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Molar Excess Volumes and Excess Isentropic Compressibilities of {2-Methylaniline (i) + Benzene (j) + Methylbenzene}, {2-Methylaniline (i) + Benzene (j) + 1,2-Dimethylbenzene (k)}, and {2-Methylaniline (i) + Benzene (j) + 1,4-Dimethylbenzene (k)} at T = 308.15 K

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Molar excess volumes, V^E_{ijk}, and speeds of sound, U_{ijk}, of {2-methylaniline (i) + benzene (j) + methylbenzene (k)}, {2-methylaniline (i) + benzene (j) + 1,2-dimethylbenzene (k)}, and {2-methylaniline (i) + benzene (j) + 1,4-dimethylbenzene (k)} have been measured as a function of composition at a temperature of 308.15 K. The observed speeds of sound data have been utilized to determine excess isentropic compressibilities, $\kappa^E_{S\ ijk}$ of ternaries (i + j + k).

1. Introduction

Randic et al.[1,2] in their recent papers have noted that while on the one hand hundreds of topological indices are known, on the other, the interpretation of topological indices has received little attention. Basically, the topological index expresses in numerical form the topology of the molecule it presents. Topological indices are designed by transforming a a molecular graph into numbers, and they possess the remarkable ability of being able to correlate and predict a very wide spectrum of properties for a vast range of molecular species. Sharma et al.[3−6] have shown that the third-degree connectivity parameter of a molecule, $^3\xi$, can be utilized to predict thermodynamic properties of binary and ternary mixtures. In our recent studies,[7] we reported molar excess volumes, V^E and molar excess enthalpies, H^E of {2-methylaniline + benzene}, {2-methylaniline + methylbenzene}, {2-methylaniline (i) + 1,4-dimethylbenzene} or {2-methylaniline (i) + 1,3-dimethylbenzene (j)} at a temperature of 308.15 K. It would be of interest to see how V^E_{ijk} and $\kappa^E_{S\ ijk}$ vary when a third component like methylbenzene or 1,4-dimethylbenzene (k) is added to {2-methylaniline (i) + benzene (j)}. These considerations prompted us to measure molar excess volumes, V^E_{ijk}, and speed of sound, U_{ijk}, data for {2-methylaniline (i) + benzene (j) + methylbenzene}, {2-methylaniline (i) + benzene (j) + 1,2-dimethylbenzene (k)}, and {2-methylaniline (i) + benzene (j) + 1,4-dimethylbenzene (k)}.

2. Experimental Section

2.1. Materials. 2-Methylaniline (MA) (Fluka, with mass fraction 0.99), benzene, methylbenzene, 1,2-dimethylbenzene, and 1,4-dimethylbenzene were all AR grade (with mass fraction purity of 0.99) and were purified by standard methods.[8]

2.2. Methods. The purities of the purified liquids were verified by measuring their densities with a pycnometer (with an fractional uncertainty of $2 \cdot 10^5$) at T = (298.15 ± 0.01) K, and the resulting densities are listed in Table 1 and agreed to within ± 0.05 kg·m^{-3} of their corresponding literature values.[8]

Molar excess values, V^E_{ijk}, for the ternary mixtures were measured in a dilatometer in the manner described elsewhere.[9] The uncertainty in the measured V^E_{ijk} values is ± 0.5 %.

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Table 1. Comparison of Densities (ρ) and Speeds of Sound (U) of Pure Liquids along with Their Literature Values at T = 298.15 K

	ρ		U	
	kg·m^{-3}		m·s^{-1}	
liquid	experimental	literature	experimental	literature
2-methylaniline	994.28	994.30[8]	1603[a]	−
benzene	873.64	873.60[8]	1298	1298.6[11]
methylbenzene	862.17	862.19[8]	1305	1304.0[12]
1,2-dimethylbenzene	875.90	875.94[8]	1344	1345.0[13]
1,4-dimethylbenzene	858.63	856.61[8]	1310	1309.6[14]

[a] Values at 308.15 K.

The speed of sound at frequency 2 MHz was determined using a quartz crystal interferometer (model-M 80, Mittal Enterprises,

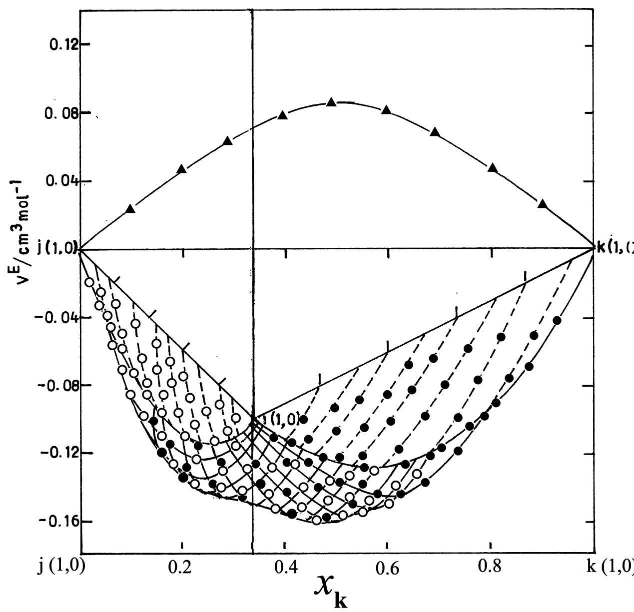

Figure 1. Molar excess volumes, V^E, for {2-methylaniline (i) + benzene (j) + methylbenzene (k)} at T = 308.15 K: ●, the V^E values obtained from eq 1 by keeping x_j (mole fraction of component j) constant and varying x_i and x_k (mole fractions of components i and k); ○, the V^E values obtained from eq 1 by keeping x_k constant and varying x_i and x_j; ▲, the V^E values for (j + k) binary mixture; —, the experimental data in front of the plane; - - -, the experimental data behind the plane.

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Table 2. V^E_{ijk} for {2-Methylaniline (i) + Benzene (j) + Methylbenzene (k)}, {2-Methylaniline (i) + Benzene (j) + 1,2-Dimethylbenzene (k)}, and {2-Methylaniline (i) + Benzene (j) + 1,4-Dimethylbenzene (k)} as a Function of Composition x_i (Mole Fraction of Component i) and x_j (Mole Fraction of Component j) and also $V_{ijk}^{(n)}$ (n = 0, 1, 2) along with Their Standard Deviation, $\sigma(V^E_{ijk})$, of Eq 1 at T = 308.15 K

		V^E_{ijk}
x_i	x_j	$cm^3 \cdot mol^{-1}$
2-Methylaniline (i) + Benzene (j) + Methylbenzene (k)		
0.2206	0.2329	−0.043
0.2536	0.5792	−0.060
0.2904	0.5182	−0.065
0.3211	0.4819	−0.069
0.3410	0.2639	−0.060
0.4021	0.2161	−0.078
0.4172	0.1882	−0.090
0.5216	0.3316	−0.085
0.6315	0.2018	−0.064
0.6802	0.1012	−0.072
0.7010	0.0820	−0.072
0.7512	0.1111	−0.052
$V_{ijk}^{(0)} = -0.935\ cm^3 \cdot mol^{-1}$; $V_{ijk}^{(1)} = 0.123\ cm^3 \cdot mol^{-1}$; $V_{ijk}^{(2)} = -103.794\ cm^3 \cdot mol^{-1}$; $\sigma(V^E_{ijk}) = 0.001\ cm^3 \cdot mol^{-1}$		
2-Methylaniline (i) + Benzene (j) + 1,2-Dimethylbenzene (k)		
0.1147	0.2785	0.163
0.1247	0.1143	0.086
0.2206	0.2329	0.118
0.2242	0.7013	0.032
0.2726	0.6243	0.053
0.3385	0.3014	0.121
0.3787	0.4414	0.096
0.4147	0.1457	0.048
0.4846	0.3252	0.085
0.5221	0.2141	0.071
0.5771	0.2998	0.047
0.6442	0.0876	0.037
0.7565	0.1008	0.031
0.8014	0.0679	0.028
$V_{ijk}^{(0)} = 0.048\ cm^3 \cdot mol^{-1}$; $V_{ijk}^{(1)} = 12.750\ cm^3 \cdot mol^{-1}$; $V_{ijk}^{(2)} = -45.243\ cm^3 \cdot mol^{-1}$; $\sigma(V^E_{ijk}) = 0.001\ cm^3 \cdot mol^{-1}$		
2-Methylaniline (i) + Benzene (j) + 1,4-Dimethylbenzene (k)		
0.1173	0.7177	0.072
0.1737	0.6019	0.077
0.2521	0.5518	0.069
0.2940	0.5128	0.065
0.3112	0.4779	0.053
0.4002	0.4186	0.041
0.4667	0.4201	0.070
0.5461	0.2443	−0.045
0.6019	0.2113	−0.049
0.6221	0.2170	−0.042
0.6586	0.1840	−0.048
0.6878	0.0436	−0.063
$V_{ijk}^{(0)} = -1.698\ cm^3 \cdot mol^{-1}$; $V_{ijk}^{(1)} = 6.132\ cm^3 \cdot mol^{-1}$; $V_{ijk}^{(2)} = 207.715\ cm^3 \cdot mol^{-1}$; $\sigma(V^E_{ijk}) = 0.001\ cm^3 \cdot mol^{-1}$		

New Delhi, India). The speeds of sound values for the purified liquids at a temperature of (298.15 ± 0.01) K are listed in Table 1 and compared with their corresponding literature values.[10−13] The uncertainty in the measured speed of sound measurements is ± 1 m·s^{-1}.

3. Results

Molar excess volumes, V^E_{ijk}, and speeds of sound, U_{ijk}, of {2-methylaniline (i) + benzene (j) + methylbenzene (k)}, {2-methylaniline (i) + benzene (j) + 1,2-dimethylbenzene (k)}, and {2-methylaniline (i) + benzene (j) + 1,4-dimethylbenzene (k)} as a function of composition at T = 308.15 K are recorded in Tables 2 and 3, respectively. The isentropic compressibilities, $\kappa_{S\,ijk}$, and excess isentropic compressibilities, $\kappa^E_{S\,ijk}$, for the ternary mixtures were determined by employing their molar excess volumes data by the procedure described elsewhere.[14] Such $\kappa_{S\,ijk}$ and $\kappa^E_{S\,ijk}$ values for various ternary mixtures are recorded in Table 3. The V^E_{ijk} and $\kappa^E_{S\,ijk}$ values, shown in Figures 1 to 3 and 4 to 6, respectively, were fitted to the Redlich−Kister equation

Table 3. Speeds of Sound, U_{ijk}, Isentropic Compressibilities, $\kappa_{S\,ijk}$, and Excess Isentropic Compressibilities, $\kappa^E_{S\,ijk}$, for {2-Methylaniline (i) + Benzene (j) + Methylbenzene (k)}, {2-Methylaniline (i) + Benzene (j) + 1,2-Dimethylbenzene (k)}, and {2-Methylaniline (i) + Benzene (j) + 1,4-Dimethylbenzene (k)} as a Function of Composition x_i (Mole Fraction of Component i) at T = 308.15 K and also $\kappa_{S\,ijk}^{(n)}$ (n = 0, 1, 2) along with Their Standard Deviation, $\sigma(\kappa^E_{S\,ijk})$, of Eq 1

		U_{ijk}	$\kappa_{S\,ijk}$	$\kappa^E_{S\,ijk}$
x_i	x_j	$m \cdot s^{-1}$	$T \cdot Pa^{-1}$	$T \cdot Pa^{-1}$
2-Methylaniline (i) + Benzene (j) + Methylbenzene (k)				
0.1968	0.6017	1096	664.0	−28.2
0.2357	0.5893	1004	649.4	−40.1
0.2873	0.5014	1000	632.1	−42.4
0.3353	0.3859	1193	618.5	−20.5
0.3981	0.4134	952	593.5	−49.5
0.4356	0.3616	1061	581.5	−38.9
0.4987	0.2816	1241	561.5	−17.8
0.6071	0.2699	1129	523.0	−35.2
0.6750	0.2513	1174	500.1	−33.3
0.7081	0.1771	1333	491.3	−13.0
0.7721	0.1782	1346	468.7	−16.9
0.8365	0.1121	1444	450.0	−6.8
$\kappa_{S\,ijk}^{(0)}$ = -100.0 T·Pa^{-1}, $\kappa_{S\,ijk}^{(1)}$ = −12000.1 T·Pa^{-1}, $\kappa_{S\,ijk}^{(2)}$ = −45166.5 T·Pa^{-1}, $\sigma(\kappa^E_{S\,ijk})$ = 0.2 T·Pa^{-1}				
2-Methylaniline (i) + Benzene (j) + 1,2-Dimethylbenzene (k)				
0.0535	0.8270	1339	704.4	9.6
0.1765	0.1386	1933	627.9	128.9
0.2767	0.2196	2215	605.6	188.7
0.3176	0.4052	1607	602.3	42.7
0.3238	0.3887	1652	599.9	50.7
0.3473	0.3590	1716	592.1	61.1
0.4893	0.2936	1646	549.8	38.7
0.5316	0.1645	2215	534.7	154.8
0.5872	0.1967	1862	519.8	71.5
0.6422	0.1452	1958	503.4	85.1
0.6820	0.1407	1842	492.0	59.5
0.7412	0.0967	1848	474.7	55.2
0.7826	0.0710	1811	462.7	45.1
0.8297	0.785	1667	449.1	19.0
$\kappa_{S\,ijk}^{(0)}$ = −2000.0 T·Pa^{-1}, $\kappa_{S\,ijk}^{(1)}$ = −33356.9 T·Pa^{-1}, $\kappa_{S\,ijk}^{(2)}$ = 125657 T·Pa^{-1}, $\sigma(\kappa^E_{S\,ijk})$ = 0.2 T·Pa^{-1}				
2-Methylaniline (i) + Benzene (j) + 1,4-Dimethylbenzene (k)				
0.1459	0.5648	1294	682.0	14.5
0.1994	0.1510	1070	668.9	−37.7
0.2969	0.2350	1047	635.8	−42.1
0.3193	0.5618	1418	618.8	12.5
0.3426	0.5160	1445	611.7	15.9
0.3739	0.4740	1461	601.6	17.1
0.4148	0.4068	1476	589.2	17.8
0.4647	0.3219	1447	574.7	10.7
0.5361	0.2816	1454	550.7	8.3
0.6285	0.2438	1472	519.0	5.7
0.6691	0.2012	1459	506.8	1.7
0.7187	0.1027	1338	495.3	−18.1
0.7616	0.1521	1477	476.0	−1.2
0.8287	0.994	1488	455.1	−3.2
$\kappa_{SS\,ijk}^{(0)}$ = −50.0 T·Pa^{-1}, $\kappa_{S\,ijk}^{(1)}$ = −13954.8 T·Pa^{-1}, $\kappa_{S\,ijk}^{(2)}$ = −5499.39 T ·Pa^{-1}, $\sigma(\kappa^E_{S\,ijk})$ = 0.1 T·Pa^{-1}				

$$X^E{}_{ijk}, X = V \text{ or } \kappa_S = x_i x_j \left[\sum_{n=0}^{2} X_{ij}{}^{(n)}(x_i - x_j)^n\right] + x_j x_k \left[\sum_{n=0}^{2} X_{jk}{}^{(n)}(x_j - x_k)^n\right] + x_i x_k \left[\sum_{n=0}^{2} X_{jk}{}^{(n)}(x_k - x_i)^n\right] + x_i x_j x_k \left[\sum_{n=0}^{2} X_{ijk}{}^{(n)}(x_j - x_k)^n x_i{}^n\right] \quad (1)$$

where x_i and x_j are the mole fractions of ith and jth components

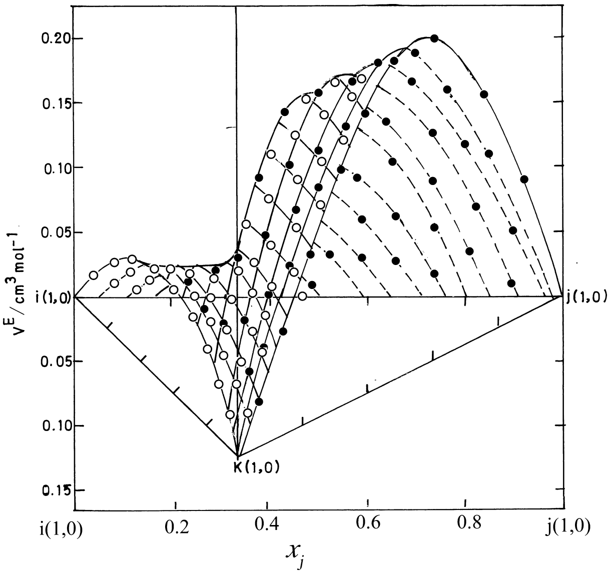

Figure 2. Molar excess volumes, V^E, for {2-methylaniline (i) + benzene (j) + 1,2-dimethylbenzene (k)} at $T = 308.15$ K: ●, the V^E values obtained from eq 1 by keeping x_i (mole fraction of component i) constant and varying x_j and x_k (mole fractions of components j and k); ○, the V^E values obtained from eq 1 by keeping x_j constant and varying x_i and x_k; —, the experimental data in front of the plane; - - -, represents the experimental data behind the plane.

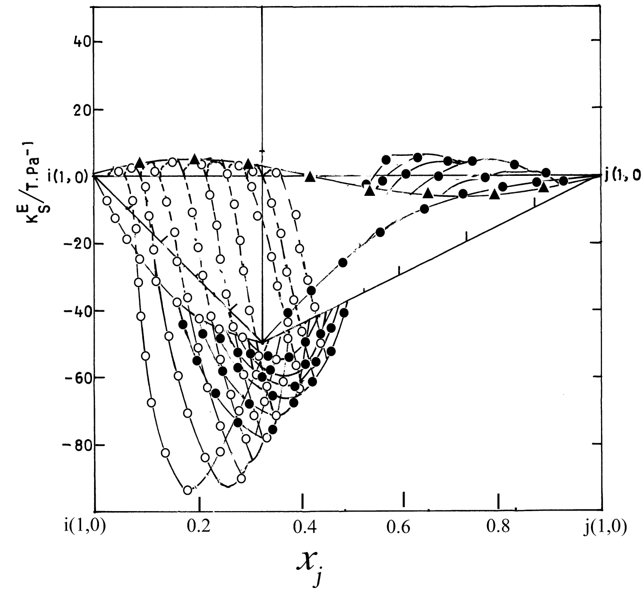

Figure 4. Molar excess volumes, κ_S^E, for {2-methylaniline (i) + benzene (j) + methylbenzene (k)} at $T = 308.15$ K: ●, the κ_S^E values obtained from eq 1 by keeping x_i (mole fraction of component i) constant and varying x_j and x_k (mole fractions of components j and k); ○, represent the κ_S^E values obtained from eq 1 by keeping x_j constant and varying x_i and x_k; ▲, represent the κ_S^E values for (i + j) binary mixture; —, the experimental data in front of the plane; - - -, the experimental data behind the plane.

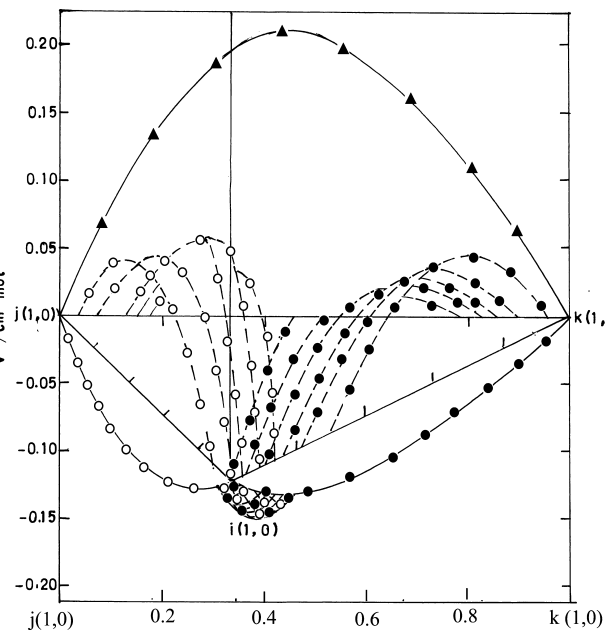

Figure 3. Molar excess volumes, V^E, for {2-methylaniline (i) + benzene (j) + 1,4-dimethylbenzene (k)} at $T = 308.15$ K: ●, the V^E values obtained from eq 1 by keeping x_j (mole fraction of component j) constant and varying x_i and x_k (mole fractions of components i and k); ○, the V^E values obtained from eq 1 by keeping x_k constant and varying x_i and x_j; ▲, the V^E values for (j + k) binary mixture; —, the experimental data in front of the plane; - - -, the experimental data behind the plane.

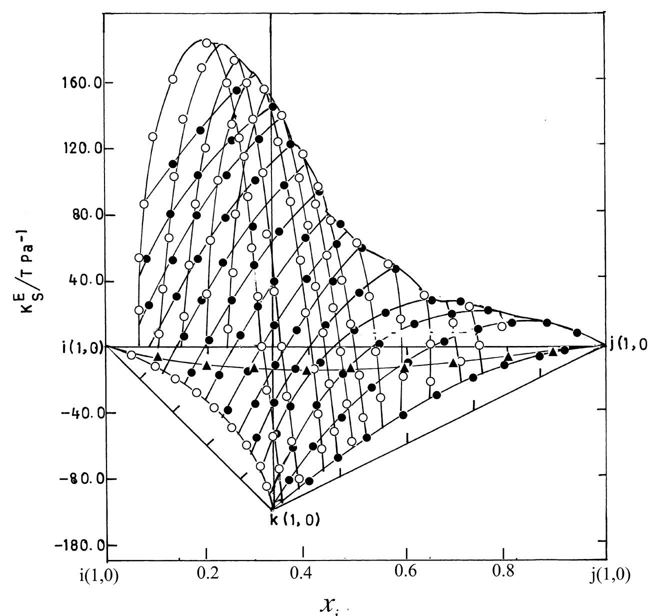

Figure 5. Molar excess volumes, κ_S^E, for {2-methylaniline (i) + benzene (j) + 1,2-dimethylbenzene (k)} at $T = 308.15$ K: ●, the κ_S^E values obtained from eq 1 by keeping x_i (mole fraction of component i) constant and varying x_j and x_k (mole fractions of components j and k); ○, the κ_S^E values obtained from eq 1 by keeping x_j constant and varying x_i and x_k; ▲, the κ_S^E values for (i + j) binary mixture; —, the experimental data in front of the plane; - - -, the experimental data behind the plane.

of (i + j + k) ternary mixtures, $X_{ij}^{(n)}$ ($n = 0, 1, 2,...$), $X = V$ or κ_S are the adjustable parameters of (i + j), (j + k), and (i + k) binary mixtures and have been taken from the literature.[7,9,15−18] $X_{ijk}^{(n)}$, $X = V$ or κ_S adjusted parameters (i + j + k) ternary mixture were determined by the least-squares method and are recorded along with their standard deviations, $\sigma(X^E_{ijk}, X = V$ or $\kappa_S)$ in Tables 2 and 3 respectively.

Figures 1 to 3 and 4 to 6 were plotted by calculating V^E_{ijk} and $\kappa^E_{S\,ijk}$ values from eq 1 keeping the mole fraction of one of the components constant and varying the other mole fractions. In Figure 1, keeping mole fraction x_j constant, V^E_{ijk} values (corresponding to i−k axis) were calculated and are shown in Figure 1. V^E_{ijk} values (corresponding to i−j axis) were obtained

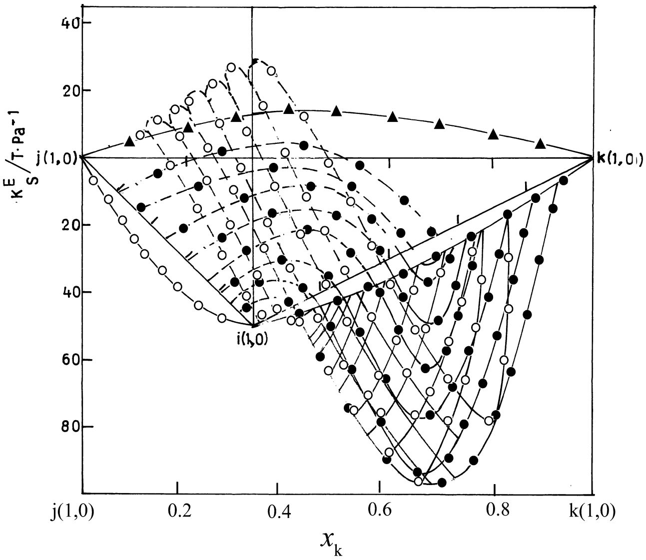

Figure 6. Molar excess volumes, κ_S^E, for {2-methylaniline (i) + benzene (j) + 1,4-dimethylbenzene (k)} at $T = 308.15$ K: ●, the κ_S^E values obtained from eq 1 by keeping x_j (mole fraction of component j) constant and varying x_i and x_k (mole fractions of components i and k); ○, the κ_S^E values obtained from eq 1 by keeping x_k constant and varying x_i and x_j; ▲, the κ_S^E values for (j + k) binary mixture; —, the experimental data in front of the plane; - - -, the experimental data behind the plane.

keeping x_k constant and varying the values of x_i and x_j and are shown (as ○) in Figure 1.

4. Discussion

We are unaware of any published V^E_{ijk} and $\kappa^E_{S\,ijk}$ data of {2-methylaniline (i) + benzene (j) + 1,2-dimethylbenzene (k)}, {2-methylaniline (i) + benzene (j) + 1,2-dimethylbenzene (k)}, and {2-methylaniline (i) + benzene (j) + 1,4-dimethylbenzene (k)} at $T = 308.15$ K with which to compare our results. The V^E_{ijk} and $\kappa^E_{S\,ijk}$ values for {2-methylaniline (i) + benzene (j) + methylbenzene} are negative and those of {2-methylaniline (i) + benzene (j) + 1,2-dimethylbenzene (k)} positive over the entire composition. However, the sign of V^E_{ijk} and $\kappa^E_{S\,ijk}$ values for {2-methylaniline (i) + benzene (j) + 1,4-dimethylbenzene (k)} are dictated by varying the composition of various components.

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