Excess Volumes of *N*,*N*-Dimethylformamide + Cyclohexanone + 1-Alkanols at 303.15 K

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Volume changes on mixing of ternary liquid mixtures of *N*,*N*-dimethylformamide and cyclohexanone with 1-alkanols have been measured as a function of composition at 303.15 K. The alkanols include 1-propanol, 1-butanol, 1-pentanol, and 1-hexanol. The ternary excess volumes were measured directly using a dilatometer. The measured data were compared with predicted values based upon an empirical relation.

Introduction

A thorough knowledge of thermodynamic properties of multicomponent liquid systems is essential in many industrial applications such as design calculation, heat transfer, mass transfer, fluid flow, etc. As a continuation of our research program of determining the thermodynamic properties of ternary liquid mixtures (Venkatesu et al., 1994; Venkatesu and Rao, 1994; Venkatesu et al., 1996), we report here the excess volumes of ternary mixtures containing *N*,*N*-dimethylformamide and cyclohexanone with 1-propanol, 1-butanol, 1-pentanol, and 1-hexanol at 303.15 K. The measured data are compared with those predicted using the Redlich−Kister relation. A survey of the literature reveals no studies of V^{E}_{123} for these mixtures.

Experimental Procedure

Apparatus. Excess volumes for ternary mixtures were measured with a three-limbed dilatometer described by Naidu and Naidu (1981). The mixing cell contained three bulbs of different capacities. Mercury was used to separate three components. One of the three bulbs was fitted with a capillary, and the other two were fitted with ground-glass stoppers. Each bulb of the dilatometer was filled with a component whose mass was determined directly by weighing. The filled dilatometer was placed in a thermostat which could be maintained to (303.15 ± 0.01) K. All the measurements were made at constant temperature employing a thermostat. The measured V^{E}_{123} values were accurate to ±0.003 $cm^3 \cdot mol^{-1}$.

Materials. All the chemicals used were of analytical grade and purchased from commercial sources. *N*,*N*-Dimethylformamide was purified by the method described by Ramadevi and Rao (1995). Cyclohexanone was purified by the method described by Venkateswarlu and Raman (1985). The 1-alkanols were further purified by the methods described by Rao and Naidu (1974). The purities of the samples were checked by comparing the measured densities of the components with those reported in the literature (Riddick et al., 1986; Rao and Reddy, 1985). Densities were determined with a bicapillary-type pycnometer, of capacity 12 cm^3, which offers an accuracy of 2 parts in 10^5. In Table 1, we compare the measured densities of the chemicals with literature values.

Results and Discussion

The measured excess volume data for the ternary mixtures are listed in Table 2. Binary V^E parameters for *N*,*N*-dimethylformamide with 1-alkanols (Rao and Reddy, 1985) and cyclohexanone with 1-alkanols (Rao and Naidu, 1976) were taken from the literature. Further, the binary V^E parameters for the system *N*,*N*-dimethylformamide with cyclohexanone, also computed from the V^E data, have been already published in our earlier paper (Venkatesu and Rao, 1996). The least-squares parameters for all these binary systems are reported in Table 3 along with standard deviations.

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[a]
cyclohexanone	0.937 58	0.937 61[a]
1-propanol	0.796 01	0.796 00[b]
1-butanol	0.802 03	0.802 06[b]
1-pentanol	0.807 61	0.807 64[b]
1-hexanol	0.812 03	0.812 01[b]

[a] Riddick et al. (1986). [b] Rao and Reddy (1985).

The dependence of experimental ternary excess volumes V^{E}_{123}(exp) on composition is expressed by the polynomial

$$V^{E}_{123}(\text{exp}) = V^{E}_{123}(\text{b}) + x_1x_2x_3[A + Bx_1(x_2 - x_3) + Cx^2_1(x_2 - x_3)^2] \quad (1)$$

where $V^{E}_{123}(\text{b}) = V^{E}_{12} + V^{E}_{13} + V^{E}_{23}$ and x_1, x_2, and x_3 are the mole fractions of *N*,*N*-dimethylformamide, cyclohexanone, and an alkanol. *A*, *B*, and *C* are ternary constants and their values obtained by the least-squares method are given in Table 4 along with the standard deviations.

The excess volumes for the ternary mixtures are positive for all the systems, except at a lower mole fraction of *N*,*N*-dimethylformamide in the system *N*,*N*-dimethylformamide + cyclohexanone + 1-propanol. These positive values suggest that the structure-breaking effect of the components is dominant in the mixtures. The data included in Table 2 show that V^{E}_{123} increases with an increase in the chain length of 1-alkanols. This may be due to the steric effect of 1-alkanols. A comparison between the positive excess volumes in the present data with negative excess volume data reported (Venkatesu et al., 1994) for ternary mixtures suggests a radical difference between an aliphatic ketone and a cyclic ketone. It is concluded that the structure-making effect dominates in systems containing an aliphatic ketone compared to systems with a cyclic ketone. Hence negative excess volumes are observed in ternary mixtures *N*,*N*-dimethylformamide + methyl ethyl ketone + 1-alkanols. Analysis of the data indicates the

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Table 2. Experimental Excess Volumes of Ternary Mixtures of *N,N*-Dimethylformamide (1) + Cyclohexanone (2) + 1-Alkanols (3) at 303.15 K

x_1	x_2	V^E_{123}(exp)/cm^3·mol^{-1}	V^E_{123}/cm^3·mol^{-1} (Redlich−Kister)	ΔV^E_{123}[a] cm^3·mol^{-1}
		N,N-Dimethylformamide (1) + Cyclohexanone (2) + 1-Propanol (3)		
0.1232	0.1029	−0.021	−0.030	0.009
0.1514	0.7272	0.063	0.041	0.022
0.2129	0.6453	0.076	0.053	0.023
0.2314	0.1214	−0.012	−0.025	0.013
0.3125	0.1514	−0.004	−0.017	0.013
0.3314	0.3228	0.080	0.016	0.064
0.3549	0.5143	0.098	0.077	0.021
0.4249	0.1418	0.025	0.008	0.017
0.4441	0.4135	0.103	0.081	0.022
0.5413	0.3158	0.098	0.066	0.032
0.5439	0.1449	0.031	0.003	0.028
0.6334	0.2513	0.087	0.062	0.025
0.6312	0.1613	0.055	0.021	0.034
0.7049	0.2108	0.076	0.060	0.016
0.7514	0.1514	0.056	0.038	0.018
0.8218	0.1214	0.049	0.037	0.012
0.8416	0.0912	0.034	0.023	0.011
0.9028	0.0491	0.015	0.009	0.006
		N,N-Dimethylformamide (1) + Cyclohexanone (2) + 1-Butanol (3)		
0.1021	0.1312	0.018	0.001	0.017
0.1413	0.7376	0.056	0.036	0.020
0.2214	0.6356	0.084	0.059	0.025
0.2419	0.1420	0.053	0.025	0.028
0.3014	0.1026	0.056	0.031	0.025
0.3445	0.1624	0.084	0.039	0.045
0.3629	0.5221	0.119	0.092	0.027
0.4132	0.1328	0.076	0.041	0.035
0.4429	0.4220	0.121	0.091	0.030
0.5242	0.3258	0.118	0.083	0.035
0.5359	0.1494	0.084	0.046	0.038
0.6035	0.2412	0.105	0.069	0.036
0.6325	0.1523	0.078	0.045	0.033
0.7132	0.2001	0.085	0.066	0.019
0.7498	0.1482	0.064	0.048	0.016
0.8042	0.1421	0.066	0.051	0.015
0.8418	0.0824	0.036	0.024	0.012
0.9054	0.0501	0.022	0.015	0.007
		N,N-Dimethylformamide (1) + Cyclohexanone (2) + 1-Pentanol (3)		
0.0982	0.1028	0.054	0.042	0.012
0.1328	0.7528	0.076	0.060	0.016
0.2289	0.6422	0.117	0.092	0.025
0.2384	0.1382	0.115	0.090	0.025
0.3122	0.1286	0.135	0.107	0.028
0.3326	0.1782	0.152	0.111	0.041
0.3438	0.5128	0.154	0.117	0.037
0.4412	0.1220	0.151	0.121	0.030
0.4028	0.4686	0.159	0.123	0.036
0.5133	0.3287	0.164	0.124	0.040
0.5228	0.1282	0.149	0.119	0.030
0.6240	0.2381	0.143	0.112	0.031
0.6185	0.1325	0.136	0.108	0.028
0.7082	0.1889	0.118	0.096	0.022
0.7254	0.1224	0.108	0.087	0.021
0.8125	0.1126	0.082	0.066	0.016
0.8257	0.0786	0.071	0.060	0.011
0.9026	0.0524	0.041	0.036	0.005
		N,N-Dimethylformamide (1) + Cyclohexanone (2) + 1-Hexanol (3)		
0.0824	0.0762	0.083	0.073	0.010
0.1628	0.1282	0.140	0.124	0.016
0.1532	0.7418	0.133	0.121	0.012
0.2385	0.6284	0.176	0.154	0.022
0.2247	0.1380	0.173	0.149	0.024
0.3028	0.1486	0.204	0.177	0.027
0.3245	0.5246	0.208	0.175	0.033
0.4252	0.1388	0.234	0.203	0.031
0.4316	0.4483	0.206	0.178	0.028
0.5244	0.3246	0.221	0.189	0.032
0.5329	0.1242	0.236	0.211	0.025
0.6132	0.2336	0.215	0.186	0.029
0.6259	0.1025	0.221	0.205	0.016
0.7125	0.1754	0.178	0.159	0.019
0.7256	0.1044	0.189	0.175	0.014
0.8047	0.1136	0.137	0.126	0.011
0.8346	0.0628	0.136	0.127	0.009
0.9004	0.0560	0.076	0.074	0.002

[a] $\Delta E^E_{123} = V^E_{123}(\text{exp}) - V^E_{123}(\text{b})$, where $V^E_{123}(\text{b})$ is the excess volume calculated from the Redlich−Kister relation.

Table 3. Values of Binary Constants and the Standard Deviation $\sigma(V^E)$ at 303.15 K

system[a]	a_0	a_1	a_2	$\sigma(V^E)$
	$cm^3 \cdot mol^{-1}$			
N,*N*-dimethylformamide (1) + cyclohexanone (2)	0.5290	−0.0136	−0.0232	0.002
N,*N*-dimethylformamide (1) + 1-propanol (3)	−0.1273	−0.0890	−0.1073	0.002
N,*N*-dimethylformamide (1) + 1-butanol (3)	0.1028	−0.1582	−0.2298	0.003
N,*N*-dimethylformamide (1) + 1-pentanol (3)	0.4808	−0.0900	−0.1486	0.004
N,*N*-dimethylformamide (1) + 1-hexanol (3)	0.7821	0.3731	0.1616	0.001
cyclohexanone (2) + 1-propanol (3)	−0.2372	0.1238	−0.0118	0.002
cyclohexanone (2) + 1-butanol (3)	−0.1470	−0.0794	−0.1077	0.004
cyclohexanone (2) + 1-hexanol (3)	0.4838	0.1269	0.1143	0.006

[a] The experimental binary V^E data reported are within the experimental error (Rao and Naidu, 1976) for the mixture of cyclohexanone (2) + 1-pentanol (3) and are not shown in the table.

Table 4. Values of Ternary Constants *A*, *B*, and *C* and $\sigma(\Delta V^E_{123})$ at 303.15 K

N,*N*-dimethylformamide (1) + cyclohexanone (2) +	$cm^3 \cdot mol^{-1}$			
	A	*B*	*C*	$\sigma(\Delta V^E_{123})$
1-propanol (3)	1.967	1.977	−77.96	0.004
1-butanol (3)	2.055	−0.534	−44.13	0.004
1-pentanol (3)	1.805	0.609	−31.00	0.003
1-hexanol (3)	1.576	0.246	−30.82	0.003

agreement between measured V^E_{123} and those calculated from the Redlich−Kister relation is satisfactory in all ternary systems.

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