Excess Molar Volumes and Speeds of Sound of *N,N*-Dimethylacetamide with Chloroethanes and Chloroethenes at 303.15 K

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Excess molar volumes (V^E) and speeds of sound (u) of the binary liquid mixtures of *N,N*-dimethylacetamide (DMA) with chloroethanes and chloroethenes at 303.15 K have been measured over the entire range of compositions. The chloroethanes are 1,2-dichloroethane, 1,1,1-trichloroethane, and 1,1,2,2-tetrachloroethane, and the chloroethenes are trichloroethene and tetrachloroethene. The V^E values are positive in mixtures of *N,N*-dimethylacetamide with 1,2-dichloroethane and tetrachloroethene. The V^E values are negative over the whole mole fraction range for *N,N*-dimethylacetamide with 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, and trichloroethene. The speed of sound data were used to compute isentropic compressibilities (κ_s) and excess isentropic compressibilities (κ_s^E). The κ_s^E values are positive for the system *N,N*-dimethylacetamide with 1,2-dichloroethane. For the remaining systems, the κ_s^E values are negative over the entire range of compositions.

Introduction

A thorough knowledge of thermodynamic properties of nonelectrolyte solutions is essential in many chemical industrial applications such as design involving chemical separations, heat transfer, mass transfer, and fluid flow. This paper forms part of our program on the measurement of thermodynamic properties of binary liquid mixtures.[1−3] We report here excess molar volumes and excess insentropic compressibilities for *N,N*-dimethylacetamide with 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, trichloroethene, and tetrachloroethene. These data are of interest because of the effect of chlorine the with C═O group present in the *N,N*-dimethylacetamide on the molecular interactions. However, no excess volumes and compressibilities for the mixtures of *N,N*-dimethylacetamide with chloroethanes and chloroethenes appear to have been measured, and there is no evidence of specific interactions between these mixtures. The main purpose of this work is to provide information on the molecular interactions between *N,N*-dimethylacetamide and chloroethanes and chloroethenes from the measurements of V^E and κ_s^E data.

Experimental Section

Procedure. The methods of V^E measurement used in our laboratory have been described previously.[4,5] The V^E values were measured with a dilatometer technique. The V^E values are accurate to ±0.003 cm^3 mol^{-1}. Speed of sound values were measured by a single-crystal ultrasonic interferometer (Mittal Enterprises, model no. M81) at 4 MHz frequency at 303.15 K. These values are accurate to 0.2%. Solutions were prepared by mass. A thermostatically controlled, well-stirred water bath with its temperaure controlled to ±0.01 K was used for all of the measurements.

Table 1. Densities of Pure Components at 303. 15 K

component	ρ/g·cm^{-3} expt	ρ/g·cm^{-3} ref
N,N-dimethylacetamide	0.936 17[a]	0.936 15[a]
1,2-dichloroethane	1.238 43	1.238 47[b]
1,1,1-trichloroethane	1.320 94	1.320 96[b]
1,1,2,2-tetrachloroethane	1.578 57	1.578 60[b]
trichloroethene	1.451 39	1.451 40[c]
tetrachloroethene	1.606 41	1.606 40[c]

[a] Reference 10 at 298.15 K. [b] Reference 8. [c] Reference 9.

The value of κ_s was calculated using the relation

$$\kappa_s = u^{-2}\rho^{-1} \tag{1}$$

$$\rho = \frac{x_1M_1 + x_2M_2}{x_1V_1^0 + x_2V_2^0 + V^E} \tag{2}$$

where u and ρ denote speed of sound and density of the binary mixtures, respectively; x_1 and x_2 denote the mole fractions of components 1 and 2, respectively; V_1^0 and V_2^0 are the molar volumes of the pure components; M_1 and M_2 are the molar masses of components 1 and 2, respectively; and V^E is the excess volume of the binary mixtures. The excess isentropic compressibilities (κ_s^E) were evaluated from the approximated equation[6]

$$\kappa_s^E = \kappa_s - \phi_1\kappa_{s1} - \phi_2\kappa_{s2} \tag{3}$$

where κ_s, κ_{s1}, and κ_{s2} are the isentropic compressibilities of the mixture and the pure components 1 and 2, respectively, and ϕ_1 and ϕ_2 are the volume fractions of the components.

Materials. All of the chemicals used were of analytical grade and were purchased from commercial sources. *N,N*-dimethylacetamide (Sisco Research Laboratory, Bombay, India, 99.5 mol %) was purified by standard methods described by Oswal and Patel.[7] 1,2-Dichloroethane (Fluka), 1,1,1-trichloroethane (Aldrich), and 1,1,2,2-tetrachloro-

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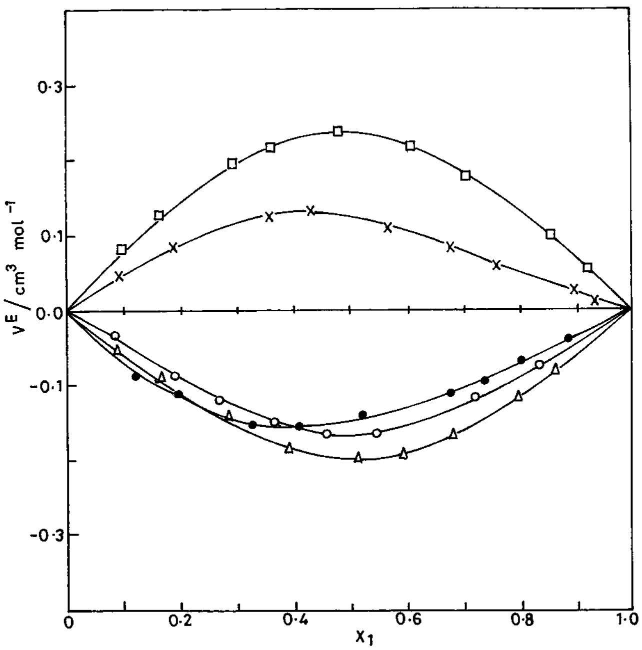

Figure 1. Excess volumes (V^E) as a function of mole fraction (x_1) for N,N-dimethylacetamide (1) with 1,2-dichloroethane (2) (□), 1,1,1-trichloroethane (2) (○), 1,1,2,2-tetrachloroethane (2) (△), trichloroethene (2) (●), and tetrachloroethene (2) (×) at 303.15 K.

Table 2. Excess Molar Volumes for N,N-Dimethylacetamide (1) + Chloroethanes and Chloroethenes (2) at 303.15 K

x_1	V^E (cm^3 mol^{-1})	x_1	V^E (cm^3 mol^{-1})
N,N-dimethylacetamide (1) + 1,2-dichloroethane (2)			
0.0934	0.082	0.6078	0.219
0.1595	0.129	0.7012	0.183
0.2974	0.197	0.8438	0.101
0.3529	0.216	0.9169	0.056
0.4718	0.231		
N,N-dimethylacetamide (1) + 1,1,1-trichloroethane (2)			
0.0814	−0.032	0.5370	−0.165
0.1950	−0.082	0.7205	−0.114
0.2696	−0.118	0.8323	−0.071
0.3636	−0.151	0.9424	−0.01
0.4548	−0.161		
N,N-dimethylacetamide (1) + 1,1,2,2-tetrachloroethane (2)			
0.1183	−0.053	0.5812	−0.192
0.1730	−0.081	0.6736	−0.169
0.2764	−0.139	0.7912	−0.114
0.3810	−0.182	0.8547	−0.080
0.5154	−0.196		
N,N-dimethylacetamide (1) + trichloroethene (2)			
0.1291	−0.091	0.6628	−0.110
0.1864	−0.116	0.7325	−0.096
0.3285	−0.153	0.8024	−0.071
0.4015	−0.155	0.8718	−0.040
0.5187	−0.142		
N,N-dimethylacetamide (1) + tetrachoroethene (2)			
0.0913	0.048	0.6666	0.084
0.1862	0.087	0.7775	0.052
0.3586	0.125	0.8469	0.036
0.4297	0.128	0.9214	0.008
0.5507	0.103		

Table 3. Volume Fraction (ϕ_1) of N,N-Dimethylacetamide and ρ, u, κ_s, and κ_s^E for the Binary Mixtures of N,N-Dimethylacetamide (1) with Chloroethanes and Chloroethenes (2) at 303.15 K

ϕ_1	ρ (g cm^{-3})	u (m s^{-1})	κ_s (TPa^{-1})	κ_s^E (TPa^{-1})
N,N-dimethylacetamide (1) + 1,2-dichloroethane (2)				
0.0000	1.232 81	1173.3	589	
0.1070	1.199 42	1189.0	589	9.1
0.1809	1.176 59	1204.0	586	11.6
0.3301	1.130 96	1234.0	580	17.9
0.3883	1.113 28	1246.0	578	20.5
0.5097	1.076 74	1284.0	563	15.1
0.6433	1.036 89	1325.0	549	11.8
0.7320	1.010 75	1359.0	535	5.3
0.8628	0.972 45	1402.0	523	3.3
0.9277	0.953 42	1425.0	516	1.9
1.0000	0.932 30	1452.0	508	
N,N-dimethylacetamide (1) + 1,1,1-trichloroethane (2)				
0.0000	1.320 96	943.0	851	
0.0814	1.291 91	986.3	795	−29.6
0.1831	1.250 82	1042.6	735	−53.1
0.2545	1.223 47	1078.5	702	−61.4
0.3458	1.188 37	1128.4	660	−71.9
0.4536	1.153 55	1174.9	628	−74.0
0.5176	1.121 67	1215.7	603	−70.7
0.7046	1.048 35	1310.5	555	−54.5
0.8211	1.002 55	1364.8	535	−34.5
0.9380	0.956 52	1419.2	519	−10.9
1.0000	0.932 30	1452.0	508	
N,N-dimetlylacetamide (1) + 1,1,2,2-tetrachloroethane (2)				
0.0000	1.578 60	1133.1	493	
0.1054	1.511 19	1168.1	484	−10.1
0.1552	1.479 30	1187.2	479	−16.2
0.2513	1.418 01	1219.1	474	−22.8
0.3510	1.354 13	1254.2	468	−29.3
0.4831	1.268 85	1295.6	469	−31.3
0.5494	1.225 80	1318.0	470	−32.2
0.6446	1.164 00	1346.7	473	−29.6
0.7690	1.082 84	1385.0	481	−23.7
0.8379	1.037 92	1404.1	488	−17.5
1.0000	0.932 30	1452.0	508	
N,N-dimetlylacetamide (1) + trichloroethene (2)				
0.0000	1.451 40	1013.6	670	
0.1327	1.383 89	1065.9	636	−13.1
0.1912	1.353 83	1091.5	619	−19.6
0.3354	1.279 35	1153.1	587	−28.4
0.4091	1.241 10	1188.3	570	−33.7
0.5266	1.179 83	1236.8	554	−31.2
0.6698	1.104 98	1300.6	535	−27.1
0.7386	1.069 05	1330.6	528	−22.8
0.8073	1.033 07	1360.1	523	−16.6
0.8753	0.997 45	1389.2	519	−09.4
1.0000	0.932 30	1452.0	508	
N,N-dimetlylacetamide (1) + tetrachloroethene (2)				
0.0000	1.606 41	1028.0	589	
0.0833	1.549 47	1067.4	566	−15.9
0.1715	1.489 46	1105.4	549	−25.8
0.3360	1.378 10	1176.8	523	−38.1
0.4054	1.331 32	1206.4	516	−40.4
0.5259	1.250 53	1261.1	502	−44.3
0.6441	1.171 60	1308.1	498	−38.5
0.7597	1.094 17	1354.7	497	−30.0
0.8335	1.044 46	1384.1	499	−30.0
0.9138	0.990 57	1417.8	502	−13.3
1.0000	0.932 30	1452.0	508	

ethane (Fluka) were purified by the method described by Reddy et al.[8] Trichloroethene (BDH) and tetrachloroethene (BDH) were purified by the method described by Venkatesulu et al.[9] The purities of the chemical products were verified by measuring the densities, determined with a bicapillary-type pycnometer of 12-cm^3 capacity, which offers an accuracy of 2 parts in 10^5, and found to be in good agreement with literature values, as can be seen in Table 1. The utmost care was taken to prevent evaporation during the experiments.

Results and Discussion

The measured excess molar volumes, V^E, as a function of mole fraction (x_1) of N,N-dimethylacetamide with 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, trichloroethene, and tetrachloroethene at 303.15

Table 4. Coefficients of Eq 4 and Standard Deviations $\sigma(V^E)$ for the Binary Systems at 303.15 K

system	a_0 ($cm^3\ mol^{-1}$)	a_1 ($cm^3\ mol^{-1}$)	a_2 ($cm^3\ mol^{-1}$)	$\sigma(V^E)$ ($cm^3\ mol^{-1}$)
N,*N*-dimetlylacetamide (1) +				
1,2-dichloroethane (2)	0.9281	−0.1304	−0.1190	0.003
1,1,1-trichloroethane (2)	−0.6706	0.0402	0.4340	0.004
1,1,2,2-tetrachloroethane (2)	−0.7947	−0.0656	−0.4062	0.002
trichloroethene (2)	−0.5934	0.2807	−0.0016	0.003
tetrachloroethene (2)	0.4804	−0.2525	−0.1638	0.004

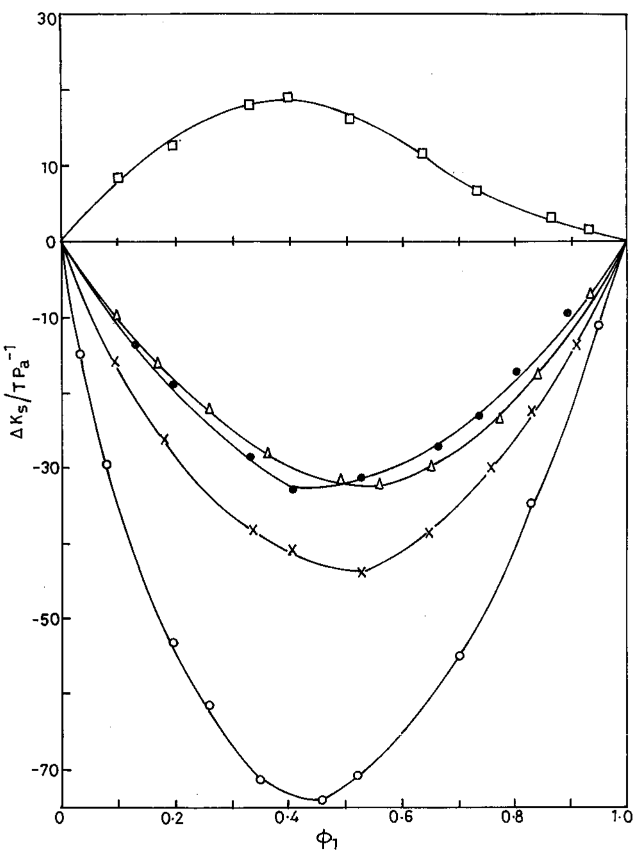

Figure 2. Excess isentropic compressibilities (κ_s^E) as a function of volume fraction (ϕ_1) for *N*,*N*-dimethylacetamide (1) with 1, 2-dichloroethane (2) (□), 1,1,1-trichloroethane (2) (○), 1,1,2,2-tetrachloroethane (2) (△), trichloroethene (2) (●), and tetrachloroethene (2) (×) at 303.15 K.

K are reported in Table 2 and represented graphically in Figure 1. The u, ρ, and κ_s^E values of *N*,*N*-dimethylacetamide with chloroethanes and chloroethenes are listed in Table 3. The κ_s^E values with volume fraction are graphically represented in Figure 2. The V^E values are fitted by the method of least squares using the polynomial

$$V^E = x_1x_2[a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2] \quad (4)$$

where a_0, a_1, and a_2 are the adjustable parameters obtained by the least-squares method and are listed in Table 4, along with the standard deviation $\sigma(V^E)$.

The depencence of κ_s^E on volume fraction has been expressed in polynomial form as

$$\kappa_s^E = \phi_1\phi_2[b_0 + b_1(\phi_1 - \phi_2) + b_2(\phi_1 - \phi_2)^2] \quad (5)$$

where b_0, b_1, and b_2 are constants obtained by the method of least squares and are given in Table 5, along with the standard deviations.

The data included in Table 2 show that the V^E values are positive in mixtures of *N*,*N*-dimethylacetamide with

Table 5. Values of the Parameters of Eq 5 and Standard Deviations $\sigma(\kappa_s^E)$ for the Binary Systems at 303.15 K

system	b_0 ($T\ Pa^{-1}$)	b_1 ($T\ Pa^{-1}$)	b_2 ($T\ Pa^{-1}$)	$\sigma(\kappa_s^E)$ ($T\ Pa^{-1}$)
N,*N*-dimetlylacetamide (1) +				
1,2-dichloroethane (2)	63.3	−43.5	−6.6	1.9
1,1,1-trichloroethlane (2)	−285.2	113.2	−25.4	2
1,1,2,2-tetrachloroethane (2)	−129.4	−9.3	13.8	0.7
trichloroethene (2)	−133.0	15.7	53.6	1
tetrachloroethene (2)	−167.6	18.2	−24.4	1

1,2-dichloroethane and tetrachloroethene over the whole range of compositions. Negative V^E values observed in Table 2 for the mixtures of *N*,*N*-dimethylacetamide with 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, and trichloroethene. The observed values of V^E in all of the systems over the entire range of compositions can be attributed to the following factors: (I) interactions between the unlike molecules, dispersion forces, dipole induced dipole interations; (II) complex formation between unlike molecules; (III) formation of new hydrogen bonds between unlike molecules of the type C−H···π-electron; and (IV) contributions due to size and shape. The experimental results suggest that the first three factors are dominant in the mixtures of *N*,*N*-dimethylacetamide with 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, and tichloroethene, whereas the last factor is dominant in the mixtures of *N*,*N*-dimethylacetamide with 1,2-dichloroethane and tetrachloroethene.

The results in Table 5 show that κ_s^E values are positive for the system of *N*,*N*-dimethylacetamide with 1,2-dichloroethane, whereas the κ_s^E values are negative for the systems of *N*,*N*-dimethylacetamide with 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, trichloroethene, and tetrachloroethene. The negative κ_s^E values can be attributed to the existence of dispersion and dipolar interactions between unlike molecules.

Literature Cited

(1) Venkatesu, P.; Rao, M. V. P. Excess Volumes of Binary Mixtures of Triethylamine with Aromatic Hydrocarbons at 308.15 K. *Fluid Phase Equilib.* **1994**, *93*, 369−376.

(2) Goud, B. B.; Venkatesu, P.; Rao, M. V. P. Excess Volumes of 1,1,2,2-Tetrachloroethane or Tetrachloroethane + 2-Chlorotoluene + 3-Chlorotoluene and 4-Chlorotoluene at 303.15 and 313.15 K. *J. Chem. Eng. Data* **1995**, *40*, 1211−1213.

(3) Venkatesu, P.; Sekhar, G. C.; Rao, M. V. P. Excess Viscosities of Organic Liquid Mixtures of Ethyl Acetate or Butyl Acetate with 2-Alkoxyethanols. *J. T. R. Chem.* **1996**, *3* (2), 50−55.

(4) Rao, M. V. P.; Naidu, P. R. Excess Volumes of Binary Mixtures of Alcohols in Methylcyclohexane. *Can. J. Chem.* **1974**, *52*, 788−790.

(5) Ramadevi, R. S.; Rao, M. V. P. Excess Volumes of Substituted Benzenes with *N*,*N*-Dimethyl Formamide. *J. Chem. Eng. Data* **1995**, *40*, 65−67.

(6) Douheret, G.; Moreau, C.; Viallard, A. Excess Thermodynamic Quantities in Binary Systems of Non Electrolytes. I. Different Ways of Calculating Excess Compressibilities. *Fluid Phase Equilib.* **1985**, *22*, 277−287.

(7) Oswal, S. L.; Patel, N. B. Speed of Sound Isentropic Compressibility, Viscosity, and Excess Volume of Binary Mixtures. 2.

Alkanenitriles + Dimethylformamide + Dimethylacetamide and + Dimethyl Sulfoxide. *J. Chem. Eng. Data* **1995**, *40*, 845−849.
(8) Reddy, K. D.; Iloukhani, H.; Rao, M. V. P. Excess Volumes of Chlorobenzene and Bromobenzene with Some Chloroethanes at 303.15 and 313.15 K. *Fluid Phase Equilib.* **1984**, *17*, 123−130.
(9) Venkatesulu, D.; Venkatesu, P.; Rao, M. V. P. Viscosities and Densities of Trichloroethylene or Tetrachloroethylene with 2-Alkoxyethanols at 303.15 and 313.15 K. *J. Chem. Eng. Data* **1997**, *42*, 365−367.
(10) Davis, M. I.; Hernandez, M. E. Excess Molar Volumes for *N*,*N*-Dimethylacetamide + Water at 25 °C. *J. Chem. Eng. Data* **1995**, *40*, 674−678.

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