

## Thermodynamical investigations of some non-electrolytic ternary mixtures

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Molar excess volume,  $V_{ijk}^E$  and molar excess enthalpies  $H_{ijk}^E$  of various nitrobenzene (i) + benzene (j) + toluene (k) nitrobenzene (i) + benzene (j) + *o*-xylene (k) and nitrobenzene (i) + benzene (j) + *p*-xylene (k) ternary mixtures have been measured as a function of composition at 298.15 K. The observed data have been analysed in terms of i) Graph theory, ii) Sanchez and Lacombe and iii) Flory's theories. The calculated  $X_{ijk}^E$  values ( $X = V$  or  $H$ ) by Graph and Flory's theories compare well with their corresponding experimental values.

Recent studies have revealed<sup>1-4</sup> that excess thermodynamic functions of a multicomponent system (i+j+k) can be evaluated from the corresponding data of (i+j), (j+k) and (i+k) binary mixtures. We report here molar excess volumes and molar excess enthalpies of nitrobenzene (i) + benzene (j) + toluene (k); nitrobenzene (i) + benzene (j) + *o*-xylene (k) and nitrobenzene (i) + benzene (j) + *p*-xylene (k) ternary mixtures at 298.15K.

### Materials and Methods

Nitrobenzene (NB), benzene, toluene, *o* and *p*-xylenes (AR grade) were purified by standard methods<sup>5-6</sup> and their purities checked by measuring their densities at 298.15 ± 0.01K and these agreed to within ± 5 × 10<sup>-5</sup> gm cm<sup>-3</sup> with their corresponding literature<sup>7</sup> values.

Molar excess volumes,  $V_{ijk}^E$  for (i+j+k) mixtures were measured by means of a dilatometer as described elsewhere<sup>8</sup> The uncertainty in the measured  $V_{ijk}^E$  values is ± 0.5%.

Molar excess enthalpies  $H_{ijk}^E$  for the ternary mixtures were measured in a flow microcalorimeter (LKB, Broma, Sweden) in the manner described elsewhere<sup>3</sup>. The uncertainty in the measured  $H_{ijk}^E$  values is about 1%.

### Results

Molar excess volumes,  $V_{ijk}^E$  and molar excess enthalpies,  $H_{ijk}^E$  for various ternary (NB(i) + benzene (j) + toluene or + *o*-xylene or + *p*-xylene (k) mixtures as a function of composition at 298.15K are recorded in Table 1 and were expressed<sup>9</sup> as

$$X_{ijk}^E (X = V \text{ or } H) = \left[ \begin{array}{l} x_i x_j \left[ \sum_{n=0}^2 X_{ij}^{(n)} (x_i - x_j)^n \right] + \\ x_j x_k \left[ \sum_{n=0}^2 X_{jk}^{(n)} (x_j - x_k)^n \right] + \\ x_k x_i \left[ \sum_{n=0}^2 X_{ki}^{(n)} (x_k - x_i)^n \right] + \\ x_i x_j x_k \left[ \sum_{n=0}^2 X_{ijk}^{(n)} (x_j - x_k)^n x_i^n \right] \end{array} \right] \dots (1)$$

where  $x_i$  and  $x_j$  are the mole fractions of the *i*th and *j*th components in the (i+j+k) mixture and  $X_{ijk}^{(n)}$  ( $n=0-2$ ) etc. are the parameters characteristic of the ternary mixture. The parameters for  $X_{ij}^{(n)}$ ,  $X_{jk}^{(n)}$  and  $X_{ki}^{(n)}$  for various binary mixtures were taken from literature<sup>1,2,10</sup> The parameters,  $X_{ijk}^{(n)}$  in Eq. (1) were evaluated by fitting  $X_{ijk}^E$  data to

$$\left[ \begin{array}{l} X_{ijk}^E (X = V \text{ or } H) - x_i x_j \left[ \sum_{n=0}^2 X_{ij}^{(n)} (x_i - x_j)^n \right] - \\ x_j x_k \left[ \sum_{n=0}^2 X_{jk}^{(n)} (x_j - x_k)^n \right] - x_k x_i \left[ \sum_{n=0}^2 X_{ki}^{(n)} (x_k - x_i)^n \right] \\ = [X_{ijk}^{(0)} + X_{ijk}^{(1)}(x_j - x_k) x_i + X_{ijk}^{(2)}(x_j - \end{array} \right]$$

by a least squares method and are recorded together with the standard deviation,  $\sigma(X^E_{ijk})$  defined by

$$\sigma[X^E_{ijk} (X = V \text{ or } H)] = \frac{[\sum \{X^E_{ijk}(\text{exptl}) - X^E_{ijk}(\text{calc Eq. 1})\}^2 / (m - n)]^{0.5}}{\dots} \quad \dots(3)$$

where  $X^E_{ijk}$  (calcd using Eq. 1) are the values evaluated from Eq. (1);  $m$  is number of data points and  $n$  is the number of adjustable parameters in Eq. (1), in Tables 1 and 2. The choice of  $n$  to have 0-2 or 3 values was dictated by consideration that the maximum deviation  $\sigma_m(X^E_{ijk})$  of  $X^E_{ijk}$  ( $X = V$  or  $H$ ) satisfies the relation  $\sigma_m(X^E_{ijk}) \leq 2\sigma(X^E_{ijk})$ .

### Discussion

There are no literature values of  $V^E$  and  $H^E$  for the studied ternary mixtures with which to compare our results:  $V^E_{ijk}$  values for NB (i) + benzene (j) + toluene (k) and NB (i) + benzene (j) + *o*-xylene (k) mixtures are negative over the whole composition range; however sign of  $V^E_{ijk}$  values for NB (i) + benzene (j) + *p*-xylene (k) mixtures are dictated by the relative proportion of components in the mixture.  $H^E_{ijk}$  values for all these mixtures are positive over the entire range of composition.

The more negative values of  $V^E_{ijk}$  for NB (i) + benzene (j) + toluene (k) than NB (i) + benzene (j) + *o*-xylene (k) or NB (i) + benzene (j) + *p*-xylene (k) mixtures suggest that addition of toluene to NB (i) + benzene (j) mixture favours more compact structure as compared to the addition of *o*- or *p*-xylene. This is due to the two-CH<sub>3</sub> groups of xylenes which hinder the approach of xylene molecules to the NB (i) + benzene (j) mixture.

The  $V^E_{ijk}$  and  $H^E_{ijk}$  data for these mixtures are analysed in terms of Graph theory.

#### Conceptual aspect of the Graph approach and results

If NB (i), in the pure state exists as associated entity, then NB (i) + benzene or + toluene or + xylene (j) binary mixture formation may be assumed<sup>10</sup> to involve (i) the establishment of  $i_n - j$  contact between  $i$  and  $j$ , (ii) the unlike contact formation between  $i_n - j$  would then cause depolymerization of  $i_n$  to yield monomer and (iii) monomers of  $i$  and  $j$  form  $i:j$  molecular entity. Consequently the overall change in the molar property ( $X = V$  or  $H$ ) due to processes (i) - (iii) were expressed<sup>10</sup> by

$$X^E = [(x_i x_j v_j) / \sum x_i v_i] [\chi_{ij} + x_i \chi_{ii} + x_j \chi_{12}] \quad \dots(4)$$

where  $\chi_{ij}$  and  $\chi_{12}$  are the molar volume or enthalpy interaction parameters of unlike  $i-j$  contact formation and specific interaction. The basic arguments in de-

veloping Eq. (4) were justified<sup>10</sup>, as the  $X^E$  data of the various (i+j) mixtures were reproduced by the  $\chi_{ij}$  and  $\chi_{12}$  parameters (evaluated from  $H^E$  data at  $x_i = 0.4$  and  $0.5$  for NB (i) + benzene, + toluene or + xylene binary mixtures). Thus the analysis of (i+j) mixtures suggests that these mixtures are characterised by the presence of 1:1 molecular entity, also the depolymerization of  $i$  contributes to measured  $X^E$  data.

If toluene or *o*-xylene or *p*-xylene (k) is added to NB (i), then ternary (i+j+k) mixture formation would involve (i) formation of (a)  $i_n - j$ , (b)  $j - k$  and (c)  $i_n - k$  contacts between  $i_n$ ,  $j$  and  $k$  components of (i+j+k) mixture, (ii) the unlike contact formation between  $i_n - j$  and  $i_n - k$  would then cause depolymerization of  $i_n$  to yield monomers of  $i$  and (iii) the monomers of  $i$  then undergo specific interaction to yield  $i - j$ ,  $j - k$  or  $i - k$  molecular entity. Consequently, if,  $\chi'_{ij}$ ,  $\chi'_{jk}$  and  $\chi'_{ik}$  are the molar interaction energies of unlike contact  $i_n - j$ ,  $j - k$  and  $i_n - k$ , then change in molar  $X$  ( $V$  or  $H$ ) property due to process (i) a,b,c would be given<sup>11,12</sup> by

$$\Delta X_1 = x_i \chi'_{ij} S_j + x_j \chi'_{jk} S_k + x_k \chi'_{ik} S_i \quad \dots(5)$$

$$\Delta X_1 = [(x_i x_j v_j) / \sum x_i v_i] [\chi'_{ij} + \chi'_{jk} + \chi'_{ik}] \quad \dots(6)$$

where  $S_i$  etc. are defined by

$$S_i = x_i v_i / \sum x_i v_i$$

Further if  $\chi'_{ii}$  and  $\chi_{12}$ ,  $\chi'_{12}$ ,  $\chi''_{12}$ , are the molar interaction energies  $i - i$  and specific interaction (leading to the formation of  $i:j$ ,  $j:k$  and  $i:k$  molecular entities) then change in molar volume due to processes (ii) and (iii) is given<sup>13</sup> by Eqs (7-10).

$$\Delta X_2 = (x_i^2 x_j v_j \chi'_{ii}) / \sum x_i v_i \quad \dots(7)$$

$$\Delta X_3 = (x_i x_j^2 v_j \chi_{12}) / \sum x_i v_i \quad \dots(8)$$

$$\Delta X_4 = (x_j x_k^2 v_k \chi'_{12}) / \sum x_i v_i \quad \dots(9)$$

$$\Delta X_5 = (x_k x_i^2 v_i \chi''_{12}) / \sum x_i v_i \quad \dots(10)$$

The overall change in thermodynamic property due to processes (i) (a,b,c), (ii) and (iii) would be expressed by Eq. (11)

$$X^E = \left[ \begin{aligned} & [(x_i x_j v_j) / \sum x_i v_i] [\chi'_{ij} + x_i \chi'_{ii} + x_j \chi_{12}] + \\ & [(x_j x_k v_k) / \sum x_i v_i] [\chi'_{jk} + x_k \chi'_{12}] + \\ & [(x_i x_k v_i) / \sum x_i v_i] [\chi'_{ik} + x_i \chi_{12}] \end{aligned} \right] \quad \dots(11)$$

since  $v_i/v_j = {}^3\xi_j/{}^3\xi_i$  where  ${}^3\xi_i$  etc. are the connectivity parameter of the third degree of pure  $i$  etc. and is defined<sup>14</sup> by Eq. (12)

$${}^3\xi = \frac{\sum_{m \neq n < o < p} (\delta_m^v \delta_n^v \delta_o^v \delta_p^v)^{0.5}}{\dots} \quad \dots(12)$$

where  $\delta_m^v$  reflects explicitly the valency of the  $m$ th vertex in the molecular graph, and is related to the

maximum valency,  $Z_m$ , and number of hydrogen atoms,  $h_m$  attached to  $m$ th vertex by  $\delta^m = Z_m - h_m$ . Equation (11) then reduces to Eq. (13)

$$X^E = \left[ \frac{\{x_i x_j ({}^3\xi_i / {}^3\xi_j)\}}{\{x_i + x_j ({}^3\xi_i / {}^3\xi_j)\}} \right] [\chi_{ij} + x_i \chi_{ij} + x_j \chi_{ij}] \\ + \left[ \frac{\{x_j x_k ({}^3\xi_j / {}^3\xi_k)\}}{\{x_j + x_k ({}^3\xi_j / {}^3\xi_k)\}} \right] [\chi_{jk} + x_j \chi_{jk}] \\ + \left[ \frac{\{x_i x_k ({}^3\xi_i / {}^3\xi_k)\}}{\{x_i + x_k ({}^3\xi_i / {}^3\xi_k)\}} \right] [\chi_{ik} + x_i \chi_{ik}] \dots (13)$$

Further if it be assumed that  $\chi'_{ij} \equiv \chi_{12}$ ;  $\chi'_{jk} \equiv \chi'_{12}$ ; and  $\chi'_{ik} \equiv \chi''_{12}$ , then Eq. (13) reduces to Eq. (14)

$$X^E = \left[ \frac{\{x_i x_j ({}^3\xi_i / {}^3\xi_j)\}}{\{x_i + x_j ({}^3\xi_i / {}^3\xi_j)\}} \right] [x_i \chi_{ij} + (1+x_j) \chi_{ij}] \\ + \left[ \frac{\{x_j x_k ({}^3\xi_j / {}^3\xi_k)\}}{\{x_j + x_k ({}^3\xi_j / {}^3\xi_k)\}} \right] [(1+x_k) \chi_{jk}] \\ + \left[ \frac{\{x_i x_k ({}^3\xi_i / {}^3\xi_k)\}}{\{x_i + x_k ({}^3\xi_i / {}^3\xi_k)\}} \right] [(1+x_i) \chi_{ik}] \dots (14)$$

Equation (14) contains four unknown parameters and for the present analysis, we employed  $X^E_{ijk}$  data at four arbitrary compositions to evaluate them. These parameters were subsequently utilized to obtain  $X^E_{ijk}$  at other values of  $x_i$  and  $x_j$ . Such  $X^E_{ijk}$  ( $X = V$  or  $H$ ) data along with  $\chi'_{ij}$ ,  $\chi'_{jk}$  and  $\chi'_{ik}$  parameters are recorded in Tables 1 and 2 and are also compared with their corresponding experimental values.

Examination of the data in Tables 1 and 2 reveals that  $V^E_{ijk}$  and  $H^E_{ijk}$  values compare reasonably well with their corresponding experimental values, (for  $x_i \leq 0.1$ , the calculated  $V^E_{ijk}$  values are not of the right magnitude) which lends additional support to our assumptions made in deriving Eq. (14).

According to Sanchez and Lacombe theory<sup>15,16</sup>  $V^E_{ijk}$  and  $H^E_{ijk}$  for a ternary mixture are given by Eqs 15 and 16

$$V^E_{ijk} = r_{mix} v_{mix}^* \left[ \bar{v}_{mix} - \sum_i \phi_i \bar{v}_i \right] \dots (15)$$

$$H^E_{ijk} = r_{mix} kT \left[ \bar{\rho}_{ijk} \sum_{i=1}^3 \sum_{j=1}^3 \phi_i \phi_j \chi_{ij} + \sum_{i=1}^3 (\bar{\rho}_i \phi_i^0 - \bar{\rho}_{ijk} \phi_i) / T_i \right] \\ = [r_{mix} \bar{\rho}_{ijk} (2\phi_i \phi_j \chi_{ij} + 2\phi_j \phi_k \chi_{jk} + 2\phi_i \phi_k \chi_{ki}) \\ + r_{mix} kT + \sum (\bar{\rho}_i \phi_i^0 - \bar{\rho}_{ijk} \phi_i) / T_i] \dots (16)$$

where

$$\phi_i = m_i (\rho_i^*)^{-1} \sum (m_j / \rho_j^*)^{-1} \dots (17)$$

$$m_i = x_i M_i \left[ \sum x_i M_i \right]^{-1}$$

$$r_{mix} = \sum_{i=1}^3 x_i r_i \dots (18)$$

$$r_i = r_i^0 \left\{ v_i^* (v_{mix}^*)^{-1} \right\} \dots (19)$$

$$v_{mix}^* = \sum \phi_i^0 v_i^* \dots (20)$$

$$\phi_i^0 = m_i (\rho_i^* v_i^*)^{-1} / \sum (m_j / \rho_j^* v_j^*) \dots (21)$$

$$\bar{v}_{mix}^* = 1 / \rho_{mix}^*$$

$$\chi_{ij} = \varepsilon_{ij}^* + \varepsilon_{ij}^* - 2\varepsilon_{ij}^* \text{ etc} \dots (22)$$

and all the terms have the same significance as described by Lacombe and Sanchez<sup>15-16</sup>.

Evaluation of  $V^E_{ijk}$  and  $H^E_{ijk}$  through Eqs (15-22) requires a knowledge of,  $\rho_{ijk}$ , reduced density of the (i+j+k) ternary mixture, which can be determined from the equation of state of the (i+j+k) mixture.

$$(\bar{\rho}_{ijk})^2 + \bar{p} + (RT/\varepsilon_{ijk}^*) [\ln(1 - \bar{\rho}_{ijk}) + \{1 - (1/r_{mix})\} \bar{\rho}_{ijk}] = 0 \dots (23)$$

where

$$\varepsilon_{ijk}^* = (\varepsilon_{ij}^* \phi_i + \varepsilon_{ij}^* \phi_j + \varepsilon_{kk}^* \phi_k) - (\phi_i \phi_j \chi_{ij} + \phi_j \phi_k \chi_{jk} + \phi_i \phi_k \chi_{ik}) \dots (24)$$

and

$$\bar{\rho}_{ijk} = \rho v_{ijk}^* (\varepsilon_{ijk}^*)^{-1} \dots (25)$$

$\chi_{ij}$  etc. parameters for the various binary mixtures have been evaluated from the single  $H^E$  value (at  $x_i = 0.5$ ) for the various binary mixtures<sup>1,2,10</sup> by employing Eq. (26)

$$H^E_{ij} = 2\phi_i \phi_j \bar{\rho}_{ij} (\varepsilon_{ij}^* + \varepsilon_{ij}^* - 2\varepsilon_{ij}^*) + RT \gamma_{mix} \left[ \sum (\bar{\rho}_i \phi_i^0 - \bar{\rho}_{ij} \phi_i) / T_i \right] \dots (26)$$

Since (i+j), (j+k) and (k+i) binary mixture of i, j and k components of the present (i+j+k) ternary mixtures satisfy Eq. (27)

$$\bar{\rho}_{ij}^2 + \bar{p} + RT/\varepsilon_{mix}^* [\ln(i - \bar{\rho}_{ij}) + (1 - r_{mix}^{-1}) \bar{\rho}_{ij}] = 0.0140 - 0.0244 \dots (27)$$

it follows that these (i+j+k) mixtures would also not satisfy Eq. (23). If the addition of kth component to the (i+j) mixture does not drastically alter the i-j, j-k and k-i interactions, then the present ternary mixtures would also satisfy an equation of state like Eq. (27). Since the ternary (i+j+k) mixture is considered to be composed of three (i+j), (j+k) and (i+k) binary mixtures, the extent to which a (i+j+k) mixture deviates from Eq. (23) would be nearly one third of the sum to which (i+j), (j+k) and (i+k) mixture deviate from Eq. (16). Thus Eq. (23) reduces to

$$(\bar{\rho}_{ijk})^2 + \bar{p} + RT/\varepsilon_{ijk}^* [\ln(i - \bar{\rho}_{ijk}) + (1 - r_{ijk}^{-1}) \bar{\rho}_{ijk}] = 1/3 [\text{S.R.H.S of Eq.27 for (i+j), (j+k) and (k+i) binary mixtures}] \dots (28)$$

Once the equation of state for a ternary mixture is established,  $V^E_{ijk}$  and  $H^E_{ijk}$  values can be easily determined from Eqs (15 and 16).

$V^E_{ijk}$  and  $H^E_{ijk}$  so evaluated for the various ternary mixtures are recorded in Tables 1 and 2 and are

Table 1—Comparison of the measured  $V_{ijk}^E$  values for the various ternary mixtures at 298.15K with the corresponding values evaluated from Graph, Flory and Sanchez & Lacombe theory; also recorded are the various  $V_{ijk}^n$  ( $n=0-2$ ) parameters, standard deviation,  $\sigma(V_{ijk}^E)$  interaction energies ( $\chi'_{ii}$ ,  $\chi'_{ij}$ ,  $\chi'_{jk}$ ,  $\chi'_{ik}$  etc.) and  ${}^3\xi_i$  etc.

$x_i$	$x_j$	$V_{ijk}^E$ ( $\text{cm}^3 \text{mol}^{-1}$ )			Sanchez & Lacombe
		Exptl.	Graph	Flory	
NB (i) + benzene (j) + toluene (k)					
0.0403	0.8608	-0.004	-0.005	-0.021	0.229
0.0643	0.7761	-0.006	-0.007	-0.042	0.188
0.1256	0.5781	-0.017	-0.017	-0.074	0.063
0.1567	0.2754	-0.048	-0.014	-0.076	0.030
0.1874	0.6628	-0.072	-0.068	-0.141	-0.144
0.2581	0.4261	-0.081	-0.078	-0.169	-0.267
0.2974	0.2169	-0.090	-0.090	-0.177	-0.326
0.3257	0.5827	-0.113	-0.110	-0.241	-0.511
0.3600	0.5156	-0.121	-0.118	-0.242	-0.578
0.3954	0.3628	-0.125	-0.127	-0.224	-0.613
0.4519	0.5042	-0.122	-0.115	-0.278	0.832
0.5268	0.4347	-0.114	-0.115	-0.268	-1.000
0.6280	0.3575	-0.099	-0.099	-0.250	-1.221
0.6614	0.1454	-0.123	-0.150	-0.210	-1.210
0.7315	0.2028	-0.171	-0.167	-0.170	-1.330
0.8100	0.0719	-0.110	-0.115	-0.136	-1.537
$V_{ijk}^{(0)} = 1.407$ ; $V_{ijk}^{(1)} = -16.352$ ; $V_{ijk}^{(2)} = 59.955$ ; $\sigma(V_{ijk}^E) = 0.001$ ( ${}^3\xi_i = 1.30$ ; ( ${}^3\xi_j) = 0.667$ ; ( ${}^3\xi_k) = 0.84$ ; $\chi'_{ii} = 0.002$ ; $\chi'_{ij} = -0.199$ ; $\chi'_{jk} = 0.280$ ; $\chi'_{ik} = -0.380$ ; $\chi_{ij} = 14.372$ ; $\chi_{jk} = 3.607$ ; $\chi_{ki} = 13.301$					
NB (i) + benzene (j) + <i>o</i> -xylene (k)					
0.0571	0.0716	-0.007	0.081	0.012	0.734
0.1008	0.7989	0.005	-0.008	-0.047	0.512
0.1306	0.3542	0.052	0.141	0.040	0.521
0.1329	0.1268	-0.043	0.064	0.006	0.535
0.1978	0.6898	-0.039	-0.040	-0.120	0.235
0.2696	0.6350	-0.069	-0.059	-0.176	0.044
0.3406	0.4825	-0.076	-0.077	-0.163	-0.112
0.3787	0.4561	-0.090	-0.088	-0.179	-0.206
0.4835	0.1901	-0.165	0.161	-0.125	-0.388
0.4969	0.2650	-0.134	-0.136	-0.154	-0.451
0.5763	0.3125	-0.107	-0.106	-0.201	-0.689
0.6872	0.2948	-0.084	-0.043	-0.216	-0.988
0.6950	0.1612	-0.115	-0.142	-0.145	-0.928
0.7591	0.1108	-0.099	-0.143	-0.118	-1.073
0.7940	0.1446	-0.072	-0.079	-0.131	-1.176
0.8476	0.0431	-0.072	-0.143	-0.071	-1.255
$V_{ijk}^{(0)} = -2.193$ ; $V_{ijk}^{(1)} = 7.541$ ; $V_{ijk}^{(2)} = 1.998$ ; $\sigma(V_{ijk}^E) = 0.002$ ; ( ${}^3\xi_i) = 1.30$ ; ( ${}^3\xi_j) = 0.667$ ; ( ${}^3\xi_k) = 1.426$ ; $\chi'_{ii} = 0.049$ ; $\chi'_{ij} = -0.089$ ; $\chi'_{jk} = 1.260$ ; $\chi'_{ik} = -1.044$ ; $\chi_{ij} = 14.372$ ; $\chi_{jk} = 9.259$ ; $\chi_{ki} = 12.247$					

(Contd.....)

Table 1—Comparison of the measured  $V_{ijk}^E$  values for the various ternary mixtures at 298.15K with the corresponding values evaluated from Graph, Flory and Sanchez & Lacombe theory; also recorded are the various  $V_{ijk}^A$  ( $n=0-2$ ) parameters, standard deviation,  $\sigma(V_{ijk}^E)$  interaction energies ( $\chi'_{ij}$ ,  $\chi'_{ij}$ ,  $\chi'_{jk}$ ,  $\chi'_{ik}$  etc.) and  ${}^3\xi_i$  etc. (Contd....)

$x_i$	$x_j$	Exptl.	$V_{ijk}^E$ ( $\text{cm}^3 \text{mol}^{-1}$ )		Sanchez & Lacombe
			Graph	Flory	
NB (i) + benzene (j) + <i>p</i> -xylene (k)					
0.0489	0.8858	0.004	-0.030	-0.021	0.213
0.0580	0.8662	0.003	-0.035	-0.021	0.192
0.0581	0.6385	0.091	-0.080	0.073	0.289
0.0963	0.5602	0.040	-0.094	0.034	0.185
0.1516	0.3330	-0.030	-0.111	-0.023	-0.085
0.1840	0.7160	-0.074	-0.072	-0.136	-0.134
0.2567	0.0414	-0.162	-0.019	-0.165	0.189
0.3270	0.1714	-0.078	-0.078	-0.163	-0.370
0.3450	0.5738	-0.098	-0.093	-0.233	-0.551
0.3931	0.5487	-0.094	0.095	-0.241	-0.674
0.5214	0.4227	-0.094	-0.094	-0.261	-0.969
0.6002	0.3840	-0.092	-0.091	-0.262	-1.164
0.6465	0.1832	-0.172	-0.061	-0.210	-1.185
0.6700	0.3184	-0.083	-0.082	-0.230	-1.316
0.7763	0.1089	-0.114	-0.037	-0.159	-1.474
0.8866	0.0653	-0.052	-0.022	-0.095	-1.704

$$V_{ijk}^{(0)} = -2.468; V_{ijk}^{(1)} = -25.342; V_{ijk}^{(2)} = 227.076; \sigma(V_{ijk}^E) = 0.001; ({}^3\xi_i) = 1.30; ({}^3\xi_j) = 0.667; ({}^3\xi_k) = 1.217;$$

$$\chi'_{ii} = 0.034; \chi'_{ij} = -0.208; \chi'_{jk} = -0.381; \chi'_{ik} = +0.077; \chi_{ij} = 14.372; \chi_{jk} = 7.866; \chi_{ki} = 12.012; \chi_{ij} \text{ etc.} - \text{are in } \text{J mol}^{-1};$$

$$V_{ijk}^{(c)} \text{ etc.} - \text{are in } \text{cm}^3 \text{mol}^{-1}; \chi'_{ij} \text{ etc. are in } \text{cm}^3 \text{mol}^{-1}$$

also compared with their corresponding experimental values.

According to Flory's theory<sup>17-18</sup>,  $V_{ijk}^E$  and  $H_{ijk}^E$  for a ternary (i+j\_k) mixtures are given by

$$V_{ijk}^E = \bar{V}_{\text{cal}}^E [x_i v_i^* + x_j v_j^* + x_k v_k^*] \quad \dots(29)$$

$$H_{ijk}^E = \sum x_i p_i^* v_i^* [\bar{v}_i^{-1} - \bar{v}_{\text{cal}}^{-1}] + x_i v_i^* \phi_j \chi_{ij} \bar{v}_{\text{cal}}^{-1} + x_j v_j^* \phi_k \chi_{jk} \bar{v}_{\text{cal}}^{-1} + x_k v_k^* \phi_i \chi_{ki} \bar{v}_{\text{cal}}^{-1} \quad \dots(30)$$

where

$$\bar{v}_i^{-1} = [\{\alpha_i T / (3\alpha_i T + 3)\} + 1]^3 \quad \dots(31)$$

$$v_i^* = v_i / \bar{v}_i \quad \dots(32)$$

$$T_i^* = T_i \bar{v}_i^{4/3} / (\bar{v}_i^{1/3} - 1) \quad \dots(33)$$

$$p_i^* = \sum \phi_i p_i^* - \sum \phi_i \theta_j \chi_{ij} \quad \dots(34)$$

$$\bar{T} = (T/p^*) \sum \phi_i p_i^* / T_i^* \quad \dots(35)$$

$$\bar{v}^0 = \sum \phi_i v_i \quad \dots(36)$$

$$\bar{T}^0 = \{(\bar{v}^0)^{1/3} - 1\} / (\bar{v}^0)^{4/3} \quad \dots(37)$$

$$\bar{V}_{\text{cal}}^E = (\bar{v}^0)^{7/3} (\bar{T} - \bar{T}^0) / \{(4/3) - \bar{v}^0\}^{4/3} \quad \dots(38)$$

and all the terms have the same significance as described elsewhere<sup>17-18</sup>.

Evaluation of  $V_{ijk}^E$  etc. and  $H_{ijk}^E$  according to this theory requires a knowledge of adjustable parameters  $\theta_j \chi_{ij}$  etc. characteristic of (i+j), (j+k) and (k+i) binary mixtures. These parameters for a particular binary mixture were evaluated by fitting the corresponding  $H_{ijk}^E$  (exptl) values<sup>2,10</sup> at  $x_i = 0.5$  via Eq. (39)

$$H_{ij}^E = \sum x_i p_i^* v_i^* [\bar{v}_i^{-1} - \bar{v}_{\text{cal}}^{-1}] + x_i v_i^* \phi_j \chi_{ij} \bar{v}_{\text{cal}}^{-1} \quad \dots(39)$$

and were subsequently employed to predict  $V_{ijk}^E$  and  $H_{ijk}^E$  values. Such  $V_{ijk}^E$  and  $H_{ijk}^E$  values evaluated by

Table 2—Comparison of the measured  $H_{ijk}^E$  values for the various ternary mixtures at 298.15K with the corresponding values evaluated from Graph, Flory and Sanchez & Lacombe theory; also recorded are the various  $H_{ijk}^n$  ( $n=0-2$ ) parameters, standard deviation  $\sigma(H_{ijk}^E)$ , interaction energies ( $\chi'_{ii}$ ,  $\chi'_{ij}$ ,  $\chi'_{jk}$ ,  $\chi'_{ik}$  and  $\chi_{ij}$ ,  $\chi_{jk}$ , &  $\chi_{ki}$ ), and  $3\xi_i$  etc.

$x_i$	$x_j$	Exptl.	Graph	$H_{ijk}^E$ (J mol <sup>-3</sup> ) Flory	Sanchez & Lacombe
NB (i) + benzene (j) + toluene (k)					
0.0433	0.7583	96.1	76.8	82.3	222.1
0.0479	0.1915	88.3	74.7	87.1	247.9
0.0915	0.7202	147.1	132.3	119.9	218.1
0.1117	0.1787	127.2	116.6	138.3	278.2
0.1534	0.6711	205.4	192.1	161.4	204.1
0.1676	0.1675	151.2	143.8	170.9	297.1
0.1847	0.6463	231.6	217.6	181.8	195.4
0.2010	0.1607	158.2	156.6	199.3	302.8
0.2319	0.6088	257.6	250.5	202.9	172.4
0.2512	0.1507	162.9	171.6	225.2	72.7
0.3117	0.5455	292.1	291.0	234.1	124.4
0.3348	0.1338	171.2	187.0	257.3	280.9
0.3765	0.4942	305.9	310.3	250.4	72.1
0.4015	0.1204	178.2	192.1	273.7	243.3
0.4753	0.4159	305.9	317.9	255.9	-23.4
0.5016	0.1003	188.1	189.3	277.6	153.0
0.6443	0.2819	274.1	274.5	226.0	-233.4
0.6681	0.0668	192.2	159.2	240.7	-74.6
0.7512	0.0501	172.2	132.5	201.2	-241.8
$H_{ijk}^{(0)} = 1466.34$ ; $H_{ijk}^{(1)} = 21498.72$ ; $H_{ijk}^{(2)} = -133636.49$ ; $\sigma(H_{ijk}^E) = 1.64$ ; $\chi'_{ii} = -111.25$ ; $\chi'_{ij} = 682.05$ ; $\chi'_{jk} = 122.29$ ; $\chi'_{jk} = 189.13$					
NB (i) + benzene (j) + <i>o</i> -xylene (k)					
0.0446	0.7659	124.8	79.7	155.7	434.7
0.0530	0.1892	137.2	109.9	153.5	414.5
0.0940	0.7263	152.4	129.6	188.3	420.3
0.1227	0.1753	180.5	170.6	203.4	427.0
0.1573	0.6756	187.2	179.3	223.3	389.1
0.1829	0.1633	214.9	213.4	235.4	425.6
0.2187	0.1561	234.4	234.9	252.8	415.3
0.2718	0.1455	261.8	261.5	274.6	403.1
0.3182	0.5466	252.1	253.6	274.4	279.0
0.3589	0.1281	290.2	292.1	300.6	360.2
0.3835	0.4942	270.4	263.3	280.4	221.8
0.4274	0.1144	304.9	304.8	306.4	311.0
0.4827	0.4147	277.9	268.6	277.9	118.3
0.5282	0.0943	307.1	305.2	300.4	213.1
0.6268	0.0745	282.9	284.1	278.1	80.4
0.6511	0.2797	250.9	229.8	235.6	-105.5
0.6913	0.0617	256.8	258.5	251.4	-25.9
0.7706	0.0458	216.1	213.9	204.6	-161.1

$$H_{ijk}^0 = -981.87; H_{ijk}^{(1)} = -2789.96; H_{ijk}^{(2)} = 34263.06; \sigma(H_{ijk}^E) = 1.49$$

$$\chi'_{ii} = -5.75; \chi'_{ij} = 413.04; \chi'_{jk} = 233.58; \chi'_{ik} = 704.22$$

(Contd.....)

Table 2—Comparison of the measured  $H_{ijk}^E$  values for the various ternary mixtures at 298.15K with the corresponding values evaluated from Graph, Flory and Sanchez & Lacombe theory; also recorded are the various  $H_{ijk}^n$  ( $n=0-2$ ) parameters, standard deviation  $\sigma(H_{ijk}^E)$ , interaction energies ( $\chi'_{ii}$ ,  $\chi'_{ij}$ ,  $\chi'_{jk}$ ,  $\chi'_{ik}$  and  $\chi_{ij}$ ,  $\chi_{jk}$ , &  $\chi_{ki}$ ), and  $3\xi_1$  etc. (Contd....)

$x_i$	$x_j$	Exptl.	$H_{ijk}^E$ (J mol <sup>-3</sup> )		Sanchez & Lacombe
			Graph	Flory	
		NB (i) + benzene (j) <i>p</i> -xylene (k)			
0.0448	0.7671	126.1	98.8	142.7	301.8
0.0944	0.7273	172.4	139.1	175.1	280.2
0.1215	0.0768	135.7	141.9	149.6	233.1
0.1579	0.6763	207.2	181.5	210.4	248.1
0.1849	0.1767	231.2	231.7	228.0	282.6
0.2209	0.1689	244.8	246.2	244.3	268.4
0.2382	0.6118	236.1	223.2	243.3	196.3
0.2461	0.0533	198.2	180.4	220.7	230.0
0.2744	0.1573	262.1	264.1	265.6	250.3
0.3192	0.5467	254.1	253.2	263.7	138.0
0.3620	0.1384	281.4	283.5	288.0	200.8
0.3847	0.4942	261.3	268.9	273.6	76.5
0.4306	0.1235	289.1	290.0	296.2	148.5
0.4541	0.2918	358.9	320.1	303.1	90.2
0.4840	0.4144	267.2	278.4	272.8	-33.5
0.5315	0.1016	289.2	284.9	288.7	44.3
0.6523	0.2793	250.4	252.7	230.9	-258.6
0.6941	0.0663	257.1	237.4	232.9	-189.3

$$H_{ijk}^{(0)} = 1563.37; H_{ijk}^{(1)} = -3130.09; H_{ijk}^{(2)} = -9562.43; \sigma(H_{ijk}^E) = 1.83; \chi'_{ii} = 248.07; \chi'_{ij} = 358.08; \chi'_{jk} = 486.94; \chi'_{ik} = 474.95$$

$H_{ijk}^{(0)}$  etc and  $\sigma H_{ijk}^E$  are in J mol<sup>-1</sup>;  $\chi'_{ii}$  etc are in J mol<sup>-1</sup>

means of Eqs (29-39) alongwith various  $\chi_{ij}$ ,  $\chi_{jk}$ ,  $\chi_{ki}$  parameters are recorded in Tables 1 and 2 and also compared with their corresponding experimental values.

Examination of data in Tables 1 and 2 has revealed that while  $V_{ijk}^E$  and  $H_{ijk}^E$  values evaluated from Flory's theory make reasonably good agreement with their corresponding experimental values  $V_{ijk}^E$  and  $H_{ijk}^E$  values calculated from Sanchez and Lacombe approach make only qualitative agreement with their experimental values.

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