Excess Volumes of Ternary Mixtures of *N,N*-Dimethylformamide + Methyl Ethyl Ketone + 1-Alkanols at 303.15 K

P. Venkatesu, D. Venkatesulu, and M. V. Prabhakara Rao*

Department of Chemistry, S. V. University College, Tirupati 517 502, Andhra Pradesh, India

Excess volumes for four ternary mixtures have been measured at 303.15 K. The mixtures are *N,N*-dimethylformamide + methyl ethyl ketone + 1-propanol, + 1-butanol, + 1-pentanol, or + 1-hexanol. Excess volumes are negative for *N,N*-dimethylformamide + methyl ethyl ketone + 1-propanol and *N,N*-dimethylformamide + methyl ethyl ketone + 1-butanol over the entire range of composition. The measured ternary excess volume exhibits inversion in sign in the mixtures containing 1-pentanol and 1-hexanol. The measured data are compared with those predicted by empirical equations.

Introduction

We report here new experimental excess volume data for four ternary mixtures. The mixtures included *N,N*-dimethylformamide and methyl ethyl ketone as common components and 1-propanol, 1-butanol, 1-pentanol, and 1-hexanol as noncommon components. The measured excess volumes have been compared with those predicted from binary data with use of semiempirical equations (*1*).

Experimental Procedure

Excess volumes for ternary mixtures were measured with the dilatometer described by Naidu and Naidu (*2*). 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 full dilatometer was placed in a thermostat that could be maintained to ±0.01 K. All the measurements were made at constant temperature employing a thermostat. The measured V^E values were accurate to ±0.003 $cm^3 \cdot mol^{-1}$.

Purification of Materials

All the chemicals used were of analytical grade. *N,N*-dimethylformamide was kept overnight over freshly ignited quick lime and distilled under reduced pressure. The middle fraction of the distillate was collected and kept over solid potassium hydroxide pellets for 24 h. It was then distilled under reduced pressure. Methyl ethyl ketone was purified by the methods described by Reddy and Naidu (*3*). The alcohols were further purified by the methods described by Rao and Naidu (*4*). The purities of the samples were checked by comparing the measured densities of the compounds with those reported in the literature (*5*, *6*). Densities were determined with a bicapillary-type pycnometer, which offers an accuracy of 2 parts in 10^5. The purities of the samples were further confirmed by GLC single sharp peaks. The measured densities and those reported in the literature are given in Table 1.

* To whom correspondence should be addressed.

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

component	ρ/(g·cm^{-3}) exptl	lit. (*5*, *6*)
N,N-dimethylformamide	0.941 18	0.941 20
methyl ethyl ketone	0.794 50	0.794 52
1-propanol	0.796 01	0.796 00
1-butanol	0.802 03	0.802 06
1-pentanol	0.807 61	0.807 64
1-hexanol	0.812 03	0.812 01

Table 2. Excess Volumes V^E for *N,N*-Dimethylformamide (1) + Methyl Ethyl Ketone (*2*) at 303.15 K

x_1	V^E/(cm^3·mol^{-1})	x_1	V^E/(cm^3·mol^{-1})	x_1	V^E/(cm^3·mol^{-1})
0.1627	−0.188	0.3883	−0.298	0.7413	−0.250
0.2683	−0.259	0.5345	−0.310	0.8503	−0.175
0.3509	−0.289	0.6087	−0.300	0.8969	−0.134

Results and Discussion

Redlich and Kister (*7*) proposed an expression for the excess volumes of a ternary mixture:

$$V^E_{123} = \sum_{i<j} V^E_{ij}(x_i, x_j) \tag{1}$$

where

$$V^E_{ij} = x_i x_j \sum_{s=0}^{n} (As)_{ij}(x_i - x_j)^s \tag{2}$$

and x_i and x_j are the mole fractions of the components in the ternary mixture.

Kohler Expression (*8*):

$$V^E_{123} = (x_1 + x_2)^2 V^E_{12} + (x_1 + x_3)^2 V^E_{13} + (x_2 + x_3)^2 V^E_{23} \tag{3}$$

where

$$V^E_{ij} = x_i' x_j' \sum_{s=0}^{n} (As)_{ij}(x_i' - x_j')^s \tag{4}$$

at composition (x_i', x_j'), such that

$$x_i' = 1 - x_j' = \frac{x_i}{(x_i + x_j)}$$

where x_i and x_j are the ternary mole fractions.

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

system	a_0/(cm³·mol⁻¹)	a_1/(cm³·mol⁻¹)	a_2/(cm³·mol⁻¹)	σV^E/(cm³·mol⁻¹)
N,*N*-dimethylformamide[a] (1) + methyl ethyl ketone (2)	−1.2412	0.0047	−0.3105	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
methyl ethyl ketone (2) + 1-propanol (3)	−0.1709	0.0122	0.0118	0.001
methyl ethyl ketone (2) + 1-butanol (3)	0.0598	0.0283	0.0156	0.002
methyl ethyl ketone (2) + 1-pentanol (3)	0.1615	0.0662	−0.0960	0.004
methyl ethyl ketone (2) + 1-hexanol (3)	0.3133	0.0051	0.1721	0.002

[a] Present study.

Table 4. Experimental Excess Molar Volumes of Ternary Mixtures of *N*,*N*-Dimethylformamide (1) + Methyl Ethyl Ketone (2) + 1-Alkanol (3) at 303.15 K

x_1	x_2	V^E_{123}(exptl)/(cm³·mol⁻¹)	V^E_{123}/(cm³·mol⁻¹) Reddlich–Kister	Kohler	Taso–Smith	ΔV^E_{123}[a]/(cm³·mol⁻¹)
N,*N*-Dimethylformamide (1) + Methyl Ethyl Ketone (2) + 1-Propanol (3)						
0.0934	0.1153	−0.049	−0.038	−0.038	−0.043	−0.011
0.2049	0.1360	−0.080	−0.066	−0.066	−0.073	−0.014
0.3081	0.1218	−0.092	−0.079	−0.085	−0.085	−0.013
0.3795	0.1399	−0.115	−0.101	−0.102	−0.106	−0.014
0.4983	0.0968	−0.104	−0.097	−0.109	−0.100	−0.007
0.5678	0.1288	−0.147	−0.129	−0.135	−0.132	−0.018
0.6306	0.1122	−0.148	−0.127	−0.137	−0.129	−0.021
0.7182	0.1081	−0.145	−0.134	−0.140	−0.136	−0.011
0.7732	0.1285	−0.153	−0.156	−0.164	−0.158	0.003
N,*N*-Dimethylformamide (1) + Methyl Ethyl Ketone (2) + 1-Butanol (3)						
0.1011	0.1571	−0.015	−0.006	−0.007	−0.010	−0.009
0.1809	0.1759	−0.024	−0.019	−0.021	−0.024	−0.005
0.2849	0.1499	−0.012	−0.028	−0.029	−0.029	0.016
0.3863	0.1741	−0.055	−0.061	−0.063	−0.057	0.006
0.4338	0.1477	−0.043	−0.060	−0.063	−0.052	0.017
0.5331	0.1440	−0.081	−0.086	−0.092	−0.074	0.005
0.5898	0.1506	−0.118	−0.109	−0.117	−0.096	−0.010
0.6659	0.1381	−0.134	−0.123	−0.132	−0.109	−0.011
0.7894	0.1271	−0.147	−0.145	−0.150	−0.136	−0.002
N,*N*-Dimethylformamide (1) + Methyl Ethyl Ketone (2) + 1-Pentanol (3)						
0.1027	0.1538	0.017	0.026	0.024	0.022	−0.009
0.1887	0.1418	0.027	0.038	0.035	0.032	−0.011
0.2988	0.1422	0.031	0.039	0.035	0.039	−0.008
0.3861	0.1305	0.030	0.035	0.031	0.038	−0.005
0.4524	0.1245	0.021	0.027	0.020	0.032	−0.006
0.5553	0.1090	0.003	0.011	0.005	0.021	−0.008
0.6330	0.1256	−0.051	−0.035	−0.042	−0.022	−0.016
0.7227	0.1367	−0.106	−0.092	−0.098	−0.076	−0.014
0.8069	0.1303	−0.125	−0.127	−0.132	−0.116	0.002
N,*N*-Dimethylformamide (1) + Methyl Ethyl Ketone (2) + 1-Hexanol (3)						
0.0782	0.1660	0.054	0.066	0.066	0.067	−0.012
0.1632	0.2178	0.044	0.067	0.065	0.068	−0.023
0.2974	0.2042	0.045	0.063	0.062	0.068	−0.018
0.3870	0.1426	0.095	0.090	0.088	0.099	+0.005
0.4791	0.1457	0.070	0.077	0.075	0.087	−0.007
0.5505	0.1521	0.033	0.051	0.052	0.063	−0.018
0.6287	0.1441	−0.003	0.028	0.029	0.041	−0.031
0.6790	0.1304	−0.008	0.020	0.020	0.033	−0.028
0.7649	0.1397	−0.080	−0.060	−0.059	−0.048	−0.020

[a] $\Delta V^E_{123} = V^E_{123}$(exptl) − V^E_{123}(b), where V^E_{123}(b) is the excess volume calculated from the Redlich–Kister equation (1).

Table 5. Values of Ternary Constants *A*, *B*, and *C* and $\sigma\Delta V^E$ at 303.15 K

system	*A*/(cm³·mol⁻¹)	*B*/(cm³·mol⁻¹)	*C*/(cm³·mol⁻¹)	$\sigma\Delta V^E$/(cm³·mol⁻¹)
N,*N*-dimethylformamide (1) + methyl ethyl ketone (2) + 1-propanol (3)	−0.30	17.02	108	0.003
N,*N*-dimethylformamide (1) + methyl ethyl ketone (2) + 1-butanol (3)	−0.56	6.47	133	0.003
N,*N*-dimethylformamide (1) + methyl ethyl ketone (2) + 1-pentanol (3)	−0.71	11.52	115	0.003
N,*N*-dimethylformamide (1) + methyl ethyl ketone (2) + 1-hexanol (3)	−1.86	−10.30	38	0.003

Tsao–Smith Expression (*9*):

$$V^E_{123} = x_2(1-x_1)^{-1}V^E_{12} + x_3(1-x_1)^{-1}V^E_{13} + (1-x_1)V^E_{23} \quad (5)$$

where V^E_{12}, V^E_{13}, and V^E_{23} are the binary excess volumes at composition (x_1', x_2') such that $x_1' = x_1$ for 1 + 2 and 1 + 3 binary systems and $x_2' = x_2/(x_2 + x_3)$ for the 2 + 3 binary system.

Binary V^E parameters for *N*,*N*-dimethylformamide with 1-alcohols (*10*) and methyl ethyl ketone with 1-alcohols (*3*) were taken from the literature. Further, the binary V^E

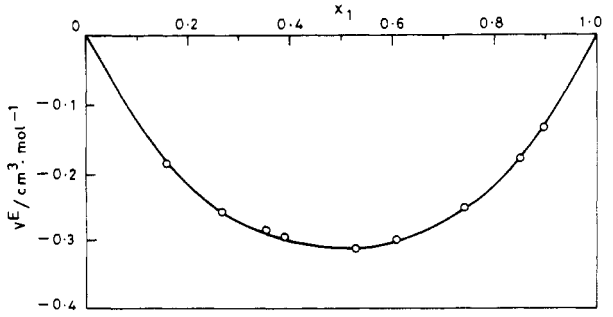

Figure 1. Excess volume (V^E) as a function of x_1 for *N*,*N*-dimethylformamide (1) + methyl ethyl ketone (2) at 303.15 K.

parameters for the system *N*,*N*-dimethylformamide with methyl ethyl ketone were also computed from the V^E data measured in the present investigation. These experimental excess volume data are given in Table 2 and are graphically represented in Figure 1. The least-squares parameters for all these binary systems are given in Table 3. The excess volume results for the four ternary mixtures are given in Table 4.

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

$$V^E_{123}(\text{exptl}) = V^E_{123}(\text{b}) + x_1x_2x_3(A + Bx_1(x_2 - x_3)) + Cx_1^2(x_2 - x_3)^2 \quad (6)$$

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, methyl ethyl ketone, and an alcohol. *A*, *B*, and *C* are ternary constants, and their values obtained by the least-squares method are given in Table 5.

The excess volumes for the binary mixture *N*,*N*-dimethylformamide + methyl ethyl ketone are negative over the entire range of composition at 303.15 K. This can be explained by (i) dipolar dissociation in pure components and (ii) dipolar interaction between unlike components. The first factor contributes to an expansion in volume, and the second factor contributes to a decrease in volume. The negative values indicate that the dipolar interaction between unlike components is dominant.

The excess volumes for the ternary mixtures are negative over the entire range of composition in the mixtures of *N*,*N*-dimethylformamide + methyl ethyl ketone + 1-propanol and *N*,*N*-dimethylformamide + methyl ethyl ketone + 1-butanol at 303.15 K. The negative V^E suggests that the factors influencing structure-making effects are dominant in these mixtures. The measured ternary excess volumes exhibit an inversion in sign in the mixtures containing 1-pentanol and 1-hexanol with an increase in the concentration of *N*,*N*-dimethylformamide at 303.15 K.

A close examination of the results and those predicted by empirical equations shows that all the equations predict V^E_{123} values that are in satisfactory agreement with the measured V^E_{123} data in all the mixtures.

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