Investigation of Molecular Association in Binary Liquid Mixture of Formamide with Propanols

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***Abstract*- Ultrasonic velocity (u), viscosity (η) and density (ρ) have been measured at atmospheric pressure and 293.15, 303.15, and 313.15 K temperatures over the entire mole fraction range for the binary mixtures of formamide with 1-propanol and 2-propanol. Deviations in isentropic compressibility (Δk_s), excess free energy of activation for viscous flow (ΔG^{*E}), and excess molar volume (V_m^E) have been calculated from the experimental data and the computed values were fitted to the Redlich- Kister polynomial equation. The observed positive and negative values of these excess parameters have been explained on the basis of the interactions among the component molecules occurring in the two binary mixtures.**

Key words: formamide, propanol-1, propanol-2, ultrasonic velocity, viscosity, density.

I. INTRODUCTION

Binary liquid mixtures have long been a favourite subject matter of study among the scientists and engineers all over the world because firstly, it provides experimental background to develop, test, and improve thermodynamic models for calculating and predicting fluid phase equilibria. Secondly, we can obtain mixtures having required properties by making a suitable choice of the components and adjusting the composition and ambience of these mixtures. Such mixtures find application in fields as diverse as food and cosmetics, chemical and pharmaceutical industries, oil extraction, lubrication engineering, scientific research, etc. This can be achieved only if we have the knowledge about the structural and interactional aspects of the mixture at the microscopic level.

For decades, the non destructive techniques of measuring macroscopic parameters like ultrasonic velocity *'u'*, viscosity *'η'*, density *'ρ'*, etc., have been found to be a cheap, reliable, and easy source of information necessary for understanding the interactions occurring at the microscopic level in liquid mixtures. The derived parameters such as deviation in isentropic compressibility *'*Δk_s*'*, excess free energy of activation for viscous flow *'*ΔG^{*E}*'*, and excess molar volume *'*V_m^E*'*, etc., which can easily be estimated from the experimental data, give a more comprehensive information about the structural and interactional aspects of the mixture [11-14]**.**

As an extension of our study in this direction, we have experimentally measured *u*, *η,* and *ρ* for two binary mixtures, namely formamide with 1-propanol (F+1-P) and formamide with 2-propanol (F+2-P), at atmospheric pressure and 293.15, 303.15, and 313.15 K, over the entire mole fraction range. We then estimated the values of Δk_s, ΔG^{*E}, V_m^E with the aim of analyzing the disruption of self association in the two alcohols and the breaking of dipole-dipole interaction of formamide along with the hydrogen bonding between oxygen of formamide and hydrogen of the hydroxyl group of the two alcohols occurring in these two binary mixtures.

II. EXPERIMENTAL DETAIL

The binary liquid mixtures were prepared in thoroughly washed and dried narrow-mouthed weighing glass-bottles, with ground-glass stoppers, by mixing the component liquids by mass on an electronic balance (Model: Sartorius BP 121S) with a stated precision of 0.1 mg. The chemicals used were obtained from Ranbaxy and E. Merck (India) Ltd. All the chemicals were purified by standard procedures discussed by Perrin and Armarego [6] before use and the purity of each of these chemicals was ascertained by literature comparison of their physical parameters.

A single-limbed dilatometer, with a bulb of volume of about 8 ml, has been used for density estimation. The dilatometer stem, with uniform fine bore, had 0.01 ml uniform graduations over it. In order to minimize the loss of

liquid due to evaporation, the open end of the dilatometer stem was closed with a teflon cap with a small orifice to ensure that the pressure inside the capillary was equal to the atmospheric pressure. The mass of thoroughly cleaned and dried empty dilatometer was measured on the electronic balance and then a suitable amount of the liquid under investigation was introduced into the bulb of the dilatometer with the help of a hypodermic glass syringe having a needle long enough to reach the bottom of the bulb so as to avoid the undesired sticking of the solution to the inner wall of the dilatometer stem. The mass of the dilatometer containing the experimental liquid was then measured on the electronic balance. The temperature of the dilatometer containing the experimental liquid was maintained by immersing it vertically in a double-walled cylindrical glass-jacket with water circulating around it from the thermostatically controlled adequately stirred water bath (accuracy $\pm$ 0.1^{o}C).

The ultrasonic velocity *u* in pure components and in their mixtures was measured using a variable path fixed-frequency interferometer (Model: M 83, Mittal Enterprises, New Delhi) operating at frequencies 1 to 10 MHz and maintained at the desired temperatures by circulating water around the liquid cell of the interferometer from thermostated water bath and covering the measuring cell along with its base with a specially made thermocol jacket with a window for noting down micrometer readings. The instrument was calibrated by measuring the velocity in AR grade benzene and carbon tetra chloride. The Experimental values of *u* agreed closely with the corresponding standard values. Standard values of *u* were calculated using the literature value [10] of u at 298.15 K and the rate of change of velocity with temperature (*–du/dt*). The maximum estimated error has been found to be $\pm$ 0.2 %.

An Ostwald's viscometer was used to determine the viscosity of pure components and their mixtures. The viscometer was kept inside a double-wall glass jacket in which water from the thermostated water bath was circulated. The inner cylinder of this glass jacket was filled with the water so as to establish and maintain the thermal equilibrium. The time of flow through the capillary tube of the viscometer was recorded using an electronic stop watch (Casio) of least count 0.01 second. The viscometer was calibrated by measuring the viscosity of the standard liquids and the maximum error was found to be $\pm$ 0.4 %.

III. THEORY

The excess parameter viz, deviations in isentropic compressibility (Δk_s) excess free energy of activation for viscous flow (ΔG^{*E}), and excess molar volume (V_M^E) were calculated using the standard equation reported earlier. [8, 18, 15]

$$\Delta k_s = 1/u^2 \rho - [x_{1/} u_1^2 \rho_1 + x_{2/} u_2^2 \rho_2] \quad \text{.....(1)}$$

$$\Delta G^{*E} = RT [\ln (\eta V_M / \eta_2 V_{M2}) - x_1 \ln (\eta_1 V_{M1} / \eta_2 V_{M2})] \quad \text{...(2)}$$

Where, R is the universal gas constant. T is the absolute temperature.

$$V_M^E = [x_1M_1 + x_2M_2 / \rho_M] \text{ --- } [x_1M_1/ \rho_1 + x_2M_2 / \rho_M] \quad \text{...(3)}$$

Here u, ρ, η, V_M, M denotes the ultrasonic velocity, density, viscosity, molar volume and molecular weight respectively. u_i , ρ_i ,η_i , $V_{Mi,}$ M_i (i= 1,2) denote respectively the ultrasonic velocity ,density, viscosity molecular volume and molecular weight of the i^{th} component .

The values of Excess parameters for each mixtures have been fitted to fitted to the Redlich-Kister polynomial equation:

$$Y^E = x_1(1-x_1)\sum_{i=1}^{5} a_i(2x_1-1)^{i-1} \quad \text{...(4)}$$

Here Y^E refer to excess / deviation parameters. The values of the coefficients a_i were calculated by the method of least squares along with the standard deviation $\sigma(Y^E)$. The coefficient a_i is an adjustable parameter for the best fit of the excess function.

The standard deviation values were obtained from

$$\sigma(Y^E) = \left[\frac{\Sigma(Y_{\exp t} - Y_{cal})^2}{n-p} \right]^{1/2} \quad \text{.(5)}$$

Where *n* is the total number of experimental points, *p* is the number of coefficients, Y_{expt} and Y_{cal} are the experimental and calculated excess parameters respectively.

IV. RESULT

The experimental values of ultrasonic velocity (u), viscosity (η) and density(ρ) at three temperature viz T= 293.15,303.15,and 313.15 k along with the derive value of deviations in isentropic compressibility (Δk_s)excess free energy of activation for viscous flow (ΔG^{*E}),and excess molar volume (V_M^E) are given in table (1)and (2) for formamide with 1-propanol and 2-propanol mixtures respectively. The excess parameters such as Δk_s, ΔG^{*E} and, V_M^E are plotted against the mole fraction of formamide and are shown in figure 1, 2, 3 respectively

V. DISCUSSION

The values of isentropic compressibility Δk_s have been found to be negative for (F+1-P) and (F+2-P) over the entire mole fraction rang at all the temperature. The sign and magnitude of Δk_s plays a vital role in assessing the molecular arrangement as the result of molecular interactions among the component molecules in the liquid mixtures. The negative Δk_s in both mixtures can be explained on the basis of complex formation through hydrogen bonding between oxygen atom of formamide and

hydrogen atom of the hydroxyl group of the alcohol a similar view has been held by many workers [5]. Negative trends in Δk_s have also been reported for binary mixtures of alcohols and alkenes. [9, 20]

Alcohols molecules form long chains through homomolecular hydrogen bonding and these chains thereby occupying larger volume. When mixed with formamide repel each other breaking of chains due to heteromolecular bonding between propanol and formamide leads to formation of smaller entities which occupy small volume due to compact arrangement. The compactness of these entities leads to decrease in compressibility of mixture and thus giving negative values of excess isentropic compressibility Δk_s. Fig-1 shows that values of Δk_s. for (F+2-P) are more negative as compared to those for the mixture (F+1-P) at all the three temperatures over the entire composition range. It indicates that formamide is more successful in breaking the homomolecular hydrogen bonding in 2-propanol than in 1-propanol further. [20-22]

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Fig-2 shows the variation of excess free energy of activation for viscous flow ΔG^{*E} with the mole fraction of formamide. For all the temperature ΔG^{*E} values are negative in 1-propanol and 2-propanol rich region and turn to small positive in formamide rich region. A negative excess in ΔG^{*E} indicate the presence of weak interaction where as a positive excess in ΔG^{*E} suggest a strong association between unlike molecules in the solvent mixture (16, 17).

In 1-propanol and 2-propanol rich region the rupture of self association in 1-propanol and 2-propanol molecules by addition of formamide governs the behaviour of mixture and gives increasingly negative contribution of ΔG^{*E} From Fig-2 increase in positive contribution to ΔG^{*E} changes sign from negative to positive.

In this region as more and more formamide molecules becomes available for forming hydrogen bonds with alcohol molecules, the positive contribution to ΔG^{*E} due to hydrogen bonding between unlike molecules acquires predominance over the negative contribution due to the rupture of hydrogen bond. Decrease in positive value of ΔG^{*E} indicate presence of Vander Walls dispersive forces between the formamide molecules which are now in majority. Mialkowaski et al. (16) have also reported similar variation in ΔG^{*E} values for γ- butyl acetone and dimethylcarbonate.

Fig-3 shows that V_m^E values are negative for both mixtures over the entire composition range at all the temperature which suggests the presence of strong intermolecular interaction between unlike molecules. This is in accordance with the view proposed by Fort and Moore (19) that the liquids of different molecular size usually mix with negative excess molar volume

V_m^E is mainly influenced by dispersive force, the dipole – dipole and donor- acceptor interactions between unlike molecules. The physical interaction due to dispersive force leads to expansion in volume hence positive contribution to V_m^E values. The other effects lead to contraction in volume resulting in a negative contribution to V_m^E value. The negative deviation of V_m^E confirms the presence of strong molecular association in the system (7). further V_m^E show more negative value in case of (F+1-P) mixture than in (F+2-P) mixture. For these mixtures V_m^E curves show the minima at or near those mole fractions of formamide where value of Δk_s also attains minimum values. This further supports the view that there is increased molecular association through hydrogen bonding between unlike molecules as suggest earlier by several other workers. (17, 18, 19, 22)

VI. CONCLUSION

The **(**Δk_s), (V_M^E) are found to be negative al most over the whole mole fraction rangefor both the mixtures which suggest the existence of strong hydrogen bonding between unlike molecules. The study of mixing rules for ultrasonic velocity gives reasonably good result.

VII. ACKNOWLEDGMENTS

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TABLE-1

ultrasonic velocity (u), , density(ρ), viscosity(η), isentropic compressibility (Δk_s) , excess molar volume (V_M^E) ,and excess free energy of activation for viscous flow (ΔG^{*E}) for (F+P-1).

x_1	u (m\s)	P g\m3)	η (Poise)	(Δk_s)	V_M^E	ΔG^{*E}
			293.15K			
0	1227	804.2	0.0219	0	0	0
0.1289	1267	824.2	0.0225	-0.0746	0.00033	-16.8155
0.2498	1301	864.1	0.0232	-0.2078	-0.0008	-81.2187
0.3639	1338	899.9	0.024	-0.2832	-0.00131	-122.3824
0.4707	1367	938.2	0.0248	-0.2674	-0.00177	-169.48883
0.5713	1411	964.5	0.0269	-0.274	-0.00136	-64.8491
0.6666	1454	997.9	0.0289	-0.2789	-0.00126	0.3281
0.757	1490	1025.1	0.0307	-0.1855	-0.00076	54.9298
0.8421	1529	1061.3	0.0319	-0.1355	-0.00061	36.5668
0.9232	1574	1102.1	0.0331	-0.1092	-0.00054	7.0255
1	1612	1132.4	0.0343	0	0	0
			303.15K			
0	1184	795.5	0.016	0	0	0
0.1289	1228	816.4	0.0164	-0.1413	0.00026	-37.3447
0.2498	1258	856.8	0.017	-0.2295	-0.00092	-103.1454
0.3639	1294	893.5	0.0173	-0.2981	-0.00149	-199.8424
0.4707	1328	931.8	0.0178	-0.3142	-0.00194	-268.9183
0.5713	1375	958.7	0.0195	-0.3336	-0.00155	-146.0232
0.6666	1419	987	0.0217	-0.2991	-0.00116	14.6297
0.757	1462	1018	0.0231	-0.242	-0.00083	58.7749
0.8421	1504	1057.1	0.0242	-0.1915	-0.00079	45.8527
0.9232	1546	1092.7	0.0251	-0.1022	-0.00049	19.1731
1	1591	1124.8	0.026	0	0	0
			313.15K			
0	1154	787	0.01333	0	0	0
0.1289	1202	804.8	0.0135	-0.1534	-0.00054	-47.2414
0.2498	1234	845.8	0.0141	-0.3737	-0.00075	-86.6697
0.3639	1265	884.2	0.0145	-0.5027	-0.00147	-153.8813
0.4707	1301	921.6	0.0147	-0.4792	-0.00187	-251.272
0.5713	1349	942.9	0.0163	-0.4228	-0.00115	-67.8266
0.6666	1394	972.9	0.0172	-0.3074	-0.00087	-36.1403
0.757	1436	1008.7	0.0186	-0.289	-0.00079	46.1871
0.8421	1478	1045.6	0.0194	-0.2179	-0.00065	34.749
0.9232	1530	1086.4	0.0201	-0.1443	-0.00056	-0.6223
1	1564	1117.2	0.0209	0	0	0

Table-2

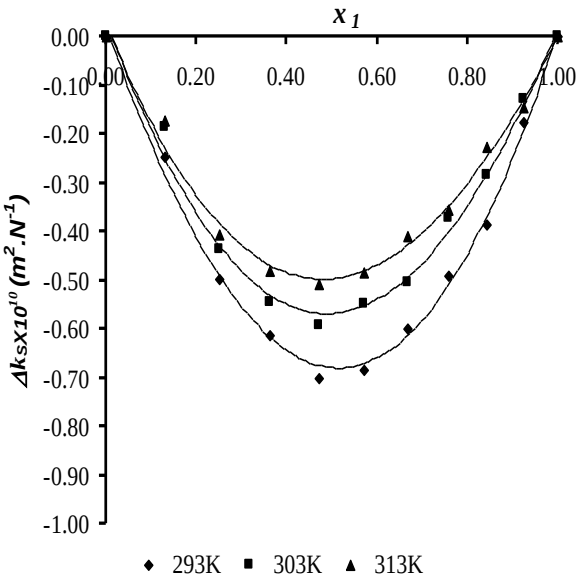
ultrasonic velocity (u), , density(ρ), viscosity(η), isentropic compressibility (Δk_s) , excess molar volume (V_M^E) ,and excess free energy of activation for viscous flow (ΔG^{*E}) for (F+P-2).

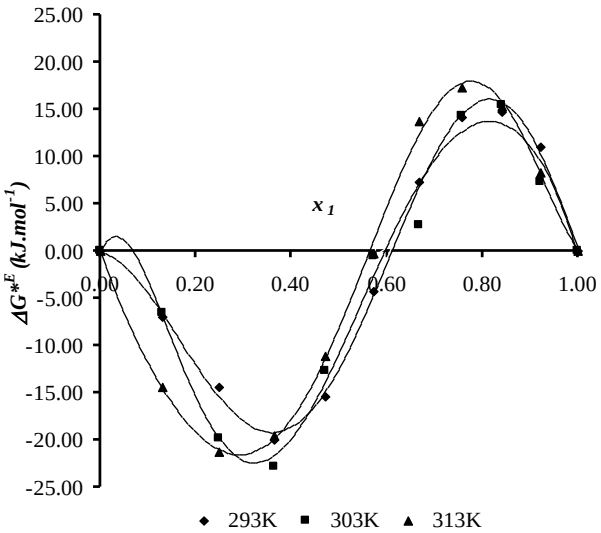
x_1	u (m\s)	P (kg\m3)	η (Poise)	(Δk_s)	V_M^E	ΔG^{*E}
			293.15K			
0	1139	785.9	0.0211	0	0	0
0.1293	1188	802.8	0.0215	-0.1534	-0.0007	-33.4467
0.2507	1242	828.2	0.0222	-0.3737	-0.3737	-0.00073
0.3638	1284	869.8	0.0227	-0.5027	-0.00032	-153.14
0.4673	1318	908.9	0.0244	-0.4792	-0.00094	-112.5431
0.5716	1357	942.2	0.0267	-0.4228	-0.00084	-11.3099
0.667	1400	976.4	0.0281	-0.3074	-0.00072	-3.5983
0.7492	1454	1002.8	0.0299	-0.289	-0.00029	55.2691
0.8423	1508	1049.2	0.0316	-0.2179	-0.00036	46.8694
0.9214	1562	1090.7	0.0329	-0.1443	-0.00027	20.9399
1	1612	1132.4	0.0343	0	0	0
			303.15K			
0	1116	777.4	0.0148	0	0	0
0.1293	1158	804.9	0.0156	-0.182	-0.00024	-7.1817
0.2507	1212	818.2	0.0161	-0.2992	-0.00087	-20.5964
0.3638	1242	872.5	0.0169	-0.4185	-0.00114	-110.7646
0.4673	1282	898.3	0.0174	-3698	-0.00082	-159.0491
0.5716	1328	931.4	0.0187	-0.3432	-0.00072	-119.5864
0.667	1372	967.5	0.0204	-0.2911	-0.00071	-44.7885
0.7492	1420	1002.6	0.0222	-0.2752	-0.00069	34.9125
0.8423	1486	1040.1	0.0237	-0.2331	-0.00033	55.8442
0.9214	1536	1081.3	0.0249	-0.1281	-0.00022	337.1202
1	1591	1124.8	0.026	0	0	0
			313.15K			
0	1086	769.1	0.01127	0	0	0
0.1293	1125	798.3	0.0118	-0.1745	-0.0004	-18.5234
0.2507	1169	829.4	0.0123	-0.3552	-0.00074	-109.5306
0.3638	1206	864.4	0.0128	-0.3909	-0.00119	-180.7485
0.4673	1240	898.2	0.0133	-0.3419	-0.00138	-244.6861
0.5716	1293	924.3	0.0142	-0.3432	-0.00081	-214.84
0.667	1338	960.1	0.0158	-0.2939	-0.00077	-97.8106
0.7492	1384	996.2	0.0177	-0.2658	-0.00079	46.8469
0.8423	1450	1041.6	0.0187	-0.2461	-0.00059	8.50644
0.9214	1518	1076.1	0.0198	-0.2054	-0.00033	15.4036
1	1564	1117.2	0.0209	0	0	0

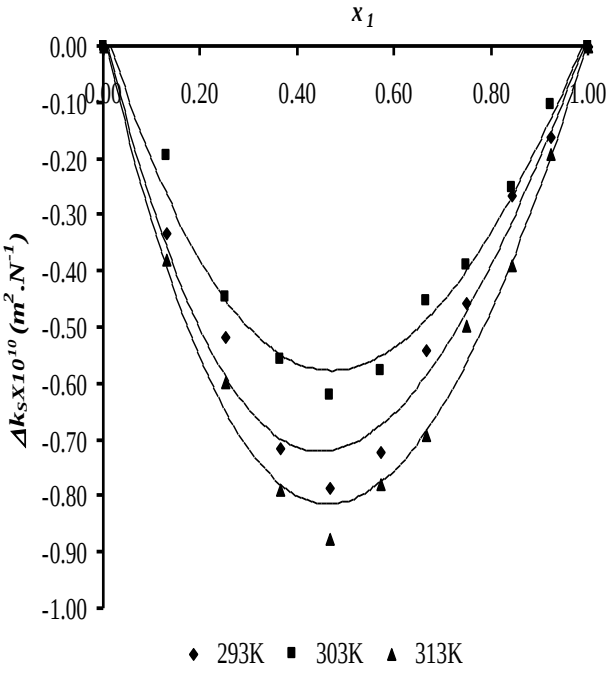
TABLE-3

Adjustable parameters a_i with the standard deviations $\sigma(Y^E)$ for excess molar isentropic compressibility (Δk_s), excess molar volume (V_m^E) and excess free energy of activation for viscous flow (ΔG^{*E}) for both the binary mixtures at varying temperatures.

Parameters	Temp. (K)	a_1	a_2	a_3	a_4	a_5	$\sigma(Y^E)$
formamide +1-propanol							
Δk_s X 10^{10} ($m^2.N^{-1}$)	293	-3.0449	-2.3681	-3.2037	5.0301	7.5612	0.0083
	303	-2.3654	0.2747	-1.5410	0.3073	3.9992	0.0140
	313	-1.9469	-1.1582	0.1243	2.4604	0.6424	0.0127
V_m^E ($cm^3.mol^{-1}$)	293	-4.8800	-0.5474	-9.1454	34.7772	30.110	0.0905
	303	-6.5405	-0.9628	-1.4815	0.3643	02.725	0.0205
	313	-9.1613	-4.7922	-3.7835	4.8922	10.008	0.0240
ΔG^{*E} ($kJ.mol^{-1}$)	293	-0.0498	-0.1864	0.2367	0.1257	-0.1825	0.0030
	303	-0.0341	-0.3001	0.1333	0.3302	-0.0262	0.0025
	313	-0.0315	-0.0089	0.0968	0.1157	-0.0887	0.0071
formamide +2-propanol							
Δk_s X 10^{10} ($m^2.N^{-1}$)	293	-3.1591	-0.1512	3.9304	-0.9188	-4.9880	0.0235
	303	-2.3782	-0.2853	-0.3640	0.6236	2.6958	0.0169
	313	-3.6439	0.4247	2.2890	-1.4708	-2.3108	0.0242
V_m^E ($cm^3.mol^{-1}$)	293	-6.6705	0.0321	4.032	-2.2504	-5.966	0.0695
	303	-9.0125	-3.4286	-9.791	7.6654	21.855	0.1786
	313	-9.9616	-2.9063	-13.939	6.0510	28.375	0.0814
ΔG^{*E} ($kJ.mol^{-1}$)	293	-0.0551	-0.2644	0.7053	0.1660	0.8349	0.0019
	303	-0.0532	-0.0294	-0.0403	-1.2462	2.3611	0.0036
	313	0.0141	0.0380	0.0023	0.3718	0.3438	0.0088







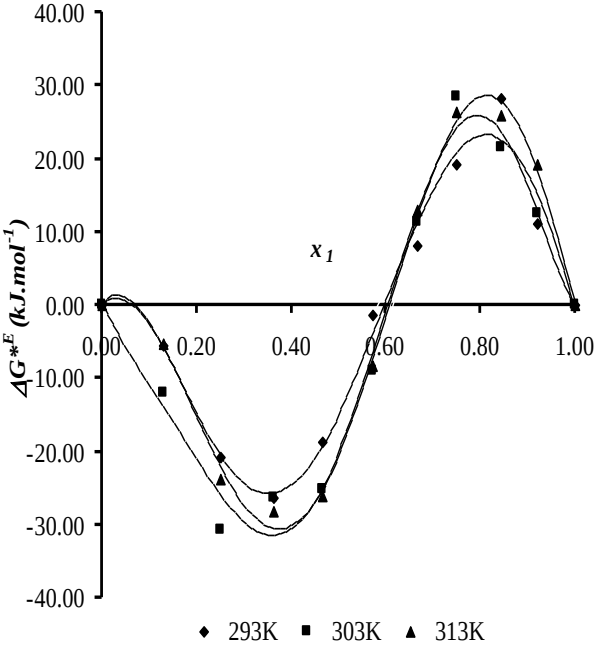


Fig.1: Deviation in isentropic compressibility Δk_s, as a function of mole fraction of formamide (x_1) for (a) formamide +1-propanol and (b) formamide +2-propanol mixtures.

Fig.2: Excess free energy of activation for viscous flow ΔG^{*E}, as a function of mole fraction of formamide (x_1) for (a) formamide +1-propanol and (b) formamide +2-propanol mixtures.

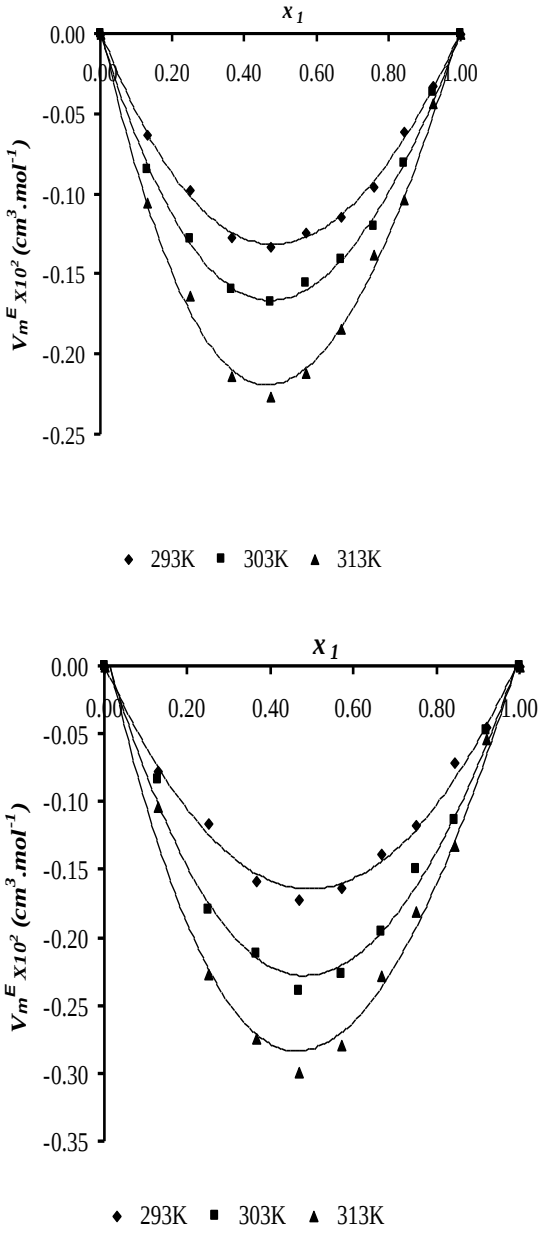


Fig.3: Deviation in excess molar volume V_m^E , as a function of mole fraction of formamide *(x_1)* for (a) formamide +1-propanol and (b) formamide +2-propanol mixtures.

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