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CORRELATION OF THERMODYNAMIC PROPERTIES OF FLUIDS BY MEANS OF EQUATIONS OF STATE

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ABSTRACT

Equations of state of different families are shortly described and reviewed. Simple models, such as the cubic equations of state, are considered in their performance to more sophisticated ones. Furthermore, different mixing rules are discussed, including the simple, random, and the complicate density-dependent mixing rules. Attention has been focused on the problem of the parameter estimation in equations of state: calculations are presented showing how an equation of state can be tuned for representing thermodynamic properties. Limitations of multiproperty and mixture prediction are also put forward.

INTRODUCTION

The deviation from perfect behaviour of real gases is a subject that has concerned chemists and chemical engineers for over a century due to the difficulties involved in the resolution of practical problems that occur in many diverse aspects of thermodynamics.

These problems require the use of different empirical equations of state (EOS) to represent the PVT properties of a given substance. Of the many EOS proposed, none is capable of simultaneously representing the properties of the solid, liquid and vapor phases and only few can be used to some extent to represent the properties of both fluid phases.

The best known EOS, that of van der Waals (vdW), was presented in 1873 [1]

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as a semi-theoretical improvement to the perfect gas equation. The vdW equation has the following form:

$$P = RT/(V_m - b) - a/V_m^2 \tag{1}$$

where P is the pressure, V_m is the molar volume, a and b are parameters which vary from one substance to another; this EOS is cubic in V.

The Van der Waals EOS has a simple form, is easy to handle and gives a qualitative description of the process of retrograde condensation and of the properties of the fluid phase. It never predicts physically absurd results. Various modifications of its form, the so called cubic EOS, have been proposed [2]. Around the 50th's other equations, such as those of Beattie-Bridgeman and Benedict-Webb-Rubin have been widely used.

This paper briefly overviews the various EOS, recent modifications of the cubic EOS applied to the prediction of vapor-liquid equilibria of pure components and mixtures, and on volumetric properties of the vapor phase. A short discussion of the mixing rules suggested by different authors is also included.

Examples are given to show the approach of obtaining EOS parameters from experimental data; consequently conclusions are taken about the applicability and limitations of phase equilibria prediction by means of equations of state.

THERMODYNAMIC PROPERTIES OF PURE COMPONENTS

In principle, all the thermodynamic properties of a pure substance could be evaluated from PVT data together with heat capacity, either C_p or C_v data as a function of T, at P or total volume V constant respectively. If accurate PVT data for condensed phases are available then the calculations may be in principle extended to the compressed liquid and solid regions.

The pure component properties measured as a function of temperature are the following:

- saturated vapor pressure
- gas phase PV measurement over a wide range of P and T
- saturated liquid density
- heat capacity at low and constant pressure
- enthalpy of vaporization.

The first step for the calculation of a complete set of thermodynamic properties for the saturated liquid and vapor and for the PVT is the determination of an accurate equation for the vapor pressure curve.

The second step should be the determination of an EOS to describe the gaseous region; in this case one of the most convenient forms is the virial expansion. By using a sufficient number of coefficients, gas density can be accurately represented by equations of this form, but extrapolation should be avoided beyond the range of P for which the experimental data have been correlated.

Since the coefficients of the virial expansion are function of T, in order to obtain $(\partial V/\partial T)_P$ empirical relations between the coefficients on T should be derived. These approaches, although following a theoretical basis, lead to a multiplicity of complex equations. Moreover, these equations do not allow continuity in the description of the behaviour of the thermodynamic properties in the phases involved. A way to overcome these difficulties is to follow the approach given by a simpler EOS such as the vdW EOS which allows the equilibrium thermodynamic properties of all the phases to be described.

CUBIC EQUATIONS OF STATE

The vdW equation consist of two parts, one is the so-called repulsive term (that containing the parameter b), the second, the attractive term (containing the parameter a).

Since the vdW EOS has displayed limitations in representing the critical isotherms, second virial coefficients and vapor phase enthalpies, many authors have tried to improve it by adjusting or modifying one of its terms.

This section presents some of the most important and best known adjustments and modifications.

Modification of the attractive term

The first important improvement was suggested by Redlich-Kwong in 1949 [3]:

$$P = RT/(v-b) - a/T^{-5}\,[V_m(V_m+b)] \qquad (2)$$

The new attractive term reflects two main ideas: it takes into account the influence of T (a/T^{-5} improves prediction of the second virial coefficient) and it introduces the correction of the covolume b, which gives a more realistic value of b/V_c (V_c is the critical Volume) and consequently a better prediction of the critical isotherms.

The same line is followed by the adjustments of Barner in 1966 [4] who suggested a = f(T), Wilson in 1964 [5] and Soave in 1972 [6] who considered a to be temperature-dependent and related to the acentric factor of the pure component. All these modifications improve the prediction of vapor enthalpies, the fugacity coefficients and consequently VLE behaviour, even if the equations are in poor agreement with the second virial coefficient.

The proposed dependence of the parameters on T generated other EOS: Joffe and Zudkevitch in 1970 [7], Kubic in 1982 [8], and Heyen in 1980 [9] suggested the use of two temperature-dependent parameters; the last two Authors even introduced a third parameter. In this way, prediction of VLE is better, but second virial coefficient prediction is not improved. Moreover, extrapolations above T_c can be dangerous when using Joffe's modification, and enthalpy calculations should be avoided.

Starting from the Redlich-Kwong EOS, Peng-Robinson proposed in 1976 [10] a new form of the attractive term by adding the term $b(V_m-b)$ to the denominator: this modification improves the prediction of liquid density (without using a temperature-dependent b), and that of VLE, but not that of the vapor density.

In order to improve the prediction of vapor density, Schmidt-Wenzel [11], Harmens-Knapp [12], and Heyen [13] all in 1980 proposed similar equations with similar capacity in predicting VLE and liquid density.

A different approach was that followed by some investigators who tried to modify the Clausius EOS published in 1880 [14]:

$$P = RT/(V_m-b) - a/T(V_m+c)^2 \tag{3}$$

Joffe in 1981 and 1983 [15,16] and Martin in 1979 [17] used the parameter a(T), and Kubic [18] two temperature dependent parameters, a and c. All these EOS calculate VLE and properties in vapor phases very well but, as generally observed, any modification of the attractive term giving better VLE prediction, degrades that of the second virial coefficient compared to the original Redlich-Kwong EOS.

A modification which improves the calculation of bulk properties (such as density and enthalpy) by using the concept of molar volume transition was proposed by Peneloux [19]. The important feature of this modification is that the improvement in density calculation does not impair the phase equilibrium calculation.

Modifications of the repulsive term

Since efforts were primarily directed to improving the expression of the attractive term, the repulsive term did not receive much attention, even if the modifications proposed are to some extent more substantial than those for the attractive term.

The theory based on hard sphere fluid does not consider the attractive term so that this term was completely neglected by some investigators. This is evidenced by Thiele in 1963 [20]; he proposed the following equation, slightly corrected by Carnahan-Starling in 1969 [21]:

$$P = RT/V[(1 + y + y^2 - y^3)/(1 + y)^3] \quad (4)$$

This modification did not greatly improve VLE prediction and that of related quantities at low and moderate pressures. Its predictions are rather innacurate when the component or one of the components in the mixture is very large. Addition of an attractive term to the Carnahan-Starling term does not improve the prediction of the thermodynamic behaviour: Ishikava in 1980 [22], Scott in 1971 [23] used the Redlich-Kwong attractive term, but VLE prediction was similar to that obtained with the Joffe EOS.

Donohue-Prausnitz in 1978 [24] presented the perturbed hard sphere EOS; Lin in 1983 [25], Kim in 1985 [26], and Chien in 1983 [27] presented application of the cubic chain of rotator EOS, where the Carnahan-Starling repulsive term was used. Once again, the results are always a compromise and no important and valid improvement is gained.

The proper form of the repulsive term is still an open question. Even if the hard sphere equation of state does not improve VLE prediction compared to cubic EOS, it should be pointed out that this repulsive term is theoretically correct and really improves the results for simple fluids at very high pressure. This arguments should be considered in developing a new equation of state.

THE BENEDICT WEBB RUBIN EQUATION OF STATE FAMILY

The Benedict-Webb-Rubin (BWR) EOS family is not so numerous as the vdW family. It is empirical, similar in form to the virial equation representing the compressibility factor as a polynomial in density. It has been the first EOS used to predict VLE in a quantitative way, and it requires 8 parameters for a pure component. Several modifications have been proposed to overcome the problems encountered at low temperature and high density.

Starling in 1973 [28] extended it to low temperatures by introducing 11 constants; Hopke and Lin in 1974 [29] investigated the applicability of BWR equation to mixtures of light hydrocarbons and sour gases: they obtained good results for pure component properties, but no particular improvements for mixtures by comparison with the Redlich-Kwong-Soave EOS. Other extension of the BWR equation have been proposed by Bender in 1970 [30], who utilized 20 constants, and by Mc Carty in 1974 [31].

CORRESPONDING STATES THEORY

The two most important formulations of the Corresponding State (CS) principle for equilibrium properties are those developed by Leach *et al* in 1968 [32] (scale and shape factors) and Pitzer [33].

Leach-Leland defined the correspondence by equating the reduced residual Helmholtz energy of the pure component (or of the mixture) with that of a reference substance:

$$A^r\ (T,V,x)/RT = A^r_o\ (T_o,V_o)/RT_o \tag{5}$$

where the reduced temperature T_o and volume V_o are calculated by using the concept of scale factor:

$$T_o = T/f_x \qquad V_o = V/h_x \tag{6}$$

where f_x and h_x are functions of the component, temperature and volume. Many authors developed different functional forms for the shape factor correlation. This method gives excellent results but is rather time consuming and depends upon the reference fluid considered.

The Lee-Kesler formulation (1965) [34] refers to an analytical BWR version of the acentric factor correlation of Pitzer *et al.* The compressibility factor of a fluid is a function of z_o (compressibility of a simple fluid) and z_r (compressibility of a reference fluid). Extension of the Pitzer correlation gives better results for mixtures, but the performance for pure components is not as accurate as the Leach-Leland formulation.

MIXTURES

The general forms of EOS applied to pure components are also used for mixtures. Parameters that were functions at most of temperature, are functions of temperature and composition.

The composition dependence of EOS is given only by that of a and b. The functions performing this are called mixing and/or combining rules. The term "combining rule" can be applied to the expression giving the property starting from the same property as the pure components, and "mixing rule" to that giving a property as a function of all the possible combinations of the properties for all the binaries contained in the mixture. In his original paper van der Waals derived a very simple set of mixing/combining rules: the random mixing theory. The algebraic form of the function is:

$$a = \sum_m \sum_n x_m x_n a_{m,n} \tag{7}$$

$$a_{m,n} = (1-k_{m,n})(a_m a_n)^{0.5} \tag{8}$$

The first equation is the mixing rule, the second the combining rule, namely the geometric mean between the interactions of the pure components corrected by a coefficient $k_{m,n}$.

In principle, one could develop a mixing/combining rule empirically, taking vdW as an example, but this is not always correct. All these functions should be derived from the statistical mechanics theory of radial distribution functions. Accordingly, for a fluid mixture with a pair intermolecular potential energy function between molecules in the form (Rowlinson-Swinton, 1982 [35])

$$v_{ij}(r) = \varepsilon_{ij} f(r/\sigma_{ij}) \tag{9}$$

the following mixing rules will be derived

$$\sigma^3 = \sum_i \sum_j x_i x_j f(r/\sigma_{ij}) \tag{10}$$

$$\varepsilon\sigma^3 = \sum_i \sum_j x_i x_j \varepsilon_{ij} \sigma^3_{i,j} \tag{11}$$

where ε_{ij} is the interaction energy parameter between molecules i and j and σ_{ij} is the intermolecular interaction distance between them. Coefficients a and b of the vdW EOS are proportional to ε and σ.The classic (random) mixing rules are therefore derived.

If we consider a different EOS, e.g. Redlich-Kwong or Peng-Robinson, the mixing rule for b will be the same as that for the original vdW. However the mixing rule for a will be different, since a is proportional to $N°(\varepsilon/k)^{1.5}\sigma^3$

instead of $N^\circ \varepsilon \sigma^3$.

As a consequence it is not correct to apply the vdW mixing rule directly to the RK equation. It must be applied to the potential in terms of ε and σ. Consistent results have been obtained by Kwak-Mansoori in 1985 [36].

The procedure outlined above shows that mixing and combining functions must be derived on a statistical mechanics basis in order to obtain an EOS for mixture consistent with the random mixing theory.

MIXING RULES

The vdW mixing rules are also called random mixing rules because they consider the interactions, size and shape of the molecules constituting the mixture to be the same. In other words, they have no preferred orientation.

All the functions developed from this theory are very simple and very fast computationally. They generally give satisfactory results, but suffer from a common weakness: they fail to describe asymmetric mixtures, namely mixtures constituted by molecules differing very much in size and shape, but especially in intermolecular energy. As a consequence the parameters in the combining rules lose their physical significance. A practical effect is that the random mixing theory can be successfully applied to mixtures containing hydrocarbons and slightly polar substances, including compounds with no marked difference in size and shape. Good results are also obtained for mixtures of polar substances (where all the molecules are strongly polar), and in some cases for ill-defined mixtures (petroleum, coal-derived liquids and vegetable oils).

To overcome the problems, implicit in the random theory, many researchers have turned their attention to the development of new mixing rules. All these attempts can be roughly classified in two categories: empirical mixing rules and statistical mechanics mixing rules.

Empirical mixing rules

The basic concept in developing a mixing rule is to use an equation giving satisfactory results in modelling the liquid state, and then extend it to high pressure calculations and the vapor phase.

Most models successfully describing the liquid phase are based on the local composition concept: they are flexible enough to describe the complex behaviour exhibited by systems containing polar compounds. We will not describe this concept here. Suffice it to say that it can quantitatively describe mixtures where non randomness is involved.

The first attempts to introduce the local composition concept in EOS were empirical: Heyen in 1981 [37] and Vidal in 1979 [38]. Although their approaches represented a significant advance in modelling complex mixture phase equilibria, they suffer from several shortcomings. The parameters have no physical significance and do not depend on density; furthermore the equation does not meet the quadratic (theoretically correct) dependence of the second virial coefficient as P tends to zero.

There have been several more recent attempts by Whiting-Prausnitz [39], Mollerup [40], Sandler [41], Mathias-Copeman [42] and so on. Excellent results in different fields of applications have been obtained, but the models failed when applied for other applications. For example, prediction of ternary liquid-liquid and vapor-liquid equilibria is normally very poor.

Statistical mechanics mixing rules

Local composition can also be derived from statistical thermodynamics and examined by using computer generated data for model fluids.

Lee in 1983 [43], Sandler in 1985 [41], Dieters in 1987 [44] have investigated the development of statistical mechanics mixing rules in depth and compared their results with computer-generated data for different kind of intermolecular potential. The agreement they found was very satisfactory. Furthermore, they demonstrated that these models can rarely be applyed to phase equilibria involving fluids of industrial interest.

In spite of the success of some researchers in describing mixtures of real fluids, the rigorous statistical mechanics treatment of complex systems for which G^E models have customarily been used is not so near; on the other hand, empiricism should be introduced at some point in the development. This theoretical approach, however, will be very useful in developing more theoretically based functional relationships for treatment of the real fluids.

PARAMETER ESTIMATION

All these equations have eventually been developed by introducing a dose of empiricism. This fact leads to the presence of adjustable parameters whose physical meaning is often doubtful. These can be divided into two categories: those which can be calculated from pure component properties and from mixture data respectively. For any EOS, the parameter estimation step is at least as important as the model development, and must be carried out in the proper way.

Parameters in EOS are usually obtained by minimization of an objective

TABLE 1

Pressure, temperature and composition derivatives of the reduced residual Helmholtz energy (F).

$$\begin{aligned}
F &= n\,A^{r}\,(T,V,n)/RT \\
(\partial F/\partial V)_{T,n} &= -P/RT + n/V \\
(\partial F/\partial T)_{V,n} &= -(\,nS^{r}(T,V,n))/RT - F/T \\
(\partial F/\partial n_i)_{T,V} &= \ln \Phi_i + \ln Z \\
(\partial^2 F/\partial V^2)_{T,n} &= -\,(\partial P/\partial V)_{T,n}/RT - n/V^2 \\
(\partial^2 F/\partial T^2)_{V,n} &= -\,(n\,C_V^{r}/RT^2 - 2/T\,(\partial F/\partial T)_{V,n} \\
(\partial^2 F/\partial n_i \partial n_j)_{T,V} &= (\partial \ln \Phi_i/\partial n_j)_{T,P} + V_i/RT\,(\partial P/\partial n_j)_{T,V} - 1/n \\
(\partial^2 F/\partial T \partial n_i)_{V} &= (\partial \ln \Phi_i/\partial T)_{P,n} - 1/T + V_i/RT\,(\partial P/\partial T)_{V,n} \\
(\partial^2 F/\partial T \partial V)_{n} &= -\,1/RT\,(\partial P/\partial T)_{V,n} + P/RT^2 \\
(\partial^2 F/\partial V \partial n_i)_{T} &= -\,1/RT\,(\partial P/\partial n_i)_{T,V} + 1/V
\end{aligned}$$

function, namely the sum of the squares of the differences between the experimental and the calculated quantities (dependent variables). Dependent variables calculation implies the solution of the equilibrium for all data points at each iteration. In this respect, it is important to have a well-defined problem; the equilibrium calculations must either converge or be suspended in a well defined way. One possibility is to take n (where n is a small number) Newton-Raphson steps from the same initial value each time: these initial values can be the experimental values. Such procedure saves computer time in the parameters estimation step and avoids convergency problems in the equilibrium calculation when the parameters are far from their optimum values.

Another possibility is to use an objective function where no equilibrium calculations are involved: the sum of the squares of the differences between the fugacity in the liquid and in the vapor phase is calculated directly from the experimental values of x, y, T and P (Michelsen 1982 [45]).

The procedure chosen for the examples of application given in the present paper is to use a "fugacity" objective function with no equilibrium calculations to generate an initial guess of the parameters for the regression of the experimental data, with an objective function written in terms of concentrations. The stop criterion in the equilibrium calculation has been used only when difficulties were encountered in starting up the final regression.

The minimization method of Lavenberg-Marquardt in the implemented version of Fletcher (1971) [46] has been used for parameter estimation. Harwell's library routine VA07A has been slightly modified to give the statistical information needed.

APPLICATION

Pure components

A general procedure for the derivation of thermodynamic properties from EOS is well presented by Vera and Prausnitz (1980) [47] and by Anderson and Prausnitz (1980) [48]; it is based upon the residual Helmholtz energy A^r, defined as:

$$A^r = A - A_{id} \tag{12}$$

where A and A_{id} are the Helmholtz energy of the compound in its actual condition and in its ideal gas state at the same T and P, respectively. They can be obtained from the partition function Q:

$$nA^r = -kT \ln Q \tag{13}$$

n is the total number of moles, k the Boltzmann's constant and T the absolute temperature. Alternatively, a simpler customary thermodynamic approach can be followed to express the A^r function in terms of P, calculated with an EOS:

$$nA^r = RT\int_V^\infty (P/RT - n/V)\,dV$$

$$P = P(V,T,n) \tag{15}$$

We refer to the reduced residual Helmholtz energy F^r:

$$F^r = nA^r/RT \tag{16}$$

It is well known that thermodynamic properties can be calculated by differentiating F with respect to T, V and n, as summarized in Table 1. Here we can see that volumetric, calorimetric and equilibrium variables can be obtained in principle by means of EOS, *via* a simple procedure that takes advantage of analitically derived equations. This leads to a remarkable improvement with respect to the analogous calculation by EOS integration.

To get reliable and consistent results from application of an EOS to a pure compound, a number of parameters have to be set and tuned on experimental data. Data reduction is performed to achieve an optimum set of parameters for a particular pure fluid; of course, the types of data used may strongly influence the parameters obtained, so that a good description of a single property may give unacceptable behaviour for another.

Several parameters can be used. They are essentially linked to: characteristic temperature, T*, and pressure, P*, the temperature dependence of each "constant" in the equation of state and other parameters (pseudo volume,....). In the case of well-defined components, the characteristic temperature and pressure are connected to respectively P_c and T_c (critical properties), which are measurable. When dealing with undefined components (such as natural products or petroleum fractions) or with components whose P_c and T_c may be difficult to measure, it is possible to obtain T* and P* from molecular information or from fitting.

Let us take as an example the CSvdW equation of state already mentioned, where the temperature dependence of a and b is expressed as:

$$a = a_c(1 + T_r^3)/(\partial + T_r^3) \quad (17)$$

$$b = b_c \quad (18)$$

where T_r is the reduced temperature T/T*. We could consider as parameters either T*, or P*, or ∂ as well as any independent set of two of them. If we write also

$$b = b_c\,[1 + \sigma \exp -(T/T_r)] \quad (19)$$

more parameters and their combination are allowed.

To perform the data reduction, we use a general purpose computer program. Different experimental data can be selected by the user, together with a weighting factor for each of them. The data input is done either on the screen or from input files. Pure compound properties are retrieved from a database. The user is then allowed to choose the number and type of parameters to be optimized, and the EOS model. At this point the main routine is run and the following objective function is calculated (M is any experimental data):

$$FOB = \sum_k w_k \sum_j [(M^{cal} - M^{exp}) / M^{exp}]^2 \quad (20)$$

A minimization criterion is set on the stability of the solution vector, thus providing the "best" fit for the selected data.

Two examples of calculation are presented in Figs. 1, 2 and 3. Fig. 1 reports

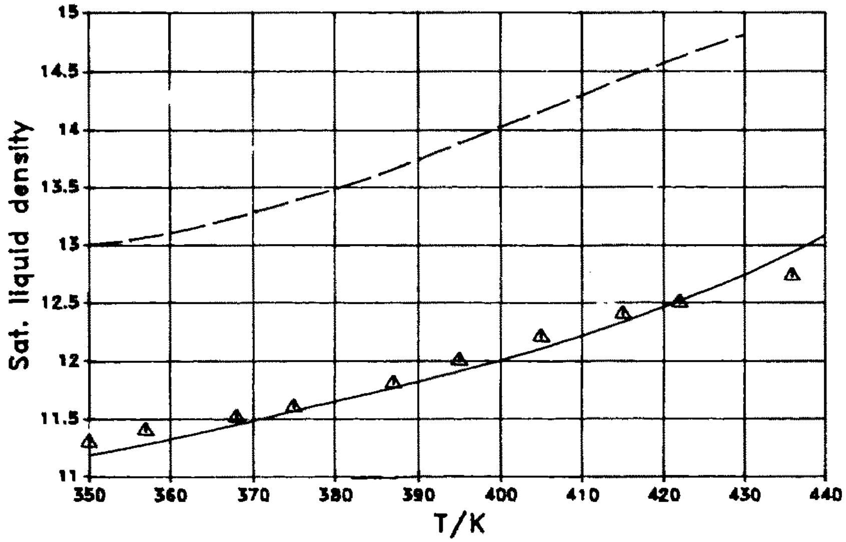

Fig. 1. Saturated liquid density (10^{-2} m^3 $kmole^{-1}$) for toluene as a function of temperature: experimental data are compared with the prediction (CSVDW with ∂ given by ref. 49) using parameters tuned on vapour pressure data (dashed line), and by using P_c as a parameter (full line).

saturated liquid volumes as a function of T for toluene. It is remarkable that poor prediction of volumetric properties is obtained by using the CSvdW EOS previously tuned on vapor pressure data according to eqn. (17). The calculation can be greatly improved if P* is taken as an adjustable parameter. The full line has been calculated with P* = 49.15 bar (instead of the value of 42.36 bar given by the critical pressure) and all the other parameters (namely ∂ and b) constant.

Figs. 2 and 3 illustrate the possibility of predicting vapour pressure data from calorimetric measurements and refer to phenol. When a generalized correlation [49] is used for computing ∂, the prediction is only acceptable for enthalpy of vaporization and vapour pressure. A regression with ∂ as a parameter leads to a much more satisfactory result. We note that the optimum ∂ depends on the data (vapour pressure or enthalpy of vaporization) used. Of course, these results can be further improved by using a better expression for a as function of temperature.

Mixtures

When applying the analytic direct method for VLE, the success of the predictions depends on the accuracy of the EOS and on the mixing rules used. The example included in this study is one for which cubic EOS (RKS or PR)

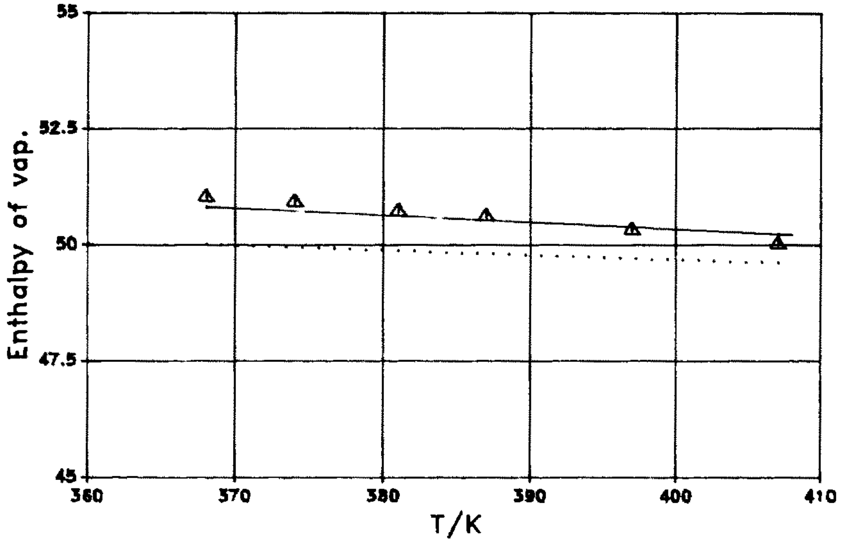

Fig. 2. Enthalpy of vaporization (kJ mole^{-1}) as a function of temperature for phenol: experimental data are compared with the prediction by using the general correlation (ref. 49; $\partial = 0.628$) (dashed line) or fitting on experimental enthalpy of vaporization ($\partial = 0.615$) (full line).

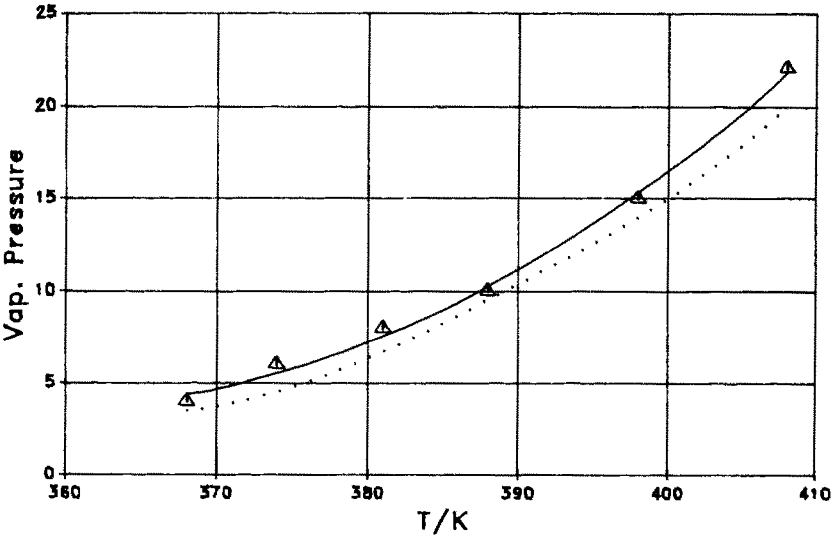

Fig. 3. Vapour pressure of phenol (kPa) as a function of temperature: comparison between experimental data, prediction from generalized correlation ($\partial = 0.628$) (dashed line) and fitting on vapour pressure data ($\partial = 0.631$) (full line).

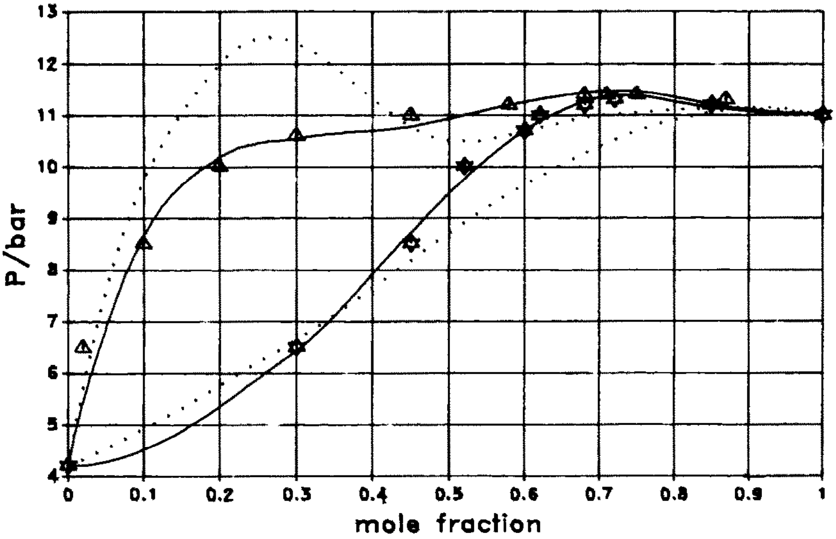

Fig. 4. VLE data for the system acetone-water at 423.15 K: experimental data are compared with the prediction using random (dashed line) and density dependent mixing rules (full line).

with their conventional mixing rules, are incapable of properly predicting its phase behaviour, namely the system acetone-water.

This system provides an interesting example of the influence of the combining and mixing rules on VLE for polar fluids. In Fig. 4 the solid line is the correlation of the system using a two-parameters density-dependent mixing rule, while the dotted line refers to the one-parameter random mixing rule.

The calculation using random mixing gives unreasonable results, since it predicts a miscibility gap which does not exist experimentally. Similar improvement on this system is obtained if we apply other mixing rules (such as proposed by Vidal [38] or Mansoori [36]), with 2 or 3 parameters.

As a conclusion, the number of parameters is more important than the real functional dependence of the mixing rule, as long as they have a physical meaning.

EOS can also be used to calculate H^E: the excess enthalpy is calculated from the derivative of the fugacity coefficient with respect to temperature.

Fig. 5 shows an example of correlation of heat of mixing data by means of a non cubic equation of state (CSvdW): this equation is considered here as an example of the performance of the random mixing and it is necessary to mention that similar results can be obtained by any other EOS , cubic or non cubic.

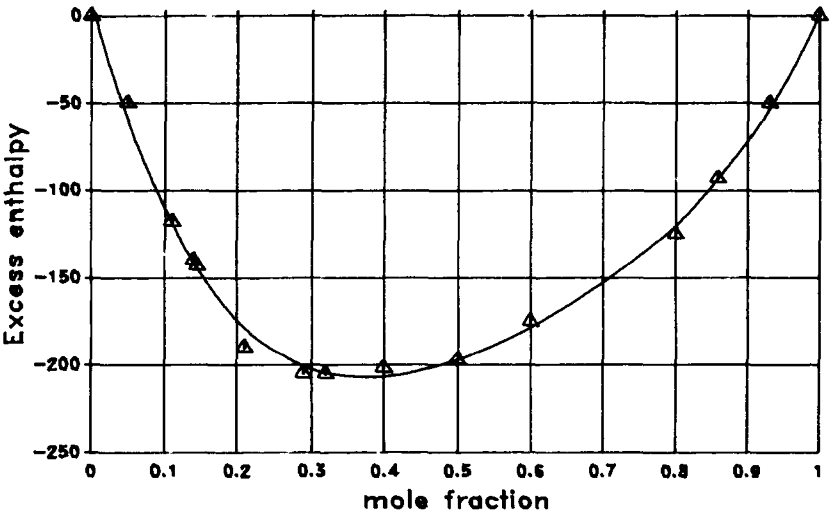

Fig. 5. Excess enthalpies (J mole^{-1}) for the system methanol-water at 298.15 K: experimental data are compared with the prediction with hard sphere EOS.

We may conclude that EOS can generally describe the concentration dependence of the excess enthalpy quite satisfactorily, even if only one temperature independent parameter is used.

CONCLUSIONS

A general conclusion [50-51] is that a perfect model is not available yet because all models contain approximations. Semiempirical models are preferred in industrial applications because of their flexibility and simplicity. On the other hand, fundamental research in the field prefer to concentrate on models whose theoretical basis is well established, even though the results are in most cases comparable to those obtained with semiempirical models.

The few applications reported show the effect of the parameters on the thermodynamic property prediction for both pure components and mixtures. It is understood from the applications that EOS are flexible enough to represent different thermodynamic properties, but incapable of representing, with the same set of parameters, all the properties of a given component or a mixture. For these reasons a good parameter estimation technique is essential when dealing with EOS for thermodynamic property calculations.

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