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MOLECULAR INTERACTIONS IN TERNARY MIXTURES OF NON-ELECTROLYTES: MOLAR EXCESS VOLUMES

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ABSTRACT

Molar excess volumes, V_{ijk}^{E}, of 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) and +γ-picoline (k) mixtures have been measured dilatometrically at 298.15 K. The data have been examined in terms of the Sanchez and Lacombe theory and the graph-theoretical approach and they were found to be described better by the latter. Self- and cross-volume interaction coefficients, V_{jk}, V_{jjk} and V_{jkk}, etc., have also been determined and the values utilized to study molecular interactions between the jth and kth in the presence of the ith molecular species in these $i+j+k$ mixtures.

INTRODUCTION

In a binary $i+j$ mixture, i–i and j–j contacts in the pure components i and j are replaced by i–j contacts in the mixture. If interactions in a ternary $i+j+k$ mixture are assumed to be closely dependent on the interactions in the constituent $i+j$, $j+k$ and $i+k$ mixtures, it should be possible to evaluate the thermodynamic excess functions for ternary mixtures of non-electrolytes when the corresponding functions for the binary $i+j$, $j+k$ and $i+k$ mixtures are known.

Singh and Sharma [1] recently employed a graph-theoretical approach that utilises connectivity parameters of the third degree, ${}^{3}\xi_{i}$, which successfully describes the molar excess volumes, V^{E}, of ternary mixtures of non-hetero-cyclic non-electrolytes. Lacombe and Sanchez [2,3] have also developed a theory of fluid mixtures which 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 the molar excess volumes, V_{ijk}^{E}, of some ternary mixtures of non-electrolytes further and to analyse data in terms of (i) the Lacombe and Sanchez theory, and (ii) the graph-theoretical approach of fluid mixtures.

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EXPERIMENTAL

1,2-Dichloroethane, pyridine, α- and γ-picolines, aniline and *n*-heptane (all BDH, Analar grade) were purified by standard procedures [4]. The purity was checked by measuring their densities at 293.15 ± 0.01 K, which agreed well with the corresponding literature values [4].

Molar excess volumes, V^{E}_{ijk}, were determined in a dilatometer similar to that used by Brown and Smith (1962) [4a], the difference being that there were now three limbs for the three components. The temperature of the water bath was controlled to within less than ±0.01 K by means of a toluene regulator, and the change in the level of the liquid in the dilatometer capillary was measured by a cathetometer that could be read to ±0.001 cm. Further, to ensure the complete mixing of the components in the capillary, the dilatometer was placed in a cold bath, so that there was a minimum amount of liquid in the capillary, and then returned to the experimental water bath. This process was repeated two or three times. The uncertainty in the measured V^{E}_{ijk} values is ~ 0.55% at most.

RESULTS

The V^{E}_{ijk} data for the various ternary $(i+j+k)$ mixtures as a function of composition at 298.15 K are recorded in Table 1 and shown graphically in Figs. 1–6. These data were expressed as [1]

$$V^{\mathrm{E}}_{ijk} = x_i x_j\left[\sum_{n=0}^{2} A^n_{ij}(x_i - x_j)^n\right] + x_j x_k\left[\sum_{n=0}^{2} A^n_{jk}(x_j - x_k)^n\right] + x_i x_k\left[\sum_{n=0}^{2} A^n_{ik}(x_i - x_k)^n\right] + x_i x_j x_k\left[\sum_{n=0}^{2} A^n_{ijk}(x_j - x_k)^n x_i^n\right] \qquad (1)$$

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

$$\left\{V^{\mathrm{E}}_{ijk} - x_i x_j\left[\sum_{n=0}^{2}(x_i - x_j)^n A^n_{ij}\right] - x_j x_k\left[\sum_{n=0}^{2}(x_j - x_k)A^n_{jk}\right] - x_i x_k\left[\sum_{n=0}^{2}(x_i - x_k)^n A^n_{ik}\right]\right\}\Big/ x_i x_j x_k$$

data to

$$\left[\sum_{n=0}^{2} A^n_{ijk}(x_j - x_k)^n x_i^n\right]$$

TABLE 1

Comparison of the measured V^E_{ijk} values for the various $(i+j+k)$ ternary mixtures at 298.15 and 308.15 K with their corresponding V^E_{ijk} values as evaluated from the graph theory and Sanchez and Lacombe theory

x_i	x_j	V^E_{ijk} (cm^3 mol^{-1})		
		Graph	Expt.	Sanchez and Lacombe
1,2-Dichloroethane (i)+pyridine (j)+ α-picoline (k) at 298.15 K $\alpha_{ij} = -7.200\ (-2.259)$ cm^3 mol^{-1}; $\alpha_{jk} = -2.6088\ (-0.434)$ cm^3 mol^{-1}; $\alpha_{ik} = -1.8517\ (-11.524)$ cm^3 mol^{-1}				
0.0299	0.0660	0.006 (0.035)	0.010	−0.239
0.0441	0.0891	0.027 (0.047)	0.013	−0.314
0.0591	0.0947	0.034 (0.052)	0.019	−0.421
0.0714	0.0596	0.038 (0.038)	0.019	−0.339
0.0784	0.3378	0.047 (0.141)	0.040	−0.084
0.1778	0.0297	0.083 (0.037)	0.052	−0.463
0.2022	0.1170	0.093 (0.083)	0.067	−0.341
0.2080	0.1018	0.095 (0.077)	0.068	−0.348
0.2095	0.7310	0.055 (0.243)	0.137	0.512
0.2184	0.3827	0.089 (0.194)	0.098	0.046
0.3494	0.4800	0.096 (0.259)	0.178	0.281
0.4470	0.3502	0.117 (0.230)	0.185	0.185
0.4678	0.3706	0.112 (0.241)	0.200	0.237
0.5771	0.2417	0.127 (0.187)	0.183	0.167
0.7520	0.1502	0.102 (0.132)	0.151	0.272
1,2-Dichloroethane (i)+ n-heptane (j)+pyridine (k) at 298.15 K $\alpha_{ij} = -94.4958$ cm^3 mol^{-1}; $\alpha_{jk} = -25.69\ (-1.327)$ cm^3 mol^{-1}; $\alpha_{ik} = -7.200\ (-2.259)$ cm^3 mol^{-1}				
0.0369	0.8619	0.122 (0.948)	0.239	−0.478
0.0568	0.8951	0.186 (1.354)	0.235	−0.515
0.0621	0.8551	0.219 (1.835)	0.268	−0.443
0.1034	0.8720	0.285 (1.346)	0.296	−0.410
0.1081	0.0595	0.313 (1.389)	0.104	0.503
0.1192	0.6755	0.277 (1.763)	0.391	−0.191
0.1462	0.7521	0.211 (0.968)	0.419	−0.236
0.1618	0.4608	1.007 (3.387)	0.380	−0.030
0.1910	0.1736	0.501 (2.785)	0.215	0.326
0.2050	0.1004	0.517 (2.456)	0.181	0.408
0.3221	0.3615	0.548 (2.236)	0.356	0.214
0.3701	0.2008	0.673 (2.461)	0.344	0.303
0.4065	0.4258	0.454 (1.387)	0.542	0.253
0.4524	0.1626	0.723 (2.228)	0.336	0.341
0.6550	0.2009	0.498 (1.072)	0.412	0.445
0.7793	0.0991	0.450 (0.842)	0.260	0.453
0.8821	0.0695	0.232 (0.364)	0.167	0.471
1,2-Dichloroethane (i)+ n-heptane (j)+ α-picoline (k) at 298.15 K $\alpha_{ij} = -94.4958$ cm^3 mol^{-1}; $\alpha_{jk} = -5.933\ (-5.078)$ cm^3 mol^{-1}; $\alpha_{ik} = -1.8517\ (-11.524)$ cm^3 mol^{-1}				
0.0474	0.8514	0.389 (0.201)	0.216	0.129
0.0666	0.9121	0.322 (0.181)	0.195	0.358

TABLE 1 (continued)

x_i	x_j	V^E_{ijk} (cm^3 mol^{-1})		
		Graph	Expt.	Sanchez and Lacombe
0.0752	0.0492	0.420 (0.254)	0.016	−0.313
0.0828	0.8310	0.411 (0.270)	0.273	0.252
0.1048	0.7829	0.422 (0.336)	0.320	0.231
0.1329	0.848	0.691 (0.389)	0.033	−0.297
0.1852	0.6128	0.703 (0.503)	0.393	0.147
0.1864	0.5269	0.852 (0.617)	0.354	0.012
0.2814	0.1694	1.149 (0.535)	0.104	−0.154
0.2881	0.5428	0.726 (0.449)	0.454	0.381
0.3343	0.3175	1.122 (0.575)	0.316	0.084
0.3676	0.4001	0.958 (0.501)	0.425	0.326
0.5574	0.0800	1.1417 (0.345)	0.121	0.205
0.6628	0.2024	0.846 (0.281)	0.360	0.734
0.8057	0.0705	0.839 (0.176)	0.177	0.693
n-Heptane (i)+pyridine (j)+ α-picoline (k) at 298.15 K $\alpha_{ij} = -25.69\ (-1.327)$ cm^3 mol^{-1}; $\alpha_{jk} = -2.6088\ (-0.434)$ cm^3 mol^{-1}; $\alpha_{ik} = -5.933\ (-5.078)$ cm^3 mol^{-1}				
0.0370	0.6448	0.064 (0.090)	−0.001	0.455
0.0412	0.0974	0.045 (0.33)	−0.002	−0.290
0.0575	0.1062	0.057 (0.39)	0.001	−0.294
0.0652	0.0354	0.052 (0.024)	0.002	−0.404
0.0858	0.0932	0.073 (0.043)	0.007	−0.413
0.0882	0.0584	0.070 (0.035)	0.008	−0.364
0.0990	0.3218	0.095 (0.094)	−0.005	−0.046
0.1114	0.8050	0.039 (0.131)	−0.006	−0.653
0.1318	0.1047	0.101 (0.057)	0.021	−0.389
0.1932	0.1970	0.133 (0.093)	0.046	−0.312
0.2754	0.5507	0.103 (0.194)	−0.160	0.268
0.4984	0.2523	0.217 (0.074)	0.181	−0.582
0.5592	0.0776	0.212 (0.084)	0.215	−0.481
0.7208	0.0558	0.178 (0.065)	0.237	−0.351
0.8484	0.0662	0.096 (0.056)	0.181	−0.101
Aniline (i)+pyridine (j)+ α-picoline (k) at 298.15 K $\alpha_{ij} = (7.505)$ cm^3 mol^{-1}; $\alpha_{jk} = -2.6088\ (-0.434)$ cm^3 mol^{-1}; $\alpha_{ik} = 62.7353\ (4709.2)$ cm^3 mol^{-1}				
0.0565	0.0431	(−6.454)	−0.141	0.081
0.0651	0.0730	(−10.667)	−0.161	0.192
0.0983	0.6585	(−42.065)	−0.243	0.364
0.1052	0.0614	(−9.036)	−0.241	0.411
0.1121	0.8213	(−28.126)	−0.211	0.533
0.1167	0.0841	(−12.137)	−0.271	0.601
0.1569	0.1136	(−16.184)	−0.345	−0.442
0.2212	0.2836	(−33.273)	−0.479	−0.820
0.2272	0.1646	(−21.936)	−0.442	−0.471
0.2433	0.1640	(−22.079)	−0.462	−0.506
0.3042	0.1744	(−22.606)	−0.509	0.566
0.3192	0.1450	(−20.478)	−0.500	0.615

TABLE 1 (continued)

x_i	x_j	V^E_{ijk} (cm^3 mol^{-1})		
		Graph	Expt.	Sanchez and Lacombe
0.4339	0.2500	(−31.916)	−0.569	−0.558
0.4350	0.1811	(−23.498)	−0.548	−0.647
0.4929	0.3817	(−38.416)	−0.420	−0.394
0.7851	0.1289	(−16.718)	−0.216	−0.621
Aniline (i)+pyridine (j)+ γ-picoline (k) at 298.15 K α_{ij} = (7.505) cm^3 mol^{-1}; α_{jk} = −6.2114 (−0.858) cm^3 mol^{-1}; α_{ik} = 36.0262 (280.42) cm^3 mol^{-1}				
0.0254	0.0764	(−0.809)	−0.042	0.184
0.0498	0.0271	(−0.304)	−0.139	0.211
0.0635	0.0914	(−0.954)	−0.111	0.082
0.0800	0.0488	(−0.534)	−0.141	0.189
0.1260	0.7680	(−2.320)	−0.191	0.242
0.1471	0.1408	(−1.374)	−0.223	0.144
0.1532	0.3158	(−2.581)	−0.216	0.144
0.2337	0.1790	(−1.671)	−0.283	−0.079
0.2357	0.5025	(−2.967)	−0.283	−0.058
0.2374	0.3002	(−2.431)	−0.290	−0.073
0.2470	0.5097	(−2.966)	−0.290	−0.086
0.4534	0.2883	(−2.187)	−0.318	−0.486
0.5648	0.1486	(−1.290)	−0.274	−0.638
0.7470	0.0819	(−0.735)	−0.152	−0.795

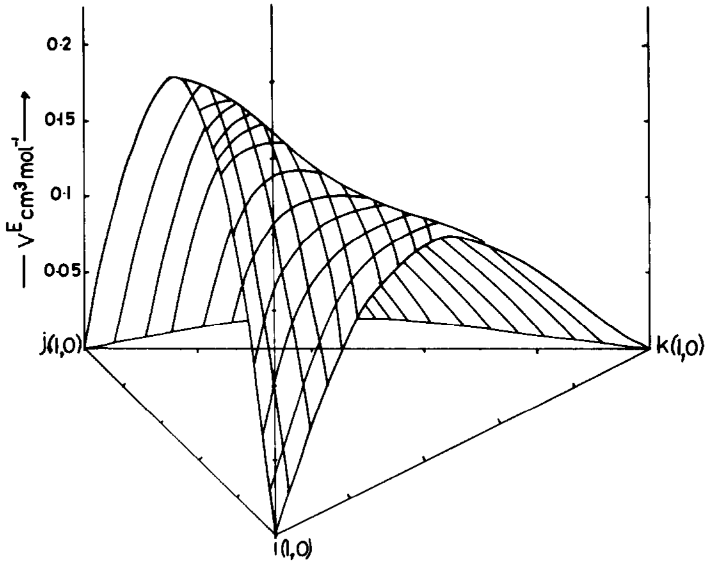


Fig. 1. Molar excess volumes, V^E, of 1,2-dichloroethane (i)+pyridine (j)+ α-picoline (k) at 298.15 K.

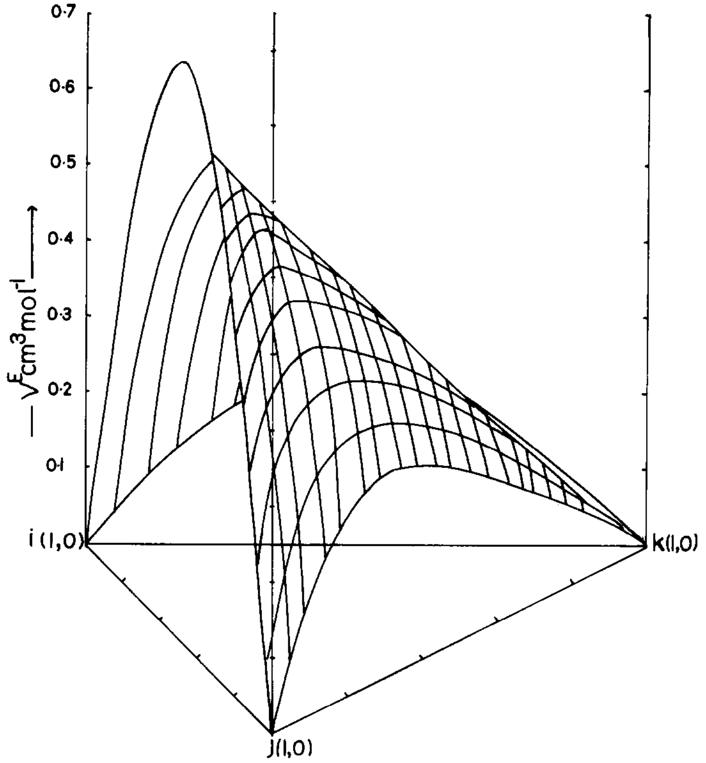


Fig. 2. Molar excess volumes, V^E, of 1,2-dichloroethane (i)+ n-heptane (j)+pyridine (k) at 298.15 K.

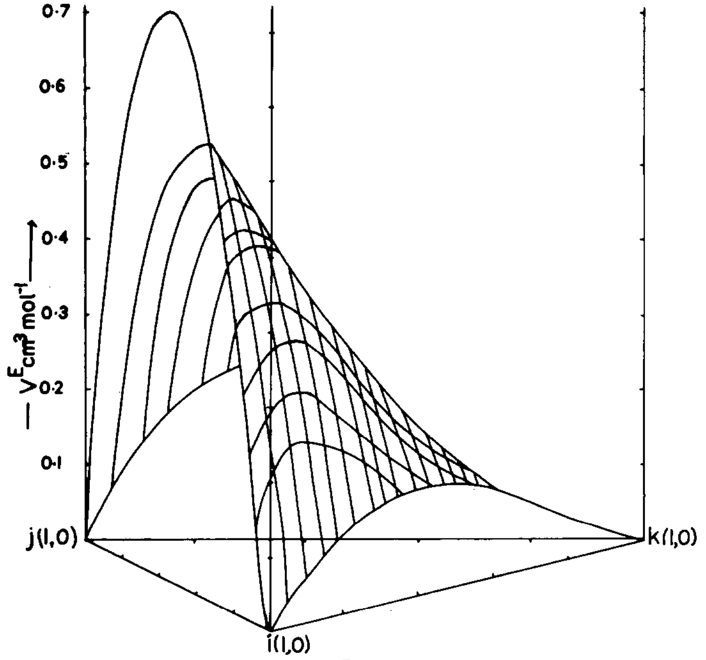


Fig. 3. Molar excess volumes, V^E, of 1,2-dichloroethane (i)+ n-heptane (j)+ α-picoline (k) at 298.15 K.

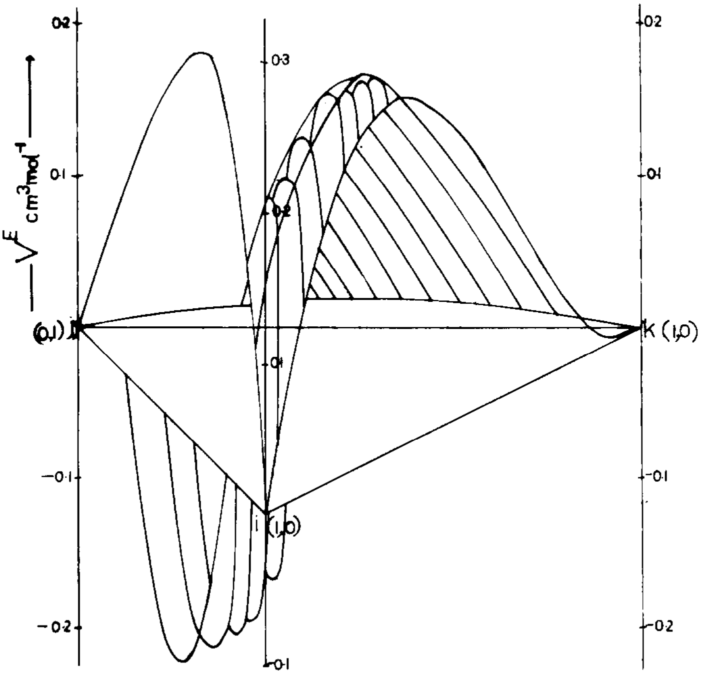


Fig. 4. Molar excess volumes, V^E, of *n*-heptane (i)+pyridine (j)+ α-picoline (k) at 298.15 K.

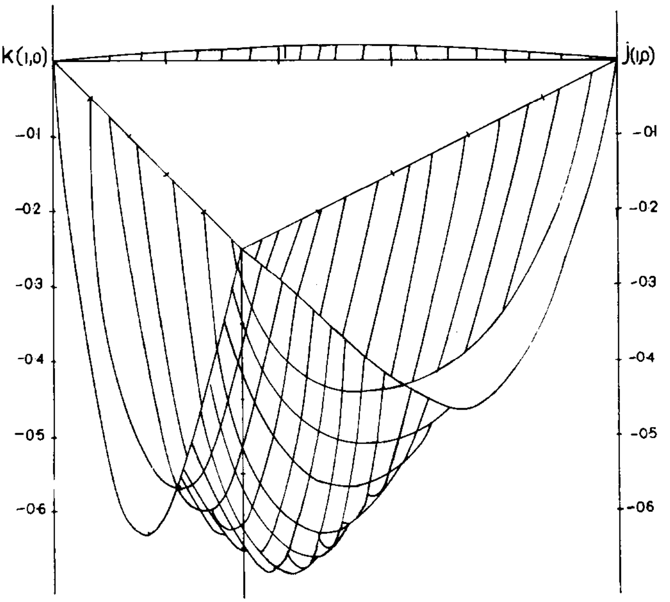


Fig. 5. Molar excess volumes, V^E, of aniline (i)+pyridine (j)+ α-picoline (k) at 298.15 K.

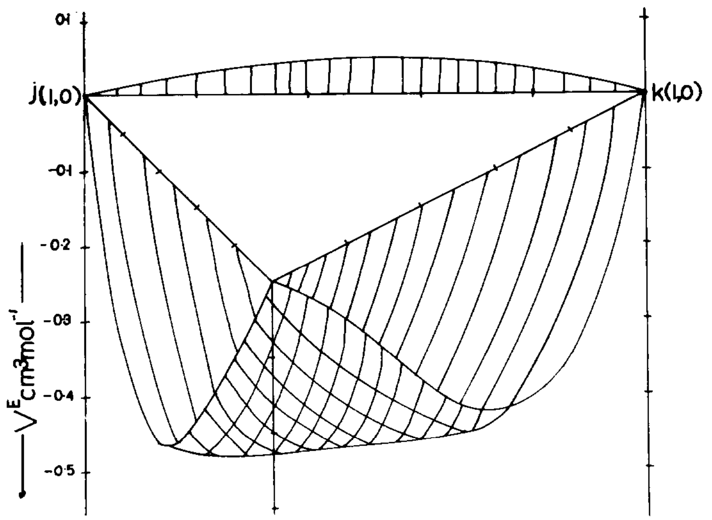


Fig. 6. Molar excess volumes, V^E, of aniline (i)+pyridine (j)+γ-picoline (k) at 298.15 K.

by the method of least squares, and are recorded in Table 2 together with standard deviations, $\sigma(V_{ijk}^E)$, defined as

$$\left[\sum\left(V_{ijk(\mathrm{exp.})}^E - V_{ijk(\mathrm{calc.\,from\,eqn.1})}^E\right)^2/(m-p)\right]^{1/2} \qquad (2)$$

TABLE 2

V_{ijk}^0, V_{ijk}^1 and V_{ijk}^2 parameters (cm^3 mol^{-1}) of eqn. (3) along with the standard deviation, $\sigma(V_{ijk}^E)$ (cm^3 mol^{-1}) of the molar excess volume for the (i + j + k) mixtures at 298.15 K

System	Temp. (K)	V_{ijk}^0	V_{ijk}^1	V_{ijk}^2	$\sigma(V_{ijk}^E)$
1,2-Dichloroethane (i) + pyridine (j) + α-picoline (k)	298.15	−1.0643	1.6922	25.0235	0.001
1,2-Dichloroethane (i) + n-heptane (j) + pyridine (k)	298.15	−2.800	−6.200	−93.400	0.002
1,2-Dichloroethane (i) + n-heptane (j) + α-picoline (k)	298.15	−4.090	0.100	−158.600	0.002
n-Heptane (i) + pyridine (j) + α-picoline (k)	298.15	−4.620	−51.114	−232.0	0.002
Aniline (i) + pyridine (j) + α-picoline (k)	298.15	−5.700	−2.800	145.000	0.003
Aniline (i) + pyridine (j) + γ-picoline (k)	298.15	−1.9925	4.7533	14.552	0.003

where m is the number of data points and p the number of adjustable parameters in eqn. (1). The parameters A_{ij}^{n}, A_{jk}^{n}, A_{ik}^{n}, etc., for the $i+j$, $j+k$ and $k+i$ binary mixtures were taken from the literature [4,5].

DISCUSSION

We are unaware of any previous V_{ijk}^{E} data with which to compare the present results for $i+j+k$ mixtures. The V_{ijk}^{E} data for the ternary mixtures were first analysed [1] using the Lacombe and Sanchez [2,3] theory of classical fluids and their mixtures.

However, it was observed that the right-hand side (RHS) of the equation of state (eqn. 34a in ref. 1) varied from 0.0124 to 0.0441 for the various binary mixtures. Since, therefore, the $i+j$, $j+k$ and $i+k$ mixtures do not satisfy the equation of state for binary mixtures, the resulting $i+j+k$ ternary mixture would also not satisfy the equation of state. Thus, V_{ijk}^{E} values evaluated in the manner originally proposed by Lacombe and Sanchez [3] would not compare well with the corresponding experimental values. The equation of state for a ternary mixture has been shown [1] to be given by

$$\begin{aligned}&\bar{\rho}_{ijk}^{2} + p_{ijk} + \left(RT/\epsilon_{ijk}^{*}\right)\left[\ln\left(1-\bar{\rho}_{ijk}\right) + \left(1 - r_{ijk}^{-1}\right)\bar{\rho}_{ijk}\right]\\ &\qquad = 1/3\left(\sum \text{RHS of the equation of state for } i+j,\ j+k \text{ and } i+k \text{ mixtures}\right)\end{aligned} \tag{3}$$

where $\bar{\rho}_{ijk}$ and ϵ_{ijk}^{*} have the same significance as explained earlier [1]. Once this equation of state for a ternary mixture has been established, $\bar{\rho}_{ijk}$ and, hence, V_{ijk}^{E} for the mixture at any composition and temperature can be evaluated readily. V_{ijk}^{E} values thus obtained for the various ternary mixtures are recorded in Table 1, where they are also compared with the corresponding experimental values.

Examination of Table 1 reveals that V_{ijk}^{E} values calculated at 298.15 K are of the right order of magnitude, but that the quantitative agreement is not very impressive. In some cases even the sign is not predicted correctly. A possible reason for this failure may be the assumption that the right-hand side of eqn. (3) for the $i+j$, $j+k$ and $i+k$ binary mixtures comprising the $i+j+k$ mixture is constant over the entire range of x_i, x_j and x_k at the given temperature. Nevertheless, the theory makes a significant theoretical attempt to evaluate V_{ijk}^{E} data for ternary mixtures of non-electrolytes from a knowledge of their binary interaction coefficients.

The V_{ijk}^{E} data for the various ternary mixtures were then analysed [1] in terms of the graph-theoretical approach [6]. V_{ijk}^{E} according to this approach is given by

$$V_{ijk}^{\mathrm{E}} = \alpha_{ijk}\left(1/\sum x_i^{3}\xi_i - \sum x_i/{}^{3}\xi_i\right) \tag{4}$$

where α_{ijk} is a constant characteristic of the $i+j+k$ mixture and is assumed to be independent of composition, and x_i, etc., are the mole fractions of the ith, etc., components in the mixture. The term ${}^3\xi_i$ is a connectivity parameter of the third degree for the ith component, and is defined [7] by

$$ {}^3\xi_i = \sum_{l<m} \sum_{m<n} \sum_{n<o} (\delta_l \delta_m \delta_n \delta_o)^{-1/2} \tag{5} $$

where δ_l, δ_m, δ_n, δ_o, etc., denote the degrees of the lth, mth, nth and oth, etc., vertices of the graph for the ith molecule [8] and were evaluated in the manner described earlier [6].

Evaluation of V^E_{ijk} for a ternary mixture thus requires a knowledge of α_{ijk} for the mixture. The latter was shown [1] to be given by

$$ \alpha_{ijk} = \tfrac{1}{5}(\alpha_{ij} + \alpha_{jk} + \alpha_{ik}) \tag{6} $$

so that eqn. (4) reduces to

$$ V^E_{ijk} = 0.2(\alpha_{ij} + \alpha_{jk} + \alpha_{ik})\left(1/\sum x_i {}^3\xi_i - \sum x_i/{}^3\xi_i\right) \tag{7} $$

Thus, from a knowledge of the binary interaction coefficients α_{ij}, α_{jk} and α_{ik} for the $i+j$, $j+k$ and $i+k$ binary mixtures, V^E_{ijk} for a ternary $i+j+k$ mixture can be evaluated readily if ${}^3\xi_i$ parameters for the constituent molecules are known.

Since aniline, pyridine and α- and γ-picolines undergo reactions that are characteristic of the aromatic ring (disregarding the basic nature of these compounds for the present analysis), and as their molar volumes are almost the same (~ 10% lower) as those of benzene and toluene, the ${}^3\xi_i$ parameters for pyridine and picolines were taken to be the same as those for benzene and toluene, respectively [6]. However, such an approach can be highly restrictive, and Singh [9] has recently advocated the use of δ^v (valence δ, which explicitly reflects the valency of the atoms forming the bonds) rather than δ to evaluate ${}^3\xi_i$ in calculating H^E and V^E values for binary mixtures of non-electrolytes. In the present analysis we thus evaluated ${}^3\xi_i$ parameters for the constituent molecules of the ternary mixtures using both these approaches and then utilised both sets of results to calculate V^E_{ijk} data for the mixtures. The V^E_{ijk} values thus obtained are recorded in Table 1 (V^E_{ijk} values obtained from eqn. (4) using ${}^3\xi$ parameters evaluated from δ^V are enclosed in parentheses), where they are also compared with the corresponding experimental values.

Examination of Table 1 reveals that the V^E_{ijk} (δ or δ^v) values calculated from eqn. (4) for all the present ternary mixtures correctly predict the sign of experimental V^E_{ijk} values; the quantitative agreement (for all except aniline (i) + pyridine (j) + α-picoline (k) and + γ-picoline (k) mixtures), however, is dictated by x_i, x_j and x_k. This suggests that, depending upon x_i, x_j, x_k, either the C–C skeleton or the valency of individual atoms in the molecular graph of the constituent molecules dictate the nature of packing of i, j and k components in the $(i+j+k)$ mixtures. For aniline (i) + pyridine (j) + α-picoline (k) and + γ-picoline (k) mixtures, the calculated V^{E}_{ijk} values are about 7 times more than the corresponding experimental values. This suggests that the addition of pyridine and α- or γ-picoline to aniline causes stronger interaction between them than that envisaged by the theory.

$V^{\mathrm{E}}_{ijk}(T,x_i,x_j)$ data were next analysed in terms of the Mayer–McMillan formalism [10] to gain information about the effect of i on the j–j and k–k, etc., interactions. According to this formalism [11], an excess function, say, $V^{\mathrm{E}*}$, of a solution containing n solute species can be expressed as

$$V^{\mathrm{E}*} = V - V_{\mathrm{sol}} - \sum_{i=1}^{n} V_i^0 m_i \tag{8}$$

$$= \sum_{i=1}^{n} \sum_{i=1}^{n} V_{ij} m_i m_j + \sum_{i=1}^{n} \sum_{i=1}^{n} \sum_{i=1}^{n} V_{ijk} m_i m_j m_k + \ldots \tag{9}$$

where V and $V^{\mathrm{E}*}$ are the volume and excess volume, respectively, of a solution containing 1 kg of solvent and $m_1, \ldots, m_n$ moles of each solute species; V_{sol} is the standard volume of 1 kg of the solvent; and V_i^0 is the partial molal volume of each solute. For a ternary solution, eqn. (9) reduces to

$$V^{\mathrm{E}*}(m_j,\ m_k) = V_{jj} m_j^2 + 2V_{jk} m_j m_k + V_{kk} m_k^2 + V_{jjj} m_j^3$$
$$+ 3V_{jjk} m_j^2 m_k + V_{jkk} m_j m_k^2 + V_{kkk} m_k^3 \tag{10}$$

and for two binary $(i+p)$, $(p=j$ or $k)$ solutions, eqn. (9) yields

$$V^{\mathrm{E}*}(m_j) = V_{jj} m_j^2 + V_{jjj} m_j^3 \tag{11}$$

$$V^{\mathrm{E}*}(m_k) = V_{kk} m_k^2 + V_{kkk} m_k^3 \tag{12}$$

In order to calculate the cross-volume coefficients V_{jk}, V_{jkk} and V_{jjk} from eqn. (10), we used an auxiliary function, $\Delta V^{\mathrm{E}*}$, defined [12] as

$$\Delta V^{\mathrm{E}*} = V^{\mathrm{E}*}(m_j,\ m_k) - V^{\mathrm{E}*}(m_j) - V^{\mathrm{E}*}(m_k) \tag{13}$$

which, in view of eqns. (11) and (12), yields

$$\Delta V^{\mathrm{E}*}(m_j,\ m_k)^{-1} = 2V_{jk} + 3V_{jjk} m_j + 3V_{jkk} m_k + \ldots \tag{14}$$

Thus, if $V^{\mathrm{E}*}(m_j,\ m_k)$ data for the $(i+j+k)$ ternary mixture, along with the $V^{\mathrm{E}*}(m_j)$ and $V^{\mathrm{E}*}(m_k)$ data for $(i+j)$ and $(i+k)$ binary mixtures are known, it should be possible to evaluate the cross-volume coefficients. Ideally, $V^{\mathrm{E}*}(m_j,\ m_k)$, $V^{\mathrm{E}*}(m_j)$ or $V^{\mathrm{E}*}(m_k)$ data for dilute solutions should be utilized to evaluate these cross-volume coefficients. This led us to use $V^{\mathrm{E}*}(m_j,\ m_k)$ data for a ternary mixture in the range $0.025 \leqslant x_j,\ x_k \leqslant 0.11$

(corresponding to $0.2 \leqslant m_j, m_k$) with the corresponding $V^{E*}(m_p)$ ($p = j$ or k) data of the $(i + p)$ binary mixtures in the range $0.2 \leqslant m_p$ to calculate V_{jk}, V_{jjk} and V_{jkk} from eqn. (14) by the method of least squares. For this purpose, $V^{E}_{ijk}(x_j, x_k)$ data (cm^3 mol^{-1}) of the $(i + j + k)$ mixture were converted to $V^{E*}(m_j, m_k)$ data (cm^3 mol^{-1}; mol kg^{-1} of i) by means of

$$V^{E*}(m_j, m_k)\ \text{cm}^3\ \text{mol}^{-1}\ (\text{mol kg}^{-1}\ \text{of}\ i)$$
$$= \left[V^{E}(x_j, x_k)\ \text{cm}^3\ \text{mol}^{-1}\ \text{of}\ (i + j + k)\ \text{mixture}\right]\left[1000/x_i\ \text{mol kg}^{-1}\ \text{of}\ i\right] \tag{15}$$

while the m_p ($p = j$ or k) values were obtained from

$$m_p = x_p\left[1000/x_i \cdot (\text{mol kg}^{-1}\ \text{of}\ i)\right] \tag{16}$$

The corresponding $V^{E*}(m_p)$ ($p = j$ or k) values (cm^3 mol^{-1}; mol kg^{-1} of i) in the $(i + p)$ binary mixtures were read from $V^{E}(m_p)$ vs. m_p plots, and for this purpose $V^{E}(x_p)$ data (cm^3 mol^{-1}) of the $(i + p)$ mixture were first converted to $V^{E}(m_p)$ data by an expression analogous to eqn. (15). Such V_{jk}, V_{jjk} and V_{jkk} data at 298.15 K are recorded in Table 3.

Examination of Table 3 reveals: (1) the V_{jk} interaction coefficients at 298.15 K of pyridine (j) with 1,2-dichloroethane (k), *n*-heptane (k) and aniline (k) in the presence of α-picoline vary in the order 1,2-dichloroethane < *n*-heptane < aniline; (2) the V_{jk} interaction coefficients at 298.15 K of 1,2-dichloroethane (j) with pyridine (k) and α-picoline (k) in the presence of *n*-heptane vary in the order α-picoline < pyridine; and the V_{jk} interaction coefficients at 298.15 K of aniline (k) with pyridine (j) in the presence of

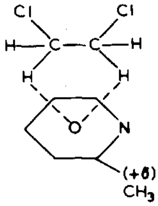
TABLE 3

Self and cross-volume interaction coefficients (cm^3 mol^{-3}; mol kg^{-1}) at 298.15 K

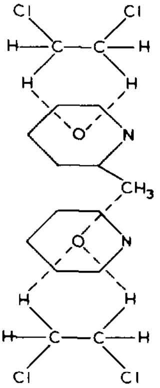
System	V_{jj}	V_{kk}	V_{jk}	V_{jjk}	V_{jkk}
1,2-Dichloroethane (k) + pyridine (j)+ α-picoline (i)	0.079	0.700	−0.1284	0.0919	0.0190
1,2-Dichloroethane (j) + *n*-heptane (i)+ pyridine (k)	6.95	4.5	0.8247	−0.0202	−0.6592
1,2-Dichloroethane (j) + *n*-heptane (i)+ α-picoline (k)	6.95	3.31	−0.0955	−0.0635	−0.0498
n-Heptane (k)+pyridine (j) + α-picoline (i)	0.079	−0.07	−0.0002	−0.0073	0.0026
Aniline (k)+pyridine (j) + α-picoline (i)	0.079	−6.45	1.8894	2.0458	−3.1540
Aniline (k)+pyridine (j) + γ-picoline (i)	0.623	−6.95	−1.4006	0.7771	0.1933

α-picoline (*i*) or γ-picoline (*i*) vary in the order α-picoline > γ-picoline.

The V_{jk} data of the pyridine with 1,2-dichloroethane, *n*-heptane and aniline in the presence of α-picoline then suggests that, compared to aniline or *n*-heptane, 1,2-dichloroethane comes closer to pyridine. This is understandable, since NMR studies on 1,2-dichloroethane + α-picoline mixtures have already suggested that 1,2-dichloroethane and α-picoline interact in the following manner

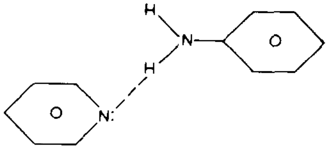


The addition of pyridine to 1,2-dichloroethane in α-picoline would then cause pyridine to approach the electron-deficient end of α-picoline in the above molecular complex with its own electron-deficient end, i.e.



The addition of *n*-heptane to pyridine in α-picoline as a solvent would not allow the components to come closer while the addition of pyridine to aniline in α-picoline may bring about additional rupture of the self association in aniline. The net effect would thus be that V_{jk} for aniline or 1,2-dichloroethane in pyridine in the presence of α-picoline would vary in the order *n*-heptane < aniline. The fact that the V_{jk} data of 1,2-dichloroethane with pyridine or with α-picoline in the presence of *n*-heptane vary in the order α-picoline < pyridine lends further support to the possible interaction of 1,2-dichloroethane with pyridine in the presence of α-picoline.

Again, NMR studies have suggested that aniline interacts with pyridine in the following manner



The introduction of α-picoline or γ-picoline into aniline + pyridine would then cause minimum disturbance in this scheme of molecular interaction when γ-picoline, rather than α-picoline, is added. The fact that V_{jk} values of aniline with pyridine in the presence of α-picoline or γ-picoline vary in the order γ-picoline < α-picoline further supports this conjecture.

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