VAPOUR–LIQUID EQUILIBRIUM AT LOW PRESSURES FROM THE BACK EQUATION OF STATE

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The BACK semiempirical equation of state was employed to determine the excess thermodynamic functions of five binary mixtures composed of benzene with cyclohexane, n-pentane, n-hexane, n-heptane, and n-octane at 298·15°K. Two sets of mixing rules are discussed and values of the excess thermodynamic functions of equimolar solutions, calculated on their basis, are compared with experimental data. The calculated and experimental equilibrium data are compared in the $x-y$ diagrams.

In several contributions[1-4] it was shown that the equation of state BACK (Boublík–Alder–Chen–Kreglewski) yields very accurate description of the P–V–T behaviour of systems of simple molecules in a broad range of the liquid and gaseous aggregation states. This fact led to an application of the BACK equation to study the equilibrium behaviour of one- and two-component systems (of relatively simple compounds) at elevated pressures. The simple form of the equation enables an easy determination of the excess thermodynamic functions of mixtures (at $P \rightarrow 0$). This fact can be used to study the mixing rules (for parameters of the equation) which often determine in a decisive way the prediction of the mixture behaviour from the given equation. This contribution is devoted to this problem.

THEORETICAL

The BACK equation of state, proposed by Chen and Kreglewski[1-3] is composed of two parts: a contribution essentially corresponding to repulsive forces, z^h, and a contribution of attractive forces, z^a,

$$z = z^h + z^a \,. \qquad (1)$$

The first contribution in the BACK equation is expressed by the equation of state proposed by the present author[5] for systems of hard convex bodies. These bodies model the short-range repulsive forces which determine "size and shape" of given molecules; denoting by a symbol z^h the compressibility factor of the one-component system of hard bodies it holds

$$z^{h} = \left(\frac{PV}{RT}\right)^{h} = \frac{1 + (3\alpha - 2)\,\xi + (3\alpha^2 - 3\alpha + 1)\,\xi^2 - \alpha^2\xi^3}{(1 - \xi)^3}\,, \tag{2}$$

where z^h is the compressibility factor and ξ the packing fraction, *i.e.* the ratio of the total volume of hard particles and the volume of the studied system, V. From the relationship for the volume V^0 of hard spheres with a diameter σ in the close packed configuration, $V^0 = N\sigma^3/\sqrt{2}$ (where N is the number of particles), the relationship between ξ and V^0 follows

$$\xi = \frac{\pi}{6}\sqrt{2}\,\frac{V^0}{V} = 0{\cdot}74048V^0/V\,. \tag{3}$$

The parameter α is a measure of the non-sphericity of molecules; for hard spheres $\alpha = 1$.

The contribution of attractive forces, z^a, is in the BACK equation expressed by the form

$$z^{a} = \sum_{n}\sum_{m} mD_{nm}(u/kT)^{n}\,(V^0/V)^{m} \tag{4}$$

which is based on the Alder's[6] study of the equilibrium behaviour of the square-well system by the method of molecular dynamics. In expression (*4*) D_{nm} denote constants adjusted to experimental data of several chosen systems of simple compounds; they are assumed to be valid for any compound.

For u/k it holds true

$$u/k = (u^0/k)\,(1 + \eta/kT)\,, \tag{5}$$

where u^0/k is the value of the intermolecular pair potential in the minimum, divided by the Boltzmann constant (it has a dimension of temperature) and the parameter η/k includes the effect of electrostatic interactions *etc.*. The effect of temperature on the thickness of the (representative) hard bodies is taken into account by expressing V^0 as a function of temperature in the following way:

$$V^0 = V^{00}(1 - C\exp(-3u^0/kT))^3\,. \tag{6}$$

V^{00} is (for spheres) the close packed-, generally the characteristic volume at zero temperature, $T = 0$ K; C stands for a constant which equals 0·12 for majority of compounds.

It is obvious that the P–V–T behaviour of pure fluids is given by the knowledge of four (eventually five) characteristic parameters: u/k, η/k, V^{00}, and α (eventually C). For approximately 20 compounds these parameters were determined from their vapour pressures, densities in the liquid phase, critical constants (eventually the P–V–T data); they are given in refs[1-4]. Their knowledge not only allows to describe the P–V–T behaviour but also the evaluation of the configurational thermodynamic functions. For example, the difference in the free energy of the system and the perfect gas at the same conditions, $F - F^*$, is

$$(F - F^*)/RT = (\alpha^2 - 1)\ln(1 - \xi) + 3\alpha\xi/(1 - \xi) + \\ + \alpha^2\xi/(1 - \xi)^2 + \sum_n\sum_m D_{nm}(u/kT)^n (V^0/V)^m . \qquad (7)$$

Further thermodynamic functions can be obtained by differentiating with respect to V or T.

The BACK equation of state was also applied to the description of the equilibrium behaviour of solutions. Though expression (2) for z^h has its counterpart in the exactly derived equation of state of hard (convex) body mixtures, expressions (1)–(2) and (4) together with mixing and combining rules for the characteristic parameters were considered in refs[2-4]. Thus, the parameter of non-sphericity in mixtures, α_s, was taken as

$$\alpha_s = \sum x_i \alpha_i , \qquad (8)$$

and u/k (eventually u^0/k)

$$u_s = \sum\sum x_i x_j u_{ij} , \qquad (9)$$

where

$$u_{ij} = (1 - \nu_{ij})(u_{ii}u_{jj})^{1/2} . \qquad (9a)$$

The rule[4]

$$V_s^0 = \sum\sum x_i x_j V_{ij}^0 \qquad (10)$$

together with

$$V_{ij}^0 = (1 - \tau_{ij})(V_{ii}^{0\,1/3} + V_{jj}^{0\,1/3})/8 \qquad (10a)$$

or (in refs[2-3])

$$V_s^0 = \sum x_i V_i^0 \qquad (11)$$

were used.

Recently[7] we have studied methods for the determination of the entropy of mixing, S^{mix}, of the hard body mixtures. By the comparison with the exact calculations (corresponding to the pseudoexperimental data) we have found that Eq. (*1*) together with the combining rule given by (*8*) yields unsufficiently accurate (always lower) values of S^{mix}. On the contrary, the mixing rule

$$\alpha_s = \sum_i x_i(\alpha_i V_i)^{1/3} \sum_i x_i(\alpha_i V_i)^{2/3} / \sum_i x_i V_i \,, \qquad (12)$$

proposed in the mentioned work, yields values of S^{mix} in a good agreement with pseudoexperiment.

In this work two sets of mixing rules were considered for the evaluation of the excess thermodynamic functions of mixtures: in the first case (Set A) the rules given by Eqs (*12*), (*9*, *9a*), and (*11*) (theoretically based), in the second case (Set B) rules (*8*), (*9*, *9a*) and (*10*, *10a*) were employed.

RESULTS

Binary systems of benzene–cyclohexane, benzene–n-pentane, benzene–n-hexane, benzene–n-heptane, and benzene–n-octane at 298·15 K were studied. The constants D_{nm} were taken from the paper by Chen and Kreglewski[1] and the characteristic parameters from ref.[4]; they are listed in Table I ($C = 0{\cdot}12$ in all the cases). Calculations were performed at pressure $P \rightarrow 0$; (owing to a very slight dependence of thermodynamic quantities of liquids on pressure and taking into account the fact that all the further considered data correspond to pressures less than 100 kPa this simplification introduces only negligible errors into the resulting values of thermodynamic quantities – and reduces considerably the computing time).

For the mixture of a given composition the volume (at $P \rightarrow 0$) and the volume of mixing were determined first and from them the Gibbs free energy and enthalpy of the mixture and the corresponding excess quantities. In the course of calculations mixing rules of sets A or B were considered. The parameter τ_{ij} was taken equal to zero in both the cases. As expected, the use of the geometric mean rule to determine u_{ij} *i.e.* the assumption $v_{ij} = 0$ does not yield good results; estimates of v_{ij} for the single binary solutions from the different semi-empirical rules vary considerably. Therefore, the unique value of $v_{ij} = 0{\cdot}035$ was chosen for all the studied systems.

In Table II values of the excess thermodynamic functions of the equimolar solutions, evaluated by employing the combining and mixing rules of sets A or B, are compared with the experimental data[3–14] of the studied systems at 298·15 K. From the comparison it follows that calculations with both the sets of mixing rules yield similar results for the first four binaries whereas for the benzene–n-octane system large differences between values, determined from sets A and B, as well as worse agreement with the experimental data results. For the first four binaries better prediction of the G^E values from the set A and of H^E from set B can be found. In all these cases the agreement with the experiment is fair and the same is true for V^E. In case of the benzene–n-octane system, however, only the prediction of G^E is of practical use.

The calculated dependences of the excess free energy on the composition make it possible to determine the vapour–liquid equilibrium diagrams for the single binary systems studied in this work. Comparison of the calculated and experimental $x - y$ curves is given in Figs 1–5. With exception of the n-pentane–benzene system, where only the experimental data at 313·15 K are at our disposal[11] (at this temperature also the G^E values were evaluated). are the other theoretical and experimental courses compared at 298·15 K. From Figs 1–5 a good accord of the predicted $x - y$ curves with the experimental data in all the cases is apparent. Very good predictions were

TABLE I

Characteristic parameters of the BACK equation of state

Compound	α	V^0, cm^3/mol	u^0/k, K	η/k, K
Benzene	1·0587	54·383	532·12	71·50
Cyclohexane	1·0583	64·772	522·46	70·72
n-Pentane	1·0566	65·751	435·83	70·72
n-Hexane	1·0720	77·228	468·33	90·11
n-Heptane	1·0799	88·351	491·00	113·77
n-Octane	1·0981	96·556	517·52	134·50

TABLE II

Excess thermodynamic functions of the equimolar solutions of benzene with cyclohexane, n-pentane, n-hexane, n-heptane, and n-octane at 298·15 K

System	V^E, cm^3/mol			G^E, J/mol			H^E, J/mol		
	A	B	exp[8–9]	A	B	exp[10–14]	A	B	exp[8–9]
C_6H_6—C_6H_{12}	0·53	0·70	0·65	464	488	290	771	797	799
C_6H_6—C_5H_{12}	−0·05	0·12	—	463	533	422[a]	758	845	857
C_6H_6—C_6H_{14}	0·10	0·38	0·50	397	460	400	691	750	870
C_6H_6—C_7H_{15}	0·55	0·88	0·60	364	431	415	713	767	950
C_6H_6—C_8H_{18}	1·89	2·39	—	435	614	318	1 773	2 012	969

[a] Interpolated from data at other temperatures.

obtained for the n-hexane–benzene and benzene–n-heptane systems. However, even in all the remaining cases – from the point of view of chemical engineering praxis – the prediction of the equilibrium behaviour is sufficiently accurate.

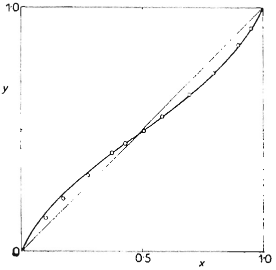

FIG. 1

Vapour–liquid equilibrium in the benzene(1)–cyclohexane(2) system at 298·15 K. ——— calculated, ○ experimental data[10,14]

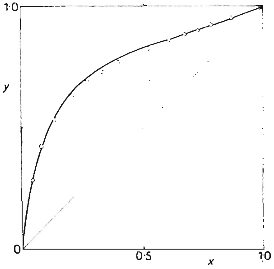

FIG. 2

Vapour–liquid equilibrium in the n-pentane(1)–benzene(2) system at 313·15 K. ——— calculated, ○ experimental data[11,14]

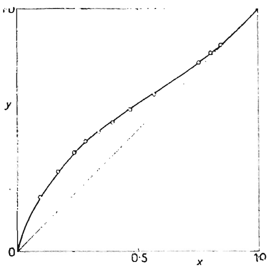

FIG. 3

Vapour–liquid equilibrium in the n-hexane(1)–benzene(2) system at 298·15 K. ——— calculated, ○ experimental data[12,14]

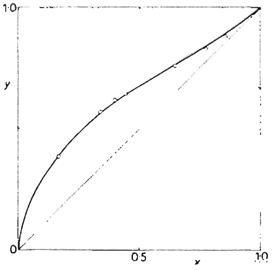

FIG. 4

Vapour–liquid equilibrium in the benzene(1)–n-heptane(2) system at 298·15 K. ——— calculated, ○ experimental data[13,14]

CONCLUSION

From the study the following conclusions about the use of the mixing and combining rules for the characteristic parameters of the BACK equation of state can be drawn: Set A (with theoretically based rules for parameters α_s and V_s^0) and set B yield essentially similar results. This situation is caused by the fact that the values of α for the studied compounds differ mutually only slightly and approach unity. In accord with this finding, differences become larger for systems with n-heptane and n-octane. In the latter case the predictions based on the rules of set A are superior to those for set B; with exception of the excess free energy, however, too great deviations from the experiment result. This disagreement could be caused by our worse knowledge of the characteristic parameters for n-octane, or – more probably – by the fact that the form of the equation of state is less suited to describe the behaviour of the longer-chain compounds in comparison with the simple-molecule systems. In view of four parameters, adjusted to properties of pure substances, the effect of the fine form of the equation of state may not play a substantial role on the accuracy of the description of a one-component system, it could, however, considerably affect the precision of the prediction of the mixture behaviour.

From the practical point of view it is important that the equilibrium behaviour of all the systems studied was described by employing only one common binary parameter ν_{ij} (lying in the interval of values which follow for the systems studied from different semi-empirical methods). This fact makes it possible to describe the equilibrium behaviour of a studied system by estimating the ν_{ij}-parameter on the basis of its values for chemically similar systems.

It can be concluded that the BACK equation of state yields sufficiently accurate predictions of the equilibrium behaviour of mixtures employing minimum number of parameters.

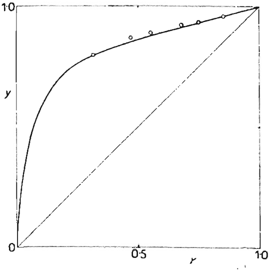

FIG. 5

Vapour–liquid equilibrium in the benzene(1)–n-octane(2) system at 298·15 K. —— calculated, ○ experimental data[13,14]

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