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EXCESS VOLUMES AND EXCESS ISENTROPIC COMPRESSIBILITIES OF BINARY MIXTURES OF *N*,*N*-DIMETHYLFORMAMIDE WITH BRANCHED ALCOHOLS AT 303.15 K

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ABSTRACT

Excess volumes and excess isentropic compressibilities for binary liquid mixtures of *N*,*N*-dimethylformamide with 2-propanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol and 3-methyl-1-butanol have been determined at 303.15 K. V^E values are positive in all the systems and K_s^E values are negative in all the systems except in the system *N*,*N*-dimethylformamide with 3-methyl-1-butanol, over the entire composition range. The results have been discussed in terms of the effects due to dissociation, association and difference in size and shape of the component molecules.

INTRODUCTION

The thermodynamic properties of liquid mixtures in which the molecular interactions are mainly due to association through hydrogen bonding between carbonyl and hydroxyl groups have been studied earlier [1–3]. We report here excess volumes, V^E, and excess isentropic compressibilities, K_s^E, for binary mixtures of *N*,*N*-dimethylformamide (DMF) with 2-propanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol and 3-methyl-1-butanol at 303.15 K. The molecular interactions in the present mixtures are also controlled mainly through the formation of hydrogen bonds of the type C=O $\cdots$ H–O, between unlike molecules. Further, the effects of difference in shape and steric factors on molecular interactions are also examined.

EXPERIMENTAL

Apparatus

Excess volumes were determined directly using a dilatometer described earlier [1] and the values were accurate to ± 0.003 cm^3 mol^{-1}. Isentropic

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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 $\pm 1\%$. Density values for the pure components were measured using a bicapillary pyknometer and, in the 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 grade *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. 2-Propanol (BDH) was dried first with calcium chloride and then with barium oxide and fractionally distilled. 2-Methyl-1-propanol (BDH) and 2-butanol (BDH) were purified by repeated fractional distillation through 1-inch-90 plate column. 2-Methyl-2-propanol (BDH) was distilled from lime and the middle fraction was distilled a number of times using a fractionating column. 3-Methyl-1-butanol (BDH) was dried with calcium chloride and then purified by careful fractional distillation. The purity of the samples was ascertained by comparing the values of density and boiling point data with literature values [4,5]. Experimental and literature values are given in Table 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 [4,5]	Present work	Literature [4,5]
DMF	425.85	426.00	0.94120	0.94120
2-Propanol	355.06	355.26	0.77741	0.77690
2-Methyl-1-propanol	380.55	380.66	0.79410	0.79437
2-Butanol	372.40	372.55	0.79888	0.79895
2-Methyl-2-propanol	355.35	355.42	0.77653	0.77570
3-Methyl-1-butanol	403.75	403.65	0.80419	0.80179

RESULTS

Experimental values of V^E are given in Table 2 and also represented as a function of mole fraction in Fig. 1. Isentropic compressibility and excess isentropic compressibility are calculated using the relations

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

$$K_s^E = K_{s(mix)} - (x_1 K_{s,1} + x_2 K_{s,2}) \tag{3}$$

The values of density, ρ, sound velocity, u, isentropic compressibility, K_s, and excess isentropic compressibility, K_s^E, are represented in Table 3. The

TABLE 2
Mole fraction of DMF, x_1, excess volume, V^E (cm^3 mol^{-1}), and ΔV^E [a] (cm^3 mol^{-1}), at 303.15 K

x_1	V^E	ΔV^E	x_1	V^E	ΔV^E
DMF + 2-propanol					
0.1418	0.052	0.003	0.6613	0.024	0.005
0.1935	0.056	0.001	0.7811	0.012	0.006
0.3522	0.049	0.009	0.8400	0.006	0.005
0.4952	0.041	0.002	0.8896	−0.007	0.005
DMF + 2-methyl-1-propanol					
0.1692	0.040	0.003	0.5278	0.031	−0.008
0.2482	0.050	−0.003	0.6634	0.019	−0.010
0.3756	0.043	−0.003	0.8398	−0.002	0.000
0.4001	0.041	−0.004	0.9008	−0.011	−0.002
0.4249	0.040	−0.005			
DMF + 2-butanol					
0.1302	0.168	−0.006	0.6781	0.159	0.002
0.3076	0.240	0.012	0.7060	0.158	−0.011
0.4845	0.244	−0.002	0.8306	0.084	−0.003
0.5860	0.210	−0.005	0.9004	0.040	0.004
DMF + 2-methyl-2-propanol					
0.1330	0.071	0.005	0.4850	0.150	−0.005
0.2273	0.120	−0.001	0.6087	0.120	0.010
0.2968	0.153	−0.012	0.7004	0.094	0.004
0.3379	0.161	−0.010	0.8834	0.030	−0.003
DMF + 3-methyl-1-butanol					
0.1499	0.052	0.000	0.5936	0.085	0.002
0.2475	0.072	0.000	0.7350	0.073	0.002
0.3378	0.081	0.001	0.7909	0.064	0.002
0.4607	0.093	−0.005	0.9132	0.036	−0.001
0.5116	0.090	−0.001			

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

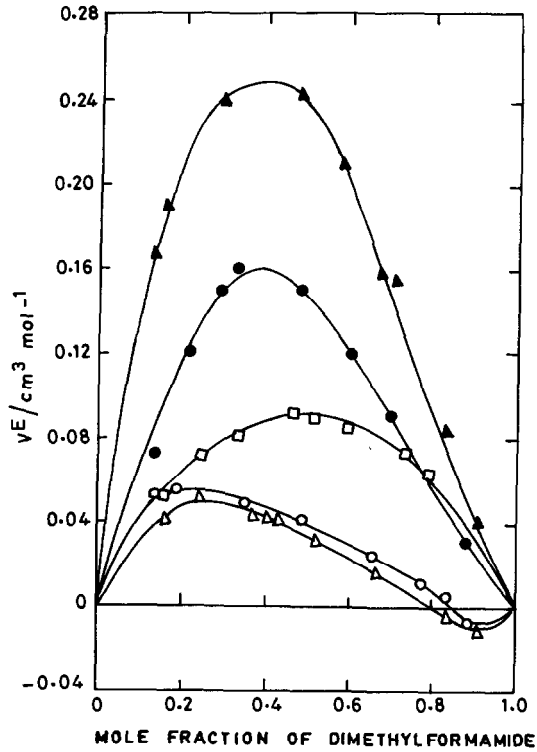

Fig. 1. Excess volumes versus mole fraction for DMF with 2-propanol (○), 2-methyl-1-propanol (△), 2-butanol (▲), 2-methyl-2-propanol (●), 3-methyl-1-butanol (□).

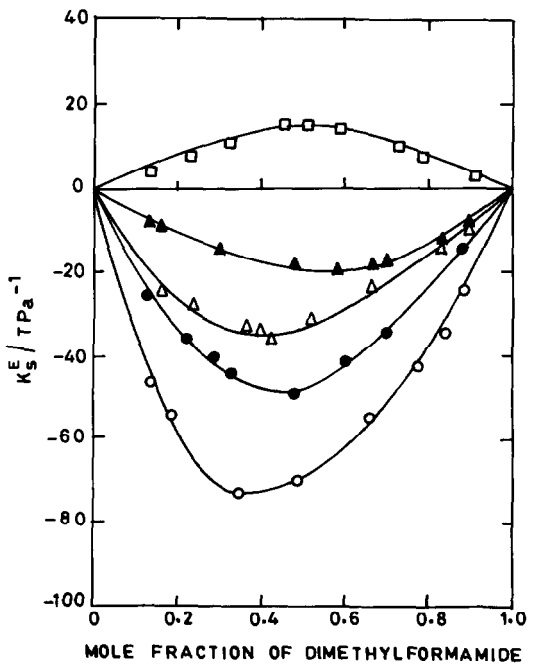

Fig. 2. Excess isentropic compressibility versus mole fraction graphs for DMF with 2-propanol (○), 2-methyl-1-propanol (△), 2-butanol (▲), 2-methyl-2-propanol (●), 3-methyl-1-butanol (□).

TABLE 3
Mole fraction of DMF, x_1, density, ρ (g cm^{-3}), sound velocity, u (m s^{-1}), isentropic compressibility, K_s (T Pa^{-1}), and excess isentropic compressibility, K_s^E (T Pa^{-1}), at 303.15 K

x_1	ρ	u	K_s	K_s^E	x_1	ρ	u	K_s	K_s^E
DMF + 2-propanol									
0.0000	0.77741	1129	1009	0	0.6613	0.88550	1358	612	−56
0.1418	0.80021	1185	890	−46	0.7811	0.90537	1400	563	−43
0.1935	0.80865	1203	854	−55	0.8400	0.91507	1420	541	−34
0.3522	0.83475	1260	754	−73	0.8896	0.92337	1435	525	−25
0.4952	0.85828	1306	683	−71	1.0000	0.94120	1466	494	0
DMF + 2-methyl-1-propanol									
0.0000	0.79410	1181	903	0	0.5278	0.86469	1328	666	−31
0.1692	0.81506	1232	808	−25	0.6634	0.88531	1363	608	−24
0.2482	0.82535	1252	772	−28	0.8398	0.91383	1415	546	−13
0.3756	0.84273	1287	716	−33	0.9008	0.92418	1437	524	−10
0.4001	0.84621	1295	704	−35	1.0000	0.94120	1466	494	0
0.4249	0.84973	1302	690	−36					
DMF + 2-butanol									
0.0000	0.79888	1205	862	0	0.6781	0.88806	1378	593	−19
0.1302	0.81322	1235	806	−8	0.7060	0.89249	1386	583	−19
0.1544	0.81599	1241	795	−9	0.8306	0.91231	1422	542	−14
0.3076	0.83535	1277	734	−15	0.9004	0.92419	1441	521	−10
0.4845	0.85893	1323	665	−18	1.0000	0.94120	1466	494	0
0.5860	0.87386	1352	626	−20					
DMF + 2-methyl-2-propanol									
0.0000	0.77653	1111	1043	0	0.4850	0.84648	1274	728	−49
0.1330	0.79417	1154	945	−25	0.6087	0.86726	1313	669	−41
0.2273	0.80729	1185	896	−36	0.7004	0.88342	1347	624	−35
0.2968	0.81722	1206	841	−40	0.8834	0.91783	1416	543	−15
0.3399	0.82365	1221	814	−43	1.0000	0.94120	1466	494	0
DMF + 3-methyl-1-butanol									
0.0000	0.80419	1234	816	0	0.5936	0.87303	1337	640	15
0.1499	0.81888	1257	772	4	0.7350	0.89421	1376	590	10
0.2475	0.82949	1273	744	8	0.7909	0.90319	1393	570	8
0.3378	0.83986	1287	718	11	0.9132	0.92432	1435	525	3
0.4607	0.85509	1307	684	16	1.0000	0.94120	1466	494	0
0.5116	0.86171	1318	668	16					

profiles of K_s^E versus mole fraction are shown in Fig. 2. The variation of V^E and K_s^E with mole fraction has been represented by an empirical equation of the form

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

TABLE 4
Least-squares parameters and standard deviation for excess volumes (cm^3 mol^{-1})

DMF +	a_0	a_1	a_2	$\sigma(V^E)$
2-Propanol	0.1700	−0.2781	0.0618	0.006
2-Methyl-1-propanol	0.1035	−0.2347	0.1149	0.007
2-Butanol	0.9494	−0.6053	0.0543	0.008
2-Methyl-2-propanol	0.6147	−0.2589	−0.2595	0.008
3-Methyl-1-butanol	0.3551	0.0036	0.1225	0.002

TABLE 5
Least-squares parameters and standard deviation for excess isentropic compressibility (cm^3 mol^{-1})

DMF +	b_0	b_1	b_2	$\sigma(K_s^E)$
2-Propanol	−280.48	87.21	−65.58	1.0
2-Methyl-1-propanol	−128.14	52.24	−26.74	1.6
2-Butanol	−77.06	−21.19	−14.90	0.6
2-Methyl-2-propanol	−183.48	48.40	14.73	1.6
3-Methyl-1-butanol	61.43	9.62	−49.56	0.7

The parameters A_i are obtained by the method of least squares and are given in Tables 4 and 5 along with the standard deviations, σ, for V^E and K_s^E.

DISCUSSION

The values of V^E are positive in the systems of DMF with 2-butanol, 2-methyl-2-propanol and 3-methyl-1-butanol over the entire range of composition and the quantity changes sign from negative to positive beyond ~ 0.8 mole fraction in the systems of DMF with 2-propanol and 2-methyl-1-propanol. The values of K_s^E are negative in the systems of DMF with 2-propanol, 2-butanol, 2-methyl-2-propanol and 2-methyl-1-propanol and positive in the system of DMF with 3-methyl-1-butanol over the whole range of mole fraction. The behaviour of V^E and K_s^E is explained on the basis of the effects due to mutual dissociation of molecules and the formation of hydrogen bonds between unlike molecules. The former effect contributes to an expansion in volume and, hence, the mixtures become more compressible, while the latter effect is responsible for a contraction in volume and, hence, the compressibility of the mixtures is less than that of the pure components. The observed values of V^E and K_s^E are attributed to a net resultant of the above two opposing effects.

The sign and magnitude of V^E and K_s^E depend on the strength of hydrogen bonding of alcohols in their pure state and in mixtures. In

branched alcohols the presence of methyl groups on the α-carbon atom controls the hydrogen bond strength. These methyl groups increase the electron density at the oxygen atom and increase the association due to the electromeric effect. Further, the presence of methyl groups also decreases the association due to the steric effect. A result of the above two effects may be related to the order observed in V^E and K_s^E. Factors such as difference in size and shape of the components are also significant in the systems. As the size of the non-common component increases in the systems DMF with 2-propanol, 2-methyl-1-propanol and 3-methyl-1-butanol, the values of V^E and K_s^E also increase. However, in the system DMF with 2-propanol, V^E values are slightly more positive than in the system DMF with 2-methyl-1-propanol. This may be attributed to the dominance of the steric effect, due to the presence of two methyl groups on the α-carbon atom in 2-propanol. In the systems DMF with 2-butanol, 2-methyl-2-propanol and 2-methyl-1-propanol, the sizes of the non-common components are almost the same, but they differ significantly in their shapes. The algebraic values of V^E fall in the order 2-methyl-1-propanol < 2-methyl-2-propanol < 2-butanol whereas the values of K_s^E are in the sequence 2-methyl-2-propanol < 2-methyl-1-propanol < 2-butanol. Finally, the order indicates that the factors which are responsible for V^E and K_s^E are not the same in these mixtures.

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