Excess Volumes and Speeds of Sound of *N*-Methyl-2-pyrrolidone with Chloroethanes and Chloroethenes at 303.15 K

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

Introduction

In the chemical industry, a knowledge of the thermodynamic properties of nonelectrolyte solutions is essential in the design of processes 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] In this work, we report the molar excess volumes and speeds of sound of mixtures of *N*-methyl-2-pyrrolidone with 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, trichloroethene, and tetrachloroethene at 303.15 K. These data are of interest because of the effect of chlorine and the C═O group present in *N*-methyl-2-pyrrolidone on the molecular interactions. However, no excess volumes or sound velocities had been measured for the above binary liquid mixtures.

Experimental Section

All of the chemicals were of analytical grade. *N*-Methyl-2-pyrrolidone, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, trichloroethene, and tetrachloroethene were purified by the methods described by Reddy et al.[4] The purities of the compounds were checked by measuring the densities with a bicapillary-type pycnometer of 12-cm^3 capacity that offers an accuracy of 2 parts in 10^5, and found to be in good agreement with literature values. The measured densities and speeds of sound reported in the literature are listed in Table 1.

Excess molar volumes were measured directly using the dilatometer technique described by Rao et al.[6] The excess molar volumes are accurate to ±0.003 cm^3 mol^{-1}.

The sound velocities were measured by a single-crystal ultrasonic interferometer at 4-MHz frequency at 303.15 K. These measurements are accurate to 0.2%. A thermostatically controlled, well-stirred water bath with a temperature controlled to (303.15 ± 0.01) K was used for all measurements.

Results and Discussion

The measured excess molar volumes, V^E, as a function of mole fraction (x_1) of *N*-methyl-2-pyrrolidone in 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, trichloroethene, and tetrachloroethene at 303.15 K are reported in Table 2 and represented graphically in Figure 1.

Table 1. Speeds of Sound (u) and Densities (ρ) of Pure Components at 303.15 K

component	u (m s^{-1})		ρ (g cm^{-3})	
	expt	lit	expt	lit
N-methyl-2-pyrrolidone	1551.6	−	1.02340	1.01910[b]
1,2-dichlorethane	1174.0	1173.3[a]	1.23830	1.23847[c]
1,1,1-trichloroethane	944.0	943.0[a]	1.32094	1.32096[c]
1,1,2,2-tetrachloroethane	1135.0	1133.1[a]	1.57858	1.57860[c]
trichloroethene	1012.0	1013.6[a]	1.45120	1.45140[d]
tetrachloroethene	1030.0	1028.0[a]	1.60640	1.60640[d]

[a] Reference 8. [b] Reference 6 at 298.15 K. [c] Reference 4. [d] Reference 7.

The isentropic compressibility (κ_s) was calculated using the relation

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

where u and ρ denote the speed of sound and density of the binary mixture, respectively. The densities of the binary mixtures were computed using the relation

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

where x_1 and x_2 denote the mole fractions, M_1 and M_2 the molar masses, and V_1^0 and V_2^0 the molar volumes 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 calculated from the equation

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

where ϕ_1 and ϕ_2 are the volume fractions and κ_{s1} and κ_{s2} are the isentropic compressibilities of pure components 1 and 2, respectively. The values of ρ, u, κ_s, are κ_s^E are included in Table 3. The variation of κ_s^E with volume fraction is represented graphically in Figure 2.

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Table 2. Excess Molar Volumes for *N*-Methyl-2-pyrrolidone (1) + Chloroethanes and Cloroethenes (2) at 303.15 K

x_1	V^E (cm^3 mol^{-1})	x_1	V^E (cm^3 mol^{-1})
N-methyl-2-pyrrolidone (1) + 1,2-dichloroethane (2)			
0.1576	−0.066	0.6667	−0.088
0.2663	−0.094	0.7997	−0.053
0.3993	−0.116	0.8423	−0.036
0.4548	−0.121	0.9142	−0.015
0.5832	−0.107		
N-methyl-2-pyrrolidone (1) + tetrachloroethene (2)			
0.1462	−0.119	0.6614	−0.219
0.2504	−0.162	0.7148	−0.207
0.3779	−0.199	0.8389	−0.169
0.4321	−0.213	0.9198	−0.101
0.5632	−0.223		
N-methyl-2-pyrrolidone (1) + 1,1,2,2-tetrachloroethane (2)			
0.1208	−0.186	0.6018	−0.392
0.2316	−0.295	0.7312	−0.332
0.3172	−0.352	0.8174	−0.261
0.4209	−0.396	0.9248	−0.129
0.5185	−0.408		
N-methyl-2-pyrrolidone (1) + trichloroethene (2)			
0.1286	−0.258	0.6192	−0.468
0.2213	−0.361	0.7489	−0.412
0.3655	−0.442	0.8660	−0.282
0.4689	−0.471	0.9314	−0.168
0.5247	−0.478		
N-methyl-2-pyrrolidione (1) + 1,1,1-trichloroethane (2)			
0.1528	−0.283	0.6128	−0.586
0.2301	−0.389	0.7023	−0.558
0.3095	−0.461	0.8098	−0.462
0.4019	−0.524	0.9176	−0.260
0.5291	−0.580		

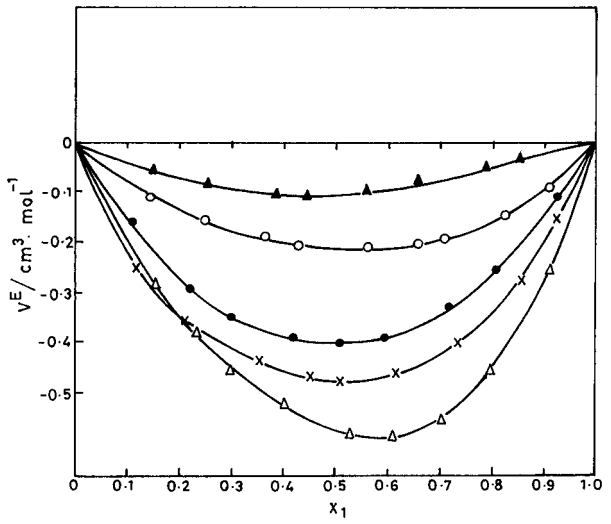

Figure 1. Excess volumes (V^E) as a function of mole fraction (x_1) for *N*-methyl-2-pyrrolidone (1) with (▲) 1,2-dichloroethane (2), (△) 1,1,1-trichloroethane (2), (●) 1,1,2,2-tetrachloroethane (2), (×) trichloroethene (2), (○) and tetrachloroethene (2) at 303.15 K.

The data included in Table 2 show that the V^E values are negative for all the mixtures investigated over the entire mole fraction range. The measured negative V^E data indicate that the effects leading to a contraction in volume are dominant over the effects leading to an expansion in volume and that the dipolar interactions between unlike components are dominant. The V^E values were fitted by the method of least squares using the polynomial

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

Table 3. Volume Fraction (ϕ_1) of *N*-Methyl-2-pyrrolidone (l), ρ, u, κ_s, and κ_s^E for the Binary Mixtures of *N*-Methyl-2-pyrrolidone 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-methyl-2-pyrrolidone (1) + 1,2-dichloroethane (2)				
0.0000	1.23830	1174.0	585	−
0.1848	1.19953	1203.0	576	23
0.3055	1.17394	1225.0	567	36
0.4462	1.14394	1263.0	548	42
0.5027	1.13181	1280.6	538	43
0.6290	1.10442	1332.0	510	37
0.7079	1.08720	1373.0	487	29
0.8287	1.06080	1447.0	450	13
0.8662	1.05255	1470.0	439	9
0.9281	1.03900	1510.0	422	3
1.0000	1.02340	1551.6	405	−
N-methyl-2-pyrrolidone (1) + 1,l,1-trichloroethane (2)				
0.0000	1.32094	944.0	849	−
0.1474	1.28074	992.0	793	−9
0.2227	1.25954	1041.2	732	−18
0.3006	1.23720	1085.4	686	−30
0.3919	1.21067	1139.0	636	−38
0.5186	1.17356	1217.0	575	−44
0.6028	1.14847	1268.0	541	−40
0.6935	1.12102	1327.0	506	−35
0.8032	1.08706	1397.2	471	−21
0.9143	1.05168	1472.0	438	−5
1.0000	1.02340	1551.6	405	−
N-methyl-2-pyrrolidole (1) + 1,1,2,2-tetrachloroethane (2)				
0.0000	1.57858	1135.0	491	−
0.1112	1.51950	1174.0	477	−4
0.2154	1.46312	1216.0	462	−11
0.2973	1.41832	1250.0	451	−14
0.3983	1.36268	1296.0	436	−20
0.4952	1.30891	1336.0	428	−21
0.5972	1.26189	1367.6	423	−18
0.7124	1.18698	1419.0	418	−12
0.8030	1.13573	1454.0	416	−6
0.9180	1.07030	1507.0	411	−1
1.0000	1.02340	1551.6	405	−
N-methyl-2-pyrrolidone (1) + trichloroethene (2)				
0.0000	1.45120	1012.0	672	−
0.1363	1.39680	1052.0	646	10
0.2331	1.35678	1080.0	631	21
0.3813	1.29423	1134.2	600	29
0.4857	1.24968	1179.0	575	32
0.5415	1.22578	1208.6	558	30
0.6349	1.18542	1262.0	529	26
0.7613	1.13036	1348.8	486	16
0.8736	1.08062	1435.2	449	9
0.9355	1.05278	1488.6	428	5
1.0000	1.02340	1551.6	405	−
N-methyl-2-pyrrolidone (1) + tetrachloroethene (2)				
0.0000	1.60640	1030.0	586	−
0.1384	1.52766	1095.0	546	−15
0.2386	1.46961	1149.6	514	−28
0.3630	1.39749	1220.0	480	−40
0.4165	1.36644	1252.2	466	−44
0.5474	1.29010	1325.4	441	−46
0.6470	1.23192	1372.0	431	−38
0.7016	1.19985	1402.0	424	−35
0.8301	1.12438	1458.0	418	−18
0.9149	1.07408	1502.0	412	−8
1.0000	1.02340	1551.6	405	−

where x_1 and x_2 are the mole fractions of components 1 and 2, respectively. 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 V^E values for equimolar mixtures were found to vary in the order 1,2-dichloroethane > tetrachloroethene > 1,1,2,2-tetrachloroethane > trichloroethene > 1,1,1-trichloroethane. Figure 2 indicates that the excess isentropic

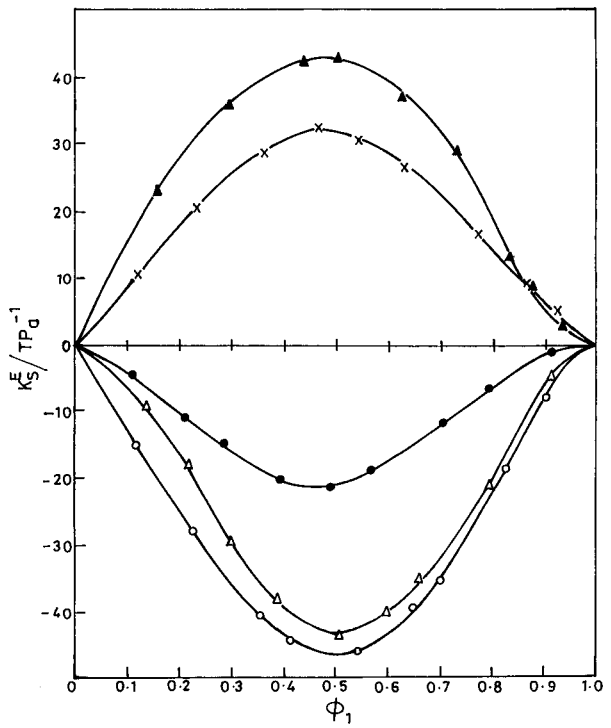

Figure 2. Excess isentropic compressibilities (κ_s^E) as a function of volume fraction (ϕ_1) for *N*-methyl-2-pyrrolidone (1) with (▲) 1,2-dichloroethane (2), (△) 1,1,1-trichloroethane (2), (●) 1,1,2,2-tetrachloroethane (2), (×) trichloroethene (2), (○) and tetrachloroethene (2) at 303.15 K.

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

system	a_0 / $cm^3 \cdot mol^{-1}$	a_1 / $cm^3 \cdot mol^{-1}$	a_2 / $cm^3 \cdot mol^{-1}$	$\sigma(V^E)$ / $cm^3 \cdot mol^{-1}$
N-methyl-2-pyrrolidone (1) +				
1,2-dichloroethane (2)	−0.4703	0.1535	0.1986	0.002
1,1,1-trichloroethane (2)	−2.2798	−0.6678	0.8349	0.003
1,1,2,2-tetrachloroethane (2)	−1.6165	−0.0436	0.2733	0.002
trichloroethene (2)	−1.9002	−0.1142	0.8546	0.003
tetrachloroethene (2)	−0.8676	−0.2124	0.4660	0.003

compressibilities are negative in the mixtures of *N*-methyl-2-pyrrolidone with 1,1,2,2-tetrachloroethane, 1,1,1-trichloroethane, and tetrachloroethene over the entire volume fraction range at 303.15 K. The dependence of κ_s^E on volume fraction was expressed in polynomial form as

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

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

system	b_0 / TPa^{-1}	b_1 / TPa^{-1}	b_2 / TPa^{-1}	$\sigma(\kappa_s^E)$ / TPa^{-1}
N-methyl-2-pyrrolidone (1) +				
1,2-dichloroethane (2)	177.6	−40.1	−129.9	0.5
1,1,1-trichloroethane (2)	−176.8	−23.5	183.1	1.2
1,1,2,2-tetrachloroethane (2)	−80.3	14.3	82.5	0.8
trichloroethene (2)	121.3	−5.9	−58.1	1.6
tetrachloroethene (2)	−182.9	3.6	114.4	0.8

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 κ_s^E values are positive for the mixtures of *N*-methyl-2-pyrrolidone with trichloroethene and 1,2-dichloroethane over the whole volume fraction range.

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