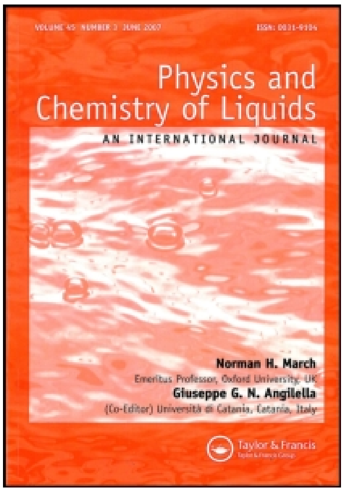

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Study on molecular interactions by antagonism, synergy and excess functions of ternary mixtures of tetrahydrofuran with dimethylsulphoxide and monoalkanols

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Study on molecular interactions by antagonism, synergy and excess functions of ternary mixtures of tetrahydrofuran with dimethylsulphoxide and monoalkanols

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The densities and viscosities of eight ternary mixtures of tetrahydrofuran, dimethylsulphoxide and monoalkanols: methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, amyl alcohol and *i*-amyl alcohol are determined over the entire range of composition at 298.15 K. From the experimental measurements, excess molar volumes (V^E), viscosity deviation ($\Delta\eta$), antagonism and antagonic index (I_A) are derived by the equations developed by Kalentunc-Gencer, Peleg and Howell, respectively. A power factor, F_η, has also been introduced here. Also, the speeds of sound of these ternary mixtures have been measured over the whole composition range at the same temperature and thus, the isentropic compressibility (K_S) and excess isentropic compressibility (K_S^E) have been evaluated from the experimental data. The results are discussed in terms of molecular packing, specific interactions and nature of liquid mixtures. The systems studied here exhibit very strong cross association through 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 inter-molecular 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]. Because of the close connection between liquid structure and macroscopic properties, determination of density, viscosity and ultrasonic speeds are valuable tools for understanding the liquid state [3,4].

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 determined that viscosity influences the drug absorption rate in the body.

The liquids examined here were selected on the basis of their industrial use [7]. Tetrahydrofuran (THF) and monoalcohols are important liquids which find a variety of applications in pharmaceuticals, cosmetics, etc., which, in turn, have

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greatly stimulated the need for extensive information on their various properties. Beside this, dimethylsulphoxide (DMSO) is a powerful broad spectrum solvent for a wide variety of inorganic and organic reactants. Having low toxicity, DMSO can be used in biology and medicine, especially for low-temperature preservation [8]. Viscosity, density and speed of sound help in understanding molecular interactions between the components of the mixture to develop new theoretical models and also for engineering applications [9]. The thermodynamic properties of various alkanols have been studied in numerous solvents [10–14]. In our previous investigation of the properties, we have reported viscosities, densities and speeds of sound of various polar mixtures [15–17].

The present work contributes to the study of viscosity deviations, viscous antagonism, excess molar volumes and isentropic compressibility in ternary mixtures formed from THF represented as (A), DMSO represented as (B) and monoalkanols represented as (C). The monoalkanols include methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH), 2-propanol (2-PrOH), 1-butanol (1-BuOH), 2-butanol (2-BuOH), amyl alcohol (AmOH) and *i*-amyl alcohol (*i*-AmOH). These have been chosen for better comparison.

The cyclic ether (A), DMSO (B) and monoalkanols (C) have proton donor and proton acceptor groups leading to self association in pure state and mutual association in combined state through significant degree of H-bonding [18,19]. Thus, determination of density, viscosity, speeds of sound helps in understanding both synergy and antagonism along with the isentropic compressibility in this type of ternary mixtures containing polar components.

2. Experimental

The monoalkanols; methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, *t*-butanol and *i*-amyl alcohol with richness values of over 98% by volume (Merck, USA) were purified by methods as described in [20,21]. THF (C_4H_8O, FW = 72.11) and DMSO (C_2H_6SO, FW = 78.13) were obtained from Merck and LR. These were further purified by standard methods [20]. Triply distilled water was used for the experimental purpose. After purification the chemicals were 99.9% pure and their purity was ascertained by GLC and also by comparing experimental values of densities, viscosities and sound velocities at 298.15 K with those reported in literature [5,11,22–30] and are listed in Table 1.

Densities were measured with an Ostwald–Sprengel-type pycnometer having a bulb volume of about 25 cm^3 and an internal diameter of the capillary of about 0.1 cm. The measurements were done in a thermostated bath controlled to ±0.01 K. The weighings were done on a Mettler AG-285 electronic balance with a precision of ±0.01 mg. The precision of density measurements was $\pm 3 \times 10^{-4}\,\mathrm{kg\,m^{-3}}$. The viscosity was measured by means of a suspended Ubbelohde type viscometer, calibrated at 298.15 K with triply distilled water and purified methanol using density and viscosity values from the literature. The flow times were accurate to ±0.1 s, and the uncertainty in the viscosity measurements, based on our work on several pure liquids, was $\pm 2 \times 10^{-4}\,\mathrm{mPa\,s}$. The details of the methods and techniques have been described earlier [17,31].

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

		$\rho \times 10^{-3}$ (kg m^{-3})		η (mPa s)		u (m s^{-1})	
Solvents	T(K)	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
Tetrahydrofuran	298.15	0.8801	0.8807 [22]	0.4627	0.463 [22]	1292.2	1288.0 [23]
DMSO	298.15	1.0951	1.0960 [24]	2.0418	2.0422 [24]	1492.0	1488.0 [23]
Methanol	298.15	0.7864	0.7869 [5]	0.5041	0.5100 [26]	1105.1	1103.0 [25]
Ethanol	298.15	0.7844	0.7850 [5]	1.0753	1.0760 [5]	1143.0	1144.9 [27]
1-Propanol	298.15	0.7958	0.7958 [11]	1.7624	1.7843 [11]	1206.5	1207.2 [27]
2-Propanol	298.15	0.7773	0.7779 [26]	1.6241	1.7732 [26]	1126.6	
1-Butanol	298.15	0.8049	0.8060 [5]	2.5343	2.5420 [5]	1240.2	1240.2 [28]
2-Butanol	298.15	0.8025	0.8035 [5]	2.3424	2.4170 [22]	1178.5	
Amyl alcohol	298.15	0.8106	0.8110 [29]	3.3500	3.3500 [29]	1280.6	1277.2 [28]
Iso-amyl alcohol	298.15	0.8071	0.8071 [29]	3.1175	3.1111 [30]	1197.4	

Speeds of sound were determined by a multi-frequency ultrasonic interferometer (Mittal Enterprise, New Delhi) working at 2 MHz, which was calibrated with water, methanol and benzene at 298.15 K. The precision of the speed measurements was $\pm 0.2\,\mathrm{m\,s^{-1}}$. The details of the methods and the techniques have been described earlier [17]. The mixtures were prepared by mixing known volumes of pure liquids in airtight stopper bottles. Each solution thus prepared was distributed into three recipients to perform all the measurements in triplicate, with the aim of determining possible dispersion of the results obtained. Adequate precautions were taken to minimise evaporation losses during the actual measurements.

3. Results and discussion

In Table 2, the experimentally determined values of densities ρ, excess molar volume, V^E and the calculated and experimentally determined viscosities, η_{calc} and η_{exp}, respectively, of the ternary mixtures of the ternary mixtures of THF (A), DMSO (B) and monoalkanols (C), i.e. methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, amyl alcohol and *i*-amyl alcohol have been presented along with the mole fractions of THF(x_A) and DMSO(x_B).

Viscosity deviation $\Delta\eta$ and antagonic index I_A values are presented together in Table 3. A perusal of Table 3 gives a clear comparison between those two, which appears to be same but are different properties.

Quantitatively, as per the absolute reaction rates theory [32], the deviations of viscosities from the ideal mixture values can be calculated as

$$\Delta\eta = \eta - \sum_{i=1}^{j} x_i \eta_i, \tag{1}$$

where η is the dynamic viscosity of the mixture; x_i and η_i are the mole fraction and viscosity of *i*-th component in the mixture, respectively.

In Figure 1, $\Delta\eta$ values for the ternary mixtures (A) + (B) + monoalkanols (C) have been plotted against the mole fraction of THF (x_A) at 298.15 K.

From the value of $\Delta\eta$ as shown in Table 2, the positive values of $\Delta\eta$ follow the trend:

$$\begin{aligned}&(\mathrm{A}) + (\mathrm{B}) + \cdots\\ &\mathrm{MeOH} > \mathrm{EtOH} > 2\text{-}\mathrm{PrOH} > 1\text{-}\mathrm{PrOH} > 2\text{-}\mathrm{BuOH} > 1\text{-}\mathrm{BuOH}\\ &\quad > i\text{-}\mathrm{AmOH} > \mathrm{AmOH}\end{aligned}$$

It is observed that $\Delta\eta$ values increases to attain a maximum and then decreases as the mole fraction of THF increases. This trend is observed for all the ternary mixtures examined here. However, the mixtures have maximum $\Delta\eta$ at $x_A = 0.79$–0.84 for all the compositions 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 THF, DMSO and monoalkanol molecules resulting in negative $\Delta\eta$ but with the increase of x_A of THF, the hydrogen bonding interactions come into play leading to the formation of complex species between unlike molecules thereby resulting in positive $\Delta\eta$ [33].

Table 2. Densities (ρ), excess molar volumes (V^E), calculated (η_{calc}) and experimental viscosities (η_{exp}) of tetrahydrofuran (THF), dimethylsulphoxide (DMSO) and different monoalkanols as a function of mole fractions of THF (x_A) and DMSO (x_B) at 298.15 K.

T(K)	x_A	x_B	$\rho_{exp} \times 10^{-3}$ (kg m^{-3})	$V^E \times 10^6$ (m^3 mol^{-1})	η_{calc} (mPa s)	η_{exp} (mPa s)
			THF + DMSO + methanol			
298.15	0.0000	0.2908	0.9229	−0.402	0.9513	0.8965
	0.0654	0.2718	0.9194	−0.430	0.9193	0.8723
	0.1361	0.2512	0.9159	−0.458	0.8848	0.8434
	0.2127	0.2290	0.9118	−0.490	0.8474	0.8113
	0.2958	0.2048	0.9075	−0.509	0.8068	0.7770
	0.3866	0.1784	0.9030	−0.526	0.7624	0.7407
	0.4859	0.1495	0.8984	−0.542	0.7139	0.7033
	0.5952	0.1177	0.8932	−0.482	0.6605	0.6697
	0.7160	0.0826	0.8886	−0.373	0.6015	0.6220
	0.8501	0.0436	0.8841	−0.212	0.5359	0.5588
	1.0000	0.0000	0.8801	0.000	0.4627	0.4627
			THF + DMSO + ethanol			
298.15	0.0000	0.3706	0.9194	−0.366	1.4335	1.3407
	0.0819	0.3402	0.9163	−0.422	1.3539	1.2781
	0.1672	0.3086	0.9130	−0.448	1.2712	1.2087
	0.2560	0.2757	0.9092	−0.468	1.1849	1.1336
	0.3487	0.2414	0.9051	−0.486	1.0950	1.0557
	0.4454	0.2055	0.9008	−0.503	1.0011	0.9718
	0.5464	0.1681	0.8965	−0.511	0.9030	0.8982
	0.6520	0.1290	0.8921	−0.460	0.8005	0.8165
	0.7626	0.0880	0.8878	−0.347	0.6932	0.7172
	0.8785	0.0450	0.8838	−0.194	0.5807	0.6027
	1.0000	0.0000	0.8801	0.000	0.4627	0.4627
			THF + DMSO + 1-propanol			
298.15	0.0000	0.4348	0.9254	−0.290	1.8839	1.7318
	0.0948	0.3936	0.9220	−0.367	1.7492	1.6268
	0.1906	0.3519	0.9181	−0.409	1.6129	1.5131
	0.2876	0.3097	0.9140	−0.429	1.4751	1.3976
	0.3858	0.2670	0.9101	−0.460	1.3356	1.2731
	0.4851	0.2239	0.9058	−0.463	1.1945	1.1543
	0.5856	0.1802	0.9016	−0.460	1.0516	1.0446
	0.6873	0.1359	0.8966	−0.389	0.9070	0.9171
	0.7903	0.0912	0.8912	−0.276	0.7607	0.7790
	0.8945	0.0459	0.8859	−0.162	0.6126	0.6316
	1.0000	0.0000	0.8801	0.000	0.4627	0.4627
			THF + DMSO + 2-propanol			
298.15	0	0.4348	0.9131	−0.315	1.8057	1.6735
	0.0948	0.3936	0.9110	−0.391	1.7450	1.6361
	0.1906	0.3519	0.9085	−0.438	1.6092	1.5210
	0.2876	0.3097	0.9056	−0.453	1.4718	1.4032
	0.3858	0.2670	0.9028	−0.469	1.3328	1.2784
	0.4851	0.2239	0.9000	−0.486	1.1921	1.1563
	0.5856	0.1802	0.8972	−0.495	1.0497	1.0497
	0.6873	0.1359	0.8936	−0.442	0.9056	0.9206
	0.7903	0.0912	0.8894	−0.325	0.7598	0.7817
	0.8945	0.0459	0.8846	−0.153	0.6121	0.6321

(*continued*)

Table 2. Continued.

T(K)	x_A	x_B	$\rho_{exp} \times 10^{-3}$ ($kg\,m^{-3}$)	$V^E \times 10^6$ ($m^3\,mol^{-1}$)	η_{calc} (mPa s)	η_{exp} (mPa s)
	1.0000	0.0000	0.8801	0.000	0.4627	0.4627
THF + DMSO + 1-butanol						
298.15	0.0000	0.4868	0.9305	−0.231	2.2945	2.0619
	0.1065	0.4358	0.9262	−0.298	2.1023	1.9159
	0.2158	0.3852	0.9216	−0.334	1.9122	1.7593
	0.3227	0.3353	0.9172	−0.374	1.7242	1.6054
	0.4266	0.2858	0.9126	−0.398	1.5382	1.4520
	0.5259	0.2369	0.9079	−0.416	1.3541	1.3023
	0.6242	0.1885	0.9031	−0.412	1.1720	1.1598
	0.7244	0.1406	0.8975	−0.327	0.9919	1.0012
	0.8200	0.0933	0.8920	−0.252	0.8136	0.8300
	0.9146	0.0464	0.8864	−0.163	0.6373	0.6515
	1.0000	0.0000	0.8801	0.000	0.4627	0.4627
THF + DMSO + 2-butanol						
298.15	0.0000	0.4868	0.9290	−0.244	2.1961	1.9898
	0.1065	0.4358	0.9250	−0.320	2.0142	1.8506
	0.2158	0.3852	0.9207	−0.362	1.8343	1.7026
	0.3227	0.3353	0.9163	−0.395	1.6564	1.5530
	0.4266	0.2858	0.9120	−0.426	1.4803	1.4054
	0.5259	0.2369	0.9074	−0.438	1.3062	1.2686
	0.6242	0.1885	0.9027	−0.430	1.1339	1.1291
	0.7244	0.1406	0.8971	−0.330	0.9634	0.9751
	0.8200	0.0933	0.8916	−0.246	0.7948	0.8114
	0.9146	0.0464	0.8864	−0.174	0.6279	0.6426
	1.0000	0.0000	0.8801	0.000	0.4627	0.4627
THF + DMSO + amyl alcohol						
298.15	0.0000	0.5301	0.9336	−0.188	2.6565	2.3494
	0.1162	0.4701	0.9287	−0.235	2.4082	2.1512
	0.2328	0.4118	0.9239	−0.290	2.1670	1.9633
	0.3444	0.3552	0.9190	−0.331	1.9327	1.7789
	0.4505	0.3002	0.9143	−0.374	1.7050	1.5959
	0.5503	0.2467	0.9092	−0.385	1.4836	1.4197
	0.6472	0.1947	0.9041	−0.379	1.2683	1.2476
	0.7432	0.1440	0.8983	−0.311	1.0588	1.0670
	0.8339	0.0947	0.8924	−0.225	0.8548	0.8671
	0.9222	0.0468	0.8866	−0.153	0.6562	0.6653
	1.0000	0.0000	0.8801	0.000	0.4627	0.4627
THF + DMSO + iso-amyl alcohol						
298.15	0.0000	0.5301	0.9314	−0.204	2.5472	2.2650
	0.1162	0.4701	0.9268	−0.254	2.3113	2.0781
	0.2328	0.4118	0.9224	−0.325	2.0821	1.9022
	0.3444	0.3552	0.9178	−0.360	1.8595	1.7199
	0.4505	0.3002	0.9133	−0.408	1.6432	1.5461
	0.5503	0.2467	0.9083	−0.400	1.4328	1.3797
	0.6472	0.1947	0.9036	−0.414	1.2282	1.2164
	0.7432	0.1440	0.8978	−0.323	1.0291	1.0388
	0.8339	0.0947	0.8921	−0.237	0.8353	0.8489
	0.9222	0.0468	0.8866	−0.165	0.6465	0.6584
	1.0000	0.0000	0.8801	0.000	0.4627	0.4627

Table 3. Viscosity deviations ($\Delta\eta$) and Antagonic index (I_A) of tetrahydrofuran (THF), dimethylsulphoxide (DMSO) and different monoalkanols as a function of mole fractions of THF (x_A) and DMSO (x_B) at 298.15 K.

T(K)	x_A	x_B	$\Delta\eta$ (mPa s)	I_A
THF + DMSO + methanol				
298.15	0.0000	0.2908	−0.0548	0.0576
	0.0654	0.2718	−0.0470	0.0511
	0.1361	0.2512	−0.0414	0.0468
	0.2127	0.2290	−0.0361	0.0426
	0.2958	0.2048	−0.0298	0.0369
	0.3866	0.1784	−0.0217	0.0285
	0.4859	0.1495	−0.0106	0.0148
	0.5952	0.1177	0.0092	−0.0139
	0.7160	0.0826	0.0205	−0.0341
	0.8501	0.0436	0.0228	−0.0426
	1.0000	0.0000	0.0000	0.0000
THF + DMSO + ethanol				
298.15	0.0000	0.3706	−0.0927	0.0647
	0.0819	0.3402	−0.0758	0.0560
	0.1672	0.3086	−0.0624	0.0491
	0.2560	0.2757	−0.0513	0.0433
	0.3487	0.2414	−0.0393	0.0359
	0.4454	0.2055	−0.0293	0.0293
	0.5464	0.1681	−0.0049	0.0054
	0.6520	0.1290	0.0160	−0.0200
	0.7626	0.0880	0.0240	−0.0346
	0.8785	0.0450	0.0220	−0.0379
	1.0000	0.0000	0.0000	0.0000
THF + DMSO + 1-propanol				
298.15	0.0000	0.4348	−0.1520	0.0807
	0.0948	0.3936	−0.1224	0.0700
	0.1906	0.3519	−0.0998	0.0619
	0.2876	0.3097	−0.0774	0.0525
	0.3858	0.2670	−0.0625	0.0468
	0.4851	0.2239	−0.0401	0.0336
	0.5856	0.1802	−0.0070	0.0067
	0.6873	0.1359	0.0101	−0.0111
	0.7903	0.0912	0.0183	−0.0240
	0.8945	0.0459	0.0190	−0.0310
	1.0000	0.0000	0.0000	0.0000
THF + DMSO + 2-propanol				
298.15	0	0.4348	−0.1322	0.0732
	0.0948	0.3936	−0.1089	0.0624
	0.1906	0.3519	−0.0882	0.0548
	0.2876	0.3097	−0.0686	0.0466
	0.3858	0.2670	−0.0544	0.0408
	0.4851	0.2239	−0.0358	0.0300
	0.5856	0.1802	0.0000	0.0000
	0.6873	0.1359	0.0150	−0.0165
	0.7903	0.0912	0.0220	−0.0289
	0.8945	0.0459	0.0200	−0.0326

(*continued*)

Table 3. Continued.

T(K)	x_A	x_B	$\Delta\eta$ (mPa s)	I_A
	1	0.0000	0.0000	0.0000
		THF + DMSO + 1-butanol		
298.15	0.0000	0.4868	−0.2327	0.1014
	0.1065	0.4358	−0.1865	0.0887
	0.2158	0.3852	−0.1530	0.0800
	0.3227	0.3353	−0.1188	0.0689
	0.4266	0.2858	−0.0861	0.0560
	0.5259	0.2369	−0.0518	0.0383
	0.6242	0.1885	−0.0123	0.0105
	0.7244	0.1406	0.0093	−0.0093
	0.8200	0.0933	0.0164	−0.0201
	0.9146	0.0464	0.0142	−0.0223
	1.0000	0.0000	0.0000	0.0000
		THF + DMSO + 2-butanol		
298.15	0.0000	0.4868	−0.2062	0.0939
	0.1065	0.4358	−0.1636	0.0812
	0.2158	0.3852	−0.1317	0.0718
	0.3227	0.3353	−0.1034	0.0624
	0.4266	0.2858	−0.0749	0.0506
	0.5259	0.2369	−0.0376	0.0288
	0.6242	0.1885	−0.0048	0.0043
	0.7244	0.1406	0.0117	−0.0121
	0.8200	0.0933	0.0166	−0.0209
	0.9146	0.0464	0.0148	−0.0235
	1.0000	0.0000	0.0000	0.0000
		THF + DMSO + amyl alcohol		
298.15	0.0000	0.5301	−0.3071	0.1156
	0.1162	0.4701	−0.2570	0.1067
	0.2328	0.4118	−0.2037	0.0940
	0.3444	0.3552	−0.1539	0.0796
	0.4505	0.3002	−0.1091	0.0640
	0.5503	0.2467	−0.0639	0.0431
	0.6472	0.1947	−0.0207	0.0163
	0.7432	0.1440	0.0082	−0.0078
	0.8339	0.0947	0.0123	−0.0144
	0.9222	0.0468	0.0091	−0.0139
	1.0000	0.0000	0.0000	0.0000
		THF + DMSO + iso-amyl alcohol		
298.15	0.0000	0.5301	−0.2822	0.1108
	0.1162	0.4701	−0.2332	0.1009
	0.2328	0.4118	−0.1799	0.0864
	0.3444	0.3552	−0.1397	0.0751
	0.4505	0.3002	−0.0971	0.0591
	0.5503	0.2467	−0.0531	0.0371
	0.6472	0.1947	−0.0118	0.0096
	0.7432	0.1440	0.0097	−0.0094
	0.8339	0.0947	0.0137	−0.0164
	0.9222	0.0468	0.0118	−0.0183
	1.0000	0.0000	0.0000	0.0000

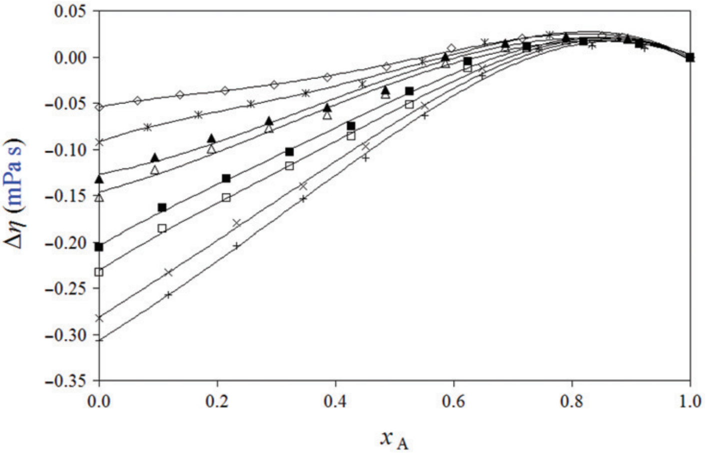


Figure 1. Viscosity deviations (Δη) of THF (A) + DMSO (B) + monoalkanol (C) mixtures with mole fraction of THF (x_A) at 298.15 K; C: (◇) methanol, (∗) ethanol, (Δ) 1-propanol, (▲) 2-propanol, (□) 1-butanol, (■) 2-butanol, (+) amyl alcohol, (×) *i*-amyl alcohol.

The method most widely used to analyse the synergic and antagonic behaviour of the ternary liquid mixtures used here is that developed by Kalentunc-Gencer and Peleg [34] allowing quantification of the synergic and antagonic interactions taking place in the 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_{calc}, defined by the simple mixing rule as,

$$\eta_{\mathrm{calc}} = x_A\eta_1 + x_B\eta_2 + x_C\eta_3, \tag{2}$$

where x_A, x_B, x_C are the mole fraction of the systems A, B, C and η_1, η_2, η_3 are the viscosities, measured experimentally, of the systems A, B and C, respectively. The method used to analyse volume contraction and expansion is similar to that applied to viscosity, i.e. the density of the mixture is determined experimentally, ρ_{exp}, and a calculation is made for ρ_{calc} based on the following expression:

$$\rho_{\mathrm{calc}} = x_A\rho_1 + x_B\rho_2 + x_C\rho_3, \tag{3}$$

where ρ_1, ρ_2, ρ_3 are the densities, measured experimentally, of the systems A, B and C, respectively.

The results have been explained graphically in Figure 2, where η_{exp} has been compared for the monoalkanols with increasing C-atoms, i.e. methanol, ethanol, 1-propanol, 1-butanol, 2-butanol, amyl alcohol and *i*-amyl alcohol.

Thus, when $\eta_{\mathrm{exp}} < \eta_{\mathrm{calc}}$ the system is considered to exhibit viscous antagonism. Hence, it is defined as the interaction between the components of a system causing the net viscosity of the latter to be less than the sum of the viscosities of each component considered separately.

In contraposition to viscous antagonism, viscous synergy is the term used in application to the interaction between the components of a system that causes the total viscosity of the system to be greater than the sum of the viscosities of

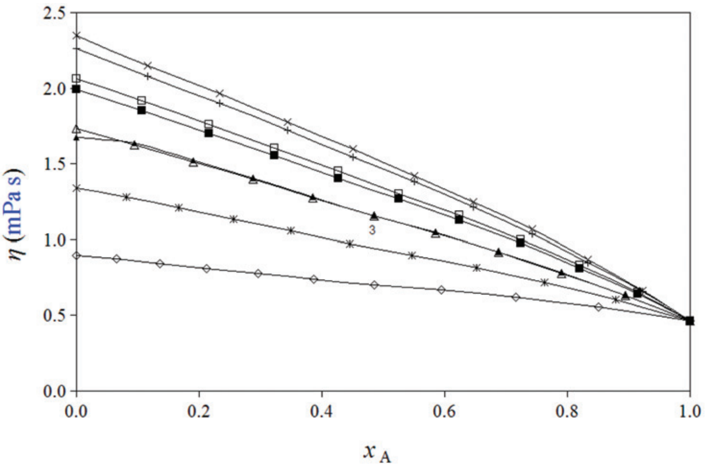


Figure 2. Viscosity (η) of THF (A) + DMSO (B) + monoalkanol (C) mixtures with mole fraction of THF (x_A) at 298.15 K; C: (◇) methanol, (∗) ethanol, (Δ) 1-propanol, (▲) 2-propanol, (□)1-butanol, (■) 2-butanol, (+) amyl alcohol, (×) *i*-amyl alcohol.

each component considered separately. So, when $\eta_{\text{exp}} > \eta_{\text{calc}}$, viscous synergy exists.

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 [35]. In order to secure more comparable viscous antagonism results, the so-called antagonic interaction index (I_A), introduced by Howell [36] is taken into account:

$$I_A = \frac{\eta_{\text{calc}} - \eta_{\text{exp}}}{\eta_{\text{calc}}} = \frac{\Delta\eta}{\eta_{\text{calc}}}. \tag{4}$$

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 [37].

In Figure 3, antagonic interaction index (I_A) values for the ternary mixtures (A) + (B) + monoalkanols (C) have been plotted against the x_A of THF 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. The estimated uncertainty for I_A is ±0.002.

The explanation of antagonic behaviour is based on the known phenomenon of molecular dissociation, which is 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 [5,38]. The maxima observed indicate strong specific interaction between the unlike molecules which is predominated by non-covalent interaction.

From Table 2, it is observed that $\eta_{\text{exp}} < \eta_{\text{calc}}$ for the ternary mixtures, thus indicating antagonism as mentioned earlier. The viscosity is found to be maximum at $x_A = 0.0$ of THF for all the monoalkanol ternary mixtures. The value gradually decreases with increasing amount of the cyclic ether (A). So, it has been observed that when (B) and (C) are in maximum proportion in the absence of (A) in the mixture, there is maximum mutual interaction. As (A) comes into play, there is

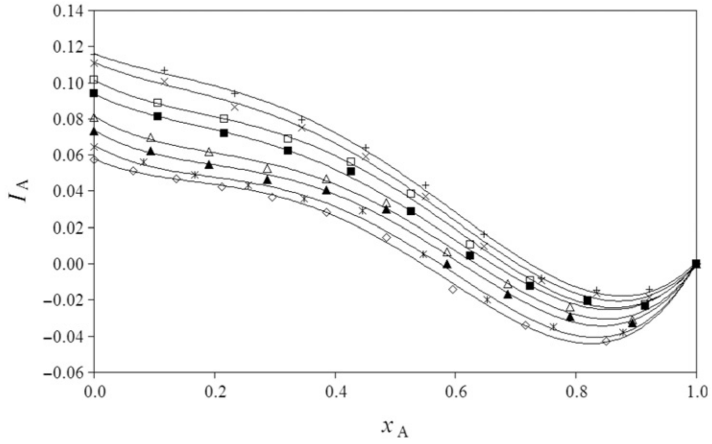


Figure 3. Antagonic index (I_A) values of THF (A) + DMSO (B) + monoalkanol (C) mixtures with mole fraction of THF (x_A) at 298.15 K; C: (◇) methanol, (∗) ethanol, (Δ) 1-propanol, (▲) 2-propanol, (□) 1-butanol, (■) 2-butanol, (+) amyl alcohol, (×) *i*-amyl alcohol.

self-interaction and gradual breaking of the mutual interactions, thus causing decrease in viscosity for the ternary mixtures. Pure liquids thus have easier flow than the system.

In Figure 2 the experimental viscosities have been compared for the monoalkanols with increasing C-chain. The order it follows is

(A) + (B) + ⋯
MeOH > EtOH > 1-PrOH > 2-PrOH > 1-BuOH > 2-BuOH
> AmOH > *i*-AmOH

This may be attributed to the known phenomenon of solvation, as a consequence of the hydrogen bonds formed between the molecules of the components of the mixture-producing an increasing in size of the resulting molecular package, which logically implies rise in viscosity.

In Table 3, the antagonic index values for the ternary mixtures are presented in the following trend:

(A) + (B) + ⋯
MeOH < EtOH < 2-PrOH < 1-PrOH < 2-BuOH < 1-BuOH
< *i*-AmOH < AmOH

The two properties $\Delta\eta$ and $I_{A,}$ as their observed trend suggest, 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.

I_A value increases for the mixtures with increasing C-chain length in the monoalkanols. This indicates that the interaction between unlike molecules of (B) and (C) decreases and that between like molecules of (A) increases. As the chain length of the alkane groups in the alkanols increases, their electron releasing ability increases, thereby decreasing the polarity of the –OH group. So the bonding between the DMSO and alkanol molecules decreases.

But in the case of isomers, the steric effect becomes the deciding factor. Here, due to large and complex size of the secondary alkanols compared to the primary ones, the THF molecules cannot easily disrupt the molecular package formed between (B) and (C). Thus, the mutual attraction remains greater for 2° -isomers.

Further, it has also been observed from Figure 3 that with increasing proportion of (A), I_A which has a maxima at $x_A = 0.0$, gradually decreases and becomes negative, thus exhibiting synergy, for each of the monoalkanol mixtures. As proportion of A increases, there is gradual increase in size of molecular package leading to predominance of interaction between unlike molecules causing synergy.

A power factor, F_η, which is the enhancement index of the viscosity, has also been introduced for these ternary liquid mixtures containing the monoalkanols [5],

$$F_\eta = \frac{\eta_{\max}}{\eta_0}, \tag{5}$$

where $\eta_{\max}$ is the maximum viscosity attained in the THF–DMSO–monoalkanol mixtures, and η_0 is the experimental viscosity of the pure monoalkanols. Table 4 gives the $\eta_{\max}$, η_0 and F_η for the mixtures.

In Table 4, the power factor, F_η, has been presented. This is the enhancement factor which represents the factor by which alkanol viscosity can be multiplied by adding a certain amount of THF. The value decreases as the chain length increases for the C-atom of the monoalkanols. However, 2° alkanols have greater F_η than 1° alkanols.

The values recorded in Table 4 allow us to plot the graphic representations shown in Figures 4–6. Figure 4 presents the viscosities $\eta_{\max}$ as a function of the number of carbon atoms for the alkanols with terminal hydroxyl group along with the hydroxyl group at the second carbon atom of the molecular chain and shows that the values $\eta_{\max}$ increases almost linearly with the number of carbon atoms.

Figure 5 shows the viscous antagonic index, I_A, as a function of the number of carbon atoms corresponding to the monoalkanols with the hydroxyl group at the end of the molecular chain and the second carbon atom. This figure reflects an increasing tendency. This figure also shows that the antagonic indices of the

Table 4. Pure state viscosity (η_0), maximum viscosity ($\eta_{\max}$, i.e. $\eta_{\exp}$ as in Table 2), antagonic indices (I_A) and enhancement or power factor (F_η) for the monoalkanols at 298.15 K.

Monoalkanols	η_0 (mPa s)	$\eta_{\max}$ (mPa s)	I_A	F_η
Methanol	0.5041	0.8965	0.0576	1.7784
Ethanol	1.0753	1.3407	0.0647	1.2468
1-propanol	1.7624	1.7318	0.0807	0.9827
2-propanol	1.6241	1.6735	0.0732	1.0304
1-butanol	2.5343	2.0619	0.1014	0.8136
2-butanol	2.3424	1.9898	0.0939	0.8495
Amyl alcohol	3.3500	2.3494	0.1156	0.7013
i-amyl alcohol	3.1175	2.2650	0.1108	0.7265

monoalkanols with the hydroxyl group at the second carbon atom of the molecular chain are lower than those of the monoalkanols with terminal hydroxyl group.

Figure 6 depicts the enhancement or power factor, F_η, as a function of the number of carbon atoms in the monoalkanol structure and shows a linear, sharp gradient decrease for the monoalkanols.

The excess molar volume, V^E, was calculated using the equation [39,40],

$$V^E = \sum_{i=1}^{j} x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i} \right), \tag{6}$$

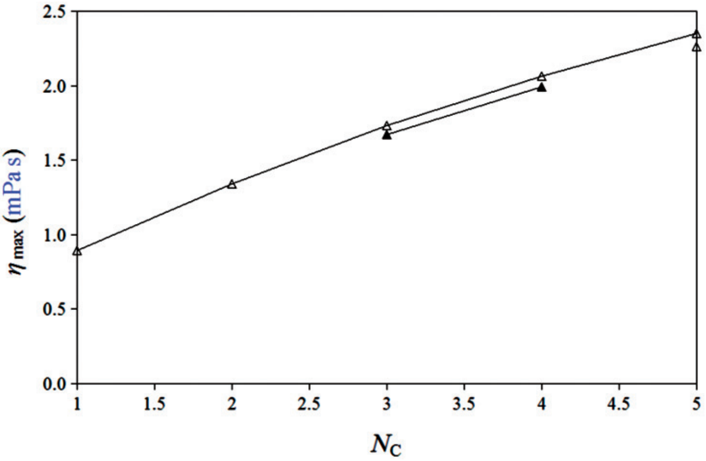


Figure 4. Viscosity values, η_{max} (mPa s), of the monoalkanols in THF + DMSO systems as a function of the number of carbon atoms, N_C: (Δ) OH – terminal, (▲) OH – 2° carbon.

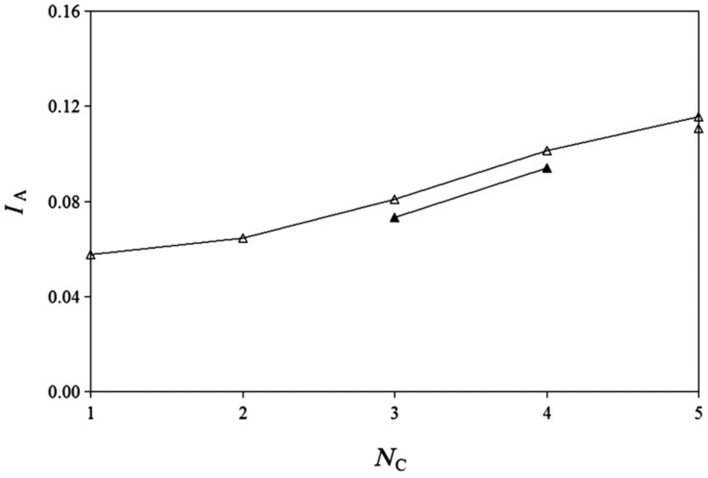


Figure 5. Viscous antagonic index, I_A, of the monoalkanols as a function of the number of carbon atoms, N_C: (Δ) OH – terminal, (▲) OH – 2° carbon.

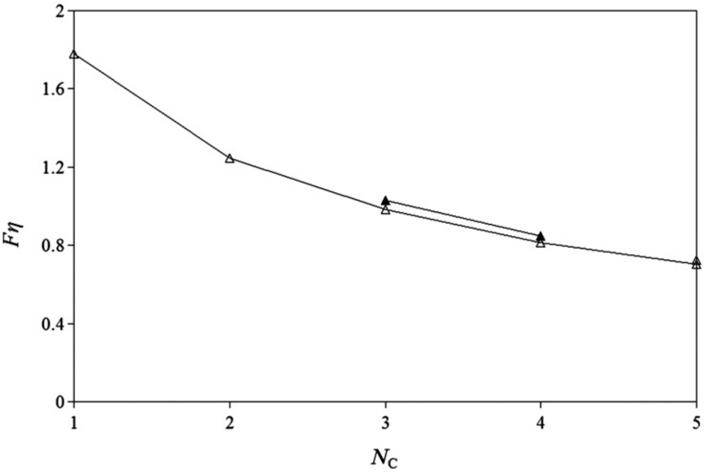


Figure 6. Enhancement or power factor (F_η), of the monoalkanols in THF + DMSO systems as a function of the number of carbon atoms, N_C: (Δ) OH – terminal, (▲) OH – 2° carbon.

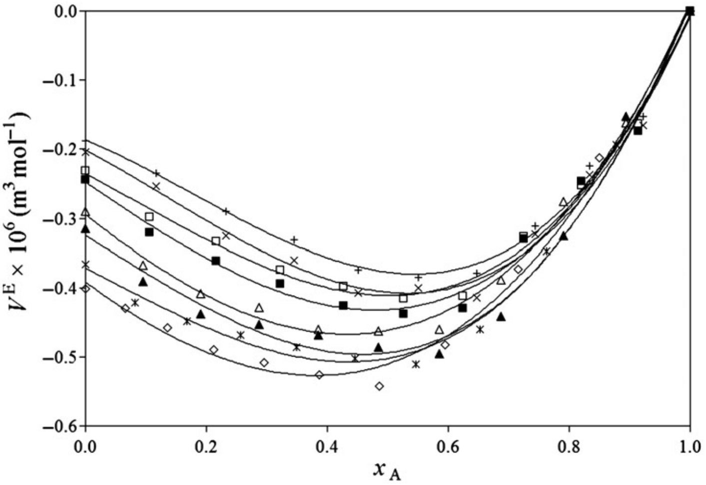


Figure 7. Excess molar volumes (V^E) of THF (A) + DMSO (B) + monoalkanol (C) mixtures with mole fraction of THF (x_A) at 298.15 K; C: (◇) methanol, (∗) ethanol, (Δ) 1-propanol, (▲) 2-propanol, (□)1-butanol, (■) 2-butanol, (+) amyl alcohol, (×) *i*-amyl alcohol.

where ρ is the density of the mixture; M, x_i and ρ_i are the molecular weight, mole fraction and density of *i*-th component in the mixture, respectively.

It can be seen from Table 2 and Figure 7 that V^E is negative for all the THF (A) + DMSO (B) + monoalcohol mixtures over the entire range of composition. The magnitude of the negative values of V^E decreases with increasing chain length of the monoalcohol in THF (A) + DMSO (B) + monoalcohol mixture series. The value of V^E at first decreases to minima and then increases over the entire range of compositions for all ternary mixtures.

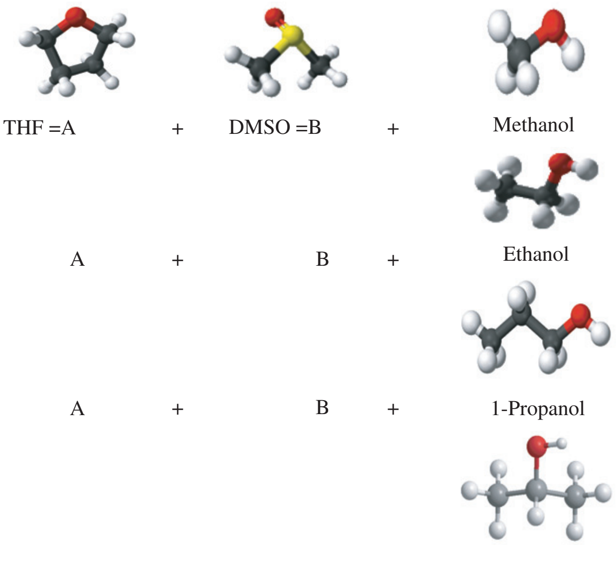
For the THF (A) + DMSO (B) + monoalcohol mixture, the minima are observed at $x_A = 0.48$–0.64. The estimated uncertainty for V^E is $\pm 0.5 \times 10^{-4}\,\mathrm{m^3\,mol^{-1}}$.

From the values of V^E as shown in Table 2, the observed trend is as follows:

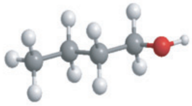
$$\begin{aligned}&(\mathrm{A}) + (\mathrm{B}) + \cdots\\ &\mathrm{MeOH} < \mathrm{EtOH} < \text{2-PrOH} < \text{1-PrOH} < \text{2-BuOH} < \text{2-BuOH}\\ &\quad < i\text{-AmOH} < \mathrm{AmOH}\end{aligned}$$

The negative V^E indicates the presence of strong molecular interactions between the components of the mixture. Volume changes for a mixed system result from changes in the free volume of the liquids, since the bond lengths and the bond distances in the molecules themselves do not change. The optimum packing condition is directly related to differences in molecular sizes and intermolecular attractions, in particular, when hydrogen bonding occurs between unlike molecules creating association complexes, as well as being effected by the breaking of interactions between like molecules [41]. As stated earlier, with the increase in chain length of the alkane groups in the alkanols, their electron releasing ability, that is, +I effect increases, thereby decreasing the polarity of the –OH group. Hence, dipolar interaction and H-bonding between the unlike molecules decreases, thereby decreasing the interaction between the components in the mixture and thus the negative values of V^E decreases with increasing chain length of alkanols. Also, since the molar volume of the monalkanols increase with the chain length, non-associated methanol molecules, having the smallest molar volume, are interstitially accommodated into the cluster of THF and DMSO molecules thereby yielding the highest negative V^E values and the same decreases as the chain length of monoalkanols increase.

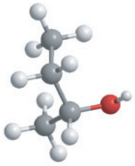
The 2° monoalkanols are more symmetric compared to their corresponding 1° monoalkanols, thus, rendering higher negative values of V^E, which is explained in view of more interaction predominated by H-bonding between the unlike molecules. The diagrammatic representation of the various components is shown below:



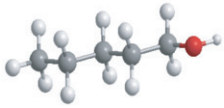
A + B + 2-Propanol



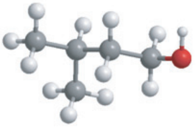
A + B + 1-Butanol



A + B + 2-Butanol



A + B + Amyl alchol



A + B + Iso-amyl alcohol

Isentropic compressibilities, K_S, and excess isentropic compressibility, K_S^E, are calculated from the experimental densities, ρ, and speeds of sound, u, using the following equations [9,42–44]

$$K_S = \frac{1}{u^2 \rho} \tag{7}$$

$$K_S^E = K_S - \sum_{i=1}^{j} x_i K_{S,i} \tag{8}$$

where K_S is the isentropic compressibility of the mixture, and x_i and $K_{S,i}$ are the mole fraction, isentropic compressibility of *i*-th component in the mixture, respectively. Experimental values of u, K_S and K_S^E are compiled in Table 5, and the plots of K_S^E, against x_1 are shown in Figure 8.

K_S^E values are negative for all the mixtures under investigation, and they increase as the length of the molecular chain of the monoalkanols increases. The donor–acceptor interactions between the mixing components play a pivotal role to yield negative K_S^E values, which are more negative for the lower monoalkanols. However, K_S^E values are less negative for linear compared to branched isomers. Similar results were reported by some authors earlier [9,30,42,43]. This is explained by the

Table 5. Experimental speeds of sound (u), isentropic compressibilities (K_S) and deviations in isentropic compressibility (K_S^E) for the mixtures of tetrahydrofuran (THF), dimethylsulphoxide (DMSO) and different monoalkanols as a function of mole fractions of THF (x_A) and DMSO (x_B) at 298.15 K.

x_A	x_B	u (m s^{-1})	$K_S \times 10^{12}$ (Pa^{-1})	$K_S^E \times 10^{12}$ (Pa^{-1})
THF + DMSO + methanol				
0	0.2908	1149.7	819.7	−38.0
0.0654	0.2718	1197.0	759.1	−87.0
0.1361	0.2512	1259.2	688.6	−145.0
0.2127	0.2290	1326.4	623.4	−196.6
0.2958	0.2048	1392.5	568.3	−237.0
0.3866	0.1784	1438.3	535.3	−253.9
0.4859	0.1495	1465.1	518.6	−253.0
0.5952	0.1177	1446.6	535.0	−217.2
0.7160	0.0826	1406.3	569.0	−161.8
0.8501	0.0436	1353.1	617.7	−89.3
1	0	1292.2	680.5	0.0
THF + DMSO + ethanol				
0	0.3706	1205.8	748.1	−18.2
0.0819	0.3402	1262.2	685.0	−74.2
0.1672	0.3086	1315.9	632.5	−119.4
0.2560	0.2757	1372.1	584.3	−160.0
0.3487	0.2414	1423.9	544.9	−191.4
0.4454	0.2055	1450.3	527.7	−200.3
0.5464	0.1681	1463.2	521.0	−198.4
0.6520	0.1290	1438.3	541.9	−168.4
0.7626	0.0880	1395.7	578.2	−122.6
0.8785	0.045	1348.8	621.9	−69.0
1	0	1292.2	680.5	0.0
THF + DMSO + 1-propanol				
0	0.4348	1265.9	674.3	8.1
0.0948	0.3936	1304.7	637.2	−30.4
0.1906	0.3519	1341.8	605.0	−64.0
0.2876	0.3097	1388.0	567.9	−102.5
0.3858	0.2670	1417.8	546.7	−125.1
0.4851	0.2239	1442.9	530.3	−142.9
0.5856	0.1802	1452.1	526.0	−148.6
0.6873	0.1359	1436.3	540.6	−135.4
0.7903	0.0912	1409.9	564.5	−113.0
0.8945	0.0459	1344.5	624.4	−54.5
1	0	1292.2	680.5	0.0
THF + DMSO + 2-propanol				
0	0.4348	1219.6	736.3	−15.0
0.0948	0.3936	1266.3	684.6	−60.0
0.1906	0.3519	1311.5	640.0	−97.8
0.2876	0.3097	1360.7	596.4	−134.5
0.3858	0.2670	1403.7	562.2	−161.8
0.4851	0.2239	1434.3	540.1	−176.8
0.5856	0.1802	1450.3	529.9	−179.9
0.6873	0.1359	1431.0	546.5	−156.1
0.7903	0.0912	1398.0	575.3	−120.0

(*continued*)

Table 5. Continued.

x_A	x_B	u (m s^{-1})	$K_S \times 10^{12}$ (Pa^{-1})	$K_S^E \times 10^{12}$ (Pa^{-1})
0.8945	0.0459	1345.3	624.6	−63.4
1	0	1292.2	680.5	0.0
THF + DMSO + 1-butanol				
0	0.4868	1282.9	653.0	38.8
0.1065	0.4358	1314.0	625.4	4.2
0.2158	0.3852	1353.0	592.7	−35.3
0.3227	0.3353	1394.8	560.4	−74.4
0.4266	0.2858	1424.2	540.3	−101.3
0.5259	0.2369	1441.4	530.1	−118.1
0.6242	0.1885	1457.2	521.4	−133.4
0.7244	0.1406	1429.8	545.0	−116.3
0.8200	0.0933	1396.1	575.2	−92.6
0.9146	0.0464	1339.5	628.8	−45.4
1	0	1292.2	680.5	0.0
THF + DMSO + 2-butanol				
0	0.4868	1250.1	688.8	28.7
0.1065	0.4358	1292.7	647.0	−15.3
0.2158	0.3852	1329.6	614.4	−50.0
0.3227	0.3353	1370.3	581.2	−85.3
0.4266	0.2858	1406.6	554.2	−114.3
0.5259	0.2369	1427.0	541.2	−129.4
0.6242	0.1885	1455.5	522.9	−149.7
0.7244	0.1406	1423.5	550.1	−124.5
0.8200	0.0933	1394.2	577.0	−99.6
0.9146	0.0464	1339.2	629.0	−49.5
1	0	1292.2	680.5	0.0
THF + DMSO + amyl alcohol				
0.0000	0.5301	1312.8	621.5	50.6
0.1162	0.4701	1335.3	603.9	20.6
0.2328	0.4118	1360.4	584.9	−10.5
0.3444	0.3552	1385.0	567.2	−39.9
0.4505	0.3002	1410.2	550.0	−68.5
0.5503	0.2467	1428.6	538.9	−90.6
0.6472	0.1947	1454.6	522.7	−117.5
0.7432	0.1440	1419.9	552.2	−98.5
0.8339	0.0947	1395.4	575.5	−85.4
0.9222	0.0468	1340.0	628.2	−42.7
1.0000	0	1292.2	680.5	0.0
THF + DMSO + *i*-amyl alcohol				
0.0000	0.5301	1266.6	669.2	45.7
0.1162	0.4701	1297.5	640.9	11.0
0.2328	0.4118	1328.9	613.9	−22.4
0.3444	0.3552	1362.2	587.2	−55.1
0.4505	0.3002	1396.4	561.5	−86.7
0.5503	0.2467	1416.7	548.6	−105.4
0.6472	0.1947	1452.9	524.3	−135.3
0.7432	0.1440	1409.1	561.0	−104.0
0.8339	0.0947	1376.5	591.7	−78.6
0.9222	0.0468	1339.5	628.7	−46.8
1.0000	0	1292.2	680.5	0.0

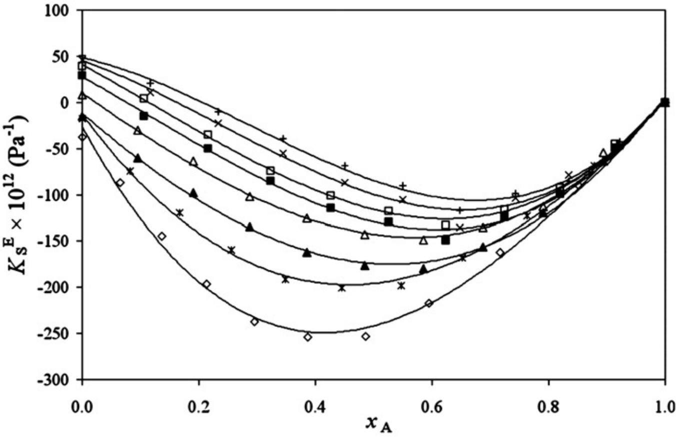


Figure 8. Excess isentropic compressibility (K_S^E) of THF (A) + DMSO (B) + monoalkanol (C) mixtures with mole fraction of THF (x_A) at 298.15 K; C: (◇) methanol, (∗) ethanol, (Δ) 1-propanol, (▲) 2-propanol, (□) 1-butanol, (■) 2-butanol, (+) amyl alcohol, (×) *i*-amyl alcohol.

interstitial accommodation and changes in free volume. The branched isomers fit into the structure of A and B more easily compared to the linear isomers, thereby possessing more negative deviations.

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 has given the clear distinction.

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