VLE Calculations for Mixtures Containing Multipolar Compounds Using the Perturbed Anisotropic Chain Theory

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Predicting the properties of mixtures, especially without adjustable binary interaction parameters, is difficult when the system exhibits large nonidealities. Nonidealities can result from differences in molecular size and shape, differences in the strength of intermolecular forces, and differences in the nature of the intermolecular forces (i.e., van der Waals dipolar and quadrupolar forces). Predictions are especially difficult when the molecules in the mixture differ both in size and in the nature of the potential function. For example, in coal processing, intermediate molecular weight compounds (molecular weight of 150 to 1,000) with numerous benzene rings and functional groups that have strong anisotropic potential functions, are found. When carbon dioxide flooding is used for enhanced oil recovery one encounters both nonpolar and multipolar molecules differing in size; when light polar gases are dissolved in polymers the large differences in the size and nature of intermolecular forces dominate the phase behavior.

The perturbed anisotropic chain theory (PACT) has been developed in an attempt to predict properties of such systems by including the effects of anisotropic multipolar forces explicitly into the perturbed soft chain theory (PSCT) (Vimalchand and Donohue, 1985; Vimalchand et al., 1986). In this paper, we discuss the effect of including the dipole-dipole and dipole-quadrupole interactions in the PACT. Binary mixture calculations have been carried out for systems containing dipolar molecules, dipolar and nonpolar molecules, and dipolar and quadrupolar molecules. Calculations indicate that the inclusion of multipolar interactions allow the properties of highly nonideal mixtures to be predicted with reasonable accuracy without the use of a binary interaction parameter.

$$\frac{Pv}{RT} = 1 + c(z^{\text{rep}} + z^{\text{iso}} + z^{\text{ani}}) \tag{1}$$

where z is the compressibility factor. In the PACT (Vimalchand, 1986; Vimalchand and Donohue, 1985), repulsions due to hard chains are calculated using the parameter c (external density-dependent degrees of freedom) and the equation of Carnahan-Starling for hard-sphere molecules. The attractive Lennard-Jones isotropic interactions are calculated by extending the perturbation expansion of Barker and Henderson (1967) for spherical molecules to chainlike molecules with the parameter c and the following reduced quantities:

$$\tilde{T} = \frac{T}{T^*} = \frac{ckT}{\epsilon q} \quad \text{and} \quad \tilde{v}_d = \frac{v}{\tilde{v}_d^*} = \frac{v\sqrt{2}}{N_A r d^3} \tag{2}$$

where N_A is Avogadro's number. The PACT equation of state for pure nonpolar molecules contains three characteristic parameters. Besides c, the parameters are molecular soft core size, v^* (or the related hard core size, v_d^*), and characteristic temperature, T^*. The other parameters, ϵ/k, q, r, and d, are only necessary for mixture calculations. Parameter q is proportional to the molecular surface area, ϵ/k is the energy per unit external surface area, and r is the number of segments of hard core diameter d (or soft core diameter σ) in a chainlike molecule. For pure fluids, the parameters ϵ/k and q and parameters r and σ^3 always appear as a product. For mixtures, σ and ϵ/k are determined by correlating v^* and cT^* for a large number of similar fluids.

In the PACT equation, Eq. 1, the anisotropic multipolar interactions are calculated using the perturbation expansion of

Gubbins and Twu (1978) assuming the molecules to be effectively linear. The anisotropic multipolar forces are treated as a perturbation over isotropic Lennard-Jones forces. Gubbins and Twu's results for small molecules are extended to chainlike molecules using the parameter c and the reduced quantities given by Eq. 2, and by defining characteristic reduced temperatures for dipolar and quadrupolar interactions,

$$\tilde{T}_\mu = \frac{T}{T^*_\mu} = \frac{ckT}{\epsilon_\mu q} \quad \text{and} \quad \tilde{T}_Q = \frac{T}{T^*_Q} = \frac{ckT}{\epsilon_Q q} \tag{3}$$

where ϵ_μ and ϵ_Q characterize the segment-segment dipolar and quadrupolar interaction potentials, respectively. Again, for pure fluids parameters ϵ_μ and q and parameters ϵ_Q and q always appear as a product. This product can be evaluated from known values of dipole and quadrupole moments of molecules μ and Q.

The PACT equation is extended to mixtures using a one-fluid approximation, however, without the usual random-mixing assumption. Following Donohue and Prausnitz (1978) the mixing rules for both the isotropic and anisotropic terms are derived using a lattice theory model. Complex molecules are divided into r segments, with σ and d as the soft core and hard core diameter of each segment, respectively. Each molecule has an external surface area q and a characteristic segment-segment potential (ϵ, ϵ_μ, etc.) for various intermolecular interactions. Mixing rules for isotropic Lennard-Jones interactions and anisotropic quadrupolar interactions are given by Vimalchand and Donohue (1985). In a similar manner, mixing rules for dipole-dipole and dipole-quadrupole (as in the system acetone-benzene) interactions are given by

$$\sum_i \sum_j x_i x_j \epsilon_{\mu_{ij}} q_i r_j \sigma^3_{ji} \quad \text{and} \quad \sum_i \sum_j x_i x_j \epsilon_{\mu Q_{ij}} q_i r_j \sigma^3_{ji} \tag{4}$$

respectively. The cross-terms, $\epsilon_{\mu_{ij}}$ and $\epsilon_{\mu Q_{ij}}$, can be obtained from pure-component parameters using the geometric mixing rules

$$\epsilon_{\mu_{ij}} = \sqrt{\epsilon_{\mu_{ii}} \epsilon_{\mu_{jj}}} \quad \text{and} \quad \epsilon_{\mu Q_{ij}} = \sqrt{\epsilon_{\mu_{ii}} \epsilon_{Q_{jj}}} \tag{5}$$

The mixing rules given by Eqs. 4 and 5 represent the interaction between segmental anisotropies, and give better predictions for mixtures containing molecules of different sizes than mole fraction averaged interactions between molecular dipoles and quadrupoles.

Corrections due to molecular clustering leading to nonrandom mixing are taken into account by expanding the attractive Helmholtz energy as a power series in reciprocal temperature (perturbation expansions). The attractive Lennard-Jones interactions have the form

$$\frac{A^{LJ}_{(i)}}{NkT} = f^{LJ}_{(i)}(\tilde{v}_d, \langle T^{*i} \rangle, \langle c \rangle), \quad i = 1, 2 \tag{6}$$

The functions $f^{LJ}_{(i)}$ are fitted to polynomials in inverse $\tilde{v}_d$. In any theory of fluid mixtures of the van der Waals type, the first-order term in the perturbation expansion for Lennard-Jones molecules is random (for molecules of similar size but different intermolecular potential energies) with respect to composition. Nonrandomness due to molecular clustering is accounted for by using different composition averages for $\langle T^{*i} \rangle$ occurring in each term of the perturbation expansion. The anisotropic terms in the perturbation expansion have the form

$$\frac{A^{\text{ani}}_{(i)}}{NkT} = f^{\text{ani}}_{(i)}(\tilde{v}, \tilde{T}, \langle c \rangle, \langle T^{*i}_{\text{ani}} \rangle) \quad i = 2, 3 \tag{7}$$

The functions $f^{\text{ani}}_{(i)}$ are based on the perturbation expansion of Gubbins and Twu (1978) for anisotropic multipolar interactions. The mixing rules for $\langle T^{*i}_{\text{ani}} \rangle$ are based on expressions similar to Eq. 4, but they are different for each term in the perturbation expansion. Details of the derivation are given by Vimalchand and Donohue (1985) and Vimalchand (1986).

Results and Discussion

The perturbed anisotropic chain theory has been tested with a wide variety of fluids in which molecules interact with dipolar and quadrupolar forces. Pure-component parameters have been obtained for over 60 fluids (Vimalchand, 1986) by fitting the PACT equation to experimental vapor pressure and liquid density data and then correlating these parameters to ensure reliability of data and data reduction. With these parameters, errors in calculated vapor pressure and liquid density are typically within 2% over a wide range of temperature and pressure. Also, saturated liquid and vapor volumes usually are predicted within 2% error (from triple point to 0.95 of the critical temperature).

The pure-component parameters calculated using the PACT are different from those calculated with the perturbed hard chain theory (PHCT) by Donohue and Prausnitz (1978), where segmental interactions were calculated with square-well potential. The soft sphere molecular volume, v^*, determined using the PACT is consistently larger than the hard sphere volume determined by the PHCT by about 15%. The characteristic energy parameter, T^*, has about the same value for both the PACT and the PHCT. However, the parameter c is found to be about 10 to 20% less when calculated with the PACT. This results because in the PHCT, where only square-well interactions are considered, the dipole interactions are converted into equivalent dispersive interactions. The decrease in the values of fitted parameters c and T^*, and the increase in the values of v^* (compared to the PHCT), has the effect of decreasing the ratio of the derived parameters, q/r. The normalized external surface area of a molecule q can be obtained from $cT^*/(\epsilon/k)$, while the number of segments in a molecule is given by

$$r = \frac{v^*}{v^*_{-\text{CH}_2-}} \tag{8}$$

where the soft sphere volume of a segment, $v^*_{-\text{CH}_2-} = N_A\sigma^3/\sqrt{2}$, is found from the slope v^* of normal alkanes (Vimalchand, 1986) vs. carbon number and has a value of 0.0107 L/mol. The ratio q/r, which depends on molecular shape, should have a value between 0 and 1. For a monomer, q/r is 1, while for a chain molecule it is ⅔. For dipolar and quadrupolar compounds the values of q/r calculated with the PHCT parameters (Kaul et al., 1980), are consistently greater than 1, as shown in Table 1. This suggests that the PHCT parameters do not correctly represent the actual forces with which the molecules interact. The corresponding values of q/r evaluated with PACT parameters, also shown in Table 1, are reasonable approximations to intermolecular interactions for all the compounds investigated

Table 1. Comparison of PHCT and PACT Values for Ratio of Derived Parameters q/r

Dipolar, Quadrupolar Compound	q/r, Calculated by PHCT	q/r, Calculated by PACT
Benzene	1.015	0.804
Naphthalene	1.09	0.814
Carbon dioxide	1.63	0.892
Chloroform	1.06	0.931
Acetone	1.13	0.743
Hydrogen sulfide	1.75	0.999
Sulfur dioxide	1.74	1.726

PHCT: Kaul et al. (1980); PACT: this work.

so far except sulfur dioxide, which gave a q/r ratio of 1.726. This large value also decreases when other interactions, such as induction forces are included explicitly in the PACT. From the above considerations, a correlation of the PACT parameters can be extrapolated to determine reasonable parameters for intermediate molecular weight compounds for which there are no experimental data.

For pure compounds, both the PHCT and the PACT—like many widely used equations of state such as the Peng-Robinson (1976) equation—have (three) adjustable parameters, which are regressed from experimental data. As a result, each theory fits the pure-component properties rather well. However, a much more stringent test of the theory is the prediction of mixture properties from pure-component parameters alone. Such predictions are compared in Figures 1 and 2 with experimental values for mixtures containing dipolar fluids. The K factors are calculated from the PACT with $k_{ij} = 0$. For comparison, K factors calculated with $k_{ij} = 0$ using the PHCT and the Peng-Robinson equations of state also are shown.

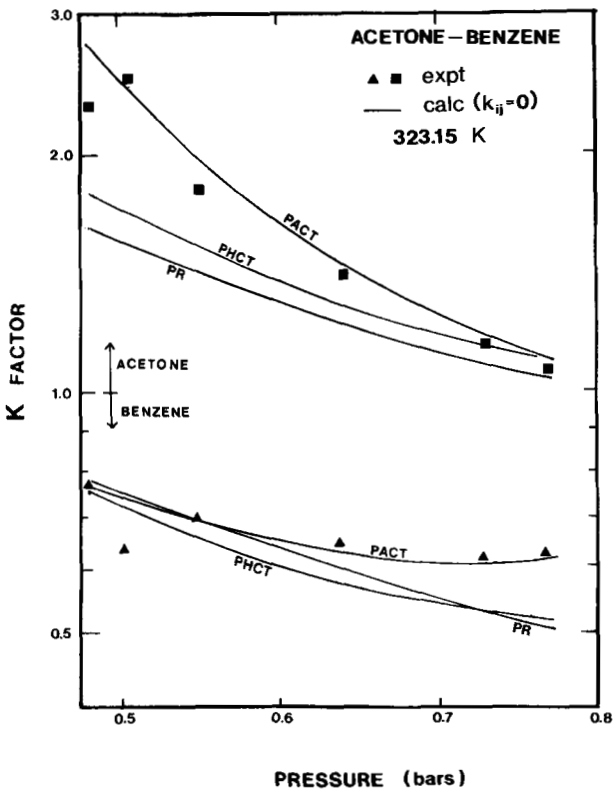

Figure 1. Comparison of experimental K factors for acetone-benzene system and calculated values, $k_{ij} = 0$.

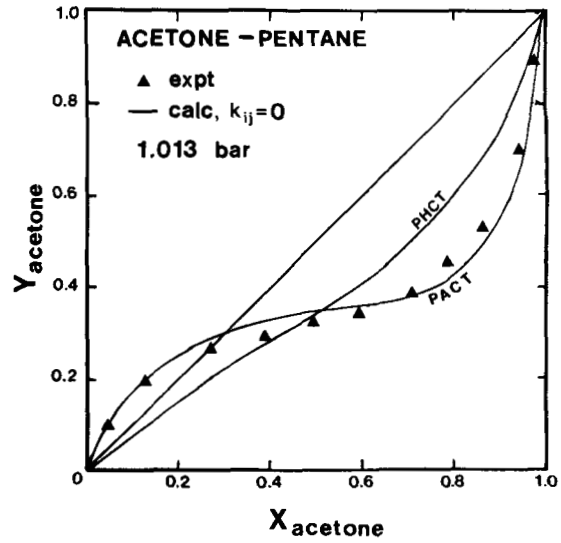

Figure 2. Comparison of experimental y-x phase equilibrium data of acetone in acetone-pentane system and calculated values, $k_{ij} = 0$.

The inclusion of multipolar interactions improves the prediction of K factors for systems containing a dipolar fluid and a quadrupolar fluid such as the acetone-benzene binary mixture shown in Figure 1. The y-x phase diagram for the system acetone-pentane, Figure 2, shows the effect of including, explicitly, the dipole interactions of acetone, rather than using an equivalent dispersion interaction in the PHCT. For this system, since acetone has a large dipole moment, the acetone parameters were evaluated including isotropic dipole-induced dipole interactions (Vimalchand, 1986). The PACT predicts the azeotrope in the acetone-pentane system and closely follows the experimental data; however, the PHCT fails to predict the azeotropes, and in addition poorly follows the experimental values. Similar results are obtained using the PACT with $k_{ij} = 0$ for over 60 binary systems (Vimalchand, 1986) containing dipolar and quadrupolar fluids. These mixture predictions by the PACT with pure-component parameters alone are quantitatively correct but usually not within experimental error. However, mixture properties usually can be fit with small errors using small values of a binary interaction parameter.

In summary, the new PACT equation takes into account the effects of differences in molecular size, shape, and intermolecular forces including anisotropic dipolar and quadrupolar forces. While prediction of properties for pure fluids is no better for the PACT than many other equations of state, the pure-component parameters obtained with the PACT are fairly reasonable and could be correlated smoothly. Calculations indicate that explicit inclusion of multipolar forces allows the properties of highly nonideal mixtures to be predicted with reasonable accuracy without the use of a binary interaction parameter.

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