

EFFECT OF DIFFERENT COMBINATION RULES FOR CONSTANTS IN THE REDLICH-KWONG EQUATION OF STATE ON CALCULATED VOLUMES OF BINARY LIQUID MIXTURES

K. HLAVATÝ

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchbát*

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Effect of different combination rules for constants a and b in the Redlich-Kwong equation of state on calculated liquid volumes 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 affected the calculated volumes only little; the differences among them were generally outweighed by inadequacy of the Redlich-Kwong equation for calculation of the liquid volumes.

The equation-of-state approach to correlations of vapour-liquid equilibria of liquid mixtures has a definite advantage in the fact that all thermodynamic quantities may be calculated simultaneously in a consistent manner. There are at least three fundamental problems inherent to this approach. Firstly, it is the question of the proper equation of state, secondly the mixing rules for the constants in this equation of state and thirdly the procedure adopted for determining these constants for pure components. Recently we have investigated effect of different combination rules on the values of equilibrium K_1 -ratios in several binary mixtures. In this work we examine the effect of different mixing rules on the resulting volumes and also the extent to which identical interaction constants may be used for calculating both the vapour-liquid equilibria and the volumes of binary liquid mixtures. We use the Redlich-Kwong equation of state

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

with constants a and b of the pure components determined by the method due to Zudkevitch and Joffe², that means by fixing these constants at each temperature to experimental orthobaric liquid volumes and pressures and by requiring simultaneously the equality of fugacities in both the liquid and the vapour phases. For a supercritical component, we employ the values determined at the critical point of this component for the value of the fugacity coefficient ϕ proposed by Zudkevitch and Joffe³

$$-\log \phi = 0.1754 + 0.0361\omega, \quad (2)$$

where ω is the eccentric factor.

In our previous work we proposed a simple method^{1,4} based on the one-fluid corresponding states theory of liquid mixtures for the determination of mixing

rules for constants in an arbitrary equation of state. Here we shall use the following ones:

the original rules

$$a = \sum x_i x_j a_{ij}, \quad b = \sum x_i b_i, \quad (3)$$

$$a_{ij} = (1 - k)(a_i a_j)^{0.5}, \quad (4)$$

the Van der Waals's (VdW) rules

$$a = \sum^{3/2} x_i x_j (a_{ij}/b_{ij})^{2/3} b_{ij}/b^{1/2}, \quad b = \sum x_i x_j b_{ij}, \quad (5)$$

$$(a_{ij}/b_{ij})^{2/3} = (1 - c)(a_i a_j/b_i b_j)^{1/3} \quad \text{and} \quad b_{ij}^{1/3} = (b_i^{1/3} + b_j^{1/3})/2, \quad (6)$$

and the $4/3$ rules

$$a = \sum^{9/8} x_i x_j (a_{ij}/b_{ij})^{8/9} b_{ij}/b^{1/8}, \quad (7)$$

$$b = \sum^{3/4} x_i x_j b^{4/3} \quad \text{and} \quad \text{Eq. (6)}.$$

The interaction constant c serves as a measure of the intermolecular interaction of molecules i and j and it is related to the well depths ε_i and ε_j of corresponding intermolecular potential functions of pure components i and j by the relation

$$\varepsilon_{ij} = (1 - c)(\varepsilon_i \varepsilon_j)^{0.5}. \quad (8)$$

The meaning of constant k in Eq. (4) is by far not so clear. If we want to incorporate the constant c into the original mixing rules we must replace Eq. (4) by Eq. (6) with

$$b_{ij} = (b_i + b_j)/2. \quad (9)$$

A similar approach to the interaction constant c in connection with the original mixing rules was used by other investigators^{5,6}.

CALCULATIONS

We have performed with the Redlich-Kwong equation with the original, VdW, or $4/3$ rules two sets of calculations. In the first set we minimized the differences between the calculated and experimental volumes of several binary liquid mixtures with respect to the interaction constant c . In the second set we calculated the differences between the experimental and calculated volumes on the basis of values of the constant c evaluated from different sources. The results of these calculations are given in Table I for both sets. The values in the first four columns were obtained by the minimization procedure. In the column denoted by $4/3$ G, the geometric-mean rule for b_i

$$b_{ij} = (b_i b_j)^{0.5} \quad (10)$$

was used⁷ together with the $4/3$ rules for constants a and b . The results in the last three columns were obtained with the values of c determined from the vapour-liquid equilibria (VLE) of the corresponding binary systems¹, from the minimization of differences between experimental and calculated excess Gibbs free energies, enthalpies and volumes in the one-fluid corresponding states theory with the $4/3$ rules⁸ (GHV), or finally from a combination rule for the constant c due to Kramer and Herschbach⁹ (KH)

$$c = 1 - \frac{2(\varepsilon_i \varepsilon_j)^{0.5}}{\varepsilon_i b_i^2 \alpha_j / \alpha_i + \varepsilon_j b_j^2 \alpha_i / \alpha_j} \left(\frac{b_i b_j}{b_{ij}} \right)^2, \quad \varepsilon_i = (a_i / b_i)^{2/3}, \quad (11)$$

where α_i is the static dipole polarizability of molecule i and the Lennard-Jones 12 : 6 potential was assumed to hold. The values of α_i were taken from other sources^{10,11}. We have also made the calculations with the London's formula¹² for the constant c and the Lennard-Jones 12 : 6 or Mie's 28 : 7 potential, but the results were not substantially different from those in the KH column of Table I. In all calculations, at least 10 experimental points were taken from widest possible temperature, pressure and concentration ranges.

DISCUSSION

By inspecting Table I we may see that the differences between the different combination rules used in the minimization procedure are rather small. Large deviations are observed especially for systems at higher pressures, *i.e.* for the first seven systems. Partially it might be caused by a lower accuracy of the high-pressure measurements and by the somewhat arbitrarily determined values of constants a and b for supercritical components in the Zudkevitch and Joffe's treatment, but even when this is taken into account, the results are unsatisfactory. Better results are obtained for the low-pressure systems, but here we must realize that the experimental results are usually determined with a much higher accuracy and that in most cases the mean percent deviation as low as 0.1 might be unacceptable. From this point of view, the results for the last three systems are quite unsatisfactory and of the systems studied, only the volumes in the benzene-1,2-dichloroethane, benzene-cyclohexane, carbon disulphide-tetrachloromethane, nitrogen-argon, and oxygen-argon are correlated within the experimental accuracy by this method. We may thus see that the results of the minimization procedure are somewhat worse than in the case of vapour-liquid equilibria¹. Similar results were obtained by Chang and Lu⁵. With respect to the compatibility among different sources for the interaction constant c it is obvious from the last three columns of Table I that the situation is still worse here and that the only system whose volumes may be calculated satisfactorily by the Redlich-Kwong equation with independently determined constants c is the nitrogen-argon system.

TABLE I

Mean Percent Deviations between Experimental and Calculated Volumes and the Values of the Interaction Constant c

Quantity	Original	VdW	4/3	4/3 G	4/3(VLE)	4/3(GHV)	4/3(KH)
propane-pentane ¹³							
c	-0.034	-0.040	-0.043	-0.041	0.007	—	—
Mean	1.10	1.24	1.17	1.21	3.0	—	—
argon-neopentane ¹⁴							
c	-0.194	0.035	-0.106	0.036	0.169	—	—
Mean	5.30	3.93	4.54	3.99	6.3	—	—
methane-neopentane ¹⁴							
c	-0.057	-0.018	-0.067	-0.029	0.092	—	—
Mean	2.42	1.83	1.78	1.85	7.3	—	—
hydrogen sulphide-pentane ¹⁵							
c	0.097	0.101	0.061	0.071	0.099	—	—
Mean	2.01	3.54	2.59	3.49	4.0	—	—
ethane-pentane ¹⁶							
c	0.006	0.003	-0.010	-0.003	0.019	—	—
Mean	2.34	2.17	2.23	2.14	3.3	—	—
nitrogen-heptane ¹⁷							
c	0.191	0.400	0.318	0.582	0.172	—	—
Mean	1.07	3.24	2.23	3.30	2.6	—	—
hydrogen sulphide-carbon dioxide ¹⁸							
c	0.013	0.011	0.013	0.013	0.070	—	0.029
Mean	2.21	2.21	2.19	2.18	6.7	—	2.4
benzene-1,2 dichloroethane ¹⁹							
c	0.023	0.025	0.023	0.025	-0.001	—	—
Mean	0.0098	0.0104	0.0101	0.0080	0.26	—	—
ethanol-toluene ²⁰							
c	-0.004	0.098	0.036	0.088	0.067	—	—
Mean	0.0534	0.0602	0.0638	0.0465	0.30	—	—
benzene-cyclohexane ²¹							
c	0.040	0.049	0.043	0.048	0.018	—	—
Mean	0.0076	0.0087	0.0082	0.0091	0.33	—	—

TABLE I
 (Continued)

Quantity	Original	VdW	4/3	4/3 G	4/3(VLE)4/3(GHV)	4/3(KH)	
carbon disulphide-tetrachloromethane ²²							
<i>c</i>	0.019	0.076	0.041	0.070	0.015	0.039	0.063
Mean	0.0033	0.0295	0.0205	0.0242	0.33	0.030	0.28
carbon monoxide-methane ²³							
<i>c</i>	0.039	0.035	0.037	0.038	—	0.025	0.003
Mean	0.1148	0.1001	0.1105	0.1134	—	0.26	0.62
argon-methane ²³							
<i>c</i>	0.051	0.062	0.055	0.062	—	0.033	0.012
Mean	0.0674	0.0877	0.0825	0.0997	—	0.34	0.67
nitrogen-oxygen ²³							
<i>c</i>	0.001	0.005	0.002	0.005	-0.009	0.003	0.003
Mean	0.0860	0.0985	0.0926	0.1002	0.18	0.092	0.092
nitrogen-argon ²³							
<i>c</i>	0.002	0.005	0.003	0.005	-0.002	0.002	0.003
Mean	0.0178	0.0248	0.0213	0.0263	0.088	0.028	0.018
oxygen-argon ²³							
<i>c</i>	0.023	0.023	0.023	0.023	0.010	0.015	0.004
Mean	0.0104	0.0107	0.0100	0.0100	0.21	0.13	0.30
acetone-chloroform ²⁴							
<i>c</i>	-0.007	—	-0.007	-0.006	-0.037	—	—
Mean	0.078	—	0.078	0.078	0.36	—	—
carbon disulphide-acetone ²⁵							
<i>c</i>	0.099	—	0.102	0.107	0.073	—	—
Mean	0.120	—	0.121	0.122	0.34	—	—
water-propanol ²⁶							
<i>c</i>	-0.096	—	0.139	0.369	-0.002	—	—
Mean	0.481	—	0.381	0.281	1.12	—	—
methanol-water ²⁷							
<i>c</i>	-0.225	—	-0.145	-0.052	-0.032	—	—
Mean	0.318	—	0.188	0.091	0.98	—	—

In conclusion we may say that the effect of the different combination rules on calculated volumes of mixtures is most probably smaller than it has been so far usually to suppose and that once these rules have been determined close to some reasonable ones, *i.e.* Van der Waals's or other, no large improvement can be expected. The basic problem lies in the choice of a proper equation of state and unless this is not solved satisfactorily, we cannot hope that we will be able to describe properties of liquid mixtures in the whole relevant range of temperatures, pressures and concentrations with only one interaction constant per each binary system.

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