CALCULATION OF HIGH- AND LOW-PRESSURE VAPOUR–LIQUID EQUILIBRIA IN BINARY MIXTURES USING THE REDLICH–KWONG EQUATION OF STATE WITH DIFFERENT COMBINATION RULES FOR CONSTANTS a AND b

K.Hlavatý

Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, Prague - Suchdol

Effect of different combination rules for constants a and b in the Redlich–Kwong equation of state on calculated values of the equilibrium constant $K_i = y_i/x_i$ was examined for several binary liquid mixtures at both high and low pressures and for the systems containing nonpolar as well as polar components. The different combination rules used had only a little effect on the resulting deviations between experiments and the calculations. On the other hand, the values of the interaction constant c differed markedly from one another according to the combination rules employed.

THEORETICAL

The Redlich–Kwong equation of state has proved very useful in correlating and predicting high-pressure vapour–liquid equilibria in mixtures containing nonpolar compounds[1]. However, the combination rules for constants a and b in this equation

$$p = RT/(V - b) - a/T^{0.5}V(V + b), \qquad (1)$$

$$a = \sum x_i x_j a_{ij}, \qquad (2)$$

$$b = \sum x_i b_i, \qquad (3)$$

$$a_{12} = (1 - k_{12})(a_1 a_2)^{0.5} \qquad (4)$$

are based on the virial expansion of Eq. *(1)* and as such are of uncertain validity when used for calculating properties of the liquid state. On the other hand, the one-fluid corresponding states theory is very useful for liquid mixtures and can be easily employed to derive combination rules for constants in any equation of state, once the necessary relations between these constants and force constants of the intermolecular potential have been established[2]. The constants a and b of pure components in the Redlich–Kwong equation are related to critical properties by the relations

$$a \sim T_c^{1.5} V_c \quad \text{and} \quad b \sim V_c. \tag{5}$$

The critical properties can be related in turn to the force constants σ and ε of an conformal potential as

$$V_c \sim \sigma^3 \quad \text{and} \quad T_c \sim \varepsilon. \tag{6}$$

It follows from Eqs (5) and (6) that

$$\varepsilon_{ij} \sim \left(a_{ij}/b_{ij}\right)^{2/3} \quad \text{and} \quad \sigma_{ij}^3 \sim b_{ij}. \tag{7}$$

For the equivalent substance parameters ε_x and σ_x in the one-fluid corresponding states theory, the following equations were investigated[3]

$$\sigma_x^{3v} = \sum x_i x_j \sigma_{ij}^3 \tag{8}$$

and

$$\varepsilon_x^\mu \sigma_x^3 = \sum x_i x_j \varepsilon_{ij}^\mu \sigma_{ij}^3. \tag{9}$$

These rules reduce to the van der Waals (VdW) ones for $v = \mu = 1$, but an approximation $v = \mu = 4/3$ yielded better results[3]. It is usual to suppose for ε_{12}

$$\varepsilon_{12} = \left(1 - c_{12}\right) \left(\varepsilon_1 \varepsilon_2\right)^{0.5} \tag{10}$$

and for σ_{12} the arithmetic-mean

$$\sigma_{12} = \left(\sigma_1 + \sigma_2\right)/2 \tag{11}$$

or the geometric-mean rule[4]

$$\sigma_{12} = \left(\sigma_1 \sigma_2\right)^{0.5}. \tag{12}$$

The original mixing rules in Eqs (2) and (3) correspond to $v = 1$, $\mu = 1.5$ and $\delta_{12}^3 = \left(\sigma_1^3 + \sigma_2^3\right)/2$.

The interaction constant k_{12} in Eq. (4) is not identical with c_{12} in Eq. (10); interpretation of the interaction constant in terms of intermolecular forces is obviously more straightforward with the constant c_{12}. New mixing rules for the constants a and b may now be deduced from Eqs $(7)-(9)$. Thus, the $4/3$ rules assume the form of

$$b = \sum {}^{3/4} x_i x_j b_{ij}^{4/3}$$

and

$$a = \sum {}^{9/8} x_i x_j (a_{ij}/b_{ij})^{8/9} \, b_{ij}/b^{1/8} \tag{13}$$

and the VdW ones

$$b = \sum x_i x_j b_{ij}$$

and

$$a = \sum{}^{3/2} x_i x_j (a_{ij}/b_{ij})^{2/3} \, b_{ij}/b^{1/2} \, . \tag{14}$$

The interaction constant c_{12} enters Eqs (2), (13) and (14) *via* the relation

$$(a_{ij}/b_{ij})^{2/3} = (1 - c_{12}) \, (a_i a_j/b_i b_j)^{1/3} \, . \tag{15}$$

RESULTS AND DISCUSSION

We have correlated several binary high- and low-pressure vapour–liquid equilibrium data by the method due to Zudkevitch and Joffe[1] with the single exception of replacing the original mixing rules by Eqs (13) or (14). Where available, at least 10 experimental points were taken for each system from the widest possible temperature, pressure and concentration range. Deviations between the experimental and calculated values of the equilibrium constant $K_i = y_i/x_i$ were minimized with respect to the constant c_{12}. For the fugacity coefficients Φ_k of individual component in the mixture, the following formula may be deduced

$$\ln \Phi_k = \frac{B_k}{V - b} + \ln \frac{RT}{p(V - b)} - \frac{1}{bRT^{1.5}} \left(\ln \frac{V}{V + b} \right) \left(\frac{aB_k}{b} - A_k \right) -$$

$$- \frac{aB_k}{b(V + b) RT^{1.5}} \, , \tag{16}$$

where for the original mixing rules

$$A_k = 2 \sum x_i a_{ki} \quad \text{and} \quad B_k = b_k \, , \tag{17}$$

for the 4/3 rules

$$A_k = {}^9\!/_4 (a/b)^{1/9} \sum x_i (a_{ki}/b_{ki})^{8/9} \, b_{ki} - {}^3\!/_{16} ab^{-4/3} \sum x_i b_{ki}^{4/3} - a/16$$

and

$$B_k = {}^3\!/_2 b^{-1/3} \sum x_i b_{ki}^{4/3} - b/2 \tag{18}$$

and for the VdW ones

$$A_k = 3(a/b)^{1/3} \sum x_i (a_{ki}/b_{ki})^{2/3} \, b_{ki} - a \sum x_i b_{ki}/b$$

and

$$B_k = 2 \sum x_i b_{ki} - b \,. \tag{19}$$

The results are given in Tables I and II. They are denoted by 4/3A or 4/3G for the 4/3 rules with the arithmetic- (Eq. (11)) or geometric-mean rule (Eq. (12)) for b_{12}. For the VdW mixing rules, only Eq. (11) was employed. From Tables I and II we may see that there is little to choose among the different combination rules used. If one set of rules fails to correlate a particular system, the others fail inevitably, too. This refers especially to the systems containing supercritical components (H_2, N_2) and to highly nonideal systems (ethanol–toluene, water–methanol, water–propanol). The failure in the former case could be removed by finding some other way of determining the pure component constants a and b as in the Zudkevitch and Joffe's method the values are employed as calculated at the critical point of the pure components. The failure in the latter case is most probably connected with inadequacy of the Redlich–Kwong equation at describing the thermodynamic properties of non-ideal liquid mixtures. Some other equation of state will perhaps prove better.

In Table II the results are given of calculations with the interaction constant c_{12} determined preliminary from the Kramer and Herschbach's (KH) (ref.[5]) or London's (L) (ref.[6]) formulas for the attractive term in the intermolecular potential of nonpolar molecules. For the Lennard-Jones 12 : 6 potential these are as follows

$$\text{KH} \quad 1 - c_{12} = \frac{2(\varepsilon_1\varepsilon_2)^{0.5}}{\varepsilon_1\sigma_1^6\alpha_2/\alpha_1 + \varepsilon_2\sigma_2^6\alpha_1/\alpha_2}\left(\frac{\sigma_1\sigma_2}{\sigma_{12}}\right)^6 \tag{20}$$

and

$$\text{L} \quad 1 - c_{12} = \frac{2(I_1I_2)^{0.5}}{I_1 + I_2} \cdot \frac{(\sigma_1\sigma_2)^3}{\sigma_{12}^6} \,, \tag{21}$$

where α_1 is the static dipole polarizability and I_1 the ionization potential of component 1. The corresponding columns in Table II are denoted by KH or L. The values of I_i and α_i were taken from other sources[32,33]. We may see from this Table that in the absence of any direct experimental data, Eqs (20) or (21) may be used equally successfully to calculate the interaction constant c_{12} in systems containing nonpolar components. It must be stressed that this is possible only with the interaction constant c_{12}, as the physical meaning of constant k_{12} in Eq. (4) is by far not so clear. Similar calculations with the Mie 28 : 7 potential were somewhat less successful than those with the 12 : 6 potential.

We may conclude this by stating that the Redlich–Kwong equation in the Zudkevitch and Joffe's treatment is capable to describe fairly well the properties of liquid mixtures containing nonpolar components, but that for the mixtures with polar compo-

TABLE I

Mean Percent Deviations of the Equilibrium K_i-Ratios and the Values of the Interaction Constant c_{12} as Obtained by the Minimization Procedure

Quantity	Original	VdW	4/3 A	4/3 G
methane–neopentane[7]				
c_{12}	0·152	0·080	0·092	0·079
Mean	14·0	10·7	11·7	9·4
argon–neopentane[7]				
c_{12}	0·243	0·155	0·169	0·165
Mean	3·8	5·0	4·8	7·1
methane–hexane[8]				
c_{12}	0·145	0·116	0·147	0·155
Mean	8·7	11·7	9·8	12·8
propane–pentane[9]				
c_{12}	0·017	0·009	0·007	0·006
Mean	4·7	4·1	4·4	4·3
hydrogen sulphide–pentane[10]				
c_{12}	0·140	0·126	0·099	0·095
Mean	5·5	4·1	4·3	4·3
carbon dioxide–hydrogen sulphide[11]				
c_{12}	0·071	0·067	0·070	0·070
Mean	2·4	2·2	2·3	2·3
nitrogen–hexane[12]				
c_{12}	0·232	0·116	0·147	0·155
Mean	6·2	7·9	8·2	13·6
ethane–pentane[13]				
c_{12}	0·043	0·023	0·019	0·018
Mean	4·9	5·1	4·9	5·0
ethane–heptane[14]				
c_{12}	0·085	0·038	0·027	0·013
Mean	1·9	4·7	2·3	5·3
nitrogen–heptane[15]				
c_{12}	0·266	0·153	0·172	0·172
Mean	18·0	17·3	19·2	24·7

TABLE I (continued)

Quantity	Original	VdW	4/3 A	4/3 G
		nitrogen–butane[16]		
c_{12}	0·229	0·104	0·160	0·161
Mean	14·1	13·1	13·9	14·6
		neon–argon[17]		
c_{12}	0·134	0·054	0·099	0·103
Mean	3·1	1·5	2·5	3·2
		carbon disulphide–tetrachloromethane[18]		
c_{12}	0·023	0·021	0·015	0·014
Mean	0·5	0·5	0·5	0·5
		benzene–1,2-dichloroethane[19]		
c_{12}	−0·001	0·000	−0·001	−0·001
Mean	1·6	1·7	1·6	1·6
		ethanol–toluene[19]		
c_{12}	0·082	0·077	0·067	0·067
Mean	12·7	12·6	12·7	12·6
		chloroform–acetone[20]		
c_{12}	−0·036	−0·037	−0·037	−0·037
Mean	2·9	3·0	2·9	2·9
		benzene–cyclohexane[21]		
c_{12}	0·148	0·019	0·018	0·018
Mean	0·6	0·6	0·6	0·6
		carbon disulphide–acetone[19]		
c_{12}	0·075	—	0·073	0·073
Mean	3·1	—	3·1	3·1
		propanol–water[19]		
c_{12}	0·047	—	−0·002	−0·013
Mean	12·9	—	13·4	7·9
		methanol–water[19]		
c_{12}	−0·011	—	−0·032	−0·035
Mean	9·6	—	9·3	8·9

TABLE II

Mean Percent Deviation of the Equilibrium K_i-Ratios and the Values of the Interaction Constant c_{12} as Obtained by the Minimization Procedure or on the Basis of the KH or L rules

Quantity	Minimization			KH			L		
	Orig.	4/3 A	4/3 G	Orig.	4/3 A	4/3 G	Orig.	4/3 A	4/3 G
methane–ethane[22]									
c_{12}	0·023	0·015	0·014	0·017	0·017	0·004	0·014	0·014	0·001
Mean	4·3	4·5	4·5	5·5	4·8	5·9	6·3	4·5	6·6
methane–propane[23]									
c_{12}	0·037	0·013	0·014	0·050	0·050	0·011	0·042	0·042	0·003
Mean	6·9	7·8	9·0	7·7	13·3	9·0	7·0	11·7	9·2
methane–carbon dioxide[24]									
c_{12}	0·002	0·031	0·031	0·013	0·013	0·012	0·001	0·001	0·000
Mean	3·2	3·4	3·4	6·4	5·5	5·6	8·4	7·5	7·6
ethane–propane[23,25]									
c_{12}	0·008	0·006	0·005	0·009	0·009	0·002	0·008	0·008	0·000
Mean	3·5	3·6	3·6	3·6	3·7	3·5	3·6	3·7	3·4
ethane–butane[26]									
c_{12}	0·041	0·023	0·019	0·028	0·028	0·004	0·025	0·025	0·001
Mean	1·9	1·8	1·8	2·1	2·0	3·0	2·4	2·0	3·5
ethane–ethylene[27,28]									
c_{12}	0·012	0·010	0·010	0·016	0·016	0·014	0·004	0·004	0·002
Mean	1·8	1·8	1·8	1·9	1·9	1·9	2·2	2·1	2·3
ethylene–acetylene[27,28]									
c_{12}	0·045	0·045	0·045	0·020	0·020	0·019	0·001	0·001	0·001
Mean	1·0	1·0	1·0	7·9	7·9	7·9	12·8	12·6	12·6
carbon dioxide–hydrogen sulphide[11]									
c_{12}	0·071	0·070	0·070	0·029	0·029	0·028	0·009	0·009	0·009
Mean	2·4	2·3	2·3	9·1	8·8	8·8	12·7	12·4	12·4
argon–oxygen[29]									
c_{12}	0·010	0·010	0·010	0·004	0·004	0·003	0·008	0·008	0·008
Mean	0·5	0·5	0·5	3·1	3·6	3·6	1·1	1·1	1·1
nitrogen–argon[30]									
c_{12}	0·000	−0·002	−0·002	0·003	0·003	0·000	0·003	0·003	0·000
Mean	0·6	0·6	0·6	1·5	2·0	0·9	1·5	2·0	0·9
oxygen–nitrogen[31]									
c_{12}	−0·006	−0·009	−0·009	0·003	0·003	0·002	0·009	0·009	0·007
Mean	1·6	1·5	1·5	4·6	4·6	4·3	6·4	7·0	6·4
carbon disulphide–tetrachloromethane[18]									
c_{12}	0·023	0·015	0·014	0·063	0·063	0·045	0·020	0·020	0·001
Mean	0·5	0·5	0·5	37·0	46·0	27·0	2·2	2·0	8·6

nents it yields less satisfactory results and should be replaced by some other relation. The original mixing rules for constants a and b appear to be the best ones as they produce good results with less computational effort; however, correct interpretation of the interaction constant c_{12} should be employed in cases when this constant is to be determined preliminarily from independent formulas or experiments.

REFERENCES

1. Zudkevitch D., Joffe J.: A.I.Ch.E. J. *16*, 112 (1970).
2. Hlavatý K.: This Journal *38*, 2029 (1973).
3. Hlavatý K.: This Journal *37*, 2141 (1972).
4. Good R. J., Hope C. J.: J. Chem. Phys. *53*, 540 (1970).
5. Kramer H. L., Herschbach D. R.: J. Chem. Phys. *53*, 2792 (1970).
6. London F.: Z. Physik *63*, 245 (1930).
7. Rogers B. L., Prausnitz J. M.: J. Chem. Thermodyn. *3*, 211 (1971).
8. Poston R. S., McKetta J. J.: J. Chem. Eng. Data *11*, 362 (1966).
9. Sage B. H., Lacey W. N.: Ind. Eng. Chem. *32*, 992 (1940).
10. Reamer H. H., Sage B. H., Lacey W. N.: Ind. Eng. Chem. *45*, 1805 (1953).
11. Bierlein J. A., Kay W. B.: Ind. Eng. Chem. *45*, 618 (1953).
12. Poston R. S., McKetta J. J.: J. Chem. Eng. Data *11*, 364 (1966).
13. Reamer H. H., Sage B. H., Lacey W. N.: J. Chem. Eng. Data *5*, 44 (1960).
14. Mehra V. S., Thodos G.: J. Chem. Eng. Data *10*, 211 (1965).
15. Akers W. W., Kehn D. M., Kilgore C. H.: Ind. Eng. Chem. *46*, 2536 (1954).
16. Akers W. W., Attwell L. L., Robinson J. A.: Ind. Eng. Chem. *46*, 2539 (1954).
17. Streett W. B., Hill J. L. E.: J. Chem. Phys. *54*, 5088 (1971).
18. Hlavatý K.: This Journal *35*, 2878 (1970).
19. Hála E., Wichterle I., Polák J., Boublík T.: *Vapour Liquid Equilibrium Data at Normal Pressures*. Pergamon Press, Oxford 1968.
20. Von Zawidzki J.: Z. Phys. Chem. (Leipzig) *35*, 129 (1900).
21. Scatchard G., Wood S. E., Mochel J. M.: J. Phys. Chem. *43*, 119 (1939).
22. Wichterle I., Kobayashi R.: J. Chem. Eng. Data *17*, 4 (1972).
23. Price A. R., Kobayashi R.: J. Chem. Eng. Data *4*, 40 (1959).
24. Donnelly H. G., Kobayashi R.: J. Chem. Eng. Data *4*, 40 (1959).
25. Matschke D. E., Thodos G.: J. Chem. Eng. Data *7*, 232 (1962).
26. Mehra V. S., Thodos G.: J. Chem. Eng. Data *10*, 307 (1965).
27. McCurdy J. L., Katz D. L.: Ind. Eng. Chem. *36*, 674 (1944).
28. Hogan R. J., Nelson W. T., Hanson G. H., Cines M. R.: Ind. Eng. Chem. *47*, 2210 (1955).
29. Narinskij G. B.: Kislorod *10* (3), 9 (1957).
30. Narinskij G. B.: Ž. Fiz. Chim. *40*, 2022 (1966).
31. Dodge B. F., Dunbar A. K.: J. Am. Chem. Soc. *49*, 591 (1927).
32. Moelwyn-Hughes E. A.: *Physical Chemistry*, 2nd Ed.. Macmillan, New York 1964.
33. Vedeneyev V. I., Gurvich L. V., Kondratyev V. N., Medvedev V. A., Frankevich Y. L.: *Bond Energies, Ionization Potentials, and Electron Affinities*. Arnold, London 1966.

Translated by the author.