Excess Volumes of *N*,*N*-Dimethylformamide with Ketones at 303.15 K

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Excess volumes, V^E, of binary liquid mixtures of *N*,*N*-dimethylformamide with methyl propyl ketone, diethyl ketone, methyl isobutyl ketone, methyl isopropyl ketone, and cyclohexanone at 303.15 K have been measured with a dilatometer. Excess volumes are negative for the systems of *N*,*N*-dimethylformamide with methyl propyl ketone, diethyl ketone, methyl isobutyl ketone, and methyl isopropyl ketone and are positive for *N*,*N*-dimethylformamide with cyclohexanone at 303.15 K.

Introduction

This paper forms part of our program on the measurement of thermodynamic properties of nonelectrolyte solutions (Venkatesu and Rao, 1994; Goud et al., 1995). We report in this paper excess volumes, V^E, for *N*,*N*-dimethylformamide with methyl ethyl ketone, methyl propyl ketone, diethyl ketone, methyl isobutyl ketone, methyl isopropyl ketone, and cyclohexanone at 303.15 K. The aim of this work is to provide information on the molecular interactions between ketones and *N*,*N*-dimethylformamide from measurements of excess volumes.

Experimental Procedure

Apparatus. Excess volumes were measured directly using the dilatometer technique described earlier (Rao and Naidu, 1974; Ramadevi and Rao, 1995). The excess volumes are accurate to ± 0.003 $cm^3 \cdot mol^{-1}$. A thermostatically controlled, well-stirred water bath with temperature controlled to ± 0.01 K was used for all the measurements.

Materials. All the chemicals used were of analytical grade. *N*,*N*-Dimethylformamide was purified by the method described previously (Venkatesu et al., 1994). All the ketones were further purified by the methods described by Venkateswarlu and Raman (1985). The purities of the samples were checked by comparing the measured densities of the compounds with those reported in the literature (Dharmaraju et al., 1982; Rao and Reddy, 1985; Rintelene et al., 1937). Densities of pure components were determined with a bicapillary type pycnometer, which offers an accuracy of 2 parts in 10^5. The measured densities and those reported in the literature are listed in Table 1.

Table 1. Densities (ρ) of Pure Components at 303.15 K

component	ρ/g·cm^{-3} exptl	ρ/g·cm^{-3} lit.
N,*N*-dimethylformamide	0.941 18	0.941 20 (1985)
methyl propyl ketone	0.796 53	0.796 60 (1982)
diethyl ketone	0.804 58	0.804 61 (1982)
methyl isobutyl ketone	0.796 07[a]	0.796 10[a] (1982)
methyl isopropyl ketone	0.805 18	0.805 20 (1937)
cyclohexanone	0.937 58	0.937 57 (1982)

[a] At 298.15 K.

Results and Discussion

The experimental excess volumes for binary mixtures of *N*,*N*-dimethylformamide with methyl ethyl ketone, methyl propyl ketone, diethyl ketone, methyl isobutyl ketone, methyl isopropyl ketone, and cyclohexanone at 303.15 K are reported in Table 2 and graphically represented in Figure 1. The V^E values are fitted by the method of least squares using the polynomial

$$V^E = x_1x_2[a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2] \qquad (1)$$

where x_1 and x_2 are the mole fractions of components 1 and 2, respectively. a_1, a_2, and a_3 are the adjustable parameters

Table 2. Excess Volumes (V^E) for the Binary Mixtures of *N*,*N*-Dimethylformamide (1) with Ketones (2) at 303.15 K

x_1	V^E/cm^3·mol^{-1}	x_1	V^E/cm^3·mol^{-1}
N,*N*-Dimethylformamide (1) + Methyl Propyl Ketone (3)			
0.1242	−0.079	0.5523	−0.181
0.2195	−0.119	0.6252	−0.169
0.3312	−0.156	0.7134	−0.147
0.4025	−0.172	0.8325	−0.098
0.5174	−0.179	0.9147	−0.051
N,*N*-Dimethylformamide (1) + Diethyl Ketone (2)			
0.1440	−0.100	0.6540	−0.197
0.1957	−0.133	0.7694	−0.167
0.3324	−0.183	0.8618	−0.115
0.4195	−0.201	0.9227	−0.074
0.5508	−0.213		
N,*N*-Dimethylformamide (1) + Methyl Isobutyl Ketone (2)			
0.1556	−0.144	0.6662	−0.253
0.2665	−0.215	0.7615	−0.218
0.3061	−0.231	0.8897	−0.130
0.4299	−0.268	0.9328	−0.086
0.5339	−0.272		
N,*N*-Dimethylformamide (1) + Methyl Isopropyl Ketone (2)			
0.1303	−0.133	0.6007	−0.293
0.2193	−0.201	0.7125	−0.254
0.3178	−0.263	0.7649	−0.226
0.4002	−0.295	0.8526	−0.159
0.5175	−0.309	0.9314	−0.082
N,*N*-Dimethylformamide (1) + Cyclohexanone (2)			
0.1342	0.064	0.5849	0.126
0.2048	0.085	0.6425	0.119
0.3268	0.115	0.7580	0.092
0.4213	0.128	0.8249	0.072
0.5214	0.132	0.9098	0.044

Table 3. Binary Parameters of Eq 1 and Standard Deviation $\sigma(V^E)$ at 303.15 K

	cm^3·mol^{-1}			
N,*N*-dimethylformamide (1) +	a_0	a_1	a_2	$\sigma(V^E)$
methyl propyl ketone (2)	−0.7220	0.0141	0.0528	0.003
diethyl ketone (2)	−0.8361	−0.0733	−0.1839	0.003
methyl isobutyl ketone (2)	−1.0895	−0.1180	−0.2281	0.003
methyl isopropyl ketone (2)	−1.2270	−0.0612	−0.0078	0.003
cyclohexanone (2)	0.5290	−0.0136	−0.0232	0.002

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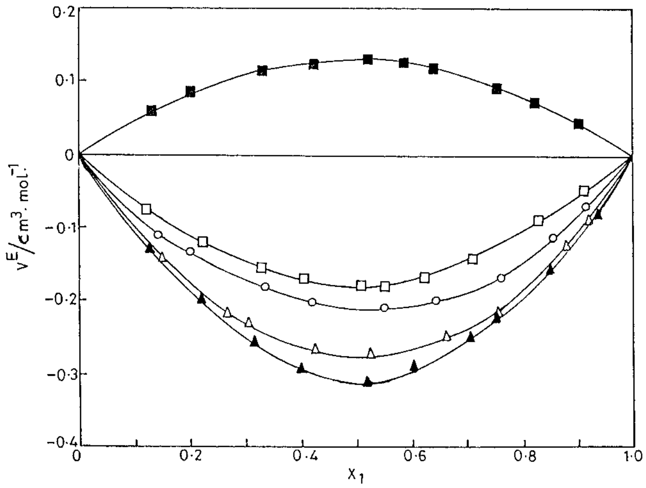

Figure 1.

obtained by the least squares method and are listed in Table 3 along with the standard deviation $\sigma(V^E)$.

The excess volumes are negative for the systems of *N*,*N*-dimethylformamide with methyl propyl ketone, diethyl ketone, methyl isobutyl ketone, and methyl isopropyl ketone at 303.15 K. The negative V^E data indicate dipole−dipole interactions between the unlike components which leads to contraction in volume. The observed V^E data for *N*,*N*-dimethylformamide with cyclohexanone are positive at 303.15 K. The positive V^E data contribute to an expansion in volume.

The values of V^E for equimolar mixtures are found to vary in the following order: cyclohexanone > methyl propyl ketone > diethyl ketone > methyl isobutyl ketone > methyl isopropyl ketone.

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