APPLICATION OF THE REDLICH-KWONG-SOAVE EQUATION OF STATE TO THE SOLUBILITY OF WATER IN COMPRESSED GASES

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Dedicated to the Academician O. Wichterle on the occasion of his 70th birthday.

Published data on the solubility of water in compressed gases were employed for calculating the interaction coefficients k_{ij} in the Redlich-Kwong-Soave equations of state for binary systems of water with argon, nitrogen, CO_2, N_2O, CH_4, C_2H_6, or C_2H_4. With these coefficients, the estimate of the solubility of water in these gases has been improved by more than one order.

The content of water in gases and, especially, in gaseous mixtures plays an important role during their compression and transportation, further also in engineering calculations of technological units, in air-conditioning, *etc.*

The dependence of the partial pressure of water in various gases is illustrated in Fig. 1. In an ideal system, this dependence should be weak and it should be corrected by using only the Poynting correction, which, at a temperature of 323 K and a pressure of 10 MPa, increases the partial pressure of water by approximately 7%. The observed substantially higher increase in the partial pressure of water is due above all to the nonideal behaviour of the vapour phase, or by a low value of the fugacity coefficient of water in the gaseous phase, respectively.

At lower pressures, the nonideal behaviour of the gaseous phase is expressed usually through the virial equation of state with the second virial coefficient. In calculations and correlations of dissolved water at higher pressures, the Redlich-Kwong equation[1-3], or possibly more complex equations[4], is being used. In this work we employ the Soave[5] form of the Redlich-Kwong equation, whose efficiency in calculations of phase equilibria has been proved by many authors[6-9]. The Soave equation is given by[5]

$$P = RT/(V - b) - a/[V(V + b)] , \tag{1}$$

where V is molar volume, P is pressure, T is absolute temperature and R is the universal gas constant. The constants a, b of pure components are calculated from the relations

$$\begin{aligned} a &= a_{ii} = 0{\cdot}42748 R^2 T_{c,i}^2 P_{c,i}^{-1} \{1 + m[1 - (T/T_{c,i})^{1/2}]^2\} , \qquad (2) \\ b &= b_{ii} = 0{\cdot}08647 R T_{c,i}/P_{c,i} , \\ m &= 0{\cdot}480 + 1{\cdot}574\omega_i - 0{\cdot}176\omega_i^2 , \end{aligned}$$

where $T_{c,i}$, $P_{c,i}$, ω_i are the critical temperature, critical pressure and accentric factor of substance i, respectively.

For a mixture of the composition $y_1, y_2, \ldots, y_{N-1}$, the constants are calculated from the relations

$$b = \sum_{i=1}^{N} y_i b_{ii}\,, \tag{3}$$

$$a = \sum_{i=1}^{N} \sum_{j=1}^{N} y_i y_j a_{ij}\,.$$

In the case of similar substances (*e.g.*, a mixture of hydrocarbons), the cross-terms a_{ij} are estimated either from the geometric mean (the classical version) as

$$a_{ij} = (a_{ii}a_{jj})^{1/2}\,, \tag{4}$$

or from the relation

$$a_{ij} = (1 - k_{ij})\,(a_{ii}a_{jj})^{1/2}\,, \tag{5}$$

with the interaction coefficient k_{ij} whose value is determined from experimental data.

As it has been shown, these interaction coefficients must be necessarily known for a successful calculation of the solubility of water. Since we did not find these coefficients in the literature, we calculated the values of k_{ij} for seven gases (Ar, N_2, CO_2, N_2O, CH_4, C_2H_6, C_2H_4) and water from available experimental data[10–13] on the solubility of water in these gases at higher pressures.

In binary water (1)–gas (2) systems, the equilibrium between the liquid and gaseous

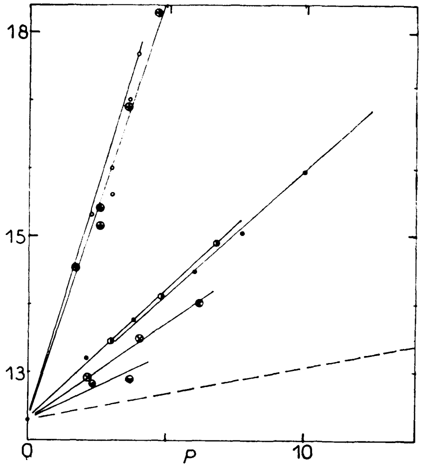

FIG. 1

The dependence of the partial pressure of water P_{H_2O} (kPa) in various gases on pressure P (MPa) at 50°C: ○ N_2O (ref.[11]); + CO_2 (ref.[11]); ◑ CH_4 (ref.[10]); ● N_2 (ref.[10,12]); × Ar (ref.[10]); △ C_2H_6 (ref.[11]); — — — the Poynting correction phases can be expressed through the relations[14]

$$P y_1 \nu_1 = x_1 f_1^{\mathrm{L}} \tag{6}$$

$$P y_2 \nu_2 = x_2 \, \mathrm{H}_2 \exp \left[\bar{V}_2^{\infty} (P - P_1^0) / RT \right] ,$$

where y_i, resp. x_i, is the mole fraction of component i in the vapour, resp. liquid phase, ν_i is the fugacity coefficient of component in the vapour phase, which we calculated from the Redlich–Kwong–Soave equation as

$$\ln \nu_i = \ln \frac{RT}{P(V - b)} - \frac{V b_{ii}}{V - b} - \frac{a b_{ii}}{RT \, b(V + b)} +$$

$$+ \left(a b_{ii} - 2b \sum_{j=1}^{N} y_j a_{ij} \right) (RT \, b^2)^{-1} \ln \frac{V + b}{V} . \tag{7}$$

The molar volume V of the vapour phase must be determined preliminarily by solving the equation of state (1) at given values of T, P, y_1.

The fugacity f_1^{L} of pure liquid water at pressure P was calculated from the relation

$$\ln f_1^{\mathrm{L}} = \ln P_1^0 + B_1 P_1^0 / RT + V_1^{\mathrm{L}} (P - P_1^0) / RT . \tag{8}$$

The temperature dependence of the saturated vapour pressure of water, P_1^0, was determined from the Antoine equation[15]. For the second virial coefficient of water,

TABLE I

The dependence of Henry's constant H (MPa) on temperature and $\bar{V}^{\infty}$ for the gases investigated

$$\ln H = A + B/T + C \ln T + DT$$

Gas	Temperature range, °C	A	B	C	D	$\bar{V}^{\infty}$ cm^3/mol
Argon	0—74	167·17550	− 8 137·38	−23·2546	3·06355 . 10^{-3}	30·5 (ref.[17])
Nitrogen	0—74	162·69062	− 8 432·73	−21·5579	8·43620 . 10^{-3}	40 (ref.[18])
CO_2	0—80	157·56183	− 8 741·50	−21·6689	1·10259 . 10^{-3}	33 (ref.[18])
N_2O	0—40	88·76789	− 6 645·40	−10·0844	−1·20040 . 10^{-2}	33 [a]
CH_4	0—80	181·47810	− 9 111,60	−25·0379	1·41170 . 10^{-4}	39·3 (ref.[17])
C_2H_6	0—80	266·1231	−13 367·98	−37·5521	2·3013 . 10^{-3}	55[a]
C_2H_4	15—80	150·6333	− 7 959·79	−20·5108	0	55 (ref.[13])

[a] Estimated values.

B_1 (in cm^3/mol), we employed the Keyes relation[16]

$$B_1 = 37{\cdot}15 - (52\,274/T)\exp(1{\cdot}7095 \,.\, 10^5/T^2)\,. \tag{9}$$

The temperature dependence of the molar volume of liquid water, V_1^L (= 18·07 cm^3/mol), was neglected.

TABLE II

Experimental[10] and calculated values of y_1 for the H_2O(1)–methane(2) system (k_{ij} = 0·48)

t, °C	P, MPa	$y_{1,\mathrm{exp}} \,.\, 10^3$	$y_{1,\mathrm{calc}} \,.\, 10^3$	% Dev.
25	2·353	1·483	1·456	1·83
25	3·051	1·175	1·156	1·65
25	4·055	0·915	0·907	0·92
50	3·014	4·474	4·472	0·03
50	4·838	3·921	2·960	1·35
50	6·817	2·185	2·242	2·63
75	3·121	13·55	13·32	1·71
75	5·472	8·03	8·09	0·76
75	6·726	6·71	6·80	1·40
100	5·741	19·92	19·91	0·05
100	7·188	16·43	16·42	0·07
100	9·343	13·09	13·19	0·75

TABLE III

The interaction parameters k_{ij}

Gas	k_{ij}	Temperature range, °C	Maximum pressure, MPa	Lit.
Argon	0·52	25–100	10	10
Nitrogen	0·36	25–100	10	10
	0·40	50	100	12
CO_2	0·25	25–100	5	11
N_2O	0·24	25–100	5	11
Methane	0·48	25–100	9	10
Ethane	0·48	25–100	4	11
Ethylene	0·34	37–140	13·8	13

Values of Henry's constant of the corresponding gas were calculated from the relation

$$\ln H_j = A_j + B_j/T + C_j \ln T + D_j T, \qquad (10)$$

in which the constants A_j, B_j, C_j, D_j as well as the partial molar volume $\bar{V}_j^\infty$ at infinite dilution were taken from the literature[17] and they can be found in Table I. The temperature dependence of $\bar{V}^\infty$ was also neglected.

If we know the value of y_1 at a given temperature and pressure, we obtain by connecting relations (*1*), (*2*), (*3*), (*5*)–(*10*) a complicated relation for the independent variable a_{12}, resp. k_{12}, in relation (*5*). During the optimization of k_{12}, we calculated the value of y_1 for the given temperature and pressure and for a selected value of k_{12}. Then, those values of k_{12} were considered as being optimal, which gave the lowest value of the sum over all experimental points,

$$S = \sum |y_{1,\text{exp}} - y_{1,\text{calc}}| \, . \qquad (11)$$

In Fig. 2 we report this dependence of S for the $H_2O(1)$–$CH_4(2)$ system and in Table II we give the experimental[10] and calculated values of y_1 for the optimal value of $k_{12} = 0{\cdot}48$. The values of k_{12} for the seven gases are summarized in Table III.

Obviously it follows from Fig. 2 that the minimum found on the S *vs* k_{12} curve is extremely sharp and that the calculated deviation in the composition of the vapour phase with the optimal value of k_{12} is in the case of methane lower almost by two orders in comparison with the classical version, where it is assumed that $k_{12} = 0$.

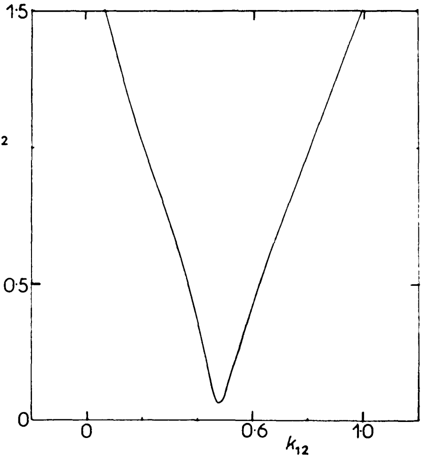

FIG. 2

The dependence of the deviation in the vapour phase composition (*11*) on the interaction parameter k_{12} for the $H_2O(1)$–$CH_4(2)$ system

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