VAPOUR–LIQUID EQUILIBRIUM AT LOW PRESSURES FROM THE BACK EQUATION OF STATE. II. TERNARY SYSTEMS

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Ternary equilibrium diagrams in the n-hexane–cyclohexane–benzene system at temperature 298·15 K and n-hexane–benzene–toluene system at pressure 101·325 kPa were determined from the BACK equation of state. In the course of the determination of excess thermodynamic functions of mixtures the values of the BACK equation parameters for pure compounds and binary interactions parameters, k_{ij}, adjusted to G^E and H^E of the corresponding binaries were employed. The comparison of theoretical and experimental data shows very good quality of the prediction of the equilibrium behaviour of polycomponent systems from the BACK equation of state.

In the previous communication of this series[1] the mixing and combining rules were studied which made it possible to apply the equation of state BACK (Boublík–Alder–Chen–Kreglewski) to the description of the equilibrium behaviour of mixtures. Two sets of the mixing and combining rules were studied with one or two binary interaction parameters and it was shown that the set of rules designated as the A-set with one binary parameter, k_{ij}, yielded a fair description of the equilibrium behaviour of the studied binary systems. For practical applications it is important to know whether the binary interaction parameters suffice for a full description of ternaries. This question is studied in this work.

Because values of parameters of the equation of state for pure components may affect considerably the quality of the description of mixtures were in this work for the sake of objectivity studied only those systems the values of the BACK parameters of which were found in the original literature[2–3]. This fact, together with an effort to study both the isothermal and isobaric systems, led to the choice of the abovementioned n-hexane–cyclohexane–benzene and n-hexane–benzene–toluene systems.

THEORETICAL

The BACK equation of state is given by a sum of two contributions, one corresponding to steep repulsive forces and the other to attractive forces. The compres-

sibility factor of a system, z, is given as

$$z = z^{(h)} + z^{(a)}, \tag{1}$$

where for the term $z^{(h)}$ the authors[1] employed the expression for the compressibility factor of hard convex body fluids proposed from our laboratory[4]

$$z = \frac{1}{(1 - y)} + \frac{3\alpha y}{(1 - y)^2} + \frac{\alpha^2 y^2 (3 - y)}{(1 - y)^3}. \tag{2}$$

In Eq. (2) y stands for the packing fraction and α is the nonsphericity parameter of molecules of the given compound; $\alpha \geqq 1$.

The contribution of attractive forces is described by the relationship

$$z^{(a)} = \sum\sum m D_{nm} \left(\frac{u}{kT}\right)^n \left(\frac{V^0}{V}\right)^m, \tag{3}$$

employed first by Alder and coworkers[5] to fit analytically their results obtained by the molecular dynamic simulations in the systems of square-well molecules. In the last expression V^0 stands for the close-packed and V for molar volume (V^0/V and y are related through $y = \pi\sqrt{2V^0/6V}$), u^0 is essentially the well-depth of the potential curve and k is the Boltzmann constant (the ratio u^0/k has the dimension of temperature and its value for the low-molecular compounds tends to the critical temperature in K for the given compound. An effect of softness of repulsive forces (with respect to repulsive forces of hard bodies considered in Eq. (2)) and the contribution of multipole interactions is taken into account by the relations

$$V^0 = V^{00}(1 - C \exp(-3u^0/kT))^3, \tag{4}$$

and

$$u = u^0(1 + \lambda/kT). \tag{5}$$

The equation of state comprises five parameters characterizing individual compounds V^{00}, α, u^0/k, λ/k and C; for majority of compounds is $C = 0{\cdot}12$. D_{nm} are universal constants.

For mixtures of several compounds the form of the equation (1)–(3) remains unchanged, the mixing and combining rules, however, must be used for parameters V^{00}, α, u^0/k and λ/k of a mixture. In this work we employ the following relationships (set *A*):

$$V_s^0 = \sum x_i V_i^0, \tag{6}$$

$$\alpha_s = \sum x_i(\alpha V_i^0)^{1/3} \sum x_i(\alpha V_i^0)^{2/3} / \sum x_i V_i^0 , \quad (7)$$

$$u_s = \sum\sum x_i x_j u_{ij} , \quad (8)$$

where

$$u_{ij} = (u_{11}u_{jj})^{1/2}(1 - k_{ij}) . \quad (9)$$

This set of mixing rules comprises one binary interaction parameter, k_{ij}, the value of which must be estimated from some semiempirical relationships or adjusted to experimental data. The estimation methods for compounds of more complicated molecules (in comparison with mono- and diatomic ones) do not yield sufficiently accurate values of k_{ij}; it appears, however, that k_{ij} possesses values $<0{\cdot}050$. In this study the k_{ij} parameters were adjusted to the experimental dependences of G^E and H^E on concentration.

RESULTS AND DISCUSSION

Excess thermodynamic functions of binary and ternary systems were determined at pressure $P \to 0$. This condition can be considered in view of the fact that the molar volume change with pressure of a mixture and pure components in the liquid phase at pressures 0–100 kPa is negligible and, moreover, mutual compensation takes place.

In the course of calculation of the excess thermodynamic functions the molar volume of the solution of given concentration (including the pure components) was determined first by an iterative procedure; the knowledge of these volumes made it possible to determine further thermodynamic functions from the expressions obtained by differentiating (*1*)–(*5*). The excess thermodynamic functions were then obtained from the respective thermodynamic functions of mixing. In the course of calculations the rounded values of k_{ij} (to 0·005) were employed; the single value was considered for the whole temperature range. The values of this binary parameter for the n-hexane(1)–cyclohexane(2), n-hexane(1)–benzene(3), cyclohexane(2)–benzene(3), benzene(3)–toluene(4) and n-hexane(1)–toluene(4) systems are given in Table I.

In the same table also the mean deviations in the composition of the vapour phase, y, for the studied binary systems are listed. These deviations denote differences, with respect to the experimental data, of the vapour phase compositions determined from the theoretical G^E course (for the given composition) and the vapour pressures of pure components. In the third row of the table the mean deviations in y, determined from the Wilson correlation expression, are listed for comparison; these values as well as the experimental data were taken from the literature[6]. Last two rows give similarly the maximum deviations (from the experiment) in the vapour phase

compositions obtained from the theoretical approach – the equation of state – and from the correlation expression. The comparison shows that the calculations based on the BACK equation of state yield data with deviations max. 1·5 mol%, which usually amount approximately twice the mean deviations obtained from the optimal correlation treatment. Values of the maximum deviations are always closer, in case of the n-hexane–toluene system is the maximum deviation of the theoretical method even lower than that from the correlation method.

Comparison of theoretical and experimental $x-y$ dependences for the binaries which form the first ternary system is shown in Figs 1 – 3. From these figures a good accord of the theoretical curves with experimental data for all three systems is apparent. In case of the binary system n-hexane–toluene (which is included in the second ternary system) the deviations are somewhat larger, obviously – as it follows from the results of the correlation method (Table I and ref.[6]) – as a result of lower precision of the experimental data. In contrast to this the deviations for the benzene–toluene system are so small that are indiscernible in the scale of the diagram.

The calculated course of the composition dependence of the excess thermodynamic function G^E/RT in the n-hexane(1)–cyclohexane(2)–benzene(3) ternary system at 298·15 K is disclosed in Fig. 4, from which the asymetric shape of this dependence is apparent. From the derivative of the G^E function with respect to composition and from the vapour pressures of pure components the values of the relative volatility coefficients were determined first for the individual (experimental) liquid phase compositions and from them the corresponding vapour phase compositions. The $x-y$ diagram of the n-hexane–cyclohexane–benzene system at 298·15 K is shown in Fig. 5. Full lines connect the experimentally determined liquid and vapour phase compositions, by the dotted lines the theoretically calculated vapour phase compositions for the same liquid compositions are indicated. From the Fig. 1 can see

TABLE I

Binary interaction parameters and the mean and maximum deviations in the vapour phase composition for the n-hexane(1)–cyclohexane(2) (at 343·15 K), n-hexane(1)–benzene(3), cyclohexane(2)–benzene(3), n-hexane(1)–toluene(4) and benzene(3)–toluene(4) systems (all at 298·15 K)

System	1–2	1–3	1–4	2–3	3–4
k_{ij}	0·010	0·035	0·015	0·020	0·000
Mean deviation theor.	0·0077	0·0107	0·0141	0·0031	0·0016
Mean deviation correl.	0·0036	0·0050	0·0109	0·0005	0·0009
Max. deviation theor.	0·0149	0·0173	0·0177	0·0051	0·0038
Max. deviation correl.	0·0073	0·0125	0·0226	0·0025	0·0023

that the determination of the vapour phase composition for the n-hexane rich liquid phase compositions is very accurate; as expected, the deviations are greater in the middle. A similar picture yields the comparison of the theoretical and experimental

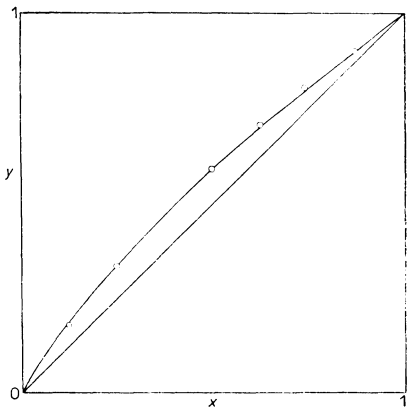

FIG. 1

$x-y$ Diagram of the n-hexane–cyclohexane system at 343·15 K. ——— calculated from the BACK equation, ○ experimental data[6]

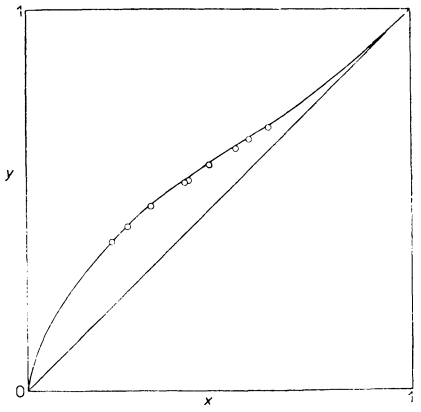

FIG. 2

$x-y$ Diagram of the n-hexane–benzene system at 298·15 K. ——— calculated from the BACK equation, ○ experimental data[6]

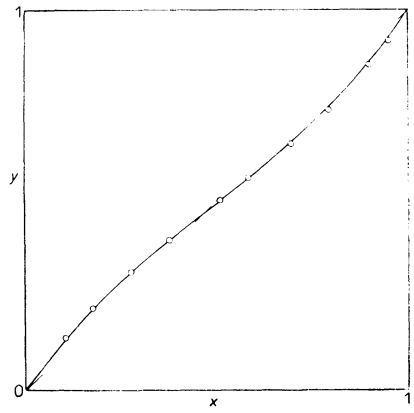

FIG. 3

$x-y$ Diagram of the benzene–cyclohexane system at 298·15 K. ——— calculated from the BACK equation, ○ experimental data[6]

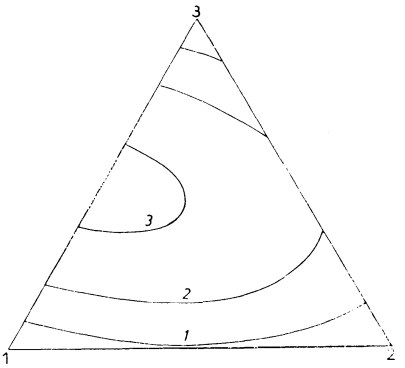

FIG. 4

The composition dependence of G^E/RT in the n-hexane(1)–cyclohexane(2)–benzene(3) system at 298·15 K. *1* $G^E/RT = 0{\cdot}05$, *2* $G^E/RT = 0{\cdot}10$, *3* $G^E/RT = 0{\cdot}15$

$x-y$ dependences in the n-hexane–benzene–toluene system at $P = 101{\cdot}3$ kPa, shown in Fig. 6., where larger differences can be found only in the region of higher toluene concentration. The comparison of the mean and maximum deviations in the determination of the vapour phase composition from the method based on BACK equation and from the correlation method is disclosed in Table II. The mean deviation in the mole fraction y (for y_1 and y_2) from the theoretical approach amounts approximately 1 mol%, *i.e.* only twice or three times the value yielded by the correlation method. It is thus of approximately same magnitude as in case of binary

TABLE II

Mean and maximum deviations in the vapour phase composition for the ternary n-hexane(1)–-cyclohexane(2)–benzene(3) (at 298·15 K) and n-hexane(1)–benzene(2)–toluene(4) (at 101·3 kPa) systems

System	1—2—3	1—3—4
Mean deviation theor.	0·0100	0·0102
Mean deviation correl.	0·0029	0·0059
Max. deviation theor.	0·0230	0·0260
Max. deviation correl.	0·0139	0·0321

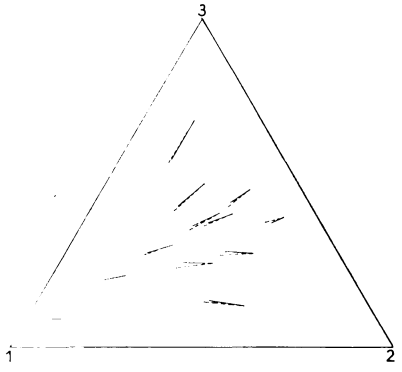

FIG. 5

$x-y$ Diagram of the n-hexane(1)–cyclohexane(2)–benzene(3) system at298·15 K. ----- calculated from the BACK equation, ——— experimental data[6]

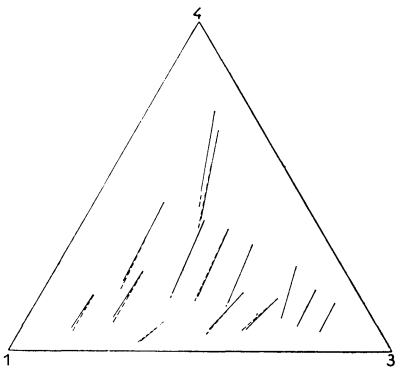

FIG. 6

$x-y$ Diagram of the n-hexane(1)–benzene(3)–-toluene(4) system at pressure 101·3 kPa. ----- calculated from the BACK equation, ——— experimental data[6]

systems and in very good agreement with experiment. The maximum deviation amounts 2·5 mol% in both the cases and is comparable with that for the optimal correlation procedures.

CONCLUSION

Results of this and previous work indicate that the BACK equation of state with the theoretically based mixing and combining rules yields a fair estimation of the equilibrium behaviour of mixtures at low pressures. The knowledge of the binary parameters k_{ij} – besides of the parameters of the equation of state for pure compound – is sufficient to determine all the thermodynamic properties of mixtures. The binary parameter k_{ij} is assumed to be independent of temperature (and further variables). The quality of estimates from the equation of state BACK is comparable with that of the correlation methods usually employed in the thermodynamics of phase equilibria at present. Estimates of the equilibrium behaviour of ternary systems is not connected with an introduction of further (ternary) parameters. Accuracy of the description of ternaries in comparison with binary systems remains unchanged and fully matches the needs of the chemical engineering praxis.

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