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Modeling bubble points of mixtures of hydrofluorocarbon refrigerants and polyol ester lubricants

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Abstract

We use a Helmholtz energy mixing model to describe the bubble point pressures of mixtures of hydrofluorocarbon refrigerants and polyol ester (POE) based lubricants. This model incorporates the best available equations of state for the refrigerants, is valid over the entire range of composition, is not limited to states below the refrigerant critical temperature, and can represent volumetric properties in addition to calculating reliable phase equilibria. As part of the approach, we developed equations that can be used to apply a simplified statistical associating fluid theory (SSAFT) equation of state to POE-based lubricants. We compare the predictions of the model with selected experimental data available in the literature for bubble point pressures and saturated liquid densities of these systems. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Density; Lubricant; Polyol ester; Refrigerant; Vapor–liquid equilibria

1. Introduction

Many models [1–8], including activity coefficient, Flory–Huggins, and equation of state, have been used to describe mixtures of refrigerants and lubricants. In this work, we use a corresponding states-based equation of state approach formulated in terms of the Helmholtz energy [9], which offers the advantage that it can be used above the critical temperature of the refrigerant. Another feature is that any equation of state for the individual components of a mixture may be selected. For the hydrofluorocarbon refrigerants of this study, we selected high accuracy equations of state available in the literature [10–12]. For lubricants, there are no high accuracy equation of state available, so another approach must be taken.

2. Model

In this work, we consider only lubricants of the class known as polyol esters (POEs). These lubricants are generally not pure fluids, but are mixtures of various POEs (for example, [13]) and may also contain

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Table 2

Results of density comparisons for the SSAFT equation of state for pure POE fluids, with parameters obtained from Eqs. (1)–(3)

Compound	Reference	Number of points	T (K)	AAD (%)	Maximum deviation (%)
Pentaerythritol tetraacetate	[15]	6	363–413	0.9	1.0
Pentaerythritol tetrapropionate	[15]	11	313–413	0.4	–0.9
Pentaerythritol tetrabutylate	[15]	12	303–413	0.6	–0.9
Pentaerythritol tetrapentanoate	[15,16]	27	298–413	0.3	–0.7
Pentaerythritol tetra-2-ethylbutanoate	[17]	10	313–368	0.6	0.7
Pentaerythritol tetraheptanoate	[15]	12	303–413	0.5	–0.8
Pentaerythritol tetraoctanoate	[15]	12	303–413	0.2	–0.5
Pentaerythritol tetra-2-ethylhexanoate	[17]	15	299–368	0.4	0.6
Pentaerythritol tetranonanoate	[15,17]	24	298–413	0.3	0.7
Pentaerythritol tetradecanoate	[15]	10	323–413	0.3	–0.6
Total		139	298–413	0.4	1.0

where T_c is in K and V_c in l/mol. The uncertainty in critical temperature for the method in [18] is estimated to be about 0.9%, and about 1.8% in critical volumes, but there is no independent information about the critical parameters of these POEs on which to base a realistic estimate of uncertainty.

Given the M_w , Eqs. (1)–(5) may be used to estimate the SSAFT and critical parameters. Unfortunately, the M_w is not always available for commercial lubricants; because these are typically complex blends, there is no single unique definition of the molar mass of the system. An alternative procedure, useful when a density point for the lubricant is available, is to approximate a value for M_w , apply Eqs. (1)–(3), and then iterate until the SSAFT calculation agrees with the density point. This “effective” M_w (denoted M_w^*) is then used to compute values for the SSAFT and critical parameters.

We tested this iterative procedure on several POE lubricants that are described as mixed- or branched-acid pentaerythritol-based lubricants, and compared the predicted densities with experimental densities. Table 3 gives the equation of state parameters we obtained, and Table 4 summarizes the results for six lubricants. The lubricants are characterized by their International Organization for Standardization (ISO) viscosity grade designation. Fig. 1a and b show the experimental [19] and calculated densities for

Table 3

Parameters for the SSAFT equation of state for POE lubricants

Compound	Density (g/l)@ T (°C)	Reference	M_w^*	$v^{(0)}$ (ml/mol)	u^0/k (K)	m
ISO 32 POE #1	993@15.6	[20]	541.74	14.137	91.323	25.973
ISO 32 POE #2	1004@5	[21]	525.65	14.051	91.470	25.216
ISO 32 POE #3	1037@15.6	[22]	432.66	13.432	92.532	20.846
ISO 32 POE#4	973.5@15	[23]	617.79	14.484	90.728	29.547
ISO 68 POE #1	1050@15.6	[22]	412.79	13.264	92.820	19.912
ISO 68 POE #2	981@19.9	[2]	575.09	14.301	91.043	27.540
ISO 100 POE#1	1058@15.6	[22]	396.58	13.115	93.075	19.150
ISO 100 POE#2	970@20	[21]	619.01	14.489	90.719	29.604

Table 4
Results of density comparisons for the SSAFT equation of state for POE lubricants

Compound	Reference	Number of points	T (K)	AAD (%)	Maximum deviation (%)
ISO 32 POE 1	[19]	12	274–373	0.4	0.7
ISO 32 POE 2	[19]	11	273–373	0.4	–0.6
ISO 32 POE 3	[19]	9	275–348	0.4	0.7
ISO 68 POE 1	[19]	11	273–373	0.3	0.4
ISO 100 POE 1	[19]	11	273–373	0.2	–0.4
ISO 100 POE 2	[19]	11	275–373	0.2	–0.4
Total		65	298–413	0.3	0.7

several different POE lubricants from various manufacturers. For the same ISO grade, there is considerable variation of the fluid properties between suppliers. The method we use to find SSAFT parameters forces the density to agree at the single experimental point used as input; Fig. 1 demonstrates that the temperature dependence of the density agrees with experimental values as well. For all 65 points for the six lubricants tested, the AAD between experimental densities and the SSAFT model is 0.3%, with a maximum deviation of 0.7%. Thus, within the class of mixed POE lubricants, knowledge of a mean molar mass or a single density point should be sufficient to establish SSAFT parameters and calculate densities over a wide range of conditions.

The mixture model we use in this paper is explicit in Helmholtz energy, and details can be found in [9]. A pseudo-excess property for the dimensionless Helmholtz energy ($\alpha = A/RT$) is defined by

$$\alpha^r(\tau, \delta, \{x\}) \equiv \alpha(\tau, \delta, \{x\}) - \alpha^{\text{idmix}}(\tau, \delta, \{x\}) \quad (6)$$

where instead of evaluating the property at a given temperature, density, and composition, we evaluate it at the equivalent inverse reduced temperature $\tau = T_{\text{red}}/T$, reduced density $\delta = \rho/\rho_{\text{red}}$ and composition $\{x\}$, with T and ρ the overall temperature and density of the mixture.

The reducing values ρ_{red} and T_{red} for the mixture are defined as

$$\rho_{\text{red}} = \left[\sum_{i=1}^n \frac{x_i}{\rho_{ci}} + \sum_{i=1}^{n-1} \sum_{j=i+1}^n x_i x_j \xi_{ij} \right]^{-1} \quad T_{\text{red}} = \sum_{i=1}^n x_i T_{ci} + \sum_{i=1}^{n-1} \sum_{j=i+1}^n x_i^{\beta_{ij}} x_j^{\phi_{ij}} \zeta_{ij} \quad (7)$$

where T_{ci} and ρ_{ci} are the critical temperature and density of component i , and ζ_{ij} , ξ_{ij} , β_{ij} and ϕ_{ij} are parameters for each binary pair, and n is the number of components (here restricted to two). ϕ_{ij} and β_{ij} were set to unity, and the remaining two parameters ζ_{ij} and ξ_{ij} were determined from fitting binary data for bubble point pressures (and densities when available).

The dimensionless Helmholtz energy for an “ideal mixture” as used in this model is

$$\alpha^{\text{idmix}}(\tau, \delta, \{x\}) = \sum_{i=1}^n x_i \left[\alpha_i^{\text{ig}}(T, \rho) + \alpha_i^{\text{res}}(\tau, \delta) + \ln x_i \right]. \quad (8)$$

Fig. 1.

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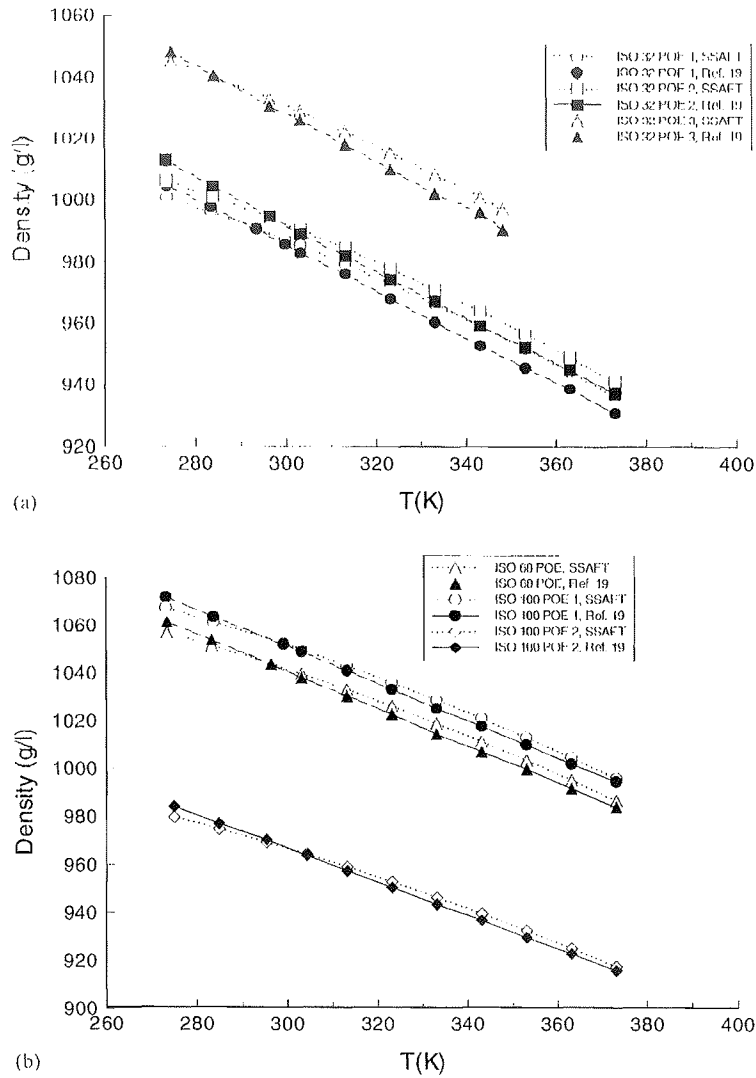


Fig. 1. Comparison of predicted and experimental densities for commercial POE lubricants: (a) ISO 32; (b) ISO 68 and ISO 100.

T and ρ are the temperature and density of the mixture; τ and δ the reduced quantities. Pure fluid (or pseudo-pure fluid) quantities α_i^{res} and α_i^{ig} are given by

$$A_i(T, \rho) = RT\alpha_i^{ig}(T, \rho) + RT\alpha_i^{res}\left(\frac{T_{ci}}{T}, \frac{\rho}{\rho_{ci}}\right) \quad (9)$$

where the superscript ig represents the value of the ideal gas contribution. The quantities in Eq. (8) are evaluated for the pure refrigerant equation of state and for the lubricant pseudo-pure fluid thermodynamic model defined by the SSAFT equation. The values of the arguments τ and δ to be used for the evaluation of α_i^{res} in Eq. (8) are determined from the reducing parameters of Eq. (7). Since the pure fluid functions are

Table 5
Coefficients and exponents of the mixture equation, Eq. (10)

k	N_k	t_k	d_k
1	$-0.223994653303 \times 10$	-0.3	2.0
2	$0.281360956592 \times 10^{-5}$	10.5	7.0
3	-0.836867755643	3.4	1.0

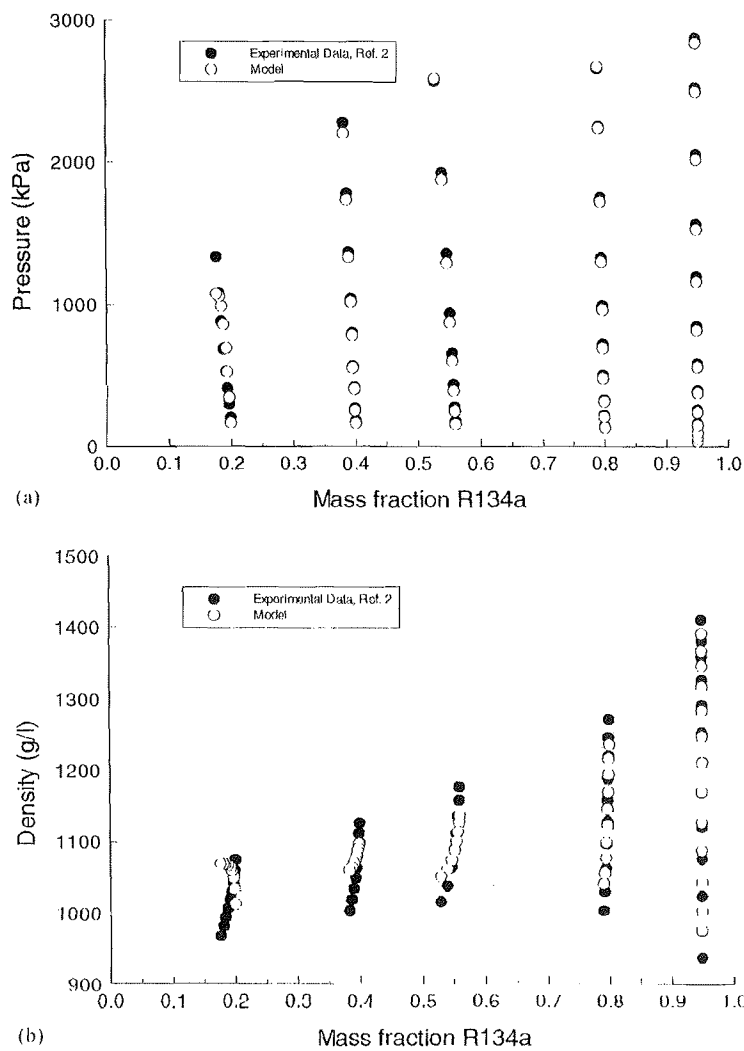


Fig. 2. Comparison of predicted and experimental: (a) bubble point pressure for R134a/commercial POE lubricant (ISO 68) mixtures; (b) liquid densities for R134a/commercial POE lubricant (ISO 68) mixtures.

Tab
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Table
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R134
R134
R125/
R236i

Total

Table 6
Binary parameters of the refrigerant/POE systems

d_k	Binary mixture	F_{12}	ζ_{12} (K)	ξ_{12} (J/mol)
2.0	R134a/(ISO32 POE#1)	1.0000	-373.9926	0.4434
7.0	R134a/(ISO68 POE#2)	1.0000	363.5927	0.3144
1.0	R134a/(ISO32 POE#1)	1.2920	560.4073	-0.1102
	R125/(ISO68 POE#2)	1.3676	460.6438	1.3568
	R236fa/(ISO32 POE#1)	0.7423	256.2246	1.6840

written in terms of reduced state points relative to the pure fluid critical temperature and density, Eq. (8) represents a mapping from a point on the mixture thermodynamic surface to a mole fraction-weighted average of "corresponding" points on each of the pure fluid surfaces. The remaining term in the mixture model of Eq. (6), the dimensionless excess contribution, is expressed as

$$\alpha^E(\tau, \delta, \{x\}) = \frac{A^E}{RT}(\tau, \delta, \{x\}) = \sum_{i=1}^{n-1} \sum_{j=i+1}^n x_i x_j F_{ij} \sum_{k=1}^K N_k \delta^{d_k} \tau^{t_k}, \quad (10)$$

where N_k , d_k and t_k are general mixture equation parameters, F_{ij} is an interaction parameter specific to each binary pair, and K is the number of terms (three in this work).

We selected a data set for R134a/POE mixtures [2,3,6,9,16,17] containing bubble point pressures and density data, and used a non-linear least squares fit of the experimental data to develop a new set of generalized coefficients for refrigerant/POE mixtures, given in Table 5. The density data used in the fit covered a composition range from 0.18–0.95 mass fraction R134a, temperatures from 227 to 357 K, and were limited to saturated liquid, bubble point densities. The bubble point pressures covered a composition range 0.02–0.95 mass fraction R134a and temperatures from 227 to 369 K. The success of this type of model depends almost entirely on the quality of the data used in the fitting process. We feel there is a need for a systematic study of this system to provide high quality data for *PVT* and *VLE* over the entire composition range. Currently, there are no data available for low concentrations of refrigerant (below 20 mass percent R134a). Thus, the current set of coefficients is preliminary, pending new and better data.

Fig. 2a and b illustrate the model predictions of bubble point pressures and saturated liquid densities as a function of composition for the R134a/POE system and the experimental data of Martz et al. [2].

Table 7
Summary of bubble point pressure results for refrigerant/POE systems

Binary mixture	Reference	Number of points	T (K)	AAD (%)
R134a/(ISO32 POE#1)	[3]	35	283–333	5.3
R134a/(ISO32 POE#1)	[6]	12	280–355	2.1
R134a/(ISO68 POE#2)	[2]	49	228–357	8.2
R134a/(ISO32 POE#4)	[23]	40	263–323	5.5
R125/(ISO68 POE#2)	[2]	61	232–333	12.9
R236fa/(ISO32 POE#1)	[3]	36	283–333	9.2
Total		233	228–357	8.4

Table 8
Summary of saturated liquid density results for refrigerant/POE systems

Binary mixture	Reference	Number of points	T (K)	AAD (%)
R134a/(ISO 32 POE#1)	[6]	12	280–355	0.7
R134a/(ISO68 POE#2)	[2]	49	228–357	2.5
R125/(ISO68 POE#2)	[2]	61	232–333	7.0
Total		122	228–357	4.6

The SSAFT parameters for the oil are in Table 3 (ISO68 POE#2). The bubble point pressure for this system is represented with an AAD of 8.2%, and the density with AAD of 2.5%. The model is valid over the entire composition range; however, Fig. 2 indicates that for this particular choice of coefficients, the deviations from experimental data at the high lubricant concentration end (approximately mass fraction R134A of 0.6 or less) are greater than at the high refrigerant concentration end. We continue to look for an alternative set of coefficients with better performance.

In addition to the mixtures described above (used to regress N_k , d_k and t_k), we examined additional refrigerant/POE lubricant systems. The binary parameters, determined from available data, are given in Table 6, and the results are summarized in Tables 7 and 8.

3. Conclusions

We present equations for the determination of parameters for the SSAFT equation of state that are applicable to POE fluids, and demonstrate that the liquid density can be calculated to within 1%. We also present preliminary coefficients for a mixture model that can simultaneously represent the saturated liquid densities and bubble point pressures for mixtures of refrigerants and POE lubricants. Results for R134a/POE, R125/POE and R236fa/POE demonstrate that the model can represent the bubble points and saturation density (bubble point pressures were represented with an AAD of 8.4% and saturated liquid densities with an AAD of 4.6%) over a wide composition range and over a range of temperatures. Further development work is needed before one should use the model for other properties such as heat of vaporization, speed of sound, heat capacity and density away from saturation.

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