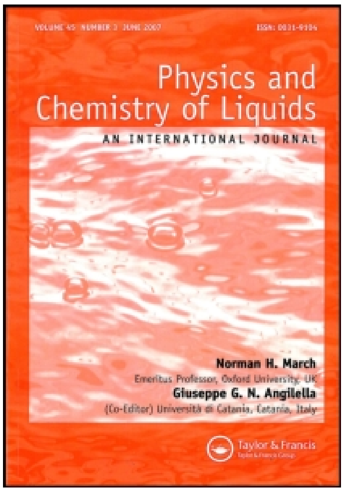

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Acoustical and excess thermodynamic studies of molecular interaction in aqueous mixed solvent systems at 303, 308 and 313 K

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Acoustical and excess thermodynamic studies of molecular interaction in aqueous mixed solvent systems at 303, 308 and 313 K

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Ultrasonic velocity (U), density (ρ) and viscosity (η) for the ternary liquid mixtures of water + propylene glycol + tetrahydrofuran, water + propylene glycol + dimethylformamide, water + propylene glycol + dimethylsulphoxide and water + propylene glycol + 1,4-dioxane have been measured as a function of the composition at 303, 308 and 313 K. The experimental data have been used to calculate some excess thermodynamical parameters such as excess viscosity (η^{E}), excess free volume ($V_{\mathrm{f}}^{\mathrm{E}}$), excess Gibb's free energy (ΔG^{E}) and interaction parameter (d). The results are discussed and interpreted in terms of structural and specific interaction predominated by hydrogen bonding.

Keywords: ultrasonic velocity; excess thermodynamic parameters; interaction parameter; hydrogen bonding

1. Introduction

In recent years, the measurement of density, viscosity and ultrasonic velocity have become valuable tools with which to learn more about the liquid state [1,2] because of the close connections between liquid structure and macroscopic properties. The calculated excess quantities from such data have been interpreted in terms of the differences in the size of the molecules as well as the strength of specific and non-specific interactions between components of the mixtures. Further, measurements of excess thermodynamic properties are found to be greatly significant in studying the structural changes associated with the liquids. They also provide important information about molecular packing, molecular motion and various types of intermolecular interactions and their strength influenced by the size, shape and the chemical nature of component molecules [3]. This in turn helps in bringing out the facts which can have positive implementation for both industry as well as the theory building process. A thorough knowledge of thermodynamic and transport properties of ternary liquid systems is essential in many industrial applications such as design calculations of heat transfer, mass transfer, fluid flow and so forth [4].

The present work deals with the study of excess thermodynamics and transport properties of some aqueous mixed solvent systems at different temperatures. The liquids under investigation have been chosen on the basis of their industrial application. These uses have greatly stimulated the need for extensive information on the thermodynamic,

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acoustic and transport properties of these solvents and their mixtures [5]. The increasing use of the solvents propylene glycol, tetrahydrofuran (THF), dimethylformamide (DMF), dimethylsulphoxide (DMSO), 1,4-dioxane and their aqueous mixtures in many industrial processes, such as battery, pharmaceutical and cosmetic have greatly stimulated the need for extensive information on their various properties. Viscosity and density of these ternary liquid mixtures are used to understand molecular interactions between the components of the mixture to develop new theoretical models and also for engineering applications [6]. 1,4-Dioxane is an aprotic solvent and it is reported to be valuable in polymer manufacture and as a solvent for natural and synthetic resins. The most important use of DMF as a dipolar aprotic solvent for polymer is in the preparation of polyacrylonitrile solutions for the manufacture of fibrous poly acrylonitride. DMSO is an aprotic polar solvent strongly associated due to a highly polar $s=0$ group in the molecule and large dipole moment (3.96 D). DMSO is called a super solvent due to its wide range of applicability as a solvent in chemical and biological processes and chemical intermediates [7]. The study of DMSO is important because of its utilisation in a broad range of applications in medicine. THF is frequently utilised as a solvent in many pharmaceutical and synthetic procedures because of its broad solvency for polar and non-polar compounds. Propylene glycol is mostly used as a co-solvent in the design and especially for the elaboration of parenteral medication [8].

Keeping these important aspects in view, the measurements on ultrasonic velocity, density and viscosity and their related excess thermodynamical and transport parameters for aqueous mixed solvent systems of water + propylene glycol + tetrahydrofuran (THF), water + propylene glycol + DMF, water + propylene glycol + DMSO and water + propylene glycol + 1,4-dioxane at 303, 308 and 313 K have been undertaken. The dependence of excess parameters on composition has been used to explain the nature and extent of intermolecular interactions in these mixtures. Moreover, a literature survey indicates that no physico-chemical study on these systems has been reported. Therefore, the study of intermolecular interactions in these systems will be interesting owing to their application in industry.

2. Materials and methods

All the chemicals used in the present research were of analytical reagent (AR) and spectroscopic reagent (SR) grades of a minimum assay of 99.9% obtained from E-Merck, Germany and Sd Fine Chemicals, India, which were without further purification. Water used in the experiments was deionised and distilled and was degassed prior to making solutions. The purities of the above chemicals were checked by density determination at 303, 308 and 313 K ± 0.1 K, which showed an accuracy of $\pm 1 \times 10^{-4}\,\mathrm{g\,cm^{-3}}$ with the reported values [9,10]. The ternary liquid mixtures of different known compositions were prepared in stopper measuring flasks. The density, viscosity and velocity were measured as a function of composition of the ternary liquid mixture at 303, 308 and 313 K for aqueous mixed solvent systems in which THF, DMF, DMSO and 1,4-dioxane were added to a binary mixtures of water and propylene glycol. For this purpose, binaries with fixed mole ratios $X_1 : X_2 \cong 3:1$ were prepared by mass. The density was determined using a specific gravity bottle by relative measurement method with an accuracy of $\pm 0.01\,\mathrm{kg\,m^{-3}}$. The weight of the sample was measured using electronic digital balance with an accuracy of ±0.1 mg (model: Shimadzu AX-200). An Ostwald's viscometer (10 mL) was used for the viscosity measurement. Efflux time was determined using a digital chronometer to within ±0.01 s. An ultrasonic interferometer having the frequency of 3 MHz (Mittal Enterprises, New Delhi, model: F-81) with an overall accuracy of ±0.1% has been used for velocity measurement. An electronic digitally operated constant temperature bath (RAAGA Industries) has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature. The accuracy in the temperature measurement is ±0.1 K.

3. Theory and calculations

Various acoustical and thermodynamical parameters are calculated from the measured data, such as

$$\text{Free volume,}\ \ V_\mathrm{f} = \left(\frac{M_\mathrm{eff}U}{K\eta}\right)^{3/2}, \tag{1}$$

where M_eff is the effective molecular weight ($M_\mathrm{eff}=\sum m_i x_i$, in which m_i and x_i are the molecular weight and the molefraction of the individual constituents, respectively). K is a temperature independent constant which is equal to 4.28×10^9 for all liquids.

The Gibb's free energy can be estimated from the following relation:

$$\Delta G = KT \ln\left(\frac{KT\tau}{h}\right), \tag{2}$$

where K is the Boltzmaan's constant ($1.23 \times 10^{-23}\ \mathrm{JK}^{-1}$), T the absolute temperature, h the Planck's constant and τ is the relaxation time ($\tau = (4/3)\eta\beta$).

Excess values of the above parameters can be determined using

$$A^\mathrm{E} = A_\mathrm{exp} - A_\mathrm{id}, \tag{3}$$

where $A_\mathrm{id} = \sum A_i X_i$, A_i is any acoustical parameters and X_i the molefraction of the liquid component. Grunberg [11] and Nissan formulated the following relation between the viscosity of a binary liquid mixture and pure components:

$$\ln \eta_\mathrm{mix} = X_1 \ln \eta_1 + X_2 \ln \eta_2 + X_1 X_2 d. \tag{4}$$

On applying to a ternary liquid mixture, this equation takes up the form

$$\ln \eta_\mathrm{mix} = X_1 \ln \eta_1 + X_2 \ln \eta_2 + X_3 \ln \eta_3 + X_1 X_2 X_3 d, \tag{5}$$

where d is an interaction parameter regarded as a measure of the strength of molecular interactions between the mixing components.

4. Results and discussion

The experimental values of density (ρ), viscosity (η) and ultrasonic velocity (U) of pure liquids and four ternary organic liquid mixtures at 303, 308 and 313 K have been given in Tables 1 and 2. The values of excess viscosity (η^E), excess free volume (V_f^E), excess Gibb's free energy (ΔG^E) and Grunberg and Nissan interaction parameter (d) have been evaluated and shown in Table 3. Further, the variation of these excess values of studied

Table 1. Comparison of experimental values of density (ρ), viscosity (η) and ultrasonic velocity (U) of pure liquids at 303, 308 and 313 K with literature values.

	ρ (kg m^{-3})						η ($\times 10^{-3}$ Nsm^{-2})						U (m s^{-1})					
	Experimental			Literature			Experimental			Literature			Experimental			Literature		
Organic liquids	303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K
Water	995.7	994.0	992.2		994.0[a]		0.7977	0.7190	0.6532		0.7190[a]		1510.4	1522.4	1532.0			
Propyleneglycol	1026.1	1025.7	1022.8				18.1097	13.5816	10.6120				1490.1	1478.5	1463.1			
THF	877.4	869.4	863.1	877.3[b]	871.8[b]	865.7[c]	0.4681	0.4378	0.3987		0.4390[a]		1278.6	1264.8	1251.2		1266.0[j]	
DMF	939.8	935.5	930.9	939.7[d]	935.6[d]	929.8[e]	0.7498	0.7022	0.6598	0.7520[h]	0.7070[h]	0.6641[h]	1476.2	1464.6	1453.5		1466.0[k]	
DMSO	1089.8	1085.6	1081.6	1089.6[f]	1084.7[f]	1080.6[f]	1.7862	1.5992	1.4286	1.7979[i]	1.6092[i]	1.4492[i]	1455.3	1450.8	1440.3			
1,4-Dioxane	1022.7	1016.2	1012.6	1022.3[g]	1016.5[g]	1011.6[g]	1.0542	0.9790	0.8691		0.9840[h]		1353.2	1342.7	1322.5		1343.9[k]	

Note: [a][12]; [b][13]; [c][14]; [d][15]; [e][16]; [f][17]; [g][18]; [h][19]; [i][20]; [j][21]; [k][22].

Table 2. Values of density (ρ), viscosity (η) and ultrasonic velocity (U) at 303, 308 and 313 K.

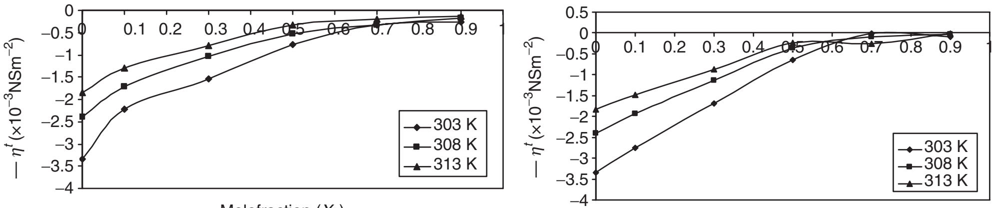
	ρ (kg m^{-3})			η ($\times 10^{-3}$ Nsm^{-2})			U (m s^{-1})		
Molefraction (X_3)	303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K
System I: Water (X_1) + Propyleneglycol (X_2) + THF (X_3) [(X_1)/(X_2) = 3 : 1]									
0	1013.6	1010.6	1008.7	1.7858	1.5347	1.3020	1642.2	1638.4	1636.8
0.1	1009.7	1004.5	1001.1	2.4533	1.8809	1.5907	1639.2	1635.5	1629.3
0.3	987.8	986.3	983.6	2.2342	1.8960	1.5781	1576.2	1572.0	1558.7
0.5	967.8	966.1	960.5	2.0911	1.7166	1.5114	1479.2	1470.2	1454.2
0.7	935.5	930.4	929.7	1.6275	1.2483	1.1239	1372.1	1366.4	1357.6
0.9	902.1	897.2	894.2	0.7927	0.7320	0.6665	1290.3	1268.3	1255.5
System II: Water (X_1) + Propyleneglycol (X_2) + DMF (X_3)									
0	1013.6	1010.6	1008.7	1.7858	1.5347	1.3020	1642.2	1638.4	1636.8
0.1	1011.4	1008.8	1006.9	1.9490	1.6848	1.4177	1653.8	1648.3	1639.8
0.3	1003.6	1002.5	999.2	2.1527	1.8587	1.5812	1665.8	1658.4	1645.7
0.5	1001.4	995.5	991.2	2.3497	2.0242	1.7018	1657.4	1640.9	1621.2
0.7	982.8	979.9	969.3	2.1662	1.8447	1.7192	1602.2	1594.2	1583.6
0.9	958.3	954.7	950.1	1.2029	1.0958	0.9787	1494.2	1485.2	1463.4
System III: Water (X_1) + Propyleneglycol (X_2) + DMSO (X_3)									
0	1013.6	1010.6	1008.7	1.7858	1.5347	1.3020	1642.2	1638.4	1636.8
0.1	1022.6	1021.2	1019.5	1.9444	1.7002	1.4443	1653.5	1649.6	1643.6
0.3	1044.5	1038.8	1037.4	2.3205	1.9826	1.6733	1669.8	1664.6	1655.7
0.5	1063.5	1061.9	1059.1	3.1105	2.6299	2.1957	1685.2	1679.0	1663.3
0.7	1076.1	1073.1	1068.2	2.9485	2.5398	2.3258	1643.2	1633.9	1605.5
0.9	1087.9	1084.8	1083.1	2.6790	2.3974	1.7906	1529.4	1516.4	1501.2
System IV: Water (X_1) + Propyleneglycol (X_2) + 1,4 Dioxane (X_3)									
0	1013.6	1010.6	1008.7	1.7858	1.5347	1.3020	1642.2	1638.4	1636.8
0.1	1021.6	1018.8	1012.2	1.9866	1.6837	1.4107	1638.7	1634.1	1631.2
0.3	1025.3	1022.5	1016.8	2.4047	1.9182	1.6481	1612.6	1601.6	1591.2
0.5	1030.8	1026.3	1022.9	2.9450	2.1994	2.0167	1566.5	1556.6	1545.9
0.7	1026.6	1021.9	1018.6	2.2285	2.0060	1.6772	1468.7	1455.7	1441.0
0.9	1024.5	1019.0	1016.1	1.5575	1.4101	1.2832	1363.5	1344.2	1328.4

Table 3. Excess values of viscosity (η^E), free volume (V_f^E), Gibbs free energy (ΔG^E) and interaction parameter (*d*) at 303, 308 and 313 K.

	$-\eta^E$ ($\times 10^{-3}$ Nsm^{-2})			$-V_f^E$ ($\times 10^{-8}$ m^3 mol^{-1})			ΔG^E ($\times 10^{-21}$ KJ mol^{-1})			*d*		
Molefraction (X_3)	303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K	303 K	308 K	313 K
System I: Water (X_1) + Propyleneglycol (X_2) + THF (X_3)[(X_1)/(X_2) = 3 : 1]												
0	3.3399	2.3999	1.8409	−0.1162	−0.2488	−0.5315	−0.5902	−0.5701	−0.6599	0.1348	0.1258	0.0384
0.1	2.2203	1.7177	1.2915	2.2488	1.9861	1.9201	0.8225	0.4003	0.2844	29.5394	21.2642	18.6153
0.3	1.5351	1.0305	0.7825	5.3811	5.3631	5.3765	1.2562	1.0976	0.8804	20.5605	18.9696	16.4734
0.5	0.7740	0.5378	0.3277	8.5715	8.3803	8.7794	1.9676	1.6045	1.5576	30.3817	26.2553	25.1794
0.7	0.3334	0.3341	0.1935	10.7801	9.6033	9.9630	2.1287	1.3927	1.3206	56.9747	41.3705	40.0584
0.9	0.2639	0.1783	0.1294	5.4248	5.0403	4.6980	0.4498	0.3704	0.2476	97.9259	87.0216	77.0056
System II: Water (X_1) + Propyleneglycol (X_2) + DMF (X_3)												
0	3.3399	2.3999	1.8409	−0.1162	−0.2488	−0.5315	−0.5902	−0.5701	−0.6599	0.1348	0.1258	0.0384
0.1	2.7514	1.9379	1.4861	1.0809	1.0249	0.8461	−0.1118	−0.0943	−0.2185	11.9697	11.7043	8.7987
0.3	1.6971	1.1402	0.8769	3.3426	3.3605	3.4472	0.6142	0.5488	0.4450	15.2135	14.4302	12.8495
0.5	0.6491	0.3509	0.2454	5.6779	5.8032	6.0571	1.3731	1.2716	1.1160	27.5206	25.8035	22.9995
0.7	0.0175	0.0934	0.2503	7.4351	7.4136	8.4052	1.7795	1.4917	1.6634	59.4142	53.6432	55.9245
0.9	0.0952	0.0319	0.0118	4.4885	4.2680	4.3746	0.5884	0.4469	0.4208	149.1674	139.0027	123.6089
System III: Water (X_1) + Propyleneglycol (X_2) + DMSO (X_3)												
0	3.3399	2.3999	1.8409	−0.1162	−0.2488	−0.5315	−0.5902	−0.5701	−0.6599	0.1348	0.1258	0.0384
0.1	2.8637	2.0202	1.5421	0.0228	0.0134	0.2390	−0.3945	−0.3021	−0.4131	5.8794	7.1207	5.1378
0.3	1.9123	1.3092	1.0001	0.3501	0.4195	0.2442	−0.0716	0.0600	−0.1292	8.1266	8.2043	6.8285
0.5	0.5271	0.2333	0.1647	1.1848	1.5019	1.5475	0.7391	0.8949	0.6426	20.2611	20.1805	18.0442
0.7	0.0939	0.1052	0.2784	1.1299	1.5817	2.1366	0.5383	0.8425	0.9443	32.1058	34.0689	37.5424
0.9	0.0232	0.0392	0.0562	1.0095	1.7359	0.8931	0.5299	0.7347	0.2424	142.9748	183.1467	85.9022
System IV: Water (X_1) + Propyleneglycol (X_2) + 1,4 Dioxane (X_3)												
0	3.3399	2.3999	1.8409	−0.1162	−0.2488	−0.5315	−0.5902	−0.5701	−0.6599	0.1348	0.1258	0.0384
0.1	2.7457	1.9691	1.5183	0.6500	0.4894	0.2097	−0.1630	−0.2051	−0.3643	11.1789	9.5947	6.5495
0.3	1.5407	1.1709	0.8538	2.3128	1.9840	1.9903	0.7485	0.4475	0.3559	15.8425	12.1571	11.1735
0.5	0.2136	0.3261	0.0579	4.2154	3.7378	4.3149	1.7932	1.1875	1.2801	30.5173	22.6492	24.0119
0.7	0.1432	0.0443	0.0229	4.4339	4.6028	4.6124	1.3433	1.3830	1.0752	43.3744	42.1384	36.5206
0.9	0.0273	0.0121	0.0633	2.9582	2.8640	3.2996	0.6630	0.0676	0.6482	136.3022	121.0371	128.3556

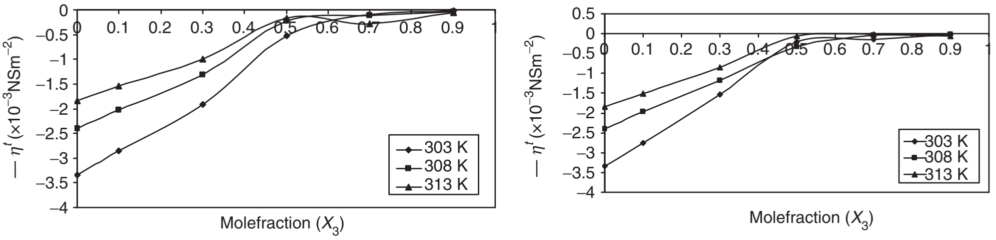
systems with molefraction of (X_3) at 303, 308 and 313 K have been recorded in Figures 1–3 and the curves are drawn using least squares fitting.

The thermodynamic excess properties are found to be more sensitive towards intermolecular interaction between the component molecules of liquid mixtures. The sign and extent of deviation of excess properties depend on the strength of interaction between unlike molecules [23].



System I: Water (X_1) + Propyleneglycol (X_2) + THF (X_3)

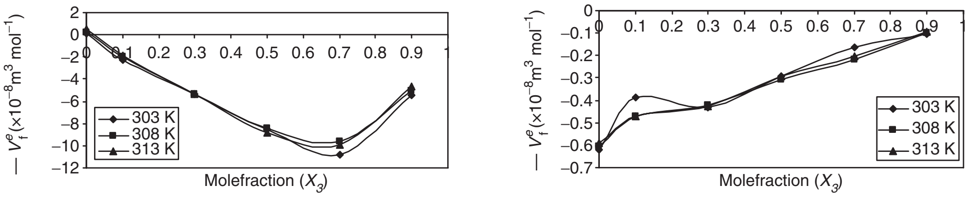
System II: Water (X_1) + Propyleneglycol (X_2) + DMF (X_3



System III: Water (X_1) + Propyleneglycol (X_2) + DMSO (X_3)

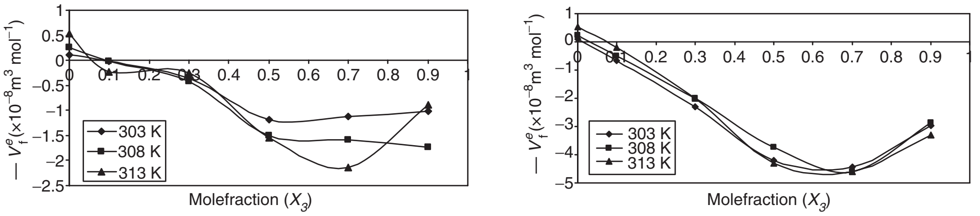
System IV: Water (X_1) + Propyleneglycol (X_2) + 1,4 Dioxane (X_3)

Figure 1. Variation of excess viscosity (η^E) of aqueous mixed solvent systems with molefraction of (X_3) at 303, 308 and 313 K.



System I: Water (X_1) + Propyleneglycol (X_2) + THF (X_3)

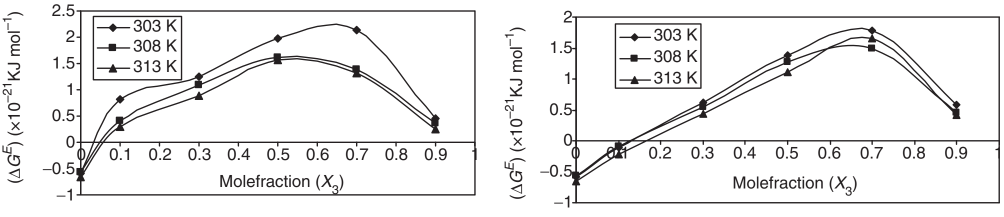
System II: Water (X_1) + Propyleneglycol (X_2) + DMF (X_3)



System III: Water (X_1) + Propyleneglycol (X_2) + DMSO (X_3)

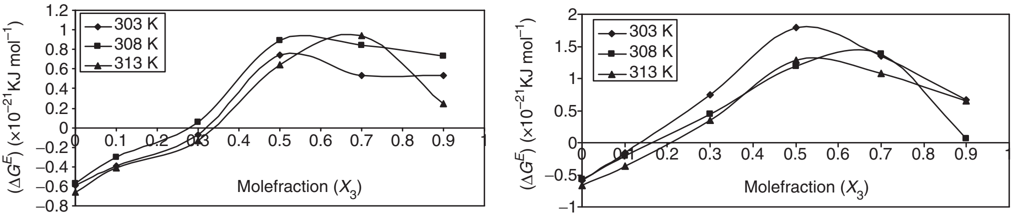
System IV: Water (X_1) + Propyleneglycol (X_2) + 1,4 Dioxane (X_3)

Figure 2. Variation of excess free volume (V_f^E) of aqueous mixed solvent systems with molefraction of (X_3) at 303, 308 and 313 K.



System I: Water (X_1) + Propyleneglycol (X_2) + THF (X_3)

System II: Water (X_1) + Propyleneglycol (X_2) + DMF (X_3)



System III: Water (X_1) + Propyleneglycol (X_2) + DMSO (X_3)

System IV: Water (X_1) + Propyleneglycol (X_2) +1,4 Dioxane (X_3)

Figure 3. Variation of excess Gibb's free energy (ΔG^E) of aqueous mixed solvent systems with molefraction of (X_3) at 303, 308 and 313 K.

According to Fort and Moore [24] the excess viscosity gives the strength of the molecular interaction between the interacting molecules. Systems where dispersion, induction and dipolar forces which are operated by the values of excess viscosity are found to be negative; whereas the existence of specific interactions leading to the formation of complexes in liquid mixtures tends to make excess viscosity positive. The excess viscosity (Figure 1) is negative through the whole range of concentration in all four systems. From the analysis and close observation it is found that they increase with an increase in molefraction of X_3, and also with the rising of temperature. This increasing behaviour shows the existence of molecular interaction between the components of mixture for all the systems studied.

Figure 2 gives a qualitative picture of the excess free volume for the four ternary liquid systems. This indicates the extent of deviation from ideal with the molefraction of the mixtures. The excess values for all the four systems are found to be negative, except the molefraction of X_3 at 0. Further, these values decrease to reach a minima at $X_3 = 0.7$ and beyond this they increase for every mixture, whereas it is found to be increasing with the rising of temperature. The results can be explained in terms of molecular interaction, structural effect and interstitial accommodation, along with changes in free volume. The sign of V_f^E depends upon the relative strength between the contractive forces and expansive forces. The factors responsible for volume contraction are:

(a) Specific interaction between component molecules.
(b) Interstitial accommodation of molecules of one component into the vacant spaces of molecules of the other components. This occurs preferentially when the size difference between the component molecules is large, or when large gaps are available in the structural network of molecules.
(c) Weak physical forces, such as dipole–dipole or dipole–induced-dipole interactions or van der Waal's forces.

The factors that cause expansion in volume are the following:

(a) dispersion force,
(b) steric hindrance of component molecules,
(c) unfavourable geometric fitting,
(d) electrostatic repulsion, etc.

The negative part of V_f^E curves of the system asserts that the combined effect of the factors responsible for volume contraction outweigh the combined effect of the factors causing volume expansion, and vice-versa [25]. Adgaonkar and Agnihotri [26] showed a positive value of V_f^E, indicating the existence of weak molecular interaction in the liquid mixtures. Fort and Moore [24] noticed that negative excess free volume tends to decrease as the strength of the interaction between the unlike molecules increases, although they do not parallel with the excess compressibilities. However, in the present investigation the observed behaviour of V_f^E shows the strength of molecular interaction greater up to the level of 0.7 molefraction of X_3; however, the strength of interaction is less beyond this level, and also increasing in temperature. The magnitude of V_f^E values follows the sequence:

$$\text{THF} < \text{DMF} < 1,4\text{-Dioxane} < \text{DMSO}.$$

The variation of excess Gibb's free energy shown in Figure 3 is found to be positive, except for lower mole fraction ranges of X_3, in all systems studied. The values of ΔG^E are found to be increasing with increasing the mole fraction of X_3, whereas they are found to be decreasing with higher mole fraction of X_3. However, these values decrease with rising temperature. According to Reed and Taylor [27], the positive ΔG^E may be attributed to specific interactions like hydrogen bonding and charge transfer, while negative values may be ascribed to the dominance of dispersion forces [28]. In the present investigation, it is found that the magnitude of the positive value of ΔG^E is an excellent indicator of the strength of specific interaction. The larger magnitude of positive ΔG^E values is observed in THF, which shows the strongest interaction between the molecules compared to the other three systems. Recently, Ali and Nain [29] attribute the increasing positive values of ΔG^E in liquid mixtures to hydrogen bond formation between unlike molecules, which supports the present investigation.

The interaction parameters, *d*, in the Grunberg and Nissan equation is a measure of the strength of interaction between the mixing components. *d*-values were said to indicate various types of interaction [30], as follows. Large and positive *d*-values indicate strong specific interaction; small positive values indicate weak specific interaction and large negative values indicate no specific interaction. It is evident from Table 3 that the *d*-values are positive in all of the four systems studied. It is seen that the values of *d* increase with increasing the mole fraction of X_3 for every mixture, and the same decreases with the rising temperature. Positive *d*-values may be attributed to the dominance of specific interactions arising from the making of hydrogen bonds in the associated components of the mixtures. Further, the increasing behaviour of *d*-values exhibits the stronger interaction between the unlike molecules. However, the strength of interaction gets weakened with the rising of temperature, which may be due to the decreasing behaviour of the *d*-values for all systems studied.

5. Conclusion

The ultrasonic method is a powerful tool for characterising the physico-chemical properties and existence of molecular interaction in mixtures. Excess ultrasonic properties of ternary mixtures of THF, DMF, dimethylsulfoxide and 1,4-dioxane in water and propylene glycol at 303, 308 and 313 K are considered to be reflecting agents of magnitude of polarity and size of interaction in the molecules. The results of excess properties reveal that a strong molecular interaction exists in the mixtures, which may be due to the dominance of hydrogen bonding and charge transfer between the mixing components. From the magnitude of V_f^E and ΔG^E, THF possesses stronger molecular interaction between the molecules than the other three systems. The strength of interaction tends to be weaker with an increase in temperature, due to the presence of weak intermolecular forces and thermal dispersion forces.

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