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To study volumetric analysis of binary liquid mixtures of ethylene glycol with formamide/N,N-dimethyl formamide/N,N-dimethyl acetamide

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Abstract

The densities, ρ and viscosities, η of binary mixtures of ethylene glycol with formamide, N,N-dimethyl formamide and N,N-dimethyl acetamide were calculated at 308.15 K over the whole formulation spectrum were reported in the present study. These deviation/excess properties have been fitted to Redlich-Kister type polynomial. The strength of interactions follows the order EG+DMA > EG+DMF > EG+FA. The values of the experimental viscosity are contrasted with the values of the viscosity derived from various observational relations and are in good accordance with the values of the experiment.

Keywords: Densities, viscosities and Redlich-Kister type polynomial

Introduction

Measuring the speed of sound in liquids allows some useful acoustic and thermodynamic parameters to be calculated, which are shown to be very sensitive to molecular interactions. Ultrasonic velocity and its associated properties have been widely used in a number of liquid mixtures to study physio-chemical activity and molecular interaction^[1]. The volumetric and viscometric properties of binary mixtures have been very useful in extracting knowledge on the relationships of solvents and geometric results in structures^[2, 3]. Direct uses in the pharmaceutical and biochemical industries are found in the study of the properties of liquid mixtures and solutions. Quantitative and qualitative data on the ultrasonic speed, density and viscosity of liquid mixtures are needed for many engineering and technical problems^[4].

Ultrasonic, volumetric and viscometric experiments on binary mixtures, glycol as one component and +2-methoxy ethanol, +formamide, +2-butoxy ethanol, +water as another component have been conducted by so many researchers in previous years^[5-9]. The volumetric properties of (acetonitrile + amide) binary mixtures at temperatures between 293.15 K and 318.15 K were stated by Nain^[10]. Volumetric properties of 2-alkoxyethanol binary mixtures of N, N-dimethyl formamide and N,N-dimethyl acetamide at 298.15 K have been recorded by A. Pal *et al.*^[11]. Anjali Awasthi and Aashees Awasthi^[12] have been researching the intermolecular interactions of multi-temperature formamide+2-alkoxyethanols in recent years. The volumetric properties of N,N Dimethyl acetamide + water binary mixtures were reported by Das *et al.*^[13] at temperatures from 298.15 K to 318.15 K.

In view of the industrial importance of liquid mixtures, in this study we reported ultrasonic velocities (u), densities (ρ) viscosities (η) of the liquid mixtures. The ultrasonic properties such as isentropic compressibility, free length, acoustic impedance, isothermal compressibility, thermal expansion coefficient, enthalpy and relaxation time are measured at a fixed temperature 308.15 K. Thermodynamic properties are measured, such as free space, internal pressure and excess Gibb's free viscous flow activation energy, viscosity variance, excess molar volume, partial molar volume and excess partial molar volume. In this analysis, partial molar volumes at infinite dilution are measured and recorded for excess partial molar volumes at infinite dilution and properties such as molar isentropic compressibility and partial values. In terms of molecular interactions occurring within the molecules of these mixtures, the differences of these properties with composition are discussed. Nomoto, Van

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Dael, Impedance relationships and viscosity data are compared to separate viscosity models such as Grunberg and Nissan, Hind *et al.*, and Frenkel with the experimental ultrasonic velocity data of all binary liquid mixtures.

Materials and Methods

Ethylene glycol (EG), formamide (FA), N,N-dimethyl formamide (DMF) and N,N-dimethyl acetamide (DMA) compounds of high purity and analytical reagent (AR) grade were obtained from LOBA Chemicals, India. By standard methods, the above chemicals used in the present investigation are further purified^[14]. liquids obtained is > 0.995. Binary mixtures of EG with FA/DMF/DMA are prepared so that the entire composition range is covered (i.e. 0-100% of EG). The mixtures were prepared by mass in airtight bottles. The mass measurements have been performed with a METTLER TOLEDO (Switzerland) ABB5-S/FACT digital balance with an accuracy ± 0.01 mg. The uncertainty in the mole fraction is 10^{-4} . The density and viscosity measurements of liquid mixtures have been measured using a two stem double-walled Parker & Parker type pycnometer^[15] and Ostwald viscometer respectively. The reproducibility

in the measured parameters of density and viscosity are 3 in 10^{-5} parts and ± 0.2 %, respectively.

Results and Discussion

Table 1 presents experimentally measured values of density and viscosity. The density in the EG+FA system is found to decrease as reported in Table 1, and it is observed to increase monotonically in EG+DMF/DMA systems where the viscosity is found to increase monotonically, non-linearly in all binary systems with an increase in EG concentration. This non-linear variation is a deviation from ideal behaviour that indicates that there are interactions between molecules of the mixture's component liquids. The deviation/excess properties such as deviation in viscosity ($\Delta\eta$), excess molar volume (V_m^E), excess Gibbs free energy of activation of viscous flow (ΔG^{*E}) are computed from the experimental values of density and viscosity. These deviation/excess properties have been adapted to the polynomial equation of the Redlich-Kister^[16] type. The R-K polynomial values of A_i coefficients were determined using the least square method and the standard deviations $\sigma(YE)$ calculated using the standard equations are presented in Table 2.

Table 1: Shows the experimental values of densities (ρ) and viscosities (η) with mole fraction of EG, x for all binary systems at 308.15 K

EG+FA			EG+DMF			EG+DMA		
x	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\eta/10^{-3}\text{N}\cdot\text{s}\cdot\text{m}^{-2}$	x	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\eta/10^{-3}\text{N}\cdot\text{s}\cdot\text{m}^{-2}$	x	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\eta/10^{-3}\text{N}\cdot\text{s}\cdot\text{m}^{-2}$
0.0000	1120.20	2.653	0.0000	935.60	0.707	0.0000	927.50	0.806
0.0761	1118.92	2.392	0.1399	953.84	0.956	0.1632	947.44	1.166
0.1538	1117.64	2.439	0.2568	970.24	1.132	0.2752	962.32	1.388
0.2311	1116.66	2.487	0.3715	987.72	1.288	0.4068	981.77	1.611
0.3245	1115.24	2.636	0.4762	1004.62	1.898	0.5162	1000.26	2.416
0.4125	1114.34	2.996	0.5807	1022.84	2.801	0.6269	1021.82	3.622
0.5236	1113.72	4.026	0.6745	1040.62	3.878	0.7125	1039.62	4.662
0.6337	1112.98	5.164	0.7677	1059.36	5.167	0.7974	1056.30	5.882
0.7468	1111.24	6.594	0.8456	1074.22	6.582	0.8652	1071.44	7.289
0.8596	1108.64	8.193	0.9229	1088.28	8.355	0.9339	1087.54	8.916
1.0000	1102.60	10.968	1.0000	1102.60	10.968	1.0000	1102.60	10.968

Table 2: Coefficients A_i of Redlich-Kister type polynomial equation (3.28) and the corresponding standard deviations, σ (3.29) of all the systems under investigation

property	A_0	A_1	A_2	A_3	A_4	σ
EG+FA						
$\Delta\eta/10^{-3}\text{N.s.m}^{-2}$	-12.349	-1.43	3.796	5.097	-8.354	0.054
$V_m^E/10^{-6}\text{m}^3.\text{mol}^{-1}$	-0.67	1.02	-0.81	-0.23	0.44	0.008
$\Delta G^{*E}/\text{kJ.mol}^{-1}$	-3.78	-4.79	1.47	3.66	-4.32	0.053
EG+DMF						
$\Delta\eta/10^{-3}\text{N.s.m}^{-2}$	-15.118	5.131	1.487	6.844	-6.037	0.034
$V_m^E/10^{-6}\text{m}^3.\text{mol}^{-1}$	-0.78	1.17	-2.07	0.27	2.04	0.015
$\Delta G^{*E}/\text{kJ.mol}^{-1}$	-3.08	-4.49	1.84	9.30	2.19	0.077
EG+DMA						
$\Delta\eta/10^{-3}\text{N.s.m}^{-2}$	-14.384	4.517	1.814	6.318	-3.146	0.074
$V_m^E/10^{-6}\text{m}^3.\text{mol}^{-1}$	1.35	1.74	-1.14	-1.68	0.30	0.029
$\Delta G^{*E}/\text{kJ.mol}^{-1}$	-2.56	-3.64	3.87	8.78	0.68	0.097

The deviation from the ideal behaviour of the physical and chemical properties of the liquid mixture is a measure of the interaction between molecules of liquid mixture components, and dipole-dipole interactions and hydrogen bonds between unlike molecules are normally due to such a form of deviation [17]. The variation of excess molar volume in the present investigation is negative over the entire mole fraction range. The molar volumes of EG, FA, DMF and DMA are 56.29, 40.21, 78.12 and 93.93 $\text{cm}^3.\text{mol}^{-1}$ at 308.15 K respectively. EG molecules are self-associated by inter- and intra-molecular hydrogen bonding [18], while FA molecules are closely associated by hydrogen bonding due to the presence of a large proton-acceptor group ($>\text{C}=\text{O}$) and a proton-donor group ($-\text{NH}_2$) in their pure molecules, and this association decreases with an increase in the number of methyl groups in the molecules. Thus DMF and DMA are practically unassociated [19, 20].

On the other hand, DMF and DMA contain only a hydrogen bond accepting carbonyl group. FA molecules that have hydrogen atoms bound to nitrogen have both hydrogen-bond donating and hydrogen-bond accepting capabilities. The addition of amide molecules allows the hydrogen bonds between EG molecules to dissolve and the resulting

formation of solid hydrogen bonds between the glycol molecules' hydrogen atom-OH group and the amide molecules' oxygen molecule $>\text{C}=\text{O}$ group.

The variation of deviation in viscosity, $\Delta\eta$ with the mole fraction of EG is shown in figure 1. Generally, negative values of $\Delta\eta$ indicate the presence of dispersion forces or mutual loss of specific interactions in like molecules operating in the systems arising due to weak intermolecular interactions, and positive values of deviation in viscosity indicate strong specific interactions [21, 22]. The sign and magnitude of $\Delta\eta$ depend on the combined effect of factors such as molecular size, shape, and intermolecular forces. The molecules of FA, DMF and DMA are highly polar $\mu = 3.37, 3.86$ and 3.72 D respectively at $T = 298.15$ K.

The variation in excess Gibbs free energy of activation of viscous flow, ΔG^{*E} with the mole fraction of secondary alcohols is shown in figure 2. The excess Gibbs free energy of activation of viscous flow is negative over the entire composition range studied. The less negative ΔG^{*E} values for EG+DMA system indicates the interactions are predominant compared to EG+FA and EG+DMF systems. Such type of behaviour was also observed by Liisa Pikkarainen [23].

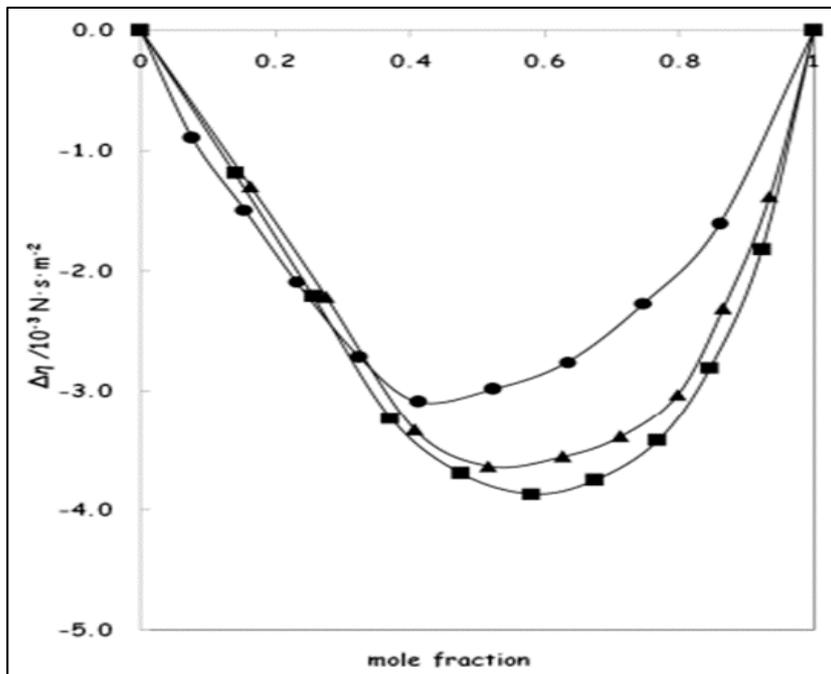


Fig 1: Shows plots of deviation in viscosity.

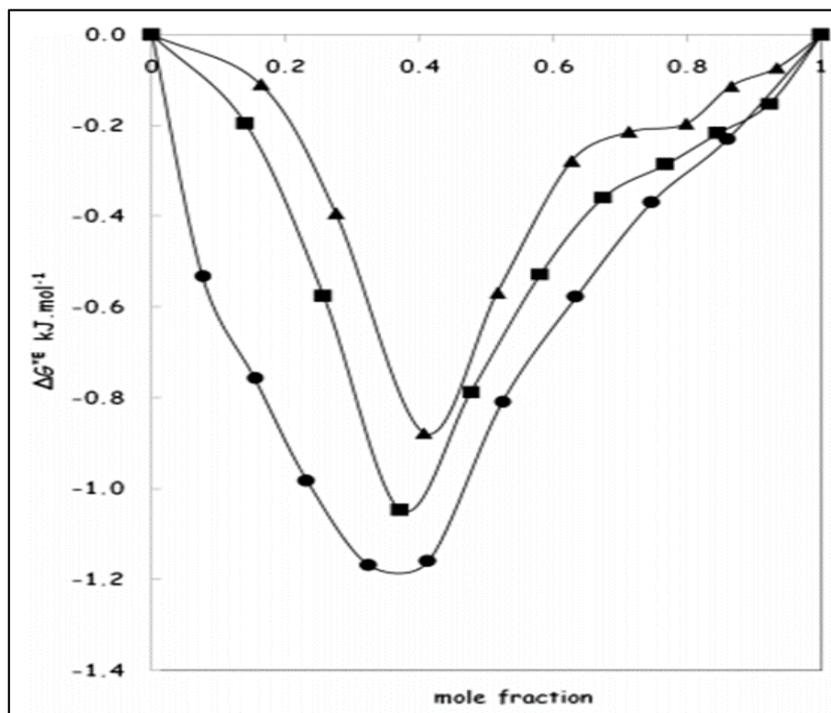


Fig 2: shows excess Gibbs free energy of activation of viscous flow

Using different analytical relationships such as Kendall and Monroe, Grunberg and Nissan, Tamura and kurata, Frenkel, Hind and Ubbelohde, Katti and Chaudari, and Heric and Brewer, the complex viscosities of the binary liquid mixtures have been determined and the related interaction parameters are also evaluated. Table 3 provides the potential viscosity values of liquid mixtures determined using the

above equations. The values of interaction parameters are provided in Table 4 along with the standard deviations, σ . The predicted values of σ was observed to be lower, suggesting that viscosity experimental values are well-correlated with those derived from various models of viscosity.

Table 3: Shows Partial molar volumes $\bar{V}_{m,1}$, $\bar{V}_{m,2}$ and excess partial molar volumes $\bar{V}_{m,1}^E, \bar{V}_{m,2}^E$ of all binary systems with mole fraction of ethylene glycol at 308.15 K

mole fraction of ethylene glycol (x)	$\bar{V}_{m,1}$ $10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$	$\bar{V}_{m,2}$	$\bar{V}_{m,1}^E$	$\bar{V}_{m,2}^E$
EG+FA				
0.0000	56.04	40.21	-0.25	0.00
0.0761	56.00	40.21	-0.29	0.00
0.1538	56.02	40.20	-0.27	-0.01
0.2311	56.02	40.20	-0.27	-0.01
0.3245	55.97	40.20	-0.32	-0.01
0.4125	55.91	40.22	-0.39	0.01
0.5236	55.87	40.25	-0.42	0.04
0.6337	55.92	40.19	-0.37	-0.02
0.7468	56.07	39.96	-0.22	-0.25
0.8596	56.22	39.56	-0.07	-0.65
1.0000	56.29	39.18	0.00	-1.03
EG+DMF				
0.0000	56.92	78.12	0.63	0.00
0.1399	55.68	78.16	-0.61	0.04
0.2568	55.90	78.07	-0.39	-0.05
0.3715	55.96	78.00	-0.33	-0.12
0.4762	55.83	78.06	-0.46	-0.06
0.5807	55.74	78.19	-0.55	0.07
0.6745	55.80	78.19	-0.49	0.07
0.7677	55.99	77.95	-0.30	-0.17
0.8456	56.17	77.60	-0.12	-0.52
0.9229	56.27	77.39	-0.02	-0.73
1.0000	56.29	77.93	0.00	-0.19
EG+DMA				
0.0000	54.16	93.93	-2.13	0.00
0.1632	55.88	93.82	-0.41	-0.11
0.2752	55.85	93.81	-0.44	-0.12
0.4068	55.58	93.92	-0.71	-0.01
0.5162	55.52	93.95	-0.77	0.02
0.6269	55.69	93.75	-0.60	-0.18
0.7125	55.91	93.39	-0.38	-0.54
0.7974	56.12	92.90	-0.17	-1.03
0.8652	56.24	92.55	-0.05	-1.38
0.9339	56.29	92.43	0.00	-1.50
1.0000	56.29	92.81	0.00	-1.12

Table 4: Theoretical values of viscosities $\eta/10^{-3} \text{ N} \cdot \text{s} \cdot \text{m}^{-2}$ calculated with mole fraction of EG, x for all binary systems at 308.15 K

x	Kendall & Monroe	Grunberg & Nissan	Tamura & Kurata	Frenkel	Hind & Ubbelohde	Katti & Chaudari	Heric & Brewer
EG+FA							
0.0000	2.653	2.653	2.653	2.653	2.653	2.653	2.653
0.0761	3.037	2.619	2.429	2.644	2.425	2.617	2.619
0.1538	3.465	2.639	2.345	2.685	2.338	2.635	2.638
0.2311	3.929	2.714	2.408	2.779	2.399	2.710	2.713
0.3245	4.542	2.886	2.678	2.971	2.667	2.881	2.885
0.4125	5.176	3.142	3.125	3.245	3.115	3.139	3.142
0.5236	6.057	3.634	3.957	3.757	3.952	3.636	3.635
0.6337	7.023	4.377	5.075	4.515	5.080	4.386	4.380
0.7468	8.118	5.534	6.533	5.675	6.547	5.548	5.537
0.8596	9.317	7.304	8.302	7.423	8.323	7.323	7.308
1.0000	10.968	10.968	10.968	10.968	10.968	10.968	10.968
EG+DMF							
0.0000	0.707	0.707	0.707	0.707	0.707	0.707	0.707
0.1399	1.249	0.924	0.166	0.927	0.146	0.923	0.924
0.2568	1.873	1.189	0.206	1.196	0.175	1.187	1.189
0.3715	2.659	1.562	0.681	1.574	0.644	1.559	1.562
0.4762	3.544	2.050	1.489	2.066	1.454	2.046	2.050
0.5807	4.605	2.746	2.652	2.767	2.625	2.743	2.746
0.6745	5.722	3.634	3.996	3.660	3.985	3.635	3.634
0.7677	6.997	4.883	5.613	4.911	5.625	4.892	4.883
0.8456	8.197	6.331	7.194	6.357	7.217	6.343	6.331
0.9229	9.517	8.288	8.978	8.307	8.996	8.296	8.288
1.0000	10.968	10.968	10.968	10.968	10.968	10.968	10.968
EG+DMA							
0.0000	0.806	0.806	0.806	0.806	0.806	0.806	0.806
0.1632	1.487	1.118	0.343	1.122	0.316	1.118	1.118
0.2752	2.127	1.430	0.503	1.438	0.464	1.430	1.431
0.4068	3.086	1.956	1.187	1.969	1.143	1.954	1.957
0.5162	4.074	2.587	2.160	2.604	2.122	2.584	2.588
0.6269	5.269	3.494	3.516	3.515	3.496	3.493	3.494
0.7125	6.338	4.462	4.822	4.486	4.823	4.465	4.461
0.7974	7.532	5.747	6.357	5.772	6.367	5.745	5.744
0.8652	8.587	7.088	7.744	7.109	7.763	7.087	7.084
0.9339	9.752	8.825	9.303	8.839	9.325	8.828	8.822
1.0000	10.968	10.968	10.968	10.968	10.968	10.968	10.968

Conclusion

The densities, ρ and viscosities, η of binary mixtures of Ethylene glycol with formamide, N,N-dimethyl formamide and N,N-dimethyl acetamide have been measured over the entire composition range at 308.15 K and also the excess

properties V_m^E , $\Delta\eta$ and ΔG^{*E} have been determined.

These deviation/excess properties have been generalised to polynomials of the Redlich-Kister form. These observed properties are negative values due to the addition of amide molecules causing the breakup of hydrogen bonds between EG molecules and the subsequent forming of strong hydrogen bonds between the glycol molecules of the hydrogen atom-OH group and the amide molecules of the oxygen molecules $>C=O$ group and the fitting of smaller molecules into the voids created by the larger molecules.

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