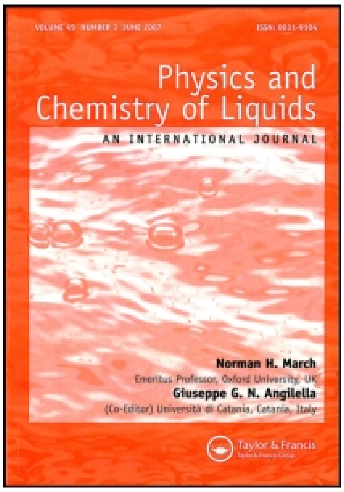

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Studies of viscous antagonism, excess molar volume and isentropic compressibility in aqueous mixed solvent systems at different temperatures

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Studies of viscous antagonism, excess molar volume and isentropic compressibility in aqueous mixed solvent systems at different temperatures

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Densities and viscosities for the ternary liquid mixtures of water + ethylene glycol + tetrahydrofuran, water + ethylene glycol + 1,4-dioxane, water + ethylene glycol + *N*,*N*-dimethylformamide and water + ethylene glycol + dimethyl sulphoxide have been measured as a function of the composition at 298.15, 308.15 and 318.15 K. From the experimental measurements, viscosity deviations ($\Delta\eta$), antagonic index (I_A) and excess molar volumes (V^E) have been evaluated. The speeds of sound have been also measured and excess isentropic compressibilities (K_S^E) are calculated at 298.15 K. The results are discussed and interpreted in terms of molecular package and specific interaction predominated by hydrogen bonding.

Keywords: Viscous antagonism; Viscosity deviations; Excess molar volumes; Isentropic compressibilities

1. Introduction

Grouping of solvents into classes is often based on the nature of the intermolecular forces because the manner whereby solvent molecules are associated with each other brings about a marked effect on the resulting properties. After the introduction of the concept of ionisation power of solvents [1], much work has been devoted to the solvent effects on the rate and equilibrium processes [2]. The determination of density, viscosity and speeds of sound is a valuable tool to learn about the liquid state [3,4] because of the close connection between liquid structure and macroscopic properties.

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Rheology is the branch of science [5] that studies material deformation and flow, and is increasingly applied to analyse the viscous behaviour of many pharmaceutical products [6], and to establish their stability and even bio-availability, since it has been firmly established that viscosity influences the drug absorption rate in the body.

The increasing use of the solvents: ethylene glycol, tetrahydrofuran, 1,4-dioxane, *N*,*N*-dimethylformamide, dimethyl sulphoxide and their aqueous mixtures in many industrial processes such as battery, pharmaceutical and cosmetics 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 [7]. In the author's systematic investigation of the properties, they have reported viscosities, densities and speeds of sound in their previous papers [8,9].

The present work contributes to the study of viscosity deviations, viscous antagonism, excess molar volumes and isentropic compressibility in ternary solutions of water (A), ethylene glycol (B) and THF, DO, DMF, DMSO (C).

2. Experimental

2.1. *Source and purity of samples*

Ethylene glycol ($C_2H_6O_2$, FW = 62.07), THF (tetrahydrofuran, C_4H_8O, FW = 72.11), DO (1,4-dioxane, $C_4H_8O_2$, FW = 88.11), DMF (*N*,*N*-dimethylformamide, C_3H_7NO, FW = 73.10), DMSO (dimethyl sulphoxide, C_2H_6SO, FW = 78.13) were obtained from Merck and LR. These were further purified by standard methods [10]. Triply distilled water was used for the experimental purpose. The purity of the liquids was checked by measuring their densities, viscosities and sound velocities at 298.15 K which was quite in agreement with the literature values [11,12]. The purity of the solvents finally obtained were >99%.

2.2. *Method*

Densities (ρ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm^3 and an internal diameter of the capillary of about 1 mm. The pycnometer was calibrated at 298.15, 308.15 and 318.15 K with triply distilled water and THF. The pycnometer with the test solution was equilibrated in a thermostatic water bath maintained at ±0.01 K of the desired temperature by means of a mercury in glass thermoregulator and the temperature was determined with a calibrated thermometer and a Muller bridge [13]. The viscosities (η) were measured by means of a suspended Ubbelohde type viscometer [14] which was calibrated at the desired temperatures. The ultrasonic speeds (u) were determined using a single-crystal variable path ultrasonic interferometer (Mittal Enterprises, New Delhi) working at 5 MHz [15] which was calibrated and the temperature stability was maintained within ±0.01 K by circulating thermostatic water around the cell with a circulating pump.

The solutions were prepared by mixing known volumes of pure liquids in airtight stoppered bottles at 298.15 K. The weights were taken on a Mettler electronic analytical balance (AG285) accurate to 0.0002 g. The uncertainties in the liquid composition, density, viscosity and speeds of sound measurements were estimated to be 1×10^{-4}, $0.3\,\mathrm{kg\,m^{-3}}$, 3×10^{-6} poise, and $0.2\,\mathrm{m\,s^{-1}}$ respectively.

3. Results and discussion

The comparison of the experimentally determined densities, viscosities at 298.15, 308.15 and 318.15 K and sound velocities at 298.15 K of the pure components with the literature values [11,12,16,25] have been presented in table 1.

3.1. *Viscosity deviations*

In table 2, the calculated and experimentally determined viscosities of the ternary mixtures are shown along with the mole fraction of water (x_A) and ethylene glycol (x_B) at the three temperatures.

Viscosity deviation ($\Delta\eta$) and antagonic index (I_A) values presented together in table 3 for clear comparison between the two that appears to be same but are different properties.

Quantitatively, as per the absolute reaction rates theory [17], the deviations of viscosities from the ideal mixture values can be calculated as

$$\Delta\eta = \eta - \sum_{i=1}^{n=3} x_i \eta_i \tag{1}$$

Table 1. Comparison of experimental densities (ρ), viscosities (η) and ultrasonic speeds (u) of the pure components with literature values.

		$\rho \times 10^{-3}$ (kg m^{-3})		$\eta \times 10^{2}$ (poise)		u (m s^{-1})	
Liquids	T (K)	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.
Water	298.15	0.9971	0.9971(11)	0.8904	0.8903(11)	1498.0	1497.4(25)
	308.15	0.9941	0.9940	0.7194	0.7190		
	318.15	0.9903	0.9902	0.5960	0.5972		
Ethylene glycol	298.15	1.1063	1.1100(16)	16.3876	16.4716(16)	1666.0	1662.0(25)
	308.15	1.1029	1.1029	10.7719	10.4700		
	318.15	1.0964	1.0956	7.7029	7.6938		
THF	298.15	0.8807	0.8829(11)	0.4630	0.4850(11)	1279.0	1288.0(25)
	308.15	0.8712	0.8712	0.4277	0.4390		
	318.15	0.8614	–	0.3902	–		
DO	298.15	1.0273	1.0276(12)	1.2236	1.1600(12)	1344.0	1347.0(25)
	308.15	1.0160	1.0162	0.9268	0.9840		
	318.15	1.0056	–	0.7991	–		
DMF	298.15	0.9461	0.9445(12)	0.8586	0.8020(12)	1465.0	1462.0(25)
	308.15	0.9399	0.9356	0.7763	0.7070		
	318.15	0.9316	–	0.7125	–		
DMSO	298.15	1.0954	1.0960(11)	2.0418	2.0422(11)	1493.0	1488.0(25)
	308.15	1.0859	1.0856	1.5682	1.6450		
	318.15	1.0767	–	1.4847	–		

Table 2. Calculated (η_{calcd}) and experimental viscosities (η_{exp}) of water (A) + ethylene glycol (B) + THF, DO, DMF and DMSO (C) at 298.15, 308.15 and 318.15 K.

		T (K)					
		298.15		308.15		318.15	
x_{A}	x_{B}	$\eta_{\mathrm{calcd}} \times 10^2$ (poise)	$\eta_{\mathrm{exp}} \times 10^2$ (poise)	$\eta_{\mathrm{calcd}} \times 10^2$ (poise)	$\eta_{\mathrm{exp}} \times 10^2$ (poise)	$\eta_{\mathrm{calcd}} \times 10^2$ (poise)	$\eta_{\mathrm{exp}} \times 10^2$ (poise)
Water (A) + ethylene glycol (B) + THF (C)							
0.0000	0.5374	8.4253	2.5089	5.5998	1.8657	4.0465	1.5580
0.2917	0.3807	7.6718	3.0132	5.1118	2.1278	3.7015	1.7702
0.4809	0.2789	6.9183	3.2529	4.6237	2.2389	3.3564	1.8577
0.6137	0.2076	6.1648	3.2052	4.1357	2.0902	3.0114	1.7386
0.7119	0.1548	5.4113	2.8614	3.6476	2.0876	2.6663	1.6777
0.7875	0.1142	4.6579	2.5922	3.1596	1.8937	2.3213	1.4754
0.8476	0.0819	3.9044	2.2505	2.6716	1.6581	1.9762	1.3085
0.8964	0.0557	3.1509	1.8361	2.1835	1.3794	1.6312	1.1199
0.9368	0.0339	2.3974	1.5022	1.6955	1.1586	1.2861	0.9499
0.9709	0.0156	1.6439	1.1334	1.2074	0.9263	0.9411	0.7761
1.0000	0.0000	0.8904	0.8904	0.7194	0.7194	0.5960	0.5960
Water (A) + ethylene glycol (B) + DO (C)							
0.0000	0.5867	8.8056	4.3863	5.8493	3.3599	4.2509	2.6606
0.3102	0.4047	8.0141	4.6841	5.3363	3.3688	3.8855	2.6591
0.5029	0.2917	7.2225	4.4134	4.8233	3.2323	3.5199	2.5678
0.6343	0.2146	6.4310	4.0934	4.3103	2.9890	3.1545	2.4148
0.7296	0.1587	5.6395	3.5120	3.7974	2.6999	2.7889	2.1916
0.8018	0.1163	4.8479	3.0150	3.2844	2.3145	2.4235	1.9302
0.8585	0.0829	4.0565	2.5926	2.7714	2.0389	2.0579	1.7051
0.9042	0.0562	3.2649	2.0955	2.2584	1.6466	1.6925	1.4275
0.9418	0.0341	2.4734	1.6589	1.7454	1.3502	1.3269	1.1692
0.9733	0.0157	1.6819	1.3144	1.2324	1.0865	0.9615	0.9308
1.0000	0.0000	0.8904	0.8904	0.7194	0.7194	0.5960	0.5960
Water (A) + ethylene glycol (B) + DMF (C)							
0.0000	0.5408	8.6231	3.0647	5.7741	2.4529	4.2077	1.9599
0.2929	0.3824	7.8498	3.5692	5.2686	2.6729	3.8465	2.1575
0.4825	0.2799	7.0766	3.7485	4.7631	2.6966	3.4853	2.1779
0.6152	0.2081	6.3033	3.4817	4.2577	2.5674	3.1242	2.1075
0.7132	0.1551	5.5300	3.2008	3.7522	2.4000	2.7630	1.9306
0.7886	0.1143	4.7568	2.8546	3.2467	2.1559	2.4018	1.7646
0.8484	0.0820	3.9835	2.4439	2.7413	1.8837	2.0407	1.5409
0.8969	0.0557	3.2102	1.9531	2.2358	1.5390	1.6795	1.3014
0.9372	0.0339	2.4369	1.6778	1.7303	1.3388	1.3183	1.1293
0.9711	0.0156	1.6637	1.3057	1.2249	1.0679	0.9572	0.9164
1.0000	0.0000	0.8904	0.8904	0.7194	0.7194	0.5960	0.5960
Water (A) + ethylene glycol (B) + DMSO (C)							
0.0000	0.5573	9.2147	5.1947	6.1700	3.9014	4.5938	3.1081
0.2993	0.3905	8.3823	5.2372	5.6249	3.8752	4.1940	3.1009
0.4900	0.2842	7.5499	4.9627	5.0799	3.7189	3.7942	2.9574
0.6222	0.2105	6.7174	4.3772	4.5348	3.3605	3.3945	2.7177
0.7193	0.1564	5.8849	3.8823	3.9898	2.9391	2.9947	2.4509
0.7935	0.1151	5.0526	3.2904	3.4447	2.5760	2.5949	2.2202
0.8522	0.0824	4.2201	2.7917	2.8997	2.2892	2.1951	1.9817
0.8997	0.0559	3.3877	2.3008	2.3546	1.8950	1.7953	1.6577
0.9389	0.0340	2.5553	1.8725	1.8095	1.5362	1.3956	1.3437
0.9719	0.0157	1.7228	1.3859	1.2645	1.1737	0.9958	1.0216
1.0000	0.0000	0.8904	0.8904	0.7194	0.7194	0.5960	0.5960

Table 3. Viscosity deviations ($\Delta\eta$) and antagonic index (I_A) of water (A) + ethylene glycol (B) + THF, DO, DMF and DMSO (C) at 298.15, 308.15 and 318.15 K.

		T (K)					
		298.15		308.15		318.15	
x_A	x_B	$\Delta\eta \times 10^2$ (poise)	I_A	$\Delta\eta \times 10^2$ (poise)	I_A	$\Delta\eta \times 10^2$ (poise)	I_A
Water (A) + ethylene glycol (B) + THF (C)							
0.0000	0.5374	−6.512	0.702	−4.121	0.667	−2.762	0.615
0.2917	0.3807	−3.637	0.607	−2.323	0.584	−1.464	0.522
0.4809	0.2789	−1.857	0.529	−1.214	0.516	−0.671	0.447
0.6137	0.2076	−0.826	0.48	−0.664	0.495	−0.296	0.423
0.7119	0.1548	−0.371	0.471	−0.149	0.428	0.009	0.371
0.7875	0.1142	−0.026	0.443	0.055	0.401	0.088	0.364
0.8476	0.0819	0.121	0.424	0.136	0.379	0.145	0.338
0.8964	0.0557	0.103	0.417	0.114	0.368	0.138	0.313
0.9368	0.0339	0.099	0.373	0.107	0.317	0.119	0.261
0.9709	0.0156	0.007	0.311	0.054	0.233	0.072	0.175
1.0000	0.0000	0.000	0.000	0.000	0.000	0.000	0.000
Water (A) + ethylene glycol (B) + DO (C)							
0.0000	0.5867	−5.734	0.502	−3.343	0.426	−2.189	0.374
0.3102	0.4047	−2.573	0.416	−1.478	0.369	−0.871	0.317
0.5029	0.2917	−1.066	0.389	−0.462	0.329	−0.143	0.270
0.6343	0.2146	−0.173	0.363	0.081	0.307	0.263	0.234
0.7296	0.1587	0.125	0.377	0.362	0.289	0.445	0.214
0.8018	0.1163	0.295	0.378	0.409	0.295	0.491	0.204
0.8585	0.0829	0.398	0.361	0.474	0.264	0.508	0.171
0.9042	0.0562	0.321	0.358	0.354	0.271	0.424	0.157
0.9418	0.0341	0.232	0.329	0.283	0.226	0.326	0.119
0.9733	0.0157	0.177	0.219	0.207	0.118	0.221	0.032
1.0000	0.0000	0.000	0.000	0.000	0.000	0.000	0.000
Water (A) + ethylene glycol (B) + DMF (C)							
0.0000	0.5408	−6.192	0.645	−3.729	0.575	−2.533	0.534
0.2929	0.3824	−3.237	0.545	−1.909	0.493	−1.194	0.439
0.4825	0.2799	−1.472	0.470	−0.850	0.434	−0.435	0.375
0.6152	0.2081	−0.628	0.448	−0.254	0.397	0.012	0.325
0.7132	0.1551	−0.089	0.421	0.114	0.360	0.217	0.301
0.7886	0.1143	0.196	0.399	0.282	0.336	0.345	0.265
0.8484	0.0820	0.285	0.386	0.336	0.313	0.354	0.245
0.8969	0.0557	0.201	0.392	0.257	0.312	0.304	0.225
0.9372	0.0339	0.263	0.312	0.277	0.226	0.289	0.143
0.9711	0.0156	0.174	0.215	0.191	0.128	0.208	0.043
1.0000	0.0000	0.000	0.000	0.000	0.000	0.000	0.000
Water (A) + ethylene glycol (B) + DMSO (C)							
0.0000	0.5573	−4.842	0.436	−2.796	0.368	−1.842	0.323
0.2993	0.3905	−2.062	0.375	−1.033	0.311	−0.546	0.261
0.4900	0.2842	−0.592	0.343	−0.049	0.268	0.141	0.221
0.6222	0.2105	0.032	0.348	0.383	0.259	0.477	0.199
0.7193	0.1564	0.425	0.340	0.542	0.263	0.633	0.182
0.7935	0.1151	0.511	0.349	0.622	0.252	0.725	0.144
0.8522	0.0824	0.549	0.338	0.686	0.211	0.742	0.097
0.8997	0.0559	0.493	0.321	0.576	0.195	0.625	0.077
0.9389	0.0340	0.424	0.267	0.452	0.151	0.482	0.037
0.9719	0.0157	0.238	0.195	0.286	0.072	0.303	−0.026
1.0000	0.0000	0.000	0.000	0.000	0.000	0.000	0.000

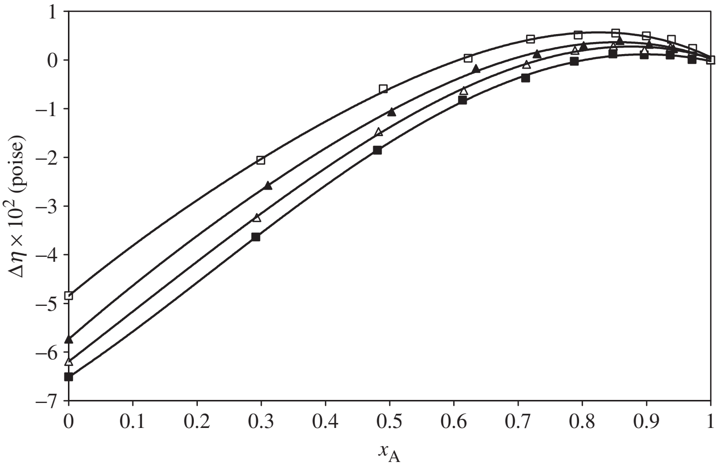

Figure 1. Viscosity deviations ($\Delta\eta$) of: (■), water (A) + ethylene glycol (B) + THF (C); (▲), water (A) + ethylene glycol (B) + 1,4-dioxane (C); (△), water (A) + ethylene glycol (B) + *N*,*N*-dimethylformamide (C); and (□), water (A) + ethylene glycol (B) + dimethylsulphoxide (C) mixtures with mole fraction of water (x_A) at 298.15 K.

where η is the viscosity of the mixture and x_i, η_i are the mole fraction and viscosity of pure component *i* respectively.

In figure 1, $\Delta\eta$ values for the ternary mixtures (A) + (B) + THF, DO, DMF and DMSO (C) have been plotted against the mole fraction of water (x_A) at 298.15 K. It is observed that $\Delta\eta$ values increases to attain a maximum and then decreases as the mole fraction of water increases. Similar curves are obtained at 308.15 and 318.15 K. This trend is observed for all the ternary mixtures examined here. The values become more and more positive as the temperature rises from 298.15 to 318.15 K. However, the mixtures have maximum $\Delta\eta$ at $x_A = 0.85$ for all the temperatures indicating strong specific interaction between the unlike molecules. The estimated uncertainty for $\Delta\eta$ is ± 0.0004 poise.

Here, dispersion and dipolar interactions are operating between water, ethylene glycol and THF/DO/DMF/DMSO molecules resulting in negative $\Delta\eta$ but with the increase in temperature and x_A of water, the hydrogen bonding interactions come into play leading to the formation of complex species between unlike molecules thereby resulting in positive $\Delta\eta$ [18].

3.2. *Viscous antagonism*

The method most widely used to analyse the antagonic behaviour of various mixtures studied here is that developed by Kalentunc-Gencer and Peleg [19], allowing the quantification of the antagonic interactions taking place in mixtures involving variable proportions of the constituent components. The method compares the viscosity of the system, determined experimentally, η_{exp} with the viscosity expected in the absence of interaction, η_{calcd}.

Thus, when $\eta_{\text{exp}} < \eta_{\text{calcd}}$ the system is considered to exhibit viscous antagonism. Hence, it is defined as the interaction between the components of a system causing the

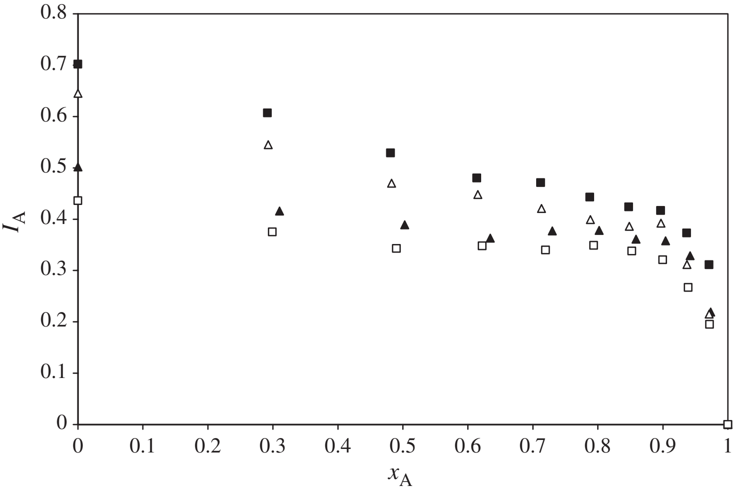

Figure 2. Antagonic Index (I_A) values of: (■), water (A) + ethylene glycol (B) + THF (C); (▲), water (A) + ethylene glycol (B) + 1,4-dioxane (C); (△), water (A) + ethylene glycol (B) + *N*,*N*-dimethylformamide (C); and (□), water (A) + ethylene glycol (B) + dimethylsulphoxide (C) mixtures with mole fraction of water (x_A) at 298.15 K.

net viscosity of the latter to be less than the sum of the viscosities of each component considered separately. So, if the total viscosity of the system is equal to the sum of the viscosities of each component considered separately, the system would lack interaction [20].

In order to secure more comparable viscous antagonism results, the so called antagonic interaction index (I_A), introduced by Howell [21] is taken into account.

$$I_A = \frac{(\eta_{calcd} - \eta_{exp})}{\eta_{calcd}} \tag{2}$$

This procedure is used when Newtonian fluids are involved, since in non-Newtonian systems shear rate must be taken into account, and other synergy indices are defined in consequence [22].

In figure 2, antagonic interaction index (I_A) values for the ternary mixtures (A) + (B) + THF, DO, DMF and DMSO (C) have been plotted against the x_A of water at 298.15 K. It is found that each mixture, has a maxima at $x_A = 0.0$ and then it decreases as x_A increases. Furthermore, the magnitude falls as the temperature rises from 298.15 to 318.15 K. The estimated uncertainty for I_A is ±0.002.

A perusal of table 2 shows that the experimentally determined viscosities, η_{exp} for all mixtures for various mole fraction at various temperatures are lower than those of its calculated values, η_{calcd} which demonstrates viscous antagonism in the four mixtures studied here. The explanation of this behaviour is based on the known phenomenon of molecular dissociation, as a consequence of weakening the non-covalent bondings formed between the molecules producing a decrease in size of the molecular package which logically implies an increase in I_A [5,9]. The maxima observed indicates strong specific interaction between the unlike molecules which is predominated by non-covalent interaction. Thus, the molecular package increases gradually with the addition of water to the mixtures which implies a decrease in I_A at higher temperatures.

3.3. *Comparison of viscosity deviations and viscous antagonism for the ternary mixtures*

It is observed that although $\Delta\eta$ is a mixture of positive and negative values, I_A is positive throughout. Again $\Delta\eta$ has maximum at $x_A = 0.85$ for all the mixtures but I_A shows maxima at $x_A = 0$. Further, the sequence it followed for $\Delta\eta$ values is

$$(A) + (B) + \text{DMSO} > \text{DO} > \text{DMF} > \text{THF}$$

but the opposite trend is observed for I_A values

$$(A) + (B) + \text{THF} > \text{DMF} > \text{DO} > \text{DMSO}$$

The two properties are clearly distinguishable as $\Delta\eta$ explains the behaviour through dipolar interactions whereas I_A indicates the nature of liquid mixtures in terms of non-covalent interaction as mentioned earlier in this text.

3.4. *Excess molar volume*

The experimentally determined density values along with the derived parameter, V^E which is the excess molar volume are listed in table 4.

The excess molar volumes, V^E, are calculated from density data according to the following equation [23]:

$$V^E = \sum_{i=1}^{n} x_i M_i (1/\rho - 1/\rho_i) \tag{3}$$

where M_i, ρ_i and ρ are the molar mass, density of the ith component and density of the mixture respectively.

Figure 3 represent the V^E values for the four ternary mixtures under examination. In general, V^E is found to be negative throughout all the temperatures for all the ternary mixtures. However, the values at first decreases to a minima and then it increases with increasing x_A. V^E increases systematically from 298.15 to 318.15 K over the whole range of mole fractions. The four ternary mixtures shows the minima at the same point i.e. at $x_A = 0.6$. The estimated uncertainty for V^E is $\pm 0.5 \times 10^{-4}\,\text{m}^3\,\text{mol}^{-1}$. The trend is:

$$(A) + (B) + \text{THF} > \text{DMF} > \text{DO} > \text{DMSO}$$

The negative V^E indicates the presence of strong molecular interaction between the components of the mixture. Several effects contribute to the value of V^E, such as [24]: (1) dipolar interaction, (2) interstitial accommodation of one component into the other and (3) possible hydrogen bonded interactions between unlike molecules. The actual volume change would, therefore, depend on the relative strength of these three effects.

3.5. *Isentropic compressibility*

Table 5 contains the sound velocity (u), isentropic compressibility (K_S) and excess isentropic compressibility (K_S^E) data for the mixtures observed and calculated at 298.15 K.

Table 4. Experimental densities (ρ) and excess molar volumes (V^E) of water (A) + ethylene glycol (B) + THF, DO, DMF and DMSO (C) at 298.15, 308.15 and 318.15 K.

		T (K)					
		298.15		308.15		318.15	
x_A	x_B	$\rho \times 10^{-3}$ (kg m^{-3})	$V^E \times 10^3$ (m^3 mol^{-1})	$\rho \times 10^{-3}$ (kg m^{-3})	$V^E \times 10^3$ (m^3 mol^{-1})	$\rho \times 10^{-3}$ (kg m^{-3})	$V^E \times 10^3$ (m^3 mol^{-1})
Water (A) + ethylene glycol (B) + THF (C)							
0	0.5374	0.9845	−0.261	0.9741	−0.047	0.9649	−0.013
0.2917	0.3807	0.9914	−0.487	0.9812	−0.311	0.9712	−0.215
0.4809	0.2789	0.9964	−0.553	0.9883	−0.483	0.9789	−0.417
0.6137	0.2076	1.0009	−0.574	0.9927	−0.496	0.9842	−0.456
0.7119	0.1548	1.0035	−0.529	0.9938	−0.402	0.9868	−0.399
0.7875	0.1142	1.0048	−0.456	0.9949	−0.328	0.9875	−0.296
0.8476	0.0819	1.0052	−0.376	0.9956	−0.255	0.9879	−0.209
0.8964	0.0557	1.003	−0.252	0.9957	−0.184	0.9877	−0.122
0.9368	0.0339	1.001	−0.155	0.9946	−0.101	0.9878	−0.059
0.9709	0.0156	0.999	−0.071	0.9944	−0.047	0.9888	−0.022
1	0	0.9971	0	0.9941	0	0.9903	0
Water (A) + ethylene glycol (B) + DO (C)							
0	0.5867	1.0709	−0.358	1.0604	−0.178	1.0509	−0.121
0.3102	0.4047	1.0695	−0.563	1.06	−0.454	1.0498	−0.356
0.5029	0.2917	1.0666	−0.631	1.0583	−0.574	1.0492	−0.517
0.6343	0.2146	1.0624	−0.636	1.0546	−0.585	1.0457	−0.531
0.7296	0.1587	1.0567	−0.591	1.0475	−0.493	1.0396	−0.457
0.8018	0.1163	1.0488	−0.501	1.0404	−0.419	1.0328	−0.383
0.8585	0.0829	1.0397	−0.397	1.0323	−0.337	1.0249	−0.297
0.9042	0.0562	1.0302	−0.302	1.0225	−0.228	1.0162	−0.205
0.9418	0.0341	1.0193	−0.191	1.0129	−0.141	1.0072	−0.119
0.9733	0.0157	1.0076	−0.078	1.0033	−0.061	0.9983	−0.047
1	0	0.9971	0	0.9941	0	0.9903	0
Water (A) + ethylene glycol (B) + DMF (C)							
0	0.5408	1.0248	−0.313	1.0168	−0.127	1.0082	−0.056
0.2929	0.3824	1.0279	−0.522	1.02	−0.371	1.0111	−0.285
0.4825	0.2799	1.0294	−0.584	1.0234	−0.533	1.0146	−0.459
0.6152	0.2081	1.0301	−0.605	1.0237	−0.542	1.016	−0.503
0.7132	0.1551	1.0291	−0.568	1.0214	−0.465	1.0147	−0.452
0.7886	0.1143	1.0259	−0.482	1.0185	−0.392	1.0116	−0.362
0.8484	0.082	1.0222	−0.397	1.0149	−0.314	1.0079	−0.277
0.8969	0.0557	1.0156	−0.266	1.0102	−0.228	1.003	−0.178
0.9372	0.0339	1.0094	−0.164	1.0041	−0.125	0.9979	−0.092
0.9711	0.0156	1.0028	−0.068	0.9985	−0.046	0.9937	−0.035
1	0	0.9971	0	0.9941	0	0.9903	0
Water (A) + ethylene glycol (B) + DMSO (C)							
0	0.5573	1.1085	−0.434	1.0989	−0.265	1.0896	−0.185
0.2993	0.3905	1.1034	−0.624	1.0943	−0.496	1.0851	−0.419
0.49	0.2842	1.0968	−0.686	1.0894	−0.632	1.0805	−0.564
0.6222	0.2105	1.0891	−0.694	1.0818	−0.638	1.0738	−0.595
0.7193	0.1564	1.0799	−0.657	1.0716	−0.566	1.0643	−0.538
0.7935	0.1151	1.0681	−0.556	1.0594	−0.456	1.0528	−0.437
0.8522	0.0824	1.0549	−0.438	1.0477	−0.373	1.0412	−0.349
0.8997	0.0559	1.0417	−0.337	1.0339	−0.257	1.0287	−0.252
0.9389	0.034	1.0269	−0.216	1.0213	−0.176	1.0158	−0.158
0.9719	0.0157	1.0119	−0.102	1.0074	−0.079	1.0023	−0.061
1	0	0.9971	0	0.9941	0	0.9903	0

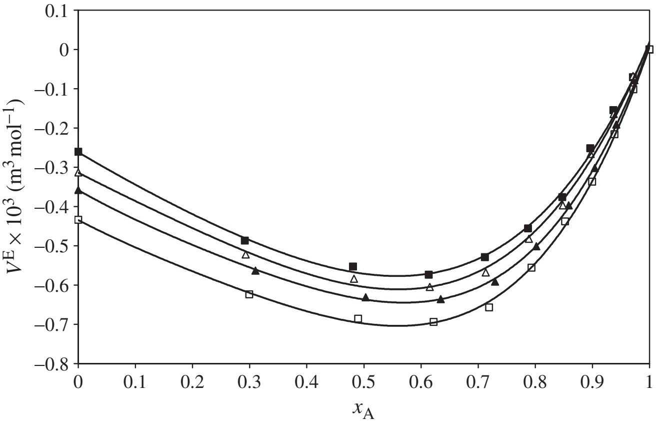

Figure 3. Excess molar volumes (V^E) of: (■), water (A) + ethylene glycol (B) + THF (C); (▲), water (A) + ethylene glycol (B) + 1,4-dioxane (C); (Δ), water (A) + ethylene glycol (B) + *N*,*N*-dimethylformamide (C); and (□), water (A) + ethylene glycol (B) + dimethylsulphoxide (C) mixtures with mole fraction of water (x_A) at 298.15 K.

Table 5. Experimental sound velocities (u), isentropic compressibility (K_S) and excess isentropic compressibility (K_S^E) of water (A) + ethylene glycol (B) + THF, DO, DMF and DMSO (C) at 298.15 K.

x_A	u ($m\,s^{-1}$)	$K_S \times 10^{12}$ (Pa^{-1})	$K_S^E \times 10^{12}$ (Pa^{-1})	x_A	u ($m\,s^{-1}$)	$K_S \times 10^{12}$ (Pa^{-1})	$K_S^E \times 10^{12}$ (Pa^{-1})
Water (A) + ethylene glycol (B) + THF(C)				Water (A) + ethylene glycol (B) + DO (C)			
0.0000	1436.8	492.0	−4.1	0.0000	1519.2	404.6	−9.2
0.2917	1502.4	446.9	−34.9	0.3102	1578.7	375.2	−48.9
0.4809	1554.8	415.2	−57.3	0.5029	1617.9	358.2	−72.3
0.6137	1592.8	393.8	−72.1	0.6343	1644.4	348.1	−86.7
0.7119	1623.9	377.9	−83.2	0.7296	1671.4	338.8	−99.2
0.7875	1652.0	364.7	−92.7	0.8018	1691.0	333.4	−106.9
0.8476	1663.0	359.7	−94.7	0.8585	1697.6	333.7	−108.5
0.8964	1633.2	373.8	−78.2	0.9042	1659.1	352.6	−91.1
0.9368	1593.7	393.3	−56.7	0.9418	1606.2	380.3	−64.7
0.9709	1546.3	418.6	−29.7	0.9733	1559.8	407.9	−38.1
1.0000	1498.0	446.9	0.0	1.0000	1498.0	446.9	0.0
Water (A) + ethylene glycol (B) + DMF (C)				Water (A) + ethylene glycol (B) + DMSO (C)			
0.0000	1584.4	388.7	−13.6	0.0000	1617.3	344.9	−17.9
0.2929	1650.9	356.9	−58.4	0.2993	1687.9	318.1	−69.9
0.4825	1688.8	340.6	−83.2	0.4900	1728.1	305.3	−98.7
0.6152	1713.8	330.5	−99.2	0.6222	1747.9	300.5	−114.6
0.7132	1733.4	323.4	−110.7	0.7193	1769.6	295.7	−127.6
0.7886	1752.5	317.4	−120.1	0.7935	1789.3	292.4	−137.1
0.8484	1756.6	317.0	−123.1	0.8522	1789.9	295.9	−138.6
0.8969	1705.3	338.6	−103.7	0.8997	1719.0	324.9	−113.6
0.9372	1641.9	367.5	−76.6	0.9389	1645.5	359.6	−82.1
0.9711	1576.5	401.2	−44.4	0.9719	1581.3	395.2	−49.3
1.0000	1498.0	446.9	0.0	1.0000	1498.0	446.9	0.0

Isentropic compressibility (K_S) and excess isentropic compressibility (K_S^E) were obtained using the following equation [7]:

$$K_S = 1/(u^2 \cdot \rho) \tag{4}$$

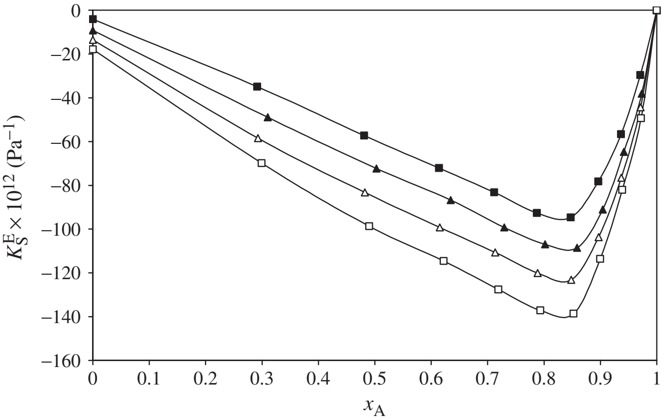

Figure 4. Excess isentropic compressibility (K_S^E) of: (■), water (A) + ethylene glycol (B) + THF (C); (▲), water (A) + ethylene glycol (B) + 1,4-dioxane (C); (Δ), water (A) + ethylene glycol (B) + *N*,*N*-dimethylformamide (C); and, (□), water (A) + ethylene glycol (B) + dimethylsulphoxide (C) mixtures with mole fraction of water (x_A) at 298.15 K.

$$K_S^E = K_S - \sum_{i=1}^{n} x_i K_{S,i} \tag{5}$$

where $K_{S,i}$ gives the isentropic compressibility for the ith component of the mixture.

Figure 4 predicts the curves for the ternary mixtures. K_S^E is negative over the whole composition range for all the mixtures. However, the values decreases to reach a minima at $x_A = 0.85$ and thereafter increases for every mixture. The estimated uncertainty for K_S^E is $\pm 0.2\,\mathrm{Pa}^{-1}$. The K_S^E values follow the sequence:

$$(A) + (B) + \mathrm{THF} > \mathrm{DO} > \mathrm{DMF} > \mathrm{DMSO}$$

The results can be explained in terms of molecular interactions, structural effects, interstitial accommodation along with changes in free volume. Negative K_S^E indicates the formation of molecular order in the pure components due to dipole–dipole interactions between the molecules. The more easily the molecules fit into each others structure, K_S^E values become more and more negative.

4. Conclusion

The study of the aqueous ternary mixtures in this work has given us an idea about antagonism. The similarity in the working formula of antagonic interaction index and viscosity deviation would probably indicate that the two properties are similar but a close comparison between these two parameters have given the clear distinction.

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