic solvation model

3.6 Forces of interactions

Solution is homogenous mixture of substances which consists of solvent and solute. The solvent is the component of solution that is presentin the greatest amount. It is the solvent that dissolve the solute. All other components, except the solvent constitute the solute. In the formation of a solution, several interactions exist. These are,

i. Solvent- solvent interaction
ii. Solute- solute interaction
iii. Solvent- solute interaction

Among the above three interaction, it is the solvent-solute interaction that is significant in determining the possibility of solute dissolution. Generally, if solvent and solute intermolecular forces are similar, then , the pair will be soluble and as a rule, like dissolve like. Dissolution is effective when the solvent-solute interaction is strong enough to overcome solvent- solvent and solute- solute interactions.

Solute can be classified into ionic solid, polar covalent solute and polar non covalent solute. as According to coloumbic law opposite charges attracts while like charges repel. Solvent must be able to attract solute before solution can be formed. The formation of solution generally depends on the nature of solute, the nature of solvent and on the nature of interaction between the two. Four types of interactions can be examined with respect to the formation of a solution. These are

i. Charge-dipole interaction
ii. Dipole-dipole interaction
iii. Dipole-induced dipole interaction
iv. Induced dipole-induced dipole interaction

These forces are called intermolecular interactions and exist in the range of 2 to 10 kCal/mol as distinct from intramolecular forces (such as covalent bond) that has a long range of operation (50 to 125 kCal/mol). Because of the low range of operation of intermolecular forces, they are so much less than typical covalent bonding forces and are sometimes called secondary bonding interactions.

3.6.1 Charge dipole interaction

This type of interaction occurs when a charge solute interact with a dipolar solvent. A molecule with a permanent dipole can interact significantly with cations and anions through charge-dipole or ion-dipole interaction. Example is the interaction between sodium chloride and water. There will be a Coulombic interactions between a positively charged sodium ion and 6 water molecules as well as the corresponding interactions between a negatively charged chloride ion and 6 other water molecules (as shown in Fig. 6)

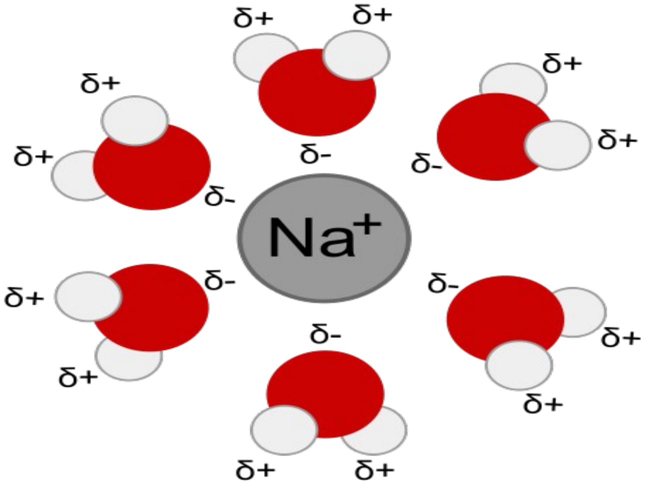
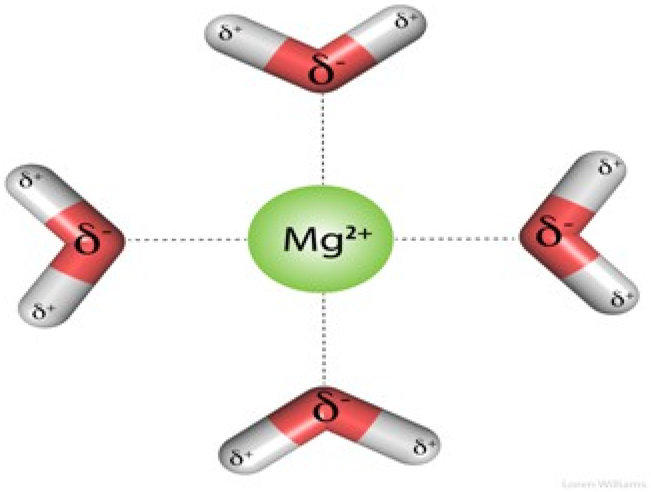


Fig.6: Representation of Coulombic interactions between a positively charged sodium ion and 6 water molecules

In the case of the sodium ion, the positive charge attracts the negative end of each water molecule's dipole. The negative charge of the chloride ion attracts the positive end of the O-H bond dipole. Each ion is encased in a shell of water molecules. The shells insulate the ions from each other, allowing the oppositely charged particles to separate. Molecules that have high dielectric constants are good electrical insulators because of their ability to shield the oppositely charged ions in this way. Another example is the interaction between Mg^{2+} and water, which is symbolically represented by the diagram below

In the diagram given below (Fig. 7), four water molecules are shown interacting favorably with a magnesium dictation. The negative ends of the water dipoles are directed toward the positively charged magnesium ion. Six water molecules coordinate magnesium in solution. Two are omitted for clarity. For an anion like chloride, the water molecules switch direction and direct the positive ends of their dipoles toward the anion. Here the dashed lines do not represent hydrogen bonds. There are no hydrogen atoms between the Mg^{2+} cation and the water oxygen atoms.



(Source: https://ww2.chemistry.gatech.edu)

Fig. 7: Interaction of water with Mg

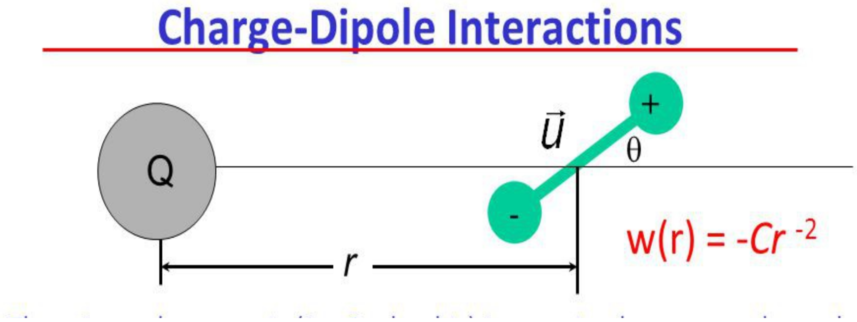


Fig. 8: Model representing dipole moment

Consider a charge at a distant of r experiencing a dipole moment, as shown in Fig. 8. The potential in charge dipole interaction is expressed as,

This interaction potential can be compared with the Colombic potential between two charges

where, and are the stationary point charges and r is the separation between them in the air vacuum.

Also, = 9.0 × N./

where = permittivity of free space = 8.85419 × /N.

The force between two charges and located at a distance r in the medium other than free space may be expressed as

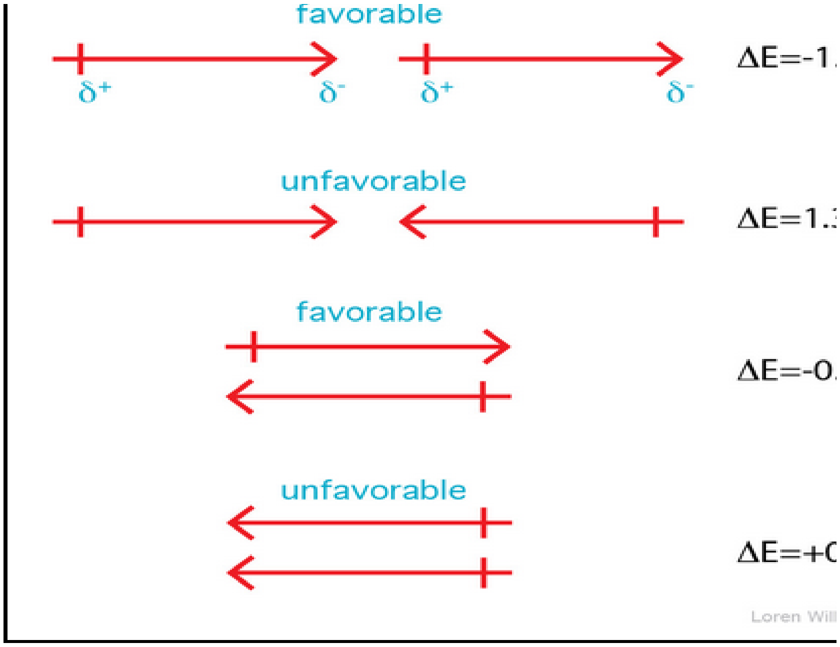
where is the relative permittivity of the medium also called the dielectric constant of the medium. In vector form, the equation can be written as

or

3.6.2 **Dipole dipole interaction**(Keesom Interactions)

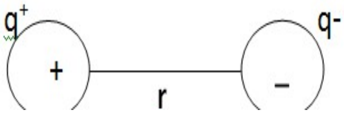
Two dipoles feel each other at a distance. The positive end of the first dipole is attracted to the negative end of the second dipole and is repelled by positive end. The strength of a dipole-dipole interaction depends on the size of both dipoles and on their proximity and orientations. The net interaction energy between two dipoles can be positive or negative. Parallel end-to-end dipoles attract while antiparallel end-to-end dipoles repel. The Figure below shows the energies of interaction for various orientations of two dipoles with moments of 1 Debye at a distance of 5 Å in a medium of $\varepsilon = 4$.

Knowledge of dipole-dipole interaction is very essential in choosing the right non aqueous solvent. For example if we are interested in a solvent that will dissolve both 1-bromobutane and the KOH.



(Source:https://ww2.chemistry.gatech.edu)

KOH is very soluble in water but 1-bromobutane is not but is dissolved in hexane in which KOH is completely insoluble. The solution is a solvent that has just the right balance of polar and non-polar character. For example, methanol and ethanol are suitable choices.

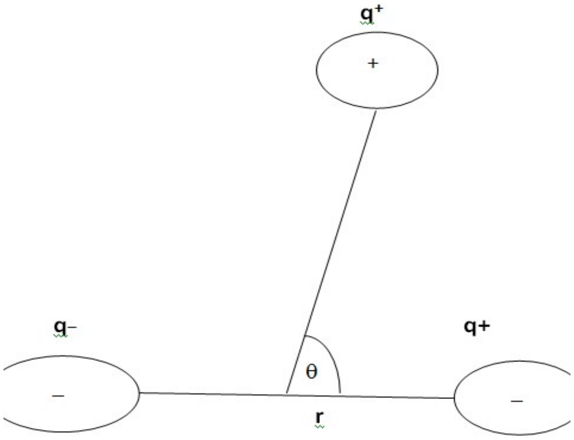


For two positively charged particles interacting, (as shown in the above, the potential energy of the system can be written as

where k is the Coulomb constant, r is the distant of separation and q_1 and q_2 are the magnitude of the charges. The Coulomb equation given above is most useful for point charge. Consequently, since molecules of solvents are often larger than point charge, there is a need to amend the equation. Two polar atoms interacting with each other are strongly influenced by the dipole moment, distanceof separation and the nature of charge orientation. In dipole-dipole interaction, partially positive and negative charges interact with each other and the Coulomb equation can be amended to the following equation, where is the permitivity of space. If the molecular dipoles are not interacting in a straight line, the equation is amended to incorporate the associated angles. The expected equation is,

where is the angle between the two oppositely charged dipoles, is the distance between the two molecules., and   are the angles formed by the two dipoles relative to the line connecting their centres.

In the case of multiple charges, it is significant to state that like charges repel and unlike charges attract. If the charges are three, two of them will be similar while the other will differ (as shown in the diagram below).



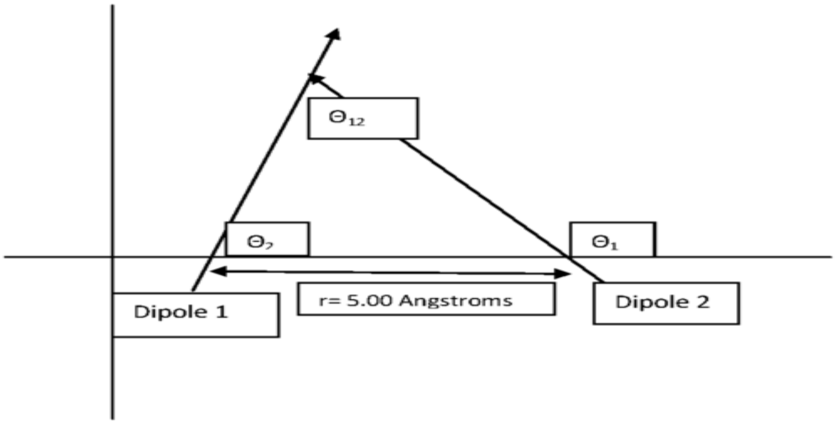
Hence the angle between the attractive and repellant forces are considered and the potential can be estimated using the formula,

where k is the Coulomb constant and r is the distance between the molecules

Solved problem 2

(a) Calculate the potential energy of the dipole-dipole interaction between 2 HF molecules oriented along the x axis in an XY coordinate plane whose area of positive charge is separated by 7.00 Angstroms from the area of negative charge of the adjacent molecule (The Dipole moment of the HF molecules, μ=1.92 D). Assume the molecules exist in a vacuum such that $\epsilon_0=8.8541876\times10^{-12} C^2 N^{-1} m^{-2}$.

(b) If the orientation of HF given above coincided with the under listed, calculate the potential energy,



Solution

(b) The formula for calculating the potential, V is

(**Note 1 Debye = 3.3356 x 10^{-30} Ams (ampere meter second) = 3.3356 x 10^{-30} Cm. Therefore, to convert from Debye to Ams or Cm, we multiply by 3.3356 x 10^{-30} but to convert from Cm to Debye, we divide by 3.3356 x 10^{-30}**)

(b) In this case, the required formula is

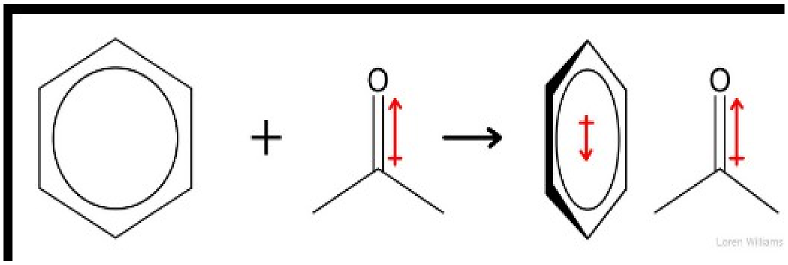
Hence

= -1.47 x 10^{20} Nm = = -1.47 x 10^{20} J

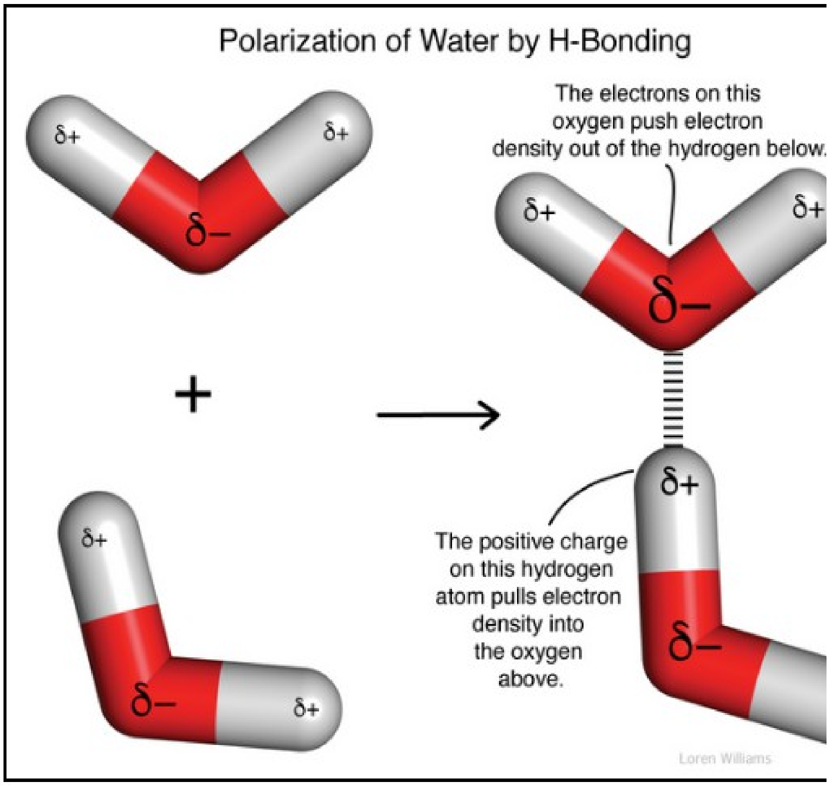
3.6.3 Dipole-Induced Dipole Interactions

Polar protic and dipolar aprotic molecules both have permanent bond dipoles. Non-polar molecules do not, or if they do, their dipole moments are very small. However, when a molecule with a permanent bond dipole comes close to one with no bond dipole, the electric field associated with the permanent dipole can temporarily distort the electron distribution in the non-polar molecule, thereby inducing a temporary bond dipole.

The electron density of a polarizable molecule is shifted and deformed by the electric fields of polar molecules. Any molecule with a dipole moment (or any ion) is surrounded by an electrostatic field. This electrostatic field shifts the electron density (alters the dipole moments) nearby molecules. A change in the dipole moment of one molecule by another (or by any external electric field) is called *polarization*. The ease with which electron density is shifted by an electronic field is called polarizability. For example, benzene is a symmetric molecule that does not have a permanent dipole moment but can be polarized as shown below



The static dipole can induce a dipole in an adjacent molecule. When two isolated molecules (left) come together in a liquid or solid (right), the static dipole 'polarizes' the adjacent molecule. π Electrons are more polarizable (more easily perturbed by an adjacent dipole) than σ electrons. The strength of a dipole-induced dipole interaction depends on the size of the dipole moment of the first molecule and on the polarizability of the second molecule. Another example of Induced dipole-dipole interaction is the polarization of water molecule by hydrogen bond as shown in the diagram below.



Each water molecule polarizes neighboring water molecules and increases neighboring dipole moments. When the two water molecules approach each other and form a hydrogen bond as shown here, the partial negative charge on the oxygen of the top water molecule is increased in magnitude, and the partial positive charge on the proton of the bottom water molecule is also increased. Here the symbol size is scaled to the magnitude of the partial charge.

Dipole-induced dipole interactions are important even between molecules with permanent dipoles. A permanent dipole is perturbed by an adjacent dipole. For example, in liquid water (where molecules are close together), *all* water molecules are polarized. The permanent dipole of each water molecule polarizes all adjacent water molecules. The dipole of a water molecule induces change in the dipoles of all nearby water molecule.

Dipole-induced dipole interactions are always attractive and can contribute as much as 0.5 kcal/mole to stabilization of molecular associations. Dipole-induced dipole interactions fall off with $1/r^4$. Formally charged species (Na^+, Mg^{2+}, $-COO^-$, etc.) also polarize nearby molecules and induce favorable dipoles. The resulting interactions, called charge-induced dipole interactions (or ion-induced dipole interactions). These interactions are important, for example in protein structure.

3.6.4 Induced dipole induced dipole interaction (The London force or dispersion interaction)

The London dispersion force is the weakest intermolecular force. The **London dispersion** force is a temporary attractive force that results when the electrons in two adjacent atoms occupy positions that make the atoms form temporary dipoles. This force is sometimes called an induced dipole-induced dipole attraction

Molecules resonate too. Electrons, even in a spherical atom like Helium or Xenon, fluctuate over time according to the natural resonant frequency of that atom. As electron density fluctuates, dipole moments also fluctuate. Therefore, all molecules and atoms contain oscillating dipoles. In all molecules that are close together (any liquid or solid, but not a perfect gas) the oscillating dipoles sense each other and couple. They oscillate in synchrony, like the strings of a violin. The movements of electrons in adjacent molecules are correlated. Electrons in one molecule tend to flee those in the next, because of electrostatic repulsion. Coupled fluctuating dipoles experience favorable electrostatic interaction known as dispersive interactions.

4.0 Summary

Intermolecular interactions include solute-solute, solvent-solvent and solvent-solute interaction. A solution is formed when the solvent-solute interaction is greater than the other two interactions. Solvation is a process whereby solvent molecules surrounds solute. Without solvation, molecular interactions and subsequent formation of solution will not be feasible. Thermodynamics of solvation involves enthalpy, entropy and free energy and changes at various stages (or level of interaction).

8.0 **Conclusion**

Formation of solution involves the coming together of solute and solvent. Solvent and solute must interact before solution is formed. The mechanismof solvent molecules surrounding the solute, in order to drive it towards the formation of solution is governed by the rule of solvation. After solvation, the solvent solute interaction must overcome the solute solute and the solvent solvent interaction before solution can be formed. These interactions that leads to solution formation may be, Charge-dipole interaction, Dipole dipole interaction or Dipole-induced dipole interaction or Induced dipole-induced dipole interaction.

5.0 Tutor marked assignment

1. Explain why XeF_4 and CO has no dipole moment
2. Write short notes on the following terms,
   i. Polarization
   ii. Polarizability
   iii. Polarity
   iv. Dipole moment
3. Give one example of molecule in which each of the following interactions are applicable,
   i. Charge dipole interaction
   ii. Dipole dipole interaction
   iii. Induced dipole interaction
   iv. Induced dipole induced dipole interaction.

7.0 References

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MODULE 3

UNIT 1: OXYHALIDE

1.0 **Introduction**

2.0 **Objectives**

3.0 **Main content**

3.1 **Nitrosyl chloride**

3.2 **Phosphoryl chloride**

4.0 **Summary**

5.0 **Conclusion**

6.0 **Tutor marked assignment**

7.0 **References**

1.0 Introduction

Oxyhalides are often use as non-aqueous solvents and in the preparation of several useful products. However, their action as non-aqueous solvent is widely acceptable. Nitrosyl chloride and phosphoryl chloride are the commonest oxyhalide solvent and are discuss in this section.

2.0 Objectives

i. To understand physical properties of nitrosyl chloride as a solvent

ii. To know physical properties of phosphoryl chloride as a solvent

ii. To be able to explain the solvent properties of nitrosyl chloride and phosphoryl chloride based on their physical properties.

iv. To know chemical reactions (and write equations) that involves phosphoryl chloride and nitroyl chloride as solvents.

3.0 Main content

3.1 Nitrosyl chloride

Physical properties of nitrosyl chloride as a solvent arepresented in the Table 1. On account of its reasonable high dielectric constant, the solvent is expected to bea strong ionizing solvent. However, some materials such as KCl are not soluble in the solvent while others like tetra-alkyl ammonium halides are soluble, which conflicts with the expected ionic behaviour. Nitrosyl chloride has remarkable solvent properties for nitrosonium salts.

Table 1: Physical properties of nitrosyl chloride

Property	
Melting point	−64.5 °C
Boiling point	−5.55 °C
Liquid range	5.9 °C
Viscosity	0.586 centipoise (at 21 °C)
Density	1.50 g/dm^3 (at -6 °C)
Dipole moment (Debye)	1.83
Dielectric constant	18.2

These salts have very similar lattice energies to the corresponding potassium salts. Therefore, there must be a fairly specific solvation interaction. Also both $(NO)AlCl_4$ and $(NO)FeCl_4$ form solid adducts, (i.e.$(NO)AlCl_4NOCl$ and $(NO)FeCl_4NOCl$) indicating that the interaction involving the formation of species such as $[O=N\text{-}Cl=O]^+$, $(NO)ALCl_4$ and $(NO)FeCl_4$makes them to be readily soluble and behaves as strong electrolytes. Conductometric titration have been carried out in the solvent. Isotopic studies using radioactive chlorine, ^{35}Cl reveals that rapid exchange of chlorine takes place between $AlCl_3$, $GaCl_3$, $InCl_3$ and $FeCl_3$ and the solvent. All chlorine atom in these compounds are equivalent.

Some exchange of ^{15}Cl between $ZnCl_2$, $CaCl_2$ and $HgCl_2$ which are not significantly soluble in nitrosyl chloride also takes place at fairly rapid rate. This occurs as a result of the 1:1 complex which is insoluble. This is followed by a slower heterogeneous exchange of chlorine between the complex and the solvent.

Although studies on chemical reactions occurring in the solvent, notable reactions involving silver phosphates are examples,

The reactions produce additional P-O-P bond formation, rather surprisingly in the case of the silver tri and tetra-metaphosphates.

NOCl behaves as an electrophile (an oxidant) in most of its reactions. It can react with halide acceptors (such as antimony pentachloride) to form nitrosonium slats as shown in the under listed equations

Tetraoxosulphate (VI) acid reacts with NOCl to give nitrosylsulphuric acid, which is a mixed anhydride of nitrous and sulphuric acid:

NOCl reacts with silver thiocyanate to give silver chloride and pseudohalogen nitrosyl thiocyanate:

Nitrosyl chloride is used to prepare metal nitrosyl complexes. For example, NOCl gives the dinitrosyldichloride complex with molybdenum hexacarbonyl:

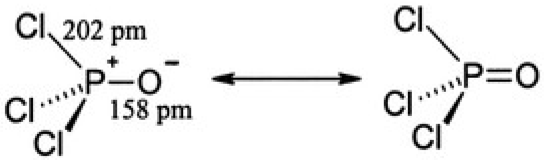
Solved problem 1

Write suitable equations show the reaction of NOCl with various forms of silver phosphate

Solution

3.2 Phosphoryl chloride ($POCl_3$)

Phosphoryl chloride (phosphorus oxychloride) is a colourless liquid with the formula, $POCl_3$. It hydrolyses in moist air releasing phosphoric acid and a characteristic choking fumes of hydrogen chloride. On industrial scale, the oxyhalide is manufactured from phosphorus trichloride and oxygen or phosphorus pentaoxide.



Posphoryl chloride has the same tetrahedral shape like phosphate. It has three P-Cl bonds and one strong P=O double bond, with an estimated bond dissociation energy of 533.5 kJ/mol. The

Schomaker-Stevenson rule suggests that the double bond form is very dominant (in contrast with POF_3). Quantum chemical calculations shows that P=O bond does not utilize the d orbital on phosphorus. It is currently believe that the donation of the lone pair electrons from oxygen p-orbitals to the antibonding phosphorus-chlorine bonds account for □ bonding in the molecule.

As shown in Table 2. $POCl_3$ has a melting and boiling points of 1 and 108 □C respectively. The viscosity of the oxohalide is 11.5 at 25 □C. It has a density of 1.17 at 0 □C while its dielectric constant is 13.9 at 22 □C.It has a long solvent range which is much higher than that of NOCl inspite of the lower dielectric constant.

Table 2: Physical properties of phosphoryl halide

Property	
Melting point (°C)	1
Boiling point (°C)	108
Liquid range (°C)	107
Viscosity (centipoises)	1.15 (25 °C)
Density (g/cm^3)	1.71 0 °C)
Dipole moment (Debye)	1.83
Dielectric constant	13.9 (at 22°C)
Specific conductivity ($Ohm^{-1} cm^{-1}$)	$<2 \times 10^{-8}$
Trouton's constant	24.9
Enthalpy of vapourization	9.5

Therefore $POCl_3$ is more associated than HOCl. Generally, the Solubilites of alkali halides in phosphoryl chloride are low but are higher than in nitrosyl chloride, even if its dielectric constant is lower. The alkaline halides, silver chloride, mercurious chloride and thallous chloride are insoluble.

Quaternary ammonium salts are very soluble. Compounds such as $SiCl_4$, $SiBr_4$ and $SnBr_4$ dissolve readily and undergo polymerization in the solvent. $AsCl_3$, $SiCl_4$ and BiI_3 are readily soluble but cryoscopy measurements indicate that they are dissociated. $AlCl_3$, $SbCl_5$, $BBr_3$and $SnCl_4$ are readily soluble but form adducts with the solvent.

The dielectric constant of $POCl_3$ is sufficiently low for soluble ionic compounds to show a molar conductivity minimum in the solvent just as in SO_2. However at concentrations close to 5 x 10^{-3}M triple ions are in negligible concentration and the datacan be interpreted in the terms of an ion pair free equilibrium given below,

$$[M^+X^-] = M^+ + X^-$$

The value of limiting equivalent conductivity of $POCl_3$is rather low when compared with other solvents, perhaps due to viscosity of the solvent. Consequently, the mobility of the chloride ion is not anomalous. This is important relation to the proposed self-ionization of the solvent,

Triethylamine dissolves in phosphoryl chloride to give a conducting solution. The behaviour can be represented by the equilibrium,

In spite of the fact that all the solid adducts of $POCl_3$ with Lewis acids which have been investigated, contained an oxygen link to the Lewis acid, solutions of Lewis acids in $POCl_3$ are conducting and is a consequence of the following equilibrium,

3.2.1 Mechanism of adducts formation

All the chloride ions that forms $FeCl_4^-$ come from $FeCl_3$ as shown below

In the above equation, is a unstable specie. Addition of the above two equations yields,

Literature reveals that it is possible to interpret the conductivity in terms of the following equilibrium reactions

3.2.2 Chemical reactions in phosphoryl chloride

Conventional conductometric titrations between tetramethyl ammonium chloride and in ferric chloride and antimony trichloride can be performed in $POCl_3$to obtain a sharp 1:1 end point according to the following equations

Similar titrations can also be carried out in triethyl phosphate and in whatsoever system, as long as the equillibria (in the underlisted equations) lies to the right, a sharp 1:1 end point is expected.

+

+

`The ratio of iron to chlorine in $FeCl_3$ is 1:3. Therefore only one mole for chlorine is required to convert all the iron to $FeCl_4$.

Pyridine also gives conducting solution in $POCl_3$ just as triethylamine, even with similar mechanism:

These solutions can be titrated with VCl_4, PCl_5 and $TaCl_5$ solutions and such titrations show end points at 1:2, 1:1 and 1:1 mole ratios of pyridine to Lewis acid respectively. The equations for the reactions are

Solved problem 2

Explain in details, the features of conductometric titration between tetramethyl ammonium chloride and in ferric chloride and antimony trichloride in $POCl_3$ solvent.

Solution

Conventional conductometric titrations between tetramethyl ammonium chloride and in ferric chloride and antimony trichloride can be performed in $POCl_3$to obtain a sharp 1:1 end point according to the following equations

Similar titrations can also be carried out in triethyl phosphate and in whatsoever system, as long as the equillibria (in the underlisted equations) lies to the right, a sharp 1:1 end point is expected.

`The ratio of iron to chlorine in $FeCl_3$ is 1:3. Therefore only one mole for chlorine is required to convert all the iron to $FeCl_4$.

4.0 Summary

Nitrosyl chloride has a high dielectric constant but does not confer solubility in some ionic compound such as KCl indicating that its chemistry is slightly deviated from normal solvent, probably due to its organic and inorganic characters. It is reactive to various phosphates of silver, tetraoxosulphate (VI) acid and sometimes behaves as an electrophile. Phosphoryl chloride has a long liquid range which permits it for special utilization. It has a high dielectric constant and undergoes several reactions including adducts formation. It is suitable as a solvent for conductometric titration between tetramethyl ammonium chloride and in ferric chloride and antimony trichloride

5.0 Conclusion

NOCl and $POCl_3$ are major type of oxyhalides that are suitable as solvents. The solvent have some similarities with other solvents and exhibit long liquid range and high dielectric constant which makes them suitable for conductometric titration and other laboratory and industrial applications.

6.0 Tutor marked assignment

1. Write suitable equation for the underlisted reactions involving $POCl_3$
    - i. Reaction with pyridine
    - ii. Formation of adduct with $FeCl_3$
2. Write equation to show the use of nitrosyl chloride in preparing metal nitrosyl complexes
3. Write a suitable equation to show the behaviour of NOCl as an electrophile

7.0 References

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MODULE 3

UNIT 2: Liquid oxides and halides

1.0 **Introduction**

2.0 **Objectives**

3.0 **Main content**

  3.1 **Liquid nitrogen tetroxide**

  3.2 **Liquid sulphur (IV) oxide**

  3.3 **Liquid halides**

4.0 **Summary**

5.0 **Conclusion**

6.0 **Tutor marked assignment**

7.0 **References**

1.0 Introduction

One of the most unique properties of protonic solvent (those containing replaceable hydrogen) can donate electron under certain conditions and can also accept electron under other conditions. Bronsted- Lowry concept is satisfactory in studying the behaviour of these solvent . However, non-protonic solvents do not contain hydrogen indicating that this concept may not be applicable. Therefore, Lewis acid-base concept is a better theory for these solvent. In this section, liquid nitrogen tetroxide, liquid sulphur dioxide and liquid halides are discussed. These solvents are ionizing and covalent solvents.

2.0 Objectives

i. To study the solvent properties of dinitorgen tetroxide, liquid $SO_2$and liquid halides

ii. To understand various chemical reactions that directly involves dinitorgen tetroxide, liquid $SO_2$and liquid halides

iii. To understand chemical reactions in which dinitrogen tetroxide, liquid $SO_2$and liquid halides act as a solvent and not as reactants

iv. To understand the application of conductometric titration using these solvents.

3.0 Main content

3.1 Liquid dinitrogen tetroxide

It is a type of non-protonic solvent which contains no hydrogen atoms and on self-ionization does not yield a proton (). For this type of solvent, it is best to use the Lewis definition of acids and bases (acids are electron pair acceptors; bases as electron pair donors).

Because of its covalent liquid range, its special chemical properties, its ease of preparation and purification, etc. dinitrogen tetroxide has been widely used as a medium for chemical reactions and as a reactant in liquid phase.

In gaseous and liquid state, N_2O_4 is in mobile equilibrium with the brown monomeric species, NO_2 (i.e nitrogen (IV) oxide or nitrogen dioxide).

Nitrogen dioxide contained an odd number of electrons, it is paramagnetic indicating that a change in temperature may be readily followed by measuring the magnetic susceptibility of the equilibrium mixture. The differences in the adsorption spectra of the monomer and the dimer also provide convenient reason for spectrophotometric instrumentation in studying them. Results obtained from the above two studies reveals that the equilibrium constant (K) for the reaction () in liquid phase is of the order of 1.0×10^{-6} gcm^{-1} at 20 °C.

Therefore, in the liquid state concentration of NO_2 is very low but in the vapour state, concentration of NO_2 is about 16 % at the boiling point and tend to increase rapidly with increasing temperature

The character of dinitrogen tetroxide as a medium for conducting chemical reactions is determined mainly by:

i. Its Lewis acid character
ii. Its oxidizing properties
iii. Its low dielectric constant which renders it a poor solvent for ionic compounds
iv. The variety of dissociation equilibria exhibited by it

v. Its explosive reactions with many reducing agents, particularly those of an organic nature.

Physical properties of liquid N_2O_4

Melting point	-12.3°C
Boiling point	21.3°C
Density	1.49 gm./c.c
Dielectric constant	2.42 at 18°C
Specific conductivity	2.36 × at 17°C

Due to the very low value of dielectric constant, liquid N_2O_4 is a poor solvent for ionic substances. Many organic solutes like alkanes, aromatic hydrocarbons. Halo and nitro compounds and carboxylic acids dissolve in N_2O_4 without change. Many oxygen and nitrogen compounds like ethers, esters and tertiary amines are also soluble. However, many organic compounds containing an active hydrogen atom, such as primary and secondary amines, alcohols and ketones, dissolve in the solvent.

Solved problem 1

(a) Write an equation to shows that liquid N_2O_4 exist as anequilibrium of a dimer and comment on the equation.

(b) Comment on the magnetic property of N_2O_4 as a guide for analytical purpose

(c) Provide reason for suitability of spectrophotometric instrumentation for studying N_2O_4

Solution

(a) In gaseous and liquid state, N_2O_4 is in mobile equilibrium with the brown monomeric species, NO_2 (i.e nitrogen (IV) oxide or nitrogen dioxide).

(b) Nitrogen dioxide contained an odd number of electrons, it is paramagnetic indicating that a change in temperature may be readily followed by measuring the magnetic susceptibility of the equilibrium mixture.

(c) The differences in the adsorption spectra of the monomer and the dimer also provide convenient reason for spectrophotometric instrumentation in studying them.

Solved problem 2

What are the featuresto support the use of N_2O_4 as suitable solvent

Solution

The character of dinitrogen tetroxide as a medium for conducting chemical reactions is determined mainly by:

I. Its Lewis acid character
II. Its oxidizing properties
III. Its low dielectric constant which renders it a poor solvent for ionic compounds
IV. The variety of dissociation equilibria exhibited by it
V. Its explosive reactions with many reducing agents, particularly those of an organic nature.

3.1.1 Chemical reactions in liquid dinitrogen tetroxide

3.1.1.1 Acid-base Reaction

The proposed auto-ionization of liquid N_2O_4 may be

Studies have shown that in addition to the equilibrium existing between NO_2 and N_2O_4, additional equilibrium due to autoionization also exist in the liquid phase. The auto-ionization must occur to an exceedingly small extent since the specific electrical conductivity of the purified liquid is very low. Therefore, any compounds yielding NO^+ ions would be acids in the solvent and those giving NO_3^- ions would be bases. This accounts for the acidic behaviour of NOCl and NOBr in liquid N_2O_4while nitrates such as $(C_2H_5)_4N^+NO_3^-$ behaves as bases in liquid N_2O_4 The low dielectric constant of N_2O_4 does not favor ionic reactions.

However, when a solution of NOCl in liquid N_2O_4 reacts with solid silver nitrate, a precipitateof AgCl is formed.

This reaction is analogous to the typical neutralization reactions occurring in water and ammonia systems.

3.1.1.2 Reaction with metals

Metals that are very active metals (such as lithium, sodium, potassium etc.) react with liquid N_2O_4 in the same manner with water. For example,

Zinc nitrate react with soluble diethyl ammonium nitrate to form tetranitrozincate as follows

3.1.1.3 Solvolysis

Significant number of solvolytic reactions in liquid N_2O_4 have been reported. For example diethyl ammonium chloride undergoes solvolysis in accordance with the following reactions:

The second reaction is reversible in liquid N_2O_4 depending upon the solubility of MCl in the system and the removal of NOCl from the system. Other solvolysis reactions are:

Lithium carbonate is solvolysed by liquid N_2O_4 in the presence of traces of water

Also calcium oxide, calcium carbonate, sodium carbonate, sodium hydroxide, zinc carbonate and zinc sulphide are solvolysed to yield anhydrous nitrates and sometimes mixed with nitrates. These reactions are quite slow and can be made faster in some cases by adding traces of water.

Solvate formation reactions: Nitrates of some metals such as Zn, U and Fe react with liquid N_2O_4 to form the solvates e.g. $Zn(NO_3)_3.2N_2O_4$, $UO_2(NO_3)_2$. N_2O_4 and $Fe(NO_3)_3$, N_2O_4 respectively. These solvates may also be formulated as complex salts: $(NO)_2[Zn(NO_3)_4]$, $NO[UO_2(NO_3)_2]$ and $NO[Fe(NO_3)_4]$.

Amphoteric metals such as zinc displaces reactive behaviour to liquid dinitrogen tetraoxide in the same way it does to aqueous system, although the reaction is relatively slow. On the other hand, zinc reacts rapidly with solutions of NaOCl or $[Et_2NH_2]NO_3$ in N_2O_4 solvent, The product,   is called diethyl ammonium nitrato-zincate and its exact composition is not fully known. The reaction can be viewed as been analogous to the under listed reactions involving zinc in aqueous medium,

Zinc nitrate is readily soluble in a solution of diethyl ammonium nitrate in liquid dinitrogen tetraoxide to yield a nitrato-zincate complex.

Again, this reaction is analogous to the one in aqueous and other media,

3.1.1.4 Adducts formation with organic compounds

Dinitrogen tetroxide forms adducts with numerous inorganic and organic compounds. An adduct is a product of a direct addition of two or more distinct molecules, resulting in a single reaction product containing all atoms of all components. The resultant is considered a distinct molecular species. Examples of adducts formation reactions with inorganic compounds are

The unusual stability of   is explained by its formulation as the ionic compound NO^+ $[SnCl_4(NO_3)]^-$. The nitrate ligand is assumed to be probably bidentates such that tin atom has 6-coordination. This formulation is supported by the infrared spectrum, and by the hydrolysis products in water and sodium hydroxide solution. On thermal decomposition at 170°, a sublimate of composition $SnCl_4$,2NOCl is obtained.

Cobalt (II) nitrate also forms a 1:1 and a 1:2 adducts with dinitrogen tetroxide according to the following equations

Anhydrous cobalt(II) nitrate forms both 1:1 and 1:2 adducts with dinitrogen tetroxide. The formation process first leads to the 1:2 adduct, which is a deep purple crystal. The decomposition in vaccum at about 50 °C leads to the formation of the 1:1 adduct. Further heating in vaccum gives a pale purple anhydrous $Co(NO_3)_2$. Thermogravimetric analysis and vapour-pressure measurements on the 1:2 adduct confirms the formation of the 1:1 adduct as intermediate during thermal decomposition. Dissociation of both adducts is irreversible. Cobalt(II) nitrate is an ionic compound, but the solid adducts contain coordinated nitrate groups entirely. Infrared spectra support the structures $NO^+[Co(NO_3)_3]^-$ and $NO^+[Co(NO_3)_3]^-,N_2O_4$, and electrical conductivity of the 1:2 adduct in acetonitrile indicates that the ionic form exists in solution also to a small extent. Visible spectra are consistent with an essentially octahedral environment for cobalt in the simple nitrate and its adducts both in the solid state and in solution in organic solvents. Table 1 below shows some organic adducts of dinitrogen tetroxide

Table 1 : Adducts of N_2O_4 with organic compounds

Organic compound	Adduct composition	Melting point	Stability
$(C_5H_5)_2O$	$2((C_5H_5)_2O.N_2O_4$	-74.8	Very low
$(CH_3)_2NNO$	$2(CH_3)_2NNO.N_2O_4$	-20.5	moderate
CH_3COOH	$2\ CH_3COOH.N_2O_4$	+2	Moderate
$C_6H_5.COOC_2H_5$	$2\ C_6H_5.COOC_2H_5.N_2O_4$	-13	Moderate
$(CH_3)_2CO$	$2(CH_3)_2CO.N_2O_4$	-40	Low
$(CH_3)_2SO$	$(CH_3)_2SO.N_2O_4$	+38	Stable
$(C_2H_5)_2SO$	$(C_2H_5)_2SO.N_2O_4$	+14	Stable
C_6H_6	$C_6H_6.N_2O_4$	-7	Moderate
$C_6H_5.CN$	$C_6H_5.CN.N_2O_4$	-26	low

Solved problem 2

Write at least one equation to show the involvement of N_2O_4in the following,

i. Reaction with metals
ii. Solvolysis
iii. Adduct formation with inorganic compound
iv. Adduct formation with organic compound

Solution

i. or

ii.

Or

iii. The equation is or

iv.

3.2 Liquid sulphur (IV) oxide

Physical properties of sulphur (IV) oxide arepresented in Table 2

Table 2: Physical properties of SO_2

Parameter	Values
Melting point (°C)	-75.46
Boiling point (°C)	-10,02
Liquid range (°C)	65.5
Viscosity (millipoise)	4.285 (at -10 °C)
Dielectric constant	15.4
Specific conductivity ($ohm^{-1}cm^{-1}$)	3 -4 x 10^{-8} (at -10°C)
Trouton's constant	22.7
Dipole moment (Debye)	1.62
Enthalpy of fusion (kcal/mol)	1.97
Enthalpy of vapourization (kcal/mol)	5.96

Some special features of liquid SO_2 as a solvent are,

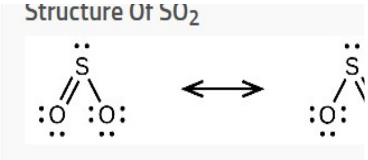
i. it has low boiling point that favours ease of evaporation which encourage its removal from the reaction mixture.

ii. Liquid SO_2 is an inert solvent

iii. it has unique solvating powers for both covalent and electrovalent compounds.

iv. Liquid SO_2 is used as diluent for the super acid medium ($CHSO_3F$-SbF_5) which helps in reducing its viscosity without compromising its acidity.

Some of the physical properties of liquid sulphur dioxide are liquid range(-75.5 to -10.2 ℃), viscosity (0.428 cp at -10 ℃), dipole moment (1.61 Debye) and specific conductance (4 x 10^{-8} $Ohmm^{-1}$). Liquid SO_2 is a non-protonic solvent because it does not contain any hydrogen atom. Its dielectric constant is small (15.6 at 0℃) .Therefore it is a good solvent for covalent compounds. The structure of the solvent exist in a resonance form as shown below



In spite of its low electrical conductivity (3 -4 x 10^{-8}Ohm^{-1}cm^{-1}, SO_2 offers useful medium for some substances to be conductive. Electrical conductors as liquid SO_2 solutions or constant equilibria exist in solution not only between ions and ion pairs (uncharged) but also in more concentrated solutions between ion pairs and ion triplets (charged). Literature reveals that a plot of equivalent conductivity against concentration for liquid SO_2 shows a minimum at concentration above 0.1M. The conductivity is largely attributed to ion triplets; a minimum is found at about 0.1M, and below this the equivalent conductivity increases with decreasing concentration, obeying Ostwald's dilution law. Triple ion formation can be disregarded at concentrations below 0.01M, and at this concentration association constants for ion pair formation may be determined.

The data for a number of salts at 0°C are given in **Table 3**. The limiting conductivities of the salts in the Table show that there must be considerable hydrodynamic transport of solvent associated with the lithium ion. With constant cation the association constants increase from <<, and with constant anion they increase from <<<Me_4<Et_4.

Triphenylchloromethane and some of its chloro and methyl derivates are moderately good conductors in liquid SO_2. The conductivity results may be explained in terms of the following reactions;

Table 3: Conductivity and ion pair association parameters in liquid SO_2

Lone pair	Limiting molar conductance ($cm^{-1}Ohm^{-1}mol^{-1}$)	**K (mol^{-1} x 10^4)**
LiBr	189	0.27
NaBr	265	0.46
KCl	243	0.74
KBr	249	1.43
KI	244	3.00
Me_4NCl	243	10.30
Me_4NBr	236	11.90
Me_4NI	234	13.90

Me_4NClO_4	218	8.40
Me_4NBF_4	215	7.90
Et_2NBr	215	21.00
Et_4NI	197	39.00

Solutions of trisubstituted hydronium salts in the solvent are also fairly good electrical conductors. Salts like $(CH_3)_3B$,$(C_2H_5)_3Sb$ have conductivities of about the same order of magnitude as solutions of KI. It is also worth noting that, though neither water nor hydrogen bromide by themselves are electrical conductors in sulphur dioxide, a mixture of both gives a conducting solution in the solvent, presumably due to H_3O.

Solved question 3

(i) Why is liquid SO_2 a good solvent for covalent compounds

Solution

(i) Liquid SO_2 is a non-protonic solvent because it does not contain any hydrogen atom. Its dielectric constant is small (15.6 at 0) .Therefore it is a good solvent for covalent compounds

3.2.1 Autoionisation of SO_2

Electrical conductivity of liquid SO_2 is oftenattributed to its autoionization. It undergoes autoinonization to give positive thionyl ion and negative sulphate ion. According to the following equation

The autoionization can be viewed as analogous to that of water and ammonia, i.e,

Thus SO^{2+} ion is analogous to H_3O^+ and ions while is analogous toOH^- and ions. Consequently, substances which gives SO^{2+}in liquid SO_2 are acidic (e.g thionyl chloride) while those that gives are bases (e.g ccaesium trisilicate),

Solved problem 4

(a) With the aid of suitable equations, explain the similarity of autoionization reaction of liquid $SO_2$with that of water and liquid ammonia**.**

(b) Comment on the acidic or basic behaviour of liquid SO_2 with respect to autoionization. Give example, where necessary.

Solution

(a) According to the following equation

The autoionization can be viewed as analogous to that of water and ammonia, i.e,

Thus SO^{2+} ion is analogous to H_3O^+ and ions while is analogous toOH^- and ions.

(b) Substances which gives SO^{2+} in liquid SO_2 are acidic (e.g thionyl chloride) while those that gives are bases (e.g caesium trisilicate),

3.2.3 Neutralization reaction

Liquid SO_2 undergoes neutralization reaction to produce salt and SO_2 . The produce SO_2 can be viewed in terms of combination of the product of autoionization, just like in water

Example of neutralization reaction involving SO_2 is

Typical acid-base reactions, which have been carried out using liquid sulphur dioxide as a solventinclude the following,

It cannot really be concluded that the reaction involves ionic mechanism between sulphide and thionyl ion compared with those of hydroxyl and hydroxonium ion, involving neutralization reaction carried out in aqueous medium. That is, Studies of the kinetics of exchange of radioisotopes of sulphur between thionyl halides and sulphur dioxide, as well as between tetramethylammonium pyrosulphite and sulphur dioxide reveals that the free ion SO^{++} plays no important role in the mechanism of reactions where the solvent is liquid sulphur dioxide. However, experimental evidence supports the partial ionization of thionyl halides. For example,

3.2.4 Solvolysis reaction

Solvolytic reactions in liquid SO_2 is not very common as they are in other protonic solvents such as NH_3 ,H_2O. However, examples of solvolysis reaction in liquid SO_2 are

3.2.5 Precipitation reaction

A large number of precipitation reactions can be carried out in liquid sulphur dioxide due to selective solubility of compounds

Zinc diethyl reacts with SO_2 to produce diethyl sulphoxide and zinc oxide according to the following equation,

Ammonium acetate is also solvolysed in liquid SO_2 according to the following equations,

Although it has not been confirmed that solutions of alkali bromides and iodides are slowly solvolysed in SO_2 solvent, some reactions of these nature have been reported as the following summation of equations reveals,

---

Similar reaction with KI in SO_2 has been affirmed. However, S_2I_2 break down to sulphur and iodine

There are some binary halides that do not react in liquid $SO_2$for example, halides of group IV do not react while phosphorus pentachloride and penta bromide are solvolysed by SO_2, even at a low temperature. Thus the following equations are valid,

Other examples of solvolysis reactions are

3.2.6 Metathetical reactions

A metathesis reaction (double replacement reaction or double displacement reaction) is a chemical process involving the exchange of bonds between two reacting chemical species, which results in the creation of products with similar or identical bonding. Most reactions called neutralization reactions or acid-base reactions are probably better described as metathetical reactions. Thus, sulphites react with thionyl halides in the solvent to produce chlorides and sulphur dioxides:

It has been found that the isolated $SO(CH_3.CO_2)_2$is broken up to acetic anhydride and sulphur dioxide. However, $(C_6H_5.CH_2.CO_2)_2SO$ and $(ClCH_2.CO_2)_2SO$ have been isolated from similar reactions. Ammonium thiocyanate also reacts with thionyl chloride according to the following equation

Stability of in dilute solution has been affirmed by several experiments . The compound can be titrated with K_2SO_4 using conductometric method.

3.2.7 Amphoteric reactions

Several amphoteric reactions in liquid sulphur dioxide that are analogous to the behaviour of amphoteric substances in water have been identified and confirmed. For example, when a solution of tetramethylammonium sulphide is added to a solution of aluminium chloride in liquid sulphur dioxide, a voluminous white precipitate of aluminium sulphite is formed;

The precipitate [can be converted to a complex anion by addingtetramethylammonium sulphite in excess

Also, if thionyl chloride is added to the solution, aluminium sulphite will be re-precipitated

Reactions similar to those explain above are also observed with gallium trichloride in liquid SO_4 and also with stannic chloride.

Phosphorus trichloride react with liquid SO_2 to produce a white flocculent precipitate of phosphorus trioxide, in the presence of tetramethylammonium sulphate according to the following equation,

On addition of excess sulphite the precipitate redissolves, and form a another compound, $Me_4NPO_2SO_2$ has been isolated:

The reaction can be followed conductometrically and results obtained from some experiments reveals two major end point at sulphite to PCl_3 ratios of 2:3 and 4:2.

Metals which have amphoteric hydroxides generally dissolve in aqueous alkali with the liberation of hydrogen. However, most of these metals (except tin), including beryllium, aluminium, gallium, antimony and lead, give no reaction with tetramethylammonium sulphite in liquid sulphur dioxide.

3.2.8 Complex formation reaction

Equations for some of the complex formation reactions that occurs in liquid ammonia medium are given below

Addition of iodine increases the conductivity of potassium iodine and rubidium iodide in liquid SO_2, and the solubility of iodine itself is greatly increased by the addition of potassium iodide or rubidium iodide. These effects are a maximum at an iodine:iodide ratio of 1:1 and are due to the formation of tri-iodide ion:

Also the solubilities of cadmium iodide and mercuric iodide are found to increase with the addition of potassium iodide and rubidium iodide to the solvent and is attributed to the formation of complex ions:

Also, a precipitate of K_3SbCl_6 is obtained from the addition of $SbCl_3$ to a solution of KCl . Again, addition of excess of antimony pentachloride causes this complex to dissolve and decomposes to hexachloroantimonate:

The preparation of a number of hexachloroantimonates in liquid SO_2 has been followed conductometrically. For example, titration of NOCl, CH_3.COCl, and C_6H_6.COCl, and C_6H_6 against $SbCl_5$ in SO_2 reveal a sharp break at a ratio of 1:1 and the compounds N $SbCl_{6}$,,CH_3.C Sb and C_6H_5.C Sb were isolated.

3.2.9 Reactions with organic compounds.

Liquid SO_2 is a good solvent for several organic compounds because it is relatively inert solvent. Some examples are given below,

i. **Sulphonation**

ii. **Friedal Craft reaction**

iii. **Adducts**

iv. SO_2 is capable of forming molecular adducts with some organic compounds as shown in the Table 4.

Table 4: Molecular adducts of SO_2 with some organic compounds

Compound	Adduct
$(CH_3)_3N$	$(CH_3)_3N.SO_2$
$(C_2H_5)_3N$	$(C_2H_5)_3N.SO_2$
$C_6H_5.N(CH_3)_2$	$C_6H_5.N(CH_3)_2.SO_2$
$C_6H_{5.}NH_2$	$C_6H_{5.}NH_2.SO_2$
C_5H_5	$C_5H_5.SO_2$
$p\text{-}C_6H_4(NH_2)_2$	$p\text{-}C_6H_4(NH_2)_2.SO_2$
$(C_2H_5.).CH_3$	$(C_2H_5.).CH_3.SO_2$
CH_3COOH	$CH_3COOH.SO_2$
$(C_2H_5)_2S$	$(C_2H_5)_2S.SO_2$

SO_2crystallisation (Solvation Reaction)

SO_2crystallisation are formed with the highly soluble salts and are analogous to hydrates. Examples include, $NaI.4SO_2$,$LiI.2SO_2$,$AlCl_3.SO_2$,$BaI_2.4SO_2$.

3.2.10 Redox reaction :

liquid SO_2 does not show any marked reducing or oxidising tendency butt simply act as a medium for certain redox reaction such as .

3.3 Liquid halides

Most liquid halides are usually considered as a covalent compound which functions as ionizing solvents. Liquid halides that are considered in this section are AsF_3, $AsCl_3$. $AsBr_3$ and $SbCl_3$ as well as interhalogen compounds of ICl and BrF_3.Physical properties ofAsF_3, $AsCl_3$and $AsBr_3$ are presented in the Table 5 below,

Table 5: Physical properties of arsenic trihalides

Parameter	**AsF_3**	**$AsCl_3$**	**$AsBr_3$**
Melting point (°C)	-6	-13	35
Boiling point (°C)	63	136	220
Liquid range (°C)	69	143	185
Viscosity (centipoises)	8.57 (at 20°C)	1.225 (at 20°C)	5.41 (35 °C)
Density (gcm^{-3})	2.45 (at 20°C)	2.16 (at 20°C)	3.33 (at 50°C)
Dielectric constant	5.7 (at -6°C)	12.6 (17°C)	8.8 (at 35°C)
Specific conductivity ($ohmcm^{-1}$)	2.4×10^{-5}	1×10^{-7}	1.6×10^{-7}

Self-ionization equations for arsenic chloride, arsenic bromide and arsenic fluoride are given in the equations below,

Solved problem 5

Write autoionization equation for at least three liquid halides

Solution

Self-ionization equations for arsenic chloride, arsenic bromide and arsenic fluoride are given in the equations below,

3.3.1 Arsenic chloride

The dielectric constant of arsenic chloride is relatively low which justifies why the solubilities of alkaline metal chlorides and ammonium chlorides in $AsCl_3$ are very low. However, tetra alkylammonium halides are highly soluble, $NbCl_5$ and $TaCl_5$ are sparingly soluble but $AlCl_3$,

$SnCl_4$, VCl_4 and $FeCl_3$ are very soluble in the solvent ($AsCl_3$). Some non-metals including sulphur, phosphorus and iodine readily dissolve in this solvent, although the chemistry of this solution has not been fully explored. $AsCl_3$ is not a good solvent for most metals, metal oxides and oxysalts such as sulphate and nitrate because they are either insoluble or sparingly soluble.

3.3.1.1 Chemical reactions in $AsCl_3$

Solutions of trimethylammonium chloride and antimony pentachloride have high conductivities in $AsCl_3$. A conductometric titration of these solutions gives a break at a ratio of 1:1. The salts Me_4NSbCl_6 can be isolated from the solvent according to the following reaction equation,

The feasibility of the above reaction is because antimony pentachloride has a high conductivity. Tellurium tetrachloride is also soluble in $AsCl_3$ and it dissolves to give a conducting solution. This solution when subjected to conductometric titration against Me_4NCl, gives an end point at a molar ratio of 1:1 and 1:2. The 1;1 results is associated with the possibility of isolating a solid with chemical formula, $Me_4NCl.TeCl_4AsCl_3$ while from a 1:2 solution, a solid of composition, is isolated. When $TeCl_4$ is titrated with $SbCl_5$ in $ArCl_3$, end point occurs at a molar ratios of 2:1 and 1:1 $TeCl_4$ to $SbCl_4$. From the 2:1 solution a solid of composition, $2TeCl_4SbCl_5.AsCl_2$ [in ionic form,]. However, from the 1:1 ratio, a solid compound of formula, $TeCl_4.SbCl_5$ (is formed.
Pyridine solution is also a good conductor in arsenic trichloride solvent as shown by the following equation,

The formed solution can be titrated against $SnCl_4$ and VCl_4. In both cases, the end point will be obtained at a 1:2 ratio. During the conductometric solids of compositions, $2C_5H_5N.2AsCl_3SnCl_4$ and $2C_5H_5N.2AsCl_3VCl_4$ will be respectively obtained. The ionic forms of these complexes are and respectively.

Solved problem 6

Provide suitable explanation for conductometric titration of solutions of trimethylammonium chloride and antimony pentachloride

Solution

Solutions of trimethylammonium chloride and antimony pentachloride have high conductivities in $AsCl_3$. A conductometric titration of these solutions gives a break at a ratio of 1:1. The salts Me_4NSbCl_6 can be isolated from the solvent according to the following reaction equation,

3.3.2 Arsenic triflouride

AsF_3 has a fairly high specific conductivity which has been attributed to impurities because the dielectric constant of the solvent is low. In spite of this, potassium fluoride (which is an ionic compound), rubidium fluoride and caesium flouride dissolve readily in this solvent. From the product of the dissolution, , and . This suggest that the formation of complex ion () and higher complexes in solution accounts for the solubility of these metal fluoride in AsF_3

Antimony pentaflouride also dissolves in AsF_3 solvent to yield a conductive solution from which a compound of composition, AsF_3SbF_6 can be isolated. Conductometric titration of solution of potassium fluoride and antimony pentaflouride approaches end point at a molar ratio of 1:1 and the product, $KSbF_6$ is obtained.

3.3.2.1 Chemical reactions in AsF_3

A white crystalline substance is formed when chlorine is passed into AsF_3 at 0 C. Consequently, many chlorine containing substances react feasibly with AsF_3For example,

3.3.2.2 NMR study of AsF_3

^{19}F NMR study of AsF_3 and solution of alkaline metal fluorides indicates that the alkaline fluoride has only one resonance line which was shifted slightly from that of AsF_3. The explanation was that the solvated fluoride ion or the solvated exchanges flourides sufficiently (and at rapid rate) with AsF_3 to give a single NMR resonance. Also the ^{19}F NMR spectrum of an arsenic triflouride-antimony pentaflouride mixtures reveals only one resonance peak located between the resonances of the two pure compounds. This suggests that rapid exchange of fluoride between AsF_3 and SbF_5 must have taken place.

3.3.3 Arsenic tribromide

Arsenic tribromide is not a good solvent for alkali, alkaline earth, and divalent transition metal bromides. Also salt of oxy-acids and metal oxides do not appear to have significant solubility in $AsBr_3$. $HgBr_2$, $InBr_3$, $TeBr_4$, and $BiBr_3$ are moderately soluble in $AsBr_3$. Quaternary ammonium bromides and BBr_3, $AlBr_3$, $GaBr_3$, $SnBr_4$, $TiBr_4$, Pr_5, $SbBr_3$ and $SeBr_4$ are readily soluble. Many organic compounds, including aromatic hydrocarbons, alcohols, ketones, aldehydes, esters and amines are freely soluble in the solvent.

Solvates of the type R_4NBr, $AsBr_3$ are formed with quaternary ammonium bromides and with other organic bases, B, solvates of the type *B*HBr.$AsBr_3$ are found. Both types should perhaps be formulated as containing the $^-$ ion. Cryoscopic measurements show that with anhydrous bases such as triethylamine and pyridine an equilibrium given below would be observed,

Addition of silver salts, such as silver perchlorate, at 50 °C produces diluents, which decreases the conductivity of the mixture. However, the mixture is relatively better solvent than either thionyl chloride or iodine monochloride by itself. Potassium chloride is much more soluble in the mixture than in either of the pure components. This may be due to the ability of thionyl chloride to coordinate the cation and iodine monochloride to coordinate the anion.

The significance of self-ionization in the solvent is attributed to the high specific conductivity while the dissolution affinity for chlorine and iodine contradict this assertion. The degree of dissociation of the solvent is 0.4 % at 25 °C and 1.1 % at 100 °C. The equation for self-ionization is represented by,

The existence of in $^-$ and in $KICI_2$ and $RbICI_2$ is confirmed by X-ray studies. The phase diagrams of the systems $AICI_3^-$ ICI and $SbCI_5$ICI show the existence of compounds $AICI_3$, 2ICI and $SbCl_5$, 2lCl show the existence of compounds $AlCl_3$, 2lCl and $SbCl_5$, 2lCl, which may be formulated as and . Limiting conductivities values, A_o, of 32 $ohm^{-1}cm^2\ mol^{-1}$ for KCl and 26 $ohm^{-1}\ cm^2\ mol^{-1}$ for HN_4Cl at 35 ^{0}C have been reported. Conductometric titrations of RbCl against $SbCl_5$ and KCl against $NbCl_5$ reveals end point at molar ratio of 1:1 while conductometric titrations of NH_4Cl against $SnCl_4$ show a base: acid break of 2:1.

3.3.4 Bromine Trifluoride

Fundamental solvent/ physical properties of bromine trifluoride listed in the Table shown below. Bromine trifluoride fluorinates virtually everything which dissolves in it, so studyon the solubilities is restricted to soluble inorganic fluorides. The alkali metal fluorides, silver fluoride and barium fluorides are readily soluble in the solvent. AuF_3, BF_3, TiF_4, SiF_4, GeF_4, VF_4, NbF_5, TaF_5, PF_5, AsF_5, SbF_5, PtF_4, and RuF_5 are also readily soluble. All the above are conductors in

BrF_3. Any of the alkali metal or silver or barium fluorides reacts with the Lewis fluorides to give a complex halide.

In BrF_3, several adducts are formed both by the alkali metal fluorides and by Lewis acid fluorides. Consequently the alkali metal fluorides form the adducts MF, BrF_3, which can be formulated as , Stannic fluoride forms the adduct $2BrF_3$, SnF_4 and antimony pentafluoride the adduct BrF_3, SbF_5, which may be formulated as and respectively

Table 6 : Physical Properties of Bromine Trifluoride

Properties	Value
Melting point (*C)	9
Boiling Point (*C)	126
Liquid range (*C)	117
Viscosity (centipoises	2.22(25*C)
Density (g cm^{-3})	2.8 (25*C)
Specific conductivity (ohm^{-1} cm^{-1})	8.0 x 10^{-3} (25*C)
Trouton's constant	25.6
Enthalpy of vaporization (kcal mol^{-1})	10.2

Solved problem 7

Write an equation to show the formation of adducts between BrF_3 and the following compounds

i. SbF_5

ii. NaF

iii. SnF_4

Solution

3.3.4.1 Chemical reactions in BF_3

BF_3a solvent of choice for the preparation of large number of complex flouro-compounds. For example auric fluoride can be prepared from the reaction of metallic gold with BrF_3 according the following equation,

Nitrosonium compounds may be produced from nitrosyl chloride and Lewis acid fluorides,

4.0 Summary

Liquid N_2O_4, liquid SO_2 and liquid halides are examples of aprotic solvents, which do not contain hydrogen, which means their basic and acidic character cannot be viewed in terms of Arrhenius theory but by Bronsted –Lowry and Lewis theory. Liquid dinitrogen tetroxide does undergo autoionization, reacts with metals and is a solvent suitable for solvolytic and adduct formation reaction. Liquid SO_2 undergoes autoionization, neutralization reaction, precipitation reaction, metathetical reaction, amphoteric reaction, sulphonation reaction and Fredel- Craft reaction. Common liquid halides are AsF_3, $AsCl_3$. $AsBr_3$ and $SbCl_3$. Bromine triflouride is an ionic liquid solvent. It dissolves several fluorides of metalloid

5.0 Conclusion

Liquid N_2O_4, liquid SO_2 and liquid halides are essential non- aqueous solvent that play solvent roles that cannot be met by aqueous solvent. For example, Dinitrogen tetroxide has been widely used as a medium for chemical reactions and as a reactant in liquid phase. Liquid SO_2 has low boiling point that favours ease of evaporation, which encourage its removal from the reaction mixture. It has unique solvating powers for both covalent and electrovalent compounds. Liquid SO_2 is an inert solvent and is also used as diluent for the super acid medium ($CHSO_3F$-SbF_5) which helps in reducing its viscosity without compromising its acidity. Liquid $BrF_3$is a solvent of choice for the preparation of large number of complex flouro-compounds

6.0 Tutor marked assignment

1. Write suitable equation to show how BrF_3 can act as a solvent for the production of nitrosonium compounds.
2. What are the special properties of liquid SO_2
3. Write (one for each) suitable equation to support the following properties of liquid SO_2
   i. Neutralization reaction
   ii. Solvolysis reaction

   iii. Precipitation reaction
   iv. Metathetical reaction
   v. Amphoteric reaction
   vi. Complex formation reaction
   vii. Sulphonation reaction
   viii. Fridel Craft reaction
   ix. Adducts formation with organic compound
   x. Redox reaction

4. List four liquid halides that are appropriate as solvents

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MODULE 3

UNIT 3: Protic solvents

1.0 **Introduction**
2.0 **Objectives**
3.0 **Main content**
    3.1 **Liquid ammonia**
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1.0 Introduction

This section considers solvent properties of some protic solvents including liquid ammonia, aceticacid anhydrous tetraoxosulphate (VI) acid and hydrogen fluoride. The commonest feature of these solvents is their ability to produce proton, which implies that they are aligned to Bronsted-Lowry acid and base. For example, they undergoes self-ionization according to the following equation,

The self-ionization equation reveals that these solvents can behave as an acid or base depending on the proton affinity of the substance that they solvate. For example, any substance that will produced, , and in liquid ammonia, acetic acid, anhydrous sulphuric acid and hydrogen fluoride will be an acid respectively. Similarly if any substance produces, , and in liquid ammonia, acetic acid, anhydrous sulphuric acid and hydrogen fluoride respectively will be regarded as a base. Among these solvents, liquid ammonia seems to be more universal than others. Therefore much reaction details are available for liquid ammonia than acetic acid, anhydrous tetraoxosulphate (VI) acid and hydrogeflouride. Brief introduction is also provided for superacids solvents.

2.0 Objectives

i. To know physical properties of liquid ammonia, acetic acid and anhydrous sulphuric acid that enhances its solvent properties

ii. To study autoionization property of liquid ammonia, acetic acid and anhydrous sulphuric acid

iii. To compare the autoionization property of liquid ammonia, acetic acid and anhydrous sulphuric acid with each other and with aqueous medium.

iv. To study and comprehends the various reactions that are carried out in liquid ammonia, acetic acid and anhydrous sulphuric acid

v. To compare the solvent behaviours of ammonia, acetic acid and anhydrous sulphuric acid with that of water

vi. To introduce super acids and hydrogen fluoride as solvents

3.0 Main content

3.1 Liquid ammonia

Liquid ammonia is a widely use nonaqueous solvent. At atmospheric pressure, ammonia(NH_3), is present as aliquid at temperatures below -33.6 °C (-28.5 °F). At 10 bar, the condensation/boiling point is 25 °C (77 °F) The melting and boiling points of liquid NH_3 are lower than those of water while its liquid range is -77 to -33℃ , which make it difficult for handling. Just like in water, liquid NH_3 also show hydrogen bonding but NH_3 molecules are less strongly associated because nitrogen is less electronegative than oxygen. Therefore freezing point and boiling point of ammonia are less. The dielectric constant of liquid ammonia (22 at -33℃) is lower than that of water (78.5 at 25℃). Therefore liquid ammonia is expected to be a poor solvent forionic compounds. However, the solvent has lower viscosity (0.254cp at -33℃) than water (0.959cp at 25℃).. Consequently, liquid ammonia exhibit greater ionic mobility and thereby compensate to some extent for the effect of dielectric constant.

Solved problem 1

Give reasons for the following solvent property of liquid ammonia

i. liquid ammonia exhibit greater ionic mobility

ii. Liquid ammonia is difficult for handling

iii. Liquid ammonia is expected to be a poor solvent for polar substances compared to water.

iv. Hydrogen bond is weaker in liquid ammonia than in water

Solution

i. Liquid ammonia has lower viscosity than water

ii. The liquid range of liquid ammonia is -77 to -33℃

iii. The dielectric constant of liquid ammonia (22 at -33℃) is lower than that of water (78.5 at 25℃).

iv. Nitrogen is less electronegative than oxygen

3.1.1 Self ionization

As stated before, liquid ammonia undergoes self-ionization according to the following equation,

This can be compare to that of water which is represented as,

The extent of auto ionization of liq.NH_3 is less than that of water because oxygen is more electronegative than nitrogen. Besides, the specific conductance of ammonia is low compared to water. The ionization constant of water and that of ammonia are expressed below,

3.1.2 Solvent advantages of liquid ammonia over water

Inspite of its low dielectric constant and specific conductivity, liquid ammonia has some advantages as a solvent over water. Some of these advantages are listed below,

i. Liquid ammonia is a poor conductor of electricity indicating that it can be used to study poorly ionize compounds that are not soluble (or too soluble) in water.

ii. Specific heat of liquid ammonia is more than that of water. This property gives a wider temperature tolerance range than water

iii. Unlike water, liquid ammonia has critical temperature and pressure

iv. Liquid ammonia is a solvent than is less associated than water and could be a better solvent for some organic compounds.

However, some of the disadvantages of liquid ammonia as a solvent are,

i. It is not suitable for a high temperature and pressure study because its liquid range is -77 to -33 °C.

ii. It requires seal tubes for reactions to be carried out because it is hygroscopic.

iii. It has a very offensive odour

Liquid ammonia is a good solvent for some organic compounds including ester, amines and alcohol. SCN^-, I^-,NO_2^-, NO_2^- and ClO_4^- are also soluble in liquid ammonia but fluoride ion, chloride , bromide, carbonate, sulphate, hydroxyl and sulphide ions are not soluble in liquid ammonia.

The differences in solvent properties of water and ammonia can give some advantages in chemical analysis as the underlisted example suggests,

In the above equations, it is clearly evidence that synthesis of ammonium nitrite using ammonium chloride can best be carried out using liquid ammonia as a solvent instead of water because the product is soluble in water (and not soluble in liquid ammonia) indicating that after formation, it will dissolve in water and generate nitrogen gas whereas in liquid ammonia, it can easily be precipitated out.

3.1.3 Reactions of liquid ammonia

3.1.3.1 Acid base reaction

Acid is definedas substances that produces hydrogen ion or proton. That means any substance that contain replaceable hydrogen ion is an acid. Liquid ammonia can behave as an acid or as abase according to the following equation,

Consequently, substance that produces ammonium ions (NH_4^+) in liquidNH_3 behave as acid while those that produces amide ions(NH_2^-) behave as base. For examples NH_4Cl is an acid because it produces in liquid ammonia while KNH_2 is a base because it produces in liquid ammonia

3.1.3.2 Protolysis

Protolysis is a term use to describe the process of proton transfer. This means the substance that donate proton is the acid while the one that accepts is the base. Most compounds are capable of donating proton to liquid ammonia. Some of them are urea, acetamide ,sulphamide etc. In the process, this compounds act as acid in liquid NH_3.

Acid- base neutralization

In aqueous medium, acid base neutralization yields salt and water (i,e. the water is regenerated). Similarly acid base neutralization in liquid ammonia yields salt and ammonia as shown in the following example,

The generation of ammonia can be compared with the generation of water as shown in the following equations,

Some compounds such as $Zn(NH_2)_2$ exhibit amphoteric behaviour in liquid ammonia depending on the salt. That means it can acts as an acid or as a base (see equations below)

In the first case, $Zn(NH_2)_2$ acts as a base because it produces NH_3 while it acted as an acid in the second case.

Substances which furnishes in liquid ammonia are called ammono acid (example, $Zn(NH_2)_2$) while those that furnishes are called ammono base (Example KNH_2)

3.1.3.3 Ammonolysis

Ammonolysis can be likened to hydrolysis reaction in water. It involves dissociation of ammonia solvent to produce and . Some ammonolysis reactions are given below

The common feature of the above equations is that and ions are produced. Another example of ammonolysis is

Halides which undergo ammonolysis at the boiling point of liquid ammonia give rise to mixtures of primary, secondary and tertiary amines. For example,

where X = Cl, Br or I

3.1.3.4 Ammoniation

Ammoniation is defined as a reaction in which ammonia is added to other molecules or ion by covalent bond formation utilizing the unshared pair of electrons on the nitrogen atom through ion dipole electrostatic interaction. In most cases of ammonation, the ammonia acts as a Lewis base to the Lewis acid (as shown in the under listed equations),

Thus the reaction of SiF_4 with NH_3 produces $SiF_4(NH_3)_2{\cdot}2NH_3$ at −40°C. Warming the compound to 25°C leads to $SiF_4(NH_3)_2$, which is stable at room temperature (Baer and Kraus, 2016). Summary of similar ammoniation reaction with BF_3 is also presented in the equation below.

Ammonation can also occur if the ammonia is a ligand to a cation. For example, in the formation of $[Pt(NH_3)_4]^{2+}$, $[Ni(NH_3)_6]^{2+}$ and $[Cr(NH_3)_6]^{3+}$

3.1.3.5 Precipitation reaction

Precipitation involving liquid ammonia is a double decomposition reaction and is attributed to the differences in solubilities of various substances in the solvent. Liquid ammonia display better precipitation reaction than water. For example, in aqueous medium,

However, in liquid ammonia,

3.1.3.6 Complex formation reaction

Liquid ammonia is capable of encouraging the formation of complexes similar to the reactions occurring in the aqueous systems. For example

Aqueous solution prepared from copper(II) chloride contain a range of copper(II) complexes depending on concentration, temperature, and the presence of additional chloride ions. These species include blue color of $[Cu(H_2O)_6]^{2+}$ and yellow or red color of the halide complexes of the formula $[CuCl_{2+x}]^x$

3.1.3.7 Formation of ammoniates

Just as aqueous medium forms hydrates with some inorganic salt. Liquid ammonia forms ammoniates with many inorganic salts. For example,

3.1.3.8 Redox reaction

Strong oxidizing agent exhibit weaker oxidizing properties in liquid ammonia compared to aqueous solvent. For example, in aqueous medium, trioxonitrate (V) acid is a strong oxidizing agent but in liquid ammonia, it does not act as an oxidizing agent. On the other hand, reducing agents display increasing reactivity in liquid ammonia. Some reduction reactions involving liquid ammonia are given below,

In the above reactions, it is seen that liquid ammonia reduces CuI ,$KMnO_4$ to Cu and $KMnO_4$respectively. Therefore, liquid ammonia is not a good solvent for oxidation reaction but for a reduction reaction. Other examples are,

Liquid ammonia dissolves group 1metals and other electropositive metals including calcium, strontium, barium, magnesium, aluminium and others. At low concentration (about 0.06 M), deep blue solution is formed due to the production of $Na(NH_3)^{n+}$, and the anion i.e. solvated electron $e(NH_3)^{n-}$. The solvated electrons (which are readily available) provide a strong reducing property to liquid ammonia. The blue colour is independent of the metal that is dissolved.

Increase in the concentration of the metal ion will change the colour to bronze and reveals metallic appearance. Such solutions are good conductor (the electrical conductivity is also due to the ammoniated cations and ammoniated electrons)and are paramagnetic. The paramagnetic character decreases with increasing concentration.

3.2 Acetic acid

Acetic acid is an associated solvent and exists as a dimer in the liquid state. It has a wide range liquid range extending from 16.6 to 118 °C. It is non- ionic and stable under ordinary conditions. However, its major disadvantage is the difficulty involves in the preparation of anhydrous acid. The dipole moment of acetic acid is zero and the dielectric constant is as low as 9.7. Due to some shortcomings arising from its physical properties, acetic acid is expected to be a poor solvent for ionic compounds. However, several ionic compounds are soluble in acetic acid. Some of the major solvent properties of acetic acid are highlighted below,

3.2.1 Autoinonization and acid base reactions

Acetic acid undergoes autoinonization according to the following equation,

Application of solvent system of acid base definition indicates that the solvated proton is an acid while is a base. Neutralization reaction between acetate which behaves as a base is shown by the following equation,

Weak organic bases like acetamide and acetanilide cannot be titrated in aqueous medium but they could be titrated in CH_3COOH medium. Perchloric acid which is a strong acid that exhibit the highest dissociation in CH_3COOH serves as a titrant. The neutralization reaction is normally monitored potentiometrically and by indicators. The weak organic bases function as very strong bases because of the possibility of the following reaction,

3.3.2 Precipitation reactions

Possible precipitation reactions that can occur in liquid acetic acid are presented below,

3.3.3 Amphoteric reaction

Compounds such as $Zn(CH_3COO_2)$displays amphoteric behaviour with liquid CH_3COOH according to the following equation,

3.3.4 Complex formation reactions

As in aqueous medium, several complex formation reactions are feasible in liquid CH_3COOH. For example Fe^{3+} and CNS^- react in the solvent medium to form red soluble complex according to the following equations,

Similar reaction also occurs in water. This reaction is often used in qualitative test for Fe^{3+} in aqueous medium because of the formation of reddish brown complex.

3.3.5 Solvolysis reactions

Some of the solvolysis reactions in liquid acetic acid are given below,

3.3 Anhydrous sulphuric acid

Boiling point of anhydrous sulphuric acid is 300 and its dielectric constant is 110. The viscosity of anhydrous H_2SO_4 is about 25 times higher than that of water. Therefore,solutes dissolve very slowly in sulphuric acid and it is difficult to crystallise from H_2SO_4.

3.3.1 Autoinonization

Anhydrous H_2SO_4autoionises to give $H_3SO_4^+$ and $H_2SO_4^-$ ions according to the following equation,

It follows from the above that any species producing HSO_4^- ion will act as base and any chemical species producing $H_3SO_4^+$ ion acts as acid in H_2SO_4.

3.3.2 Acid base reaction

$KHSO_4$ acts as a base in anhydrous sulphuric acid

Species that are basic in water are also basic in H_2SO_4 as the following equations compares, Water behaves as base in anhydrous sulphuric acid because its proton donation affinity is greater than that of water

Species containing lone pair of electrons can easily accept a proton from H_2SO_4 and acts as bases. Consequently, amides such as urea ,which acts as acid in liquid NH_3 and neutral in water but are bases in anhydrous H_2SO_4

Most acids behave as base in anhydrous sulphuric acid. The very strong perchloric acid behaves as weak acids in anhydrous H_2SO_4.

3.3.3 Dehydrating Action

H_2SO_4 is a strong dehydrating agent and extract water even from chemical compounds for example,

3.3.4 Super-Acids:

Acids which behave as strong acid solvents are termed as super acids . Example of such acid is $[HB(HSO_4)_4]$,whose solution can be prepared in sulphuric acid. It behvaves as exceptionally strong acid. However, it is not isolated as such but its solution can only be prepared. Other super acids in H_2SO_4 solution are $H_2Sn(HSO_4)_4$ and $H_2Pb(HSO_4)_4$.

Solved problem 2

(a) Use suitable equations to explain the acid and basic behaviour of water, amide and perchloric acids in sulphuric acid solvent.
(b) Write equation to show dehydrating action of sulphuric acid

Solution

(a) Water behaves as base in anhydrous sulphuric acid because its proton donation affinity is greater than that of water

Species containing lone pair of electrons can easily accept a proton from H_2SO_4 and acts as bases. Consequently, amides such as urea ,which acts as acid in liquid NH_3 and neutral in water but are bases in anhydrous H_2SO_4

Most acids behave as base in anhydrous sulphuric acid. The very strong perchloric acid behaves as weak acids in anhydrous H_2SO_4.

(b)

3.4 Hydrogen fluoride

Liquid hydrogen fluoride is a protonic solvent whose solvent properties and dissociating power are greater than that of water . Its viscosity is very low. It has a density of 1.015 g/cm^3, boiling point, 19.37 °C and melting point, -83.55 °C. It is an excellent solvent for a large number of organic and inorganic substances. Behavioural differences as a solvent from water towards electrolytes capable of dissociating have been observed. These differences are due to the higher tendency for liquid HF to donate proton more than water. The autoionization equation for liquid HF is given below,

By convention, any substance which produces from HF is an acid while those that produce F^- from HF are base.

4.0 Summary

Protic solvents closely behave like aqueous solvent due to their abilities to undergo autoionization and closely related reactions. For example, liquid ammonia has some advantageous solvent properties over water because of its long liquid range. Among the studied protic solvent (i.e liquid ammonia, anhydrous sulphuric acid, acetic acid and hydrogen fluoride), liquid ammonia is the most reactive solvent. Unlike water, it has critical temperature and pressure. Anhydrous sulphuric acid is excessively reactive and is a suitable solvent for reactions that are relatively inert.

5.0 Conclusion

Protic solvents have unique potential of undergoing autoionization, which makes them to behave closely like water. They can behave as an acid or as a base and are therefore versatile in their laboratory and industrial applications.

6.0 Tutor marked assignment

1. What are the common features of liquid ammonia, acetic acid, anhydrous sulphuric acid and hydrogen fluoride as a solvent?
2. Write suitable equations to show that species that are basic in water are also basic in H_2SO_4 solvent.
3. What are the factors that differentiate solvent behaviourable characters of HF from that of H_2SO_4
4. List two advantageous and two disadvantageous solvent properties of liquid ammonia
5. With suitable equations, compare self-ionization potential of liquid ammonia and that of water and comment on their acid –base behaviour.
6. Define protolysis and give example of protolysis in liquid ammonia (equation is required)
7. Define ammonolysis and give example of protolysis in liquid ammonia (equation is required)
8. Define ammonation and give example of protolysis in liquid ammonia (equation is required)
9. Write at least one equation to show the following solvent properties of acetic acid

i. Autoionization
ii. Precipitation
iii. Solvolysis
iv. Amphoterism

7.0 References

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