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Shear viscosities of the *N*-methylformamide– and *N,N*-dimethylformamide–(C$_1$–C$_{10}$) alkan-1-ol solvent systems

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Viscosities of some *N*-methylformamide– and *N,N*-dimethylformamide–(C$_1$–C$_{10}$) alkan-1-ol binary mixtures have been measured at 298.15 K over the whole composition range. The excess viscosities and excess Gibbs energies of activation for viscous flow, compared with values for other amide–alcohol mixed solvents, suggest that the alcohol size does not play a significant role in the mixture behaviour. The alcohol mixtures with aliphatic amides gave heteroaggregates to a greater extent, the lower the self-association of the pure amides. An analysis in terms of solvent solubility parameters gave good agreement with experimental results.

The important role played by solvents in chemistry has long been recognized. After the first quantitative description of solvent effects on chemical reactions, much work has been devoted to solvent effects on rate and equilibrium processes.[1] Changes in energy of reacting states upon solvation are of critical importance both in proton-transfer and electron-transfer reactions. However, although more important than pure solvents in practical work, the properties of mixed solvents are less well known.

Alcohol–amide mixed solvents are interesting liquid systems, but only very few experimental data on their behaviour are available. *N*-Methylformamide (NMF) and *N,N*-dimethylformamide (DMF) are among the most representative of non-aqueous amidic solvents. In addition to its high dipole moment, NMF possesses the basic (—CO) and acidic (—NH) groups of the very common, naturally occurring —CO—NH— peptide bond. The —NH···OC— hydrogen bond plays a central physiological role in biological systems. According to Reichardt's grouping of solvents, NMF and DMF may be classified as weakly structured solvents.[2] Alcohols, on the other hand, are strongly self-associated in the pure state owing to the H-bonding ability of the OH group, with behaviour ranging from the presence of cyclic dimers in methanol to a 1 : 1 equilibrium of monomers and open dimers in the C$_5$–C$_{10}$ alkanols.[3] Although less structured than water and with a lower solvation ability,[4] alcohols can mimic some of the features of water and constitute an excellent medium for experimental work.

Previously, we reported on the excess volumes, V^E, of alkan-1-ol binary mixtures with pyrrolidin-2-one,[5] formamide,[6] and NMF and DMF.[7] In order to gain a deeper insight into the behaviour of alcohol–amide mixed solvents, we report here the excess viscosities, η^E, and excess Gibbs energies of activation for viscous flow, $\Delta_a G^{*E}$, of binary mixtures of (C$_1$–C$_{10}$) alkan-1-ols with NMF and DMF. The interactions between unlike molecules were also interpreted in terms of solubility parameters.

Experimental

The reactants NMF (Fluka, >99%), DMF (Carlo Erba, >99.5%), methanol (MET: 99.97%), ethanol (ETH, Aldrich, >99%), propan-1-ol (PRO: Carlo Erba, 99.5%), butan-1-ol (BUT: Aldrich, >99%), pentan-1-ol (PEN: Aldrich, >99%), hexan-1-ol (HEX: Sigma, 99%), heptan-1-ol (HEP: Fluka, >99%), octan-1-ol (OCT: Fluka, >99,5%), nonan-1-ol (NON: Aldrich, 99%), and decan-1-ol (DEC: Aldrich, 99%), of the highest purity commercially available, were used without further purification. They were degassed with ultrasound for several days before use and kept out of the light over Fluka Union Carbide 3A molecular sieves. The purity of the liquids was checked by comparing their densities and viscosities with literature values. In order to prevent the mixtures from preferential evaporation, they were prepared by syringing amounts (weighed to $\Delta m = 0.00001$ g with a Mettler AT 261 Delta Range balance) of the pure components into stoppered bottles. The mixtures were entirely miscible over the whole composition range.

The densities were measured with a microcomputer-controlled DMA-58 Anton Paar digital precision densimeter (0.7 ml sample size, stated accuracy 1×10^{-5} g cm^{-3} and precision 5×10^{-6} g cm^{-3}); a built-in thermostat controlled the temperature to ± 0.01 K. The densimeter functions under the oscillating U-tube measuring principle, and was calibrated with doubly distilled water and *n*-nonane as references. Viscosities were measured with an automated AMV-200 Anton Paar microviscometer (0.12 ml sample size, stated accuracy better than 0.5%); the apparatus measures the time taken (± 0.01 s) for a gold-covered steel ball to roll down a fixed distance between two magnetic sensors inside an inclined sample-filled glass capillary. The shear stress may be varied by changing the inclination angle; the instrument is well suited even for non-Newtonian fluids, as shear rates ranging from 10 to 1000 s^{-1} can be covered. The temperature was controlled by placing the capillary in a thermostatted block connected to a Julabo F30 circulating bath. The temperature within the capillary block was measured with a sensor close to the capillary's surface. The capillaries used (0.9 and 1.0 mm inner diameter) were calibrated with adequate standard liquids, and the viscosities (η mPa) evaluated as an average of four readings at each of ten different inclination angles.

Results and Discussion

The experimental viscosity–mole fraction data of the (C$_1$–C$_{10}$) alkan-1-ol–NMF and –DMF mixed-solvent systems are avail-

able as supplementary material.† Many properties of binary liquid mixtures normally are not additive with respect to pure cosolvents, for additional effects may arise as a result of mutual interactions. The extent to which real liquid mixtures deviate from ideality is best expressed through the use of thermodynamic excess functions. Excess viscosities, η^E, determined at different mole fractions represent a measure of the type of intermolecular interaction and are approximately proportional to the extent of the interactions. On the other hand, excess Gibbs energies of activation, $\Delta_a G^E$, may also be considered a reliable measure of the interactions between unlike molecules.[8] The η^E and $\Delta_a G^E$ values were calculated using the equations

$$\eta^E = \eta - X_1 \eta_1 + X_2 \eta_2 \qquad (1)$$

$$\Delta_a G^E = RT[\ln \eta V - (X_1 \ln \eta_1 V_1 + X_2 \ln \eta_2 V_2)] \qquad (2)$$

where η_i and V_i are the viscosities and molar volumes of the two components ($i = 1$ for the amide, absence of subscript refers to the mixture), R is the gas constant, T is the absolute temperature and X is the mole fraction. The molar volumes V_i and V were calculated from the densities of the pure components.[7] The excess viscosities for the NMF– and DMF– alcohol systems were negative throughout, and increased with the alcohol chain length; as an example, Fig. 1 shows the variation of η^E with X_1 for the DMF binary mixtures. These values and those already reported for PYR[5] and FOR[6] with the same alcohols are plotted in Fig. 2 for an equimolar alcohol–amide mixture. The V^E values were negative for binary mixtures with the smallest alkanols, and increased with chain length, their values being strongly influenced by the alcohol size and to a lesser extent by the nature of the amide.[7] Although the V^E vs. n curves (number of alcohol carbon atoms) for the four amides displayed a similar shape, the η^E vs. n plots (Fig. 2) were quite different from each other in this work. The η^E values were negative throughout except for the FOR–PRO and –PEN mixtures. Negative η^E values are common in mixtures of molecules of unequal size in which dispersion forces are dominant.[9,10]
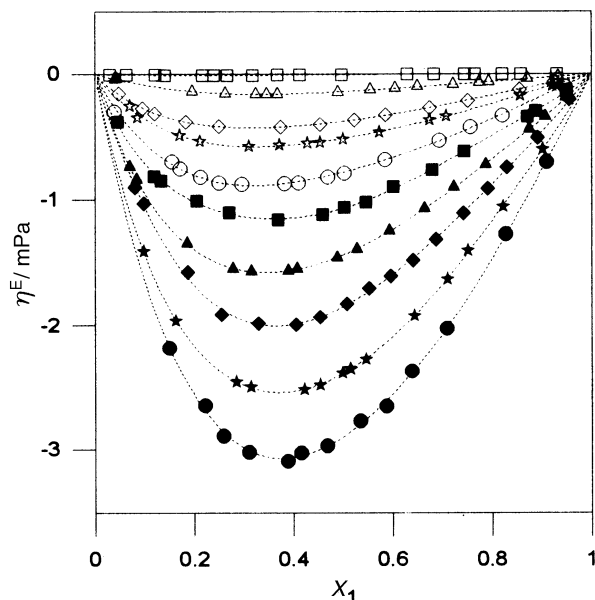

Fig. 2 Variation of η^E vs. n (number of alcohol carbon atoms), for: (○) FOR, (■) NMF, (□) DMF and (●) PYR

Fig. 3 shows the variation, $\Delta_a G^{*E}$ vs. X_1, for the NMF mixtures. The variation, $\Delta_a G^{*E}$ vs. n, for alcohol mixtures of the four amides with equimolar alcohol–amide composition (Fig. 4) shows that $\Delta_a G^{*E}$ was nearly zero with methanol for all four amides; it was positive and increased with the alcohol chain length for FOR, and gave minima for PYR, NMF and DMF, always being negative for PYR and changing from negative to positive for NMF and DMF. The sign of the $\Delta_a G^{*E}$ values provides a qualitative interpretation of the nature of the interactions;[8-10] positive values can be seen in binary mixtures where specific interactions (dipole–dipole and H-bond) between molecules are prevalent, whereas negative values are characteristic of mixtures in which dispersion forces are predominant.[10] As shown in Fig. 2 and 4, the dispersion forces increase in the order FOR < NMF < DMF < PYR. The small $\Delta_a G^{*E}$ values indicate a balance between two opposing effects: dispersion forces, which tend to restructure the solvents (of greater intensity for PYR with BUT and PEN)

Fig. 1 Excess viscosities, η^E vs. X_1, at 298.15 K for X_1 DMF–(1 − X_1) alkan-1-ol mixtures: (□ MET, (△) ETH, (◇) PRO, (☆) BUT, (○) PEN, (■) HEX, (▲) HEP, (◆) OCT, (★) NON and (●) DEC

Fig. 3 $\Delta_a G^{*E}$ for viscous flow at 298.15 K for X_1 NMF–(1 − X_1) alkan-1-ol mixtures: (□) MET, (△) ETH, (◇) PRO, (☆) BUT, (○) PEN, (■) HEX, (▲) HEP, (◆) OCT, (★) NON and (●) DEC

† Supplementary material (**SUP 57209**, 2 pages) deposited with the British Library. Details are available from the Editorial Office.
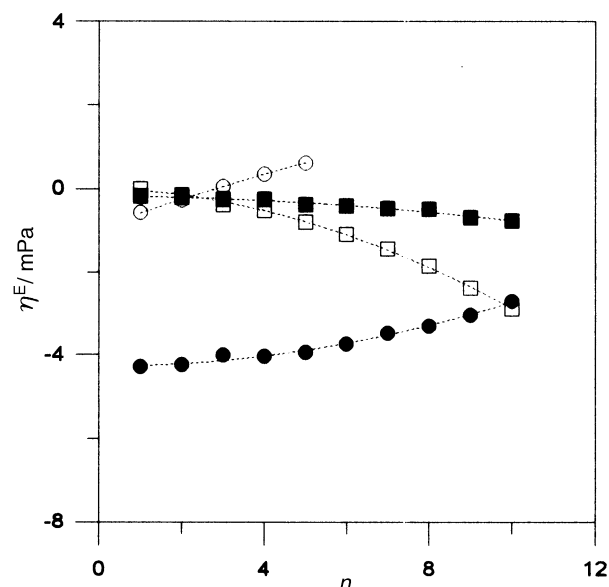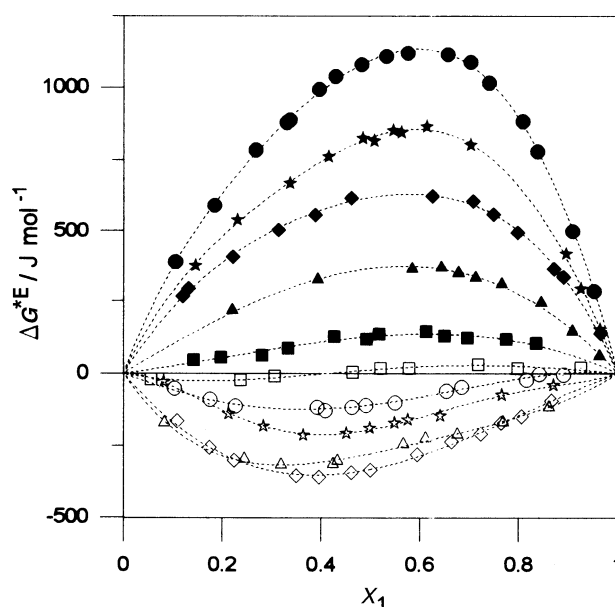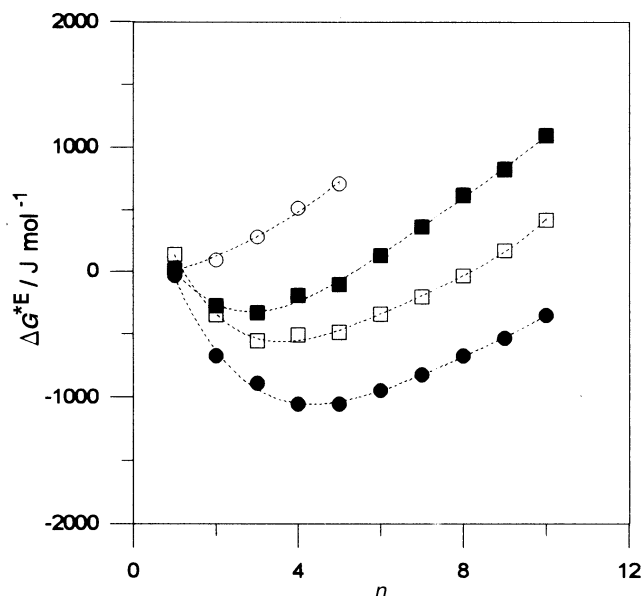
Fig. 4 Variation of $\Delta_a G^{*E}$ *vs. n* for the mixtures in Fig. 2

and specific interactions (mostly heteroassociations through hydrogen bonding), which were greatest for the FOR mixtures. The DMF mixtures gave the same $\Delta_a G^{*E}$ values for MET and NON, as occurs in the NMF mixtures with MET and HEX. The geometrical effect has a major influence on the V^E values of these mixtures, but seems to have no significant effect on the $\Delta_a G^{*E}$ values.[7]

PYR is known to be strongly self-associated in the pure state, forming dimers, trimers and higher oligomers.[11] The FOR molecules possess three hydrogen-bond donors (the three hydrogen atoms) and three acceptors (one lone pair of electrons on nitrogen and two on oxygen) so that complete saturation of all the potential valencies is possible giving a 3D hydrogen-bond network structure in pure formamide.[12] NMF forms a linear hydrogen-bonded structure.
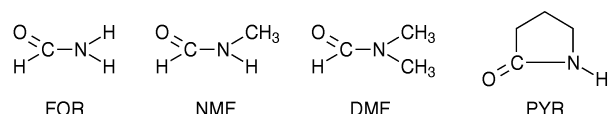
DMF, however, is not self-associated by hydrogen bonding and manifests no significant structural effects, although a certain degree of association due to dipole–dipole interactions is excepted, the extent of this is still a matter of dispute.[13] Alcohols, on the other hand, are highly structured solvents, although less so than water or formamide. Fig. 2 and 4 show that the FOR–alkan-1-ol associations are stronger than for FOR–FOR ones. In the NMF and DMF alcohol mixtures, the ability to form hetero- and self-aggregates is similar, but for PYR the dispersion forces are predominant.

The solubility parameter concept related to the internal pressure exerted by the solvent was first proposed by Hildebrand *et al.*[14] The internal pressure is defined as the energy required to vaporize a unit volume of a substance. Hildebrand suggested that molecules with similar internal pressures would interact with each other. The cohesive energy density (CED) is a description of such an internal pressure and can be calculated from thermophysical properties. Solvents with similar CED values will be miscible. Hansen[15] introduced the concept that the total solubility parameter of a mixed solvent, δ_i, can be represented in terms of three components: dispersion or non-polar (δ_D), polar (δ_P) and hydrogen bonding (δ_H), and expressed as:

$$\delta_i = \sqrt{(\delta_D^2 + \delta_P^2 + \delta_H^2)}$$

Liquids with similar total solubility values will be miscible, otherwise they will not be totally compatible. Using the solubility parameters available for the alkanols and amides investigated,[15,16] the δ_i values for the equimolar alcohol–amide mixed solvents were calculated from

$$\delta_i = X_1\delta_1 + X_2\delta_2 \tag{3}$$

Fig. 5 shows the δ_i *vs. n* plots for the FOR–, DMF– and PYR–alcohol mixtures (solubility parameters for NMF were not available). The values for the dispersion contribution, δ_D, were similar for DMF, PYR and FOR; however, the polar, δ_P, and hydrogen bonding, δ_H, components were substantially greater for FOR than for PYR and DMF.

In summary, the conclusions drawn in terms of the Hansen solubility parameters are in convincingly good agreement with those arising from the excess Gibbs energies of activation for viscous flow analysis, as inferred from Fig. 4 and 5.
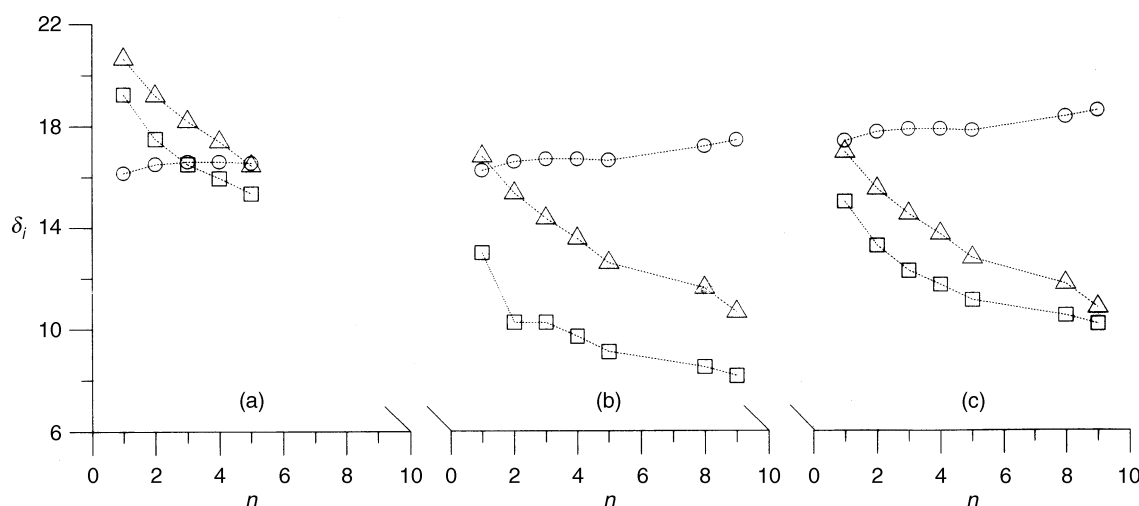
Fig. 5 Plot of the δ_i Hansen solubility parameters: (○) δ_D, (□) δ_P and (△) δ_H for equimolar alkan-1-ol binary mixtures with (a) FOR, (b) DMF and (c) PYR

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