Molar Excess Volumes of Binary and Ternary Mixtures Containing Chloroaniline

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Molar excess volumes, V^E, for *m*-chloroaniline + benzene, + toluene, + *o*-xylene, + *m*-xylene, and + *p*-xylene, *m*-chloroaniline + benzene + toluene, and *m*-chloroaniline + benzene + *o*-xylene have been measured as a function of composition at 308.15 K. V^E values for the binary mixtures are negative for all the systems over the entire range of composition and for an equimolar composition vary in the order *o*-xylene > toluene > *m*-xylene > benzene > *p*-xylene. On the other hand while V^E values for *m*-chloroaniline + benzene + toluene are negative over the whole composition range, those for *m*-chloroaniline + benzene + *o*-xylene vary from positive to negative depending on the mole fraction of each of the components.

Introduction

A binary mixture is formed by the replacements of like contacts in the pure state by unlike contacts in the mixture. Consequently if interactions in a ternary $i + j + k$ mixture are closely dependent on the interactions in $i + j$, $j + k$, and $k + i$ mixtures, then it appears that it should be possible to predict V^E_{ijk} values of ternary mixture from the corresponding data for constituent binary mixtures.

Experimental Section

m-Chloroaniline (Aldrich, purris-quality with a stated purity of >99 mol %) was used without further purification. Benzene (Ranbaxy, analytical reagent grade) was purified (*1*) of thiophene by shaking it with 15% of its volume of concentrated sulfuric acid. It was then shaken with 10% sodium carbonate solution, washed with distilled water, dried over anhydrous calcium chloride, and then fractionally distilled and stored over sodium wire. Toluene, *o*-xylene, and *m*-xylene (Ranbaxy, analytical reagent grade) were purified in the same manner as described for benzene except that during shaking with concentrated sulfuric acid the temperature was kept below 30 °C (*1*) by occasional cooling. The purities of the purified compounds were checked by measuring their densities at 298.15 + 0.01 K, and these agreed to within $\pm 5 \times 10^{-5}$ g cm^{-3} with their corresponding literature values (*2-5*) as reported in Table 1.

Molar excess volumes for binary and ternary mixtures were measured in a V-shaped dilatometer explained elsewhere (*6*). The temperature of the water thermostat was controlled to 0.01 K. The change in the level of the liquid in the dilatometer was measured by a cathetometer with a precision of ±0.001 cm. The uncertainty in our measured V^E values is 0.003 cm^3 mol^{-1} at the worst.

Results and Discussion

The molar excess volumes V^E for various binary and ternary mixtures are given in Tables 2 and 3 and plotted in Figures 1 and 2. The V^E values for binary mixtures were fitted to the equation

$$V^E/(\text{cm}^3\cdot\text{mol}^{-1}) = x_1x_2[\sum_{n=0}^{2} A(n)(x_1 - x_2)^n] \qquad (1)$$

where x_1 is the mole fraction of component 1 and $A(n)$ (n = 0-2) are parameters that were evaluated by the method of least squares. The values are recorded together with the standard deviation $\sigma(V^E)$ of V^E defined by

$$\sigma(V^E) = \{[\sum(V^E - V^E(\text{calcd})]/(m - n)\}^{0.5} \qquad (2)$$

where V^E is the experimentally measured value of V^E and V^E(calcd) is the value calculated from eq 1, m is the number of experimental values, and n is the number of adjustable parameters in eq 1, in Table 2.

Table 1. Densities at 298.15 K

material	density/(gm·cm^{-3}) present work	density/(gm·cm^{-3}) lit.	material	density/(gm·cm^{-3}) present work	density/(gm·cm^{-3}) lit.
benzene	0.873 75	0.873 72 (*2*)	*p*-xylene	0.856 70	0.856 73 (*4*)
toluene	0.862 21	0.862 24 (*3*)	*m*-xylene	0.860 01	0.859 99 (*4*)
o-xylene	0.875 85	0.875 83 (*3*)	*m*-chloroaniline	1.216 03[a]	1.216 06 (*5*)

[a] At 293.15 K.

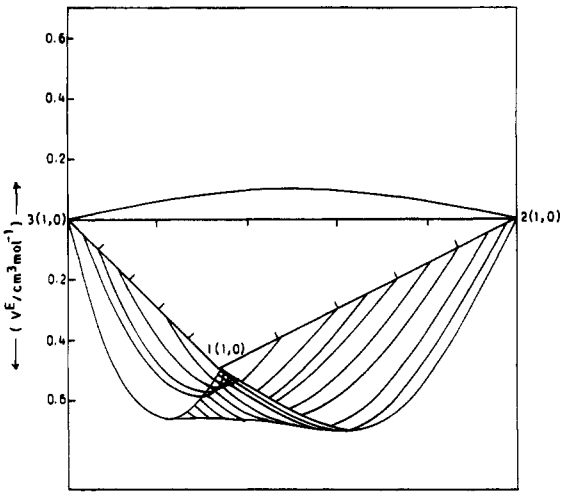

Figure 1. Molar excess volumes, V^E, of the *m*-chloroaniline (1) + benzene (2) + toluene (3) mixture at 308.15 K.

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Table 2. Molar Excess Volumes of Binary Systems and Parameters in Equation 1 Along with Standard Deviations $\sigma(V^E)$ at 308.15 K

x_1	$V^E/(cm^3 \cdot mol^{-1})$	x_1	$V^E/(cm^3 \cdot mol^{-1})$
	m-Chloroaniline (1) + Benzene (2)		
0.0724	−0.101	0.5568	−0.439
0.1842	−0.262	0.5913	−0.417
0.2846	−0.376	0.6748	−0.349
0.4246	−0.460	0.7591	−0.253
0.4861	−0.464	0.8346	−0.160
0.5124	−0.459	0.9125	−0.067
	$A(0) = -1.834$, $A(1) = 0.416$, $A(2) = 0.929$		
	$\sigma(V^E) = 0.002$ cm^3 mol^{-1}		
	m-Chloroaniline (1) + Toluene (2)		
0.0852	−0.131	0.4736	−0.401
0.1452	−0.208	0.5826	−0.385
0.2207	−0.281	0.6518	−0.352
0.2884	−0.335	0.7415	−0.291
0.3915	−0.387	0.8352	−0.207
0.4382	−0.393	0.9216	−0.106
	$A(0) = -1.591$, $A(1) = 0.112$, $A(2) = 0.033$		
	$\sigma(V^E) = 0.002$ cm^3 mol^{-1}		
	m-Chloroaniline (1) + *o*-Xylene (2)		
0.1216	−0.094	0.5358	−0.227
0.2439	−0.168	0.5886	−0.226
0.2926	−0.183	0.6473	−0.209
0.3374	−0.200	0.7154	−0.191
0.4186	−0.213	0.8206	−0.142
0.4627	−0.229	0.9127	−0.076
	$A(0) = -0.912$, $A(1) = -0.052$, $A(2) = 0.030$		
	$\sigma(V^E) = 0.002$ cm^3 mol^{-1}		
	m-Chloroaniline (1) + *p*-Xylene (2)		
0.0935	−0.204	0.5441	−0.597
0.1978	−0.392	0.6528	−0.516
0.2684	−0.495	0.7246	−0.437
0.3215	−0.550	0.7851	−0.353
0.3924	−0.595	0.8752	−0.209
0.4836	−0.610	0.9358	−0.107
	$A(0) = -2.439$, $A(1) = 0.368$, $A(2) = 0.471$		
	$\sigma(V^E) = 0.003$ cm^3 mol^{-1}		
	m-Chloroaniline (1) + *m*-Xylene (2)		
0.0825	−0.064	0.5524	−0.432
0.1574	−0.151	0.6235	−0.403
0.2251	−0.237	0.7234	−0.315
0.3241	−0.345	0.8240	−0.190
0.3975	−0.404	0.8857	−0.111
0.4870	−0.439	0.9448	−0.048
	$A(0) = -1.760$, $A(1) = -0.101$, $A(2) = 1.203$		
	$\sigma(V^E) = 0.002$ cm^3 mol^{-1}		

Molar excess volumes for ternary $i + j + k$ mixtures were expressed (7) as

$$V^E_{ijk} = x_i x_j[\sum_{n=0}^{2} A_{ij}(n)\,(x_i - x_j)^n] + x_j x_k[\sum_{n=0}^{2} A_{jk}(n)\,(x_j - x_k)^n] + x_k x_i[\sum_{n=0}^{2} A_{ki}(n)\,(x_k - x_i)^n] + x_i x_j x_k[\sum_{n=0}^{2} A_{ijk}(n)\,(x_j - x_k)^n x_i^n] \quad (3)$$

where x_i and x_j are the mole fractions of the ith and jth components in the $i + j + k$ mixture and $A_{ijk}(n)$ (n = 0–2) etc. are the parameters characteristic of the $i + j + k$ mixture. The parameters $A_{jk}(n)$ for $j + k$ binary mixtures were taken from the literature (8). The parameters in eq 3 were evaluated by fitting X data to

$$X = A_{ijk}(0) + A_{ijk}(1)\,(x_j - x_k)x_i + A_{ijk}(2)\,(x_j - x_k)^2 x_i \quad (4)$$

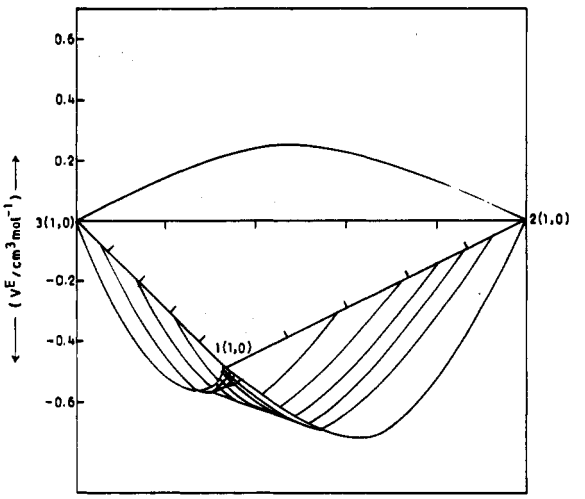

Figure 2. Molar excess volumes, V^E, of the *m*-chloroaniline (1) + benzene (2) + *o*-xylene (3) mixture at 308.15 K.

Table 3. Molar Excess Volumes of Ternary Systems and Parameters Along with Standard Deviations $\sigma(V^E)$ at 308.15 K

x_1	x_2	$V^E/(cm^3 \cdot mol^{-1})$	x_1	x_2	$V^E/(cm^3 \cdot mol^{-1})$
		m-Chloroaniline (1) + Benzene (2) + Toluene (3)			
0.0370	0.0959	−0.031	0.2892	0.5178	−0.242
0.0530	0.9390	−0.069	0.3850	0.3008	−0.278
0.0612	0.1662	−0.044	0.4302	0.4001	−0.313
0.0728	0.6612	−0.023	0.5208	0.0812	−0.359
0.1034	0.7889	−0.105	0.5691	0.2550	−0.300
0.1425	0.5301	−0.085	0.6421	0.3021	−0.316
0.1602	0.6128	−0.123	0.6817	0.1231	−0.273
0.1830	0.7202	−0.204	0.7228	0.1419	−0.238
0.1856	0.1532	−0.186	0.7468	0.2018	−0.299
0.2210	0.4492	−0.162	0.7889	0.0912	−0.199
		$A_{123}(0) = 2.500$, $A_{123}(1) = 7.207$, $A_{123}(2) = -1.730$			
		$\sigma(V^E) = 0.002$ cm^3 mol^{-1}			
		m-Chloroaniline (1) + Benzene (2) + *o*-Xylene (3)			
0.0162	0.9064	0.032	0.4212	0.0912	−0.244
0.0430	0.5506	0.167	0.4982	0.0754	−0.258
0.0446	0.6623	0.136	0.5106	0.4006	−0.359
0.0630	0.2629	0.071	0.5817	0.2822	−0.306
0.0721	0.7128	0.050	0.6206	0.1702	−0.261
0.1399	0.1214	−0.074	0.6923	0.1721	0.260
0.1530	0.5830	−0.052	0.7108	0.0506	−0.206
0.2569	0.0105	−0.175	0.7817	0.0312	−0.169
0.3127	0.2889	−0.199	0.8006	0.0818	−0.158
0.3652	0.4574	−0.282	0.9408	0.0280	−0.043
		$A_{123}(0) = -0.758$, $A_{123}(1) = 7.643$, $A_{123}(2) = 1.054$			
		$\sigma(V^E) = 0.003$ cm^3 mol^{-1}			

where

$$X = \{V^E_{ijk} - x_i x_j[\sum_{n=0}^{2} A_{ij}(n)\,(x_i - x_j)^n] - x_j x_k[\sum_{n=0}^{2} A_{jk}(n)\,(x_j - x_k)^n] - x_k x_i[\sum_{n=0}^{2} A_{ki}(n)\,(x_k - x_i)^n]\}/x_i x_j x_k \quad (5)$$

by a le ast-squares method. The values along with the standard deviation $\sigma(V^E)$ of V^E are recorded in Table 3. The choice of n to have 0–2 or 3 values was dictated by consideration that the maximum deviation $\sigma_m(V^E)$ of V^E satisfies the relation $\sigma_m(V^E) \leq 2\sigma(V^E)$.

There are no literature values of V^E for the binary and ternary mixtures with which to compare our results. V^E values for studied binary mixtures are negative over the entire range of composition and for an equimolar mixture vary in the order *o*-xylene > toluene > *m*-xylene > benzene > *p*-xylene. V^E values for *m*-chloroaniline (1) + benzene (2) + toluene (3) mixtures are negative over the whole composition range; the

sign of V^E for *m*-chloroaniline (1) + benzene (2) + *o*-xylene (3) mixtures are dictated by the relative proportion of various components.

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