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THERMODYNAMICS OF TERNARY MIXTURES OF NON-ELECTROLYTES: MOLAR EXCESS ENTHALPIES

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ABSTRACT

Molar excess enthalpies, $H^{E}_{ijk}(T_1, x_i, x_j)$ for 1,2-dichloroethane (i)+pyridine (j)+ α-picoline (k), + n-heptane (j) +pyridine (k), + α-picoline (k); n-heptane (i)+pyridine (j) + α-picoline (k); aniline (i)+pyridine (j) + α-picoline (k), + γ-picoline (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 the graph theoretical approach. It has been observed that the $H^{E}_{ijk}(T, x_i, x_j)$ data calculated from the graph theoretical approach better reproduce the corresponding experimental H^{E}_{ijk} data.

INTRODUCTION

A recent study [1,2] utilized a "graph theoretical approach" (that employed the graph theoretical parameters of the third degree of the constituent molecules) to successfully describe molar excess volumes of ternary mixtures of non-electrolytes. This approach [1,2] makes use of the interactions in $(i+j)$, $(j+k)$ and $(i+k)$ mixtures. Furthermore, the Lacombe and Sanchez theory of ternary 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) the graph theoretical approach and (ii) the Lacombe and Sanchez theory of fluid mixtures.

EXPERIMENTAL

1,2-Dichloroethane, n-heptane, pyridine, α- and γ-picolines and aniline (BDH AR grade) were purified by standard methods [4]. The purity of the final samples was checked by measuring their density at 293.15 K and these agreed [4] to within ± 0.00005 g cm^{-3} with the corresponding literature values [4].

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 elsewhere [5]. 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 separate by a column of mercury and their compositions were determined by direct weighings of 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 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) that could read to 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 $H^E_{ijk}(T, x_i, x_j)$ data are accurate to about 1.0%.

RESULTS

Molar excess enthalpies, $H^E_{ijk}(T, x_i, x_j)$ for the various $(i+j+k)$ 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. 1–6) were expressed

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

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

$$\left\{H^E_{ijk}(T, x_i, x_j) - x_i x_j\left[\sum_{n=0}^{2} H^n_{ij}(x_i - x_j)^n\right] - x_j x_k\left[\sum_{n=0}^{2} H^n_{jk}(x_j - x_k)^n\right] - x_i x_k\left[\sum_{n=0}^{2} H^n_{ik}(x_i - x_k)^n\right]\right\} / x_i x_j x_k$$

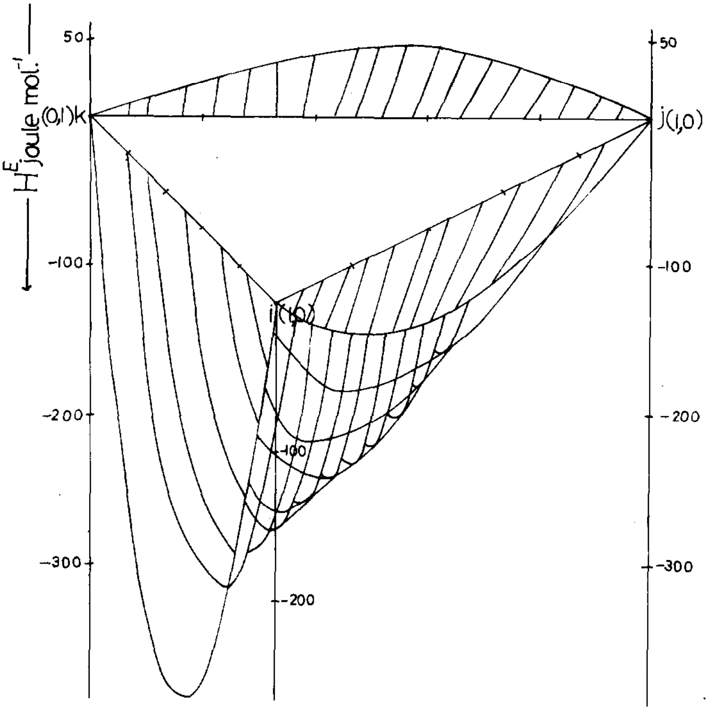

Fig. 1. Molar excess enthalpies, H^E, of 1,2-dichloroethane (i) + pyridine (j) + α-picoline (k) at 308.15 K.

to the equation

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

by the method of least squares; the necessary H^n, etc., parameters of some of the binary mixtures were taken from the literature [6,7]. These parameters, along with standard deviation $\sigma H^E_{ijk}(T, x_i, x_j)$ of $H^E_{ijk}(T, x_i, x_j)$ are defined by

$$\sigma H^E_{ijk}(T, x_i, x_j)/\text{J mol}^{-1} = \left[\frac{\Sigma\left(H^E_{ijk(\text{expt})}(T, x_i, x_j) - H^E_{ijk(\text{calc.eqn.1})}(T, x_i, x_j)\right)^2}{(m^* - z)}\right]^{0.5}$$

where m^* is the number of data points and z the number of adjustable parameters in eqn. (1) (Table 2).

DISCUSSION

Molar excess enthalpies for 1,2-dichloroethane (i) + pyridine (j) + α-picoline (k) are negative for most of the x_i and x_j at 298.15 and 308.15 K.

TABLE 1

Comparison of measured H^E_{ijk} values for various ternary mixtures with the corresponding values as evaluated from graph theory and Sanchez and Lacombe theory

x_i	x_j	H^E_{ijk} (J mol^{-1})		
		Graph	Experimental	Sanchez and Lacombe
1,2-Dichloroethane (i)+pyridine (j) + α-picoline (k) at 298.15 K: $\chi'_{ij} = -95.12$ J mol^{-1}; $\chi'_{jk} = 390.75$ J mol^{-1}; $\chi'_{ik} = -1394.41$ J mol^{-1}				
0.0769	0.5263	−46.9	21.7	22.2
0.1639	0.1478	−71.5	−105.9	−307.3
0.1888	0.0583	−82.5	−162.1	−392.9
0.2316	0.2032	−98.8	−123.0	−301.7
0.2420	0.4267	−104.8	−73.6	−116.1
0.3717	0.3725	−124.1	−115.1	−158.5
0.4002	0.3093	−129.4	−133.3	−215.8
0.5797	0.1623	−120.8	−176.8	−249.9
0.7303	0.1231	−78.0	−125.2	−118.0
0.8204	0.0963	−45.6	−84.1	−4.8
At 308.15 K: $\chi'_{ij} = -188.17$ J mol^{-1}; $\chi'_{jk} = 137.50$ J mol^{-1}; $\chi'_{ik} = -1416.40$ J mol^{-1}; $\chi^0_{ij} = 9.39$ cal mol^{-1}; $\chi^0_{jk} = 5.252$ cal mol^{-1}; $\chi^0_{ik} = 17.712$ cal mol^{-1}				
0.0846	0.8667	−51.0	−15.8	226.1
0.1541	0.1015	−83.0	−148.8	−347.4
0.2184	0.6144	−133.4	−78.1	35.7
0.2267	0.5344	−150.6	−94.9	−22.0
0.2454	0.1718	−138.7	−170.0	−160.1
0.2785	0.2658	−168.6	−156.7	−238.8
0.3998	0.1278	−163.1	−217.0	−563.2
0.4529	0.3651	−179.4	−156.8	43.6
0.5198	0.2216	−183.4	−188.1	−207.0
0.5655	0.2974	−168.1	−150.8	−65.7
0.8388	0.0907	−89.5	−96.0	72.4
1,2-Dichloroethane (i)+ n-heptane (j)+pyridine (k) at 298.15 K: $\chi'_{ij} = 5372.66$ J mol^{-1}; $\chi'_{jk} = 5656.05$ J mol^{-1}; $\chi'_{ik} = -95.12$ J mol^{-1}				
0.1033	0.0727	441.4	370.9	642.6
0.1060	0.3362	915.1	1236.0	1677.8
0.1684	0.4477	1272.1	1299.6	1227.4
0.1907	0.6402	965.5	1080.2	898.2
0.2252	0.7333	662.0	1055.5	1693.0
0.2677	0.3262	1353.4	1112.1	1213.2
0.3271	0.0529	720.2	262.9	423.9
0.4795	0.2689	1288.8	970.8	1138.8
0.5714	0.1985	1116.9	830.0	1019.1
0.7832	0.0919	576.7	503.8	601.1
0.7954	0.1106	586.2	604.5	786.6
At 308.15 K: $\chi'_{ij} = 4813.54$ J mol^{-1}; $\chi'_{jk} = 5391.80$ J mol^{-1}; $\chi'_{ik} = -188.17$ J mol^{-1}; $\chi^0_{ij} = 46.5225$ cal mol^{-1}; $\chi^0_{jk} = 27.8822$ cal mol^{-1}; $\chi^0_{ik} = 9.39$ cal mol^{-1}				
0.0564	0.2701	792.1	1105.3	1292.4
0.0619	0.7628	533.4	1044.3	698.6
0.0846	0.3474	947.5	1296.5	1338.9

TABLE 1 (continued)

x_i	x_j	H^E_{ijk} (J mol^{-1})		
		Graph	Experimental	Sanchez and Lacombe
0.1040	0.1149	519.2	562.0	842.8
0.1686	0.6566	780.7	1235.0	932.0
0.1763	0.1734	801.0	807.1	1024.2
0.1820	0.6302	836.6	1275.6	983.1
0.4273	0.2211	1075.2	981.1	1102.4
0.4415	0.1771	1002.1	815.6	988.9
0.4478	0.1180	866.3	550.2	768.2
0.6141	0.2219	891.0	954.4	1150.0
0.7965	0.0796	444.2	406.1	698.4
1,2-Dichloroethane (*i*) + *n*-heptane (*j*) + α-picoline (*k*) at 298.15 K: χ'_{ij} = 5372.66 J mol^{-1}; χ'_{jk} = 4968.87 J mol^{-1}; χ'_{ik} = −1394.41 J mol^{-1}				
0.0814	0.1866	599.5	601.5	519.0
0.1466	0.7385	586.6	880.0	719.6
0.2272	0.2193	816.4	555.2	582.1
0.2324	0.6378	830.8	998.3	903.7
0.2436	0.1018	514.0	126.2	167.0
0.2585	0.6122	886.6	1022.7	892.7
0.2658	0.3156	1002.1	799.9	815.1
0.3936	0.4300	1094.3	993.6	1093.3
0.4514	0.2642	978.9	747.0	870.9
0.5963	0.2516	890.0	865.4	1074.2
0.6501	0.2510	853.4	946.8	1177.4
0.8202	0.0866	382.5	415.7	721.1
At 308.15 K: χ'_{ij} = 4813.54 J mol^{-1}; χ'_{jk} = 3689.76 J mol^{-1}; χ'_{ik} = −1553.90 J mol^{-1}; χ^0_{ij} = 46.5225 cal mol^{-1}; χ^0_{jk} = 18.4086 cal mol^{-1}; χ^0_{ik} = 17.7121 cal mol^{-1}				
0.1021	0.1369	417.2	371.0	362.2
0.1291	0.3673	790.5	929.8	890.4
0.1628	0.2056	605.9	627.7	567.5
0.1799	0.7403	452.3	996.7	821.6
0.2152	0.5292	790.2	1202.4	1017.0
0.3354	0.2008	693.3	738.3	604.1
0.3441	0.3888	850.1	962.6	1057.2
0.3630	0.6123	597.5	1323.9	1174.6
0.5110	0.2052	647.6	617.3	812.3
0.6609	0.1245	432.3	436.2	695.0
0.7658	0.1389	413.2	531.7	955.9
n-Heptane (*i*) + pyridine (*j*) + α-picoline (*k*) at 298.15 K; χ'_{ij} = 5656.05 J mol^{-1}; χ'_{ik} = 390.75 J mol^{-1}; χ'_{ik} = 4968.87 J mol^{-1}				
0.1187	0.1150	583.1	547.2	434.4
0.1562	0.7977	574.2	770.4	1142.2
0.1786	0.3952	1007.6	932.9	863.5
0.2516	0.5016	1112.1	1148.5	1156.2
0.3034	0.0998	978.4	992.9	858.3
0.3304	0.5526	1085.8	1213.8	1144.4
0.3922	0.0403	927.4	1221.0	882.1

TABLE 1 (continued)

x_i	x_j	H^E_{ijk} (J mol^{-1})		
		Graph	Experimental	Sanchez and Lacombe
0.5222	0.0681	973.9	1184.5	924.4
0.5984	0.0810	910.8	1221.9	881.5
0.7444	0.1327	665.4	1162.8	759.3
At 308.15 K: $\chi'_{ij}=5391.80$ J mol^{-1}; $\chi'_{jk}=137.5$ J mol^{-1}; $\chi'_{ik}=3689.76$ J mol^{-1}; $\chi^0_{ij}=27.8822$ cal mol^{-1}; $\chi^0_{jk}=5.2522$ cal mol^{-1}; $\chi^0_{ik}=18.4086$ cal mol^{-1}				
0.0400	0.1541	353.1	125.5	137.1
0.0768	0.4942	733.2	280.3	574.4
0.1013	0.7490	525.1	451.9	876.1
0.1938	0.0914	704.4	621.4	644.9
0.2146	0.1640	875.5	683.5	761.8
0.2179	0.5778	912.6	826.4	1171.8
0.2803	0.4047	1112.5	861.0	1145.1
0.3641	0.1732	1075.4	1026.0	1034.9
0.5302	0.2608	964.3	1145.5	1191.7
0.5666	0.0738	856.2	1203.1	952.1
0.7138	0.1015	621.3	960.2	837.0
0.8142	0.1138	406.4	871.8	682.1
Aniline (i) + pyridine (j) + α-picoline (k) at 298.15 K: $\chi'_{ij}=-8586.68$ J mol^{-1}; $\chi'_{jk}=390.75$ J mol^{-1}; $\chi'_{ik}=-9995.03$ J mol^{-1}				
0.1408	0.8028	−816.1	−864.3	−439.1
0.1612	0.0754	−843.8	−1211.8	−1157.7
0.1652	0.1097	−940.4	−1201.4	−1032.2
0.2023	0.6565	−1223.2	−1137.6	−999.7
0.2592	0.1300	−1233.8	−1589.5	−1694.7
0.3001	0.4588	−1405.3	−1402.1	−1293.1
0.4071	0.2931	−1608.8	−1575.9	−1677.8
0.5109	0.0722	−1217.2	−1920.1	−2021.9
0.6091	0.1969	−1247.5	−1477.6	−1781.3
0.7988	0.1090	−669.8	−937.4	−1279.1
At 308.15 K: $\chi'_{ij}=-8894.04$ J mol^{-1}; $\chi'_{ik}=137.5$ J mol^{-1}; $\chi'_{ik}=-10394.95$ J mol^{-1}; $\chi^0_{ij}=-77.7366$ cal mol^{-1}; $\chi^0_{jk}=5.2522$ cal mol^{-1}; $\chi^0_{ik}=-97.7335$ cal mol^{-1}				
0.0642	0.3347	−1158.2	−550.8	−309.1
0.1012	0.6219	−1262.6	−786.6	−345.7
0.1476	0.7612	−960.4	−890.0	−500.3
0.1515	0.1619	−1144.1	−1041.1	−1006.1
0.2014	0.4781	−1674.2	−1403.7	−930.3
0.2398	0.5486	−1561.7	−1352.9	−1028.2
0.2535	0.2233	−1592.9	−1512.7	−1335.6
0.2704	0.5429	−1548.7	−1361.1	−1268.2
0.3779	0.4513	−1564.1	−1475.5	−1493.4
0.5343	0.3064	−1416.7	−1526.9	−1710.1
0.5910	0.0382	−1101.5	−1358.1	−2065.9
0.6854	0.1708	−1012.3	−1209.1	−1650.8
0.8567	0.0792	−467.6	−490.0	−1098.3

TABLE 1 (continued)

x_i	x_j	H^E_{ijk} (J mol^{-1})		
		Graph	Experimental	Sanchez and Lacombe
Aniline (i) + pyridine (j) + γ-picoline (k) at 298.15 K: $\chi'_{ij} = -8586.68$ J mol^{-1}; $\chi'_{jk} = 280.90$ J mol^{-1}; $\chi'_{ik} = -9888.61$ J mol^{-1}				
0.0753	0.8177	−625.3	−485.6	−184.2
0.1128	0.1441	−795.3	−780.6	−409.8
0.1957	0.6709	−1170.9	−1168.4	−820.2
0.2341	0.5453	−1409.0	−1307.8	−980.5
0.2411	0.1310	−1162.9	−1480.5	−1028.0
0.3197	0.3696	−1588.8	−1514.4	−1296.3
0.4826	0.1493	−1366.7	−1764.9	−1687.9
0.5512	0.2292	−1361.4	−1538.8	−1702.6
0.6749	0.1655	−1046.5	−1231.2	−1641.9
0.7688	0.1241	−761.9	−900.9	−1438.4
At 308.15 K: $\chi'_{ij} = -8894.04$ J mol^{-1}; $\chi'_{jk} = 334.71$ J mol^{-1}; $\chi'_{ik} = -10790.16$ J mol^{-1}; $\chi^0_{ij} = -77.7366$ cal mol^{-1}; $\chi^0_{jk} = 6.2417$ cal mol^{-1}; $\chi^0_{ik} = -85.08$ cal mol^{-1}				
0.0700	0.3886	−814.3	−480.3	−151.5
0.1012	0.7615	−803.1	−651.2	−337.6
0.1377	0.2059	−970.1	−887.2	−556.1
0.1521	0.0761	−790.1	−968.2	−605.2
0.1962	0.6353	−1183.3	−1068.4	−825.5
0.2305	0.6830	−1102.9	−1134.8	−984.0
0.2645	0.0668	−1030.5	−1271.1	−1145.0
0.3347	0.2443	−1436.2	−1538.8	−1366.6
0.3396	0.5533	−1273.8	−1300.3	−1351.8
0.3983	0.2533	−1455.9	−1608.9	−1539.3
0.4316	0.1439	−1321.2	−1506.2	−1627.9
0.5530	0.1601	−1241.9	−1426.9	−1751.4
0.6542	0.1342	−1042.1	−1153.6	−1838.8
0.7608	0.1960	−646.0	−751.9	−1416.8

When 1,2-dichloroethane is replaced by aniline (i) in its ternary mixtures with pyridine (j) and α-picoline (k) or γ-picoline (k) the molar excess enthalpies become more negative over the entire composition range. On the other hand, molar excess enthalpies are positive over the entire composition range for heptane (i) + pyridine (j) + α-picoline (k). Thus, H^E_{ijk} for 1,2-dichloroethane (i), n-heptane (i) or aniline (i) in their ternary mixtures with pyridine (j) and picoline (k) varies in the order: n-heptane > 1,2-dichloroethane > aniline. H^E_{ijk} values for 1,2-dichloroethane (i) + n-heptane (j) + pyridine (k) or α-picoline (k) are all positive for all x_i and x_j.

The $H^E_{ijk}(T, x_i, x_j)$ data for various ternary mixtures were analysed in terms of the Sanchez and Lacombe theory [3] of fluid mixtures. $H^E_{ijk}(T_1, x_i, x_j)$ according to this theory [3] are given by

$$H^E_{ijk}(T_1, x_i, x_j) = rkT\left[\bar{\rho}_{ijk}\sum_{m=1}^{3}\sum_{l=1}^{3}\phi_l\phi_m\chi^0_{lm} + \sum_{l=1}^{3}\left(\frac{\bar{\rho}_l\phi^0_l - \bar{\rho}_{ijk}\phi_l}{\tilde{T}_l}\right)\right] \tag{2}$$

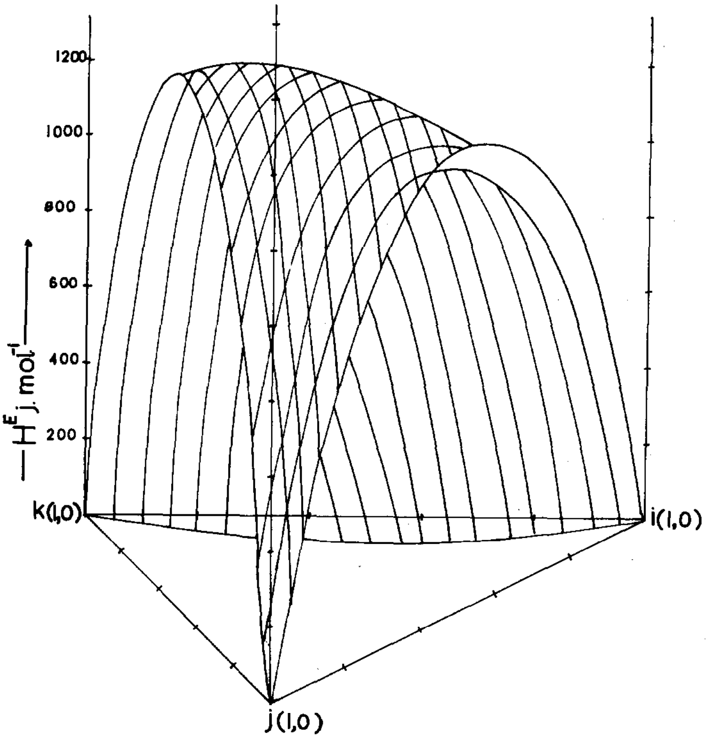

Fig. 2. Molar excess enthalpies, H^E, of 1,2-dichloroethane (i) + n-heptane (j) + pyridine (k) at 308.15 K.

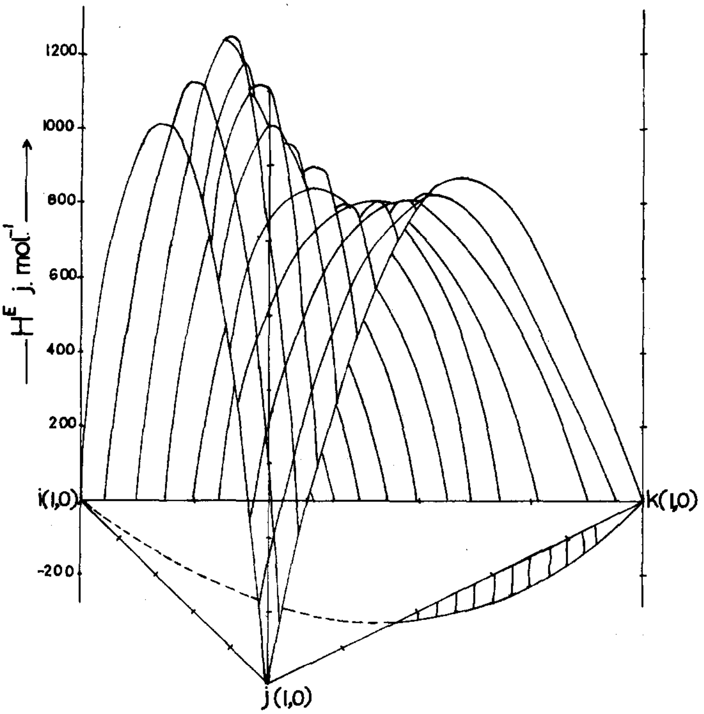

Fig. 3. Molar excess enthalpies, H^E, of 1,2-dichloroethane (i) + n-heptane (j) + α-picoline (k) at 308.15 K.

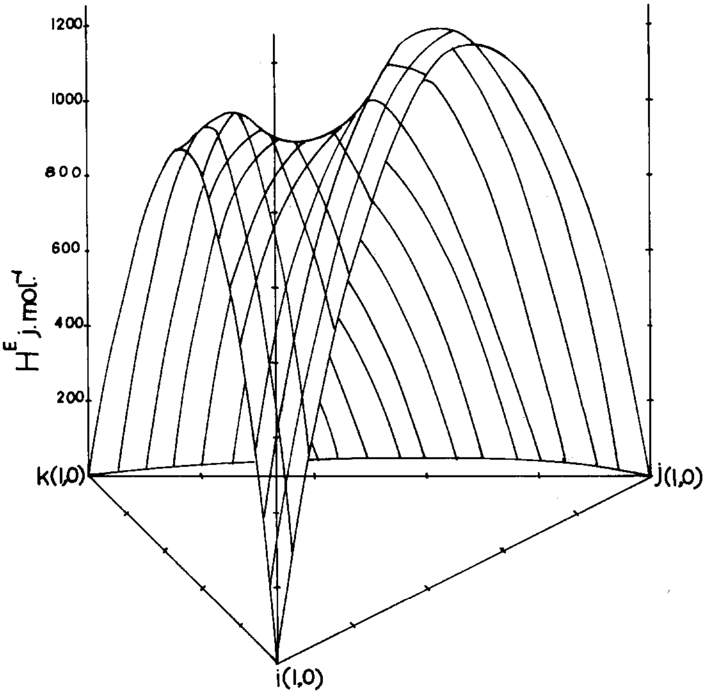

Fig. 4. Molar excess enthalpies, H^E, of *n*-heptane (i) + pyridine (j) + α-picoline (k) at 308.15 K.

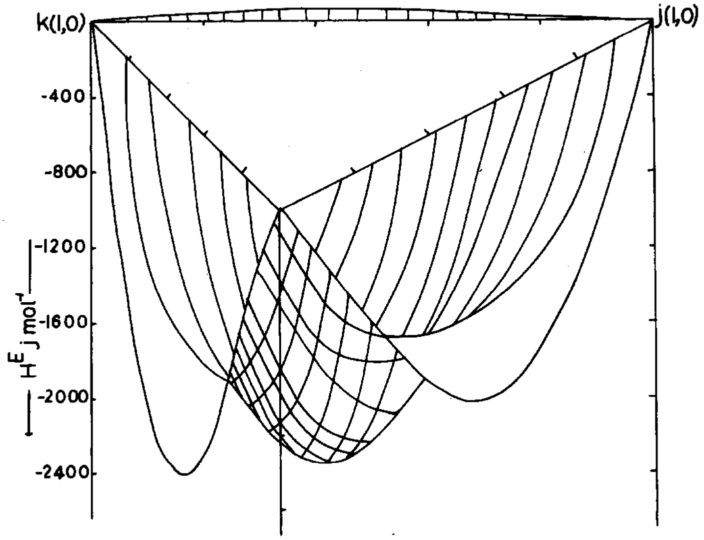

Fig. 5. Molar excess enthalpies, H^E, of aniline (i) + pyridine (j) + α-picoline (k) at 308.15 K.

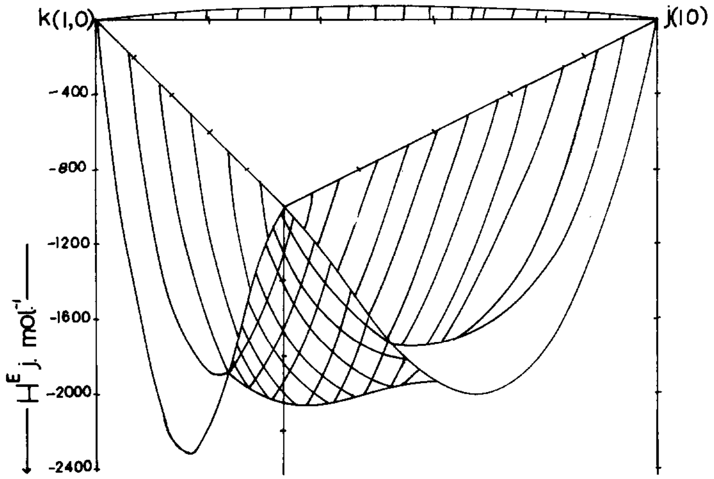

Fig. 6. Molar excess enthalpies, H^{E}, of aniline (i)+pyridine (j)+ γ-picoline (k) at 308.15 K.

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

where

$$\chi_{ij}^0 = \epsilon_{ii}^* + \epsilon_{jj}^* - 2\epsilon_{ij}^*, \text{ etc.} \tag{4}$$

$$\phi_i = m_i(\rho_i^*)^{-1}\left[\sum_{i=1}^{3}(m_i/\rho_i^*)\right]^{-1} \tag{5}$$

$$m_i = x_i M_i\left(\sum_{i=1}^{3} x_i M_i\right)^{-1} \tag{6}$$

$$r = \sum_{i=1}^{3} x_i r_i \tag{7}$$

$$r_i = \sum_{i=1}^{3} r_i^0\left[V_i^*(V_{\mathrm{mix}}^*)^{-1}\right] \tag{8}$$

$$V_{\mathrm{mix}}^* = \sum_{i=1}^{3}\phi_i^0 V_i^* \tag{9}$$

$$\phi_i^0 = m_i(\rho_i^* V_i^*)^{-1}\Big/\left[\sum_{i=1}^{3}(m_i/\rho_i^* V_i^*)\right] \tag{10}$$

and

$$\bar{\rho}_{ijk} = \left(\bar{V}_{ijk}\right)^{-1} \tag{11}$$

TABLE 2

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

	Temp. (K)	H^0_{ijk} (J mol^{-1})	H^1_{ijk} (J mol^{-1})	H^2_{ijk} (J mol^{-1})	$\sigma H^{\mathrm{E}}_{ijk}$ (J mol^{-1})
1,2-Dichloroethane (i)+ pyridine (j)+ α-picoline (k)	298.15	−113.17	−5542.0	14253.2	0.91
	308.15	−193.77	−9425.26	26283.6	0.84
1,2-Dichloroethane (i)+ n-heptane (j)+ pyridine (k)	298.15	−7199.0	−46178.0	−92590.0	4.42
	308.15	3506.45	−8213.3	−151256.0	5.53
1,2-Dichloroethane (i)+ n-heptane (j)+ α-picoline (k)	298.15	−7231.0	−15499.0	−236399.0	4.89
	308.15	−2013.22	−24894.2	894789.2	7.28
n-Heptane (i)+ pyridine (j)+ α-picoline (k)	298.15	1924.0	4864.2	−400567.0	5.53
	308.15	−5681.72	5165.61	318244.1	5.71
Aniline (i)+ pyridine (j)+ α-picoline (k)	298.15	3374.5	22976.0	−314165.0	5.68
	308.15	−10273.0	−6022.0	1026195.0	6.28
Aniline (i)+ pyridine (j)+ γ-picoline (k)	298.15	−9926.5	−44988.0	12706.0	4.49
	308.15	−3465.56	−8177.47	518969.2	7.24

and all the terms have the same significance as described by Lacombe and Sanchez [3,8].

The 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

$$\bar{\rho}^2_{ijk} + RT/\epsilon^*_{ijk}\left[\ln(1-\bar{\rho}_{ijk}) + (1 - 1/r_{ijk})\bar{\rho}_{ijk}\right] + \bar{P} = 0 \qquad (12)$$

where

$$\epsilon^*_{ijk} = \left(\epsilon^*_{ij}\phi_i + \epsilon^*_{jj}\phi_j + \epsilon^*_{kk}\phi_k\right) - \left(\phi_i\phi_j X^0_{ij} + \phi_i\phi_k X^0_{ik} + \phi_j\phi_k X^0_{jk}\right) \qquad (13)$$

and

$$\bar{P} = PV^*_{ijk}/\epsilon^*_{ijk} \qquad (14)$$

This would require a knowledge of the binary interaction energies ϵ^*_{ij}, ϵ^*_{jk} and ϵ^*_{ik} of the $(i+j)$, $(j+k)$ and $(i+k)$ binary mixtures, but since such information 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

$$H^{\mathrm{E}}_{ij} = 2\phi_i\phi_j r_{i+j}\left[\epsilon^*_{ii} + \epsilon^*_{jj} - 2\epsilon^*_{ij}\right] + RTr_{i+j}\left[\sum_i \frac{\phi_i^0\bar{\rho}_i - \bar{\rho}_{ij}\phi_i}{\bar{T}_1}\right] \tag{15}$$

where

$$\bar{T}_i = RT/\epsilon^*_{ii} \tag{16}$$

and

$$\bar{\rho}_{ij} = \left\{\left[V^E_{(i+j)}/\sum_i\left(x_i r_i^0\left(v_i^*/\sum_i \phi_i v_i^*\right)\right)\sum_i\left(\phi_i^0 v_i^*\right)\right] + \sum_i \phi_i \bar{V}_i\right\}^{-1} \tag{17}$$

Once ϵ^*_{ij}, ϵ^*_{jk} and ϵ^*_{ik} parameters of the $(i+j)$, $(j+k)$ and $(i+k)$ binary mixtures are known, $\bar{\rho}_{ij}$ for the $(i+j+k)$ mixture can be evaluated from eqns. (12)–(14). 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, χ^0_{ij}, χ^0_{jk} and χ^0_{ik}, for these binary systems are independent of composition and that these binary mixtures satisfy eqn. (18) for binary mixtures. Since

$$(\bar{\rho}_{ijk})^2 + (RT/\epsilon^*_{ijk})\left[\bar{\rho}_{ijk}(1 - r^{-1}_{ijk}) + \ln(1 - \bar{\rho}_{ijk})\right] + \bar{P} = 0 \tag{18}$$

1,2-dichloroethane (i) +pyridine (j), +α-picoline (j) and pyridine (i) +α-picoline (j) do not satisfy [6,7] eqn. (18) (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

$$(\bar{\rho}_{ij})^2 + \bar{P}_{ij} + \frac{RT}{\epsilon^*_{ij}}\left[\ln(1 - \bar{\rho}_{ij}) + (1 - r^{-1}_{ij})\bar{\rho}_{ij}\right] = 0.0124 \text{ to } 0.0441 \tag{19}$$

Since the calculated H^{E}_{ij} values compare reasonably well within corresponding experimental values [6,7], the present $(i+j+k)$ mixtures would also not satisfy eqn. (12). Consequently, H^{E}_{ijk} values evaluated at 298.15 and 308.15 K by eqn. (2), in the manner originally prepared 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 did not drastically effect the nature of the i–j interaction in the $(i+j)$, etc., mixture, it followed that the extent to which the $(i+j+k)$ mixture deviated from eqn. (12) was nearly one third of the sum to which the $(i+j)$, $(j+k)$ and $(i+k)$ equimolar mixtures deviated at 308.15 K from eqn. (18), i.e., eqn.

(12) 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

$$\bar{\rho}^2_{ijk} + \bar{P}_{ijk} + RT/\epsilon^*_{ijk}\left[\ln(1-\bar{\rho}_{ijk}) + (1-1/r_{ijk})\bar{\rho}_{ijk}\right] = \left(\tfrac{1}{3}\right) \tag{20}$$

(right-hand side of eqn. (18) for $(i+j)$, $(j+k)$ and $(i+k)$) where ϵ^*_{ijk} and $\bar{\rho}_{ijk}$ are defined by

$$\epsilon^*_{ijk} = \sum_{i=1}^{3} \phi_i \epsilon^*_{ii} - RT\Sigma\Sigma\phi_i\phi_j\chi^0_{ij} \tag{21}$$

$$\bar{V}_{ijk} = 1/\bar{\rho}_{ijk} \tag{22}$$

Once the equation of state for a ternary mixture, such as eqn. (20) 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 thus calculated are for the right order of magnitude but that 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. (20) 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 multiple component systems from a knowledge of their binary interaction coefficients.

The H^{E}_{ijk} data were next analysed in terms of the "graph theoretical" approach [9].

Graph theoretical approach

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 $(k+i)$ mixtures by means of this approach, 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

$$H^{\mathrm{E}}_{ijk}(T_1,\ x_i,\ x_j) \propto \left[H^{\mathrm{E}}_{ij'} + H^{\mathrm{E}}_{jk'} + H^{\mathrm{E}}_{ki'} + H^{\mathrm{E}}_{ij} + H^{\mathrm{E}}_{jk} + H^{\mathrm{E}}_{ik} \right] \tag{23}$$

$$= K\left[H^{\mathrm{E}}_{ij'} + H^{\mathrm{E}}_{jk'} + H^{\mathrm{E}}_{ki'} + H^{\mathrm{E}}_{ij} + H^{\mathrm{E}}_{jk} + H^{\mathrm{E}}_{ik} \right] \tag{24}$$

where K is a constant of proportionality and $H^{\mathrm{E}}_{ij'}$, 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 [9]

$$H^{\mathrm{E}}_{ij'}(T_1,\ x_i,\ x_j) = \frac{x_i(1-x_i)\chi'_{ij'}K_{ij'}\left({}^3\xi_i/{}^3\xi_{j'}\right)}{x_i + x_i(1-x_i)K_{ij'}\left({}^3\xi_i/{}^3\xi_{j'}\right)} \tag{25}$$

where ${}^3\xi_i$ denotes the connectivity parameter of the third degree for i, etc., and is defined by [9]

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

where δ_l, δ_m and δ_n, etc., denote the degrees of the lth, mth and nth, etc., vertices of the molecular graph of i. As ${}^{1/3}\xi_i$ of a molecule has been regarded [9] as a measure 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 it should be given by

$$K^1_{ij}\left({}^3\xi_i/{}^3\xi_j\right) = x_j k_{ij}\left({}^3\xi_i/{}^3\xi_j\right) + x_i K_{ik}\left({}^3\xi_i/{}^3\xi_k\right) \tag{26}$$

assuming that there are no specific interactions between i, j and k components of the $(i+j+k)$ mixture. Consequently, eqn. (25) yields

$$\begin{aligned} &H^{\mathrm{E}}_{ijk}(T_1,\ x_i,\ x_j) \\ &\quad = K\left[\sum x_i(1-x_i)\chi'_{ij'} \frac{x_j K_{ij}\left({}^3\xi_i/{}^3\xi_j\right) + x_k K_{ik}\left({}^3\xi_i/{}^3\xi_k\right)}{x_i + (1-x_i)\left[x_j K_{ij}\left({}^3\xi_i/{}^3\xi_j\right) + x_k K_{ik}\left({}^3\xi_i/{}^3\xi_k\right)\right]} \right. \\ &\qquad \left. + \sum \frac{x_i x_j \chi'_{ij} K_{ij}\left({}^3\xi_i/{}^3\xi_j\right)}{x_i + x_j K_{ij}\left({}^3\xi_i/{}^3\xi_j\right)} \right] \end{aligned} \tag{27}$$

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

$$\begin{aligned} \chi'_{ij'} &= \chi'_{ij} + \chi'_{ik} \\ \chi'_{jk'} &= \chi'_{jk} + \chi'_{ji} \\ \chi'_{ki'} &= \chi'_{ki} + \chi'_{kj} \end{aligned} \tag{28}$$

Equation (27) then yields

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

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 and 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 [10] at 293.15 K for benzene (i) + cyclohexane (j) + n-heptane (k) were utilised to find the best possible value of K for eqn. (29). 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' and 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. (30)

$$H^{\mathrm{E}}_{ij}(T_1,\, x_i) = x_i x_j \chi'_{ij} K_{ij}\left({}^3\xi_i/{}^3\xi_j\right)\Big/\left[x_i + K_{ij} x_j\left({}^3\xi_i/{}^3\xi_j\right)\right] \qquad (30)$$

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 ternary mixtures. These six binary contacts taken two at a time will give rise to ${}^6C_2$ or fifteen ijk ternary contacts. In actual fact, however, 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. (29) 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} and K_{ij}, etc., of the $(i+j)$, $(j+k)$ and $(k+i)$ binary mixtures. Such $H^{\mathrm{E}}_{ijk}(T_1, x_i, x_j)$ values for the 1,2-dichloroethane (i) + pyridine (j) + α-picoline (k), + n-heptane (j) + pyridine (k), + α-picoline (k), n-heptane (i) + pyridine (j) + α-picoline (k), aniline (i) + pyridine (j) + α-picoline (k), + γ-picoline (k) mixtures are recorded in Table 1 and are also compared with their corresponding experimental values for all these mixtures.

Examination of Table 1 shows that $H^{\mathrm{E}}_{ijk}(T_1, x_i, x_j)$ values evaluated from $H^{\mathrm{E}}(T_1;\ x_i = 0.4$ and $0.5)$ data compare well with their corresponding experimental values for all these mixtures.

The analysis of $H^{\mathrm{E}}_{ijk}(T_1, x_i, x_j)$ data of the various $(i+j+k)$ mixtures studied here suggests that the $H^{\mathrm{E}}_{ijk}(T_1, x_i, x_j)$ data of the present ternary mixtures evaluated from the graph theoretical approach reproduce the experimental $H^{E}_{ijk}(T_1, x_i, x_j)$ data better than the Sanchez and Lacombe theory.

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