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VOLUMETRIC BEHAVIOUR OF *N*-METHYLFORMAMIDE–(C_1–C_{10})ALKAN-1-OL AND *N*,*N*-DIMETHYLFORMAMIDE–(C_1–C_{10})ALKAN-1-OL SOLVENT SYSTEMS

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Densities were measured for the *N*-methylformamide–(C_1–C_{10})alkan-1-ol and *N*,*N*-dimethylformamide–(C_1–C_{10})alkan-1-ol solvent mixtures at 298·15 K over the whole miscibility range ($0 < X_1 < 1$). The excess volumes (V^E), which are discussed in terms of intermolecular interactions, are negative for the mixtures with the smallest alkanols in the series and increase with increase in the chain length. Comparison with other amide–alcohol mixtures previously investigated (formamide and pyrrolidin-2-one) indicates that the excess volumes are strongly influenced by the size of the alcohol and to a lesser extent by the nature of the amide. In contrast with the amide–water system, neither the amide size nor its degree of sustitution plays an important role in the amide–alcohol systems investigated. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

In previous papers, we reported the excess viscosities and excess free energies of activation of the liquid mixtures of alkan-1-ols with pyrrolidin-2-one[1] and formamide,[2] calculated from density and viscosity measurements, and discussed the interactions of the alcohol and amide groups in terms of these excess quantities. In this work, we continued the systematic study of the amide–alcohol interactions by obtaining the excess volumes of binary mixtures of C_1–C_{10} alkan-1-ols with *N*-methylformamide and *N*,*N*-dimethylformamide, calculated from density measurements at 298·15 K.

N-methylformamide (NMF, relative permittivity $\varepsilon = 182$) and *N*,*N*-dimethylformamide (DMF, $\varepsilon = 36{\cdot}7$) are polar, non-aqueous compounds representative of amidic solvents;[3] they are widely used as solvents in many settings, such as solvent–reactivity relationships, owing to the ability of the solvent to modify the potential reactivity of reacting states in electron- and proton-transfer reactions, and as a medium solvent in electrochemistry studies.[4] However, very little has been published on NMF binary mixtures; only data on excess volumes[5] and excess free energies of activation[6] for NMF–methanol and excess enthalpies for mixtures with methanol[7] and butanol[8] have been reported. There is more extensive literature on DMF–alcohol mixtures, focused mainly on the excess volumes with C_1–C_{10} alkanols[9, 11] and excess volumes and excess enthalpies with methanol,[12] the results being discussed in terms of intermolecular interactions and geometrical effects between the two components.

We report here the excess volumes (V^E) for *N*-methylformamide–(C_1–C_{10})alkan-1-ol and *N*,*N*-dimethylformamide–(C_1–C_{10})alkan-1-ol solvent systems calculated from density measurements at 298·15 K. The V^E behaviour is discussed in terms of interactions and geometrical effects between the two components.

EXPERIMENTAL

The reactants *N*-methylformamide (NMF, Fluka, >99%), *N*,*N*-dimethylformamide (DMF, Carlo Erba, >99·5%), methanol (MET, Aldrich, 99·97%) ethanol (ETH, Aldrich, >99·8%), 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 in the dark

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Table 1. Properties of the pure compounds at 298·15 K

	Density (g cm^{-3})		Viscosity (cP)	
Compound	Exp.	Lit.	Exp.	Lit.
N,*N*-dimethylformamide	0·94406	0·9444[a] 0·94387[b] 0·9445[c] 0·94393[d] 0·94376[e] 0·94539[f]	0·805	0·80[a] 0·802[b]
N-Methylformamide	0·99929	0·9988[a] 1·0000[b]	1·76	1·65[a]

[a] Ref. 13.
[b] Ref. 14.
[c] Ref. 15.
[d] Ref. 16.
[e] Ref. 17.
[f] Ref. 18.

over Fluka Union Carbide 3A molecular sieves. The purity of the liquids was checked by measuring their densities and viscosities at 298·15 K (Table 1). Binary mixtures were prepared by syringing amounts (weighed to $\Delta m = 0{\cdot}00001$ g with a Mettler AT 261 Delta Range balance) of the pure components into stoppered bottles. The mixtures were fully miscible over the whole composition range.

The densities (ρ, g cm^{-3}) were measured with a microcomputer-controlled DMA-58 Anton Paar digital precision densitometer (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 within 0·01 K. It functions under the oscillating U-tube measuring principle, and was calibrated with doubly distilled water and *n*-nonane as references. Viscosities (η, cP) were measured with a rolling ball automated AMV-200 Anton Paar microviscometer (0·12 ml sample size, stated accuracy better than 0·5%) described elsewhere.[2]

RESULTS AND DISCUSSION

The excess volumes of the binary mixtures, V^E, were calculated with equation (1) from density measurements of the pure components (ρ_i) and of the mixtures (ρ),

$$V^E = (X_1M_1 \times X_2M_2)/\rho - (X_1V_1 + X_2V_2) \quad (1)$$

where V_i and M_i are the molar volumes and molar masses of the pure components ($i = 1$ for the amide). The Redlich Kister-type equation (2) was fitted to the data pairs (V^E, X_1):[19]

$$V^E = X_1(1 - X_1)\sum_{j=0}^{n} a_j(1 - 2X_1)^j \quad (2)$$

Table 2 lists the densities for the NMF–(C_1–C_{10})alkan-1-ol mixtures and Table 3 the densities for the DMF–(C_1–C_{10})alkan-1-ol mixtures measured at 298·15 K. Figures 1 and 2 show the fits to equation (2) of the isothermal variations V^E vs X_1 for the NMF– and DMF–alcohol mixtures, and Table 4 lists the parameters of the least-squares fitting. The excess volumes of the two systems increased as the alcohol chain length increased.

Alcohols are strongly hydrogen-bonded in the pure state; the degree of association decreases as the chain length increases, and is lower for secondary and tertiary alcohols.[20] The OH free fraction remains small at room temperature; at the same time, the enthalpies of H-bond formation are not significantly different for the various alcohols, the mean value being -25 ± 2 kcal mol^{-1} (1 kcal = 4·184 kJ) for several pure low molecular mass alcohols.[21] Addition of solvent to an alcohol leads to break-up of the hydrogen bonds, which produces a positive contribution to V^E; also, an increase in the alcohol chain length causes a steric effect that is accompanied by an increase in the mixture volume. Figure 3 shows the V^E values calculated for the NMF and DMF binary mixtures; for comparison purposes the V^E values of the systems FOR ($\varepsilon = 110$)–(C_1–C_5)alkan-1-ols (from hexanol and above the liquids were only partly miscible) and PYR ($\varepsilon = 28$)–(C_1–C_{10})alkan-1-ols are also included. All four binary systems exhibit a similar pattern, with constant variation (roughly) between the curves along the alcohol series; for the same alcohol the V^E values varied in the order V^E (PYR) < V^E (FOR) < V^E (DMF) < V^E (NMF); V^E (PIR) was always negative (except for larger alkanols), whereas V^E (NMF) was always positive (except for smaller alkanols); thus the positive contributions to V^E strongly depend on the nature of the amide.

The volume cavities, FOR (95·94), NMF (97·00), PYR (127·64) and DMF (128·50), indicate that the difference in amide size is not the principal factor accounting for such an effect; the volume cavities were chosen to be equal to the molecular volume of ther amides at room temperature in the liquid state or in a solution, and were determined using the MINDO/3 computational method.[21] Also, the breaking effect of the self-associations in the amide structures does not account satisfactorily for the observed behaviour, as the degree of association varies markedly with the particular amide. The very high degree of self-association by H-bonding in pyrrolidin-2-one depends on the PYR concentration and may be disturbed by the solvent, even by solvents incapable of forming hydrogen bonds; PYR may form dimers at low concentrations and dimers,[22] trimers and higher oligomers at high concentrations, the aggregates behaving as independent entities.[23] On the other hand, DMF shows no significant structural effects due to the lack of H-bonds;[24] although evidence for dipole–dipole self-association has been reported, some controversy about its extent still remains;[25] for instance, dielectric relaxation studies of *N*,*N*-dimethylacetamide (DMA) have suggested a low degree of association (*ca* 10%) in pure DMA. With this in mind, it is not immediately obvious how one explains the order of the V^E values reported, as the addition of alcohol should have a considerable influence on the structure

breaking of PYR, little effect on DMF and an intermediate effect for NMF and FOR. The difference in the ability of these amides to form hetero-aggregates with alcohols may account for the V^E behaviour.

The partial molar volumes of NMF and DMF ($\bar{V}_1$) were evaluated from the Redlich Kister parameters (Table 4)

Table 2. Densities (ρ, g cm^{-3}) for NMF–alkan-1-ol binary systems at 298·15K

System	X_1	ρ	X_1	ρ	X_1	ρ
NMF(1)–MET(2)	0·03553	0·79873	0·38698	0·89465	0·67970	0·95191
	0·06448	0·80825	0·39678	0·89683	0·68685	0·95304
	0·11398	0·82351	0·46612	0·91178	0·73824	0·96161
	0.13831	0·83083	0·49433	0·91753	0·78223	0·96854
	0.22528	0.85506	0.56469	0.93127	0.92568	0.98943
	0·26219	0·86469	0·62614	0·94272		
NMF(1)–ETH(2)	0·05280	0·79686	0·44353	0·88193	0·79740	0·95727
	0·14569	0·81708	0·49983	0·89396	0·85246	0·96874
	0·19293	0·82731	0·54850	0·90451	0·89629	0·97781
	0·24590	0·83889	0·60881	0·91737	0·93586	0·98592
	0·28598	0·84762	0·65474	0·92721		
	0·34917	0·86142	0·75887	0·94922		
NMF(1)–PRO(2)	0·06468	0·80949	0·46503	0·87981	0·79148	0·94901
	0·12917	0·81983	0·51319	0·88932	0·83306	0·95865
	0·19302	0·83041	0·55844	0·89857	0·87893	0·96943
	0·34728	0·85749	0·65660	0·91909	0·95829	0·98878
	0·39836	0·86703	0·70569	0·92984		
NMF(1)–BUT(2)	0·06551	0·81360	0·54149	0·88741	0·78406	0·94015
	0·13248	0·82203	0·56829	0·89271	0·81976	0·94901
	0·23123	0·83561	0·60000	0·89902	0·87262	0·96282
	0·29679	0·84534	0·64982	0·90943	0·89662	0·96925
	0·33653	0·85159	0·70785	0·92220	0·92987	0·97857
	0·40597	0·86298	0·73881	0·92934	0·95543	0·98586
NMF(1)–PEN(2)	0·07476	0·81781	0·38047	0·85046	0·84817	0·91688
	0·13662	0·82386	0·41025	0·85406	0·89167	0·92443
	0·20902	0·83130	0·50636	0·86607	0·91909	0·92922
	0·25108	0·83582	0·67008	0·88878		
	0·28772	0·83984	0·73340	0·89833		
NMF(1)–HEX(2)	0·14127	0·82757	0·55474	0·88038	0·77465	0·92663
	0·23086	0·83653	0·60241	0·88889	0·83559	0·94306
	0·33345	0·84826	0·61281	0·89089	0·86555	0·95215
	0·47928	0·86812	0·69597	0·90803	0·88967	0·95967
	0·50079	0·87152	0·74973	0·92047	0·94778	0·98014
NMF(1)–HEP(2)	0·13133	0·82846	0·58427	0·88199	0·76527	0·91954
	0·21998	0·83623	0·64345	0·89275	0·79154	0·92644
	0·39397	0·85454	0·67800	0·89971	0·84558	0·94168
	0·45571	0·86237	0·67890	0·89982	0·90891	0·96254
	0·52862	0·87288	0·71363	0·90733	0·96302	0·98336
NMF(1)–OCT(2)	0·13143	0·83030	0·52517	0·87005	0·70810	0·90218
	0·31405	0·84537	0·57520	0·87766	0·74947	0·91163
	0·38844	0·85291	0·62573	0·88615	0·79845	0·92410
	0·46167	0·86157	0·66140	0·89277	0·87163	0·94621
NMF(1)–NON(2)	0·14536	0·83251	0·50834	0·86568	0·89516	0·95118
	0·23068	0·83838	0·54659	0·87083	0·92538	0·96325
	0·33620	0·84693	0·61407	0·88112	0·96338	0·98026
	0·41499	0·85469	0·70289	0·89764		
	0·48397	0·86261	0·77451	0·91411		
NMF(1)–DEC(2)	0·10499	0·83152	0·48260	0·86117	0·74062	0·90269
	0·18409	0·83603	0·53236	0·86739	0·80891	0·91990
	0·33075	0·84650	0·57530	0·87311	0·83811	0·92855
	0·33612	0·84698	0·63933	0·88313	0·90898	0·95380
	0·39636	0·85228	0·65644	0·88585	0·95179	0·97304
	0·42888	0·85547	0·70330	0·89472		

Table 3. Densities (ρ, g cm^{-3}) for DMF–alkan-1-ol binary systems at 298·15 K

System	X_1	ρ	X_1	ρ	X_1	ρ
DMF(1)–MET(2)	0·04687	0·80229	0·30922	0·86622	0·60652	0·90929
	0·10532	0·81964	0·36350	0·87566	0·70921	0·92030
	0·14924	0·83157	0·40584	0·88255	0·77576	0·92657
	0·20468	0·84475	0·46293	0·89117	0·81441	0·92998
	0·23891	0·85208	0·50523	0·89713	0·87290	0·93471
	0·27309	0·85919	0·58176	0·90641		
DMF(1)–ETH(2)	0·04030	0·79455	0·37406	0·85811	0·57840	0·89032
	0·06988	0·80088	0·38928	0·86078	0·69760	0·90688
	0·10675	0·80842	0·41586	0·86518	0·73155	0·91139
	0·11084	0·80932	0·43343	0·86783	0·74484	0·91329
	0·20707	0·82844	0·46762	0·87350	0·89136	0·93173
	0·26012	0·83817	0·49918	0·87718	0·94563	0·93787
	0·32711	0·85004	0·54253	0·88502		
DMF(1)–PRO(2)	0·05872	0·80859	0·27894	0·84141	0·83554	0·92138
	0·06501	0·80953	0·35034	0·85192	0·85648	0·92429
	0·08857	0·81308	0·42756	0·86319	0·89663	0·92987
	0·10107	0·81495	0·56695	0·88333	0·94059	0·93596
	0·13898	0·82067	0·57408	0·88432	0·94316	0·93631
	0·19777	0·82942	0·70555	0·90304		
	0·20993	0·83125	0·78682	0·91467		
DMF(1)–BUT(2)	0·05823	0·81256	0·39350	0·85449	0·69411	0·89660
	0·09416	0·81680	0·44506	0·86143	0·78673	0·91045
	0·16127	0·82490	0·54869	0·87563	0·82414	0·91639
	0·16780	0·82566	0·57894	0·87993	0·86483	0·92245
	0·22216	0·83245	0·60273	0·88330	0·94919	0·93581
	0·26154	0·83737	0·64311	0·88913	0·94936	0·93579
DMF(1)–PEN(2)	0·07476	0·81781	0·38047	0·85046	0·84817	0·91688
	0·13662	0·82386	0·41025	0·85406	0·89167	0·92443
	0·20902	0·83130	0·50636	0·86607	0·91909	0·92922
	0·25108	0·83582	0·67008	0·88878		
	0·28772	0·83984	0·73340	0·89833		
DMF(1)–HEX(2)	0·04591	0·81854	0·36969	0·84804	0·68011	0·88685
	0·11821	0·82431	0·45874	0·85791	0·74409	0·89665
	0·20518	0·83187	0·50249	0·86313	0·83386	0·91156
	0·34997	0·84598	0·60202	0·87588	0·88773	0·92132
DMF(1)–HEP(2)	0·08395	0·82414	0·40771	0·85110	0·72365	0·89049
	0·18521	0·83159	0·52772	0·86412	0·78798	0·90096
	0·27747	0·83900	0·61591	0·87507	0·80537	0·90403
	0·31296	0·84212	0·66465	0·88181	0·87497	0·91677
	0·39000	0·84936	0·70816	0·88814	0·90753	0·92322
DMF(1)–OCT(2)	0·07938	0·82591	0·50835	0·86021	0·83054	0·90600
	0·18586	0·83284	0·59648	0·87036	0·89197	0·91822
	0·25409	0·83762	0·66138	0·87878	0·95512	0·93254
	0·32941	0·84351	0·68696	0·88237		
	0·47068	0·85635	0·79121	0·89891		
DMF(1)–NON(2)	0·09770	0·82901	0·45384	0·85402	0·75184	0·89009
	0·20533	0·83525	0·49835	0·85822	0·82225	0·90242
	0·28418	0·84046	0·51565	0·85992	0·85818	0·90948
	0·31315	0·84252	0·57369	0·86616	0·90171	0·91875
	0·40456	0·84966	0·69345	0·88123	0·94818	0·92979
DMF(1)–DEC(2)	0·14912	0·83312	0·54691	0·86193	0·82716	0·90111
	0·25804	0·83911	0·60140	0·86773	0·90967	0·91895
	0·31034	0·84237	0·70956	0·88139	0·94306	0·92747
	0·48795	0·85621	0·74997	0·88761		
	0·53474	0·86068	0·78707	0·89373		

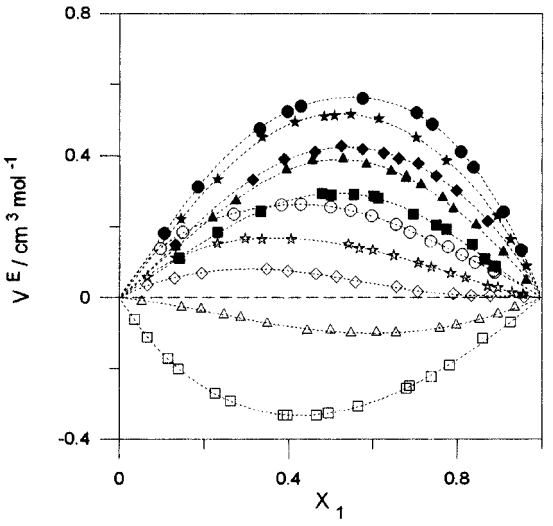

Figure 1. Molar excess volumes (V^E) vs X_1 at 298·15 K of X_1(NMF)+$(1-X_1)$ alkan-1-ols: (□) methanol; (△) ethanol; (◇) propan-1-ol; (☆) butan-1-ol; (○) pentan-1-ol; (■) hexan-1-ol; (▲) heptan-1-ol; (◆) octan-1-ol; (★) nonan-1-ol; (●) decan-1-ol

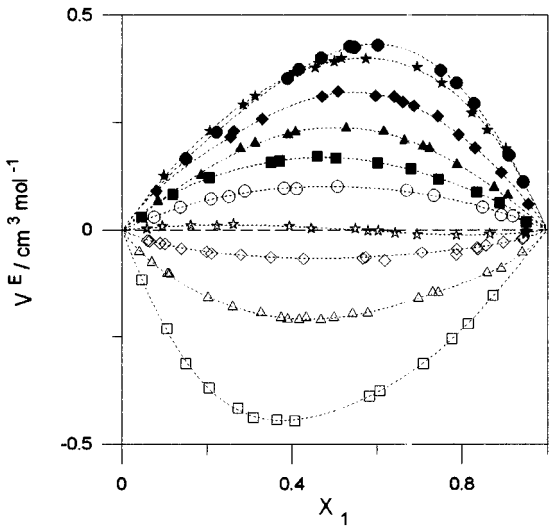

Figure 2. Molar excess volumes (V^E) vs X_1 at 298·15 K of X_1(DMF)+$(1-X_1)$ alkan-1-ols: (□) methanol; (△) ethanol; (◇) propan-1-ol; (☆) butan-1-ol; (○) pentan-1-ol; (■) hexan-1-ol, (▲) heptan-1-ol; (◆) octan-1-ol; (★) nonan-1-ol; (●) decan-1-ol

using

$$(\bar{V}_1)=V_1+(V_1^E) \tag{3}$$

where (V_1^E), the amide excess partial molar volumes, were calculated as

$$(V_1^E)=(V^E)_{1,2}+(1-X_1)[\partial(V^E)_{1,2}/\partial X_1]_{P,T} \tag{4}$$

Figures 4 and 5 show the $(\bar{V}_1)$ curves for NMF and DMF as a function of the amide mole fraction; according to de Viesser *et al.*,[26] a pronounced minimum in the curve indicates the strength of the interaction. Addition of 1 mol of amide to a large volume of the different alkan-1-ols produces a volume contraction in DMF with MET to PRO, and expansion with the other alkan-1-ols, whereas for NMR a volume contraction is produced only with MET and ETH.

Table 4. Coefficients and standard deviations for equation (2) (Units: $cm^3\ mol^{-1}$)

Mixture	a_0	a_1	a_2	a_3	a_4	σ
NMF–MET	−1·3051	−0·3710	−0·1095	−0·1134		0·0021
NMF–ETH	−0·3767	0·1993	0·0688			0·0024
NMF–PRO	0·2390	0·3776	−0·0354	−0·1363	0·1753	0·0025
NMF–BUT	0·6183	0·3622	0·0793	0·1100	−0·1075	0·0024
NMF–PEN	1·0228	0·3340	−0·1114	0·3060	0·5125	0·0027
NMF–HEX	1·1741	−0·0956	−0·4489	0·1407		0·0039
NMF–HEP	1·5533	−0·1612	−0·4954	−0·0919	0·2799	0·0047
NMF–OCT	1·6855	−0·2626	−0·1182	−0·3086		0·0045
NMF–NON	2·0629	−0·1594	−0·0197	−0·4383		0·0047
NMF–DEC	2·2342	−0·3496	−0·5266	−0·3523	−0·4532	0·0027
DMF–MET	−1·7206	−0·6763	−0·3716			0·0062
DMF–ETH	−1·6866	−0·6701	−0·6617	−0·0555	0·4071	0·0035
DMF–PRO	−0·2670	−0·0379	−0·0391	0·0143	−0·1467	0·0015
DMF–BUT	0·0121	0·1180	−0·0320			0·0020
DMF–PEN	0·4012	0·0047	0·1143	0·0410	−0·1118	0·0028
DMF–HEX	0·6697	0·0730	−0·2257	0·0582	0·1832	0·0021
DMF–HEP	0·9512	−0·0207	−0·1428			0·0036
DMF–OCT	1·2690	−0·2644	−0·2329	0·2498	0·4207	0·0023
DMF–NON	1·5759	−0·3972	−0·1982			0·0051
DMF–DEC	1·6564	−0·7462	0·0558	0·3790		0·0026

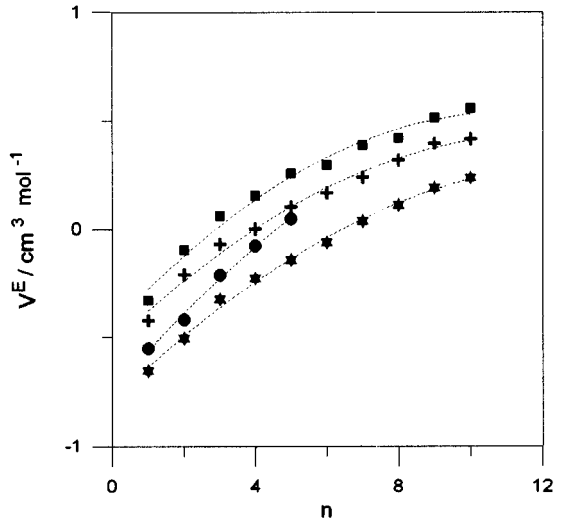

Figure 3. Plot of molar excess volumes (V^E) vs n (number of alcohol carbon atoms) of mixtures of (0·5) amide + (0·5) alkan-1-ol at 298·15 K: (■) *N*-methylformamide; (+) *N*,*N*-dimethylformamide; (●) formamide; (★) pyrrolidin-2-one

The high dipole moments of the four amides (NMF, $\mu = 3{\cdot}78$ D; DMF, $\mu = 3{\cdot}86$ D; FOR, $\mu = 3{\cdot}70$ D; and PYR, $\mu = 3{\cdot}55$ D) and of the alkanols (ranging from $\mu = 1{\cdot}66$ D for ethanol to 3·09 D for propanol)[27] result in strong dipole–dipole interactions, which favour the formation of amide–alcohol complexes. Kinart and Kinart[28] investigated the structure of FOR–propanol, DMF–ethanol and DMF–propanol binary mixtures by ^{1}H NMR spectroscopy and

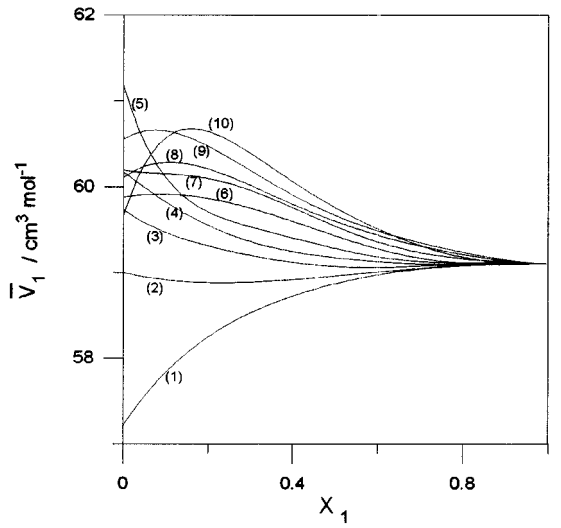

Figure 4. Plot of partial molar volumes vs NMF mole fraction: 1, MET; 2, ETH; 3, PRO; 4, BUT; 5, PEN; 6, HEX; 7, HEP; 8, OCT; 9, NON; 10, DEC

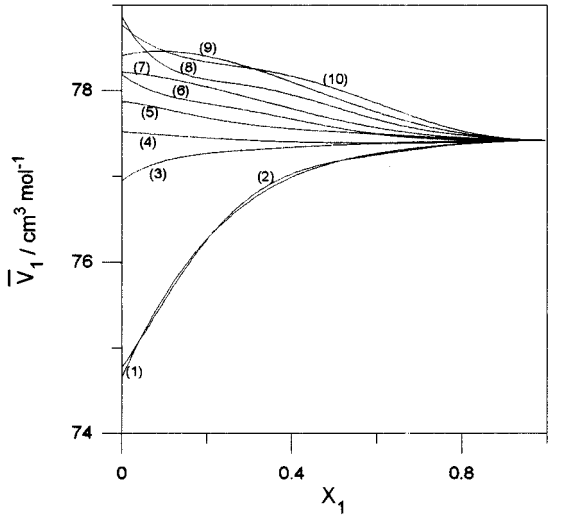

Figure 5. Plot of partial molar volumes vs DMF mole fraction: 1 MET; 2, ETH; 3, PRO; 4, BUT; 5, PEN; 6, HEX; 7, HEP; 8, OCT; 9, NON; 10, DEC

suggested the formation of the most stable complexes (subunits) of the types 3FOR–2PRO and 2FOR–PRO in the FOR–PRO mixtures, DMF–ETH in the DMF–ETH mixtures, DMF–PRO in the DMF–PRO mixtures and DMF–MET in the DMF–MET mixtures. The V^E values reported for these alcohol–amide mixtures cannot be interpreted only in terms of dispersion forces and/or hetero-associations, as the two opposing effects are present in each of the mixtures; the increase in the V^E values with increase in the alcohol chain length reveals a preponderant role of the geometrical effects.

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