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MOLAR EXCESS ENTHALPIES OF TERNARY MIXTURES OF NON-ELECTROLYTES

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ABSTRACT

Molar excess enthalpies, $H^E_{ijk}(T_1, x_i, x_j)$, for methylenebromide (i)+pyridine (j)+β-picoline (k); pyridine (i)+β-picoline (j)+cyclohexane (k); benzene (i)+toluene (j)+1,2-dichloroethane (k); benzene (i)+ o-xylene (j)+1,2-dichloroethane (k); and benzene (i)+ p-xylene (j)+1,2-dichloroethane (k) mixtures have been measured calorimetrically as a function of temperature and composition. The data have been analysed in terms of the Sanchez and Lacombe theory and using an approach employing the "graph theoretical" concept of connectivity parameters to characterize its pure components. It has been observed that the $H^E_{ijk}(T, x_i, x_j)$ data calculated from the "graph theoretical" approach using $^3\xi$ values based on δ^v considerations (that take into consideration the valency of individual atoms of the molecular graph constituent components) best reproduces the corresponding experimental H^E_{ijk} data.

INTRODUCTION

A recent study [1,2] utilized a "graph theoretical approach" (that employed the graph theoretical connectivity parameters of the third degree of the constituent molecules) which successfully described molar excess volumes of ternary mixtures of non-electrolytes. The approach [1,2] makes use of the fact that the interactions in a ternary ($i + j + k$) mixture are closely dependent on the interactions in the ($i + j$), ($j + k$) and ($k + i$) mixtures. Furthermore, the Lacombe and Sanchez theory of fluid mixtures [3] suggests that the thermodynamic properties of ternary mixtures of non-electrolytes are determinable from the corresponding properties of the constituent binary mixtures. This prompted us to study molar excess enthalpies, H^E_{ijk}, of some ternary mixtures of non-electrolytes and to analyse the data in terms of: (i) graph theoretical approach; and (ii) Lacombe and Sanchez theory of fluid mixtures.

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TABLE 1

Comparison of the measured H^{E}_{ijk} (T,x_i,x_j) values for various ternary mixtures with the corresponding values as evaluated from graph theory and the Lacombe and Sanchez theory at $T = 298.15$ and 308.15 K

x_i	x_j	H^{E}_{ijk} (J mol^{-1})		
		Graph	Experimental	Lacombe and Sanchez
Methylenebromide (i)+pyridine (j)+ β-picoline (k) at 298.15 K				
$\chi''_{ij} = -5403.68$ J mol^{-1}; $\chi''_{jk} = -2338.43$ J mol^{-1}; $\chi''_{ik} = -2558.64$ J mol^{-1}				
0.0628	0.7295	−194.67	−174.71	−30.55
0.0889	0.8444	−157.53	−205.58	−29.87
0.0900	0.6200	−258.66	−266.55	−50.96
0.1022	0.3172	−281.44	−348.56	−39.72
0.1287	0.0792	−243.63	−348.00	−216.08
0.1389	0.7389	−282.46	−296.41	−141.69
0.1827	0.7500	−276.00	−326.40	−223.73
0.2893	0.4619	−450.29	−590.43	−423.01
0.4976	0.1043	−449.29	−794.00	−749.32
0.5822	0.2400	−383.02	−655.00	−649.63
0.7377	0.1393	−281.85	−476.43	−409.39
0.8293	0.0772	−119.57	−330.55	−372.09
At 308.15 K				
$\bar{\chi}_{ij} = -163.06$ J mol^{-1}; $\bar{\chi}_{jk} = 22.1576$ J mol^{-1}; $\bar{\chi}_{ik} = -57.4668$ J mol^{-1};				
$\bar{\chi}''_{ij} = -3760.43$ J mol^{-1}; $\chi''_{jk} = -1841.28$ J mol^{-1}; $\chi''_{ik} = -1601.89$ J mol^{-1}				
0.1006	0.0943	−133.75	−219.34	−133.17
0.1287	0.7772	−180.94	−236.94	−125.03
0.1620	0.3966	-280.65	−356.12	−228.60
0.1818	0.2139	−247.11	−451.82	−314.51
0.2129	0.6145	−284.75	−369.29	−287.61
0.3404	0.5957	−307.46	−514.82	−448.32
0.3876	0.4928	−339.31	−539.19	−501.22
0.4624	0.4032	−339.08	−539.11	−573.47
0.4723	0.2979	−335.43	−526.80	−670.80
0.6524	0.1048	−210.56	−505.81	−672.03
0.8478	0.1043	−113.19	−237.91	−235.18

Pyridine (i)+β-picoline (j)+cyclohexane (k) at 298.15 K

χ''_{ij} = 6753.94 J mol^{-1}; χ''_{jk} = 6822.38 J mol^{-1}; χ''_{ik} = 13064.08 J mol^{-1}

0.0914	0.8057	499.08	408.46	871.86
0.0952	0.1012	495.85	947.31	−96.86
0.1179	0.6821	792.87	726.21	968.35
0.1183	0.5444	993.15	1058.00	959.13
0.2604	0.1657	992.21	1236.45	692.24
0.2848	0.1582	1020.20	1280.12	709.59
0.3061	0.3333	1200.66	1061.06	1006.05
0.5455	0.0788	1013.38	1211.97	1035.27
0.6348	0.2135	826.19	620.02	1053.40
0.7500	0.1394	619.12	82.82	1015.41
0.7551	0.1633	537.38	386.42	964.25
0.8381	0.0905	417.65	356.78	971.21

At 308.15 K

χ''_{ij} = 7037.12 J mol^{-1}; χ''_{jk} = 12203.60 J mol^{-1}; χ''_{ik} = 18891.07 J mol^{-1}; $\bar{\chi}_{ij}$ = 22.1576 J mol^{-1};
$\bar{\chi}_{jk}$ = 213.70 J mol^{-1}; $\bar{\chi}_{ik}$ = 205.68 J mol^{-1}

0.0569	0.8699	401.80	132.67	432.40
0.0820	0.1639	729.51	1106.45	686.29
0.0885	0.0592	453.73	747.78	445.23
0.1193	0.3028	1025.88	1043.12	956.57
0.1239	0.3186	1051.85	1414.88	973.59
0.1550	0.7132	811.98	412.85	619.05
0.1833	0.6583	952.01	702.11	685.48
0.2155	0.3017	1292.81	1440.27	1073.82
0.2848	0.4901	1317.99	895.39	854.77
0.3577	0.4234	1408.33	674.79	855.55
0.4537	0.2778	1497.42	886.62	871.02
0.5028	0.1769	1442.88	1084.72	1037.99
0.5896	0.0708	1435.96	1138.08	1079.85
0.6250	0.1964	1239.14	800.46	828.44
0.8269	0.0577	702.97	474.48	678.40
0.9118	0.0515	330.13	19.39	392.13

TABLE 1 (continued)

x_i	x_j	H^E_{ijk} (J mol^{-1})		
		Graph	Experimental	Lacombe and Sanchez
Benzene (i)+toluene (j)+1,2-dichloroethane (k) at 298.15 K				
χ''_{ij} = 550.10 (230.99*) J mol^{-1}; χ''_{jk} = 254.88 (67.23*) J mol^{-1}; χ''_{ik} = 290.20 (396.09*) J mol^{-1}				
0.0926	0.2407	35.0 (32.11*)	55.41	19.23
0.1068	0.0631	16.91 (19.07*)	52.11	−61.72
0.1180	0.6067	60.49 (−138.99*)	−19.42	49.56
0.1629	0.0899	23.75 (26.81*)	74.82	−79.83
0.2241	0.4741	−214.48 (12.51*)	6.00	49.41
0.2336	0.5327	70.07 (−70.99*)	−7.07	70.61
0.3122	0.3463	9.06 (10.31*)	45.25	18.24
0.3184	0.2870	18.36 (−182.42*)	72.28	13.87
0.3298	0.3246	17.02 (10.56*)	52.43	13.55
0.3609	0.1302	93.64 (42.13*)	110.52	−112.03
0.4114	0.3608	7.89 (43.52*)	22.14	58.20
0.6045	0.1455	31.06 (35.37*)	71.41	−1629.99
0.8100	0.0672	18.59 (22.00*)	35.21	−6.06
0.8571	0.0591	14.74 (17.22*)	24.20	12.86
At 303.15 K				
χ''_{ij} = 711.63 (259.99*) J mol^{-1}; χ''_{jk} = 330.63 (40.29*) J mol^{-1}; χ''_{ik} = 388.97 (523.83*) J mol^{-1}; $\bar{\chi}_{ij}$ = 50.75 J mol^{-1}; $\bar{\chi}_{jk}$ = 115.14 J mol^{-1}; $\bar{\chi}_{ik}$ = −14.2256 J mol^{-1}				
0.0483	0.8621	18.48 (21.64*)	−7.89	54.08
0.0739	0.3068	295.31 (46.74*)	13.64	−27.26
0.0988	0.2284	52.27 (37.15*)	29.13	34.29
0.0995	0.1990	24.64 (33.72*)	32.99	19.68
0.1221	0.5954	131.63 (−64.83*)	−28.99	84.65
0.1238	0.0524	22.91 (23.61*)	42.97	−102.75
0.1508	0.5196	107.40 (35.60*)	−28.04	41.75
0.1778	0.4978	−68.22 (31.01*)	−24.41	47.65
0.2105	0.6184	62.75 (162.63*)	−8.54	80.45
0.3128	0.5475	70.66 (194.25*)	6.04	216.91

0.3881	0.5323	63.97 (70.56*)	30.99	143.80
0.4366	0.2441	45.94 (44.97*)	6.10	−8.09
0.5799	0.0769	37.41 (38.02*)	19.20	156.92
0.6071	0.2429	46.40 (77.25*)	29.89	57.83
0.8750	0.0380	17.10 (13.71*)	19.38	14.36

Benzene (*i*) + *o*-xylene (*j*) + 1,2-dichloroethane (*k*) at 298.15 K

$\chi''_{ij} = 1007.74\ (559.768^*)\ \mathrm{J\ mol^{-1}}$; $\chi''_{jk} = 721.96\ (67.2315^*)\ \mathrm{J\ mol^{-1}}$; $\chi''_{ik} = 299.92\ (396.0895^*)\ \mathrm{J\ mol^{-1}}$

0.1077	0.3692	−38.53 (157.69*)	−14.42	80.02
0.1218	0.0714	39.29 (35.82*)	41.96	23.85
0.1341	0.7378	51.92 (75.60*)	5.92	114.46
0.1611	0.0948	51.54 (45.72*)	44.05	17.44
0.2650	0.1950	−50.03 (83.69*)	21.25	37.07
0.2681	0.1830	−114.18 (79.50*)	26.84	30.20
0.2717	0.6416	79.53 (88.36*)	98.20	221.55
0.3558	0.5215	97.06 (48.22*)	102.52	221.91
0.4598	0.3851	65.32 (37.58*)	77.02	215.90
0.5359	0.1215	56.12 (51.02*)	40.47	−8.15
0.6300	0.1100	51.79 (60.60*)	31.45	23.80
0.8084	0.0884	33.74 (33.12*)	26.94	114.39

At 308.15 K

$\chi''_{ij} = 1280.82\ (707.4595^*)\ \mathrm{J\ mol^{-1}}$; $\chi''_{jk} = 890.72\ (-35.3327^*)\ \mathrm{J\ mol^{-1}}$; $\chi''_{ik} = 380.20\ (523.831^*)\ \mathrm{J\ mol^{-1}}$;
$\bar{\chi}_{ij} = 105.07\ \mathrm{J\ mol^{-1}}$; $\bar{\chi}_{jk} = 202.34\ \mathrm{J\ mol^{-1}}$; $\bar{\chi}_{ik} = -14.23\ \mathrm{J\ mol^{-1}}$

0.0441	0.2059	94.94 (48.90*)	89.71	149.41
0.0707	0.8889	33.87 (31.73*)	41.99	118.54
0.0769	0.0350	29.39 (25.42*)	51.89	66.72
0.0769	0.5220	−19.49 (−62.17*)	15.23	23.20
0.0889	0.6148	−31.06 (12.72*)	6.21	28.91
0.1863	0.7453	78.49 (74.97*)	98.01	161.88
0.3094	0.3812	77.20 (51.44*)	76.07	96.67
0.3247	0.0649	88.22 (60.93*)	133.69	−80.57
0.3373	0.3669	83.48 (57.61*)	82.44	96.93
0.4379	0.0719	60.22 (41.43*)	148.84	−92.55
0.5765	0.2529	95.58 (53.64*)	110.23	632.19

TABLE 1 (continued)

x_i	x_j	H^E_{ijk} (J mol^{-1})		
		Graph	Experimental	Lacombe and Sanchez
0.8070	0.0965	47.91 (35.65*)	77.43	96.01
0.9063	0.0547	25.45 (16.57*)	49.41	103.73
Benzene (i) + p-xylene (j) + 1,2-dichloroethane (k) at 298.15 K				
χ''_{ij} = 761.1 (411.0977*) J mol^{-1}; χ''_{jk} = 462.07 (107.7528*) J mol^{-1}; χ''_{ij} = 285.89 (396.0895*) J mol^{-1}				
0.1394	0.7163	46.76 (50.76*)	−21.54	85.43
0.1613	0.6290	59.00 (488.9*)	−21.85	75.87
0.1777	0.2769	−25.58 (90.56*)	22.15	8.25
0.2072	0.5180	129.65 (56.21*)	−12.85	58.40
0.4039	0.3744	19.26 (87.79*)	44.98	121.59
0.4851	0.3385	51.54 (102.72*)	62.12	157.38
0.5185	0.1759	62.04 (65.59*)	38.31	20.93
0.5487	0.0823	46.74 (49.77*)	21.39	−81.04
0.7185	0.1849	57.61 (70.01*)	61.85	172.09
At 308.15 K				
χ''_{ij} = 1072.78 (550.514*) J mol^{-1}; χ''_{jk} = 669.20 (98.9203*) J mol^{-1}; χ''_{ij} = 392.22 (523.831*) J mol^{-1}; $\bar{\chi}_{ij}$ = 102.59 J mol^{-1}; $\bar{\chi}_{jk}$ = 169.54 J mol^{-1}; $\bar{\chi}_{ik}$ = −14.23 J mol^{-1}				
0.0516	0.0329	18.59 (18.27*)	48.00	133.23
0.0625	0.8281	31.46 (33.57*)	—	36.84
0.0884	0.1361	48.75 (45.44*)	95.52	44.47
0.1087	0.7826	46.66 (48.45*)	18.02	67.27
0.1146	0.5796	344.86 (99.21*)	−17.23	−2810.0
0.2564	0.4615	-25.77 (69.00*)	24.07	68.17
0.2848	0.1939	−1.48 (95.37*)	120.28	−5.84
0.4074	0.1429	56.16 (108.45*)	128.96	−39.33
0.4907	0.4037	116.43 (64.31*)	81.01	217.47
0.6935	0.2339	67.91 (50.19*)	98.18	219.65
0.8101	0.1519	45.89 (36.71*)	91.21	193.48
0.8986	0.0338	18.93 (20.91*)	36.56	41.29

EXPERIMENTAL

Pyridine, β-picoline, cyclohexane, methylenebromide, benzene, toluene, 1,2-dichloroethane, *o*-xylene and *p*-xylene (BDH AR grade) were purified by standard methods [4]. The purity of the final samples was checked by measuring their density at 298.15 K and these agreed to within ± 0.00005 g cm^{-1} with the corresponding literature values [5–7].

Molar excess enthalpies, H^{E}_{ijk}, of the various $(i+j+k)$ mixtures were measured as a function of composition and temperature in a double-walled glass calorimeter that has been described in detail elsewhere [8]. In essence, the calorimeter had three limbs and the three components were introduced by means of three separate hypodermic syringes with 9-in. long needles at their ends. The liquid components in the calorimeter were kept separated by a column of mercury and their compositions were determined by directly weighing the calorimeter. The calorimeter was placed in a water bath whose temperature was controlled to better than ± 0.01 K by means of a toluene regulator. After thermal equilibrium, the contents of the calorimeter were mixed by tilting the calorimeter by about 60° from the vertical by an automatic machine and an appropriate current was passed through the calorimeter heater for compensation (for endothermic reactions only). The time for which the current was passed was noted with the help of an electronic timer (type 701, M/s Systronic, Ahmedabad) with an accuracy of ± 0.0001 s. The current in the heater circuit was measured with a vernier potentiometer (M/s OSAW, Ambala) with an accuracy of ± 0.000001 V. Our measured $H^{\mathrm{E}}_{ijk}(T, x_i, x_j)$ data are accurate to about 1.0%.

RESULTS

Molar excess enthalpies, $H^{\mathrm{E}}_{ijk}(T, x_i, x_j)$ for the various ternary mixtures as a function of composition at 298.15 and 308.15 K (recorded in Table 1 and plotted for some of the mixtures in Figs. 1–5) were fitted to the expression

$$\begin{aligned} H^{\mathrm{E}}_{ijk}(T_1, x_i, x_j)/(\mathrm{J\ mol^{-1}}) &= x_i x_j \left[\sum_{n=0}^{2} H^{n}_{ij}(x_i - x_j)^n \right] \\ &+ x_j x_k \left[\sum_{n=0}^{2} H^{n}_{jk}(x_j - x_k)^n \right] \\ &+ x_i x_k \left[\sum_{n=0}^{2} H^{n}_{ik}(x_i - x_k)^n \right] \\ &+ x_i x_j x_k \left[\sum_{n=0}^{2} H^{n}_{ijk}(x_j - x_k)^n x_i^n \right] \end{aligned} \qquad (1)$$

TABLE 2

Values of the parameters H^0_{ijk}, H^1_{ijk} and H^2_{ijk} of eqn. (2) along with the standard deviation, $\sigma(H^E_{ijk})$, of the molar excess enthalpies, $H^E_{ijk}(T,x_i,x_j)$, for the various ($i + j + k$) mixtures at 298.15 and 308.15 K

System	Temp. (K)	H^0_{ijk} (J mol^{-1})	H^1_{ijk} (J mol^{-1})	H^2_{ijk} (J mol^{-1})	$\sigma(H^E_{ijk})$ (J mol^{-1})
Methylenebromide (i) + pyridine (j)+ β-picoline (k)	298.15	−7244.7	3609.5	215535	2.12
	308.15	−5500	47046.5	305623	2.48
Pyridine (i)+ β-picoline (j)− cyclohexane (k)	298.15	−5700	11966	70650	2.54
	308.15	−295.7	8123	−78016.3	2.36
Benzene (i)+ toluene (j)+ 1,2-dichloroethane (k)	298.15	315.3	−15800	98.9	1.29
	308.15	−1626	1080.8	−30383	0.85
Benzene (i)+ o-xylene (j)+ 1,2-dichloro-ethane (k)	298.15	−3002.8	889	111347	1.25
	308.15	−993.8	−14680.5	65312	0.89
Benzene (i)+ p-xylene (j)+ 1,2-dichloro-ethane (k)	298.15	1022.3	1472.8	−43715.1	0.91
	308.15	−524	−15210.5	6997	0.97

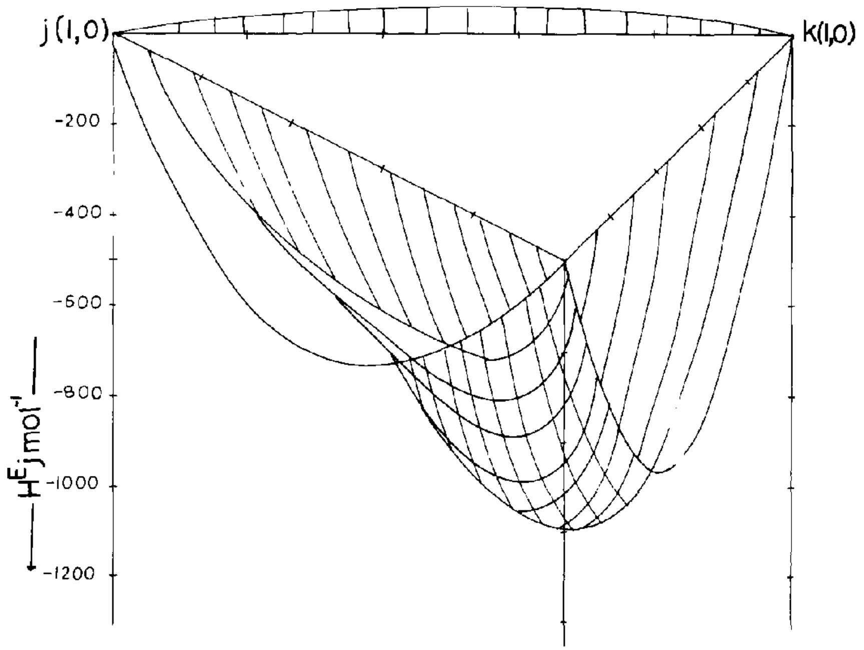

Fig. 1. Molar excess enthalpies, H^E, of methylenebromide (i)+pyridine (j)+ β-picoline (k) at 298.15 K.

where x_i, x_j and x_k are the mole fractions of the ith, jth and the kth components in the $(i+j+k)$ mixture, respectively, and $H^n_{ij}(n=0\text{–}2)$, etc., are parameters characteristic of the $(i+j)$, $(j+k)$ and $(k+i)$ binary mixtures. The parameters H^n_{ijk} $(n=0\text{–}2)$ of eqn. (1) were evaluated by fitting

$$\left[H^{\mathrm{E}}_{ijk}(T_1, x_i, x_j) - x_i x_j\left(\sum_{n=0}^{2}(x_i - x_j)^n H^n_{ij}\right) - x_j x_k\left(\sum_{n=0}^{2}(x_j - x_k)^n x^n_{jk}\right)\right.$$
$$\left. - x_i x_k\left(\sum_{n=0}^{2}(x_i - x_k)^n H^n_{ik}\right)^2\right] / (x_i x_j x_k)$$

to

$$\left[H^0_{ijk} + H^1_{ijk}(x_j - x_k)x_i + H^2_{ijk}(x_j - x_k)^2 x_i^2\right] \tag{2}$$

by the method of least squares; the necessary H^n, etc., parameters of some of the binary mixtures were taken from the literature [9]. These parameters,

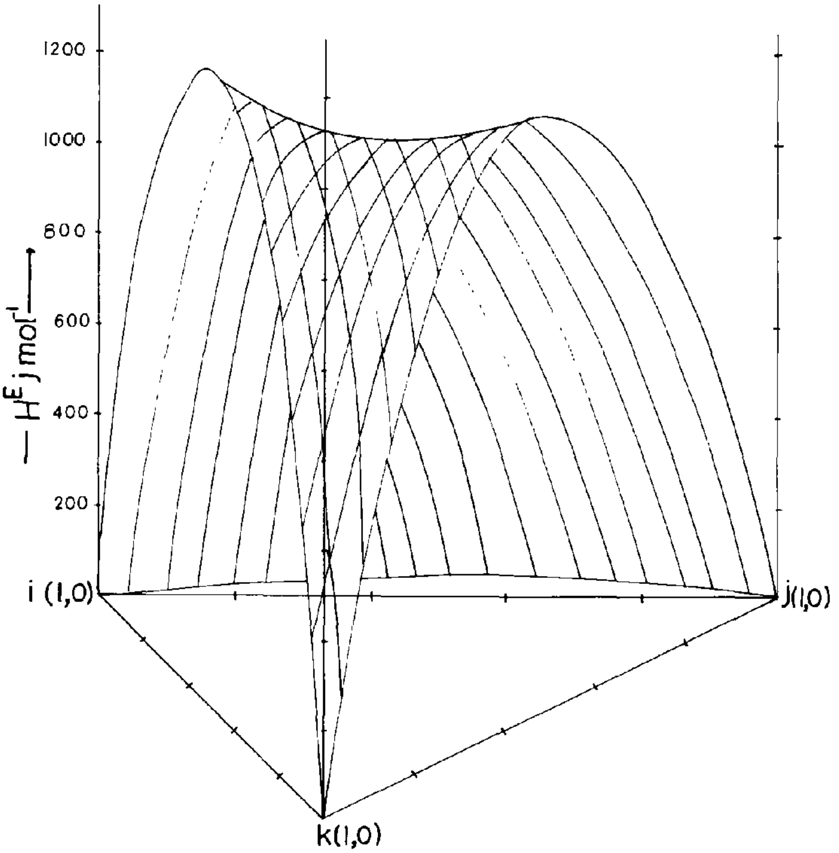

Fig. 2. Molar excess enthalpies, H^{E}, of pyridine (i)+β-picoline (j)+cyclohexane (k) at 298.15 K.

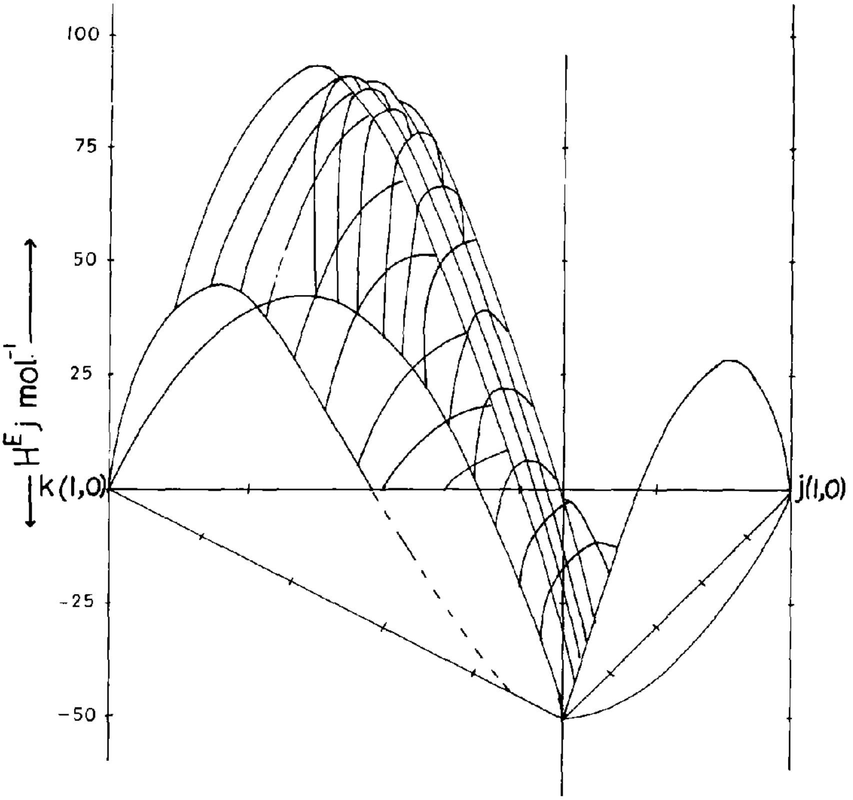

Fig. 3. Molar excess enthalpies, H^E, of benzene (*i*)+toluene (*j*)+1,2-dichloroethane (*k*) at 298.15 K.

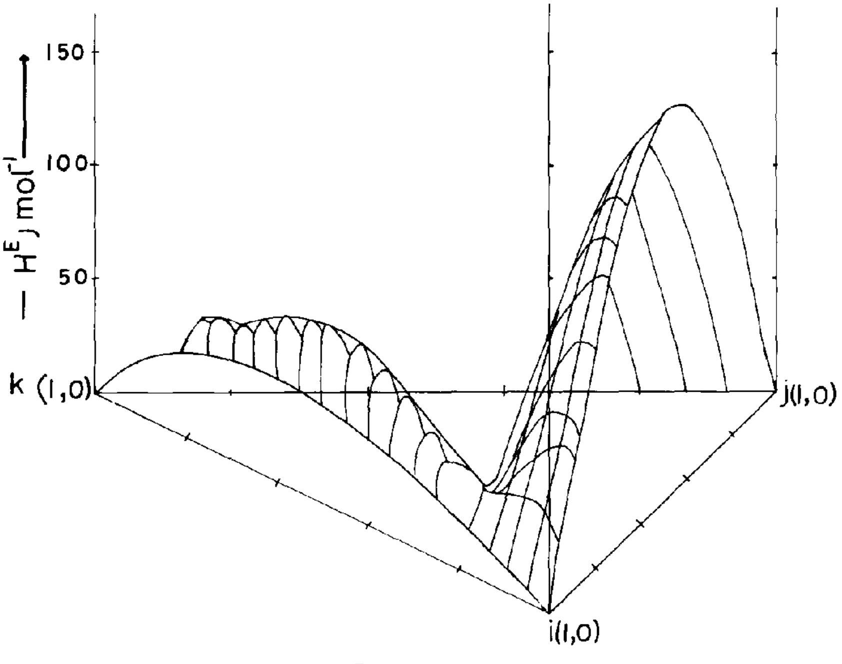

Fig. 4. Molar excess enthalpies, H^E, of benzene (*i*)+ *o*-xylene (*j*)+1,2-dichloroethane (*k*) at 298.15 K.

along with the standard deviation $\sigma(H^{E}_{ijk})$ of $H^{E}_{ijk}(T, x_i, x_j)$ defined by

$$\sigma(H^{E}_{ijk}) = \left\{ \frac{\Sigma\left[H^{E}_{ijk}(T_1, x_i, x_j)_{(\mathrm{exp})} - H^{E}_{ijk}(T, x_i, x_j)_{(\mathrm{calc\ eqn.1})}\right]^2}{(m - n')} \right\}^{0.5} \tag{3}$$

where m is the number of data points and n' is the number of adjustable parameters in eqn. (2), are recorded in Table 2.

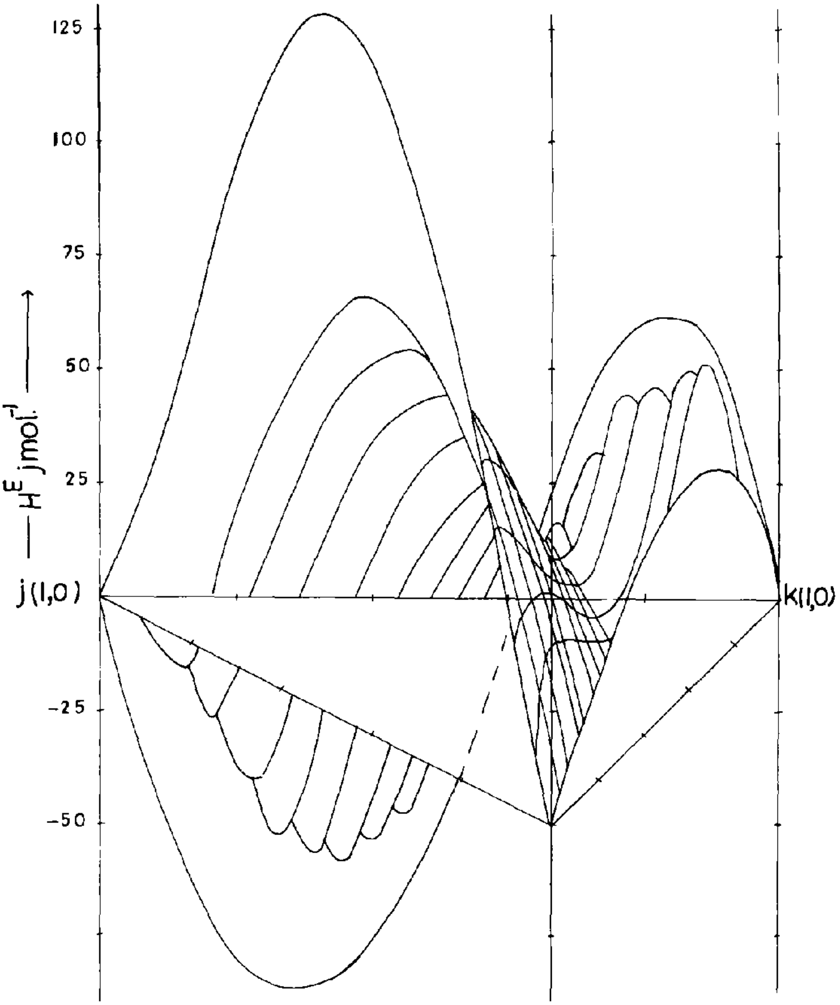

Fig. 5. Molar excess enthalpies, H^E, of benzene (i)+ p-xylene (j)+1,2-dichloroethane (k) at 298.15 K.

DISCUSSION

Molar excess enthalpies for methylenebromide(i) + pyridine(j) + β-picoline(k) are negative at 298.15 and 308.15 K. On the other hand, when methylenebromide is replaced by cyclohexane in its ternary mixtures with pyridine and β-picoline, the molar excess enthalpies become positive over the entire composition range. H^E_{ijk} for benzene (i) + 1,2-dichloroethane (j) + toluene (k), + o-xylene (j), and + p-xylene (j) mixtures is positive over most of the x_i and x_j composition, and decreases in the order: toluene > o-xylene > p-xylene.

The $H^E_{ijk}(T, x_i, x_j)$ data for the various ternary mixtures were next analysed in terms of the Sanchez and Lacombe theory [3] of fluid mixtures. $H^E_{ijk}(T, x_i, x_j)$ according to this theory is given by

$$H^E_{ijk}(T_1, x_i, x_j) = rkT\left[\bar{\rho}_{ijk}\sum_{m=1}^{3}\sum_{l=1}^{3}\phi_l\phi_m\bar{\chi}_{lm} + \sum_{l=1}^{3}\left(\frac{\bar{\rho}_l\phi_l^0 - \bar{\rho}_{ijk}\phi_l}{\bar{T}_1}\right)\right] \tag{4}$$

$$= r\bar{\rho}_{ijk}(2\phi_i\phi_j\bar{\chi}_{ij} + 2\phi_j\phi_k\bar{\chi}_{jk} + 2\phi_i\phi_k\bar{\chi}_{ik}) + rkT\sum_{i=1}^{3}\left(\frac{\bar{\rho}_1\phi_i^0 - \bar{\rho}_{ijk}\phi_i}{\bar{T}_1}\right) \tag{5}$$

where

$$\bar{\chi}_{ij} = \epsilon^*_{ii} + \epsilon^*_{jj} - 2\epsilon^*_{ij}, \text{ etc.} \tag{6}$$

$$\phi_i = m_i(\rho_i^*)^{-1}\left[\sum_{i=1}^{3}(m_i/\rho_i^*)\right]^{-1} \tag{7}$$

$$m_i = x_i M_i\left(\sum_{i=1}^{3} x_i M_i\right)^{-1} \tag{8}$$

$$r = \sum_{i=1}^{3} x_i r_i = r_{ijk} \tag{9}$$

$$r_i = r_i^0\left[V_i^*(V^*_{\text{mix}})^{-1}\right] \tag{10}$$

$$V^*_{\text{mix}} = \sum_{i=1}^{3}\phi_i^0 V_i^* \tag{11}$$

$$\phi_i^0 = m_i(\rho_i^* V_i^*)^{-1} \Big/ \left[\sum_{i=1}^{3}(m_i/\rho_i^* V_i^*)\right] \tag{12}$$

and

$$\bar{\rho}_{ijk} = \left(\bar{V}_{ijk}\right)^{-1} \tag{13}$$

and all terms have the same significance as described by Lacombe and Sanchez [3,10].

Evaluation of $H^{\mathrm{E}}_{ijk}(T_1, x_i, x_j)$ by this theory requires a knowledge of $\bar{\rho}_{ijk}$, the reduced density of the mixture, which in principle could be calculated [3] from the following equation of state of the mixture

$$\bar{\rho}^2_{ijk} + RT/\epsilon^*_{ijk}\left[\ln(1-\bar{\rho}_{ijk}) + (1 - 1/r_{ijk})\bar{\rho}_{ijk}\right] + \bar{P} = 0 \tag{14}$$

where

$$\epsilon^*_{ijk} = \left(\epsilon^*_{ii}\phi_i + \epsilon^*_{jj}\phi_j + \epsilon^*_{kk}\phi_k\right) - \left(\phi_i\phi_j\bar{\chi}_{ij} + \phi_i\phi_k\bar{\chi}_{ik} + \phi_j\phi_k\bar{\chi}_{jk}\right) \tag{15}$$

and

$$\bar{P} = PV^*_{ijk}/\rho^*_{ijk} \tag{16}$$

This would require a knowledge of the binary interaction energies ϵ^*_{ij}, ϵ^*_{jk}, ϵ^*_{ik} of the $(i+j)$, $(j+k)$ and $(i+k)$ binary mixtures but as such information, however, is not readily available, these were evaluated from the $H^{\mathrm{E}}_{ij}(T_1, x_i = 0.5)$ datum of the $(i+j)$, $(j+k)$ and $(k+i)$ mixtures by means of

$$H^{\mathrm{E}}_{ij} = 2\phi_i\phi_j r_{ij}\left[\epsilon^*_{ii} + \epsilon^*_{jj} - 2\epsilon^*_{ij}\right] + RTr_{ij}\left[\sum\left(\frac{\phi^0_i\bar{\rho}_i - \bar{\rho}_{ij}\phi_i}{\bar{T}_i}\right)\right] \tag{17}$$

where

$$\bar{T}_i = RT/\epsilon^*_{ii} \tag{18}$$

and

$$\bar{\rho}_{ij} = \left[\left\{V^{\mathrm{E}}_{(i+j)}/\sum_i\left(x_i r^0_i\left(V^*_i/\sum_i\phi_i V^*_i\right)\left(\sum_i\left(\phi^0_i V^*_i\right)\right)\right\} + \sum_i\phi_i V_i\right]^{-1} \tag{19}$$

Once the ϵ^*_{ij}, ϵ^*_{jk} and ϵ^*_{ik} parameters of the $(i+j)$, $(j+k)$ and $(i+k)$ binary mixtures, respectively, are known, $\bar{\rho}_{ij}$ for the $(i+j+k)$ mixture can be evaluated from eqns. (14)–(16). It should thus be possible to predict $H^{\mathrm{E}}_{ijk}(T_1, x_i, x_j)$ data for a ternary $(i+j+k)$ mixture if it is assumed that the binary interaction coefficients $\bar{\chi}_{ij}$, $\bar{\chi}_{jk}$ and $\bar{\chi}_{ik}$ for these binary system are independent of composition and that these binary mixtures satisfy eqn. (14) for binary mixtures. Since

$$(\bar{\rho}_{ijk})^2 + (RT/\epsilon^*_{ijk})\left[\bar{\rho}_{ijk}(1 - r^{-1}_{ijk}) + \ln(1-\bar{\rho}_{ijk})\right] + \bar{P} = 0 \tag{20}$$

methylenebromide (i) + pyridine (j), + β-picoline (j) and pyridine (i) + α-picoline (j) do not satisfy [9] eqn. (20) (as the experimental and calculated H^{E}_{ij} values make very poor agreement with the corresponding experimental H^{E}_{ij} values) but satisfy the following equation reasonably well

$$(\bar{\rho}_{ij})^2 + \bar{P} + \frac{RT}{\epsilon^*_{ij}}\left[\ln(1-\bar{\rho}_{ij}) + (1 - r_{ij})\bar{\rho}_{ij}\right] = 0.01 \text{ to } 0.051 \tag{21}$$

(the calculated H^{E}_{ij} values compare reasonably well with their corresponding experimental values [9]), it follows that the present $(i+j+k)$ mixtures would also not satisfy eqn. (14). Consequently, H^{E}_{ijk} values evaluated at 298.15 and 308.15 K by eqn. (4) in the manner originally proposed by Sanchez and Lacombe would not compare well with their corresponding experimental values. It was, therefore, imperative to know how much a particular $(i+j+k)$ mixture deviated from eqn. (14). A useful approximation, however, would be to consider an $(i+j+k)$ mixture, as a mixture of $(i+j)$, $(j+k)$ and $(i+k)$ binary mixtures and if the addition of, say, the kth component does not drastically effect the nature of the i–j interaction in the $(i+j)$, etc., mixture, it follows that the extent to which the $(i+j+k)$ mixture deviates from eqn. (14) would be nearly one third of the sum to which the $(i+j)$, $(j+k)$ and $(i+k)$ equimolar mixtures deviate at 308.15 K from eqn. (20). Therefore, eqn. (14) for a ternary $(i+j+k)$ mixture (assuming it to be composed of three binary $(i+j)$, $(j+k)$ and $(i+k)$ mixtures) would reduce to

$$\bar{\rho}^2_{ijk} + \overline{P}_{ijk} + RT/\epsilon^*_{ijk}\left[\ln(1-\bar{\rho}_{ijk}) + (1 - 1/r_{ijk})\bar{\rho}_{ijk}\right]$$

$$= \tfrac{1}{3}\left[\sum \text{RHS of eqn. (20) for } (i+j),\ (j+k) \text{ and } (i+k)\right] \tag{22}$$

where ϵ^*_{ijk} and $\bar{\rho}_{ijk}$ are defined by

$$\epsilon^*_{ijk} = \sum_{i=1}^{3} \phi_i \epsilon^*_{ii} - RT\sum\sum \phi_i \phi_j \bar{\chi}_{ij} \tag{23}$$

$$\overline{V}_{ijk} = 1/\bar{\rho}_{ijk} \tag{24}$$

Once the equation of state for a ternary mixture, such as eqn. (22), has been established, $\bar{\rho}_{ijk}$ and hence $H^{\mathrm{E}}_{ijk}(T_1, x_i, x_j)$ for the mixture at any composition can be readily evaluated. Such $H^{\mathrm{E}}_{ijk}(T_1, x_i, x_j)$ values for the various ternary $(i+j+k)$ mixtures are recorded in Table 1 and are also compared with the corresponding experimental values.

An examination of Table 1 reveals that the $H^{\mathrm{E}}_{ijk}(T_1, x_i, x_j)$ values so calculated are of the right order of magnitude but the quantitative agreement is not very impressive. The failure of the Sanchez and Lacombe theory to describe the $H^{\mathrm{E}}_{ijk}(T, x_i, x_j)$ data of these ternary mixtures well for low values of x_i, x_j or x_k at 298.15 and 308.15 K may lie in the assumption that the right-hand side of eqn. (22) for the constituent $(i+j)$, $(j+k)$ and $(i+k)$ binary mixtures (evaluated from their $H^{\mathrm{E}}(T = 308.15\ \mathrm{K}, x = 0.5)$ data) was constant over the entire range of values of x_i, x_j or x_k and T. Nevertheless, this theory makes a significant theoretical attempt to predict thermodynamic excess functions of multicomponent systems from a knowledge of their binary interaction coefficients.

The H^{E}_{ijk} data were next analysed in terms of the graph theoretical approach [11].

In order to evaluate $H^{\mathrm{E}}_{ijk}(T_1, x_i, x_j)$ from the H^{E} data of $(i+j)$, $(j+k)$ and $(k+i)$ by means of this approach [11], a ternary $(i+j+k)$ mixture was assumed to be characterised by the following contacts

$$\underline{i}\,\underline{\underline{j}\,\underline{k}} = \underline{i}\,\underline{j}'$$

$$\underline{j}\,\underline{\underline{k}\,\underline{i}} = \underline{j}\,\underline{k}'$$

$$\underline{k}\,\underline{\underline{i}\,\underline{j}} = \underline{k}\,\underline{i}'$$

so that H^{E}_{ijk} should be due essentially to H^{E} data due to the *ij'*, *jk'* and *ki'*, *jk*, *ki* and *ij* contacts. If the contribution due to each of these unlike contacts to the measured H^{E}_{ijk} is assumed to be additive then H^{E}_{ijk} should be given by

$$H^{\mathrm{E}}_{ijk}(T_1, x_i, x_j) \propto \left[H^{\mathrm{E}}_{ij'} + H^{\mathrm{E}}_{jk'} + H^{\mathrm{E}}_{ki'} + H^{\mathrm{E}}_{ij} + H^{\mathrm{E}}_{jk} + H^{\mathrm{E}}_{ik}\right] \tag{25}$$

$$= K\left[H^{\mathrm{E}}_{ij'} + H^{\mathrm{E}}_{jk'} + H^{\mathrm{E}}_{ki'} + H^{\mathrm{E}}_{ij} + H^{\mathrm{E}}_{jk} + H^{\mathrm{E}}_{ik}\right] \tag{26}$$

where K is a constant of proportionality and H^{E}_{ij}, etc., represent the contribution of H^{E} (due to *i*–*j* contacts) to the measured H^{E}_{ijk} value. $H^{\mathrm{E}}_{ij'}$ for an $(i+j')$, or an $(i+j+k)$ mixture containing x_i mole fraction of i is given by [11]

$$H^{\mathrm{E}}_{ij'}(T_1, x_i, x_j) = \frac{x_i(1-x_i)\chi''_{ij'}K_{ij'}\left({}^3\xi_i/{}^3\xi_{j'}\right)}{x_i + x_i(1-x_i)K_{ij'}\left({}^3\xi_i/{}^3\xi_{j'}\right)} \tag{27}$$

where ${}^3\xi_i$ denotes the connectivity parameter of the third degree for i, etc., and is defined by [11]

$${}^3\xi = \sum_{l<m}\ \sum_{m<n}\ \sum_{n<o} (\delta_l\delta_m\delta_n\delta_o)^{-0.5}$$

where δ_l, δ_m, δ_n, etc., denote the degrees of the lth, mth and nth, etc., vertices of the molecular graph of i.

As $1/{}^3\xi$ of a molecule has been regarded [11] as a mesure of the probability that its surface area interacts effectively, $K_{ij'}({}^3\xi_i/{}^3\xi_{j'})$ simply measures the relative probability of the surface area of j' to interact effectively with the surface area of i so that for an $(i+j+k)$ mixture containing x_i, x_j and x_k mole fractions of i, j and k, respectively, it should be given by

$$K_{ij'}\left({}^3\xi_i/{}^3\xi_{j'}\right) = x_j K_{ij}\left({}^3\xi_i/{}^3\xi_j\right) + x_i K_{ik}\left({}^3\xi_i/{}^3\xi_k\right) \tag{28}$$

assuming that there are no specific interactions between i, j and k components of the $(i+j+k)$ mixture. Consequently, eqn. (27) yields

$$H^{\mathrm{E}}_{ijk}(T_1, x_i, x_j) = K\left[\sum x_i(1-x_i)\chi''_{ij} \times \frac{x_j K_{ij}\left({}^3\xi_i/{}^3\xi_j\right) + x_k K_{ik}\left({}^3\xi_i/{}^3\xi_j\right)}{x_i + (1-x_i)\left[x_j K_{ij}\left({}^3\xi_i/{}^3\xi_j\right) + x_k K_{ik}\left({}^3\xi_i/{}^3\xi_k\right)\right]} + \sum \frac{x_i x_j \chi''_{ij} K_{ij}\left({}^3\xi_i/{}^3\xi_j\right)}{x_i + x_j K_{ij}\left({}^3\xi_i/{}^3\xi_j\right)}\right] \tag{29}$$

Further, as the i, j and kth components of the $(i+j+k)$ mixture are assumed to undergo non-specific interactions, it is reasonable to assume that

$$\begin{aligned} \chi''_{ij'} &= \chi''_{ij} + \chi''_{ik} \\ \chi''_{jk'} &= \chi''_{jk} + \chi''_{ji} \\ \chi''_{ki'} &= \chi''_{ki} + \chi''_{kj} \end{aligned} \tag{30}$$

and $\chi''_{ij} = \chi''_{ji}$

Equation (29) then yields

$$H^{\mathrm{E}}_{ijk}(T_1, x_i, x_j) = K\left(\sum x_i(1-x_i)(\chi''_{ij} + \chi''_{ik}) \times \left\{\frac{x_j k_{ij}\left({}^3\xi_i/{}^3\xi_j\right) + x_k k_{ik}\left({}^3\xi_i/{}^3\xi_k\right)}{x_i + (1-x_i)\left[x_j k_{ij}\left({}^3\xi_i/{}^3\xi_j\right) + x_k k_{ik}\left({}^3\xi_i/{}^3\xi_k\right)\right]}\right\} + \sum \frac{x_i x_j \chi''_{ij} K_{ij}\left({}^3\xi_i/{}^3\xi_j\right)}{x_i + x_j K_{ij}\left({}^3\xi_i/{}^3\xi_j\right)}\right) \tag{31}$$

It should therefore be possible to evaluate $H^{\mathrm{E}}_{ijk}(T_1, x_i, x_j)$ of a ternary mixture from the H^{E} data of the $(i+j)$, $(j+k)$ and $(k+i)$ mixtures if K is known. It is further assumed that K is dependent only on the i–j–k contacts so that it would be the same for all the $(i+j+k)$ mixtures. To evaluate the magnitude of K, $H^{\mathrm{E}}_{ijk}(T_1, x_i, x_j)$ data [12] at 293.15 K for benzene (i) + cyclohexane (j) + n-heptane (k) was utilized to find the best possible value of K for eqn. (31). It was observed that $K = 0.2$ best reproduced the observed $H^{\mathrm{E}}_{ijk}(T_1, x_i, x_j)$ of this $(i+j+k)$ mixture. (The χ'', K, etc., parameters of the $(i+j)$, $(j+k)$ and $(i+k)$ binary mixtures were evaluated from their $H^{\mathrm{E}}(T_1, x_i = 0.4$ and $0.5)$ data by means of eqn. (32))

$$H^{\mathrm{E}}_{ij}(T_1, x_i) = x_i x_j \chi''_{ij} K_{ij}\left({}^3\xi_i/{}^3\xi_j\right)/\left[x_i + K_{ij} x_j\left({}^3\xi_i/{}^3\xi_j\right)\right] \tag{32}$$

Alternatively, i and j components of an $(i+j)$ mixture may interact as ij or ji, and if a ternary $(i+j+k)$ mixture is assumed to be composed of three binary, $(i+j)$, $(j+k)$ and $(i+k)$, mixtures there would then be six different binary contacts in these binary mixtures. These six binary contacts taken two at a time will give rise to $^{6}C_{2}$ or fifteen ijk ternary contacts. But in actual fact, i, j and k molecules interact as ijk, jik and jki. The number of ijk contacts evaluated from binary contacts would thus be five times more than the actual ijk contacts. Hence, K in eqn. (31) should be $1/5 = 0.2$. This value of K was then used to evaluate H^{E}_{ijk} values for the present $(i+j+k)$ ternary mixture utilizing the binary interaction parameters like χ''_{ij}, K_{ij}, etc., of the $(i+j)$, $(j+k)$ and $(k+i)$ binary mixtures. Such $H^{E}_{ijk}(T_1, x_i, x_j)$ values for the methylenebromide (i) + pyridine (j) + β-picoline (k), pyridine (i) + β-picoline (j) + cyclohexane (k), benzene (i) + toluene (j) + 1,2-dichloroethane (k), benzene (i) + o-xylene (j) + 1,2-dichloroethane (k), benzene (i) + p-xylene (j) + 1,2-dichloroethane (k) mixtures using $^{3}\xi$ values based on δ and δ^{v} considerations [11,13] are recorded in Table 1 and are also compared with their corresponding experimental values. ($H^{E}_{ijk}(T_1, x_i, x_j)$ values based on δ considerations [11] of the molecular graph of the constituents of benzene (i) + toluene (j) + 1,2-dichloroethane (k), benzene (i) + o-xylene (j) + 1,2-dichloroethane (k) and benzene (i) + p-xylene (j) + 1,2-dichloroethane (k) mixtures at 298.15 and 308.15 K are denoted by an asterisk in Table 1. For benzene, toluene, 1,2-dichloroethane and o-, and p-xylene, since $\delta = \delta^{v}$, $^{3}\xi_{(\delta)}$ should be the same as $^{3}\xi_{(\delta^{v})}$ so that the $H^{E}_{ijk}(T, x_i, x_j)$ data for benzene (i) + toluene (j) + 1,2-dichloroethane (k), + o-xylene (j) and p-xylene (j) ternary mixtures as evaluated from eqn. (31) would be the same whether $^{3}\xi$ values are based on δ or δ^{v} considerations (of the molecular graphs of the constituent molecules) are taken into consideration.)

Examination of Table 1 shows that the $H^{E}_{ijk}(T_1, x_i, x_j)$ data evaluated from $H^{E}(T = 308.15, x_i = 0.4$ and $0.5)$ data of the $(i+j)$, $(j+k)$ and $(k+i)$ mixtures using $^{3}\xi$ values based on δ^{v} considerations best reproduces the experimental $H^{E}_{ijk}(T = 308.15$ K, $x_i, x_j)$ data of benzene (i) + toluene (j) + 1,2-dichloroethane (k), benzene (i) + o-xylene (j) + 1,2-dichloroethane (k) and benzene (i) + p-xylene (j) + 1,2-dichloroethane (k) mixtures. Consequently, $H^{E}_{ijk}(T_1, x_i, x_j)$ data of benzene (i) + toluene (j) + 1,2-dichloroethane (k), benzene (i) + o-xylene (j) + 1,2-dichloroethane (k) and benzene (i) + p-xylene (j) + 1,2-dichloroethane (k) mixtures at 298.15 and 308.15 K were evaluated from the $H^{E}(T_1, x_i)$ data of the $(i+j)$, $(j+k)$ and $(k+i)$ mixtures using $^{3}\xi$ values based on δ^{v} considerations. Such $H^{E}_{ijk}(T_1, x_i, x_j)$ values are recorded in Table 1 and they describe the experimental $H^{E}_{ijk}(T_1, x_i, x_j)$ data of all the mixtures well.

The analysis of $H^{E}_{ijk}(T_1, x_i, x_j)$ data of the various $(i+j+k)$ mixtures studied here suggests that the $H^{E}_{ijk}(T_1, x_i, x_j)$ data of the present ternary mixtures are determined by interactions that involve primarily the valency of individual atoms in the molecular graphs of i, j and k mixtures.

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