Excess Volumes of Ternary Mixtures of 1,2-Dichlorobenzene and Methyl Ethyl Ketone as Common Components and 1-Alkanols at 303.15 K

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Excess volumes for four ternary mixtures were measured at 303.15 K. The mixtures included 1,2-dichlorobenzene and methyl ethyl ketone as common components. 1-Propanol, 1-butanol, 1-pentanol, and 1-hexanol were noncommon components. Excess volumes are negative over the entire range of composition in the four mixtures. The measured data were compared with those predicted by empirical equations.

Introduction

Hwang et al. (*1*) have recently developed a semiempirical equation that includes contributions from both two-body and three-body interactions. It has been shown that the expression satisfactorily predicts ternary free energies of several aqueous-organic systems. Recently Acree and Naidu (*2*) extended the semiempirical relation to excess volumes of six ternary mixtures and noted that the equation gives a satisfactory estimate of the excess property. We report here new experimental excess volume data for four ternary mixtures, and the data are compared with those predicted by the new semiempirical expression (*1*) and also those by the Redlich-Kister equation (*3*).

Experimental Procedure

Excess volumes for ternary systems were measured with the dilatometer described by Naidu and Naidu (*4*). The mixing cell contained three bulbs of different capacities. Mercury was used in the bottom to separate three components. One of the three bulbs was fitted with a capillary, and the other two were fitted with ground-glass stoppers. Four dilatometers of the aforesaid types were used to cover the entire range of composition. All the measurements were made at constant temperature employing a thermostat that could be maintained to ±0.01 K. The measured V^E values were accurate to ±0.003 $cm^3\ mol^{-1}$.

Purification of Materials. All the chemicals used were of analytical grade. 1,2-Dichlorobenzene, methyl ethyl ketone, and 1-alcanols were purified by the methods described by Reddick and Bunger (*5*). 1,2-Dichlorobenzene (Merck) was passed through alumina in a 30 × 2 cm column and fractionally distilled. Methyl ethyl ketone (S.D. Fine Chemicals) was dried over potassium carbonate for 3 days and then boiled for 2 h and distilled. 1-Propanal (S.D. Fine Chemicals) and 1-butanol (S.D. Fine Chemicals) were refluxed over freshly ignited calcium oxide for 6 h and distilled by employing a fractionating column. 1-Pentanol (Merck) and 1-hexanol (Merck) were dried over Drierite and fractionally distilled. The purity of the sample was 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 measured densities and those reported in the literature are given in Table I.

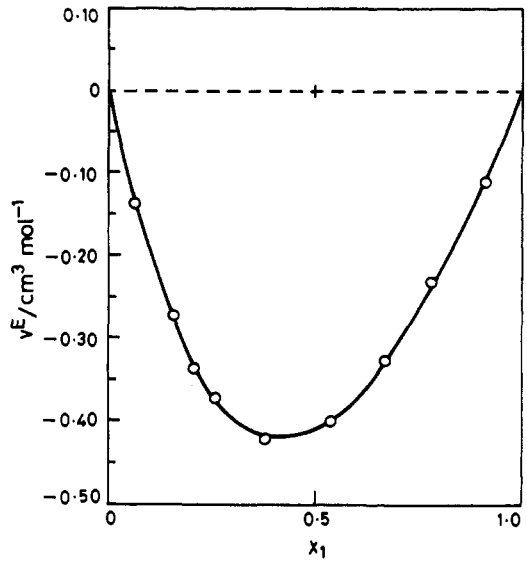

Figure 1. Excess volume (V^E) plotted against the mole fraction of 1,2-dichlorobenzene (x_1) with methyl ethyl ketone at 303.15 K.

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

component	ρ/(g·cm^{-3}) lit. (*5*, *6*)	ρ/(g·cm^{-3}) present study
1,2-dichlorobenzene	1.299 22	1.299 20
methyl ethyl ketone	0.794 52	0.794 57
1-propanol	0.796 00	0.796 02
1-butanol	0.802 06	0.802 03
1-pentanol	0.807 64	0.807 64
1-hexanol	0.812 01	0.812 05

Table II. Excess Volumes (V^E) for 1,2-Dichlorobenzene (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})
0.0656	−0.136	0.2643	−0.372	0.6692	−0.325
0.1587	−0.272	0.3781	−0.419	0.7836	−0.228
0.2131	−0.333	0.5358	−0.399	0.9062	−0.109

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Table III. Binary Parameters Obtained by the Method of Least Squares Using the Redlich–Kister Equation

system	a_0/(cm³·mol⁻¹)	a_1/(cm³·mol⁻¹)	a_2/(cm³·mol⁻¹)
1,2-dichlorobenzene (1) + methyl ethyl ketone (2) + 1-propanol (3)			
1,2-dichlorobenzene (1) + methyl ethyl ketone (2)	−1.6321	0.5602	−0.1223
1,2-dichlorobenzene (1) + 1-propanol (3)	−0.1687	1.0945	−0.3017
methyl ethyl ketone (2) + 1-propanol (3)	−0.1709	0.0122	0.0118
1,2-dichlorobenzene (1) + methyl ethyl ketone (2) + 1-butanol (3)			
1,2-dichlorobenzene (1) + methyl ethyl ketone (2)	−1.6321	0.5602	−0.1223
1,2-dichlorobenzene (1) + 1-butanol (3)	−0.4557	0.8071	0.3557
methyl ethyl ketone (2) + 1-butanol (3)	0.0598	0.0283	0.0156
1,2-dichlorobenzene (1) + methyl ethyl ketone (2) + 1-pentanol (3)			
1,2-dichlorobenzene (1) + methyl ethyl ketone (2)	−1.6321	0.5602	−0.1223
1,2-dichlorobenzene (1) + 1-pentanol (3)	−0.5347	0.8027	0.2762
methyl ethyl ketone (2) + 1-pentanol (3)	0.1615	0.0662	−0.0960
1,2-dichlorobenzene (1) + methyl ethyl ketone (2) + 1-hexanol (3)			
1,2-dichlorobenzene (1) + methyl ethyl ketone (2)	−1.6321	0.5602	−0.1223
1,2-dichlorobenzene (1) + 1-hexanol (3)	−0.5565	0.8476	0.1454
methyl ethyl ketone (2) + 1-hexanol (3)	0.3133	0.0051	0.1721

Table IV. Binary Parameters Obtained by Using the Hwang et al. Equation (Equation 4)

system	$V_0(ij)$/(cm³·mol⁻¹)	$V_1(ij)$/(cm³·mol⁻¹)	$V_2(ij)$/(cm³·mol⁻¹)
1,2-dichlorobenzene (1) + methyl ethyl ketone (2) + 1-propanol (3)			
1,2-dichlorobenzene (1) + methyl ethyl ketone (2)	−1.5910	0.5034	−0.8310
1,2-dichlorobenzene (1) + 1-propanol (3)	−0.0682	0.9000	−1.7046
methyl ethyl ketone (2) + 1-propanol (3)	−0.1744	0.0282	0.0007
1,2-dichlorobenzene (1) + methyl ethyl ketone (2) + 1-butanol (3)			
1,2-dichlorobenzene (1) + methyl ethyl ketone (2)	−1.5910	0.5034	−0.8310
1,2-dichlorobenzene (1) + 1-butanol (3)	−0.5744	1.4368	−0.4864
methyl ethyl ketone (2) + 1-butanol (3)	0.0552	0.0530	−0.0147
1,2-dichlorobenzene (1) + methyl ethyl ketone (2) + 1-pentanol (3)			
1,2-dichlorobenzene (1) + methyl ethyl ketone (2)	−1.5910	0.5034	−0.8310
1,2-dichlorobenzene (1) + 1-pentanol (3)	−0.5842	1.0615	−0.6664
methyl ethyl ketone (2) + 1-pentanol (3)	0.1891	−0.0359	−0.1969
1,2-dichlorobenzene (1) + methyl ethyl ketone (2) + 1-hexanol (3)			
1,2-dichlorobenzene (1) + methyl ethyl ketone (2)	−1.5910	0.5034	−0.8310
1,2-dichlorobenzene (1) + 1-hexanol (3)	−0.6049	1.2034	−0.8148
methyl ethyl ketone (2) + 1-hexanol (3)	0.2559	0.2342	0.2241

Results and Discussion

Redlich and Kister (*3*) proposed the following equation for binary excess volume data:

$$V^{E(12)} = x_1x_2(a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2 \quad (1)$$

where x_1 and x_2 denote mole fractions of components 1 and 2 and a_0, a_1, and a_2 are the constants. The equation, when extended to a ternary mixture, takes the form

$$V^{E(123)} = x_1x_2x_3(a_0 + a_1x_1(x_2 - x_3) + a_2x_1^2(x_2 - x_3)^2) \quad (2)$$

Hwang et al. (*1*) developed the relation

$$A^{E(12)} = G^{E(12)} = x_1x_2(a_0 + a_1x_1^3 + a_2x_2^3) \quad (3)$$

where $A^{E(12)}$ or $G^{E(12)}$ represents an excess thermodynamic property. x_1 and x_2 denote the mole fractions of components 1 and 2. a_0, a_1, and a_2 are the constants for binary mixtures, taking into account two-body and three-body interactions.

Acree and Naidu (*2*) adopted the equation for excess volume in the following form:

$$V^{E(12)} = x_1x_2(a_0 + a_1x_1^3 + a_2x_2^3) \quad (4)$$

These workers also extended the predictive approach to ternary excess volume and employed the equation

$$V^{E(123)} = x_1x_2(V_0^{(12)} + V_1^{(12)}x_1^3 + V_2^{(12)}x_2^3) + x_1x_3(V_0^{(13)} + v_1^{(13)}x_1^3 + V_3^{(13)}x_3^3) + x_2x_3(V_0^{(23)} + V_2^{(23)}x_2^3 + V_3^{(23)}x_3^3) \quad (5)$$

to predict the ternary V^E data on the basis of binaries.

We analyze here V^E data of four ternary mixtures in terms of eq 5. Binary V^E parameters for 1,2-dichlorobenzene with 1-alcanols and methyl ethyl ketone with 1-alcanols were taken from the literature (*7–9*). Further, the binary V^E parameters for the system 1,2-dichlorobenzene 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 II and are graphically represented in Figure 1. All these binary parameters are included in Table III. The V coefficients in eq 5 were computed from the smoothed binary experimental data at mole fractions x_i = 0.2, 0.5, and 0.8. The values of the V coefficients are given in Table IV.

The experimental V^E data for the mixtures and those predicted by Redlich–Kister and Hwang et al. are given in columns 3, 4, and 5 of Table V, respectively. Further, the differences between measured and computed data are also included in columns 6 and 7 of Table V.

The binary parameters computed on the basis of the Redlich–Kister equation for the mixture of 1,2-dichlorobenzene with methyl ethyl ketone were calculated, and the constants obtained were

$$a_0 = -1.6321 \quad a_1 = 0.5602 \quad a_2 = -0.1223$$

Values of V^E at 0.2, 0.5, and 0.8 mole fractions were then estimated using the Redlich–Kister equation:

$$V^{E(12)} = x_1x_2(a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2)$$

The values of V^E thus computed were then substituted in

Table V. Experimental and Predicted Excess Molar Volumes for 1,2-Dichlorobenzene (1) + Methyl Ethyl Ketone (2) + 1-Alkanols (3) at 303.15 K

x_1	x_2	$V^{E(123)}$(exptl)/ ($cm^3 \cdot mol^{-1}$)	$V^{E(123)}$(Redlich–Kister)/ ($cm^3 \cdot mol^{-1}$)	$V^{E(123)}$(Hwang et al.)/ ($cm^3 \cdot mol^{-1}$)	$\Delta V^{E(123)}$(Redlich–Kister)[a]/ ($cm^3 \cdot mol^{-1}$)	$\Delta V^{E(123)}$(Hwang et al.)[b]/ ($cm^3 \cdot mol^{-1}$)
			1,2-Dichlorobenzene (1) + Methyl Ethyl Ketone (2) + 1-Propanol (3)			
0.1624	0.0644	−0.215	−0.145	−0.132	−0.070	−0.083
0.1597	0.1545	−0.269	−0.149	−0.125	−0.120	−0.144
0.1114	0.2649	−0.232	−0.136	−0.110	−0.096	−0.122
0.1194	0.3026	−0.248	−0.144	−0.116	−0.104	0.132
0.1259	0.4552	−0.267	−0.165	−0.138	−0.102	−0.129
0.1261	0.5071	−0.267	−0.171	−0.147	−0.096	−0.120
0.1490	0.6023	−0.294	−0.207	−0.176	−0.087	−0.118
0.1732	0.7172	−0.319	−0.259	−0.250	−0.060	−0.069
0.1087	0.8431	−0.219	−0.200	−0.198	−0.019	−0.021
			1,2-Dichlorobenzene (1) + Methyl Ethyl Ketone (2) + 1-Butanol (3)			
0.1994	0.0716	−0.235	−0.134	−0.130	−0.101	−0.105
0.1711	0.1239	−0.224	−0.125	−0.118	−0.099	−0.106
0.1253	0.2220	−0.170	−0.103	−0.095	−0.067	−0.075
0.1314	0.2832	−0.186	−0.113	−0.102	−0.073	−0.084
0.1435	0.3875	−0.186	−0.134	−0.123	−0.052	−0.063
0.1375	0.4869	−0.176	−0.144	−0.133	−0.032	−0.043
0.1369	0.5713	−0.178	−0.160	−0.149	−0.018	−0.029
0.1914	0.7363	−0.292	−0.281	−0.274	−0.011	−0.018
0.1299	0.7931	−0.217	−0.211	−0.207	−0.006	−0.010
			1,2-Dichlorobenzene (1) + Methyl Ethyl Ketone (2) + 1-Pentanol (3)			
0.2040	0.0919	−0.149	−0.148	−0.138	−0.001	−0.011
0.1576	0.2678	−0.213	−0.126	−0.109	−0.087	−0.104
0.1497	0.3704	−0.246	−0.126	−0.108	−0.120	−0.138
0.0856	0.4976	−0.163	−0.073	−0.059	−0.090	−0.104
0.1468	0.5896	−0.289	−0.162	−0.148	−0.127	−0.141
0.1776	0.6659	−0.332	−0.227	−0.215	−0.105	−0.117
0.1933	0.7488	−0.327	−0.284	−0.279	−0.043	−0.048
0.1041	0.8659	−0.204	−0.190	−0.189	−0.014	−0.015
			1,2-Dichlorobenzene (1) + Methyl Ethyl Ketone (2) + 1-Hexanol (3)			
0.2367	0.1043	−0.220	−0.152	−0.145	−0.068	−0.075
0.1967	0.1826	−0.223	−0.129	−0.119	−0.094	−0.104
0.1571	0.3047	−0.201	−0.102	−0.090	−0.099	−0.111
0.1467	0.4025	−0.199	−0.101	−0.089	−0.098	−0.110
0.1088	0.4871	−0.149	−0.072	−0.060	−0.077	−0.089
0.1367	0.5641	−0.199	−0.119	−0.108	−0.080	−0.091
0.1470	0.5971	−0.217	−0.141	−0.131	−0.076	−0.086
0.1822	0.6717	−0.273	−0.215	−0.209	−0.058	−0.064
0.1143	0.8093	−0.194	−0.172	−0.170	−0.022	−0.024

[a] $\Delta V^{E(123)} = V^{E(123)}$(exptl) − $V^{E(123)}$(Redlich–Kister). [b] $\Delta V^{E(123)} = V^{E(123)}$(exptl) − $V^{E(123)}$(Hwang et al.).

the equation of Hwang et al. at mole fractions 0.2, 0.5, and 0.8:

$$V^{E(12)} = x_1 x_2 (V_0 + V_1 x_1^3 + V_2 x_2^3)$$

The three unknown equations was then solved to estimate the values of V_0, V_1, and V_2.

An examination of the results included in Table V shows that the newly proposed equation predicts correctly the sign of the excess function in all the mixtures. However, the equation gives a rough estimate of the excess function in the quantitative sense. Further, the data predicted by the new equation are comparable to those of the Redlich–Kister relation.

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