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Employment of Vapor Pressure Data in the Description of Vapor-Liquid Equilibrium with Direct Method

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A procedure for inserting vapor pressure data in the equations of state is presented. It provides a straightforward scheme for the extension of direct methods to the study of phase equilibria of polar mixtures and of solutions containing nonvolatile electrolytes. Some examples of application are also given.

SCOPE

Equations of state are always more often employed to estimate thermodynamic properties of fluids. Specifically this paper will focus on their use to describe vapor-liquid equilibria in multicomponent systems, where equations of state represent an alternative method to the so-called "indirect methods." The accuracy of the prediction of the multicomponent equilibrium data depends on the ability of the equation of state to represent the vapor pressure of the pure components present in the mixture. For this reason, parameters of the cubic equations of state (Soave, 1972; Peng and Robinson, 1976) are given as functions of the temperature, obtained through a regression procedure in order to fit the vapor pressure data of a set of compounds in a specific range of temperature.

A general procedure will be developed to introduce the vapor pressure of pure component in the van der Waals-type equations of state, so that, at any given temperature, the equality of the liquid and vapor fugacity occurs at a pressure value exactly equal to the vapor pressure. This procedure will improve the multicomponent vapor-liquid equilibria prediction and allow use of the equation of state in all compounds and in the whole temperature range.

Furthermore, such a procedure can also be regarded as a useful tool to study the intrinsic ability of equations of state with different structure to describe the vapor-liquid equilibrium of multicomponent system, once they all exactly describe the vapor pressure of the pure components, without any previous regression analysis.

CONCLUSIONS AND SIGNIFICANCE

A general procedure is introduced for the vapor pressure data of pure components in the equations of state derived from the van der Waals theory.

The procedure has been applied to the PR (Peng and Robinson, 1976) and RSRK (Carnahan and Starling, 1972) equations of state. We have thus overcome lack of accuracy in the prediction of the vapor pressure of pure components at temperatures below the boiling points. Besides, in this region, the proposed procedure improves the vapor liquid equilibria prediction of multicomponent mixtures, obtained by using the two equations of state in the common way.

Further, this procedure is expected to be of some use in the approximate prediction of the effect of electrolytes on vapor-liquid equilibrium of multicomponent mixtures, once you know only the effect of the electrolytes themselves on the pure components vapor pressure.

Finally, we deem it worthwhile to point out that the present analysis does not consider any adjustable parameter. However, such parameters can be easily introduced, as it is usually done in the application of the equations of state, to improve the agreement between the experimental and the predicted values.

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The simplest and most widespread way to study vapor-liquid equilibria implies a direct evaluation of the fugacity coefficients of both phases. The advantages of this procedure have recently been reviewed by Witchterle (1978). It relies on the availability of an equation of state able to describe the behavior of both vapor and liquid phases.

Though many equations have been suggested, it is well known that prominent position must be attributed to equations derived from the van der Waals theory, in which the compressibility factor is given by the sum of two contributions:

$$Z = \frac{PV}{RT} = Z^{hs}(V) + \frac{1}{RT}\psi(V, T) \qquad (1)$$

The former reflects the structure of the fluid, described as a collection of rigid bodies, while the latter reflects the attractive interactions between the molecules.

The most common procedure employed in the application of such direct methods relies on the possibility of adjusting some semiempirical parameters present in the second of the above-mentioned contributions, in order to fit the vapor pressure of pure components. This approach implies the application of a regression analysis for each component and the attempt to correlate the values of the obtained parameters to some typical property of the molecules under consideration (for instance the acentric factor, Peng and Robinson, 1976; Soave, 1972). Such a procedure involves a certain lack of accuracy due either to the limit of the regression analysis or to the necesity of limiting the regression to a fixed range of temperature and to a restricted number of compounds. For these reasons, the method has been basically applied only to mixtures of nonpolar molecules, as hydrocarbons.

In a recent paper, Gmehling et al. (1979) have proposed a modification of the equation of state based on the perturbed hard-chain theory (Beret and Prausnitz, 1975) to describe the vapor-liquid equilibria, in the presence of one or more polar components. The obtained results show an excellent agreement with the experimental data, even if they require the introduction of few adjustable parameters to describe the interaction between the indissociate molecules and the ions present in the mixture.

In this paper, a procedure for inserting the vapor pressure data in the equation of state is presented. It provides an exact method to determine the function $\psi(V, T)$, so that for *any temperature* the equality of the fugacities of *pure* components in the two phases in equilibrium:

$$f_i^v(T, p_i^o) = f_i^l(T, p_i^o) \qquad (2)$$

is exactly satisfied.

The suggested procedure, besides the remotion of the already mentioned lack of accuracy, provides the advantages of a higher flexibility. This fact yields, as it will be shown, a straightforward tool for the extension of direct methods to the study of phase equilibria in the case of polar mixtures and in the presence of nonvolatile electrolytes.

DESCRIPTION OF THE METHOD

Equation 1 can be rewritten in the form:

$$P = \frac{RT}{V} Z^{hs}(V) + \frac{\psi(T,V)}{V} = P_R(V,T) + P_A(V,T) \qquad (3)$$

where P_R and P_A are the repulsive and the attractive contribution to the pressure, respectively. This latter term can be expressed as:

$$P_A = -\frac{f(T)}{g(V)} \qquad (4)$$

where $g(V)$ gives the general functional dependence from the volume.

For instance it is: $V(V + b)$ in Redlich-Kwong-Soave (RKS) (1972) equation; $V(V + b) + b(V - b)$ in Peng-Robinson (PR) (1976) equation.

From the equation of state (Eq. 3), the fugacity coefficient can be evaluated as:

$$\ln \varphi = \frac{1}{RT}\int_{\infty}^{V}\left(\frac{RT}{V} - P\right) dV + Z - 1 - \ln Z \qquad (5)$$

therefore, the equilibrium condition of a pure component given by Eq. 2, recalling that $f_i = \varphi_i P$, can be obtained, substituting Eqs. 3 and 4 in Eq. 5, as follows:

$$\begin{aligned}\int_{\infty}^{V^v}\left(\frac{RT}{V} - P_R\right) dV + f(T)\int_{\infty}^{V^v}\frac{dV}{g(V)} + Z^v - \ln Z^v \\ = \int_{\infty}^{V^l}\left(\frac{RT}{V} - P_R\right) dV + f(T)\int_{\infty}^{V^l}\frac{dV}{g(V)} + Z^l - \ln Z^l\end{aligned} \qquad (6)$$

Further, the equation of state (Eq. 3) can be applied to the two phases in equilibrium, liquid and vapor, separately:

$$p^o(T) = P_R(V^v, T) - \frac{f(T, V^l, V^v)}{g(V^v)} \qquad (7a)$$

$$p^o(T) = P_R(V^l, T) - \frac{f(T, V^l, V^v)}{g(V^l)} \qquad (7b)$$

The solution of the system of Eqs. 6, 7a and 7b gives, for a given value of T and $p^o(T)$, the values of V^v, V^l and $f(T)$. Then, it is possible to introduce in Eqs. 7a and 7b either an empirical relationship between the vapor pressure and the temperature (Antoine, Riedel . . .) or the single experimental datum. The value of $f(T)$ which is evaluated from the solution of Eqs. 6, 7a, 7b satisfies exactly the equilibrium condition (Eq. 2) of the pure component at a pressure equal to the vapor pressure at the given temperature.

The numerical solution of the previous system can be quickly obtained with the Newton method. Namely, it requires very few iterations since two good first attempt values for V^v and V^l are available: the volume of ideal gas and the covolume of liquid, respectively.

Such a general procedure has been applied to two particular state equations.

Rigid Sphere Redlich-Kwong (RSRK) (Carnahan and Starling, 1972):

$$P = \frac{RT}{V}\frac{(V_R^3 + V_R^2 + V_R - 1)}{(V_R - 1)^3} - \frac{f(T)}{V(V + b)} \qquad (8)$$

where $V_R = V/V^*$ and $b = 4V^*$.

From Eq. 8, the terms P_R and P_A of the general Eq. 3 can be identified and substituted in Eq. 6 to give the following explicit expression of $f(T)$:

$$f(T) = RT\,V^*\,\frac{\dfrac{8V_R^{v^2} - 9V_R^v + 3}{(V_R^v - 1)^3} - \dfrac{8V_R^{l^2} - 9V_R^l + 3}{(V_R^l - 1)^3} + \ln\dfrac{V_R^l}{V_R^v}}{\dfrac{1}{b_R}\ln\dfrac{V_R^l(V_R^v + b_R)}{V_R^v(V_R^l + b_R)} + \dfrac{1}{(V_R^v + b_R)} - \dfrac{1}{(V_R^l + b_R)}} \qquad (9)$$

being $b_R = b/V^* = 4$.

Peng and Robinson (PR) (1976):

$$P = \frac{RT}{V - b} - \frac{f(T)}{V(V + b) + b(V - b)} \qquad (10)$$

Substituting in Eq. 6, and solving, for $f(T)$, it follows:

$$f(T) = \frac{\ln\frac{(V^l - b)}{(V^v - b)} + b\left(\frac{1}{V^v - b} - \frac{1}{V^l - b}\right)}{\frac{1}{2\sqrt{2}b}\ln\frac{[V^l - b(\sqrt{2} - 1)]\,[V^v + b(\sqrt{2} + 1)]}{[V^v - b(\sqrt{2} - 1)]\,[V^l + b(\sqrt{2} + 1)]} + \frac{V^v}{V^v + 2bV^v - b^2} - \frac{V^l}{V^l + 2bV^l - b^2}} \qquad (11)$$

where $b = V^*$.

THERMODYNAMIC STABILITY CRITERIA

It is worthwhile to note that the employed procedure for the evaluation of $f(T)$ brings to an equation of state which contains only one undetermined parameter, V^*. On the other hand in all the equations of the state derived from the van der Waals theory there are always two such parameters. These parameters are usually evaluated (Beret and Prausnitz, 1975; Peng and Robinson, 1976; Soave, 1972) on the basis of the thermodynamic stability criteria at the critical point:

$$\left(\frac{\partial P}{\partial V}\right)_{T_C,P_C} = 0; \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_C,P_C} = 0 \qquad (12)$$

In our case, it is easy to verify that the first of Eqs. 12 is identically satisfied by Eqs. 8 and 9 or 10 and 11 for all values of the parameter V^*.

This finding is a consequence of the equality of vapor and liquid fugacities of pure components at each temperature, along the vapor-liquid equilibrium, provided by our procedure.

The parameter V^* can then be evaluated from the second of conditions (Eq. 12). In particular for RSRK equation it follows:

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_C,P_C} = \frac{2V_{RC}^5 + 14V_{RC}^4 + 20V_{RC}^3 - 20V_{RC}^2 + 10V_{RC}^{-2}}{(V_{RC} - 1)^3}$$

$$- \frac{(V_{RC}^4 + 4V_{RC}^3 + 4V_{RC}^2 - 4V_{RC} + 1)\,(6V_{RC}^2 + 6V_{RC}\,b_R + 2b_R)^2}{(V_{RC} - 1)^4\,(2V_{RC} + b_R)\,(V_{RC} + b_R)} \qquad (13)$$

The only physically significant solution of the previous equation is:

$$V_{RC} = 12.0273$$

while the covolume is equal to:

$$V^* = V_C/12.0273$$

The critical compressibility Z_C can be obtained from Eq. 8, by substituting in it the value of $f(T)$ given by Eq. 9 at $T = T_C$. Since, in such a condition, Eq. 9 results undetermined, it is necessary to apply a limit procedure, from which the following expression is obtained:

$$f(T_C) = RT_C\,V^*\,\frac{(V_{RC}^4 + 4V_{RC}^3 + 4V_{RC}^2 - 4V_{RC} + 1)\,(V_{RC} + b_R)^2}{(V_{RC} - 1)^4\,(2V_{RC} + b_R)} \qquad (14)$$

Therefore, it follows:

$$Z_C = \frac{V_{RC}^3 + V_{RC}^2 + V_{RC} - 1}{(V_{RC} - 1)^3} - \frac{(V_{RC}^4 + 4V_{RC}^3 + 4V_{RC}^2 - 4V_{RC} + 1)\,(V_{RC} + b_R)}{(V_{RC} - 1)^4\,(2V_{RC} + b_R)} = 0.3157 \qquad (15)$$

Similarly the following expressions are obtained for PR Eq. 10:

$$V_{RC} = 3.9514$$

$$f(T_C) = RT_C\frac{(V_C + 2b\,V_C - b^2)^2}{2(V_C - b)^2\,(V_C + b)} \qquad (16)$$

and

$$Z_C = \frac{V_{RC}}{(V_{RC} - 1)} - \frac{(V_{RC}^2 + 2V_{RC} - 1)\,V_{RC}}{2(V_{RC} - 1)^2\,(V_{RC} + 1)} = 0.3074 \qquad (17)$$

Clearly enough, the obtained values of the critical compressibilities are the same as the ones given by the normal procedure. However, the proposed method allows us to introduce in the equation of state all the available informations on the vapor-liquid equilibrium of pure components. These informations can be introduced either as any vapor pressure equation or also as experimental data. This fact, as it will be shown, will prove advantageous in the study of vapor-liquid equilibrium in multicomponent systems.

MULTICOMPONENT MIXTURES

The equation of state obtained by the procedure above outlined can also be written for multicomponent systems. This aim can be pursued, in the same way as it is usually done in previous works (Peng and Robinson, 1976; Soave 1972), by evaluating V^*

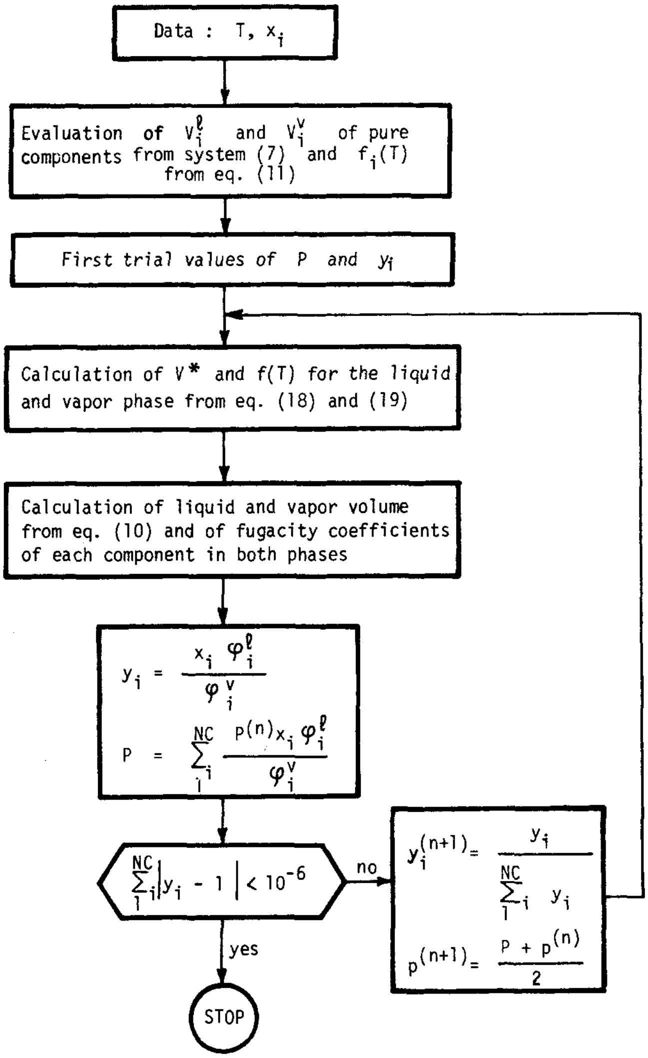

Figure 1. Scheme for the calculation of vapor-liquid equilibria (Eqs. 10 and 11).

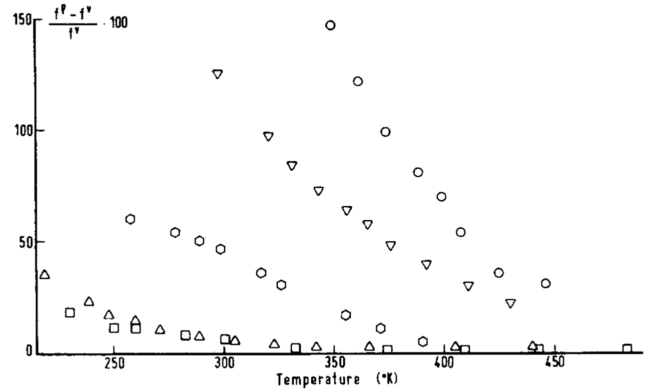

Figure 2. Differences between the liquid and vapor fugacities of pure components, at the equilibrium, predicted by PR equation (▽ hexanol, ○ 1-octanol, △ *n*-hexane, □ ethylacetate ○ 1-propanol).

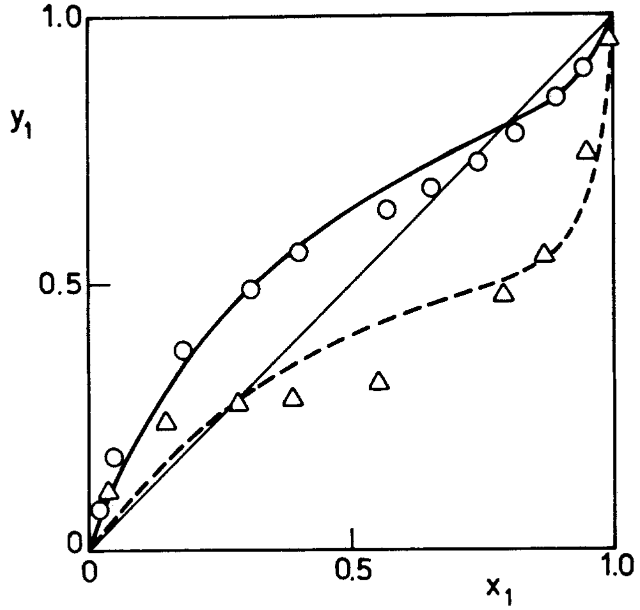

Figure 3. *x-y* plot for the system: methanol (1)—ethylacetate (2). ○ experimental data, continuous line calculated with Eqs. 10 and 11. △ experimental data for the system saturated with LiCl. Dotted line calculated with the method described in the paper. (P = 1.01 × 10^5 Pa) (Data source: Dernini et al., 1975).

and $F(T)$ for the mixture by the corresponding values of pure components, through the employment of appropriate mixing rules. In the present paper the following mixing rules have been applied:

$$V^* = \Sigma_i\, x_i\, V_i^* \tag{18}$$

$$f(T) = \Sigma_i\, \Sigma_j\, x_i\, x_j \{f_i(T)\, f_j(T)\}^{\frac{1}{2}} \tag{19}$$

It follows that the bubble point calculation of a multicomponent system implies the solution for each component at a given temperature of the non linear system of Eqs. 7a and 7b in order to evaluate the vapor and liquid volume of the pure components. The values of the equilibrium pressure and vapor composition can be then obtained, in the same way as for all previous equations of state, following the scheme reported in Figure 1 for the case of the PR equation. An extensive review of the computational method of vapor-liquid equilibria for multicomponent systems has been recently published by Anderson and Prausnitz (1980).

Application of the Method

The described procedure has been applied both to pure compounds and to binary mixtures.

In the case of pure compounds the aim of the calculations was to verify the accuracy in the evaluation of the fugacity out of the temperature range in which the parameters of the equation of state in the normal way, have been calibrated. It has been confirmed that in the above mentioned range of temperature the difference between the values obtained the normal way and with our procedure, is practically negligible. But it follows that differences of this kind take on some significance when the temperature falls out of such a range, and in particular below the boiling point of the considered compound.

This difference is due to the fact that the parameters present in the original form of PR or RSRK equations are calibrated in a restricted range of temperature, while, with the procedure outlined above, Eq. 2 is always exactly satisfied. Further this procedure can be applied to all compounds, without any *a priori* analysis, simply on the basis of an expression of the vapor pressure of the pure compound itself.

For instance, Figure 2, shows, the percentage differences between liquid and vapor fugacities, evaluated by means of PR equation at bubble point conditions. The influence of this on the prediction, through Eq. 2, of vapor pressure of pure components is reported in Table 1.

The described method does not significantly affect the evaluation of liquid and vapor density, which essentially depends on the type of equation of state employed in the calculation. Then, as already evidenced (Peng and Robinson, 1976), the Peng and Robinson equation is more accurate than RSRK equation in predicting liquid densities.

The differences, of course, may affect the description of binary mixtures. An example is offered in Table 2, in which the results of some calculations performed on the system ethylacetate-propanol are given. The table reports percentage differences between pressure and vapor compositions predicted by PR Eqs. 10 and 11. It is significant to observe that the difference increases by increasing the percentage of propanol in the mixture. This finding is consistent with the data of Figure 2, where it appears that Eq. 2, for the pure component, is more aptly satisfied for ethylacetate than for propanol.

PR equation has been also applied, both in the original form,

TABLE 1. PERCENTAGE ERROR (ϵ%) IN THE VAPOR PRESSURE PREDICTION OF PURE COMPOUNDS BY EQS. 2 AND 10.

Ethyl Acetate		Propanol		Hexyl Alcohol		Octanol		Hexane	
T	ϵ%	*T*	ϵ%	*T*	ϵ%	*T*	ϵ%	*T*	ϵ%
229.8	18.6	258.2	63.8	297.6	127.4	327.2	250.4	219.3	36.4
249.7	11.9	378.2	53.1	320.4	95.9	349.7	145.1	238.7	22.3
270.2	8.3	287.9	49.4	331.4	83.0	361.5	121.0	248.2	16.4
289.8	6.6	298.5	46.6	343.5	72.8	374.2	99.0	259.1	14.4
300.2	6.3	309.6	39.3	356.9	63.7	388.4	81.1	270.9	15.5
332.5	1.6	326.0	30.4	365.2	57.6	397.0	69.2	289.0	7.4
373.8	0.9	334.0	−4.8	376.0	47.9	408.4	54.5	304.8	5.8
409.8	0.4	355.2	17.1	392.8	39.9	425.2	36.6	341.9	3.1
482.7	2.1	371.0	11.1	411.2	30.8	447.0	32.5	366.2	3.5
508.2	1.2	390.2	5.1	430.2	22.7	468.4	24.3	404.9	4.0

TABLE 2. DIFFERENCES IN THE PREDICTION OF VAPOR PRESSURE AND VAPOR-PHASE COMPOSITION FOR THE SYSTEM: ETHYL ACETATE (1)—PROPANOL (T = 333°K)*

x_1	P%**	y_1%***
0.048	−18.2	−20.8
0.064	−16.7	−19.8
0.091	−14.9	−18.2
0.160	−11.3	−14.9
0.219	−9.4	−12.7
0.277	−7.8	−10.9
0.416	−5.3	−7.6
0.528	−3.1	−5.6
0.626	−2.2	−4.1
0.702	−1.7	−3.3
0.814	−0.4	−1.9
0.916	−0.6	−0.8

*Murti and van Winkle (1958). The differences refer to the normal procedure and to the application of the proposed method (Eqs. 10 plus 11).

** P% = percentage error in vapor pressure.

*** y_1% = percentage error in vapor phase composition.

and coupled with Eq. 11, to evaluate the bubble point data of some binary mixtures. The obtained results are collected in Tables 3 and 4, and compared with experimental data. It can be observed that the suggested procedure gives a better prediction of the system composition. Only some of the pressure values reported in Table 4 are better described by the normal procedure; but in these cases the error made in the evaluation of pure compounds vapor pressure gives rise to a fortuitous approach to the experimental values.

Finally, some typical binary mixtures, including polar components, have been studied with RSRK Eq. 8 coupled with Eq. 9. Only critical data and normal boiling temperatures have been employed to perform the calculations. Vapor pressure has been described by the Riedel equation. The obtained values of mean absolute errors are summarized in Table 5, compared with the ones obtained by applying Wilson equation with two adjustable parameters.

TABLE 3. ERRORS IN VAPOR-LIQUID EQUILIBRIUM PREDICTION FOR THE SYSTEM: 1-HEXANOL (1)—1-OCTANOL (2) (P = 1.3375 × 10^4 Pa)*

		Peng-Robinson		Eqs. 10 and 11		Eqs. 8 and 9	
x_1	T	Δy_1%	ΔP%	Δy_1%	ΔP%	Δy_1%	ΔP%
0.417	391.0	−3.3	56.1	+1.4	+3.0	+1.1	+2.1
0.549	386.6	−3.6	52.3	−0.4	0.0	+0.2	+0.5
0.707	382.6	−2.1	51.5	−0.2	−0.7	−0.3	−0.3
0.830	379.7	−0.7	50.0	+0.3	−2.3	−0.2	−2.5

* Rose and Supina (1961).

On the whole it appears that the inclusion of the function $f(T)$ in Eqs. 8 and 10 gives better results than the normal procedure. Improvement of this kind, due to the accurate description of the pure compounds vapor pressure, is effective in both the examined equations.

It is worthwhile to investigate also the possibility to predict the vapor-liquid equilibrium, when accurate values of vapor pressure are not available. For this aim, some calculations have been performed by using, in the RSRK equation of state, the Antoine equation, obtained by fitting experimental vapor pressure data, and the Riedel equation obtained by critical properties. Some results, for the mixture acetone-ethanol, taken as example, will now be given. At 48°C, the vapor pressure difference, between Riedel and Antoine equations are: 1.91% for acetone, 2.58% for ethanol, respectively.

Then 12 bubble-point calculations, at different liquid-phase composition, and always at temperature 48°C, have been performed. The percentage difference in vapor composition is 1.99% and in the pressure 3.68%. These errors are comparable with the ones corresponding to vapor pressure. Therefore the proposed method appears to be insensitive to small variations of vapor pressure. It is worthwhile to point out that the errors in the prediction of experimental results by means of Riedel vapor pressure equation is of the order of 7.78% for the vapor compositions, and 7.23% for the pressure. These predictions, which require only the knowledge of critical constants, bring to lower errors than the ones obtained through the application of the Wilson two parameters model, as illustrated in Table 5.

SALT EFFECT ON VAPOR-LIQUID EQUILIBRIUM

The described procedure can also be applied to the prediction of the effect of nonvolatile electrolyte on vapor-liquid equilibrium of multicomponent mixtures.

This aim can be pursued by simply introducing in Eqs. 7a and 7b the vapor pressure of the pure component corrected by the presence of the electrolyte.

It may be of interest to point out that this procedure requires only the knowledge of the effect of a fixed amount of salt on the vapor-liquid equilibrium of the pure components, without any experimental information on the ternary system. Therefore, this procedure can be considered as a *predictive method*, although it is approximate, to describe the vapor-liquid equilibrium of multicomponent mixture in the presence of a *fixed* amount of nonvolatile components.

Unfortunately, the experimental data of vapor-liquid equilibrium of pure components in the presence of electrolytes are seldom available.

For this reason, a simple procedure has been applied to evaluate the influence of dissolved salts on vapor pressure of pure liquid components. It is based on boiling point elevation for system at constant pressure, or on the vapor pressure lowering for system at constant temperature, respectively. In a first

TABLE 4. ERRORS IN VAPOR-LIQUID EQUILIBRIUM PREDICTION FOR THE SYSTEM: ETHYL ACETATE (1)—1-PROPANOL (2) (T = 333.16°K)*

		Peng-Robinson		Eqs. 10 and 11		Eqs. 8 and 9	
x_1	$P \cdot 10^{-4}$(Pa)	Δy_1%	ΔP%	Δy_1%	ΔP%	Δy_1%	ΔP%
0.048	2.3811	−31.3	+13.2	−13.3	−4.2	−10.8	−3.8
0.064	2.5331	−29.3	+9.2	−11.9	−6.4	−9.9	−5.6
0.091	2.7358	−26.8	+5.6	−10.3	−8.1	−8.4	−7.4
0.160	3.1917	−24.8	−0.3	−11.7	−10.5	−10.4	−9.5
0.277	3.8098	−16.6	−5.1	−6.3	−11.9	−5.7	−11.1
0.416	4.3266	−9.7	−6.3	−2.2	−11.0	−2.2	−10.0
0.528	4.5698	−5.6	−4.4	0	−7.5	−0.1	−7.1
0.626	4.8332	−1.8	−4.2	+2.5	−6.3	+2.3	−5.9
0.702	5.0561	−1.3	−4.4	+1.9	−6.0	+1.7	−5.6
0.814	5.2385	+0.3	−2.5	+2.2	−2.9	+2.0	−2.7
0.916	5.3601	+0.7	0	+1.6	+0.5	+1.5	+0.5

* Murti and van Winkle (1948).

TABLE 5. EXAMPLES OF STUDY OF SOME BINARY MIXTURES
(The numbers give the mean absolute errors of compositions in vapor phase: $\Sigma|y_{i,calc} - y_{i,exp}|$/number of data).

System (1)-(2)	Two Parameter Wilson Model*	Eqs. 8 and 9
Metane-Ethane	0.0536	0.0086
Ethylene-Ethane	0.0123	0.0119
Propylene-1, Butene	0.0298	0.0052
Octane-Ethyl Benzene	0.0037	0.0050
n-Hexane-Chlorobenzene	0.0063	0.0054
p-Xilene-Aniline	0.0402	0.0441
Ethylacetate-Propanol	0.0117	0.0222
Acetone-Ethanol	0.0125	0.0256

* M. Hirata et al. (1975).

approximation, a proportionality relationship can be employed to express the vapor pressure of a salted liquid through the vapor pressure of the pure liquid, once the boiling temperature of the base component, with the fixed amount of electrolyte, is known. So to describe ternary systems, at a fixed pressure of 1.01 × 10^5 Pa, a sufficient approximation of the vapor pressure of each salted component can be expressed as follows:

$$p_i^{oS}(T) = \frac{760}{p_i^o(T_{b,i}^S)}\, p_i^o(T) \tag{20}$$

$T_{b,i}^S$ is the boiling temperature of the salted component.

Calculations have been made for some binary mixtures in the absence or in the presence of salts. The results are reported in Figures 3, 4 and 5. The calculated curves are compared with experimental data. Actually the considered mixtures are always saturated with salts and therefore the employment of Eq. 20, which has been derived for a fixed amount of salt, is not altogether reliable.

Despite all this, the analysis of the mentioned figures reveals some significant features of the proposed procedure. In fact, it allows the prediction of the influence of the salt in terms of modification of the volatilities of the components. For example, if we look at Figure 4, the salting-out effect on component 1 (acetone) is well predicted. Besides, also the influence of the salts on the azeotropic behavior of some mixtures is well predicted. Namely, the disappearance of the azeotrope in the acetone-methanol system when saturated with LiCl (Figure 4), and the movement of the azeotrope in the methanol ethylacetate system when saturated with LiCl (Figure 3).

Finally, the system methanol (1)-ethylacetate (2) (Figure 6) has been examined at different salt concentrations. The calculated behaviors of *T*-*x* curves give rise to a shift of the mentioned curves, in agreement with experimental data.

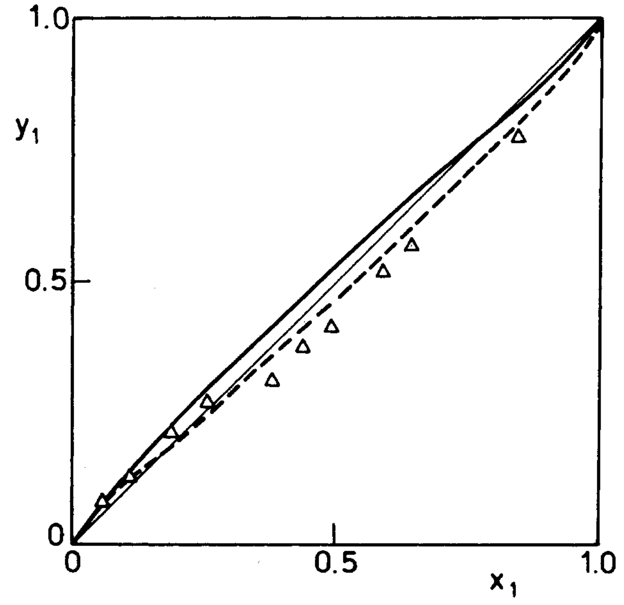

Figure 5. x-y plot for the system: ethanol (1)—acetonitrile (2). △ experimental data for the system saturated with NaI (*P* = 1.01 × 10^5 Pa). Dotted line calculated with the method described in the paper. Continuous line calculated for the system in the absence of salt.
(Data source: Cruccu et al., 1975).

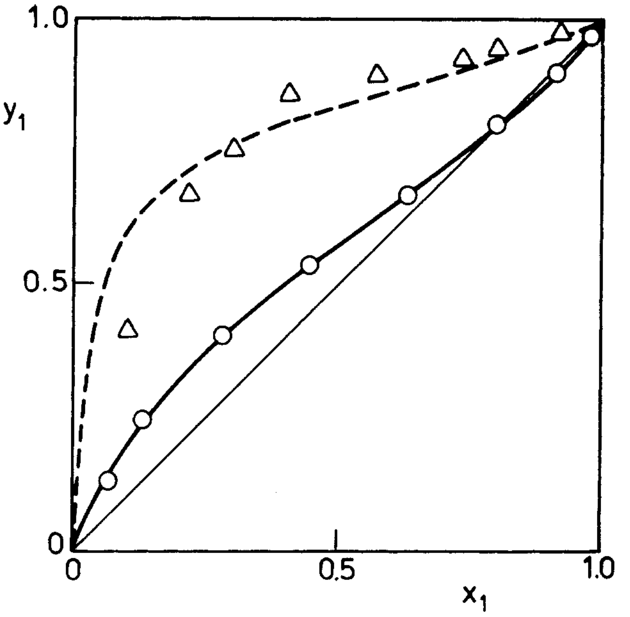

Figure 4. x-y plot for the system: acetone (1)—methanol (2). ○ experimental data, continuous line calculated with Eqs. 10 and 11. △ experimental data for the system saturated with LiCl. Dotted line calculated with the method described in the paper (*P* = 1.01 × 10^5 Pa)
(Data source: Dernini et al., 1976).

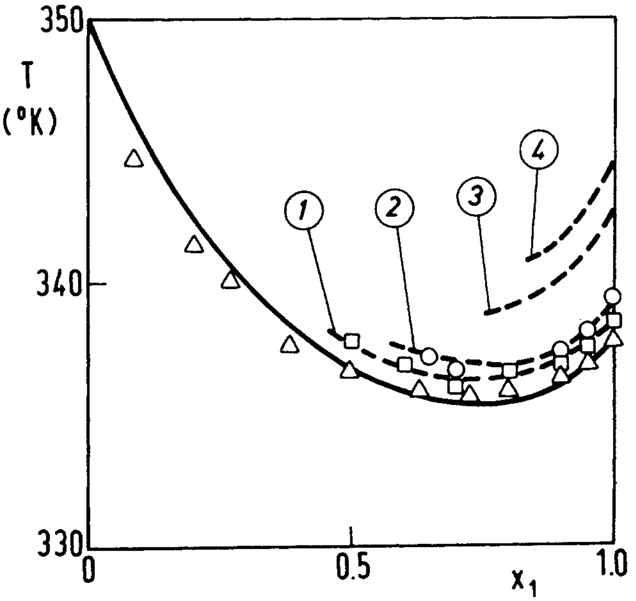

Figure 6. *T*-*x* plot for the system: methanol (1)—ethylacetate (2). Continuous line calculated for the system in the absence of salt (*P* = 1.01 × 10^5 Pa). Dotted lines calculated for the system in the presence of $CaCl_2$ at different weight percentage:
① 5%, □ experimental data
② 10%, ○ experimental data
③ 20%,
④ saturated.
△ experimental data for unsalted system.
(Data source: Ohe et al., 1971).

FINAL REMARKS

The procedure for the evaluation of the attractive term in a van der Waals type of equation allows introduction in the equation of state of the exact values of the vapor pressure of pure components.

This makes the equation of state applicable to all compounds and to the whole temperature range, and more accurate in the prediction of both multicomponent and pure vapor-liquid equilibria. This procedure gives a qualitative description of the effects of the presence of nonvolatile components on the multicomponent vapor-liquid equilibria, using only informations about the influence of the electrolyte on pure components.

Of course, the quantitative agreement with the experimental data can be improved by giving a description of the influence of the electrolytes on pure compounds, which is more accurate than Eq. 20. Besides, the introduction of a semi-empirical interaction parameter in the mixing rule (Eq. 19) will contribute to a better quantitative description of the system under examination, either with or without nonvolatile components.

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NOTATION

b = parameter of the equation of state
f_i = fugacity of component i
P = pressure
p_i^0 = vapor pressure of component i
T = temperature
V = volume
V^* = covolume
x_i = mole fraction of component i in the liquid phase
y_i = mole fraction of component i in the vapor phase
Z = compressibility factor
Z^{hs} = hard sphere compressibility factor
φ = fugacity coefficient

Superscripts

l = liquid phase
v = vapor phase
s = nonvolatile compound

Subscripts

C = value at the critical point
R = reduced value

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Diffusion and Reaction in a Stagnant Boundary Layer About a Carbon Particle

Part 7: Transient Behavior and Effect of Water Vapor

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The dynamics of carbon combustion is studied. It is shown that the carbon particle will not ignite if the furnace temperature is below a certain critical value. In addition, carbon particles display thermal instabilities which can be delayed or eliminated by increasing the water vapor concentration and/or the furnace temperature.

SCOPE

Due to its practical importance the combustion of carbon has attracted an enormous amount of theoretical and experimental work. Carbon combustion involves an interaction of heterogeneous and homogeneous reactions, and transport limitations. This gives rise to a complex pathology, understanding which is of fundamental importance in the context of coke

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