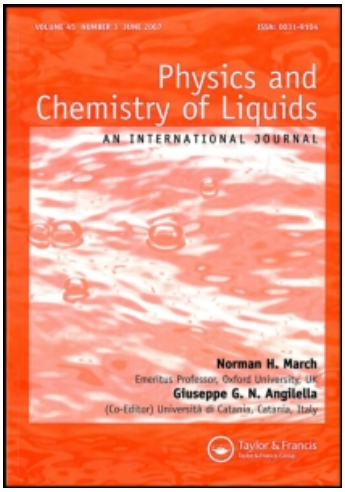

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EXCESS VOLUMES AND ULTRASONIC STUDIES OF N,N-DIMETHYL ACETAMIDE WITH SUBSTITUTED BENZENES AT 303.15 K

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Molar excess volumes, (V^E) and the ultrasonic sound volocity (U) of binary mixtures of N,N-dimethylacetamide with chlorobenzene, bromobenzene, fluorobenzene, nitrobenzene and aniline have been measured at 303.15 K. The speed of sound data were used to compute isentropic compressibilities (K_s) and deviation in isentropic compressibilities (ΔK_s). V^E values and ΔK_s values are negative in all the systems, over the entire range of composition. The results are interpreted on the basis of intermolecular interactions between unlike molecules.

Keywords: Binary mixtures; Substituted benzenes; N,N-dimethylacetamide

1. INTRODUCTION

In recent years there has been considerable progress in the experimental investigation of the excess thermodynamic properties of liquid mixtures. Excess thermodynamic functions have been used as a qualitative guide to predict the extent of complex formation in binary liquid mixtures. As a part of our continuing study on thermodynamic properties of non-electrolyte solutions [1–3], in this work, we report molar excess volumes and speed of sound and related properties of

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N,N-dimethylacetamide with chlorobenzene, bromobenzene, fluorobenzene, nitrobenzene and aniline at 303.15 K. We have undertaken this work to investigate the effect of aromatization and the influence of different substituents in the aromatic ring on V^E and ΔK_s values.

2. EXPERIMENTAL

In the present investigation all the chemicals used were of analytical grade. N,N-dimethylacetamide, chlorobenzene, bromobenzene, fluorobenzene, nitrobenzene and aniline were purified by the methods described by Ramadevi and Rao [4]. The purities of samples were checked by comparing the measured densities of the compounds with those reported in the literature [5, 6]. The purities of the samples were further confirmed by GLC single sharp peaks. The measured densities and ultrasonic sound velocities which reported in the literature are listed in Table I.

Molar excess volumes were measured directly using the dilatometer technique described by Rao and Naidu [7]. The molar excess volumes are accurate to $\pm$ 0.003 $cm^{-3} mol^{-1}$. The sound volocities were measured by a single crystal ultrasonic interferometer at 4 MHz frequency at 303.15 K. These were accurate to 0.02%. Densities of pure components were measured with a bicapillary pycnometer, which offers an accurary of 2 parts in 10^5. In the case of mixtures, the density data were obtained from measured excess volumes. A thermostatically controlled, well-stirred water bath with temperature controlled to 303.15 $\pm$ 0.01 K, was used for all the measurements.

TABLE I Ultrasonic sound velocities (U) and densities (ρ) of pure components at 303.15 K

	$U/m \cdot s^{-1}$		$\rho/g \cdot cm^{-3}$	
Compound	*Exptl.*	*Lit.* [8, 9]	*Exptl.*	*Lit.* [5, 6]
N,N-dimethylacetamide	1452	1451	0.932 40	0.932 43
chlorobenzene	1249	1248	1.095 47	1.095 50
bromobenzene	1137	1136	1.481 47	1.481 50
fluorobenzene	1171	1172	1.013 16	1.013 14
nitrobenzene	1441	1441	1.193 38	1.193 41
aniline	1620	1619	1.017 53	1.107 50

3. RESULTS AND DISCUSSION

The V^E data at 303.15 K of all the mixtures are reported in Table II and are graphically represented in Figure 1.

The isentropic compressibility (K_s) was calculated using the relation:

$$K_s = U^{-2}\rho^{-1} \tag{1}$$

TABLE II Molar excess volumes (V^E) for the binary mixtures of N,N-dimethyl acetamide (1) with substituted benzenes (2) at 303.15 K

x_1	V^E $cm^3 \cdot mol^{-1}$	x_1	V^E $cm^3 \cdot mol^{-1}$
N,N-Dimethylacetamide (1) + Chlorobenzene (2)			
0.1496	−0.131	0.5704	−0.219
0.2204	−0.156	0.6890	−0.181
0.2848	−0.205	0.7707	−0.148
0.3711	−0.231	0.8724	−0.084
0.5292	−0.235		
N,N-Dimethylacetamide (1) + Bromobenzene (2)			
0.1428	−0.081	0.6350	−0.121
0.2123	−0.113	0.6854	−0.106
0.3059	−0.131	0.8464	−0.046
0.4167	−0.142	0.8855	−0.038
0.5406	−0.135		
N,N-Dimethylacetamide (1) + Fluorobenzene (2)			
0.1357	−0.261	0.6621	−0.305
0.1283	−0.309	0.7109	−0.264
0.2495	−0.379	0.7723	−0.198
0.3561	−0.438	0.8679	−0.103
0.5173	−0.399		
N,N-Dimethylacetamide (1) + Nitrobenzene (2)			
0.1395	−0.018	0.6370	−0.027
0.2118	−0.031	0.6883	−0.019
0.3193	−0.039	0.8449	−0.011
0.3616	−0.045	0.8921	−0.009
0.4912	−0.033		
N,N-Dimethylacetamide (1) + Aniline (2)			
0.1366	−0.278	0.6466	−0.613
0.1855	−0.345	0.7014	−0.586
0.2916	−0.468	0.7537	−0.534
0.3916	−0.554	0.8503	−0.400
0.3925	−0.609		
0.4874			

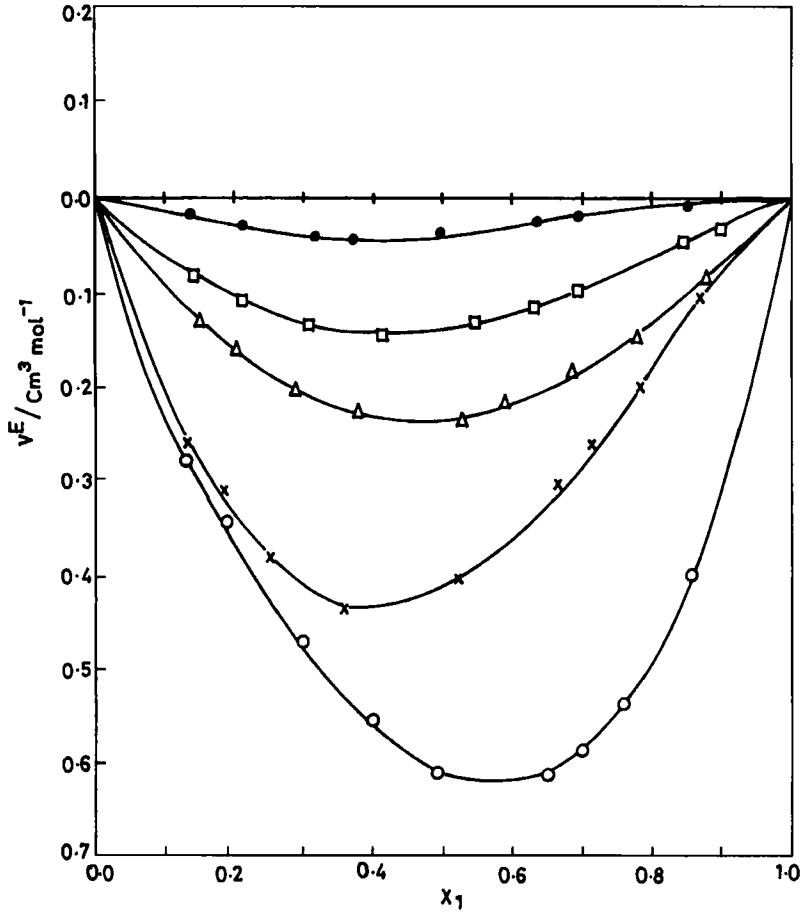

FIGURE 1 Excess volumes (V^E) for N,N-dimethylacetamide + fluorobenzene (x); + chlorobenzene (Δ); + bromobenzene (□); + aniline (○) and + nitrobenzene (●) at 303.15 K.

where U and ρ denote the speed of sound and density of binary machines respectively. The density of the binary mixtures was computed using the relation:

$$\rho = \frac{x_1 M_1 + x_1 M_2}{V + V^E} \tag{2}$$

where x_1 and x_2 are the mole fractions, M_1 and M_2 are the molar masses of pure components. V is the ideal molar volume and V^E the molar excess volume of the mixture.

Deviation in isentropic compressibility (ΔK_s) was calculated using the expression

$$\Delta K_s = K_s - \phi_1 K_{s1} - \phi_2 K_{s2} \quad (3)$$

where Φ_1, Φ_2 and K_{s1}, K_{s2} are volume fractions and isentropic compressibilities of pure components respectively. The values of ρ,U,K_s and ΔK_s are included in Table III. The variation of ΔK_s with volume fraction in graphically represented in Figure 2.

TABLE III Volume fraction (ϕ_1) of N,N-dimethylacetamide, ρ,U, K_s and ΔK_s for N,N-dimethylacetamide (1) + Substituted benzenes (2) at 303.15 K

ϕ_1	ρ $g \cdot cm^{-3}$	$U exp.$ ms^{-1}	K_s TPa^{-1}	ΔK_s TPa^{-1}
N,N-Dimethylacetamide (1) + Chlorobenzene (2)				
0.000	1.09550	1252	582	–
0.1379	1.07437	1279	568	−3.7
0.1856	1.06681	1290	563	−5.6
0.2658	1.05426	1306	555	−7.4
0.3492	1.04092	1324	547	−9.1
0.5055	1.01543	1356	535	−9.7
0.5470	1.00842	1365	531	−10.4
0.6890	0.98825	1387	525	−7.4
0.7707.	0.97403	1403	520	−5.9
0.8724	0.95575	1424	515	−3.4
1.0000	0.93230	1452	508	–
N,N-Dimethylacetamide (1) + Bromobenzene (2)				
0.0000	1.48151	1130	528	–
0.1280	1.41226	1175	512	−13.2
0.1920	1.37755	1197	506	−18.5
0.2789	1.32951	1229	497	−25.6
0.3864	1.27105	1265	491	−29.3
0.5092	1.20345	1306	487	−31.3
0.6007	1.20530	1334	486	−29.9
0.6576	1.12154	1350	488	−26.9
0.8293	1.02653	1402	495	−13.7
0.8721	1.00291	1415	497	−13.5
1.0000	0.93230	1452	508	–
N,N-Dimethylacetamide (1) + Fluorobenzene (2)				
0.0000	1.01314	1171	719	–
0.1339	1.00508	1202	688	−2.9
0.1761	1.00217	1214	677	−5.5
0.2467	0.99719	1238	654	−13.4
0.3526	0.98922	1274	622	−22.5
0.5135	0.97575	1331	578	−32.9
0.6587	0.96301	1374	550	−30.7
0.7078	0.95861	1386	543	−27.3
0.7696	0.95293	1401	534	−22.7

TABLE III (Continued)

ϕ_1	ρ $g \cdot cm^{-3}$	$U exp.$ ms^{-1}	K_s TPa^{-1}	ΔK_s TPa^{-1}
0.8661	0.94415	1421	524	−12.4
1.0000	0.93230	1452	508	–
N,N-Dimethylacetamide (1) + Nitrobenzene (2)				
0.0000	1.19341	14441.0	403	–
0.1280	1.16018	1442.0	414	−2.4
0.1957	1.14264	1443.1	420	−3.8
0.2982	1.11598	1444.0	429	−5.1
0.3391	1.10536	1444.6	433	−5.7
0.4665	1.07195	1445.9	446	−6.4
0.6138	1.03341	1447.2	462	−6.0
0.6667	1.01952	1447.9	467	−5.8
0.8314	0.97641	1449.3	487	−3.4
0.8822	0.96314	1449.9	493	−2.4
1.0000	0.93230	1452.0	508	–
N,N-Dimethylacetamide (1) + Aniline (2)				
0.0000	1.01340	1620	376	–
0.1385	0.00519	1604	386	−7.7
0.1880	1.00190	1595	392	−8.6
0.2950	0.99450	1576	404	−10.3
0.3964	0.98715	1559	416	−11.8
0.4915	0.97997	1546	426	−14.3
0.6504	0.96703	1529	442	−20.0
0.7048	0.96229	1519	450	−19.2
0.7567	0.95751	1504	461	−14.7
0.8524	0.94833	1487	476	−12.2
1.000	0.93230	1452	508	–

The composition dependent of the V^E and ΔK_s volume were fitted by the method of least squares using the polynomial form,

$$Z = x_1 x_2 \sum_{i=0}^{2} a_i (x_1 - x_2)^i \tag{4}$$

where if Z is the excess volume, the composition is mole fraction, and if Z is deviation in compressibility, the volume fraction is the composition variable are the adjustable parameters obtained by the least squares method and are listed in Tables IV and V along with standard deviation.

The data include in Table II show that V^E values are negative in mixture of N,N-dimethylacetamide with chlorobenzene, bromobenzene, fluorobenzene, nitrobenzene and aniline at 303.15 K. The excess

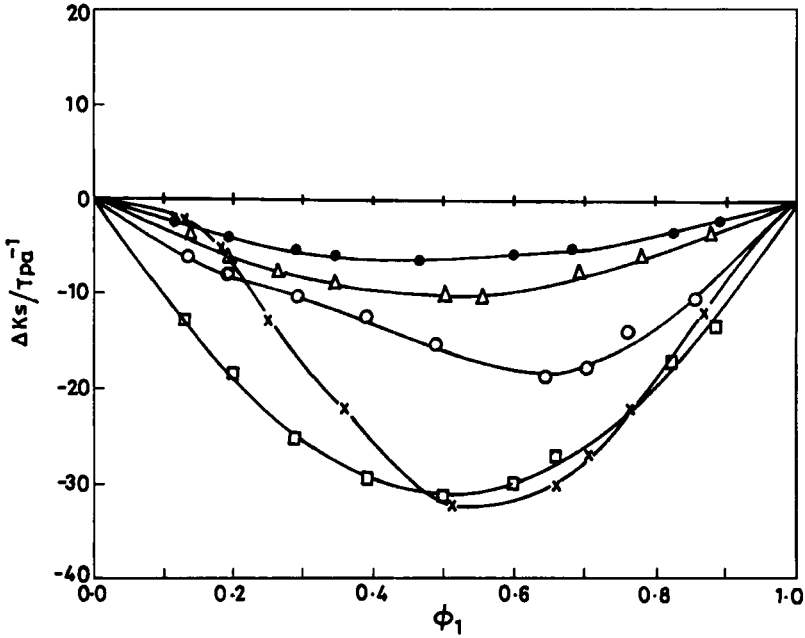

FIGURE 2 Deviation in isentropic compressibilities (ΔK_s) for N,N-dimethylacetamide + fluorobenzene (x); + chlorobenzene (Δ); + bromobenzene (□); + aniline (o), and + nitrobenzene (•) at 303.15 K.

TABLE IV Parameters of Eq. (4) and standard deviation $\sigma(V^E)$ at 303.15 K

System	a_0	a_1 $cm^3 \cdot mol^{-1}$	a_2	$\sigma(V^E)$
N,N-dimethylacetamide (1) + chlorobenzene (2)	−0.9395	0.1716	0.0965	0.004
N,N-dimethylacetamide (1) + bromobenzene (2)	−0.5645	0.2037	0.0836	0.003
N,N-dimethylacetamide (1) + fluorobenzene (2)	−1.6552	0.8699	0.1853	0.005
N,N-dimethylacetamide (1) + nitrobenzene (2)	−0.1449	0.0665	0.0285	0.004
N,N-dimethylacetamide (1) + aniline (2)	02.4368	−0.5961	−0.6072	0.004

volumes are possibly influenced by two effects: (1) expansion in volume because of the loss of dipolar association, and the difference in size and shape of the component molecules (2) contraction in volume

TABLE V Parameters of Eq. (4) and standard deviation $\sigma(\Delta K_s)$ at 303.15 K

System	b_0 (Tpa^{-1})	b_1 (Tpa^{-1})	b_2 (Tpa^{-1})	$\sigma(\Delta K_s)$ (Tpa^{-1})
N,N-dimethylacetamide (1) + chlorobenzene (2)	−40.1	2.4	16.4	0.3
N,N-dimethylacetamide (1) + bromobenzene (2)	−124.4	0.6	10.0	0.5
N,N-dimethylacetamide (1) + fluorobenzene (2)	−127.0	−59.2	123.8	0.4
N,N-dimethylacetamide (1) + nitrobenzene(2)	−26.0	−0.8	5.8	0.1
N,N-dimethylacetamide (1) + aniline (2)	61.6	−31.7	−37.6	1.9

because of dipole–dipole and dipole–induced dipole intiractions. The actual volume of V^E would depend upon the relative strength of the two opposing effects. The experimental results suggest that the later effect is dominent in the present investigation. The V^E values for equimolar mixtures are found to vary in the following order.

nitrobenzene > bromobenzene > chlorobenzene
> fluorobenzene ≃ aniline

Figure 2 indicates that deviation in isentropic compressibilities are negative in all systems. The negative deviations are attributed to dipolar interactions between unlike molecules which lead to increase in free length and decrease in sound velocity. The algebraic values of ΔK_s at equimolar mixtures are found to vary in the following order:

nitrobenzene > chlorobenzene > aniline
> bromobenzene ≃ fluorobenzene

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