

CHAPTER: 5

CONCLUSIONS AND SCOPE FOR FUTURE WORK

Conclusion:

The study undertaken by the author broadly can be categorised into five parts .They are

1. Dielectric studies
2. Thermodynamic studies
3. Ultrasonic studies
4. Densimetric studies
5. Optical studies.

It is essential to point out that the experimental methods chosen for this studies in the ETIPM (Eigen and Tomm Ion Pair Mechanism) using copper sulphate (penta hydrate) ionic liquid in the binary solvent mixture of water and ethylene glycol for the ultrasonic, densimetric , and optical studies, supplement those worked by Chandrika Akilan of Murdoch University in her Doctoral work in the year 2008. C. Akilan used UV-Visible Spectrophotometry, Cu (II) ion selective Electrode Potentiometry, Dielectric Relaxation Spectroscopy and titration calorimetry. It is interesting to note that there is an excellent agreement in the findings of the author and those of C. Akilan.

1.Dielectric studies:

In these studies, Glueckauff model for the lowering of dielectric constant of an electrolytic solution was applied to chosen sulphates, nitrates and chlorides (all put together twelve electrolytes) of transition metal cations. The molal concentrations of the electrolytes studied are from 0.1 to 1.4 in steps of 0.05.

The operational amplifier circuitry, including a precise temperature variation determination is used in this studies, is designed and fabricated by the author. A dielectric cell is designed for the experimental determination of the dielectric constant of the

chosen electrolytic solutions. This cell in principle is a parallel plate capacitor, and the inter space can be filled with the electrolytic solution. Knowing the capacitance with and without the solution and the pre estimated cell constant, the dielectric constant can be evaluated. A very good agreement is found between the experimental dielectric data, and that of the literature.

2. Thermodynamic studies:

The above obtained dielectric data is used to apply Pitzer model and Bromley model, which are the developments for the Debye- Huckel model, for the evaluation of the activity and osmotic coefficients. The data so obtained when presented as plots with square root of concentration as abscissa and activity and osmotic coefficients and Debye-Huckel coefficient A_ϕ as ordinate. The discrete evidences for the formation of ion pairs are reflected from the graphs, in the form of changes in slope. The findings from our plots were compared with the values from literature. The Pitzer's model gave conspicuous dissonance in the case of variation of activity coefficient and osmotic coefficient data with \sqrt{m} . This has to be attributed to the inaccuracies in the crude approximations about the virial coefficients involved in the basic principles of the Pitzer's model. Also the evaluations did not account for the Glueckauf's lowering of the dielectric constant and they are to be corrected suitably with the impregnation of the variation of dielectric constant with concentration of the electrolyte solution. This can be done if a suitable model would become available in the near future for this purpose.

The Osmotic coefficient data with Pitzer's model were observed to become negative for sulphates of copper, nickel and manganese and cobalt cations, at molal concentration of 0.6 and more. However the values cited from the Robinson and Stokes [82] did not show this variation. Deviations are explained on the basis of erroneous approximations involved in the model. Bromley's four presumptions applied several approximations to the Guggenheim's equation, which end up to mask the microscopic delicacies in the ETIPM. So the author failed to draw any good outcome out of the application to the Bromley's model. It is interesting to point out that this data showed reasonable agreement, with that available from the standard reference of Robinson and Stokes.

The activity and osmotic coefficient and A_ϕ data with Pitzer's model revealed conspicuous traces of the ETIPM in the case of all the chosen electrolytic systems. All the characteristics pointed out by C. Akilan were traced in the results, and were later confirmed in the other studies discussed below.

Excess Gibbs energy evaluation is done using the equations of Lu and Maurer model, developed by combining ionic solvation equilibriums and physical interaction forces. However the equations used are not in a position to reflect the details of the happenings about the various interactions involving ions and solvents.

3. Ultrasonic studies:

The experimental methods chosen for our studies in the ETIPM, using copper sulphate (penta hydrate) ionic liquid in the binary solvent mixture of water and ethylene glycol, were all available Antonpaar, Austrian made setup. This setup utilises modern design and principles and is most accurate to the pharmaceutical precision. As little as 5ml of the ionic liquid of a composition can deliver Acoustic, Densimetric and Refractive index data at all the five chosen temperatures in a span of a few minutes. The details of the setup are presented in the experimental techniques chapter. A very accurate electronic digital micro balance, Sartorius CPA- 225D with six and half digit display, for weight determination, is used. In the ultrasonic studies chapter, data of Ultrasonic Velocity, Density, Adiabatic Compressibility, Acoustic Impedance, Inter molecular free length, Relative association, Apparent Molal Volume, Apparent Molal Compressibility, Surface Tension and Refractive Index for the Ionic liquid of copper sulphate in the aqueous Ethylene Glycol binary solvent system were presented.

The data appears in the form of tables as well as two sets of plots. In the first set, each of the six parameters is chosen as ordinate separately and concentration as abscissa. Separate plots of each of the composition and temperature are presented. Similarly in the second set the ordinates remain the same but the abscissa is the composition of the binary solvent system. Separate plots of each of the concentration and temperature are presented.

A detailed analysis of all these plots in the light of all the possible Ion- Ion interaction, Ion-Solvent interactions and Solvent- Solvent interaction is presented. Since

the data was available up to a molal concentration of 0.6, the author was unable to trace all the ion pairs obtained in the similar studies of C. Akilan. All the traits about the formed ion pairs were critically analysed. Striking confirmation, including the arguments about the physio- chemical mechanisms, by several other studies by a host of authors from literature were cited in confirmation of the findings of the author.

4. Densimetric studies:

This chapter presents the data on apparent molal volume and apparent molal compressibility, both of which depend on the variations in density and ultrasonic velocity. The data appeared in the form of tables as well as two sets of plots. In the first set each of the two parameters is chosen as ordinate separately and concentration as abscissa. Separate plots of each of the composition and temperature are presented. Similarly in the second set the ordinates remain the same but the abscissa is the composition of the binary solvent system. Separate plots of each of the concentration and temperature are presented. A detailed analysis of all these plots in the light of all the possible Ion-Ion interaction, Ion- Solvent interaction, and Solvent- Solvent interaction is presented. Since the data was available up to a molal concentration of 0.6, the author was unable to trace all the ion pairs obtained in the similar studies of C. Akilan. All the traits about the formed Ion pairs were critically analysed. Striking confirmation, including the arguments about the physio- chemical mechanisms, by several other studies by a host of authors from literature was cited in confirmation of the findings of the author.

5. Optical studies:

Refractive index, data obtained by Antonpaar's Abbe type refractometer setup, is presented in this chapter. Surface tension of ionic liquid also presented in this part. The data appears in the form of tables as well as two sets of plots. In the first set, the refractive index and surface tension are chosen as ordinates separately and concentration as abscissa. Separate plots of each of the composition and temperature are presented. Similarly in the second set, the ordinates remain the same but the abscissa is the composition of the binary solvent system. Separate plots of each of the concentration and temperature are presented. A detailed analysis of all these plots is attempted. However to

detail some of the physiochemical happenings supplementary data is necessary and this would be included for the future scope of the work. However broadly The features analysed suggest the outlines about the ETIPM, for which several literature supporting outlines are given.

Scope For future Work:

The following aspects are proposed to be taken up in the extension work of this Thesis.

1. Determination of temperature dependent dielectric constant data using the operational amplifier set up for the chosen electrolytes for which the data is available at the authors end in aqueous alcoholic solution and aqueous ethylene glycol binary solvent of solutions and evaluation of their Claussius Mossoti Factor (CMF), and polarizability for the ionic liquid systems and also to incorporate them (on an emperical basis to start with) into the NRTL and UNIQUAC thermodynamic models for the evaluation of thermodynamic parameters, with the available data.
- 2 To apply Wang and Anderko models for the evaluation of the dielectric constants of the binary solvent ionic liquid systems, as functions of temperature and concentration. Also Monte-Carlo simulations using Molecular Dynamics and to study details of ETIPM using that data in conjunction with data available at the authors end, for the evaluation of Association Constants, for all the possible parameters, for which results are reported in this thesis.

Appendix- A

Electrolytes used in the dielectric and thermodynamic studies

S.No	Electrolyte	Formula	Molecular Weight
1.	Copper sulphate	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	249.69
2.	Nickel sulphate	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	262.86
3.	Cobalt sulphate	$\text{CoSO}_4 \cdot \text{H}_2\text{O}$	173.01
4.	Manganese sulphate	$\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$	223.06
5.	Copper chloride	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	170.48
6.	Nickel chloride	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	237.71
7.	Cobalt chloride	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	237.93
8.	Manganese chloride	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	197.91
9.	Copper nitrate	$\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	295.64
10.	Cadmium nitrate	$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	308.47
11.	Cobalt nitrate	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	291.04
12.	Chromium nitrate	$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	400.15

Preparation of Solutions in Acoustic Study

Copper Sulphate : Molecular Weight: 249.69 gm/mole.

50 ml water + 1.2484 gm Copper Sulphate gives 50 ml of 0.1M (gr.mol/lit)salt solution.

50 ml water + 2.4968 gm ,, gives 50 ml of 0.2M salt solution.

50 ml water + 3.7452 gm ,, gives 50 ml of 0.3M salt solution.

50 ml water + 4.9936 gm ,, gives 50 ml of 0.4M salt solution.

50 ml water + 6.2420 gm ,, gives 50 ml of 0.5M salt solution.

50 ml water + 7.49048 gm ,, gives 50 ml of 0.6M salt solution.

Salt Solution	Solvent (EthyleneGlycol)	Percentage composition	Ratio
0 ml	5.0 ml	0%	0:100
0.5 ml	4.5 ml	10%	10:90
1.0 ml	4.0 ml	20%	20:80
1.5 ml	3.5 ml	30%	30:70
2.0 ml	3.0 ml	40%	40:60
2.5 ml	2.5 ml	50%	50:50
3.0 ml	2.0 ml	60%	40:60
3.5 ml	1.5 ml	70%	30:70
4.0 ml	1.0 ml	80%	20:80
4.5ml	0.5 ml	90%	10:90
5.0ml	0 ml	100%	100:0

Dielectric Constant Data of Aqueous Ethylene Glycol at different temperatures.

% weight of Ethylene glycol in BSM	298K	303K	308K	313K	318K
0(pure water)	78.303	76.546	74.823	73.151	71.511
10	75.7194	73.8875	72.1266	70.4237	68.7682
20	73.1554	71.3151	69.5491	67.8437	66.1877
30	70.1839	68.3618	66.6151	64.9300	63.2950
40	66.8050	65.0277	63.3248	61.6827	60.0901
50	63.0186	61.3128	59.6781	58.1018	56.5731
60	58.8246	57.2168	55.6749	54.1871	52.7438
70	54.2232	52.7401	51.3153	49.9388	48.6023
80	49.2137	47.8819	46.5990	45.3569	44.1490
90	43.7979	42.6441	41.5270	36.3422	39.3829
100(pure EG)	37.9740	37.0248	36.0981	31.7460	34.3049