

## ESTIMATION OF EXCESS VOLUME AND DENSITY OF TERNARY LIQUID MIXTURES OF NON-ELECTROLYTES FROM BINARY DATA

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Several methods for estimating the excess volume and density of ternary liquid mixtures of non-electrolytes from binary data are tested using 27 sets of data from the literature. The mean error of the excess volume estimation is lower than  $0.1 \text{ cm}^3 \text{ mol}^{-1}$ . The use of the tested methods for estimating the density of ternary mixtures results in a significant reduction of the error compared to the estimation when the mixture is considered to be ideal. In decisive majority of the data sets, the maximum error in the density estimation is lower than 0.1%.

The data on excess volumes are known for a number of binary liquid mixtures of non-electrolytes and the literature survey can be found in several review articles<sup>1-3</sup>. On the other hand the experimental data on excess volume or density of more than two-component mixtures are rather rare in the literature. It is therefore useful to attempt to estimate the excess volume and density of mixtures with more than two components from binary data.

Several methods for estimating the excess volume of multicomponent mixtures from binary data are tested in this work. Considering that the reliable data on density or excess volume of more than three-component mixtures are absent in the literature, the test is limited to three-component mixtures. The use of the methods, however, can be extended easily to multicomponent mixtures.

To estimate excess volume of multicomponent mixtures from binary data the relation is usually used

$$v^E = \sum_{i < j} v_{ij}^E(x_i, x_j), \quad (1)$$

where  $v_{ij}^E$  is the contribution of binary system  $i-j$  evaluated from the correlation relation used for the respective binary system. It is evident that the values of binary contributions depend on the form of the correlation relations used because they are evaluated at the points of composition which, from the point of view of binary systems, have no physical sense, i.e.  $x_i + x_j = 1$  does not hold here.

Voňka and coworkers<sup>4</sup> studied the estimation of vapour-liquid equilibrium of more than two-component systems from binary data and used an equation which can be written for excess volume in the form

$$v^E = \sum_{i < j} \frac{x_i x_j}{x'_i x'_j} v_{ij}^E(x'_i, x'_j), \quad (2)$$

where the mole fractions  $x'_i, x'_j$  are defined so that  $x'_i + x'_j = 1$ . The binary contribution  $v_{ij}^E$  is then the excess volume of the binary system  $i-j$  at the point  $x'_i, x'_j$ .

The mole fractions  $x'_i, x'_j$  can be obtained as projections of the ternary point composition onto the axis of respective binary system in the triangle diagram. For the normal projection we obtain the relations:  $x'_i = (1 + x_i - x_j)/2$  and  $x'_j = (1 + x_j - x_i)/2$  and then

$$v^E = \sum_{i < j} \frac{4x_i x_j}{1 - (x_i - x_j)^2} v_{ij}^E \left( \frac{1 + x_i - x_j}{2}, \frac{1 + x_j - x_i}{2} \right). \quad (3)$$

It is possible to prove easily that relation (3) is equivalent to Eq. (1) if the Redlich-Kister equation (Eq. (8) below) is used for binary data. For the direct projection of the ternary point from the apex of the triangle diagram we get:  $x'_i = x_i/(x_i + x_j)$  and  $x'_j = x_j/(x_i + x_j)$  and consequently

$$v^E = \sum_{i < j} (x_i + x_j)^2 v_{ij}^E \left( \frac{x_i}{x_i + x_j}, \frac{x_j}{x_i + x_j} \right). \quad (4)$$

For the parallel projection, the binary contribution can be written as the arithmetic mean of contributions at the points of composition  $x'_i(1) = x_i, x'_j(1) = 1 - x_i$  and  $x'_i(2) = 1 - x_j, x'_j(2) = x_j$  and

$$v^E = \frac{1}{2} \sum_{i < j} \left[ \frac{x_j}{1 - x_i} v_{ij}^E(x_i, 1 - x_i) + \frac{x_i}{1 - x_j} v_{ij}^E(1 - x_j, x_j) \right]. \quad (5)$$

The estimation methods based on Eq. (2) (i.e. Eqs (3)–(5)) have the following substantial advantage compared to Eq. (1): On the assumption that binary data are correctly described by correlation relations, the values of the estimate do not depend on the form of these correlation relations and, in addition, the methods mentioned can be used even in those cases when the binary data are known only in a graphical or tabular form.

Nissema<sup>5</sup> used the relation for the estimation of excess volume of ternary mixtures:

$$v^E = \sum_i x_i \bar{v}_i^E, \quad (6)$$

where  $\bar{v}_i^E$  is the partial molar excess volume of component  $i$  in ternary mixture. For this quantity, Nissema proposed the relation

$$\bar{v}_i^E = \frac{x_j}{x_j + x_k} \bar{v}_{i(ij)}^E \left( \frac{x_i}{x_i + x_j}, \frac{x_j}{x_i + x_j} \right) + \frac{x_k}{x_j + x_k} \bar{v}_{i(ik)}^E \left( \frac{x_i}{x_i + x_k}, \frac{x_k}{x_i + x_k} \right), \quad (7)$$

where  $\bar{v}_{i(ij)}^E$  and  $\bar{v}_{i(ik)}^E$  are the partial molar excess volumes of the component  $i$  in binary systems  $i-j$  and  $i-k$ .

The estimation methods given by Eqs (3)–(7) were tested using experimental data available in the literature. Nissema tested relations (6) and (7) by ternary mixtures with two components exhibiting the mutual limited miscibility<sup>5–7</sup>; in this work only the data of mixtures with completely miscible components are used for the test. As binary data we always used the data of authors who measured the corresponding ternary system, too. The binary data were correlated by the Redlich–Kister equation

$$v_{ij}^E = x_i x_j \sum_{s=0}^{N_{ij}} A_s^{(ij)} (x_i - x_j)^s. \quad (8)$$

On the basis of Eq. (8), the partial molar excess volumes (Eq. (7)) were evaluated as well.

Results of the test are given in Table I. The values of standard deviation given in the fourth column of the table are those obtained on correlating the ternary data by the relation

$$v^E = \sum_{i < j} x_i x_j \sum_{s=0}^{N_{ij}} A_s^{(ij)} (x_i - x_j)^s + x_1 x_2 x_3 (B_0 + B_1 x_1 + B_2 x_2) \quad (9)$$

(except for the data of Heric and Brewer<sup>14</sup>, where the values of standard deviation, given with an accuracy of  $0.01 \text{ cm}^3 \cdot \text{mol}^{-1}$ , were taken from the original work) and can serve for a rough illustration of the accuracy of experimental data. In the fifth column of Table I there are the values of standard deviation of the excess volume estimates of ternary mixtures in terms of Eqs (3)–(5) for it was proved that these relations yielded practically identical results.

The knowledge of value of excess volume allows to calculate also the density of mixture. Here we have

$$\rho = \frac{\sum x_i M_i}{v^E + \sum x_i v_i^0}, \quad (10)$$

TABLE I  
Standard deviations of the excess volume estimates and maximum errors in the density estimates of ternary mixtures

System	Ref.	$N^a$	Eq. (9)	Eq. (3)-(5) <sup>b</sup>	Eq. (6), (7) <sup>a</sup>	Eq. (3)-(5)	Eq. (6), (7)	$ \delta v_{id}^E _{\max}, \%$
Cyclohexane + benzene + <i>n</i> -hexane	8	24	60	67	64	0-21	0-19	0-54
Cyclohexane + benzene + tetrachloromethane	9	8	3-7	6-7	77	0-015	0-091	0-48
Cyclohexane + toluene + tetrachloromethane	10	10	1-4	9-0	61	0-014	0-076	0-46
Cyclohexane + <i>p</i> -xylene + tetrachloromethane	10	10	2-5	17	69	0-019	0-097	0-44
Cyclohexane + benzene + tetrachloroethene	11	6	13	98	51	0-12	0-070	0-58
Cyclohexane + toluene + tetrachloroethene	11	9	4-7	17	41	0-024	0-077	0-47
Cyclohexane + <i>p</i> -xylene + tetrachloroethene	11	7	4-1	33	66	0-037	0-081	0-43
Cyclohexane + tetrachloromethane + tetrachloroethene	11	6	6-1	6-8	60	0-015	0-075	0-31
Cyclohexane + tetrachloromethane + quinoline	9	11	6-2	10	42	0-026	0-054	0-23
Cyclohexane + toluene + chloroform	10	10	4-0	41	41	0-054	0-061	0-48
Cyclohexane + <i>p</i> -xylene + chloroform	10	8	3-1	28	45	0-040	0-054	0-42
Cyclohexane + toluene + dichloromethane	10	9	3-1	88	42	0-13	0-061	0-80
Cyclohexane + benzene + acetone	10	10	4-7	98	62	0-12	0-077	0-78
Cyclohexane + benzene + dichloromethane	12	38	9-6	18	88	0-040	0-21	1-20
Benzene + <i>p</i> -xylene + tetrachloromethane	10	10	2-2	7-6	24	0-012	0-032	0-13
Benzene + methanol + acetone	13	100	2-0	13	24	0-048	0-082	0-27
<i>n</i> -Hexadecane + <i>n</i> -hexane + 2-bromobutane	14	15	40	67	59	0-10	0-095	0-18
<i>n</i> -Hexadecane + <i>n</i> -hexane + benzene	14	15	10	97	37	0-10	0-036	0-47
<i>n</i> -Hexadecane + benzene + tetrachloromethane	14	14	10	97	235	0-11	0-25	0-66
<i>n</i> -Hexadecane + <i>n</i> -hexane + tetrachloromethane	14	14	60	76	59	0-093	0-079	0-20
<i>n</i> -Hexadecane + <i>n</i> -hexane + 4-methylcyclohexanone	14	13	40	50	39	0-054	0-045	0-22
<i>n</i> -Tetradecane + <i>n</i> -hexane + 2-bromobutane	14	14	30	32	34	0-037	0-033	0-17
<i>n</i> -Tetradecane + <i>n</i> -hexane + 4-methylcyclohexanone	14	14	30	58	27	0-048	0-048	0-19
<i>n</i> -Hexadecane + <i>n</i> -tetradecane + 2-bromobutane	14	15	30	31	30	0-033	0-067	0-30
<i>n</i> -Hexadecane + <i>n</i> -tetradecane + <i>n</i> -hexane	14	15	20	51	46	0-053	0-050	0-31
<i>n</i> -Hexadecane + <i>n</i> -tetradecane + 4-methylcyclohexanone	14	14	50	55	88	0-082	0-076	0-34
<i>n</i> -Hexane + benzene + tetrachloromethane	14	14	40	39	76	0-087	0-12	0-32

<sup>a</sup>  $\sigma(v^E) = [\sum(v_{\text{est}}^E - v_{\text{exp}}^E)^2 / N]^{1/2}$ , where  $N$  is the number of ternary experimental points.

where  $M_i$  and  $v_i^0$  are the molar mass and molar volume of component  $i$ . For the relative error of the mixture density estimate it is possible to find the relation

$$\delta \varrho_{\text{est}}(\%) = \frac{\varrho_{\text{est}} - \varrho_{\text{exp}}}{\varrho_{\text{exp}}} \cdot 100 = \frac{v_{\text{exp}}^{\text{E}} - v_{\text{est}}^{\text{E}}}{v_{\text{est}}^{\text{E}} + \sum x_i v_i^0} \cdot 100, \quad (11)$$

whose maximum values are given in the seventh and eighth columns of Table I. In the last column of the table the maximum values of relative error in density obtained by means of the "ideal" estimation which characterize the non-ideality of mixture are then given for illustration:

$$\delta \varrho_{\text{id}}(\%) = \frac{\varrho_{\text{id}} - \varrho_{\text{exp}}}{\varrho_{\text{exp}}} \cdot 100 = \frac{v_{\text{exp}}^{\text{E}}}{\sum x_i v_i^0} \cdot 100, \quad (12)$$

where the density of ideal mixture,  $\varrho_{\text{id}}$ , is given by Eq. (10), for  $v^{\text{E}} = 0$ . Considering that the estimated values of excess volume were, with regard to small numbers of experimental points in data sets, compared directly with experimental data, it is evident that the values of expressions (11) and (12) are subject to an uncertainty given by the expression  $100 \Delta v_{\text{exp}}^{\text{E}}/v$ , where  $\Delta v_{\text{exp}}^{\text{E}}$  is the absolute error in the excess volume determination and  $v$  the mixture molar volume. If we replace  $\Delta v_{\text{exp}}^{\text{E}}$  by the standard deviation in excess volume obtained on correlating the ternary data (the fourth column of Table I) and if we consider that molar volume of mixtures,  $v$ , is about  $100 \text{ cm}^3 \cdot \text{mol}^{-1}$  and more, then it is evident that the mentioned uncertainty manifests itself more significantly only with less accurate data sets, especially in those cases when the estimation method yielded the value of standard deviation in excess volume close to the experimental accuracy.

The number of systems by means of which the test was carried out is limited and consequently it is difficult to generalize the results obtained. None of methods tested yielded only higher or only lower values than the experimental data. The method represented by Eq. (2) is to a considerable extent empirical<sup>4</sup> and its success will depend on many factors as *e.g.* on the form of concentration dependence of excess volume of the binary systems, on the polarity of components, on the existence of specific interactions between components, *etc.* A lucid dependence between these factors and the success of the method, however, has not been found. The method due to Nissema (Eqs (6) and (7)) yielded for about one third of the systems substantially higher values of standard deviation in excess volume than the methods according to Eq. (2), in the other cases it gave the results either comparable or better. With regard to the approximation (7), analogous conclusions will hold as in case of the method (2). A disadvantage of the Nissema method is larger numerical demands of the estimate and the fact that this method is, owing to the derivative in evaluating the partial molar excess volumes, more sensitive to the quality of correlation and the

accuracy of binary data. Consequently, the method represented by Eq. (2) appears to be more suitable for a rapid rough estimation of excess volume of ternary mixtures. It is pertinent to add that the methods tested are not the only means for estimating excess volume and density of ternary mixtures. In special cases as *e.g.* mixtures of *n*-alkanes it is possible to apply very well the principle of congruence<sup>15,16</sup>.

Use of the methods tested for estimating density of ternary mixtures results in reducing the maximum error by more than one order of magnitude for plenty of sets used compared to the estimation when the mixture is considered to be ideal. The maximum relative error in the density estimation is for majority of mixtures lower than 0.1% and for half the data sets lower than 0.05%. If we accept the conclusion that the methods tested yield the estimate of excess volume with an average error whose magnitude has an upper limit constant (from the results of the test follows for this limit the value about  $0.1 \text{ cm}^3 \cdot \text{mol}^{-1}$ ) then the relative error of the density estimate will decrease with increasing molar volume of mixture, *i.e.* the density estimation will be better for the mixtures containing components with large molar volume.

Thus, the results of the test show that the methods investigated can serve as a useful tool for estimating the excess volume and density of ternary liquid mixtures of non-electrolytes from binary data.

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