Thermodynamic properties of binary liquid mixtures of Ethylene Glycol (EG) with different amines at 308.15KΨ

Dr. K.G. Neerajakshi
Lecturer
Chemistry Department
A.A.S. College, Adoni, Andhra Pradesh, India

Abstract : Densities and viscosities of the binary liquid mixtures of Ethylene (EG) + n-butylamine (NBA), + sec-butylamine (SBA) + tert-butylamine (TBA), + n-hexylamine (NHA), + n-octylamine (NOA) and + cyclohexylamine (CHA) have been measured at 308.15K. From the experimental results the excess molar volume (V^E), excess viscosities (η^E), and excess molar Gibbs free energy of activation of viscous flow (G^{*E}) have been computed as a function of composition. The parameter d^1 of the Grunberg and Nissan expression has been computed. The values of V^E are negative whereas the values of η^E, G^{*E} and d^1 are positive. Deviations from the ideal behavior are discussed from the point of view of the molecular interactions present between the unlike molecules. The strength of these interactions is related with the chain length of the amines. The results are discussed in terms of the theories of non-electrolyte solutions.

***IndexTerms* - molar volume , Nissan expression , viscosities.**

I. INTRODUCTION

Viscosities and desitites for the binary liquid mixtures of Ethylene Glycol (EG) with a number of amines have been taken up for the first time for measurements. The results obtained for the systems of Ethylene Glycol + n-butylamine (NBA), + sec-butylamine (SBA) + tert-butylamine (TBA), + n-hexylamine (NHA), + n-octylamine (NOA) and + cyclohexylamine (CHA) are reported in this paper.

Densities and viscosities of the systems mentioned were measured at 308.15K. Excess functions like, excess molar volume (V^E), excess molar free energy of activation of viscous flow (G^{*E}) and Grunberg and Nissan interaction parameter (d^1) were calculated from the experimental results at different mole fractions of Ethylene Glycol (EG). The values obtained are discussed in terms of molecular interations

II. RESULTS AND DISCUSSIONS

The measured density (ρ) and viscosity (η) data for mixtures of ethylene glycol (EG) + n-butylamine (NBA), + sec-butylamine (SBA), + tert-butylamine (TBA), + n-hexylamine (NHA), + n-octylamine (NOA) and + cyclohexylamine (CHA) are used to calculate the excess molar volume (V^E), excess viscosity (η^E), excess Gibbs free energy of activation of viscous flow (G^{*E}) and Grunberg-Nissan interaction parameter (d^1) and the results are presented in Tables 1 to 4

The variation of these parameters η, V^E, η^E, G^{*E} with mole fraction of Ethylene Glycol (X_{EG}) for the systems under study are graphically shown in Figs. 1 to 4 respectively.

As expected, pure EG has the highest viscosity (Tables 1 to 6) than all the other amines. Fig. 1 shows the variation of viscosity of these binary systems with mole fraction of Ethylene Glycol (X_{EG}). It is observed that greater viscosity is obtained in Ethylene Glycol rich region and is in consistence with the idea that the molecules of Ethylene Glycol are strongly self-associated.

A perusal of Fig. 1 reveals that as the mole fraction EG increases, the possible hydrogen bonding and dipole-dipole interactions between EG and amine molecules-overrides. The dissociate effect leading to a sharp increase in dn/dc values. Moreover, the sharp increase in η and x, principally in EG rich region. This is supported by the view[27] that viscosity of a system is determined mainly by the bulky are less mobile entities of the system. One can assume the existence of bulky entities, EG-Amines, which might involve hydrogen bonding between unlike molecules and also the entities EG-EG in EG rich mixtures owing to its tendency to preserve structural order.[28]

It is further observed from the Fig. 1 that the viscosity of these mixtures varied non-linearly with increase in Ethylene Glycol content, which indicates the presence of intermolecular interactions between components.

It is clear from the Fig. 2 that the negative V^E values are obtained over the entire composition range for all these systems which indicates the presence of strong molecular interactions between the components of the mixture. It is also observed from the Fig. 2 and Tables 1 to 6 that the numerical values of V^E fall in the sequence.

EG + TBA < + SBA < + NBA < + NHA < + NOA < + CHA

From Fig. 2, it is further observed that V^E values become less negative as the chain length in amines increase. The negative V^E vs X_{EG} plots were found to be large and unsymmetrical with maxima between 0.4 to 0.5 mole fraction of Ethylene Glycol.

Several effects may contribute to the value of V^E and three different effects may be considered as being important.

(a) break up of hydrogen bonds and dipolar interactions in Ethylene Glycol and intermolecular hydrogen bonded interactions in amines,
(b) interstitial accommodation of one component into the other, and
(c) the possible hydrogen bond interactions between unlike molecules.

The interaction between Ethylene Glycol and amines due to the formation of strong intermolecular hydrogen bonded complexes would produce negative excess volume. The negative excess volumes of Ethylene Glycol + amines over the whole range of composition suggest that the contraction which accompanies the formation of strong hydrogen bonded complexes is sufficient to compensate the physical effect caused during mixing.

From Fig. 2 it is clear that the values of excess volumes (V^E) increases as the chain length of the normal amines increases and they fall in the following order: NBA < NHA < NOA. This order in the case of normal amines may be ascribed to the effect of chain length and the degree of polymerization of amines in pure state and the strength of complex formation between unlike molecules. This order further also ascribed to the effect of interaction between the two components becomes less predominant as the alkyl group of the normal amines increase. A similar observation was made by Pikkarainen[32] in case of excess volume studies for the binary liquid mixtures of N, N-Dimethylacetamide with aliphatic alcohols.

It is further observed from Fig. 2 that the negative V^E values increased with increase in branching of amines and they are in the following order:

n-butylamine < sec-butylamine < tert-butylamine

In the case of branched amines the excess volumes are higher than the respective normal amines. The more negative V^E values of Sec butyl amine, tert-butyl amine than their corresponding normal amine (n-butyl amine) may be due to two factors. First, it could be a result of larger positive effect due to breakdown of H-bonded structure of primary amine. Secondly it could be a result of primary amine having a more compact structure than the secondary and tertiary amine which has large Floppy alkyl groups attached. This means that Ethylene glycol molecule cannot back into the primary amine structures as easily as they could into the secondary or tertiary amines. Narayana Swamy etal.[33] made a similar observation in case of binary liquid mixtures of Acetonitrile and amines. It is also observed that in the case of cyclohexylamine the excess volume is less negative than the corresponding n-hexylamine. This abnormal behaviour of the cyclic amine may be due to the steric factors. Paul and Singh[34] made a similar observation.

Thus, in the present study the negative V^E values for Ethylene Glycol + amines indicate the predominance of hydrogen bonding interactions between them over the other effects.

Fig. 3 shows that η^E values are positive for the whole composition range for all the systems under study. A correlation between signs of η^E and V^E has been observed for a number of binary solvent systems[35,36] η^E being positive where V^E is negative or vice-versa. In general for systems, where dispersion and dipolar interactions are operating η^E values are found to be negative, whereas Charge transfer and hydrogen bonding interactions lead to the formation of complex species between unlike molecules thereby resulting in positive η^E values[37].

The algebraic values of η^E for all the mixtures of Ethylene Glycol + amines fall in the order.

EG + CHA > + NOA > + NHA > + NBA > + SBA > + TBA

This order suggests that hydrogen bonding between unlike molecules increase with increase in chain length in amines. A similar observation was reported by Krishnaiah et al.[38]

The variation of excess Gibbs free energy of activation of viscous flow (G^{*E}) with X_{EG} is shown graphically in Fig. 4.

Reed and Taylor[12] and Meyer et al.[13] reported that G^{*E} parameter can be considered as a reliable criterion to detect or exclude the presence of interactions between unlike molecules. According to these authors, the magnitude of the positive values is an excellent indicator of the strength of specific interactions. G^{*E} values for the systems under study suggest the following order.

EG + NBA > + SBA > + TBA > + NHA > + NOA > + CHA

The above said positive values of G^{*E} are in accordance with the viscosity results of these mixtures explained above. Similar behaviour was reported by Krishnaiah et al.[38] in case of G^{*E} values for mixtures of 2-alkoxy ethanols in water.

Fort and Moore[39] and Ramamoorthy[40,41] reported that for any binary liquid mixture, the positive value of d^1 indicates the presence of strong interactions and the negative value of d^1 indicates the presence of weak interactions between the components. On the basis the d^1 values obtained in the present study for all the six systems (cf. Tables 1 to 6) confirm the presence of strong interactions between the component molecules. A similar observation was made by Subha et al.[42] from the d^1 values of the binary liquid mixtures of propionic acid with alcohols.

In conclusion, it may be said that the observed variation of the properties of the mixtures studied support the view that the interactions between unlike molecules is predominant and characterized by the negative V^E and positive η^E, G^{*E} and d^1 values.

Table:1: Values of Density (□), Viscosity (□), Excess viscosity ($□^E$), Molar volume (V), Excess molar volume (V^E), Excess Gibbs free energy of activation of viscous flow (G^{*E}) and Grunberg-Nissan interaction parameter (d^1) for the binary liquid mixtures of Ethylene gylcol (EG) + n-butylamine (NBA) at 308.15 K.

Mole fraction of EG X_{EG}	□ x 10^{-3} Kg m^{-3}	□ x 10^3 Kg m^{-1} s^{-1}	$□^E$ x 10^3 Kg m^{-1} s^{-1}	V x10^5 m^3 mol^{-1}	V^E x 10^6 m^3 mol^{-1}	G^{*E} x 10^3 N mol^{-1}	d^1
0.0000	0.7239	0.4401	0.0000	101.04	0.0000	0.00	---
0.1666	0.7749	1.4653	0.2785	91.99	-1.5700	492.79	5.7670
0.3109	0.8251	2.4356	0.6021	84.45	-2.6409	620.54	4.4831
0.4353	0.8693	3.3954	1.0044	78.56	-2.9474	657.23	4.0370
0.5453	0.9084	4.3475	1.4635	73.83	-2.7424	647.25	3.9280
0.6427	0.9443	4.8762	1.5556	69.87	-2.3282	588.44	3.7168
0.7296	0.9764	5.0961	1.3861	66.58	-1.7179	480.65	3.4862
0.8076	1.0089	5.1548	1.0952	63.58	-1.2244	361.47	3.2878
0.8780	1.0414	5.0528	0.6777	60.84	-0.8030	286.95	2.9955
0.9418	1.0738	5.0126	0.3515	58.34	-0.4382	180.25	2.8973
1.0000	1.1038	4.9219	0.0000	56.17	0.0000	0.00	---

Table:2: Values of Density (□), Viscosity (□), Excess viscosity (□^{E}), Molar volume (V), Excess molar volume (V^E), Excess Gibbs free energy of activation of viscous flow (G^{*E}) and Grunberg-Nissan interaction parameter (d^1) for the binary liquid mixtures of Ethylene gylcol (EG) + sec-butylamine (SBA) at 308.15 K.

Mole fraction of EG X_{EG}	□ x 10^{-3} Kg m^{-3}	□ x 10^3 Kg m^{-1} s^{-1}	□^{E} x 10^3 Kg m^{-1} s^{-1}	V x10^5 m^3 mol^{-1}	V^E x 10^6 m^3 mol^{-1}	G^{*E} x 10^3 N mol^{-1}	d^1
0.0000	0.7078	0.3632	0.0000	103.33	0.0000	0.00	---
0.1700	0.7641	1.2235	0.0853	93.24	-2.0743	472.99	5.4681
0.3155	0.8154	2.1748	0.3733	85.39	-3.0659	584.95	4.4803
0.4413	0.8610	3.1754	0.8004	79.24	-3.2825	620.12	4.1296
0.5513	0.9027	4.1259	1.2495	74.22	-3.1123	611.63	4.0155
0.6483	0.9418	4.6935	1.3749	69.99	-2.7660	554.45	3.8128
0.7344	0.9767	4.8956	1.1845	66.51	-2.1881	450.28	3.5223
0.8114	1.0099	4.9782	0.9161	63.47	-1.5922	304.65	3.2873
0.8806	1.0418	4.9156	0.5380	60.79	-1.0119	203.78	2.9483
0.9432	1.0717	4.9182	0.2552	58.44	-0.4061	103.65	2.7499
1.0000	1.1038	4.9219	0.0000	56.17	0.0000	0.00	---

Table:3: Values of Density (□), Viscosity (□), Excess viscosity (□^{E}), Molar volume (V), Excess molar volume (V^E), Excess Gibbs free energy of activation of viscous flow (G^{*E}) and Grunberg-Nissan interaction parameter (d^1)

for the binary liquid mixtures of Ethylene gylcol (EG) + tert-butylamine (TBA) at 308.15 K.

Mole fraction of EG X_{EG}	□ x 10^{-3} Kg m^{-3}	□ x 10^3 Kg m^{-1} s^{-1}	□^{E} x 10^3 Kg m^{-1} s^{-1}	V x10^5 m^3 mol^{-1}	V^E x 10^6 m^3 mol^{-1}	G^{*E} x 10^3 N mol^{-1}	d^1
0.0000	0.6787	0.3813	0.0000	107.76	0.0000	0.00	---
0.1760	0.7411	1.1236	-0.0568	96.05	-2.6385	416.52	4.3485
0.3246	0.7944	2.0456	0.1904	87.52	-3.4995	550.26	3.8759
0.4517	0.8434	3.0452	0.6129	80.75	-3.7051	582.55	3.7248
0.5748	0.8961	4.0215	1.0303	74.47	-3.6333	562.46	3.6240
0.6578	0.9336	4.5426	1.1745	70.49	-3.3327	526.87	3.5329
0.7425	0.9720	4.7584	1.0057	66.74	-2.7182	406.54	3.2688
0.8177	1.0067	4.7952	0.7011	63.60	-1.9707	273.15	2.9537
0.8849	1.0406	4.8762	0.4769	60.81	-1.2950	170.55	2.7995
0.9454	1.0722	4.8526	0.1786	58.39	-0.5944	128.95	2.4313
1.0000	1.1038	4.9219	0.0000	56.17	0.0000	0.00	---

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Table:4: Values of Density (□), Viscosity (□), Excess viscosity (□^{E}), Molar volume (V), Excess molar volume (V^E), Excess Gibbs free energy of activation of viscous flow (G^{*E}) and Grunberg-Nissan interaction parameter (d^1)

for the binary liquid mixtures of Ethylene gylcol (EG) + n-hexylamine (NHA) at 308.15 K.

Mole fraction of EG X_{EG}	□ x 10^{-3} Kg m^{-3}	□ x 10^3 Kg m^{-1} s^{-1}	□^{E} x 10^3 Kg m^{-1} s^{-1}	V x10^5 m^3 mol^{-1}	V^E x 10^6 m^3 mol^{-1}	G^{*E} x 10^3 N mol^{-1}	d^1
0.0000	0.7507	0.6639	0.0000	134.79	0.0000	0.00	---
0.2108	0.7982	2.0754	0.5139	116.42	-1.7972	469.56	4.3135
0.3754	0.8422	3.3964	1.1340	102.68	-2.5974	540.23	3.7550
0.5075	0.8804	4.4625	1.6377	92.35	-2.5466	550.25	3.5560
0.6158	0.9148	5.0526	1.7666	84.23	-2.1437	521.65	3.3646
0.7063	0.9468	5.4236	1.7523	77.64	-1.6211	448.87	3.3049
0.7829	0.9785	5.4265	1.4290	72.06	-1.1816	362.56	3.1336
0.8487	1.0099	5.3248	1.0471	67.26	-0.8020	263.10	2.9737
0.9058	1.0417	5.2146	0.6938	63.06	-0.5140	171.35	2.8892
0.9558	1.0712	5.1136	0.3799	59.50	-0.1487	89.17	3.0009
1.0000	1.1038	4.9219	0.0000	56.17	0.0000	0.00	---

Table:5: Values of Density (□), Viscosity (□), Excess viscosity (□^{E}), Molar volume (V), Excess molar volume (V^E), Excess Gibbs free energy of activation of viscous flow (G^{*E}) and Grunberg-Nissan interaction parameter (d^1) for the binary liquid mixtures of Ethylene gylcol (EG) + n-octylamine (NOA) at 308.15 K.

Mole fraction of EG X_{EG}	□ x 10^{-3} Kg m^{-3}	□ x 10^{3} Kg m^{-1} s^{-1}	□^{E} x 10^{3} Kg m^{-1} s^{-1}	V x10^{5} m^3 mol^{-1}	V^E x 10^{6} m^3 mol^{-1}	G^{*E} x 10^{3} N mol^{-1}	d^1
0.0000	0.7702	0.9267	0.0000	167.80	0.0000	0.00	---
0.2496	0.8141	2.8417	0.9178	138.14	-1.8010	434.25	3.7580
0.4280	0.8536	4.3652	1.7285	117.69	-2.3312	520.65	3.4118
0.5620	0.8886	5.1742	2.0022	102.92	-2.1480	511.44	3.1749
0.6662	0.9199	5.6543	2.0660	91.80	-1.6343	444.58	3.1309
0.7496	0.9508	5.7142	1.7927	82.92	-1.2056	351.52	3.0234
0.8179	0.9808	5.6234	1.4290	75.70	-0.7998	264.74	2.9367
0.8957	1.0239	5.4852	0.9800	67.40	-0.4105	162.35	3.0247
0.9229	1.0438	5.3964	0.7825	64.37	-0.4113	118.85	3.1033
0.9642	1.0738	5.2145	0.4356	59.98	-0.1854	81.24	3.4054
1.0000	1.1038	4.9219	0.0000	56.17	0.0000	0.00	---

Table:6: Values of Density (□), Viscosity (□), Excess viscosity (□^{E}), Molar volume (V), Excess molar volume (V^{E}), Excess Gibbs free energy of activation of viscous flow (G^{*E}) and Grunberg-Nissan interaction parameter (d^{1})

for the binary liquid mixtures of Ethylene gylcol (EG) + cyclohexylamine (CHA) at 308.15 K.

Mole fraction of EG X_{EG}	□ x 10^{-3} Kg m^{-3}	□ x 10^{3} Kg m^{-1} s^{-1}	□^{E} x 10^{3} Kg m^{-1} s^{-1}	V x10^{5} m^{3} mol^{-1}	V^{E} x 10^{6} m^{3} mol^{-1}	G^{*E} x 10^{3} N mol^{-1}	d^{1}
0.0000	0.8527	1.3721	0.0000	116.31	0.0000	0.00	---
0.1870	0.8883	2.9241	0.8882	103.82	-1.2416	330.93	3.4064
0.3411	0.9218	4.2235	1.6406	93.84	-1.9621	442.31	3.0645
0.4702	0.9507	5.0746	2.0334	85.93	-2.0990	469.52	2.8398
0.5799	0.9750	5.6891	2.2585	79.61	-1.8262	443.69	2.7978
0.6743	0.9973	5.9532	2.1875	74.31	-1.4481	380.12	2.7610
0.7565	1.0183	5.9722	1.9147	69.78	-1.0381	294.82	2.7390
0.8285	1.0388	5.9610	1.6479	65.82	-0.6617	213.64	2.8904
0.8923	1.0597	5.7634	1.2238	62.29	-0.3612	124.55	3.0745
0.9491	1.0825	5.4499	0.7087	59.02	-0.2078	59.85	3.4559
1.0000	1.1038	4.9219	0.0000	56.17	0.0000	0.00	---

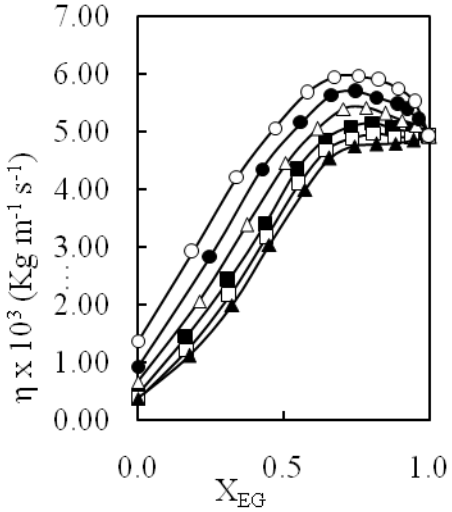

Fig. 1. Plots of viscosity (□) vs mole fraction of ethylene Gylcol (X_{EG}) at 308.15 K for the binary mixtures of EG with NBA (■), SBA (□), TBA (▲), NHA (Δ), NOA (●) and CHA (○).

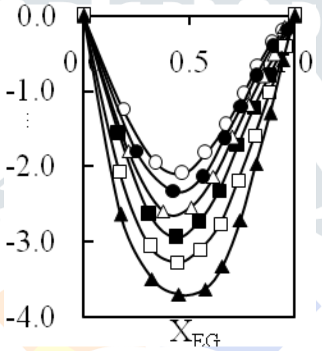

Fig.2. Plots of Excess molar volume (v^E) vs mole fraction of ethyleneglycol (X_{EG}) at 308.15 K for the binary mixtures of EG with NBA (■), SBA (□), TBA ( ), NHA (Δ), NOA (●) and CHA (○).

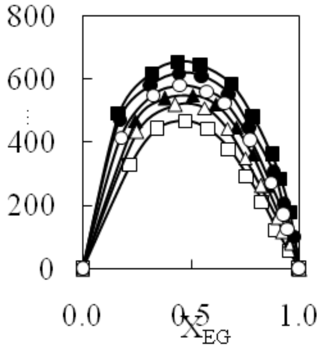

Fig.3. Plots of Gibbs free energy of activation of viscous flow (G^{*E}) vs mole fraction of ethyleneglycol (X_{EG}) at 308.15 K for the binary mixtures of EG with NBA (■), SBA (□), TBA (▲), NHA (Δ), NOA (●) and CHA (○).

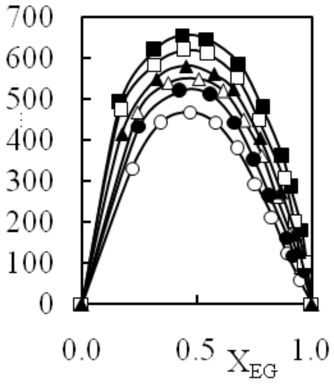

Fig.4. Plots of Gibbs free energy of activation of viscous flow (G^{*E}) vs mole fraction of ethyleneglycol (X_{EG}) at 308.15 K for the binary mixtures of EG with NBA (■), SBA (□), TBA (▲), NHA (Δ), NOA (●) and CHA (○).

III. EXPERIMENTAL

Density was measured using bicapillary pycnometer having a capillary diameter of 0.85mm, which was calibrated using double-distilled water. The necessary buoyancy corrections were applied. The density values were reproducible within ±0.2kg m^{-3}. A thermostatically controlled, well-stirred constant temperature water bath, Schott-Gerate (Model CT 050/2 made in Germany) whose temperature was controlled to ±0.02K was used for all measurements.

Viscosity was measured using an Ubbelhode viscometer. The time of efflux of a constant volume of liquid through the capillary was measured with the help of a pre calibrated ROCAR stop watch capable of recording ±0.1 s. the viscometer was kept vertical in a thermostat at 308.15K. the efflux time for the water at 308.15K was about 302 s. the flow time of pure liquids and liquid mixtures were measured a number of times and the average of the readings was taken. The viscosity was calculated from the average of efflux time t and density ρ according to:

$\eta/\rho=at-b/t$

where a and b are the characteristic constants of the viscometer. These were determined by taking water and benzene as calibrating liquids. The kinetic energy correction were calibrated from these values and they were found negligible. The viscosity measurements were accurate to ±0 X 10^{-4} kg m-1 s^{-1}.

Methoxyethanol and all the amines used were purchased from E. Merck and were used as purchased. Mixtures were prepared by mixing weighed amounts of the pure liquid adopting the method of closed system, by using Mettler balance with precision of ±0.1mg. the measurements were made with proper care in an AC room to avoid evaporation losses.

REFERENCES

[1] Aminabhavi, T.M., Patel, R.C., Bridger, K..Jayadevappa, E.S. and Prasad, B.R., *J.Chem Eng. Data.*, **27** (1982) 125.
[2] Aminabhavi, T.M. and Munk, P., *J.Phy. Chem.*, **84** (1980) 442.
[3] Glasstone, S., Laidler, K.J. and Eyring, H. "The theory of rate process", McGraw - Hill Book Company Inc., New York (1941).
[4] Doolittle, A.K., *J.Appl. Phys.*, **22** (1951) 1471; 23 (1952) 236.
[5] Williams, M.L., Landel, R.F. and Ferry, J.D., *J. Am. Chem. Soc.*, **77** (1955) 3701.
[6] Cohen, M.H. and Turnball, D., *J. Chem. Phys.*, **31** (1959) 1164.
[7] Bloomfield, A.V. and Dewan, R.K., *J. Phys Chem.*, **75** (1971) 3113.
[8] Dymond, J.H., *Chem. Soc. Rev.*, (1985) 317.
[9] Grunberg, L. and Nissan, A.H. *Nature (London).*, **164** (1949) 799.
[10] Grunberg, L., *Trans, Faraday Soc.*, **50** (1954) 1293.
[11] Katti, P.K. and Chaudhri, M.M., *J. Chem. Engg. Data*, **9** (1964) 442.
[12] Reed, T.M. and Taylor, T.E., *J.Phys. Chem.*, **63** (1959) 58.
[13] Meyer, R., Meyer, M., Metzer, J. and Peneloux, A., *Chem.Phys.*, **62** (1971) 406.
[14] Garst, J.F., In solute solvent interactions; J.F.Ritchie, C.D., Eds., Dekker, New York (1969).
[15] Franks, F. Ives, D.J.G., Q. *Rev. Chem. Soc.*, **20** (1966) 1.
[16] HSDB. 1996. Hazardous Substances Data Bank. National Library of Medicine, Bethesda, M.D (CD-ROM version) Denver Co: Micromedex, Inc. (Edition e expires 4/30/96).
[17] CARB. 1999. Air toxics emissions data collected in the Air Toxics Hot Spots Program CEIDARS Database as of January 29, 1999.
[18] Franks, F., Water – A comprehensive treatise, vol. 4, Chapter I, Plenum Press, New York (1974).
[19] Franks, F., Water – A comprehensive treatise, Vol.2, Chapters 1, 3 and 5. Plenum Press, New York (1976).