

VOLUMETRIC AND ULTRASONIC BEHAVIOUR OF BINARY MIXTURES OF N, N-DIMETHYLFORMAMIDE WITH SOME CHLOROETHANES AND CHLOROETHENES

G. Alluraiah, K. Ramanjaneyulu and A. Krishnaiah*

Department of Chemistry, College of Engineering, S.V. University, Tirupati - 517 502, India

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Excess Volumes (V^E) and deviations in isentropic compressibilities (K_s) were reported for the binary liquid mixtures of N, N-dimethylformamide (DMF) with 1, 2-dichloroethane, 1, 1, 1-trichloroethane, 1, 1, 2, 2-tetrachloroethane, trichloroethene and tetrachloroethene over the entire mole fraction range at 303.15°K. The values of V^E and K_s are positive for the system, DMF + 1, 2-dichloroethane and negative for the systems, DMF + 1, 1, 1-trichloroethane and + 1, 1, 2, 2-tetrachloroethane. For DMF + trichloroethene, the values of V^E are negative and an inversion in sign of K_s from positive to negative is observed. The V^E values for the system, DMF + tetrachloroethene, are negative and K_s values are positive. The experimental data were used to explain the effect of successive chlorination and unsaturation of ethane molecule on V^E and K_s .

Key words: Excess volumes, Sound velocity, Density.

INTRODUCTION

The present paper forms a part of our programme on the measurement of thermodynamic properties of mixtures containing chlorinated hydrocarbons as one of the components [1-3]. We report here new experimental data on excess volumes and deviations in isentropic compressibilities for the mixtures of DMF with 1, 2-dichloroethane, 1, 1, 1-trichloroethane, 1, 1, 2, 2-tetrachloroethane, trichloroethene and tetrachloroethene at 303.15 K. We have undertaken this work to investigate the effect of successive chlorination and unsaturation of ethane molecule on excess volumes and deviations in isentropic compressibilities.

EXPERIMENTAL

Excess Volumes (V^E) were measured directly using a single composition per loading type dilatometer described by Rao and Naidu [4]. Five dilatometers with different capacities were used to cover the entire composition range. The values of V^E are accurate to $\pm 0.003 \text{ cm}^3 \text{ mol}^{-1}$. Isentropic compressibilities were calculated from the relation,

$$k_s = U^2 \rho^{-1} \quad (1)$$

where U and ρ denote sound speed and density. Sound speeds in liquids and liquid mixtures were measured with a single crystal ultrasonic interferometer working at a fixed frequency. The densities of the mixtures were computed from experimental excess volume data (Table 1) using the relation,

$$\rho = \frac{x_1 M_1 + x_2 M_2}{V^o + V^E} \quad (2)$$

where x_1 and x_2 denote mole fractions and M_1 and M_2 stand for the molecular weights. V^o and V^E represent ideal molar volume and excess molar volume of the mixture. Densities of the pure components were determined using a bicapillary pycnometer. Deviation in isentropic compressibility was calculated using the relation,

$$K_s = K_s - \phi_1 k_{s,1} - \phi_2 k_{s,2} \quad (3)$$

where k_s , $k_{s,1}$ and $k_{s,2}$ are the isentropic compressibilities of the mixture and the pure components 1 and 2 respectively. ϕ_1 and ϕ_2 are the volume fractions. K_s represents the deviation in isentropic compressibility from the ideal behaviour. K_s values are accurate to $\pm 1.5\%$.

Materials. N, N-dimethylformamide (AR) was purified by the method described by Ramgopal *et al.* [5]. 1, 2-dichloroethane (BDH), 1, 1, 1-trichloroethane (Koch-light) and 1, 1, 2, 2-tetrachloroethane (BDH) were purified by the methods described by Ramanjaneyulu *et al.* [3]. Trichloroethene (BDH) and tetra-chloroethene (BDH) were purified using the method described by Riddick and Bunger [6]. The measured densities and boiling points of the purified components are in good agreement with the literature values.

RESULTS AND DISCUSSION

Experimental V^E values for the five binary liquid mixtures are included in Table 1. Dependence of V^E on mole fraction is graphically presented in Fig. 1. The values of density (ρ), sound speed (U), isentropic compressibility (k_s) and deviation in isentropic compressibility (K_s) are included in Table 2. Volume fraction versus K_s plots are shown in Fig. 2. The V^E values are fitted to an empirical equation of the form,

* To whom correspondence should be addressed.

Table 1. Excess volumes (V^E) of DMF with some chlorinated ethenes and ethenes at 303.15 K.

X_1	V^E $\text{cm}^3 \text{mol}^{-1}$	X_1	V^E $\text{cm}^3 \text{mol}^{-1}$
<i>DMF + 1, 2-dichloroethane</i>			
0.1525	0.005	0.6102	0.018
0.2028	0.007	0.6851	0.019
0.3040	0.010	0.7315	0.018
0.4093	0.013	0.8579	0.013
0.5280	0.017	0.8837	0.009
<i>DMF + 1, 1, 1-trichloroethane</i>			
0.1294	-0.015	0.5466	-0.061
0.2020	-0.025	0.5954	-0.064
0.3661	-0.045	0.6687	-0.063
0.4252	-0.051	0.7976	-0.053
0.4779	-0.056	0.8987	-0.034
<i>DMF + 1, 1, 2, 2-tetrachloroethane</i>			
0.1246	-0.031	0.5655	-0.079
0.2335	-0.060	0.6359	-0.072
0.3403	-0.074	0.7435	-0.054
0.4375	-0.082	0.7807	-0.048
0.5068	-0.083	0.8944	-0.025
<i>DMF + trichloroethene</i>			
0.1272	-0.040	0.5641	-0.047
0.2043	-0.055	0.6615	-0.038
0.2889	-0.062	0.7061	-0.034
0.3727	-0.060	0.7622	-0.026
0.4733	-0.055	0.8754	-0.014
<i>DMF + tetrachloroethene</i>			
0.1585	-0.008	0.5826	-0.020
0.2248	-0.012	0.6721	-0.017
0.3126	-0.016	0.7296	-0.015
0.3977	-0.019	0.7828	-0.014
0.4840	-0.021	0.8801	-0.009

$$V^E = x_1 x_2 [a_0 + a_1 (x_1 - x_2) + a_2 (x_1 - x_2)^2] \dots (4)$$

where x represents the mole fraction and a_0 , a_1 and a_2 are adjustable parameters. The values of the parameters, obtained by the method of least squares, are given in Table 3, along with the values of the standard deviation, σ (V^E).

The values of K_s are also represented by a polynomial similar to equation (4) wherein the mole fraction is replaced by volume fraction (ϕ) and the constants a_0 , a_1 , and a_2 are by b_0 , b_1 and b_2 . The values of the empirical constants

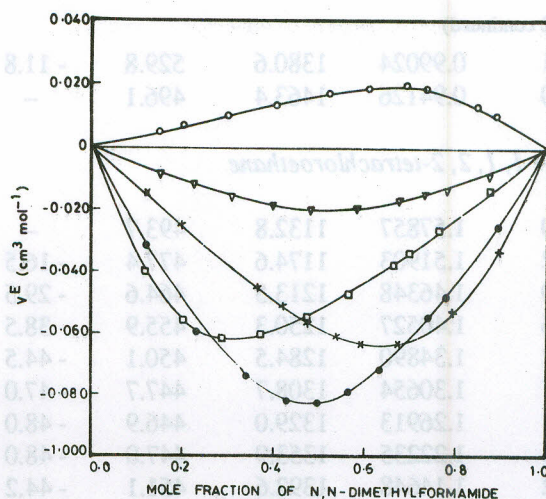


Fig. 1. N, N-dimethylformamide + 1, 2-dichloroethane (o), + 1, 1, 1-trichloroethane (x), + 1, 1, 2, 2-tetrachloroethane (•), + trichloroethene (□) and + tetrachloroethene (∇).

Table 2. Volume fraction (ϕ_1), density (ρ) sound speed (U), isentropic compressibility (k_s) and deviation in isentropic compressibility (K_s) at 303.15 K

ϕ_1	ρ g cm^{-3}	U ms^{-1}	k_s TPa^{-1}	K_s TPa^{-1}
<i>DMF + 1, 2-dichloroethane</i>				
0.0000	1.23828	1173.3	586.6	-
0.1488	1.19398	1201.2	580.5	7.4
0.1982	1.17698	1212.0	578.4	9.7
0.2979	1.14962	1233.0	572.2	12.6
0.4024	1.11857	1257.6	565.3	15.1
0.5208	1.08336	1288.2	556.2	16.7
0.6033	1.05883	1311.0	549.5	17.5
0.6789	1.03639	1333.8	542.4	17.2
0.7258	1.02247	1348.8	537.6	16.7
0.8544	0.98438	1395.0	522.0	12.7
0.8807	0.97659	1406.1	517.9	11.0
1.0000	0.94126	1463.4	496.1	-
<i>DMF + 1, 1, 1-trichloroethane</i>				
0.0000	1.32094	942.1	852.9	-
0.1026	1.28216	992.4	791.9	-23.7
0.1629	1.25938	1022.1	760.1	-34.0
0.3075	1.20475	1089.6	699.1	-43.5
0.3625	1.18393	1115.7	678.5	-44.6
0.4131	1.16482	1139.7	660.9	-44.2
0.4810	1.13908	1172.1	639.0	-41.9
0.5308	1.12021	1196.4	623.7	-39.4
0.6081	1.09084	1236.0	600.1	-35.5
0.7518	1.03615	1311.9	560.8	-23.8

(Continued)

(Table 2 continued)

0.8721	0.99024	1380.6	529.8	- 11.8
1.0000	0.94126	1463.4	496.1	-

DMF + 1, 1, 2, 2-tetrachloroethane

0.0000	1.57857	1132.8	493.7	-
0.0942	1.51903	1174.6	477.4	- 16.5
0.1820	1.46348	1213.5	464.6	- 29.5
0.2736	1.40527	1250.3	455.9	- 38.5
0.3622	1.34890	1284.5	450.1	- 44.5
0.4287	1.30654	1308.7	447.7	- 47.0
0.4873	1.26913	1329.0	446.9	- 48.0
0.5605	1.22235	1353.9	447.0	- 48.0
0.6792	1.14648	1392.6	451.1	- 44.2
0.7222	1.11896	1402.4	454.9	- 40.5
0.8608	1.03029	1437.5	470.0	- 25.8
1.0000	0.94126	1463.4	496.1	-

DMF + trichloroethene

0.0000	1.45134	1015.1	668.1	-
0.1112	1.39525	1049.7	650.5	1.5
0.1805	1.36014	1072.2	639.5	2.4
0.2584	1.320047	1098.6	627.5	3.8
0.3376	1.28005	1127.1	615.0	5.0
0.4353	1.23013	1165.8	598.1	4.9
0.5261	1.18368	1205.4	581.4	3.8
0.6263	1.13240	1253.4	562.1	1.7
0.6733	1.10839	1277.4	552.9	0.6
0.7333	1.07767	1309.1	541.4	- 0.6
0.8577	1.01405	1379.2	518.2	- 2.1
1.0000	0.94126	1463.4	496.1	-

DMF + tetrachloroethene

0.0000	1.60636	1024.5	593.1	-
0.1241	1.52390	1059.6	584.5	3.4
0.1791	1.48704	1076.1	580.6	4.9
0.2549	1.43656	1100.4	574.7	6.3
0.3318	1.38534	1126.2	568.9	8.0
0.4137	1.33090	1155.9	562.1	9.1
0.5122	1.26542	1194.6	553.5	9.9
0.6066	1.20269	1236.0	544.1	9.8
0.6699	1.16059	1266.1	537.3	9.2
0.7305	1.12030	1297.2	530.3	8.1
0.8466	1.04314	1362.3	518.4	5.4

b_0 , b_1 and b_2 , evaluated by the least square analysis, are given in Table 4 along with the values of standard deviation, σ (K_j).

The data included in Table 1 and 2 shows that the values of V^B and K_j are positive for the system, DMF + 1,2-dichloroethane and negative for the systems, DMF + 1,1,1-

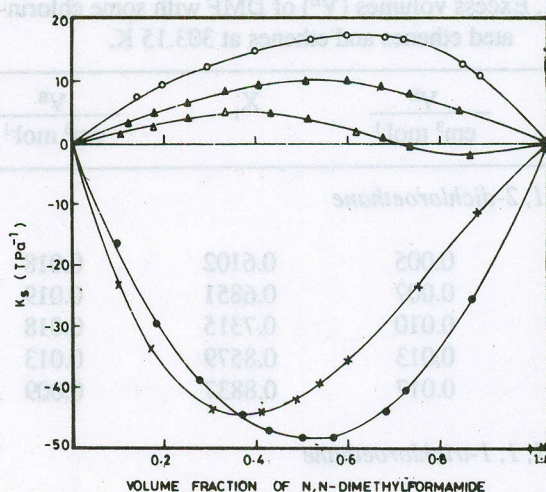


Fig. 2. N, N-dimethylformamide + 1, 2-dichloroethane (o) + 1, 1, 1-trichloroethane (x), + 1, 1, 2, 2-tetrachloroethane (●) + trichloroethene (Δ) and + tetrachloroethene (Δ).

Table 3. Values of the parameters, a_0 , a_1 and a_2 of the equation (4) and the standard deviation, σ (V^B) at 303.15 K

System	a_0	a_1	a_2	σ (V^B)
	$\text{cm}^3 \text{mol}^{-1}$			
DMF + 1, 2-dichloroethane	0.066	0.041	- 0.002	0.001
DMF + 1, 1, 1-trichloroethane	- 0.245	- 0.149	- 0.035	0.001
DMF + 1, 1, 2, 2-tetrachloro ethane	- 0.325	0.032	- 0.081	0.002
DMF + trichloroethane	- 0.215	0.161	- 0.058	0.001
DMF + tetrachloroethene	- 0.080	- 0.013	+ 0.017	0.001

Table 4. Values of the parameters, b_0 , b_1 and b_2 of the equation (4) and the standard deviation, σ (K_j) at 303.15 K

System	b_0	b_1	b_2	σ (K_j)
	TPa^{-1}			
DMF + 1, 2-dichloroethane	66.126	28.440	29.040	0.2
DMF + 1, 1, 1-trichloroethane	- 166.552	96.791	- 23.133	0.7
DMF + 1, 1, 2, 2-tetrachloro ethane	25.505	8.664	- 8.050	0.1
DMF + trichloroethane	16.362	24.217	- 34.015	0.3
DMF + tetrachloroethene	39.176	7.194	- 4.795	0.1

trichloroethane and + 1,1,2,2-tetrachloroethane. In mixtures of DMF with trichloroethene, the values of V^B are negative and an inversion in sign of K_j from positive to negative is observed. The system, DMF + tetrachloroethene is associated with negative V^B and positive K_j values.

The values of V^B and K_j may be explained on the basis of the following factors; (i) the mutual loss of dipolar association due to the addition of the second component and difference in size and shape of the components and (ii) dipolar interactions between unlike molecules. The former effect results in positive deviation whereas the latter leads to negative deviation in V^B and K_j . The experimental results

suggest that the V^E and K_s values are determined by the former effect in the system, DMF + 1, 2-dichloroethane and by the latter effect in the systems, DMF + 1, 1, 1-trichloroethane and + 1, 1, 2, 2-tetrachloroethane. In mixtures of DMF with chloroethenes the two effects operate to different extents as the composition changes. The algebraic values of V^E and K_s in mixtures containing chloroethanes and ethenes fall in the order, 1, 2-dichloroethane > 1, 1, 1-trichloroethane > 1, 1, 2, 2-tetrachloroethane and tetrachloroethene > trichloroethene.

This order suggest that increase of number of chlorine atoms in ethane results in decrease of V^E and K_s . The trend may be attributed to the increase of strength of dipolar interaction between unlike molecules as the number of chlorine atoms increases. But in the case of chloroethenes the values of V^E and K_s increase with increase in number of chlorine atoms. An inter comparison of V^E and K_s values between the mixtures containing chloroethanes and chloroethenes (with same number of chlorine atoms) as non-common components suggests that the values are larger in mixtures containing chloroethenes. This may be ascribed to the partial saturation of the interacting ability of chlorine atoms due to the presence of double bond in chloroethenes.

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INTRODUCTION

One of the logical treatments that can be conceived on the basis of law of mass action (which is essentially identical to what takes the following form:

$$\text{Species} + \text{hole} \rightleftharpoons \text{species in hole}$$

and $K = \frac{[\text{Species in hole}]}{[\text{Species}] [\text{hole}]}$ where bracket indicates the concentration in terms of number of species as well as holes per unit volume.

Testing of this model of interaction can be based on the assumption that a species entering into the holes is a part or whole of its volume. It is realized on the basis of the simple additivity rule ($V = w_1 V_1 + w_2 V_2$ where V is the specific volume of the mixture, V_1 and V_2 are those of white and solvent and $w_1 + w_2 = 1$). If V is expressed as the volume which contains one mole of A (i.e. nV) of which a fraction has entered into the holes and each cm³ of solvent has only $\frac{1}{V_2}$ moles of holes (i.e. $10^{23} \times 0.02 \times \frac{1}{V_2}$ holes per cm³) then

$$K = \frac{nV}{(1-n)(V_2 - n)}$$

where n expresses the actual volume of the solvent hole added to make the mixture.

Now the volume V contains solvent 2 and free A while the rest of A remains inside the hole without out-

indicating its volume to the bulk, that $V = 2 + (1 - \alpha)V_2$ where V_2 is the molar volume of A. Hence we can write

$$V - 2 = V_2 = (1 - \alpha)V_2$$

Now, putting $2 = V_1 - V_2$

$$\alpha = \frac{V_1 - V_2}{V_1}$$

We get, $\alpha = \frac{2V_1}{V_1 - 2}$ and $1 - \alpha = \frac{V_1 - 2V_1}{V_1 - 2}$

Hence $K = \frac{2V_1}{V_2(V_1 - 2)}$

or $KV_2 = \frac{2(V_1 - 2)}{V_1}$

Therefore, $V_1 V_2 = \frac{2(V_1 - 2)}{K}$

Putting back $2 = V_1 - V_2$, finally we have the relation

$$K(V_1 - V_2) = \frac{2(V_1 - 2)}{V_1} \quad (1)$$

Therefore, a plot of $V_1 V_2$ against $V_1 - V_2$ will give a straight line at the lower end of concentrations. The slope of this plot gives K and the intersection gives KV_1 . Since the molar volume of acetic acid monomer known to be