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Modeling of Gas Solubility Data for HFCs–Lubricant Oil Binary Systems by Means of the SRK Equation of State

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The Soave–Redlich–Kwong (SRK) equation of state (EOS) is used to describe vapor-liquid (VLE) and vapor-liquid-liquid (VLLE) equilibria of mixtures containing environmentally friendly refrigerants (hydrofluorocarbons, HFCs) and lubricant oils (polyalkylene glycols, PAGs and polyol esters, POEs) at high pressures. For refrigerants, pure component parameters are used as they were found in refrigerant properties computer program Version 6.0 of REFPROP. For the PAG and POE oils, they are either predicted by group contribution methods or obtained from thermodynamic data. Extension to mixtures is performed by using the conventional quadratic mixing rule with only one parameter for each binary pair. The binary parameters are regressed from VLE experimental data available in the literature and subsequently used for prediction of VLLE. All results of the calculations are discussed, and the necessary parameters for prediction of thermodynamic properties of these types of mixtures for the SRK EOS are presented. The computations were performed using phase equilibria software (PE2000).

KEY WORDS: equation of state; HFCs; lubricants; refrigerants; solubility; vapor-liquid (liquid) equilibria.

1. INTRODUCTION

Modeling of the thermophysical properties and phase behavior of alternative refrigerant (HFC)–lubricant oil (PAG and POE) mixtures is highly

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important for optimal design of refrigeration and air-conditioning systems and also for selecting proper lubricants for compressors.

The SRK EOS [1] is one of the most popular models for the correlation of phase equilibria at high pressures. Even for complex systems, available literature shows that the equation is quite good. When critical parameters (T_c, P_c, ω) of the pure compounds and interaction parameters for the binary mixtures are known, the SRK EOS might successfully be used in process simulators by industry for the prediction of thermodynamic properties of multicomponent HFCs–lubricant oils systems.

Due to the great difference between the volatility of the compounds, the size of lubricant oil molecules, and the high polarity of hydrofluorocarbons, the HFCs + lubricant oil systems are a special case of complexity. So far, only a little work has been done for a description of their properties. In several cases, activity coefficient models were proposed for solubility descriptions (e.g., Flory-Huggins, Wilson, Heil, NRTL, UNIQUAC, UNIFAC) [2]. A perturbed-hard-sphere-chain equation of state [3] or cubic equations of state (Sako–Wu–Prausnitz combined with a group contribution model just for the lubricant oil [4], van der Waals, Soave–Redlich–Kwong, and Peng–Robinson with a complicated temperature dependent attractive term, $\alpha(T)$ [5]) were proposed recently. Furthermore, Huber et al. [6, 7] have applied the ESD (Elliot–Suresh–Donohue) EOS and the simplified SAFT model.

Because the operating pressure of refrigeration cycles may be as high as 4 MPa, the thermodynamic model should be preferably an equation of state (EOS) rather than an activity coefficient model. For process simulators used frequently in industrial design, both the complexity of the model and the number of the parameters are important. Even though the computation is now quite feasible, the simplicity of the model still represents time savings in design and production control. These are the main reasons why in this work, for describing vapor-liquid (liquid) equilibria (VL(L)E) of mixtures containing alternative refrigerants (HFCs) and lubricant oils (PAGs and POEs) at high pressures, the Soave–Redlich–Kwong equation of state has been selected for examination using the simple quadratic mixing rule with only one adjustable parameter for each binary pair. For refrigerants, pure component parameters are used as they were found in REFPROP [8]. For the PAG oils, they are predicted generally by group contribution methods, and for POE oils, they are obtained from thermodynamic data. For the mixtures, the binary parameter k_{ij} in the conventional quadratic mixing rule is regressed from VLE experimental data from the literature. Then, the obtained parameters are used for density and vapor-liquid-liquid equilibrium predictions at several temperatures for relevant systems where experimental data have been found in the literature for comparison.

2. THERMODYNAMIC MODEL

Despite the general weakness of cubic equations of state in representing PVT data, the phase equilibria of mixtures are usually well described. It is well known that simple cubic EOS can correlate $PTxy$ (pressure-temperature-composition) data in VLE or VLLE (vapor-liquid-liquid equilibria) with sufficient accuracy. The EOS has a theoretical basis and can be derived based on the virial expansion up to 2nd order, together with physically reasonable assumptions [9]. In the present work, for the description of pure compounds (HFCs, lubricant oils of PAG and POE types) and their mixture properties, we selected the SRK equation of state [1] to be tested. The selection was made due to the wide range of application for this EOS.

The equation is written in the following form:

$$P=\frac{RT}{v-b}-\frac{a(T)}{v(v+b)} \tag{1}$$

For pure components, the parameters are functions of critical parameters (T_c, P_c, ω) and reduced temperature ($T_r=T/T_c$):

$$a(T)=a_c\alpha(T) \tag{2}$$

with

$$a_c=0.42747\,\frac{R^2T_c^2}{P_c} \tag{3}$$

$$\alpha(T)=(1+m(1-\sqrt{T_r}\,))^2 \tag{4}$$

with

$$m=0.48+1.574\omega-0.176\omega^2 \tag{5}$$

and

$$b=0.08664\,\frac{RT_c}{P_c} \tag{6}$$

When the critical parameter values led to unsatisfactory PVT calculations, following the Peneloux idea [10], a volume shift "c" in the SRK EOS can be introduced as follows:

$$P=\frac{RT}{\tilde{v}-\tilde{b}}-\frac{a(T)}{\tilde{v}(\tilde{v}+\tilde{b})} \tag{7}$$

with

$$\tilde{v} = v + c, \qquad \tilde{b} = b + c \tag{8}$$

and

$$c = 0.40768 \frac{RT_c}{P_c} (0.00385 + 0.08775\omega) \tag{9}$$

The modified SRK EOS according to Peneloux et al. [10] has the advantage that it does not modify the VLE representation. However, it might improve the PVT description.

For mixtures, the quadratic mixing rule offers a maximum of two binary interaction parameters per binary system, but usually only one is used to adjust the parameter "a." All other mixing rules available in PE2000 [11] for EOS offer a maximum of three adjustable binary parameters, whereas two are used to adjust the parameter "a." These mixing rules reduce exactly to the quadratic mixing rule, if the third parameter is not used, i.e., set to zero. Often, the quadratic mixing rule is sufficient for correlation of phase equilibria in systems that do not contain specific interactions. The use of the second adjustable parameter l_{ij} is avoided, by setting all $l = 0$, which is the case for this work. Therefore,

$$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \qquad \text{with} \quad k_{ij} = k_{ji} \tag{10}$$

$$b_{\mathrm{ij}} = \frac{b_i + b_j}{2}(1 - l_{ij}) \qquad \text{with} \quad l_{ij} = l_{ji} = 0 \tag{11}$$

3. RESULTS AND DISCUSSION

The experimental database used for this work included density, $P\rho T$ data for pure compounds and solubility, PTx data at equilibrium for 4 binary mixtures containing HFC-134a (1,1,1,2-tetrafluoroethane) + PAGs (hexaethylene glycol, HEXG, triethylene glycol, TRIG, tetraethylene glycol, TETG, tetraethylene glycol dimethyl ether, TEGDME) [12] as well as for 20 binary systems containing HFCs (HFC-32 – difluoromethane, HFC-152a – 1,1-difluoroethane, HFC-143a – 1,1,1-trifluoroethane, HFC-134a – 1,1,1,2-tetrafluoroethane, HFC-125 – 1,1,1,2,2-pentafluoroethane) + POEs (pentaerytritol-tetrapentanoate, PEC5, -tetra-2-ethylbutanoate, PEB6, -tetra-2-ethylhexanoate, PEB8, and -tetranonanoate, PEC9) [13, 14].

For the pure HFCs, the critical parameters are already reported in the literature (REFPROP [8]). They are shown in Table I together with the

Table I. Molecular Weight M_w, Boiling Point T_b, Critical Temperature T_c, Critical Pressure P_c, and Acentric Factor ω for the Refrigerants Under Study (REFPROP [8])

Refrigerant	M_w ($g \cdot mol^{-1}$)	T_b (K)	T_c (K)	P_c (MPa)	ω
HFC-32	52.02	221.50	351.26	5.782	0.2768
HFC-152a	66.05	249.13	386.41	4.517	0.2752
HFC-143a	84.04	225.93	346.04	3.776	0.2611
HFC-134a	102.03	247.08	374.21	4.059	0.3268
HFC-125	120.02	225.01	339.33	3.629	0.3035

molecular mass and normal boiling points. Unfortunately, such values led to unsatisfactory liquid density calculations at saturation. Therefore, we introduced the volume shift "*c*" in the SRK EOS, following the Peneloux et al. idea [10]. In Table II the saturation densities of HFCs at the normal boiling and critical points using SRK [1] and SRK-VT, Peneloux-3P [10] EOS are given. As can be seen in Table II, when the volume translation is considered, the PVT properties description is improved.

For the three pure PAGs (HEXG, TRIG, TETG), we estimated the boiling points and critical parameters by the Joback method [15], unless some values were used as found in other sources. For pure TEGDME, the boiling point has been evaluated from the Antoine equation given by Esteve [16]. The value was used in the prediction of the critical temperature by means of the Joback method [15]. The critical pressure and acentric factor were adjusted by using the SRK EOS for the best description of vapor pressures and saturation densities, taking into account $P\rho T$ data for pure TEGDME of Comuñas et al. [17]. Since no saturation density

Table II. Experimental (REFPROP [8]) and Calculated Densities at Normal Boiling and Critical Points for Pure Refrigerants. (Calculations have been performed with both SRK [1] and SRK-VT (Peneloux-3P) [10] equations of state)

	Experimental			SRK			SRK-VT (Peneloux-3P)		
	ρ_l ($kg \cdot m^{-3}$)	ρ_v ($kg \cdot m^{-3}$)	ρ_c ($kg \cdot m^{-3}$)	$\Delta\rho_l$ (%)	$\Delta\rho_v$ (%)	$\Delta\rho_c$ (%)	$\Delta\rho_l$ (%)	$\Delta\rho_v$ (%)	$\Delta\rho_c$ (%)
HFC-32	1213	2.988	424.0	−22.1	−1.8	−14.9	−12.9	−1.8	−11.8
HFC-152a	1011	3.376	368.0	−16.7	−1.4	−35.9	−7.1	−1.3	−33.6
HFC-143a	1168	4.760	432.9	−15.1	−1.4	−27.9	−5.9	−1.4	−25.4
HFC-134a	1377	5.259	511.9	−12.7	−1.2	−15.4	−0.8	−1.1	−11.7
HFC-125	1515	6.796	571.3	−8.5	−0.9	−17.4	2.9	−0.9	−14.2

experimental data were available, we extrapolated liquid densities at the PT data values [16], using the relation $\rho(P, T)$ given in Ref. 17 and assuming that the vapor phase densities are negligible (≈ 0). Since the $P\rho T$ experimental data are not available at saturation conditions, we found that this is a good procedure in order to obtain correct values for critical parameters. These values should be better than those predicted by group contribution methods such as Joback [15] or Lydersen [18]. The correctness of these values will be confirmed further in description of solubility data for the mixture containing TEGDME.

Since for the pure POEs the boiling points are not known and in the classical group contribution methods both critical temperature and acentric factor are very sensitive to this property, we estimated first the critical pressure, P_c, by means of the Lydersen method [18] which gives similar results as that of Joback [15]. Then, (T_c, ω) were adjusted simultaneously for the available liquid density data, $\rho(T)$ [13, 14], assuming the vapor pressure and vapor phase density are negligible in the experimental temperature range. Then, the boiling points of POEs were calculated by the Lee–Kesler method [19]. It should be noted that the same assumption was made in the literature [13, 14] for the experimental determination of the gas solubility. This should be a reliable method of critical parameter estimation since for POEs no vapor pressure or saturation density data are available in the literature. However, the correctness of these values will be confirmed further in a description of solubility data for mixtures containing HFCs with POEs. The molecular weights, normal boiling points, and critical parameters for all lubricant oils under study are shown in Table III. Using the parameters from Table III, the SRK density values of pure POE compounds agree well with the experimental results with a deviation of less than 1% for different temperatures at atmospheric pressure. This is shown graphically in Fig. 1.

For the binary mixtures, the quadratic mixing rule was applied, and by correlation of the available gas solubility data [12–14], the k_{ij} parameter values were determined. Two cases were considered: "individual fitting" when each isothermal set of experimental data was used individually and "global fitting" when no k_{ij} temperature dependence was assumed.

The deviation calculated by PE2000 [11] is based on the mole fractions of the coexisting phases at the temperature and pressure of the data points. The optimization method used for the binary parameter determination is the simplex Nelder–Mead algorithm [20]. In this work, the absolute average deviation, AADx_1, in liquid phase mole fraction x_1 was used as an objective function in the form:

$$\mathrm{AAD}x_1 = \frac{1}{n} \sum_{i=1}^{n} |x_1^{\mathrm{exp}} - x_1^{\mathrm{calc}}| \tag{12}$$

Table III. Molar Mass M_w, Boiling Point T_b, Critical Temperature T_c, Critical Pressure P_c, and Acentric Factor ω for the Lubricant Oils Under Study

Lubricant oil	M_w ($g \cdot mol^{-1}$)	T_b (K)	T_c (K)	P_c (MPa)	ω
HEXG	118.18	470.65[a]	623.95[b]	3.991[b]	1.1477[b]
TRIG	150.17	565.88[b]	723.89[b]	3.700	1.4883[b]
TETG	194.23	634.06	793.37[b]	2.912[b]	1.5999[b]
TEGDME	222.28	547.46[c]	712.80[b]	2.486[g]	0.9173[g]
PEC5	472.62	501.32[f]	585.22[e]	0.973[d]	1.5159[e]
PEB6	528.73	514.29[f]	599.01[e]	0.867[d]	1.4257[e]
PEB8	640.94	516.77[f]	594.09[e]	0.692[d]	1.3903[e]
PEC9	697.05	537.97[f]	597.05[e]	0.620[d]	2.0702[e]

[a] Experimental value from TRC tables [25].
[b] Estimated by means of Joback group contribution method [15].
[c] Estimated from the Antoine equation given by Esteve [16].
[d] Predicted by means of Lydersen group contribution method [18].
[e] Adjusted values for SRK EOS using Wahlström and Vamling [13, 14] (ρ, T) data.
[f] Estimated from T_c, P_c, ω using the Lee–Kesler method [19].
[g] Adjusted values for SRK EOS using the (P, ρ, T) data of Comuñas et al. [17].

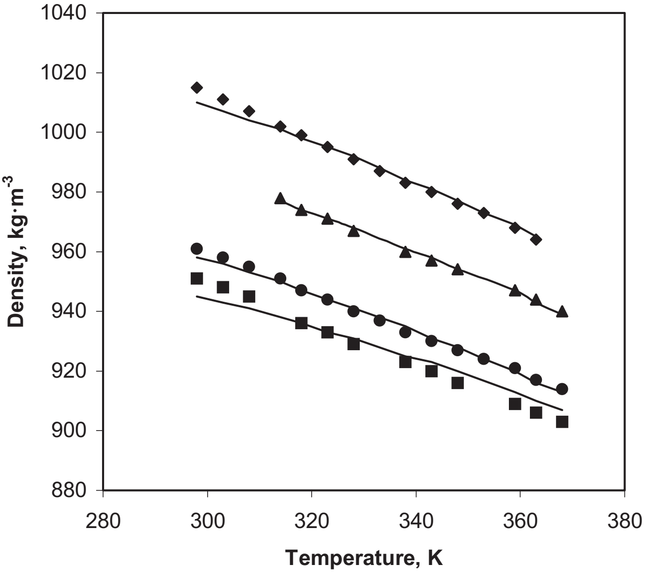

Fig. 1. Comparison between experimental (full symbols) and predicted (—) density at various temperatures for pure POEs. Experimental: (◆) PEC5 [13] and (▲) PEB6, (●) PEB 8, (■) PEC9 [14]. Prediction by means of SRK EOS using the parameters from Table III.

where n is the number of experimental points, x_1 is the mole fraction of component 1 in the liquid phase, and superscripts exp and calc denote the experimental and calculated values, respectively.

The results of the VLE data correlation for the binary mixtures of HFC-134a with each of the four PAG's under study are presented in Table IV. In this work, the vapor phase of HFC + lubricant oil (PAG or POE) mixtures was considered as pure refrigerant. Authors [12–14] who reported experimental gas solubility data made the same assumption. The k_{ij} parameters obtained for the HFC-134a + TRIG and + TETG binary

Table IV. Deviations Between Calculated and Experimental Compositions in Liquid Phase for HFC-134a (1) + PAG (2) Systems, with N_p the Number of Experimental Points

			Individual fitting		Global fitting	
PAG	N_p	T (K)	k_{12}	AADx_1	k_{12}	AADx_1
TRIG	4	283.15	−0.0874	0.028	−0.0742	0.084
	5	293.15	−0.0838	0.013		0.047
	7	303.15	−0.0793	0.008		0.020
	7	313.15	−0.0766	0.010		0.013
	9	323.15	−0.0707	0.023		0.023
	8	333.15	−0.0646	0.021		0.024
	9	353.15	−0.0567	0.012		0.026
TETG	10	283.15	−0.0809	0.038	−0.0794	0.039
	10	293.15	−0.0803	0.021		0.025
	11	303.15	−0.0773	0.028		0.028
	10	313.15	−0.0801	0.023		0.023
	12	323.15	−0.0819	0.028		0.028
	12	333.15	−0.0814	0.020		0.020
	12	353.15	−0.0742	0.009		0.014
HEXG	9	273.15	−0.0070	0.246	−0.0247	0.100
	9	283.15	−0.0224	0.105		0.085
	9	293.15	−0.0251	0.003		0.032
	5	298.15	−0.0316	0.002		0.030
	13	303.15	−0.0305	0.010		0.024
	13	313.15	−0.0297	0.013		0.024
	10	323.15	−0.0255	0.009		0.009
	8	333.15	−0.0201	0.007		0.012
	5	353.15	−0.0101	0.004		0.017
TEGDME	12	283.15	−0.0941	0.010	−0.0871	0.013
	12	293.15	−0.0888	0.007		0.009
	12	303.15	−0.0875	0.012		0.012
	12	313.15	−0.0860	0.013		0.013
	12	323.15	−0.0842	0.011		0.012
	12	333.15	−0.0857	0.009		0.010
	12	353.15	−0.0832	0.015		0.016

Table V. Experimental [21] and Calculated Densities by the SRK EOS with the Quadratic Mixing Rule for the Binary HFC134a (1) + TRIG (2) and + TETG (2) Systems at Various Temperatures and Compositions

		Exp. [19]	SRK		Deviation
T (K)	x_1	ρ_1 $(\mathrm{kg \cdot m^{-3}})$	ρ_{lc} $(\mathrm{kg \cdot m^{-3}})$	ρ_{vc} $(\mathrm{kg \cdot m^{-3}})$	$\Delta\rho_1$ (%)
		HFC-134a (1) + TRIG (2) ($k_{12} = -0.0742$)			
273.15	0	1139.0	1021.2	0	10.3
	0.089	1156.7	1037.3	0	10.3
	0.183	1176.3	1055.6	9.73	10.3
	0.236	1186.9	1066.6	8.82	10.1
	0.272	1194.6	1074.3	8.37	10.1
293.15	0	1123.3	1015.1	10.93	9.6
	0.089	1139.9	1030.5	8.86	9.6
	0.183	1157.9	1048.0	7.82	9.5
	0.236	1168.8	1058.4	7.39	9.5
	0.272	1174.5	1065.7	7.14	9.3
313.15	0	1108	1008.3	8.15	9.0
	0.089	1121.3	1023.1	7.40	8.8
	0.183	1139.2	1039.6	6.80	8.7
	0.235	1147.6	1049.2	6.52	8.6
333.15	0	1092.5	1001.0	7.00	8.38
	0.089	1104.6	1014.9	6.52	8.12
	0.183	1121.1	1030.4	6.10	8.09
	0.235	1128.4	1039.4	5.88	7.89
		HFC-134a (1) + TETG (2) ($k_{12} = -0.0794$)			
273.15	0	1139.6	956.3	0	16.1
	0.110	1160.9	973.9	0	16.1
	0.285	1197.9	1007.3	0	15.9
	0.345	1211.2	1020.6	0	15.7
293.15	0	1123.1	951.8	0	15.3
	0.109	1142.7	968.7	0	15.2
	0.285	1175.8	1000.9	0	14.9
	0.345	1187.7	1013.6	10.41	14.7
313.15	0	1107.9	947.0	0	14.5
	0.109	1124.5	963.1	0	14.4
	0.285	1154.1	993.9	9.46	13.9
	0.345	1164	1006.0	8.46	13.6
333.15	0	1091.9	941.7	0	13.8
	0.109	1107.4	957.1	11.88	13.6
	0.285	1133.3	986.3	8.01	13.0

systems were used in prediction of the vapor-liquid densities for these systems. The results were compared with experimental data taken from the literature [21], and they are presented in Table V. The deviations obtained are on average 9.2% for TRIG mixtures and 14.7% for TETG mixtures. Using the SRK-VT (Peneloux 3P) EOS, the deviation is much higher for the pure PAG component as well as for the binary mixtures with high content of lubricant. Therefore, the use of a volume translation for this type of mixture is not recommended even thought the saturation density description for pure HFCs is better in this case. Since for pure TRIG and TETG the EOS parameters have been estimated by a group contribution method without using any experimental data, we can conclude that the results of prediction are fairly good for an EOS with such a simple mixing rule. As an example of the goodness of the gas solubility correlation for

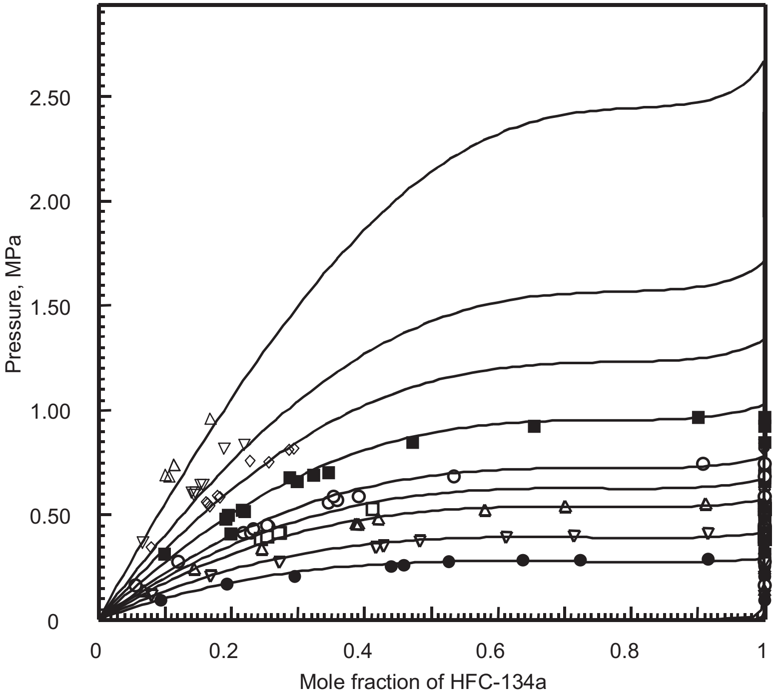

Fig. 2. Example of solubility data correlation for HFC-134a (1) + HEXG (2) binary system. Solid lines denote the calculated data by the SRK EOS with the quadratic mixing rule ($k_{12} = -0.0247$). Marked points denote experimental data [12] at 273.15 K (●), 283.15 K (▼), 293.15 K (▲), 298.15 K (□), 303.15 K (○), 313.15 K (■), 323.15 K (◇), 333.15 K (▽), and 353.15 K (△).

HFC + PAG systems, the vapor-liquid equilibria diagram for the HFC-134a + HEXG mixture is given in Fig. 2. It can be observed that the calculated values are in good agreement with experimental data, and a deviation of 0.01 to 0.10 in mole fraction for the liquid phase (Table IV) is reasonably good. In our view, these deviations are in agreement with the uncertainly of the experimental data. For the same system, within the same experimental accuracy, VLLE may be also calculated at the five lowest temperatures (273.15 to 303.15 K) by means of the same SRK EOS parameters. But in this range of temperature no LL split has been reported by the authors of the experimental data [12]. These are two contradictory calculations which cannot be reconciled at the moment with the present parameters for use in the SRK EOS in predictions for phase behavior of systems containing the both HFC-134a and HEXG components. At this

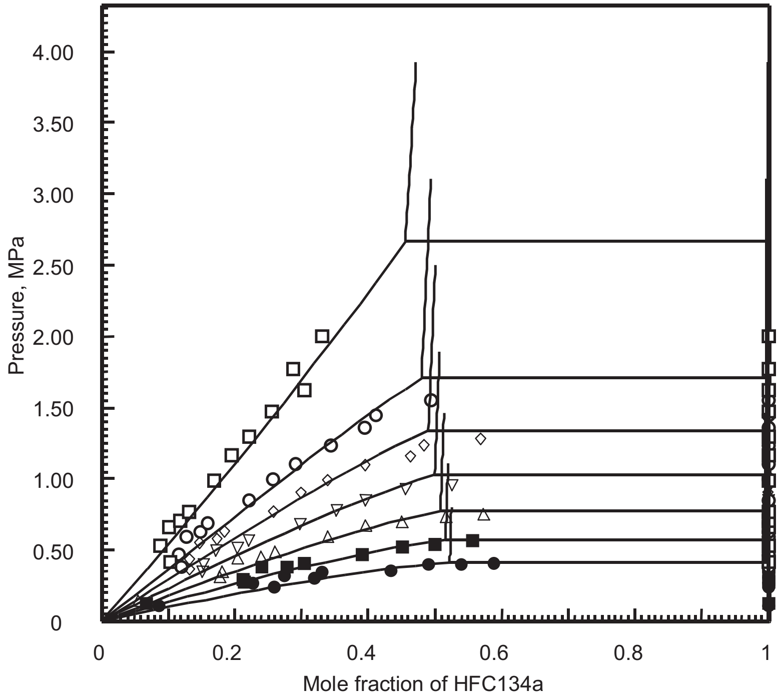

Fig. 3. Example of solubility data correlation and VLLE prediction for HFC-134a (1) + TETG (2) binary system. Solid lines denote the calculated data by the SRK EOS with the quadratic mixing rule ($k_{12} = -0.0794$). Marked points denote experimental data [12] at 283.15 K (●), 293.15 K (■), 303.15 K (△), 313.15 K (▽), 323.15 K (◇), 333.15 K (○), and 353.15 K (□). Horizontal lines represent the predicted VLLE region.

stage, they can be at most used for a correct description of the VLE experimental data of the binary system as reported in Ref. 12. Similar contradictions have been found in the literature for other type of systems (e.g., CO_2 + 1-butanol at about 313 to 314 K [22]).

For the HFC-134a + TEGDME mixtures, the results of the correlation are even better compared with TRIG, TETG, and HEXG mixtures. One explanation might be the better estimation of the pure TEGDME parameters for the EOS by the use of some experimental data [16, 17]. The VLLE region is predicted qualitatively well, too, for both HFC-134a + TRIG and + TETG systems. As an example, a diagram is presented in Fig. 3 for the HFC-134a + TETG system. For comparison, some experimental observations are given in Ref. 12.

The results of the correlation for the 20 binary systems containing HFCs (HFC-32, HFC-152a, HFC-143a, HFC-134a, HFC-125) + POEs (PEC5, PEB6, PEB8, PEC9) are presented in Tables VI to X. When the k_{ij} parameter is considered as temperature dependent (as indicated from individual isothermal fits), no significant improvement is observed in the correlation of VLE data. Using one k_{ij} parameter for each binary system, these results are good (1 to 3%) for HFC-152a and HFC-134a with all POE mixtures under study. For HFC-32, HFC-143a, and HFC-125 + POEs

Table VI. Deviations Between Calculated and Experimental Compositions in Liquid Phase for HFC-32 (1) + POE (2) Systems, with N_p the Number of Experimental Points

			Individual fit		Global fit	
POE	N_p	T (K)	k_{12}	AADx_1	k_{12}	AADx_1
PEC5	7	303.17	−0.0440	0.024	−0.0470	0.026
	7	323.28	−0.0497	0.019		0.019
	7	343.14	−0.0433	0.014		0.014
	7	363.26	−0.0508	0.074		0.075
PEB6	7	323.11	−0.0625	0.020	−0.0599	0.020
	7	343.27	−0.0553	0.014		0.014
	7	363.24	−0.0618	0.072		0.072
PEB8	7	303.14	−0.0657	0.031	−0.0589	0.031
	7	323.17	−0.0679	0.025		0.026
	7	343.18	−0.0506	0.019		0.019
	7	363.22	−0.0512	0.073		0.073
PEC9	7	303.15	−0.0271	0.041	−0.0398	0.046
	7	323.07	−0.0384	0.032		0.032
	7	343.23	−0.0483	0.024		0.024
	7	363.22	−0.0452	0.073		0.075

Table VII. Deviations Between Calculated and Experimental Compositions in Liquid Phase for HFC-152a + POE (2) Systems

			Individual fit		Global fit	
POE	N_p	T (K)	k_{12}	AADx_1	k_{12}	AADx_1
PEC5	6	303.15	−0.0208	0.014	−0.0222	0.015
	6	323.26	−0.0230	0.012		0.018
	6	343.16	−0.0251	0.010		0.010
	6	363.24	−0.0200	0.007		0.007
PEB6	6	323.13	−0.0304	0.012	−0.0338	0.012
	6	343.28	−0.0331	0.009		0.010
	6	363.28	−0.0379	0.006		0.008
PEB8	5	303.16	−0.0450	0.024	−0.0477	0.025
	5	323.14	−0.0472	0.022		0.022
	5	343.24	−0.0489	0.018		0.018
	5	363.26	−0.0498	0.015		0.016
PEC9	7	303.15	−0.0152	0.031	−0.0262	0.034
	7	323.08	−0.0221	0.026		0.027
	7	343.24	−0.0294	0.021		0.021
	6	363.21	−0.0380	0.014		0.015

Table VIII. Deviations Between Calculated and Experimental Compositions in Liquid Phase for HFC-143a (1) + POE (2) Systems

			Individual fit		Global fit	
POE	N_p	T (K)	k_{12}	AADx_1	k_{12}	AADx_1
PEC5	7	303.15	0.0535	0.018	0.0514	0.020
	7	323.23	0.0533	0.013		0.014
	7	343.15	0.0534	0.008		0.009
	7	363.22	0.0452	0.014		0.072
PEB6	7	323.11	0.0506	0.014	0.0599	0.018
	7	343.27	0.0493	0.008		0.012
	7	363.24	0.0800	0.083		0.069
PEB8	6	303.13	0.0584	0.021	0.0594	0.022
	6	323.16	0.0588	0.017		0.018
	6	343.19	0.0584	0.011		0.011
	6	363.23	0.0621	0.079		0.080
PEC9	7	303.07	0.0730	0.031	0.0676	0.036
	8	323.07	0.0695	0.020		0.020
	7	343.21	0.0669	0.014		0.014
	7	363.27	0.0609	0.072		0.072

Table IX. Deviations Between Calculated and Experimental Compositions in Liquid Phase for HFC-134a (1) + POE (2) Systems

			Individual fit		Global fit	
POE	N_p	T (K)	k_{12}	AADx_1	k_{12}	AADx_1
PEC5	7	303.15	−0.0033	0.017	0.0048	0.022
	7	323.24	−0.0007	0.013		0.015
	7	343.17	0.0021	0.010		0.010
	7	363.24	0.0067	0.007		0.008
PEB6	7	323.11	−0.0113	0.015	−0.0091	0.017
	7	343.27	−0.0096	0.015		0.016
	7	363.24	−0.0065	0.009		0.009
PEB8	5	303.15	−0.0076	0.025	0.0007	0.030
	6	323.22	−0.0035	0.020		0.022
	6	343.16	0.0024	0.015		0.015
	6	363.23	0.0116	0.010		0.012
PEC9	7	302.96	0.0266	0.033	0.0248	0.034
	7	323.09	0.0251	0.025		0.026
	7	343.24	0.0237	0.018		0.018
	7	363.27	0.0239	0.012		0.012

Table X. Deviations Between Calculated and Experimental Compositions in Liquid Phase for HFC-125 (1) + POE (2) Systems

			Individual fit		Global fit	
POE	N_p	T (K)	k_{12}	AADx_1	k_{12}	AADx_1
PEC5	8	303.15	−0.0137	0.008	0.0081	0.030
	8	323.27	−0.0048	0.006		0.014
	7	343.16	0.0084	0.069		0.069
	7	363.23	0.0182	0.004		0.076
PEB6	7	323.09	−0.0209	0.009	−0.0063	0.016
	7	343.23	−0.0101	0.067		0.067
	7	363.24	0.0121	0.067		0.073
PEB8	6	303.14	−0.0014	0.023	0.0150	0.033
	6	323.16	0.0122	0.019		0.021
	6	343.19	0.0030	0.018		0.084
	6	363.22	0.0462	0.082		0.087
PEC9	7	302.96	0.0396	0.036	0.0452	0.039
	7	323.08	0.0433	0.033		0.033
	7	343.23	0.0449	0.078		0.078
	7	363.27	0.0528	0.074		0.075

systems, the results are similarly good (1 to 3%) for low temperatures and a little bit worse for high temperature (6 to 8%). We consider these deviations as being in agreement with the estimated uncertainty of the experimental data (2% for lower pressures and 3% for higher pressures [13, 14]). For a qualitative representation of the results shown in Tables VI to X, in Figs. 4 and 5 the experimental [13, 14] and calculated VLE diagrams by means of the SRK model for the HFC-152a + PEC5 and HFC-125 + PEC9 systems are given as examples of somewhat extreme cases.

In order to test the ability of the SRK model with the quadratic mixing rule in describing the vapor-liquid-liquid equilibria (VLLE) behavior, the phase diagram have been predicted for the HFC-32 + PEB8 system using the k_{ij} parameter obtained from the VLE data correlation ($k_{ij} = -0.0589$). The VLLE behavior is expected for this system in the low temperature range. Similar behavior was observed experimentally for the

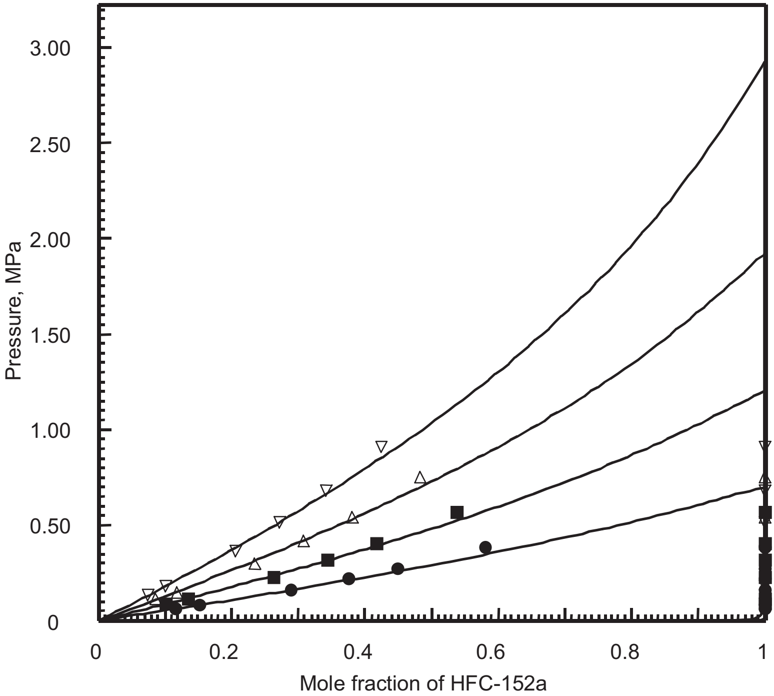

Fig. 4. Example of VLE data [13] correlation for binary HFC-152a (1) + PEC5 (2) system. Solid lines denote the calculated data by means of the SRK EOS with the quadratic mixing rule ($k_{12} = -0.0222$). Marked points denote the isothermal data [13] at 303.15 K (●), 323.15 K (■), 343.16 K (△), and 363.24 K (▽).

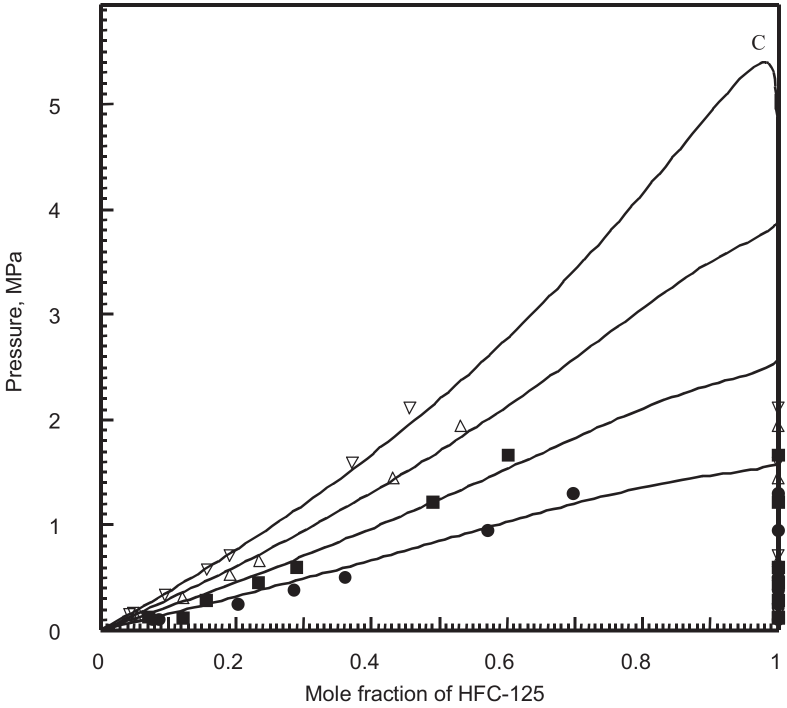

Fig. 5. Example of VLE data [14] correlation for the binary HFC-125 (1) + PEC9 (2) system. Solid lines denote the calculated data by means of the SRK EOS with the quadratic mixing rule ($k_{12} = 0.0452$). Marked points denote the isothermal data [14] at 302.96 K (●), 323.08 K (■), 343.23 K (△), and 363.27 K (▽). C, vapor-liquid critical point.

HFC-32 + synthetic POE oil ($M_w = 610$) [23]. The results of the three-phase region (VLLE) predictions are shown qualitatively in Fig. 6 for temperatures from 200 to 236 K. As can be seen, the VLLE appears at about 0.98 mole fraction (0.8 mass fraction) of HFC-32 in the liquid phase of the mixture at a temperature of 235.92 K and a pressure of 0.195 MPa. The liquid-liquid range became larger when both temperature and pressure are decreasing. In Fig. 6, the marked points have been just arbitrarily used as an initial estimate of the VLLE region. They can be selected from any part of the phase diagram (even from the VLE region). Unfortunately, no VLLE experimental data have been found in the literature for either the HFC-32 + PEB8 ($M_w = 640.96$) mixture or for any other of the investigated POE systems. Similarly, no multicomponent vapor-liquid (or liquid-liquid) equilibria data has been found for the systems investigated in this

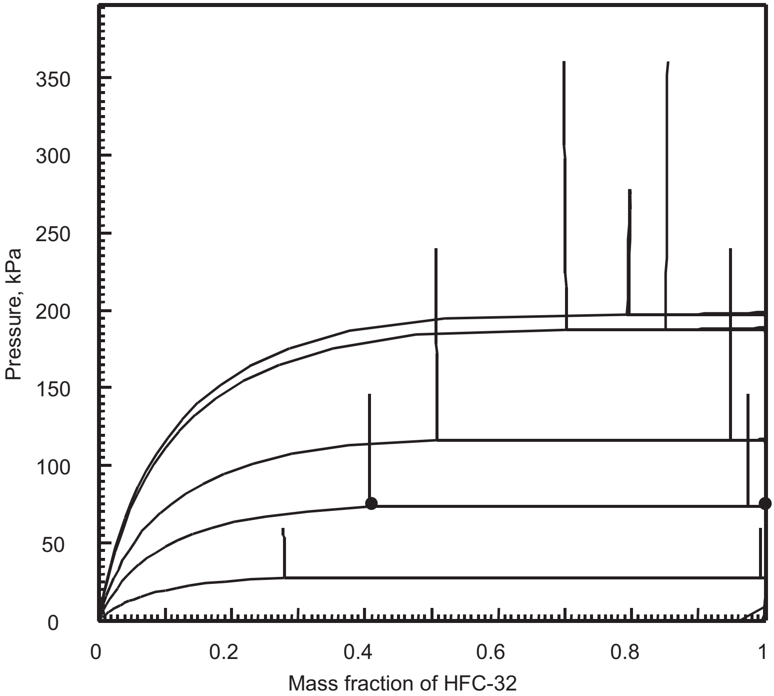

Fig. 6. Predicted VLLE behavior (at less than 236 K, 0.2 MPa) by means of the SRK EOS with the quadratic mixing rule ($k_{12} = -0.0589$) for the binary HFC-32 (1) + PEB8 (2) system. Marked points have been arbitrarily used as initial estimates of VLLE region as a requirement of the PE2000 [11] software. Horizontal lines represent the predicted VLLE region.

work containing lubricant oils in the pure state. Except for very few cases [24], synthetic oils with poorly defined chemical structure are used in measurement studies available in the literature. If the chemical structure of the investigated oils would be given with a minimum of experimental information (e.g., density-temperature data for the pure lubricant), the critical parameters could be evaluated as was done in this work. Nevertheless, with this study it was shown that the SRK model with the classical quadratic mixing rule is appropriate even for a description of the phase behavior of complex systems such as HFCs + lubricant oils (PAGs and POEs) within the uncertainty of the experimental data. Furthermore, it was shown that PE2000 software [11] is a powerful tool in estimating both pure compound and mixture thermodynamic behavior using a limited experimental database.

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