

CHAPTER IV

Viscous Synergy, Excess Molar volumes, Viscosity Deviations and Isentropic Compressibility of some Primary Monoalkanols in Aqueous N, N-dimethylformamide Mixtures.

Keywords: Viscous synergy; viscosity deviations; excess molar volumes; isentropic compressibility; molecular interactions; interstitial accommodation.

4.1. Introduction

The increasing use of N,N-dimethylformamide as a versatile solvent in the separation of saturated and unsaturated hydrocarbons, as solvents for vinyl resins, polyacrylic fibres and catalyst in carbonylation reaction as well as in organic synthesis enhance the importance to obtain information on its behavior when mixed with other solvents. On the other hand monoalkanols are useful solvents in paint, varnishes and fuel industries. So we need to require extensive information on the various properties when these monoalkanols are taken with DMF as mixed solvent systems.¹⁻⁷

The determination of density, viscosity and speeds of sound is a valuable tool to learn about the liquid state^{8, 9} because of the close connection between liquid structure and macroscopic 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.^{10,11} In our systematic investigation of the properties, we have reported viscosities, densities and speeds of sound of different solvents and their mixtures in previous papers¹²⁻¹⁸ from our laboratory. The present work contributes and extends our study of density (ρ), viscosity deviations ($\Delta\eta$), viscous syne

rgy, excess molar volumes (V^E) and isentropic compressibility (K_s^E) to the aqueous mixtures of N,N-dimethylformamide (DMF) with some monoalkanols; where water is represented as A; amide (DMF) represented as B; and monoalkanol represented as C. It is expected that there will be a significant degree of H-bonding leading to self association in the pure state in addition to mutual association in these ternaries.

4.2. Experimental Section

4.2.1. Source and purity of samples

DMF (N,N-dimethylformamide, C_3H_7NO , FW=73.10) is obtained from Merck and LR, further purified by standard methods.¹⁹ The source and purification of pure alcohols (Merck, India) methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH), 1-butanol (1-BuOH), and 1-pentanol (1-PentOH) have been described earlier.¹⁹⁻²⁵ Triply distilled water was used for the experimental purpose. The purity of the liquids was ascertained by GLC and also by comparing experimental values of densities, viscosities and sound velocities with those reported in the literature^{23, 26-31} as listed in Table 1. The purity of the solvents finally obtained were >99%.

4.2.2. Apparatus and Procedure

Densities (ρ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of 25 cm³ 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 DMF. The measurements were done in a thermostated water bath controlled to $\pm 0.01K$.⁶ The weighings were done on a Mettler electronic balance (AG-285) with a precision of $\pm 0.01mg$. The viscosities (η) were measured by means of a suspended Ubbelohde type viscometer⁷ which was calibrated at the desired temperature with triply distilled water and purified methanol using density and viscosity values from the literature. The ultrasonic speeds (u) were determined using a single-crystal variable path ultrasonic interferometer (Mittal Enterprises, New Delhi) working at 5 MHz,³² which was calibrated with water, methanol and benzene and the temperature stability was maintained within $\pm 0.01K$ by circulating thermostatic water around the cell with a circulating pump. The

solutions were prepared by mixing known volumes of pure liquids in airtight-stopper bottles at 298.15 K. The precisions of the speed of sound, density and viscosity measurements are $\pm 0.2 \text{ m s}^{-1}$, $\pm 3 \times 10^{-4} \text{ g cm}^{-3}$ and $\pm 2 \times 10^{-4} \text{ m Pa s}$, respectively.

4.3. Results and discussion

The measured density (ρ), viscosity (η) and the speeds of sound (u) data for mixtures of water (A), DMF (B), and the monoalkanols (C), i.e., methanol, ethanol, propanol, butanol, pentanol, were used to calculate the excess molar volume (V^E) and viscosity deviation ($\Delta\eta$) and excess isentropic compressibilities (K_s^E).

The method most widely used to analyze the antagonistic and synergic behavior of various solvent mixtures studied is that developed by Kalentune-Gencer and Peleg,³³ allowing the quantification of the antagonistic and synergic interactions taking place in mixtures involving variable proportions of the constituent components. Viscous synergy is the term used in application to the interaction between the components of a system that causes the total viscosity of the latter to be greater than the sum of the viscosities of each component in the system. If the total viscosity of the system is equal to the sum of the viscosities of each component considered separately, the system is considered as lack of interaction.³⁴ The method compares the viscosity of the system determined experimentally, η_{exp} with the viscosity expected in the absence of interaction, η_{calcd} , defined as,³⁵

$$\eta_{\text{calcd}} = \sum_{i=1}^{n=3} W_i \eta_i \quad (1)$$

Where, W_i and η_i are the fraction by weight and the viscosity measured experimentally, of the pure components respectively.

Viscous synergy exists when, $\eta_{\text{exp}} > \eta_{\text{calcd}}$. This procedure is used when Newtonian fluids are involved.³⁵ Quantitatively, as per the absolute reaction rates theory,³⁶ the deviations of viscosities from the ideal mixture values can be calculated as

$$\Delta\eta = \eta - \sum_{i=1}^{n=3} X_i \eta_i \quad (2)$$

where, η is the viscosity of the mixture and X_i , η_i are the mole fraction and viscosity of the pure components respectively.

In order to secure more comparable viscous synergy results, the so called synergy index (I_s), introduced by Howell³⁵ is taken into account

$$I_s = (\eta_{exp} - \eta_{calcd}) / \eta_{calcd} \quad (3)$$

The increase in density was analyzed by carrying out the following equation analogous to that used for viscosity of mixture.

$$\rho_{mix} = \sum_{i=1}^{n=3} W_i \rho_i \quad (4)$$

Where, W_i and ρ_i are the fractions by weight and densities measured experimentally of the pure components respectably. Accordingly, when $\rho_{exp} > \rho_{mix}$, volume contraction occurs. The excess molar volumes, V^E are calculated from density data according to the following equation:³⁷

$$V^E = \sum_{i=1}^{n=3} X_i M_i (1/\rho - 1/\rho_i) \quad (5)$$

Where, M_i , ρ_i and ρ are the molar mass, density of the pure components and density of the mixture respectively.

Table 4 contains the sound velocity (u), isentropic compressibility (K_s) and excess isentropic compressibility (K_s^E) data for the mixtures observed and calculated using the following equation [38]:

$$K_s = (u^2 \rho_{exp})^{-1} \quad (6)$$

$$K_s^E = K_s - \sum_{i=1}^{n=3} X_i K_{s,i} \quad (7)$$

where, $K_{s,i}$ gives the isentropic compressibility for the the pure components of the mixture.

In Fig.1, $\Delta\eta$ values for the ternary mixtures (A) + (B) + MeOH, EtOH, 1-PrOH, 1-BuOH, and 1-PentOH (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 less positive as the temperature rises from 298.15 to 318.15 K. However, the mixtures have maximum, $\Delta\eta$ at $X_A=0.70$ 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, N,N-dimethylformamide and MeOH/ EtOH/ 1-PrOH/1-BuOH/ 1-PentOH molecules resulting in negative $\Delta\eta$ but with the increase in temperature and mole fraction of water (X_A), the hydrogen bonding interactions come into play leading to the formation of complex species between unlike molecules thereby resulting in positive $\Delta\eta$.³⁹

In Fig. 2, synergy index (I_S) values for the ternary mixtures (A) + (B) + MeOH, EtOH, 1-PrOH, 1-BuOH, and 1-PentOH (C) have been plotted against the mole fraction of water (X_A) at 298.15 K. It is found that each mixture has a maximum at $X_A =0.7$ 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_S is ± 0.002 . 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 legally implies rise in viscosity. After reaching the maximum viscosity, it decreases on subsequent addition of more water, as the latter tends to approach the viscosity of water.

Such characteristics in the viscosity versus composition curve is a manifestation of specific interaction³¹ between the unlike molecules, predominated by hydrogen bonding interaction. It can be concluded that the affinity of monoalkanols molecules towards N,N-dimethylformamide (DMF) molecules in the presence of water is enhanced by the following order,



Similar results were also reported earlier.^{25,30,40,41}

In Fig. 3 $\Delta\rho$ versus mole fraction of water (X_A) behavior similar to the previous figure thus reflecting the relation between viscous synergy and volume contraction.⁶ This fact can be explained in terms of electrostriction as a consequence of solvent molecules is accommodated in the void space left in the packing of dispersed solvent molecules. Similar results were reported by some authors earlier.^{30, 40-42}

Fig. 4 represents the V^E values for the five 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 minima and then it increase with increasing X_A . V^E decreases systematically from 298.15 to 318.15K over the whole range of mole fractions. The five ternary mixtures shows the minima at the same point i.e. at $X_A = 0.5$. The estimated uncertainty for V^E is $\pm 0.5 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$. The trend is:



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:⁴³ dipolar interaction, interstitial accommodation and possible hydrogen bonded interactions between unlike molecules. The actual volume change would, therefore, depend on the relative strength of these three effects. It is known fact that as the number of C-atoms of the alkyl group increases, the electron releasing ability (+ I effect) increases, thereby decreasing the polarity of the O---H bond of the monoalkanols. Consequently, MeOH having the highest polarity achieves the most favorable intermolecular H-bonded interactions with water and DMF. Moreover, its simple structure and smaller size leads to interstitial accommodation with others molecules more easily compared to the higher monoalkanols that have greater structural complexity. Similar results have been reported earlier.^{23, 44, 45}

Fig. 5 predicts the curves for the ternary mixtures of K_s^E . The values decreases to attain a minima and then increases as the mole fraction of water increases and they also increase as the length of the molecular chain of the monoalkanols increases. However, the values

attend a minima at $X_A = 0.7$ and thereafter increases for every mixture. The estimated uncertainty for K_s^E is $\pm 0.2 \text{ Pa}^{-1}$. The K_s^E values follow the sequence:



The results can be qualitatively explained in terms (i) molecular interactions (ii) structural effects and (iii) geometrical fitting of component molecules into each other structure. Negative deviation in isentropic compressibility is an indication of strong interactions such as formation of hydrogen bonds, charge transfer complexes or strong dipole-dipole interactions between the component molecules. The more easily the molecules fit into each others structure, K_s^E values become more and more negative. Similar results have been reported by some authors earlier.^{25, 29, 41, 46, 47}

4.4. Conclusion

After a thorough study of the behavior of monoalkanols on aqueous DMF we get a clear idea about the type and amount of molecular interactions between them and also given us an idea about synergy. The lower monoalkanols are found to associate more with others molecules whereas self-association between the alcohol molecules was found to increase with increasing chain length.

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

T (K)	$\rho \times 10^{-3}$ kg m ⁻³		η m Pa s		u m s ⁻¹	
	I	II	I	II	I	II
Water						
298.15	0.99707	0.9970 ²⁶	0.8903	0.8904 ²⁶	1496.2	1497.4 ²⁷
308.15	0.99406	0.9940 ²⁶	0.7194	0.7194 ²⁶		
318.15	0.99025	0.9902 ²⁶	0.5960	0.5960 ²⁶		
N,N-dimethylformamide						
298.15	0.9460	0.9461 ²³	0.8586	0.8586 ²³	1465.2	1465.0 ²³
308.15	0.9399	0.9399 ²³	0.7763	0.7763 ²³		
318.15	0.9316	0.9316 ²³	0.7125	0.7120 ²³		
Methanol						
298.15	0.78659	0.7866 ²⁶	0.5446	0.54230 ²⁶	1108.2	1105 ²⁶
308.15	0.77728	0.7772 ²⁶	0.4747	0.47424 ²⁶		
318.15	0.76774	0.7677 ²⁶	0.4185	0.41739 ²⁶		
Ethanol						
298.15	0.78508	0.7849 ²⁹	1.088	1.0830 ²⁹	1144.3	1144.9 ²⁶
308.15	0.77809	0.7764 ²⁹	0.897	0.8930 ²⁹		
318.15	0.76391	0.7678 ²⁹	0.767	0.76304 ²⁹		
Propanol						
298.15	0.8025	0.8025 ³⁰	1.946	1.95 ²⁸	1206.5	1207 ²⁶
308.15	0.79141	0.7915 ²⁸	1.564	1.40 ²⁸		
318.15	0.7834	0.7832 ²⁸	1.178	1.10 ²⁸		
Butanol						
298.15	0.8056	0.8057 ²⁹	2.566	2.57 ²⁹	1240.2	1240 ²⁶
308.15	0.798	0.7982 ²⁹	1.998	1.981 ²⁹		
318.15	0.7905	----	1.55	----		
Pentanol						
298.15	0.8104	0.8112 ³¹	3.510	3.5104 ³¹	1277.2	1277 ³¹
308.15	0.8029	----	2.582	----		
318.15	0.78508	----	2.106	----		

Table 2. Viscosity deviations ($\Delta\eta$) and synergic index (I_S) of water (A) + N,N-dimethylformamide (B) + methanol, ethanol, propanol, butanol and pentanol (C) at 298.15, 308.15 and 318.15 K.

X_A	X_B	T (K)					
		298.15		308.15		318.15	
		$\Delta\eta$, mPa s	I_S	$\Delta\eta$, mPa s	I_S	$\Delta\eta$, mPa s	I_S
water (A)+ N,N-dimethylformamide (B)+ methanol (C)							
0.00000	0.30447	-0.12100	-0.25997	-0.14800	-0.33089	-0.02300	-0.14233
0.21555	0.23917	0.17900	0.21188	0.15600	0.19009	0.14900	0.18912
0.38205	0.18815	0.79000	1.06366	0.46800	0.69636	0.35600	0.57038
0.51453	0.14781	1.28100	1.70355	0.66700	1.00741	0.49400	0.82248
0.62245	0.11495	1.53500	1.99946	0.75800	1.14111	0.56000	0.94354
0.71206	0.08767	1.57700	2.00925	0.76900	1.14794	0.55800	0.94346
0.78766	0.06465	1.45400	1.81179	0.69400	1.02531	0.50283	0.85021
0.85230	0.04497	1.18400	1.44368	0.57500	0.83994	0.41000	0.69209
0.90819	0.02795	0.84300	1.00604	0.38200	0.55200	0.28000	0.47130
0.95700	0.01309	0.43200	0.50501	0.21000	0.29974	0.15500	0.26017
1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
water (A)+ N,N-dimethylformamide (B)+ ethanol(C)							
0.00000	0.38623	-0.38600	-0.36977	-0.33700	-0.38638	-0.14800	-0.19169
0.25847	0.28640	0.16800	0.18053	0.12900	0.14620	0.10300	0.11693
0.43954	0.21646	0.89600	0.93107	0.50000	0.58978	0.33200	0.42340
0.57346	0.16474	1.34200	1.40280	0.68800	0.82572	0.46500	0.61487
0.67652	0.12494	1.48800	1.56734	0.74200	0.90411	0.49700	0.67315
0.75828	0.09336	1.45400	1.54413	0.70000	0.86506	0.47100	0.65187
0.82473	0.06769	1.26600	1.35556	0.61800	0.77523	0.40000	0.56432
0.87980	0.04642	1.01400	1.09501	0.44600	0.56531	0.30600	0.43950
0.92619	0.02851	0.67769	0.73778	0.32300	0.41626	0.21300	0.31263
0.96579	0.01321	0.38500	0.42333	0.14799	0.19251	0.09000	0.13230
1.00000	0.00000	-0.00000	-0.00000	0.00000	0.00000	0.00000	0.00000
water (A)+ N,N-dimethylformamide (B)+ propanol (C)							
0.00000	0.45079	-0.70500	-0.46459	-0.55592	-0.44196	-0.28400	-0.27621
0.28918	0.32043	0.06983	0.00816	0.11800	0.05358	0.09000	0.04417
0.47790	0.23536	0.90000	0.60441	0.48100	0.34812	0.34200	0.29347
0.61077	0.17546	1.30000	0.93034	0.64500	0.50246	0.44500	0.41093
0.70938	0.13101	1.41200	1.05982	0.65400	0.53120	0.47100	0.45882
0.78547	0.09671	1.32000	1.03402	0.58100	0.48756	0.42600	0.42980
0.84597	0.06944	1.12100	0.91615	0.47000	0.40580	0.35200	0.36649
0.89521	0.04724	0.87700	0.74971	0.35500	0.31718	0.26500	0.28429
0.93608	0.02881	0.59400	0.53160	0.23900	0.22252	0.16800	0.18313
0.97055	0.01328	0.32481	0.30828	0.11800	0.11425	0.07700	0.08406

Viscous Synergy.....of some Pr. Monoalkanols in Aqueous DMF Mixtures.

1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
water(A)+ N,N-dimethylformamide (B)+ butanol (C)							
0.00000	0.50306	-0.96600	-0.56720	-0.77500	-0.56139	-0.47569	-0.42277
0.31224	0.34598	0.03300	-0.08897	0.07100	-0.05551	0.06000	-0.05137
0.50532	0.24886	0.87200	0.39955	0.46000	0.20284	0.31500	0.14676
0.63651	0.18286	1.23500	0.65259	0.58600	0.30328	0.40400	0.22969
0.73147	0.13509	1.27800	0.72579	0.58100	0.32022	0.41000	0.25284
0.80338	0.09891	1.17200	0.70821	0.50700	0.28832	0.36700	0.23634
0.85973	0.07057	0.97800	0.62650	0.40000	0.22914	0.29000	0.18593
0.90507	0.04776	0.74900	0.51009	0.29700	0.17365	0.22400	0.15067
0.94234	0.02901	0.47900	0.34292	0.18100	0.10052	0.14600	0.09909
0.97353	0.01332	0.24400	0.18860	0.09200	0.05445	0.07500	0.05477
1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
water (A)+N,N-dimethylformamide (B)+ pentanol (C)							
0.00000	0.54624	-1.28500	-0.64442	-0.94265	-0.61112	-0.62200	-0.48710
0.33019	0.36588	-0.27000	-0.31630	-0.02100	-0.18814	0.03700	-0.14562
0.52588	0.25898	0.61000	0.06762	0.37600	0.01590	0.29800	0.00194
0.65534	0.18827	0.99000	0.27167	0.51100	0.10148	0.37800	0.05733
0.74734	0.13802	1.06000	0.34775	0.50700	0.11777	0.36400	0.06019
0.81607	0.10047	0.98000	0.35678	0.44900	0.10865	0.31000	0.04100
0.86937	0.07136	0.79000	0.30217	0.35300	0.07574	0.24700	0.02119
0.91191	0.04812	0.62000	0.26202	0.26000	0.04890	0.17200	-0.00716
0.94666	0.02914	0.40000	0.17726	0.15600	0.01184	0.11800	-0.00620
0.97557	0.01335	0.20000	0.09730	0.07100	-0.00437	0.04900	-0.02071
1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000

Table 3. Density deviation ($\Delta\rho$) and excess molar volumes (V^E) of water (A) + N,N-dimethylformamide (B) + methanol, ethanol, propanol, butanol and pentanol (C) at 298.15, 308.15 and 318.15 K.

X_A	X_B	T (K)					
		298.15		308.15		318.15	
		$\Delta\rho \times 10^{-3}$ kg m ⁻³	$V^E \times 10^6$ m ³ mol ⁻¹	$\Delta\rho \times 10^{-3}$ kg m ⁻³	$V^E \times 10^6$ m ³ mol ⁻¹	$\Delta\rho \times 10^{-3}$ kg m ⁻³	$V^E \times 10^6$ m ³ mol ⁻¹
water (A)+ N,N-dimethylformamide (B)+ methanol (C)							
0.00000	0.30447	-0.00450	-0.17119	-0.00048	-0.44018	-0.00012	-0.48428
0.21555	0.23917	0.00626	-0.73502	0.00662	-0.78618	0.00799	-0.88910
0.38205	0.18815	0.01399	-0.98792	0.01248	-0.96290	0.01333	-1.03718
0.51453	0.14781	0.01855	-1.03907	0.01756	-1.04015	0.01703	-1.05790
0.62245	0.11495	0.02015	-0.96488	0.01949	-0.97701	0.01903	-0.99603
0.71206	0.08767	0.02043	-0.85295	0.01991	-0.86596	0.01859	-0.85711
0.78766	0.06465	0.01904	-0.70609	0.01939	-0.73755	0.01912	-0.75457
0.85230	0.04497	0.01549	-0.52399	0.01688	-0.57310	0.01644	-0.58076
0.90819	0.02795	0.01120	-0.34705	0.01267	-0.38908	0.01259	-0.39920
0.95700	0.01309	0.00598	-0.17106	0.00764	-0.20897	0.00839	-0.22963
1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
water (A)+ N,N-dimethylformamide (B)+ ethanol(C)							
0.00000	0.38623	-0.00811	0.04770	-0.00586	-0.17954	-0.00304	-0.41865
0.25847	0.28640	0.00195	-0.63493	0.00269	-0.70271	0.00467	-0.89594
0.43954	0.21646	0.00875	-0.91620	0.00897	-0.92963	0.00931	-1.01789
0.57346	0.16474	0.01180	-0.89188	0.01171	-0.91415	0.01170	-0.97783
0.67652	0.12494	0.01361	-0.82811	0.01370	-0.85407	0.01216	-0.85430
0.75828	0.09336	0.01320	-0.75508	0.01409	-0.74096	0.01480	-0.80936
0.82473	0.06769	0.01221	-0.56010	0.01274	-0.58993	0.01357	-0.64913
0.87980	0.04642	0.01145	-0.44703	0.01099	-0.44756	0.01019	-0.45438
0.92619	0.02851	0.00808	-0.28793	0.00789	-0.29145	0.00720	-0.29341
0.96579	0.01321	0.00407	-0.13570	0.00577	-0.17333	0.00639	-0.19431
1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
water (A)+ N,N-dimethylformamide (B)+ propanol (C)							
0.00000	0.45079	-0.01001	0.36101	-0.00448	-0.16769	-0.00256	-0.34810
0.28918	0.32043	-0.00006	-0.45100	0.00225	-0.65920	0.00495	-0.87107
0.47790	0.23536	0.00642	-0.73899	0.00742	-0.84074	0.00884	-0.94513
0.61077	0.17546	0.00901	-0.73901	0.01064	-0.85401	0.01050	-0.87519
0.70938	0.13101	0.01034	-0.67500	0.01195	-0.77184	0.01168	-0.78662
0.78547	0.09671	0.01019	-0.56599	0.01203	-0.65515	0.01296	-0.70610
0.84597	0.06944	0.00933	-0.45100	0.01160	-0.53804	0.01136	-0.54830
0.89521	0.04724	0.00736	-0.32300	0.00905	-0.38195	0.00892	-0.39123
0.93608	0.02881	0.00457	-0.19383	0.00651	-0.24790	0.00629	-0.25125
0.97055	0.01328	0.00125	-0.07071	0.00230	-0.09696	0.00246	-0.10394
1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000

Viscous Synergy.....of some Pr. Monoalkanols in Aqueous DMF Mixtures.

water(A)+ N,N-dimethylformamide (B)+ butanol (C)							
0.00000	0.50306	-0.01278	0.70001	-0.00590	0.01056	-0.00278	-0.30063
0.31224	0.34598	-0.00179	-0.34200	0.00124	-0.58874	0.00330	-0.76306
0.50532	0.24886	0.00392	-0.62399	0.00593	-0.76380	0.00653	-0.82100
0.63651	0.18286	0.00540	-0.59200	0.00858	-0.76193	0.00808	-0.76207
0.73147	0.13509	0.00638	-0.53400	0.00974	-0.68406	0.00932	-0.68899
0.80338	0.09891	0.00694	-0.46402	0.00972	-0.57311	0.00957	-0.58615
0.85973	0.07057	0.00547	-0.34200	0.00909	-0.45893	0.00870	-0.46248
0.90507	0.04776	0.00485	-0.25900	0.00817	-0.35248	0.00822	-0.36486
0.94234	0.02901	0.00324	-0.22900	0.00623	-0.23590	0.00604	-0.23898
0.97353	0.01332	0.00168	-0.07799	0.00343	-0.11644	0.00342	-0.11986
1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
water (A)+N,N-dimethylformamide (B)+ pentanol (C)							
0.00000	0.54624	-0.01387	0.91400	-0.01424	0.03700	-0.00540	-0.22595
0.33019	0.36588	-0.00327	-0.21600	-0.00961	-0.53900	-0.00093	-0.58971
0.52588	0.25898	0.00093	-0.44800	0.00513	-0.71800	0.01081	-1.14472
0.65534	0.18827	0.00188	-0.42200	0.00559	-0.71300	0.01135	-0.97022
0.74734	0.13802	0.00236	-0.37100	0.00370	-0.63800	0.01058	-0.77757
0.81607	0.10047	0.00226	-0.30200	0.00279	-0.52900	0.00691	-0.52411
0.86937	0.07136	0.00133	-0.21600	0.00249	-0.46400	0.00767	-0.45163
0.91191	0.04812	0.00096	-0.15500	0.00308	-0.29400	0.00505	-0.29651
0.94666	0.02914	-0.00074	-0.06900	0.00458	-0.21700	0.00570	-0.23871
0.97557	0.01335	-0.00065	-0.02900	0.00203	-0.08000	0.00261	-0.10667
1.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000

Table 4. Experimental sound velocities (u), isentropic compressibility (K_S) and excess isentropic compressibility (K_S^E) of water (A)+ N,N-dimethylformamide (B) + methanol, ethanol, propanol, butanol and pentanol (C) at 298.15.

x_A	u $m\ s^{-1}$	$K_S \times 10^{12}$ Pa^{-1}	$K_S^E \times 10^{12}$ Pa^{-1}
water (A)+ N,N-dimethylformamide (B)+ methanol (C)			
0.00000	1364.1	623.6	43.7
0.21555	1376.6	595.8	45.0
0.38205	1458.2	518.8	-9.6
0.51453	1552.4	449.1	-61.5
0.62245	1628.0	401.9	-94.1
0.71206	1674.6	374.5	-109.4
0.78766	1679.9	367.7	-106.1
0.85230	1659.7	373.0	-92.1
0.90819	1619.9	388.0	-69.5
0.95700	1569.3	410.1	-40.8
1.00000	1496.2	448.0	0.0
water (A)+ N,N-dimethylformamide (B)+ ethanol (C)			
0.00000	1385.6	607.4	69.0
0.25847	1417.2	565.3	51.0
0.43954	1513.4	484.5	-12.9
0.57346	1604.9	423.4	-61.5
0.67652	1663.3	387.9	-87.4
0.75828	1675.6	376.3	-91.4
0.82473	1665.8	376.7	-84.8
0.87980	1635.9	385.6	-70.8
0.92619	1593.1	402.5	-49.5
0.96579	1550.8	420.8	-27.5
1.00000	1496.2	448.0	0.0
water (A)+ N,N-dimethylformamide (B)+ propanol (C)			
0.00000	1391.7	597.3	95.6
0.28918	1436.8	546.4	61
0.47790	1540.0	465.8	-8.9
0.61077	1616.9	415.7	-51.5
0.70938	1656.0	390.5	-71.1
0.78547	1655.4	385.8	-71.5
0.84597	1639.2	388.8	-65.1
0.89521	1610.8	398.3	-52.8
0.93608	1575.0	412.6	-36.2
0.97055	1547.8	423.3	-23.5
1.00000	1496.2	448.0	0.0

Viscous Synergy.....of some Pr. Monoalkanols in Aqueous DMF Mixtures.

water (A)+ N,N-dimethylformamide (B)+ butanol (C)			
0.00000	1391.2	598.6	116.6
0.31224	1442.7	542.1	71.6
0.50532	1538.9	467.1	3.7
0.63651	1596.3	427.7	-30.9
0.73147	1622.3	408.3	-46.8
0.80338	1615.4	406.2	-46.2
0.85973	1602.6	408.1	-42.2
0.90507	1580.8	414.5	-34.2
0.94234	1558.5	421.8	-25.5
0.97353	1528.3	433.9	-12.2
1.0000	1496.2	448.0	0.0
water (A)+ N,N-dimethylformamide (B)+ pentanol (C)			
0.00000	1386.1	602.2	135.9
0.33019	1447.2	538.4	79.1
0.52588	1533.7	470.9	15.7
0.65534	1584.9	434.7	-17.7
0.74734	1600.2	420.8	-29.7
0.81607	1593.4	419.0	-30.0
0.86937	1583.9	419.2	-28.7
0.91191	1565.8	423.8	-23.2
0.94666	1543.5	431.6	-14.7
0.97557	1523.7	437.5	-8.2
1.00000	1505.6	448.0	0.0

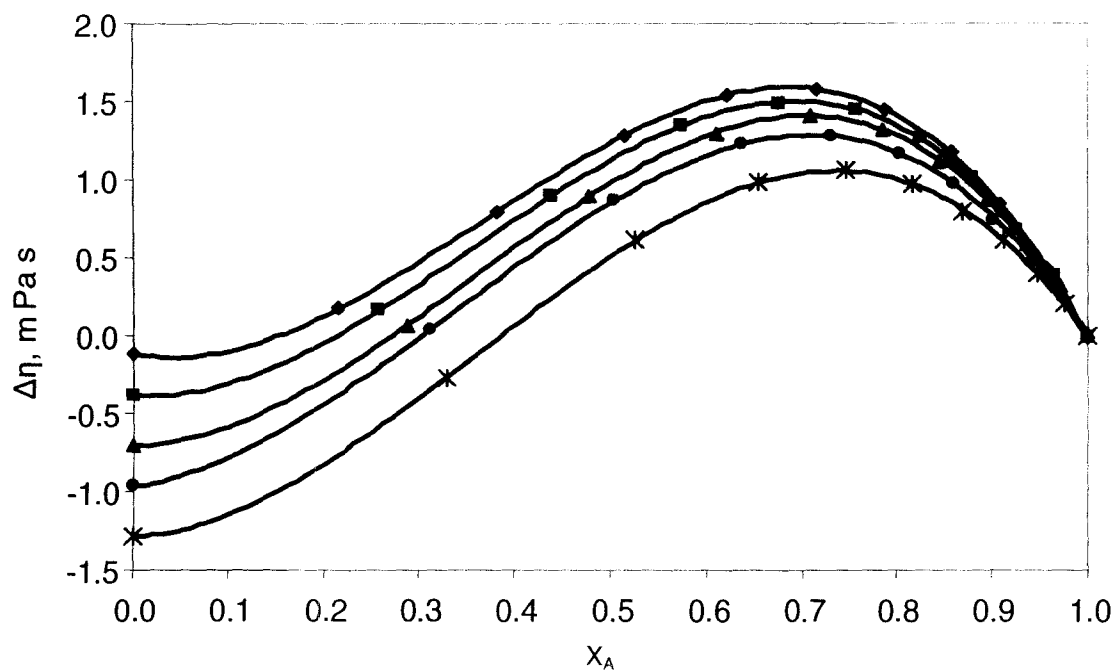


Fig. 1. Viscosity deviations ($\Delta\eta$) of: (◆), water (A)+ N,N-dimethylformamide (B) + methanol (C); (■), water (A)+ N,N-dimethylformamide (B)+ ethanol(C); (▲), water (A) + N,N- dimethylformamide (B) + propanol (C); (●), water (A) + N,N-dimethyl formamide (B)+ butanol (C); and (⋈), water (A)+N,N-dimethylformamide (B) + pentanol (C) mixtures with mole fraction of water(x_A) at 298.15 K.

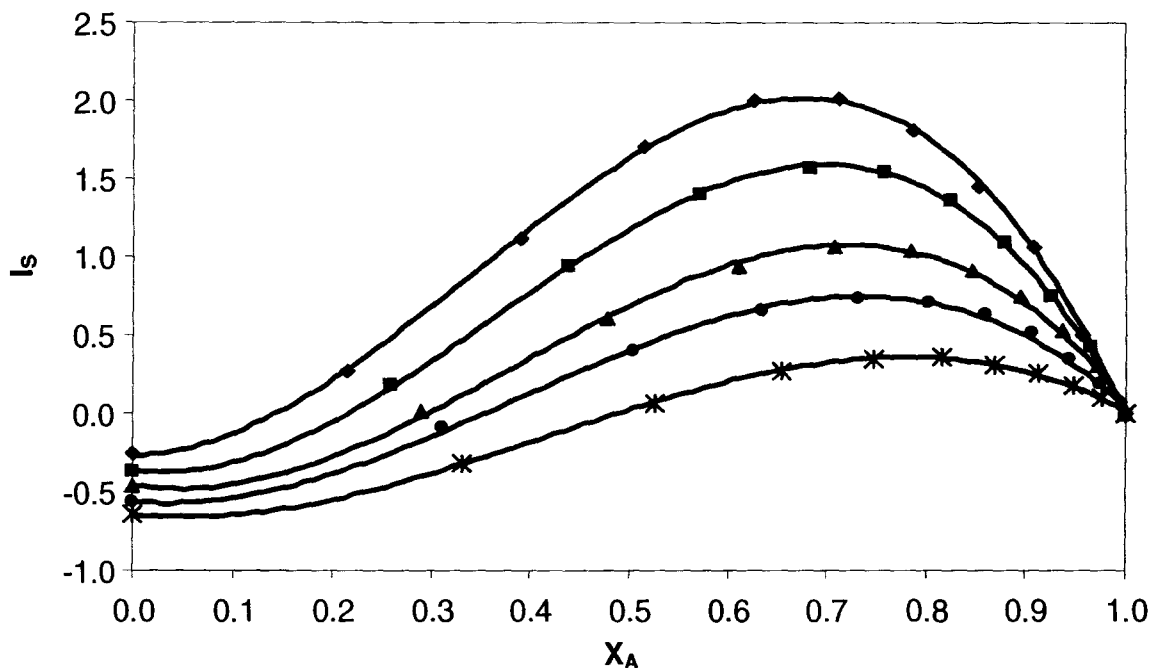


Fig. 2. Synergy Index (I_s) of: (♦), water (A)+ N,N-dimethylformamide (B)+ methanol (C); (■), water (A)+ N,N-dimethylformamide (B)+ ethanol(C); (▲), water (A)+ N,N-dimethylformamide (B)+ propanol (C); (●), water(A)+ N,N-dimethylformamide (B)+ butanol (C); and (✕), water (A)+N,N-dimethylformamide (B)+ pentanol (C) mixtures with mole fraction of water(x_A) at 298.15 K.

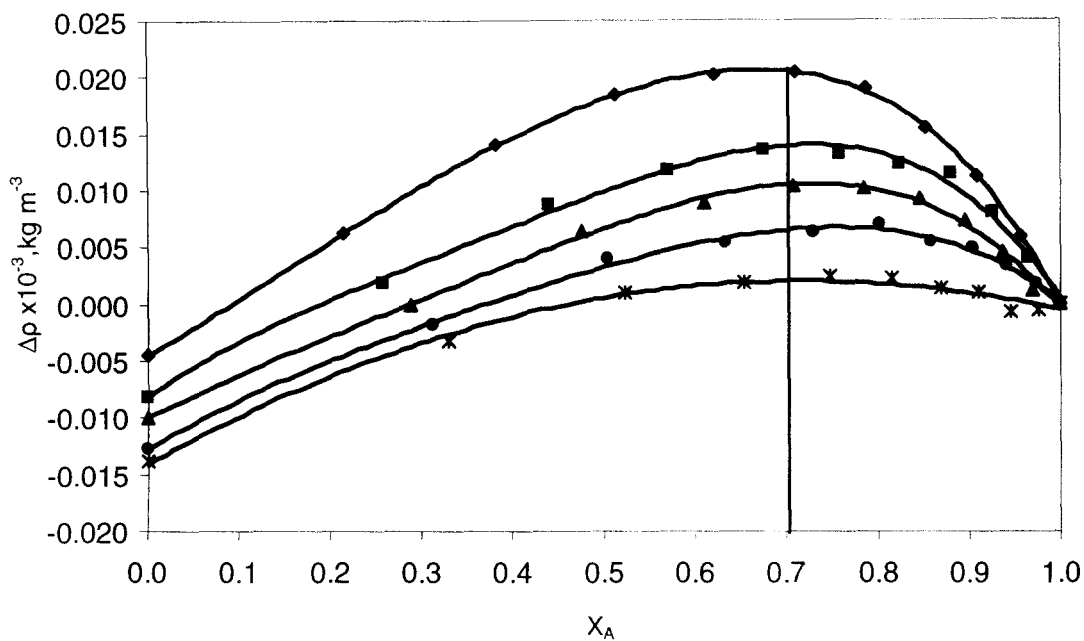


Fig. 3. Density Differences ($\Delta\rho$) of: (♦), water (A)+ N,N-dimethylformamide (B)+ methanol (C); (■), water (A) + N,N-dimethylformamide (B)+ ethanol(C); (▲), water (A)+ N,N-dimethylformamide (B)+ propanol (C); (●),water (A)+ N,N-dimethylformamide (B)+ butanol (C); and (⋈), water (A)+N,N-dimethylformamide (B) + pentanol (C) mixtures with mole fraction of water(x_A) at 298.15 K.

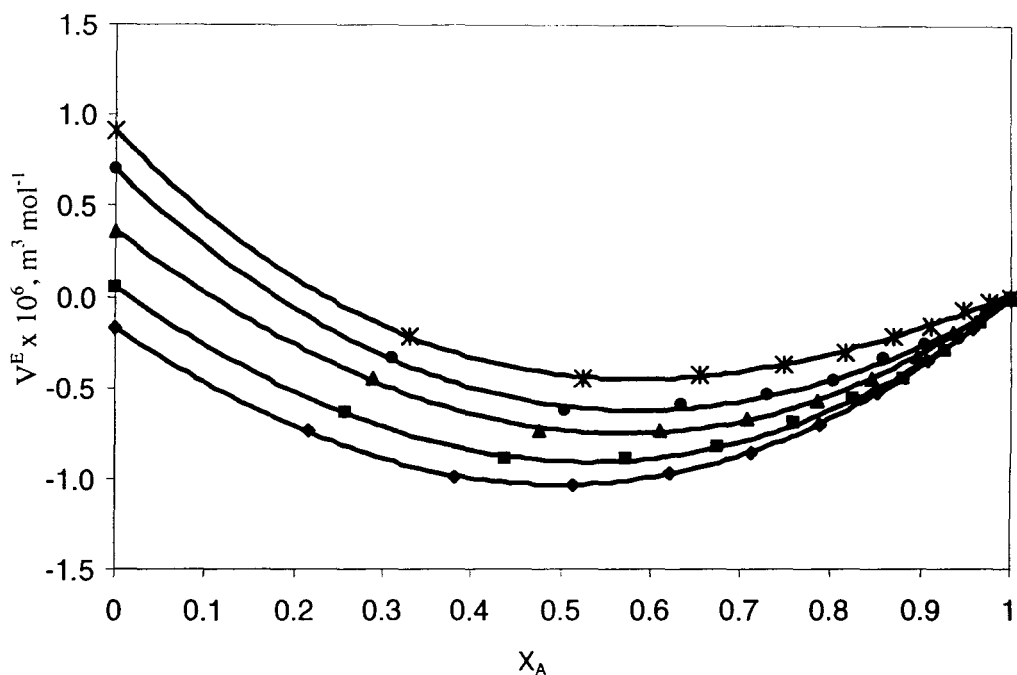


Fig. 4. Excess molar volumes (V^E) of: (♦), water (A)+ N,N-dimethylformamide (B)+ methanol (C); (■), water (A) + N,N-dimethylformamide (B)+ ethanol(C); (▲), water(A)+ N,N-dimethylformamide (B)+ propanol (C); (●), water(A)+ N,N-dimethylformamide (B)+ butanol (C); and (*), water (A)+N,N-dimethylformamide (B)+ pentanol (C) mixtures with mole fraction of water(x_A) at 298.15 K.

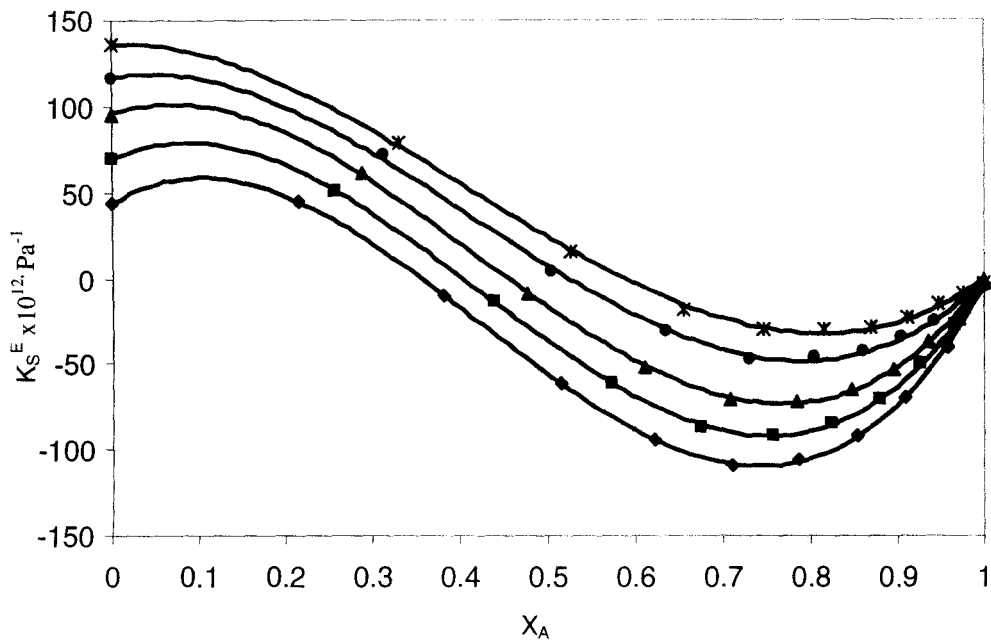


Fig. 5. Excess isentropic compressibility (K_S^E) of: (◆), water (A)+ N,N-dimethylformamide (B)+ methanol (C); (■), water (A)+ N,N-dimethylformamide (B)+ ethanol(C); (▲), water (A)+ N,N-dimethylformamide (B)+ propanol (C); (●), water(A)+ N,N-dimethylformamide (B)+ butanol (C); and (x), water (A)+N,N-dimethylformamide (B)+ pentanol (C) mixtures with mole fraction of water(X_A) at 298.15 K.