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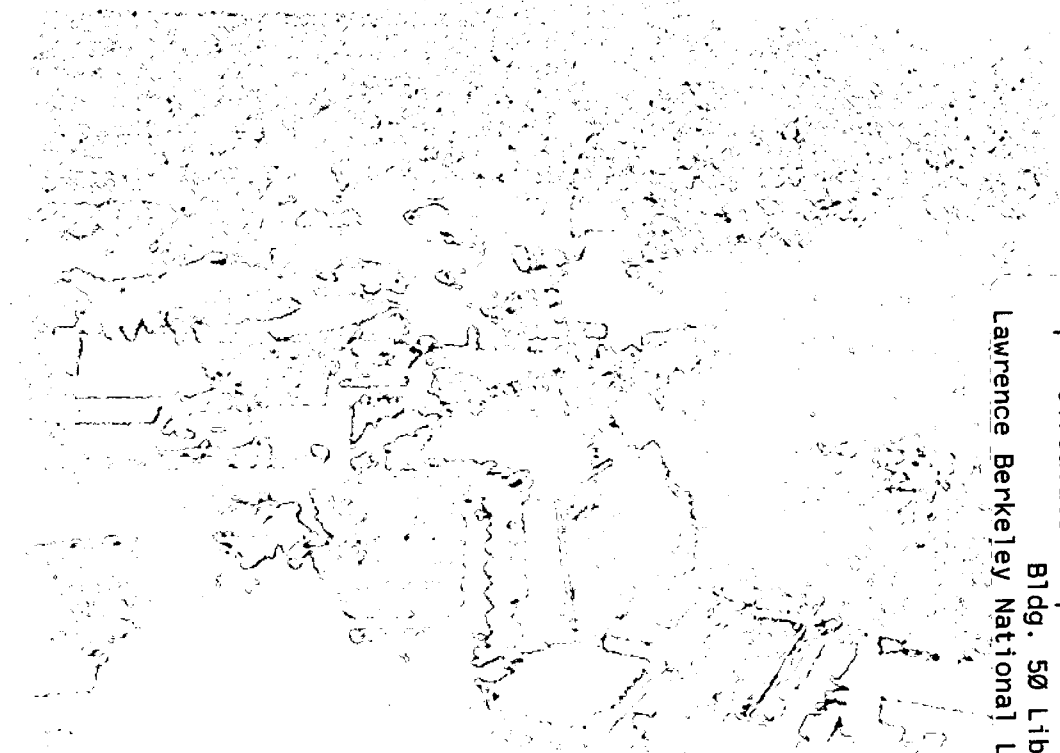
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A Perturbed-Hard-Sphere-Chain Equation of State for Phase Equilibria of Mixtures Containing a Refrigerant and a Lubricant Oil

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Chemical Sciences Division

August 1998

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A Perturbed-Hard-Sphere-Chain Equation of State

for Phase Equilibria of Mixtures

Containing a Refrigerant and a Lubricant Oil

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Abstract

A modification of the Perturbed-Hard-Sphere-Chain equation of state is used to describe vapor-liquid (VLE) and liquid-liquid equilibria (LLE) of mixtures containing new-generation refrigerants and a lubricant oil.

For refrigerants, pure-component parameters are obtained from thermodynamic data. For the oil, they are predicted by a group-contribution method, and the calculation is checked on liquid density values of polyol-ester lubricants.

Extension to mixtures is performed by using conventional one-fluid mixing rules with binary interaction parameters regressed from vapor-liquid equilibrium experimental data. VLE calculations are reported for mixtures containing a refrigerant and a polyol-ester lubricant over wide temperature and concentration ranges.

The thermodynamic condition for LLE is checked. If two liquid phases are present, LLE is calculated and compared with experimental measurements.

Introduction and Scope

In engineering practice there is a strong current need for a molecular thermodynamic model suitable to represent both volumetric and equilibrium properties of new refrigerants. In most cases these new refrigerants are mixtures of hydro-fluorocarbons and hydrocarbons. Mixtures are required because no pure fluid alternatives exist that can provide as high performance as those attained by refrigerants to be phased out because of environmental laws.

In a refrigeration cycle mutual solubility may occur between refrigerant and lubricant oil. This solubility can reduce dramatically the efficiency of a refrigeration plant. Lubricant oils modify the equilibrium pressure and the refrigerant composition, and may induce an undesired liquid-liquid phase split.

Therefore, the thermo-physical properties of mixtures of new refrigerants and lubricant oils are essential for proper design and operation of new refrigeration systems.

The phase equilibria of such mixtures has been addressed in the open literature only recently. Among others, a Flory-Huggins type model has been proposed by Thomas and Pham [1], who concentrated on the R134a-Polyalkylene Glycol system. These authors correlated vapor-liquid equilibria (VLE) by introducing a temperature and composition dependence in the Flory parameter; Martz et al [2] compared the performance of several excess Gibbs energy (G^E) models for VLE calculation of systems containing Polyol Ester oil (POE).

However, the best model for representing such systems is an equation of state (EOS). An EOS suitable to this purpose should be able to:

- describe both volumetric and equilibrium properties of pure components and mixtures;

- take into account the effect of long-chain molecules and;

- represent simultaneously VLE and liquid-liquid equilibria (LLE).

The poor volumetric behavior of cubic equations of state and their inherent difficulties for describing both long-chain molecules and LLE is well known as discussed in a previous paper [3] where models based on perturbation theories were shown to be more reliable due to their theoretical basis.

In this work the Modified Perturbed-Hard-Sphere-Chain equation of state (MPHSC EOS) proposed by Song et al. [4] is used to establish oil-refrigerant equilibria. This equation has been tested by Fermeglia et al. [5] on a large database of hydro-chloro-fluorocarbons, hydrocarbons and their mixtures, with reference to both volumetric and equilibrium properties.

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To apply the MPHSC EOS to mixtures containing lubricant oils, a method for the calculation of pure oil parameters is required. For refrigerants, parameter values are obtained from experimental data. For oils, however, PVT data are available only at atmospheric pressure.

Extension to mixtures are discussed here; binary interaction parameters (k_{ij}) are introduced to describe VLE and LLE of mixtures containing new-generation refrigerants and a lubricant oil.

The correlation presented in this work may be useful for improved design of new refrigeration systems.

Model

According to the MPHSC EOS, the Chiew [6] expression for hard-sphere chains is taken as the reference term, while the perturbation is described by the van der Waals attractive form:

$$\left(\frac{P}{\rho kT}\right) = 1 + r^2 b\rho g(d^+) - (r-1)\left[g(d^+) - 1\right] - \frac{r^2 a\rho}{kT} \tag{1}$$

where P is the pressure, T the absolute temperature, $\rho = N/V$ the number density, N the number of molecules, V the volume of the system, k the Boltzmann's constant, d the hard-sphere diameter and $g(d+)$ the pair radial distribution function of hard spheres at contact. Three segment-based parameters appear in Eq. (1): r is the number of segments per molecule, a reflects attractive forces between two non-bonded segments and b is the segment Van der Waals co-volume. Eq. 1 shows that the repulsive term accounts for chain connectivity.

Expressions for a and b are obtained by applying the method of Song and Mason [7]:

$$a(T) = \frac{2\pi}{3}\sigma^3 \varepsilon F_a(kT/\varepsilon) \tag{2}$$

$$b(T) = \frac{2\pi}{3}\sigma^3 F_b(kT/\varepsilon) \tag{3}$$

where ε is the depth of the minimum in the pair potential and σ is the separation distance between segment centers at this minimum. F_a and F_b are universal function of the reduced temperature kT/ε; they are determined from thermodynamic properties of argon and methane over large ranges of temperature and density and are expressed by empirical equations, given by Song et al. [4]. For Argon and methane, $r=1$.

The MPHSC EOS for simple fluids contains two parameters: σ and ε/k. For molecular fluids and chainlike molecules, a third parameter (r) is needed. It is convenient to redefine these parameters through a characteristic volume, V^*, a characteristic surface area, A^* and a characteristic «cohesive» energy, E^* per mole of molecules:

$$V^* = (\pi/6)r\sigma^3 N_A \tag{4}$$

$$A^* = \pi r \sigma^2 N_A \tag{5}$$

$$E^* = r(\varepsilon/k)R_g = r\varepsilon N_A \tag{6}$$

where N_A and R_g are Avogadro's and the universal gas constants.

Pure component parameters are molecular quantities that reflect the size, shape and interaction energy of the molecule.

For refrigerants, expressions for V^* and A^* are given as a function of the Bondi volume and surface area based on thermodynamic data as given in [5], while E^* is specific to reproduce the vapor pressure at the temperature of interest.

Since experimental data are insufficient for determining the EOS parameters for the oil, a group-contribution method was developed based on vapor-pressure and liquid-density data for a large number of ordinary molecular-weight compounds containing the functional groups needed to represent the oil [8]. This method is used to establish lubricant-oil parameters.

Extension of the MPHSC EOS to mixtures is obtained by applying mixing rules to the EOS parameters, leading to the following equation [9]:

$$\frac{P}{\rho kT} = 1 + \rho \sum_{ij}^{m} x_i x_j r_i r_j b_{ij} g_{ij}\left(d^+_{ij}\right) - \sum_{i}^{m} x_i (r_i - 1)\left[g_{ii}\left(d^+_{ii}\right) - 1\right] - \frac{\rho}{kT}\sum_{ij}^{m} x_i x_j r_i r_j a_{ij} \quad (7)$$

where $x_i = N_i/N$ is the number fraction of molecules of species i, r_i the number of segments for the i-th component and $g_{ij}\left(d^+_{ij}\right)$ the ij pair radial distribution function of hard-sphere mixtures at contact. The exact statistical mechanic expression for $g_{ij}\left(d^+_{ij}\right)$ is given by Boublik [10] and Mansoori et al. [11].

The molecular-weight range of typical lubricant oils is not so high to allow the assumption of an infinite number of segments, as it is for high-molecular weight polymers [4].

For each pair of components, two parameters a_{ij} and b_{ij} are needed: they are obtained by extensions of equations (2) and (3):

$$a_{ij} = (2\pi/3)\sigma^3_{ij}\varepsilon_{ij} F_a\left(kT/\varepsilon_{ij}\right) \quad (8)$$

$$b_{ij} = (2\pi/3)\sigma^3_{ij} F_b\left(kT/\varepsilon_{ij}\right) \quad (9)$$

where F_a and F_b are the same universal function as those in Eqs. (2) and (3).

The combining rule for σ is defined without any interaction parameter:

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \qquad (10)$$

A binary interaction parameter, k_{ij}, is introduced in the combining rule for the energetic parameter ε:

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}\left(1 - k_{ij}\right) \qquad (11)$$

Values for k_{ij}'s are regressed from experimental binary vapor-liquid equilibrium data.

Calculation methods

Equations (1) through (11) utilize a pressure-explicit EOS. For phase equilibrium calculations, we want the Helmholtz energy because we can then obtain all relevant thermodynamic properties by simple partial differentiation

Equations for the chemical potential and thermodynamic subroutine details are reported elsewhere [5].

Table 1 Pure component parameters. [1]POE of reference [14], [2]POE of references [15-17].

Substance	Molecular weight	$A*$ $(10^{-9}\ cm^2/mol)$	$V*$ (cm^3/mol)	$E*$ $(bar\ cm^3/mol)$
R134a	102.031	6.781	41.40	45085
R125	120.022	7.936	39.99	51191
R32	52.054	4.787	24.69	41816
POE[1]	696	73.80	458.95	483920
POE[2]	612	64.77	398.83	425258

For LLE, a Gibbs tangent plane stability test has been implemented, according to the method proposed by Michelsen [12,13]. This test distinguishes between stable and
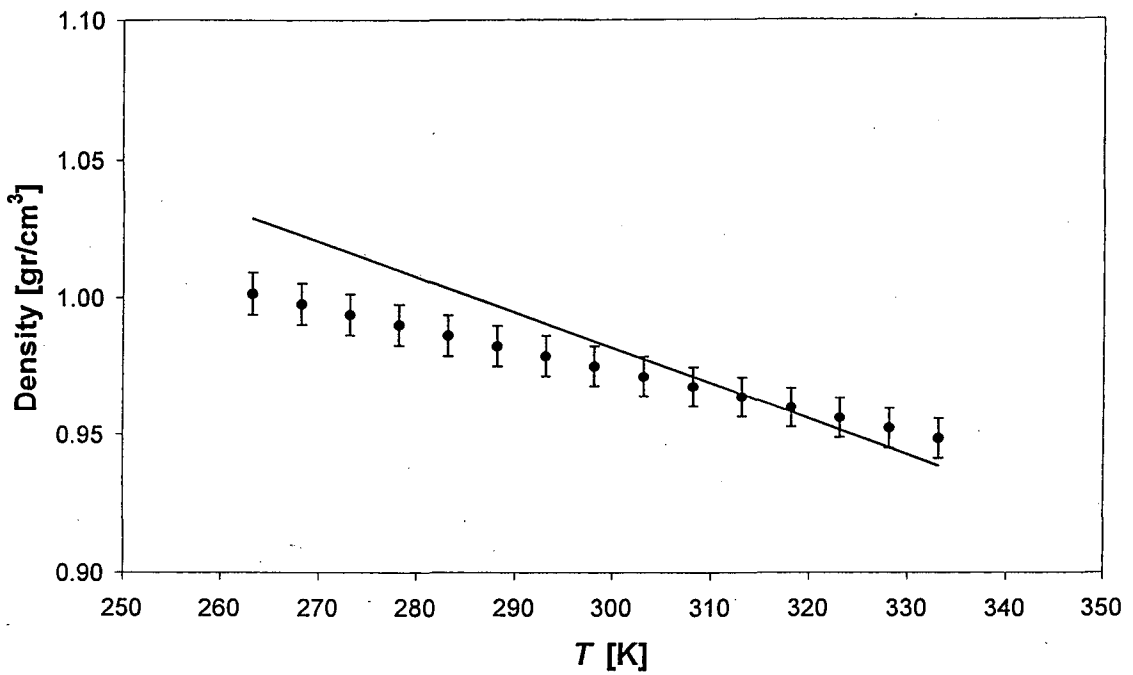
Figure 1 Density of POE: experimental [14] and calculated results. The bar corresponds to 0.75% experimental error.
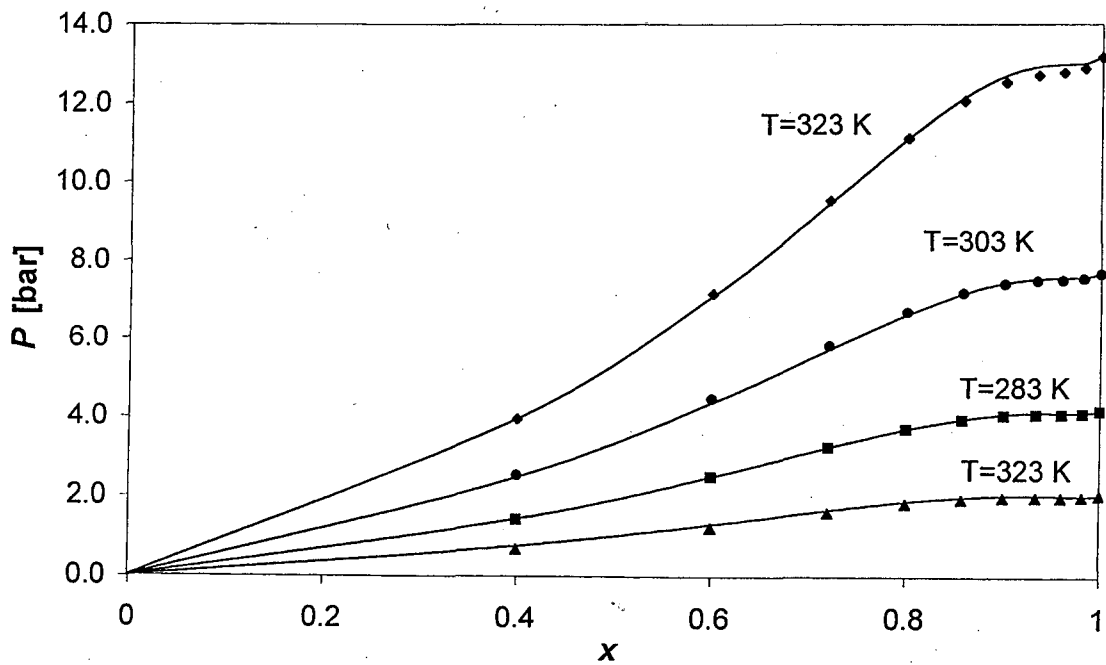

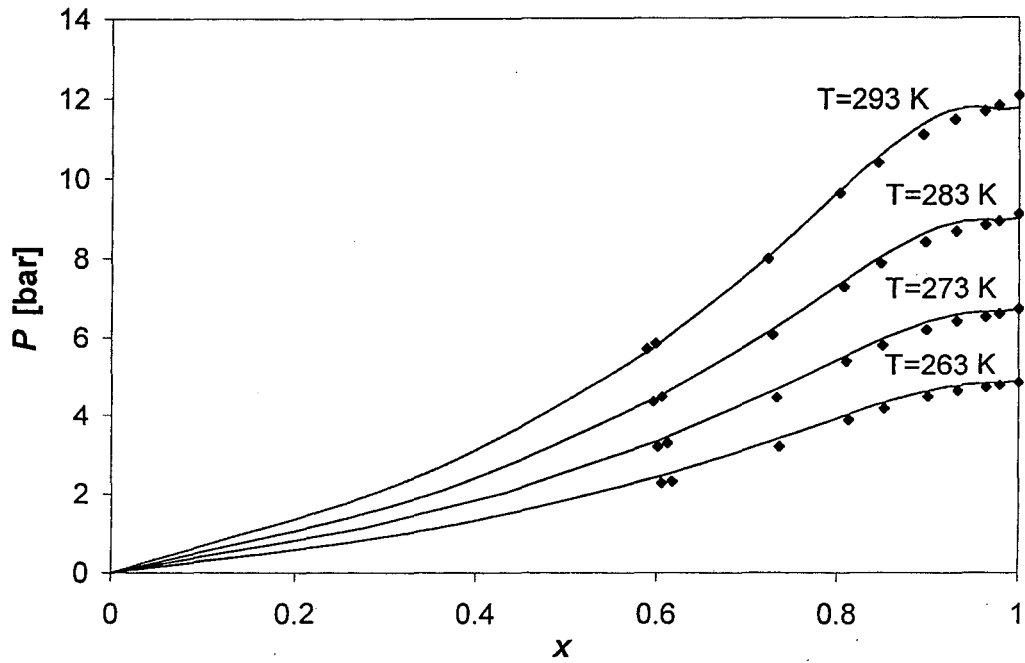**Figure 2** VLE calculation for the system R134a-POE. Data from [16]. x = molar fraction of refrigerant

Figure 3 VLE calculation for the system R125-POE. Data from [15]. x = molar fraction of refrigerant.
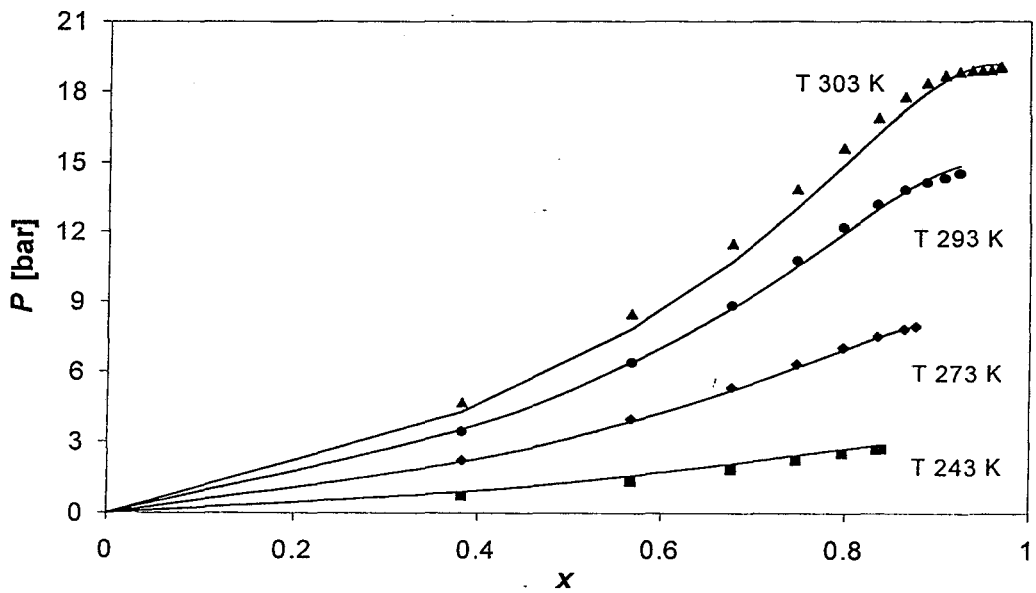

Figure 4 VLE calculation for the system R32-POE. Data from [17]. x = molar fraction of refrigerant.
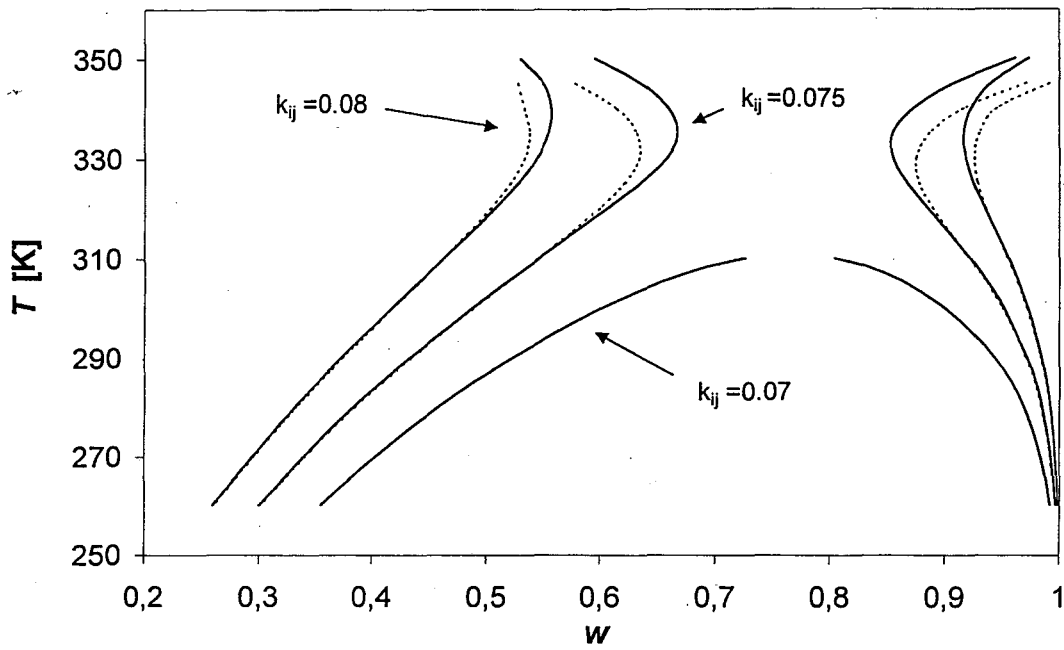
Figure 5 Parametric LLE curves for the system R32-POE. Continuous line P=20 bar and dashed line P=5 bar. w = weight fraction of refrigerant.
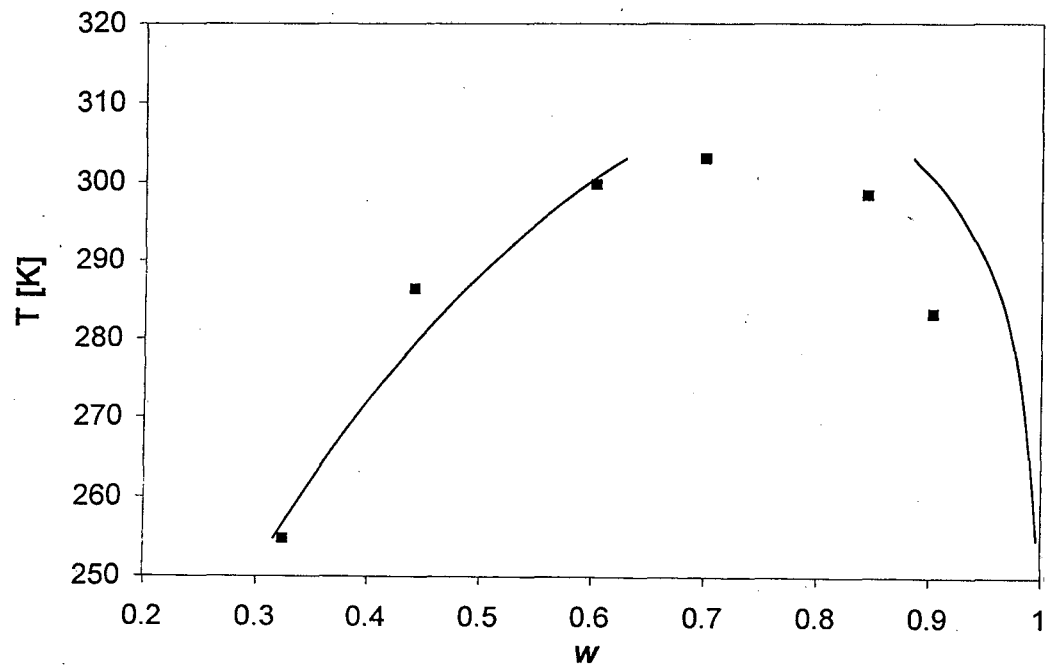

Figure 6 LLE calculation for the system R32-POE. Data from [17]. w = weight fraction of refrigerant

unstable regions of the liquid phase and provides an initial estimate for the LLE flash calculation robust enough to avoid undesirable trivial solutions.

Results

Table 1 shows pure-component parameters for refrigerants and lubricant oils as needed for VLE and LLE calculations.

Table 2 Summary of VLE calculation results. *denotes temperature where k_{ij} was fitted.

System	T (K)	k_{ij}	$\Delta P/P\%$
R134a-POE	323.15*	0.0391	0.83
	303.15	0.0391	0.95
	283.15	0.0391	0.49
	263.15	0.0391	3.76
R125-POE	293.15*	0.0202	1.41
	283.15	0.0202	1.62
	273.15	0.0202	2.85
	263.15	0.0202	4.07
R32-POE	303.15	0.0695	3.00
	293.15*	0.0695	1.61
	273.15	0.0695	1.48
	243.15	0.0695	12.40

For refrigerants, Fermeglia et al. [5] have shown that these parameters provide equilibrium and volumetric properties with a precision comparable to the experimental error. The parameter values presented in Table 1 are updated by fitting to new experimental data [18, 19]. To check the reliability of the group-contribution approach

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developed by Elvassore et al. [8] for lubricant oils, Figure 1 shows the liquid density of a POE as a function of temperature. The prediction is satisfactory. The error is larger at lower temperature; probably because the energetic parameter is taken to be independent of temperature.

In Table 2 and Figures 2, 3 and 4, VLE calculations are reported for mixtures containing a refrigerant and a POE lubricant over wide temperature and concentration ranges. A single interaction parameter k_{ij} is able to reproduce very well all data for a single system. For the system R32-POE, the thermodynamic condition for LLE is checked. First, the occurrence of two liquid phases is detected as a function of temperature, pressure and k_{ij} value, as shown in Figure 5. Then, the LLE curve is compared to experimental measurements in Figure 6. It is remarkable that, by using the value of k_{ij} regressed in VLE calculations, satisfactory agreement is obtained.

The good results obtained suggest that the physical significance of the EOS and of the parameters give a good phenomenological representation of phase behavior for the systems of interest here.

Conclusions

Calculations for prediction of phase equilibria are presented for mixtures containing hydro-fluoro-carbons and lubricant oils. Calculations are based on a modified Perturbed-Hard-Sphere-Chain equation of state.

Calculation of pure-oil parameters was performed by a predictive group-contribution method. With these values, the oil density could be predicted satisfactorily.

The ability of the proposed equation of state for calculating VLE and LLE of binary systems was shown; for all cases considered, a single value of the only binary

interaction parameter was able to reproduce with good accuracy the experimental data in a relatively wide temperature range.

To confirm these promising results, the model needs to be checked with a larger data base of phase-equilibrium data for the mixtures of interest.

Acknowledgement

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