

APPLICATION OF TWO-PARAMETER EQUATION OF STATE TO PREDICTION OF ISOTHERMAL VAPOUR-LIQUID EQUILIBRIA

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SUMMARY

The Redlich-Kwong equation of state was used to calculate liquid and vapour phase fugacities of Acetic acid (1)-n. Heptane (2) and Acetic acid (1)-Benzene (2) systems for predicting isothermal vapour-liquid equilibria. The binary interaction coefficients were obtained by a minimization technique with the help of a computer. The agreement, between the predicted and experimental equilibrium data allows the calculation of isothermal vapour-liquid data for systems containing both polar and non-polar compounds.

INTRODUCTION

In order to design industrial separation equipment and to determine their optimum operating conditions reliable vapour-liquid equilibrium (VLE) data are required.

The fundamental thermodynamic condition for equilibrium between phases is given by the equality of fugacities "f_i", in all phases for each component.

For equilibrium between a vapour and a liquid

$$f_i^v = f_i^L, \quad i = 1, 2, \dots, n \quad (1)$$

The fugacities can be expressed in terms of fugacity or activity coefficients which approach unity for nearly ideal systems:

$$f_i^v = \phi_i^v y_i P \quad \text{and} \quad f_i^L = \phi_i^L x_i \quad (2)$$

The VLE equilibrium condition becomes

$$y_i = \frac{\phi_i^L}{\phi_i^v P} x_i = K_i x_i \quad (3)$$

where K_i is called the equilibrium ratio.

The quantities φ_i^L and φ_i^V in Eq. (3) are often calculated by means of the Redlich-Kwong equation (RK) of state (Redlich and Kwong, 1949) in order to predict the required vapour-liquid equilibria at given operating conditions.

$$\underline{P} = \frac{RT}{V-b} - \frac{a}{T^{0.5}V(V+b)} \quad (4)$$

The main advantage of the two-parameter Redlich-Kwong equation of state is the ease of predicting its coefficients from the critical properties of pure compounds.

The standart values of the constants a and b in Eq (4) can be calculated by applying Eq. (4) to the conditions at critical point. (Redlich-Kwong (1949)).

$$(\partial P / \partial V)_{T_c} = 0 \quad (5)$$

$$(\partial^2 P / \partial V^2)_{T_c} = 0 \quad (6)$$

and

$$a = 0.42748 R^2 T_c^{2.5} / P_c \quad (7)$$

$$b = 0.08664 R T_c / P_c \quad (8)$$

Wilson (1966) originally proposed that constant "a" may be made temperature dependent and its value adjusted for each pure component in order to make the liquid-phase fugacity coefficient equal to the vapour-phase fugacity coefficient at the component vapour-pressure. He proposed to establish the temperature dependence of the constant "a" from the slope of the vapour-pressure curve at the critical point. The temperature function proposed by Wilson is given below.

$$(a / RT^{1.5}b) = 4.934 \times \left[1 + (1.45 + 1.62 w) \left(\frac{1}{T_R} - 1 \right) \right] (1/T_R)^{0.12} \quad (9)$$

In Wilson's treatment of the R-K equation a single set of parameters is used for the gas and liquid phases, the parameter "b" is taken as a constant calculated from Eq. (8) and the parameter "a" is a generalized function of temperature and acentric factor, "w".

Chueh and Prausnitz (1967) suggested that there must be two characteristic constants differ from one substance to another. They replace equations (7) and (8) with:

$$a = \Omega_a R^2 T_c^{2.5} / P_c \quad (10)$$

$$b = \Omega_d R T_c / P_c \quad (11)$$

The dimensionless constants $g\Omega_a$ and $g\Omega_d$ are determined for each pure component by fitting equation (4) to P-V-T data for the saturated vapour. This gives us vapour-phase values of the constants. A similar procedure is used to obtain liquid-phase values of ${}_1\Omega_a$ and ${}_1\Omega_b$ fitting Eq. (4) to P-V-T data for the saturated liquid (Prausnitz 1967).

Zudkevitch and Joffe (1970) and Asselineau and Renon (1973) considered that both of the parameters "a" and "b" were temperature dependent. Kato and Chung (1976) developed new expression for parameters at the critical region.

De Santis (1976) et al modified the pressure term ($RT/(V-b)$).

The physical properties used in the evaluation of the pure-component parameters include vapour pressure, saturated liquid and Vapour volumes, and the equal fugacity criterion for describing the vapour-liquid equilibrium since various combinations of these properties are used in the calculation of the pure component parameters. Evaluated parameters differ from one to another.

The application of R-K Equation to vapour-liquid equilibrium calculations for mixtures necessitates the proper mixing rules for pure component. The original rules given by Zudkevitch (1966) involve the geometric mean assumption.

$$a_{ij} = (a_i a_j)^{0.5} \quad \text{No empirical coefficient is required} \quad (12)$$

$$a_M = \sum_i \sum_j x_i x_j a_{ij} \quad (a_{ii} = a_i) \quad (13)$$

and

$$b_M = \sum_i \sum_j x_i x_j b_{ij} \quad (b_{ii} = b_i) \quad (14)$$

Wilson (1964) and Chueh and Prausnitz (1967) proposed that equation (14) be replaced with the simpler relationship:

$$b = \sum_i x_i b_i \quad (15)$$

Equation (15) is equivalent to assuming the combining rule

$$b_M = \frac{1}{2} (b_1 + b_2) \quad (16)$$

This simple combining rule appears to represent a reasonably good approximation in most systems.

Wilson (1964) proposed that the interaction constants, a_{ij} , of Eq. (13) be obtained from experimentally determined binary vapour-liquid equilibrium data. Chueh and Prausnitz (1968), on the other hand, used binary mixture volumetric data. (second virial coefficients of gases and saturated liquid volumes) to calculate the a_{ij} for either phase.

Zudkewitch (1970) et al proposed the more general case

$$a_{ij} = (1 - \theta_{ij}) (a_i \cdot a_j)^{0.5} \quad (17)$$

Where θ_{ij} is an empirical constant, dependent on the binary pair i - j , being involved and is independent of temperature. In other words θ_{ij} are interaction parameters to account for specific interaction forces between different molecules with

$$\theta_{ij} = \theta_{ji} \quad \text{and} \quad \theta_{ii} = 0 \quad , \quad i = 1, \dots, n$$

and n the number of components.

Fugacities From Redlich-Kwong Equation with Temperature-Dependent Coefficients

At a specified temperature and pressure, the equilibrium between the liquid and the vapour phase is determined by the Equation (1).

Various modifications of the R-K Equation have been suggested for calculating component fugacity coefficients in both the liquid and vapour phases of a mixture. For instance, the fugacity coefficient, ϕ_i , of a component in a multi-component mixture is deduced from equations, (4), (13) and (15) as (Chueh, Prausnitz, 1967)

$$\begin{aligned} \ln \phi_i = \ln \left(\frac{V}{V-b_M} \right) + \frac{b_i}{V-b_M} - \frac{2 \sum_{i=1}^N y_i a_{ij}}{RT^{1.5} b_M} \cdot \ln \left(\frac{V+b_M}{V} \right) \\ + \frac{a_M b_i}{RT^{1.5} b_M^3} \left[\ln \left(\frac{V+b_M}{V} \right) - \frac{b_M}{V+b_M} \right] \quad (18) \end{aligned}$$

by means of the relation given by Beattie (1949)

$$\ln \phi_i = \frac{1}{RT} \int_0^P \left[\left(\frac{\partial V}{\partial n_i} \right)_{T,P,n_{j \neq i}} - \frac{RT}{P} \right] dp \quad (19)$$

For a one-component system Eq. (18) reduces to Eq. (20)

$$\ln \phi = \ln \left(\frac{V}{V-b} \right) + \left(\frac{PV}{RT} \right) - 1 - \left(\frac{a}{RT^{1.5} b} \right) \ln \left(\frac{V+b}{V} \right) \quad (20)$$

In the present work equations (18), and (20) are applied to both the liquid and vapour phases. The K-ratio is evaluated as the ratio of fugacity coefficients. From Eq. (3).

$$K = \frac{\phi_i^L}{\phi_i^V} \quad (21)$$

Eq. (21) is obtained.

The molar volumes in Eq. (18) are the molar volumes of the liquid phase and vapour phase respectively which must be evaluated by solving equation (4) once for the vapour phase and then for the liquid phase.

In addition, both liquid and vapour mole fractions add up to unity:

$$\sum x_i = 1 \quad (22)$$

$$\sum y_i = 1 \quad (23)$$

The object of this work is to estimate the equilibrium system pressure P when system temperature T and liquid composition x_i are specified. Acetic acid (1)/n-Heptane (2) at 30°C (Markuzin 1971) Acetic acid (1)/Benzene (2) at 20°C (Houghton 1967) were chosen to be investigated.

In order to simplify the VLE equations, binary interaction terms are taken as

$$a_{ij} = (1 - \theta_{ij}) (a_i + a_j) / 2 \quad (24)$$

$$b_{ij} = (1 - \sigma_{ij}) (b_i + b_j) / 2 \quad (25)$$

where θ_{ij} and σ_{ij} are two adjustable coefficients, and must be determined empirically.

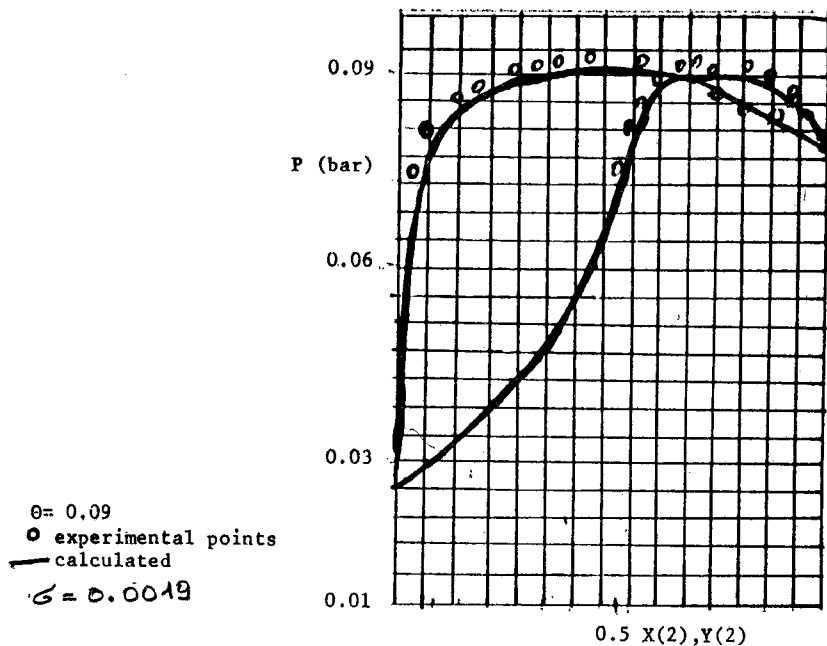


Fig.1 Vapour-liquid equilibrium of Acetic acid (1)-n-Heptane (2) at 303.15°K

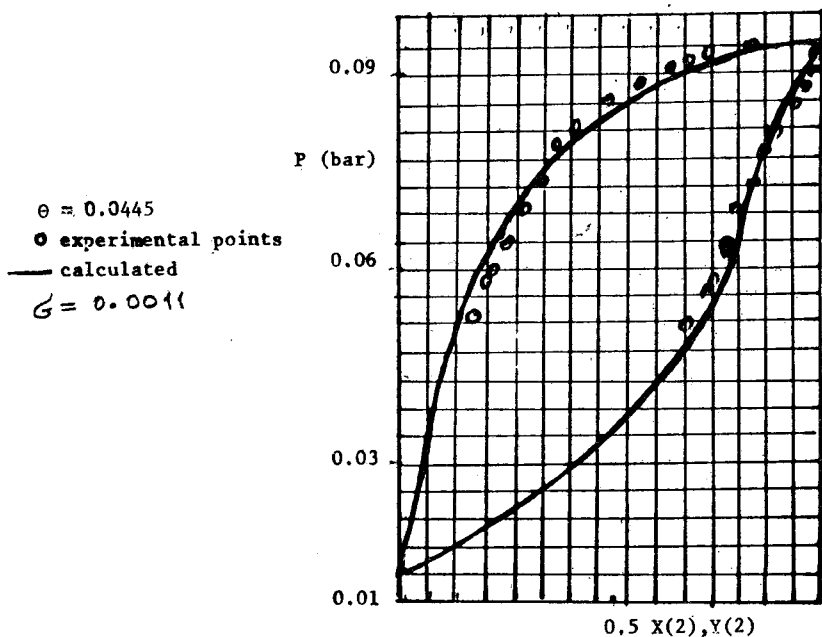


Fig.2 Vapour-liquid equilibrium of Acetic acid(1)-Benzene(2) at 293.15°K

Procedure For Finding Equation Parameters

Computations were carried out in terms of dimensionless parameters Ω_a and Ω_b , as described by equations (10) and (11) rather than the R-K parameters a and b . At any given temperature the values of the Ω parameters were established by simultaneous solution of equations (4) and (20). So that the R-K equation would reproduce for each pure component its saturated liquid density and fugacity at the experimental vapour pressure.

The fugacity coefficient at saturation was obtained by fitting on analytic form to a tabular correlation for the fugacity coefficient at saturation published by Lyckman, Eckert, and Prausnitz (1965). The pure component vapour pressure and saturated liquid densities were calculated from the Antoine (Am.Pet.Inst.Research Project 44, 1953) and Riedel's equations (Reidel, 1954).

In practice, the simultaneous solution of Equation (4) and Eq. (20) is carried out by a minimization method with the help of a computer. Determination of the parameters require many iterations and for practical purposes, the Quasi-Newton fit program has been developed to evaluate parameters by minimizing the function given by Eq. (26).

$$S^2 = \sum_1^N [[(P_{\text{assumed}} - P_{\text{expt}})/P_{\text{expt}}]^2] + \sum [[(\phi_{\text{assumed}} - \phi_{\text{Lyckman}})/\phi_{\text{Lyckman}}]^2] \quad (26)$$

Ω_a and Ω_b values are varied systematically until the best possible match is obtained between the experimentally obtained pressure and the Lyckman (1965) fugacity coefficients and the values calculated by applying equations (4) and (18) to both phases for each component,

The iteration ends when

$$S^2_{n-1} - S_n^2 < 10^{-9}. \quad (27)$$

In the current work the combining rule of Equations (24) and (25) have been used to determine θ_{ij} and σ_{ij} values. It is assumed in the present work that the binary constants θ_{ij} and σ_{ij} are independent of the temperature, pressure, or composition of the system. The interaction constants, a_{ij} and b_{ij} were then obtained from experimental binary vapour-liquid equilibrium data by means of equations (4) and (18). The interaction constants a_{ij} and b_{ij} were then used together with pure compound Ω_a and Ω_b parameters in the calculation of fugacity coefficients from. Eq. (18).

In the calculation of the Ω parameters, θ_{ij} , and σ_{ij} values by means of a single equation of state, representing both the liquid and the vapour phases, from time to time some of the calculation methods fail to converge. This is particularly true in the region close to the critical point of the mixture concerned. Eq. (4) may be rearranged to give a cubic equation in terms of compressibility factor "Z" of the mixture

$$Z^3 - Z^2 + (A - B - B^2) Z - AB = 0 \quad (28)$$

where

$$A = \frac{a P}{R^2 T^{2.5}} \quad \text{and} \quad B = \frac{b P}{RT} \quad (29)$$

The problem of non-convergence may occur when Eq. (28) yields only one identical single root for both phases as no clear distinction exist between f_1^L and f_1^V on the basis of a different Z (Harmens, 1975). In order to overcome the difficulty of non-convergence, in the present work, two modifications are used. The first modification involves the initial assumption that $\phi_1^V = 1$ and the second modification is to assume the first value of pressure \underline{P} (I) slightly less than the expected value (say 95 %).

The proposed procedure was used for prediction of vapour-liquid equilibria for binary systems containing polar and non-polar components. Such as Acetic acid (1)-n.Heptane(2) and Acetic acid (1)-Benzene (2) at constant temperature. The convergence was obtained for all the 12 data points of Acetic acid (1)-n. Heptane (2) system at 303.15 °K and for all the 17 points of Acetic acid (1)-Benzene (2) system at 293.15 ° K.

VLE prediction results of the Acetic acid (1)-n.Heptane (2) are compared with the experimental data of Markuzin (1971) in Fig. (1). Fig. (1) suggests that there are certain discrepancies between the calculated and the experimental values around the flat azeotropic region where there is a miscibility gap in the liquid. An average deviation of ± 5.3 % was observed in the calculation of \underline{P} at $T = 303.15$ °K.

The predictions on the system Acetic acid (1)-Benzene (2) are compared with the experimental data in Fig. (2). The prediction of pressure at 293.15 °K. is as good as the one be expected. An average deviation of 3.03 % is observed in the calculation of pressure for a given temperature and a system composition.

CONCLUSIONS

In the present work, two-parameter equation of state is tested whether it can be used for VLE predictions of systems containing polar groups such as organic acids.

Calculations indicates that binary constants θ_{ij} and σ_{ij} are small numbers at low pressures (Figs (1) and (2)). Thus, it appears that at low pressures (max. 0.095 bar) an arithmetic mean combining rule for constant a_{ij} and b_{ij} is a good approximation and this explains the small values of θ_{ij} and σ_{ij} in equations (24) and (25).

Results of the Acetic acid (1)-n. Heptane (2) VLE predictions by means of the two-parameter equation of state at low pressures show very good agreement between calculated and experimental values reported by Markuzin (1971), although there is a flat azeotropic region that are illustrated in Fig. 1.

The calculation on the Acetic acid (1)- Benzene (2) system shows that prediction is as good as the one be expected.

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SYMBOLS

a, b	parameters in Redlich-Kwong equation, Equation (6).
θ_{ij}, σ_{ij}	binary constants in Eqs. (24) and (25).
f	fugacity
K	vapour-liquid equilibrium constant
\underline{P}	pressure (bar)
R	Universal gas constant
T	temperature °K
T_R	Reduced temperature (°K)
V	Molar volume ($\text{m}^3/\text{k.mol}$) $V = \sum x_i M_i / \underline{P}$
w	acentric factor
x	molal concentration in liquid phase
y	molal concentration in vapour phase
Z	compressibility factor

ϕ	fugacity coefficient
ρ	liquid density.
Ω	parameters in Eqs. (10) and (11).
R-K	Redlich-Kwong Eq.
VLE	Vapour Liquid Equilibrium Data

SUBSCRIPTS

i, j	refer to component i or j
ij	pertaining to binary pair of component i and j
c	pertaining to critical state
g	pertaining to vapour or gas phase
L	pertaining to liquid state
v	pertaining to vapour state
M	pertaining to mixture property

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