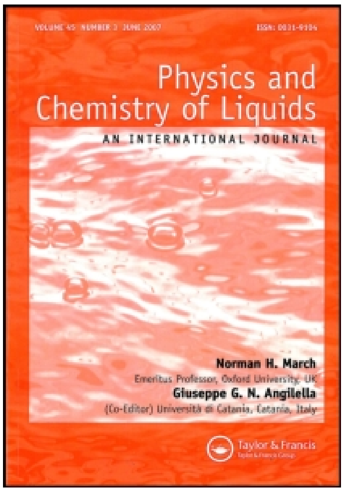

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article Rao, K. Purnachandra and Reddy, K. S.(1985) 'Excess Volumes and Excess Isentropic Compressibility of Binary Mixtures of N, N-Dimethyl for mamide with n-Alcohols at 303.15 K', Physics and Chemistry of Liquids, 15: 2, 147 — 154

To link to this Article: DOI: 10.1080/00319108508078476

URL: http://dx.doi.org/10.1080/00319108508078476

Phys. Chem. Liq., 1985, Vol. 15, pp. 147–154
0031-9104/85/1502-0147$18.50/0
1985 Gordon and Breach, Science Publishers, Inc. and OPA Ltd.
Printed in the United Kingdom

Excess Volumes and Excess Isentropic Compressibilities of Binary Mixtures of *N,N*-Dimethylformamide with *n*-Alcohols at 303.15 K

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(*Received February 18, 1985*)

Excess volumes and isentropic compressibilities for binary liquid mixtures of *N,N*-dimethylformamide with methanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol and 1-heptanol have been measured at 303.15 K. Both the excess properties are negative in the systems with lower alcohols and become positive with increase in alkane chain length of alcohols. The sign and magnitude of excess functions have been discussed in terms of the combination of the effects due to difference in size, shape and intermolecular interaction between unlike components.

1 INTRODUCTION

Dimethylformamide (DMF) due to its versatile solvent character[1] has been used as cosolvent with water to study the solvation and hydrophobic effects of alcohols[2] and other hydrophobic solutes[3]. Thermodynamic properties of mixtures of alcohols with water have been studied extensively, but there is no such systematic study on mixtures of alcohols with DMF. The results on few alcohols, methanol and ethanol have been reported in the literature.[4,5] Therefore it is interesting to gain insight into the nature of interactions in mixtures of DMF with alcohols through the measurement of their thermodynamic properties. In this paper, we report excess volumes and excess isentropic compressibilities of binary mixtures of DMF with methanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol and 1-heptanol. The results are interpreted in terms of relative strengths of the interactions and difference in sizes between like and unlike molecules.

2 EXPERIMENTAL

Apparatus

Excess volumes were determined directly using a dilatometer described earlier [6] and the values were accurate to ±0.003 $cm^3\ mol^{-1}$. Isentropic compressibilities were computed from measured sound velocity and density data. Ultrasonic sound velocities were measured with a single crystal interferometer at a frequency of 1 MHz and were accurate to ±1 per cent. Density values for the pure components were measured using a bicapillary pyknometer and in case of mixtures the data were obtained from measured excess volumes using the relation

$$\rho = \frac{x_1 M_1 + x_2 M_2}{x_1 V_1 + x_2 V_2 + V^E}. \tag{1}$$

Density values obtained from both the methods were accurate to $\pm 5 \times 10^{-5}\ g\ cm^{-3}$.

Materials

Analytical reagent *N*,*N*-dimethylformamide was kept overnight over freshly ignited quicklime and distilled under reduced pressure. The middle fraction of the distillate was collected and kept over solid potassium hydroxide pellets for 24 h. It was then distilled under reduced pressure. Methanol (BDH) was refluxed over potassium hydroxide for five hours and then distilled through a one metre fractionating column. 1-Propanol (BDH) was refluxed over lime for five hours and then distilled through a one metre fractionating column. 1-Butanol (BDH) was refluxed over freshly ignited calcium oxide for four hours. The alcohol was decanted from the lime, refluxed with magnesium turnings and then fractionally distilled. 1-Pentanol (E. Merck), 1-Hexanol (BDH) and 1-Heptanol (Koch Light Laboratories Ltd., England) were dried over drierite and fractionally distilled. The purity of the compounds was ascertained by comparing the values of densities and boiling points with literature values.[7,8] The boiling points were corrected to 1 atm pressure and the data are given in Table I along with literature values.[7,8]

3 RESULTS AND DISCUSSION

Experimental values of V^E are given in Table II and also represented as a function of mole fraction in Figure 1.

TABLE 1

Boiling points and densities of the pure components at 303.15 K

Component	Boiling point, K		Density, g cm^{-3}	
	Present work	Literature[7,8]	Present work	Literature[7,8]
DMF	425.85	426.00	0.94120	0.94120
Methanol	337.15	337.50	0.78298	0.78208
1-Propanol	370.10	370.15	0.79574	0.79567
1-Butanol	390.07	390.80	0.80231	0.80206
1-Pentanol	410.75	410.95	0.80705	0.80764
1-Hexanol	430.70	430.85	0.81261	0.81201
1-Heptanol	448.65	449.15	0.81502	—

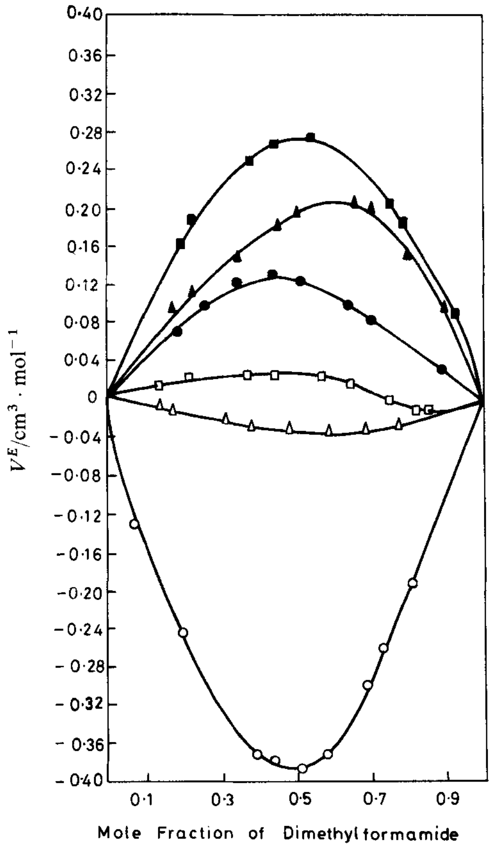

FIGURE 1 Excess volume versus mole fraction for DMF with methanol, ○; 1-propanol, △; 1-butanol, □; 1-pentanol, ●; 1-hexanol, ▲; and 1-heptanol, ■ at 303.15 K.

TABLE II

Mole fraction of DMF, x_1, excess volume, V^E, and $\Delta V^{E\,a}$ at 303.15 K

x^1	V^E cm^3 mol^{-1}	ΔV^E cm^3 mol^{-1}	x_1	V^E cm^3 mol^{-1}	ΔV^E cm^3 mol^{-1}
DMF + Methanol					
0.0773	−0.130	0.002	0.5860	−0.375	−0.005
0.2072	−0.245	−0.001	0.6935	−0.304	0.001
0.3984	−0.370	0.005	0.7376	−0.263	0.005
0.4461	−0.389	−0.001	0.8174	−0.194	−0.003
0.5176	−0.393	−0.005			
DMF + 1-Propanol					
0.1492	−0.012	0.002	0.4898	−0.035	−0.004
0.1771	−0.015	0.001	0.5904	−0.040	−0.004
0.3107	−0.024	−0.001	0.6929	−0.038	0.000
0.3878	−0.028	−0.001	0.7704	−0.036	0.000
DMF + 1-Butanol					
0.1349	0.013	0.002	0.6484	0.013	0.005
0.2148	0.019	0.001	0.7505	−0.003	0.003
0.3711	0.025	−0.004	0.8261	−0.016	−0.002
0.4450	0.025	0.003	0.8581	−0.017	−0.001
0.5684	0.022	0.003	0.		
DMF + 1-Pentanol					
0.1928	0.077	0.003	0.5154	0.120	0.001
0.2645	0.098	0.003	0.6484	0.098	−0.002
0.3416	0.122	0.011	0.7005	0.080	−0.008
0.4478	0.128	0.007	0.8958	0.029	0.009
DMF + 1-Hexanol					
0.1748	0.096	0.003	0.6819	0.203	−0.001
0.2211	0.108	0.001	0.7004	0.201	0.001
0.3532	0.155	−0.001	0.8083	0.152	−0.004
0.4574	0.187	0.000	0.9041	0.103	0.000
0.5029	0.197	0.001			
DMF + 1-Heptanol					
0.1916	0.165	−0.004	0.5418	0.272	0.004
0.2214	0.192	0.004	0.7501	0.209	−0.005
0.3806	0.256	0.003	0.7863	0.184	−0.002
0.4466	0.265	0.001	0.9204	0.093	0.002

[a] $\Delta V^E = V^E(\text{exp}) - V^E$ (Eq. 4).

Isentropic compressibility and excess isentropic compressibility are calculated using the relations

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

$$k_s^E = k_{s_{\mathrm{mix}}} - (x_1 k_{s,1} + x_2 k_{s,2}) \tag{3}$$

The values of density ρ, sound velocity u, isentropic compressibility k_s, and excess isentropic compressibility k_s^E are reported in Table III. The profiles of k_s^E versus mole fraction are shown in Figure 2. The variation of V^E and k_s^E aith mole fraction has been represented with an empirical equation of the form

$$X^E = x_1 x_2 \sum_{i=0}^{2} A_i (x_1 - x_2)^i \tag{4}$$

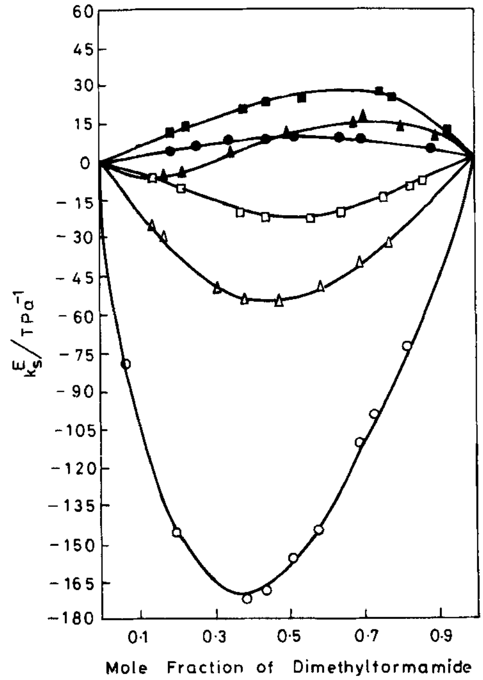

FIGURE 2 Excess isentropic compressibility versus mole fraction graphs for DMF with methanol, ○; 1-propanol, △; 1-butanol, □; 1-pentanol, ●; 1-hexanol, ▲; and 1-heptanol, ■ at 303.15 K.

TABLE III

Mole fraction of DMF, x_1, density, ρ, sound velocity, u, isentropic compressibility, k_s and excess isentropic compressibility, k_s^E, at 303.15 K

x_1	ρ $g \cdot cm^{-3}$	u ms^{-1}	k_s TPa^{-1}	k_s^E TPa^{-1}	x_1	ρ $g \cdot cm^{-3}$	u ms^{-1}	k_s TPa^{-1}	k_s^E TPa^{-1}
				DMF + Methanol					
0.0000	0.78298	1108	1040	0	0.5860	0.90322	1388	573	−146
0.0773	0.80631	1162	917	−80	0.6935	0.91403	1410	550	−111
0.2072	0.83877	1236	779	−147	0.7376	0.91950	1422	537	−100
0.3984	0.87636	1326	648	−174	0.8174	0.92689	1439	520	−73
0.4461	0.88366	1345	625	−171	1.0000	0.94120	1466	494	0
0.5176	0.89411	1365	600	−157					
				DMF + 1-Propanol					
0.0000	0.79574	1187	891	0	0.4898	0.86634	1342	640	−57
0.1492	0.81789	1231	806	−26	0.5904	0.88208	1357	615	−50
0.1771	0.82204	1239	791	−30	0.6929	0.89774	1392	574	−42
0.3107	0.84162	1287	717	−51	0.7704	0.90887	1411	552	−33
0.3878	0.85323	1310	682	−55	1.0000	0.94120	1466	494	0
				DMF + 1-Butanol					
0.0000	0.80231	1253	794	0	0.6484	0.88653	1396	578	−21
0.1349	0.81827	1280	746	−7	0.7505	0.90187	1415	553	−15
0.2148	0.828106	1295	720	−10	0.8261	0.91316	1429	536	−10
0.3711	0.84812	1334	663	−20	0.8581	0.91853	1436	527	−9
0.4450	0.85799	1351	638	−22	1.0000	0.94120	1466	494	0
0.5684	0.87505	1380	600	−24					
				DMF + 1-Pentanol					
0.0000	0.80705	1270	768	0	0.5154	0.86367	1349	636	10
0.1928	0.82590	1297	719	4	0.6484	0.88215	1377	597	8
0.2645	0.83354	1306	703	6	0.7005	0.88997	1387	584	8
0.3416	0.84214	1322	679	7	0.8958	0.92196	1435	526	4
0.4478	0.85494	1338	653	8	1.0000	0.94120	1466	494	0
				DMF + 1-Hexanol					
0.0000	0.81261	1285	745	0	0.6819	0.88388	1385	589	15
0.1748	0.82738	1319	694	−7	0.7044	0.887201	1391	584	16
0.2211	0.83096	1325	684	−5	0.8083	0.90442	1410	556	14
0.3532	0.84379	1340	659	3	0.9041	0.90677	1443	529	11
0.4574	0.85505	1353	638	8	1.0000	0.94120	1466	494	0
0.5029	0.86033	1359	628	10					
				DMF + 1-Heptanol					
0.0000	0.81502	1325	699	0	0.5418	0.86164	1376	613	25
0.1916	0.82762	1341	671	12	0.7501	0.89097	1400	572	27
0.2214	0.82979	1342	667	14	0.7863	0.89720	1406	563	25
0.3806	0.84428	1359	640	20	0.9204	0.92269	1440	522	12
0.4466	0.85090	1366	629	22	1.0000	0.94120	1466	494	0

TABLE IV

Least square parameters and standard deviation for excess volumes

	a_0	a_1	a_2	(V^E)
DMF +	cm^3 mol^{-1}			
Methanol	−1.5621	0.1455	0.4658	0.006
1-Propanol	−0.1273	0.0890	0.1073	0.002
1-Butanol	0.1028	−0.1582	0.2298	0.003
1-Pentanol	0.4808	0.0900	0.1486	0.004
1-Hexanol	0.7821	0.3731	0.1616	0.001
1-Heptanol	1.0753	0.0615	0.1597	0.004

The parameters A_i are obtained by the method of least squares and are given in Tables IV and V along with the standard deviation $\sigma(V^E)$.

The values of V^E are negative in mixtures of DMF with methanol and 1-propanol and positive in the remaining systems over the entire range of composition. The algebraic values of V^E are in the following sequence: methanol < 1-propanol < 1-butanol < 1-pentanol < 1-hexanol < 1-heptanol. k_s^E values are negative in the systems of DMF with methanol, 1-propanol and 1-butanol and the quantity is positive in DMF with 1-pentanol and 1-heptanol over the whole range of composition. In the system DMF with 1-hexanol, k_s^E values change sign from negative to positive at the mole fraction ~ 0.3. However, the order in k_s^E at the middle composition is similar to the one observed in the case of excess volumes.

The sign and magnitude of the excess functions may be attributed to a result of appropriate combination of the following three major effects. The mutual dissociation of the components due to addition of the second component, the formation of hydrogen bonds between unlike molecules

TABLE V

Least square parameters and standard deviation for excess isentropic compressibility

	b_0	b_1	b_2	$\sigma(k_s^E)$
DMF +	TPa^{-1}			
Methanol	−648.1	344.8	−137.3	1.9
1-Propanol	−225.6	35.6	89.5	1.7
1-Butanol	−92.3	16.5	69.1	0.6
1-Pentanol	37.2	8.8	5.9	0.5
1-Hexanol	37.6	107.4	−2.8	1.2
1-Heptanol	99.6	55.7	30.9	1.1

and difference in sizes of the components. Excess functions are more negative in the system DMF with methanol which may be understood in terms of strong interactions between unlike molecules and this behaviour is more significant in lower alcohols.[9] Further, a large difference in molecular sizes of DMF and methanol may also contribute to negative excess volume by interstitial occupation [10] of methanol molecules in DMF. In the system DMF with 1-hexanol, and k_s^E values are negative in the lower mole fraction range of DMF, this behaviour may be attributed to the dominance of the effect due to interstitial accommodation of the components over the dissociation effect.

The values of V^E and k_s^E in these mixtures are affected by different contributions, whose relative significance depend on the alkane chain length of alcohols.

References

1. C. V. Krishnan, H. L. Friedman, *Solute-Solvent Interactions, Vol. II*, J. F. Coetzee, C. D. Ritchie, Editors; M. Dekker (New York, 1976).
2. A. C. Rouw, G. Somsen, *J. Chem. Thermodyn.*, **13**, 67 (1981).
3. A. C. Rouw, G. Somsen, *J. Solution Chem.*, **10**, 533 (1981).
4. R. Gopal, S. Agarwal, *J. Chem. Thermodyn.*, **8**, 1205 (1976).
5. P. P. Singh, D. V. Verma, P. S. Arora, *Thermochim. Acta*, **15**, 267 (1976).
6. K. S. Reddy, P. R. Naidu, *Can. J. Chem.*, **55**, 76 (1977).
7. J. A. Riddick, W. S. Bunger, *Organic Solvents in Techniques of Chemistry, 3rd ed. Vol. II*, Wiley Interscience (New York, 1970).
8. J. Timmermans, *Physico-chemical Constants of Pure Organic Compounds*, Elsevier Publishing Company (Amsterdam, 1950, 1965).
9. M. Kato, N. Suzuki, *J. Chem. Thermodyn.*, **10**, 435 (1978).
10. O. Kiyohara, S. C. Anand, G. C. Benson, *J. Chem. Thermodyn.*, **6**, 355 (1974).