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Excess Viscosities and Volumes of Dimethylsulphoxide + Alcohols at 298.15 K

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Excess viscosities, η^E, and volumes, V^E, of dimethylsulphoxide + methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, t-butanol and water were computed from density data, over the whole range of composition at 298.15 K. η^Es are negative over the entire range of composition for all systems except water, indicating a negative deviation from Raoult's law whereas V^Es are positive indicating an expansion in volume. V^E and η^E data was fitted to polynomial function to get values of various coefficients.

INTRODUCTION

A knowledge of chemical and physical properties of solvent systems containing two (or more) components is often required in theoretical studies[1, 2] and for industrial and chemical processes at a wide range of temperatures.[3–9] The intensive properties may include density, viscosity (or fluidity) as well as dielectric constant and refractive index. We have undertaken a study of thermochemical properties of some binary systems, in order to extend our knowledge and eventually to generalize or to improve empirical/theoretical correlation with composition.

As a part of our system on binary non-aqueous liquid mixtures, we report in this paper some investigations of dynamic viscosity of dimethylsulphoxide (DMSO) with methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH), 2-propanol (2-PrOH), 1-butanol (1-BuOH), 2-butanol (2-BuOH), *t*-butanol (*t*-BuOH) and water (W) covering the whole range of composition. Many approaches have been proposed to describe the viscosity of mixed solvent systems for both polar and non-polar associated liquids but there is no generally accepted model which can predict the viscosity of liquid mixtures.[3] There are two unsolved problems, namely:

1. No comprehensive theory describing interactions between unlike molecules at molecular level.
2. Deviations from the ideality are not predicted by common thermodynamic liquid solution principles.

Some workers obtained information about the interaction phenomenon, starting from vapour-liquid equilibria (VLE) data expressed as excess free energy parameters which were applied to a local composition model for sheer viscosity.[10, 11] The Wei and Rowley[11] approach is based on the assumption of non-random two liquid model[12] involving intermolecular interaction coefficients and non-randomness parameters. In an earlier attempt Ratcliff and Khan[13] suggested a group contribution technique to predict the viscosity of mixtures. This is based on the assumption that all deviations from ideality could be represented by the same structural and group contribution terms, as mentioned above, suggesting that functional groups rather than molecular units are responsible for localized interactions.

EXPERIMENTAL

Analytical grade DMSO, MeOH, EtOH, 1-PrOH, 2-PrOH, 1-BuOH, 2-BuOH and *t*-BuOH were obtained from Merck with purities exceeding 99.5 mole %. An attempt was made to purify the samples[5], but precision refractometry indicated that the purity of each product was not significantly enhanced.

Procedures

The binary mixtures were prepared by weight in airtight stoppered bottles just before their use, using a Chyo J-180 balance (precision $\pm 1 \times 10^{-4}$ g). The more volatile component was directly weighed in the bottle and the second component was injected into it by a syringe. Necessary precautions were observed in subsequent measurement of density and viscosity.

Density, d, measurement was carried out using a pre-calibrated 25.02 cm^3 pyknometer. Deionized water and carbon tetrachloride (CCl_4) were used as density standards for pre-calibration purpose.[6] The principle of density measurement involves measurement of the mass, M, of a test sample of a definite volume, V, at a given temperature. Temperature was regulated by Lauda 6 type thermostat (precision ± 0.01 K) and density was computed by

$$d = M/V \tag{1}$$

Viscosity, η, measurement of test liquids was done by flow method using Ostwald's 04771 viscometer, which was calibrated using deionized water and CCl_4.[6] Viscosity was obtained as:

$$\eta_1 = t_1 d_1 / t_2 d_2 * \eta_2 \tag{2}$$

where t, d and η stand for time of flow, density and viscosity, while subscripts 1 and 2 stand for components 1 and 2 respectively. Each value of density and visocity is an average of at least three independent measurements. Experimental data of viscosity and density was used to compute V^E and η^E by a computer programme in Basic language.

RESULTS AND DISCUSSION

η^E and V^E values as a function of mole ratio of component X_1 (DMSO), X_2 (alcohols and water) of binary mixtures, are plotted in Figs. 1 and 2 at 298.15 K.

The excess viscosity, η^E, has been computed using the equation:

$$\eta^E = \eta - \eta_1 X_1 - \eta_2 X_2 \tag{3}$$

All the curves, except water (which gives positive excess viscosity with a maxima), show a decline in η^E and depth of minima for alcohols follows the order:

MeOH > EtOH; 2-PrOH > 1-PrOH; *t*-BuOH > 2-BuOH > 1-BuOH

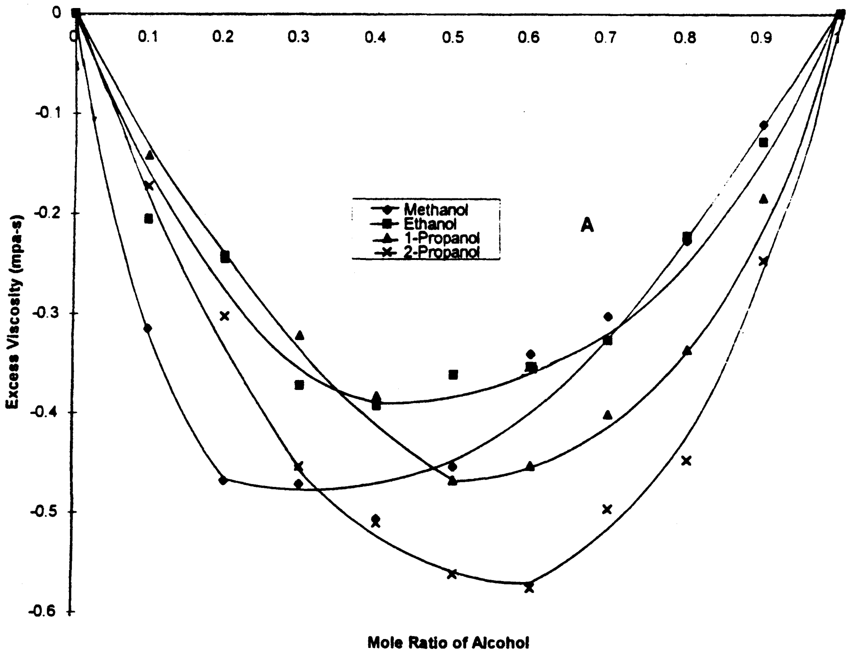

Fig. 1 Excess viscosity curves of alcohols and water *vs.* mole ratio at 298.15 K in DMSO.

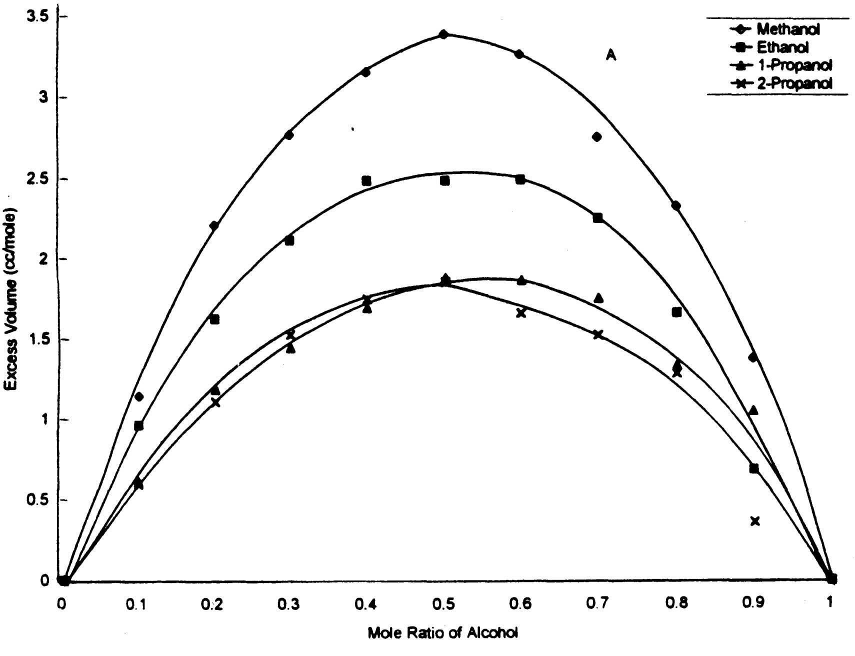

Fig. 2 Excess Volume curves of alcohols and water *vs.* mole ratio at 298.15 K in DMSO.

Alcohols are known to be extensively self-associated through hydrogen bonding and hydrophobic interactions in pure state[14], while $-\overset{O}{\overset{\|}{S}}-$ of DMSO can interact with its environment both by hydrogen bonding and dipole-dipole interactions. Therefore, on mixing of alcohols in DMSO, systems tend to casual break ups of $-\overset{O}{\overset{\|}{S}}-, -\overset{O}{\overset{\|}{S}}-$ and alcohol-alcohol interactions, followed by hydrogen bonding or dipolar interactions between unlike molecules. The results, in main, indicate that the balance between different effects in these mixtures leads to a liquid structure in which the flow is easier than expected on the basis of the viscosities of individuals in pure state. This suggests that the dissociation effects and homopolymer long-chain breakings are pre-dominant over hetero-association effects in alcohol-rich mixtures, whereas the reverse is true for DMSO-water system.

The excess volume, V^E, was computed from experimental density data, d, of binary mixtures using the relationshop:

$$V^E = X_1M_1(1/d - 1/d_1) - X_2M_2(1/d - 1/d_2) \qquad (4)$$

where d_1 and d_2 are densities of DMSO and co-solvents (alcohols and water) respectively.

Positive V^Es are observed in all systems except water. Factors already described for η^E also explain this behaviour. These observations support solute-solvent interactions and also highlight some other features of interest. The order of variation in V^E maxima is:

MeOH > EtOH; 2-PrOH > 1-PrOH; *t*-BuOH > 2-BuOH > 1-BuOH

This observatiion can be summed up by saying that alcohols are strongly associated by hydrogen bonding. Addition of alcohol to DMSO produces a molecular disorder in alcohol liquid structure and leads to positive V^E by breaking up $-\overset{O}{\overset{\|}{S}}-, -\overset{O}{\overset{\|}{S}}-$ interactions in the first half. Further addition of alcohol gives associative interactions among alcohols and —OH and $-\overset{O}{\overset{\|}{S}}-$ which results in a negative contribution to V^E.

Excess volume curve for DMSO-water system shows that there is a contraction at low water mole ratios and an expansion at high mole ratios. This is due to the fact that $\Delta V_{mix} = 0$ for ideal mixture. These positive and negative contributions to volumes are the main factors that determine the observed V^E. Furthermore, it can be seen that breaking up of the molecular order in higher alcohols is more than the lower ones indicating the participation of other factors[15], *viz.*, influence of shape, size and volumetric behaviour.

Data Fitting

The η^E and V^E data was fitted to polynomial function:

$$F = F^0 + \sum_{i=0}^{i=n} m^i F_i \qquad (5)$$

where F, m^i and F_i are functions under consideration *i.e.*, η^E and V^E, m is mole ratio and F_i is the *i*th fitting parameter. The fitting pattern of polynomial shows a non-linear behaviour. The values of coefficients obtained from weight least square fit are reported in Tables 1 and 2. The values of F_i coefficients can be used to estimate values of respective properties at other concentrations, in the entire range of mole ratios.

TABLE-1

VALUES OF VARIOUS PARAMETERS AND TOTAL STANDARD DEVIATIONS (T.S.D.) FOR EXCESS VISCOSITY OF DMSO + CO-SOLVENTS AT 298.15 K GIVEN BY:

$$\eta^E = A + Bx_1^1 + Cx_2^2 + Dx_3^3 + Ex_4^4$$

Parameters	A	B	C	D	E	T.S.D.
Methanol	–0.0042	–3.97	10.47	–10.49	4.000	0.02
Ethanol	–0.0079	–1.98	3.43	–2.38	–95.000	0.03
1-Propanol	–0.0061	–1.27	0.29	0.99	–0.005	0.02
2-Propanol	–0.0009	1.77	1.14	0.03	0.600	0.01
1-Butanol	0.0130	–2.22	5.23	–7.97	4.930	0.04
2-Butanol	3.2500	–2.54	4.74	–8.57	6.370	0.04
t-Butanol	0.0830	–8.86	38.21	–59.77	30.370	0.35
Water	–0.1100	13.80	–29.07	15.06	0.380	0.17

TABLE-2

VALUES OF VARIOUS PARAMETERS AND TOTAL STANDARD DEVIATIONS (T.S.D.) FOR EXCESS VOLUME OF DMSO + CO-SOLVENTS AT 298.15 K GIVEN BY:

$$\eta^E = A + Bx_1^1 + Cx_2^2 + Dx_3^3 + Ex_4^4$$

Parameters	A	B	C	D	E	T.S.D.
Methanol	–0.1300	17.94	–29.21	19.45	–7.99	0.34
Ethanol	0.0080	10.20	–11.10	2.38	–1.54	0.08
1-Propanol	–0.0100	7.81	–12.52	12.53	–7.77	0.08
2-Propanol	0.1200	0.33	30.47	–60.08	28.91	0.45
1-Butanol	0.0300	4.56	–15.82	25.05	–13.69	0.10
2-Butanol	2.0200	2.53	–6.93	8.98	–4.62	0.19
t-Butanol	0.0100	3.64	–0.14	–6.30	3.77	0.06
Water	0.0005	–6.26	26.12	–28.61	8.75	0.01

Conclusions

In many theories describing the behaviour of liquid complex systems, the major contribution to the deviation from ideal mixing is attributed to the dispersion forces, which generally provide positive deviations. On the other hand, negative deviations in mixtures of molecules of different sizes are accounted for by steric and geometric effects which allow an accommodation of component molecules into the structure of each other.

Negative η^E and positive V^E are indicative of the formation of hetro-associated species probably through hydrogen bonds network. This fact suggests that self-associated or clusterized aggregates of these alcohols undergo a progressive break-up as mole rato of co-solvent increases, and the hetero-association takes place.

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