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Solubility of Refrigerants in Various Lubricants[1]

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Solubility data of refrigerant/lubricant mixtures have been modeled with cubic equations of state (EOS): van der Waals (vdW), Soave-modified Redlich–Kwong (SRK), or Peng–Robinson (PR) types. The temperature dependence on the "*a*" parameter in the EOS is modeled with a common empirical function for pure refrigerants, including oils. For lubricants, a hypothetical oil (UniOIL) has been developed with universal oil EOS constants, and it is valid for any kind of lubricant oil. Only an average molecular weight is required for any type of oil. The mixing rules for the *a* and *b* parameters of EOS are more general than the ordinary van der Waals–Berthelot formula, and a justification of such mixing rules is discussed. The refrigerants studied are R-32, R-125, R-134a R-143a, R-152a, R-12, R-22, R-123 and R-13B1. The lubricants are naphthenic mineral (MO), alkylbenzene (AB/HAB), and polyol ester (POE) oils, as well as model compounds with pure component oils (hydrocarbons and POE). They are all analyzed with the UniOIL model. Good quality experimental solubility (*PTx*) data were selected from the literature and well correlated within their experimental uncertainties. All the cubic EOS (vdW, SRK, and PR) having the same type of mixing forms for the *a* and *b* parameters showed excellent fits to the experimental *PTx* data with essentially the same degree of accuracy. The results in this report are shown with the SRK type EOS.

KEY WORDS: cubic equations of state; lubricants; mixing rule; oils, phase equilibria; refrigerants; solubility.

1. INTRODUCTION

The understanding and correlation of thermophysical properties of refrigerant and lubricant oil mixtures is highly important for the design of refrigeration and air-conditioning systems and also the selection of proper

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lubricants for compressors. The solubility of refrigerant in oil significantly changes the oil viscosity and the lubricant characteristics. In addition, mutual solubility is often required for proper oil circulation in the system. Under the coexistence of oil, a blended refrigerant can alter the circulating compositions in the system due to the different solubility of each constituent compound. In order to predict the phase behavior at various operating conditions, a proper thermodynamic model must be developed for refrigerant-oil mixtures. In our earlier studies [1, 2], we have demonstrated that a simple cubic EOS with a special mixing rule is able to reproduce the experimental solubility data with sufficient accuracy and that liquid–liquid (LLE) miscibility gaps and vapor phase compositions can be correctly predicted. At the same time, we have discussed the solubility correlation with an activity (solution) model. Although such a solution model works equally well, the use is limited to below the refrigerant critical temperature.

Perhaps, one of the most difficult problems in refrigerant-oil mixtures is to obtain high quality VLE (PTx) experimental data, which are critically important for the development of accurate thermodynamic models. Fortunately, for the past several years, such reliable VLE data have become available in the literature. Among them, those by Wahlstrom and Vamling [3–5], Takaishi and Oguchi [6–11], and Burton et al. [12] are exceptionally good quality data. The majority of the present analyses are based on their experimental data.

In this report, we first describe the thermodynamic model based on cubic equations of state with non-conventional mixing rules. A justification of the use of such mixing rules is given. Next, the solubility data of various refrigerants and different types of lubricant oils are analyzed with the present model. Then, a concept of a hypothetical universal oil (UniOIL) is developed with universal oil constants for the oil EOS. Finally, a few selected examples of the model prediction are discussed with the experimental partial miscibility of binary mixtures and VLE properties of multicomponent mixtures. Then, concluding remarks follow.

2. THERMODYNAMIC MODEL

It is well known that a simple cubic type EOS can correlate $PTxy$ (pressure–temperature-compositions) data in VLE (vapor–liquid equilibria) or VLLE (vapor–liquid–liquid equilibria) with sufficient accuracy, although the volumetric correlation, particularly for the liquid phase, is poor. Furthermore, a general cubic type of EOS has a theoretical basis and can be derived based on the virial expansion up to the second order, together with physically reasonable assumptions [13]. Theoretically, there is no particular preference among all cubic EOS.

In this study, we have examined three typical cubic EOS. They are written in the following general form:

$$P = \frac{RT}{V-b} \, \frac{a(T)}{V^2 + mbV + nb^2} \tag{1}$$

$$a(T) = a_c \frac{R^2 T_c^2}{P_c} \alpha(T) \tag{2}$$

$$b = b_c \frac{RT_c}{P_c} \tag{3}$$

$m = 0$ and $n = 0$, $a_c = 0.421875$ and $b_c = 0.12500$: vdW type EOS

$m = 1$ and $n = 0$, $a_c = 0.427480$ and $b_c = 0.08664$: SRK type EOS

$m = 2$ and $n = -1$, $a_c = 0.457240$ and $b_c = 0.07780$: PR type EOS

The temperature-dependent part of the a parameter in all the EOS for pure compounds is uniformly modeled by the following empirical form [1]:

$$\alpha(T) = \sum_{k=0}^{\leqslant 3} \beta_k \left(\frac{T_c}{T} - \frac{T}{T_c} \right)^k \tag{4}$$

The coefficients, β_k, are determined so as to reproduce the vapor pressure of each pure refrigerant.

For lubricant oils, however, usually no vapor pressure data are available, and furthermore, no data for the critical parameters (T_c and P_c) exist except for some pure model compounds. In addition, actual lubricant oils are mixtures of various compounds with very high boiling points. Here, we treat such oils as a hypothetical pure compound with a proper average molecular weight and proper critical parameters. The critical parameters of oil can be estimated in various ways. For example, a simple method to estimate critical constants has been proposed by Vetere [14], based on liquid densities alone. As will be discussed later, rough estimates for the oil critical parameters are sufficient for the present purpose. On the other hand, the temperature-dependent part of the a parameter of oils (Eq. (4)) is significantly important when we try to correlate the solubility (PTx) data of refrigerant/oil mixtures, although the vapor pressure of oil is essentially zero at the temperature of interest. Therefore, the coefficients in Eq. (4) will be treated as adjustable fitting parameters. In our previous report [1], it has been found that Soave's empirical form [15] for $\alpha(T)$, in terms of the acentric factor ω of oils, works equally well, as long as we treat ω as an adjustable fitting parameter.

After analyzing various solubility data of refrigerant/oil mixtures, we have found that only one adjustable parameter, β_1, in Eq. (4) is sufficient. Then, Eq. (4) for oil can be written with just the first two terms:

$$\alpha(T) = 1 + \beta_1 \left(\frac{T_c}{T} - \frac{T}{T_c} \right) \tag{5}$$

where T_c is an estimated critical temperature of oil. The adjustable parameter, β_1, has been found to be typically 0.7 to 1.3 (or, 1 ± 0.3), which happens to be close to the acentric factor ω of high molecular weight hydrocarbons. The oil EOS constants, T_c, P_c and β_1, will be discussed further in later sections in terms of a concept of universal oil.

Then, the a and b parameters for N-component mixtures are modeled in terms of binary interaction parameters, which may be regarded as modified van der Waals–Berthelot mixing formula.

$$a(T) = \sum_{i,j=1}^{N} \sqrt{a_i a_j}\, f(T)(1 - k_{ij})\, x_i x_j, \qquad a_i = a_c \frac{R^2 T_{ci}^2}{P_{ci}} \alpha_i(T) \tag{6}$$

$$f(T) = 1 + t_{ij}/T, \qquad \text{where} \quad t_{ij} = t_{ji}, \quad \text{and} \quad t_{ii} = 0 \tag{7}$$

$$k_{ij} = \frac{l_{ij} l_{ji} (x_i + x_j)}{l_{ji} x_i + l_{ij} x_j}, \qquad \text{where} \quad k_{ii} = 0 \tag{8}$$

$$b = \frac{1}{2} \sum_{i,j=1}^{N} (b_i + b_j)(1 - m_{ij})(1 - k_{ij})\, x_i x_j, \qquad b_i = b_c \frac{R T_{ci}}{P_{ci}} \tag{9}$$

This b parameter can also be modeled with a little simpler form without the k_{ij} term.

$$b = \frac{1}{2} \sum_{i,j=1}^{N} (b_i + b_j)(1 - m_{ij})\, x_i x_j, \qquad b_i = b_c \frac{R T_{ci}}{P_{ci}} \tag{10}$$

where $m_{ij} = m_{ji}$, and $m_{ii} = 0$.

T_{ci}: critical temperature of ith species

P_{ci}: critical pressure of ith species

x_i: mole fraction of ith species

In the above model, there are four binary interaction parameters: l_{ij}, l_{ji}, m_{ij}, t_{ij}. It should be noted that when $l_{ij} = l_{ji}$ in Eq. (8) and $t_{ij} = 0$ in

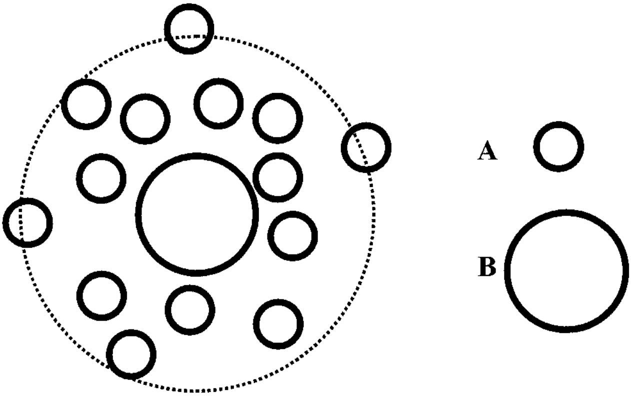
Eq. (7), Eq. (6) becomes the ordinary quadratic-mixing rule for the a parameter [van der Waals–Berthelot rule]. Then, the b parameter is also reduced to the ordinary form, $b=\sum_{i=1}^{N} b_i x_i$, with identifying m_{ij} as $m_{ij}=(k_{ij}-1)/k_{ij}$ for Eq. (9), or $m_{ij}=0$ for Eq. (10). So, this mixing rule ranges from the usual van der Waals–Berthelot rule to a more flexible general case. There are, however, some objections among researchers to use such a generalized mixing rule, k_{ij} having the mole fraction dependence [16]. The main objection is that the second virial coefficient, which is equal to $b-(a/RT)$ for all of the present EOS, becomes non-quadratic in terms of the mole fraction, x, and therefore is "theoretically" incorrect. Thus, it might be worthwhile here to discuss this matter and justify the generalized mixing rule.

The origin of the quadratic dependence on the mole fraction is based on theoretical work by Mayer [17]. The derivation is highly complicated, but the basic important assumption was to use a concept of "random mixing" of molecular species with (nearly) "equal sizes." The quadratic and symmetric $x_i x_j$ term of the second viral coefficient is a statistical weight factor for the number of possible binary interactions between i and j molecular species. Suppose two species have very different molecular sizes: small size A and large size B species, as illustrated in Fig. 1. The number of neighboring AB interactions becomes asymmetric, depending upon whether an A is surrounded by B species or a B is surrounded by A, although the interaction potential between A and B is the same and symmetric. Here we are not talking about the non-random distribution due to the existence of the intermolecular potential. This is due to the geometrical constraint in the space, and A and B species cannot be randomly distributed in the same fashion anymore. Then, the statistical weight cannot be "theoretically" a simply quadratic, $x_A x_B$, form.

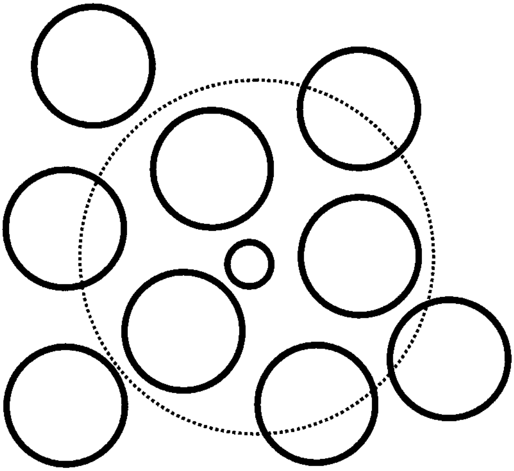
Although the present mixing rule is purely empirical, some justifications can be given. In order to apply the random mixing concept, the molecular size must be re-scaled so that the number of neighboring interactions becomes geometrically symmetric. This is equivalent to a re-normalization of the mole fraction: stretching and/or shrinking of mole fraction coordinates. To illustrate, let's take the above example of A and B binary mixtures and introduce re-normalized mole fractions, X_A and X_B, defined as:

$$X_A=\frac{l_A x_A}{l_A x_A+l_B x_B} \tag{11}$$

$$X_B=\frac{l_B x_B}{l_A x_A+l_B x_B} \tag{12}$$



(a) **B** in **A** rich mixtures



(a) **A** in **B** rich mixtures

Fig. 1. Schematic view of A/B binary mixtures with a large difference in molecular sizes, showing the asymmetry of the number of neighboring interacting molecules.

where l_A and l_B are size-scaling parameters, and $X_A + X_B = x_A + x_B$. With the new mole fraction coordinate, the ordinary mixing rule is expressed as:

$$a = \sum_{i,\, j = A,\, B} \sqrt{a_i a_j}\,(1 - K_{ij})\, X_i X_j \tag{13}$$

$$b = \tfrac{1}{2} \sum_{i,\, j = A,\, B} (b_i + b_j)(1 - M_{ij})\, X_i X_j \tag{14}$$

where K_{ij} and M_{ij} are small interaction parameters, being independent of the mole fraction. Then, it satisfies the quadratic and symmetric terms of the mole fraction in the second virial coefficient, as it should. However, in terms of the original (non-scaled) mole fraction, it is not quadratic, as illustrated above.

In order to apply this idea for general multicomponent mixtures, Eqs. (11) and (12) must be modified in order to conserve the mole number balance:

$$X_i = \frac{l_i x_i (x_i + x_j)}{l_i x_i + l_j x_j} \tag{15}$$

$$X_j = \frac{l_j x_j (x_i + x_j)}{l_i x_i + l_j x_j} \tag{16}$$

With these new mole fractions, and after rearranging, Eq. (13) is expressed in terms of the original mole fraction:

$$a = \sum_{i,\, j = 1}^{N} \sqrt{a_i a_j} \left(\frac{x_i + x_j}{\sqrt{l_i/l_j (1 - K_{ij})}\, x_i + \sqrt{l_j/l_i (1 - K_{ij})}\, x_j} \right)^2 x_i x_j \tag{17}$$

A similar expression applies for Eq. (14). Now, let's consider the first order correction of the size difference, where $\sqrt{l_i/l_j}$ is not too far from one, and $1 - K_{ij}$ is also close to one. Then, $\sqrt{l_i/l_j (1 - K_{ij})}$ and $\sqrt{l_j/l_i (1 - K_{ij})}$ can be written as $1 + \delta_{ij}$ and $1 + \delta_{ji}$, respectively, with small δ parameters, and the parenthesis in Eq. (17) can be expanded. By taking up to the first-order term, Eq. (17) becomes:

$$a = \sum_{i,\, j = 1}^{N} \sqrt{a_i a_j} \left(1 - \frac{2\delta_{ij} x_i + 2\delta_{ji} x_j}{x_i + x_j} \right) x_i x_j \tag{18}$$

This is the Margules type of mixing rule, which is often used in the literature. Also, another first-order approximation of Eq. (17) can be obtained within the same assumption used above. That is, the parenthesis part in Eq. (17) is close to unity. Then, by introducing a small parameter, δ, it can be expressed as:

$$\left(1-\frac{\delta(x_i+x_j)}{\sqrt{l_i/l_j(1-K_{ij})}\,x_i+\sqrt{l_j/l_i(1-K_{ij})}\,x_j}\right)^2$$

By expanding this and taking up to the first-order term, Eq. (17) becomes:

$$a=\sum_{i,\,j=1}^{N}\sqrt{a_i a_j}\left(1-\frac{l_{ij}l_{ji}(x_i+x_j)}{l_{ji}x_i+l_{ij}x_j}\right)x_i x_j \tag{19}$$

where $l_{ij}=2\delta/\sqrt{l_i/l_j(1-K_{ij})}$ and $l_{ji}=2\delta/\sqrt{l_j/l_i(1-K_{ij})}$. Equation (19) is the van Laar type of mixing rule and also the present mixing rule, as appeared in Eqs. (6), (8), and (9). Both the Margules and van Laar type of mixing rules look similar, but in the practical applications, there are subtle differences. Stryjek and Vera [18] have examined various type of mixing rules with the PR type EOS and applied many binary systems including mixtures with polar/nonpolar and size differences. They have found the van Laar type of mixing rule gives the best correlation for the *PTxy* (VLE) data. We have also reached the same conclusion by analyzing various binary VLE data using the SRK, PR, or vdW type EOS.

3. ANALYSES AND RESULTS

In this paper, we present results based on the SRK type of EOS only, since all other cubic EOS (vdW and PR type) have shown practically the same accuracy in fitting the experimental data as the SRK EOS. The EOS constants of pure compounds examined are given in Table I, including lubricant oils. The coefficients, β_i in Eq. (4) were determined so as to reproduce the vapor pressure of pure refrigerants in the literature [19, 20]. The critical parameters of oils were estimated with Vetere's method [14], except for the model compounds of pure hydrocarbons. We have also examined the sensitivity of estimated oil critical parameters in the analysis, and found that very rough estimates are sufficient. For example, the critical parameters of PEB8 oil [3] were replaced by those in POE32 oil [7] or in HC20 (n-eicosane) (see Table I). Re-analyses of the binary mixtures of PEB8 resulted in essentially the same degree of accuracy in the solubility correlation. This is because the oil parameter, β_1, takes care of such rough estimates of oil critical parameters by readjusting its value in the fitting.

Table I. Refrigerant and Oil Constants Used in the Present EOS Model[a]

Compound	Molar Mass	T_c (K)	P_c (kPa)	β_0	β_1	β_2	β_3
R-32	52.02	351.26	5782	1.0019	0.48333	−0.07538	0.00673
R-125	120.22	339.19	3637	1.0001	0.47736	−0.01977	−0.0177
R-134a	101.03	374.21	4059	1.0025	0.50532	−0.04983	0
R-143a	84.04	346.20	3759	1.0006	0.45874	−0.04846	−0.0143
R-152a	66.05	386.44	4520	1.0012	0.48495	−0.08508	0.0146
R-12	120.91	385.15	4116	1.0002	0.39651	−0.06152	0.0116
R-13B1	148.91	340.20	3960	1.0005	0.40042	−0.08728	0.0292
R-22	86.47	369.17	4978	1.0011	0.43295	−0.06214	0.0150
R-123	152.93	456.83	3668	1.0016	0.47925	−0.07111	0.0158
POE32	610	864	874	1.0	0.913	0	0
POE68	700	746	682	1.0	1.249	0	0
PEB8	640	793	772	1.0	0.941	0	0
HC13	184.37	676.0	1720	1.0	0.790	0	0
HC16	226.45	717.0	1419	1.0	0.731	0	0
HC20	282.56	767.0	1115	1.0	1.076	0	0
MO56	360	832	1104	1.0	1.020	0	0
AB32	390	857	1015	1.0	0.892	0	0
HAB15	311	755	1145	1.0	0.950	0	0
HAB32	328	758	1073	1.0	1.115	0	0
UniOIL	MW	800	950	1.0	1.0	0	0

[a] SRK type EOS: see Eq. (4) for β_i. POE32: Polyol ester oil (ISO 32) [7], POE68: Polyol ester oil (ISO 68) [12, 22], PEB8: Pentaerythriol tetra-2-ethylhaxanoate [3], HC13: n-Tridecane [4], HC16: n-Hexadecane [4], HC20: n-Eicosane [4], MO56: Naphthenic mineral oil [9], AB32: Alkyl benzene oil (ISO 32) [6, 10], HAB15: Hard alkyl benzene oil (ISO 15) [21], HAB32: Hard alkyl benzene oil (ISO 32) [21]. UniOIL: a hypothetical oil with the universal oil constants for any kind of oils except for molar mass (MW); see text.

The coefficient, β_1 of oils deserves a special comment, since usually it cannot be determined from the vapor pressure data. But it can be determined fairly well, together with the binary interaction parameters, from the analysis of the binary *PTx* solubility data. For example, in the case of POE32 oil [7, 8, 11], it is found to be: $\beta_1 = 0.924 \pm 0.02$ from R-32/POE32 data, $\beta_1 = 1.003 \pm 0.01$ from R-125/POE32, and $\beta_1 = 0.811 \pm 0.03$ from R-134a/POE32. These different values mean that it acts partially as a binary interaction parameter. However, the different values for the same oil will be a problem and inconsistent, when we try to calculate the solubility of multicomponent mixtures containing the same oil. So, in this example, we take a simple average value of 0.913 as the oil constant, β_1 for POE32. Then, the solubility data were re-analyzed while using a fixed value of 0.913. Usually such re-analyses result in practically the same accuracy in fitting. If this is not the case, the additional interaction parameter, t_{ij}, in Eq. (8) will be used. The oil constants, β_1 in Table I were determined in the same way as this example.

First, we have analyzed the solubility data of various refrigerant/oil mixtures with these β_1 and estimated critical parameters for individual oils, as shown in Table I. However, after careful examination of the analyses, we have discovered that solubility of any kind of oil can be modeled with the same universal constants for the oil EOS. We call this hypothetical oil "UniOIL" that has the EOS constants of $T_c = 800$ K, $P_c = 950$ KPa, and $\beta_1 = 1.0$; see the last row in Table I. Then, concerning the oil parameters, only an average molecular weight is required for any kind of oil.

Selected experimental solubility (PTx) data from the literature [3–12, 21, 22] were analyzed using a nonlinear least-squares (NLLS) method with the object function of relative pressure differences. The determined binary interaction parameters are shown in Table II, together with the average absolute deviation (AAD)% in pressure; here Eq. (9) was used for the b parameter mixing rule. All oils including model compound oils are treated as the UniOIL. The number of required interaction parameters was two to four, depending upon the binary system. High quality data were fitted within 1 to 2% in AAD.

It is worthwhile to mention about the general procedure of fitting data, since the analysis is not always straightforward. Often, there exist several local minima in the NLLS (multiple solutions), and initial guessed values in the fitting parameters are quite important in such cases. A step-by-step increase in the number of fitting parameters is an important key of the analysis, and an over-fitting of the data beyond the statistical significance may cause non-physical behaviors for EOS.

Due to the limitation of the space, only a couple of fitting examples, with AAD% of 1.5 and 0.7, is shown in Fig. 2, but they will provide some ideas for other systems in Table II, given by the overall AAD%.

4. DISCUSSION

The excellent fitting of experimental VLE (PTx) data with EOS is one important sign of the model validity, but the proper behavior of EOS predictions is another. If an EOS correlation is correct and useful, then it must provide reliable predictions of various phase behaviors, such as partial miscibility (VLLE) gaps, properties of multicomponent mixtures, and $PTxy$ properties for wide ranges of temperature, pressure, and composition.

Examples of partial miscibility (VLLE) predictions are shown in Fig. 3, in which some available experimental data are compared. By considering

Table II. Analyses of Refrigerant/Oil Mixtures and Experimental Data Information[a]

Binary Systems (1)/(2)	l_{12}	l_{21}	$m_{12,21}$	$t_{12,21}$ (K)	Np	Ref.	T range (°C)	x_1 range (mol%)	AAD (%)
R-32/POE32	0.0646	0.0266	0	0	23	8	−30 to 30	75–100	0.41
R-125/POE32	0.0179	0.0029	0.0296	0	60	11	−10 to 40	55–100	0.71
R-134a/POE32	0.0561	0.0254	−0.0106	0	40	7	−10 to 50	45–100	0.74
R-32/POE68	0.0871	0.0138	0.0128	0	30	12	9 to 52	70–100	0.82
R-125/POE68	0.0245	0.0047	0.0246	0	57*	22	−40 to 60	45–100	2.61
R-134a/POE68	0.0678	0.0351	−0.0109	0	46	22	−17 to 81	60–100	1.82
R-32/PEB8	20.058	0.0698	0.0121	−78.5	28	3	30 to 90	8–64	1.30
R-125/PEB8	0.0005	l_{12}	0.0119	0	24	3	30 to 90	7–60	1.89
R-134a/PEB8	0.0504	0.0359	−0.0193	0	23	3	30 to 90	6–65	1.03
R-143a/PEB8	−0.0845	−0.0934	0.0959	−41.9	24	3	30 to 90	7–65	1.19
R-152a/PEB8	−0.0656	−0.0820	0.0940	−14.5	24	3	30 to 90	7–65	2.00
R-125/HC16	0.1556	l_{12}	−0.2174	5.42	64	4	30 to 90	1–20	0.99
R-134a/HC16	0.0928	0.1074	−0.1630	4.19	115	4	20 to 90	1–34	1.52
R-143a/HC16	0.1167	l_{12}	−0.1544	0	56	4	20 to 90	2–30	1.75
R-152a/HC16	0.0788	0.0900	−0.1254	3.49	56	4	20 to 90	2–44	2.45
R-134a/HC13	0.0859	0.1068	−0.1734	0	25	4	20 to 90	2–24	0.67
R-134a/HC20	0.0782	0.1029	−0.1516	0	52	4	30 to 90	2–26	0.91
R-32/HAB32	0.1276	0.1422	−0.1536	0	16	21	40 to 80	15–60	2.56
R-125/HAB32	0.1587	0.1912	−0.2520	36.3	15	21	40 to 80	10–40	1.42
R-134a/HAB32	0.1146	0.1332	−0.1661	0	12	21	40 to 80	10–60	1.87
R-143a/HAB15	0.0580	0.0904	−0.0900	−3.68	25	21	40 to 80	10–60	2.23
R-125/HAB15	0.0915	0.1297	−0.1570	12.2	22	21	40 to 80	10–40	1.88
R-12/AB32	0.0339	0.0385	0	0	54	10	10 to 60	50–100	0.59
R-22/AB32	0.0569	0.0694	−0.0395	3.29	54	10	10 to 60	45–100	0.51
R-13B1/AB32	0.0598	0.1994	−0.0299	6.09	36	6	10 to 40	55–100	0.40
R-123/MO56	0.0384	l_{12}	−0.0480	7.58	61	9	20 to 80	50–100	0.57

[a] l_{12}, l_{12}, m_{12}, t_{12}: binary interaction parameters (see Text). Np: number of data points used: the symbol *: bad 7 points excluded. AAD%: average absolute deviation of fit in pressure. For the name of oils, see Table I. All oils are analyzed as UniOIL (see text).

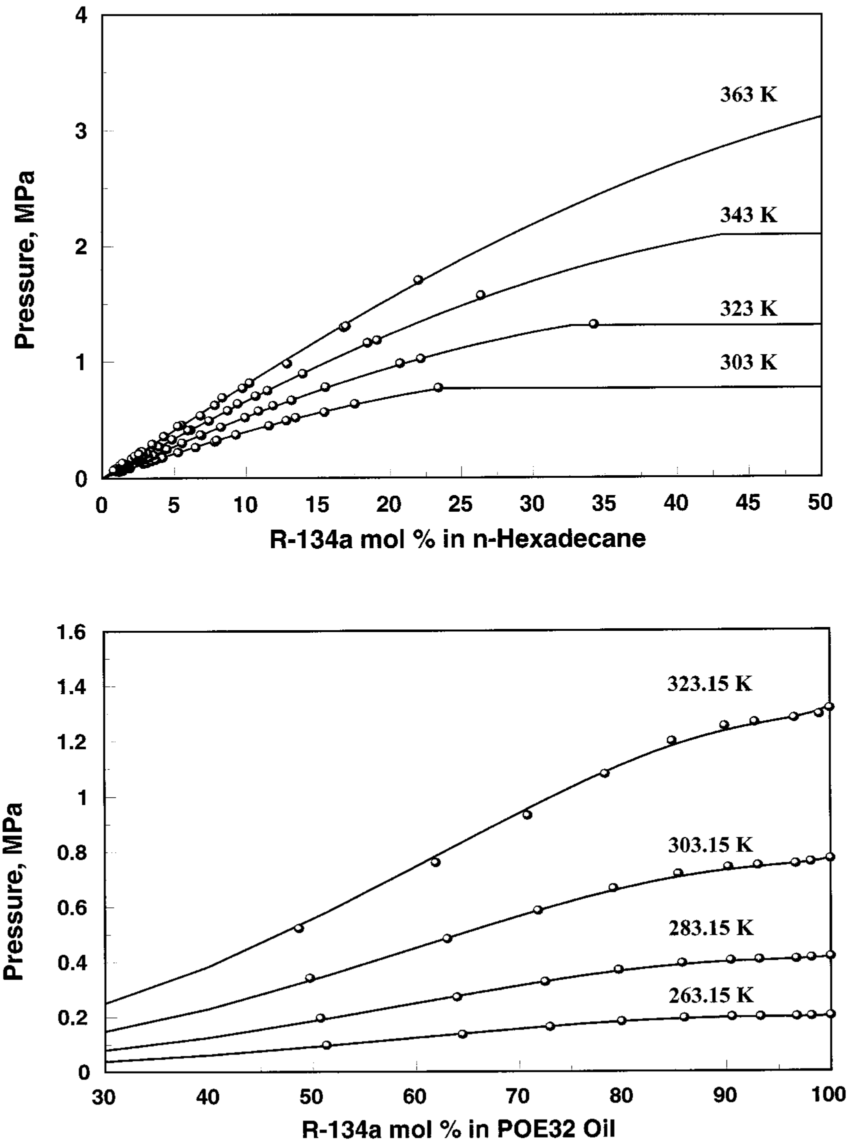


Fig. 2. Examples of the solubility data correlation. Solid lines: calculated by the present model. The regions with horizontal lines in R-134a/n-Hexadecane are in VLLE (vapor–liquid–liquid equilibria). Symbols: experimental data: R-134a/n-Hexadecane [4] and R-134a/POE32 (polyol ester oil) [7].

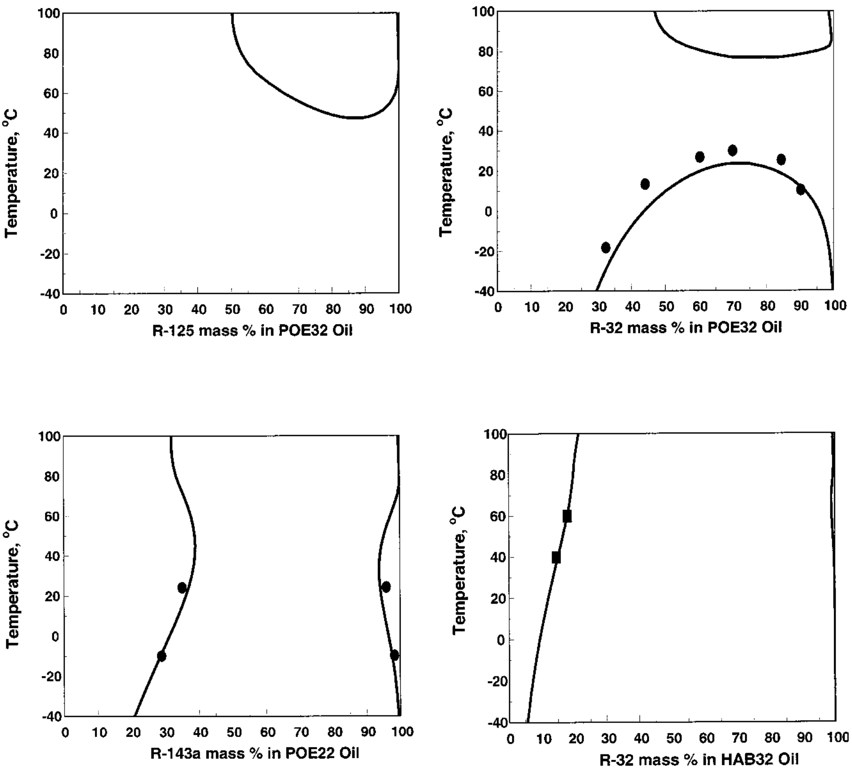


Fig. 3. Partial miscibility (VLLE, vapor–liquid–liquid equilibria). Solid lines are those predicted by the present model. Symbols are observed points: R-32/POE32 (polyol ester oil) [8], R-143a/POE22 (polyol ester oil) [2], and R-32/HAB32 (hard alkyl benzene oil) [21].

the difficulty of accurate measurements of refrigerant/oil mixtures, the predicted behaviors are in good agreement with the experimental results [2, 8, 21].

Reliable predictions for multicomponent properties based on the binary EOS parameters are important for both the validity of the model and the practical use of the EOS model. Obtaining VLE data of multicomponent systems is more difficult than the case of binary mixtures and also is time-consuming. We have demonstrated excellent predictions for *PTxy* data of R-125/R-143a/POE oil mixtures [2]. Table III shows comparisons of the present EOS predictions and experimental data for R-32/R-125/POE68 oil mixtures [12]. Although the quality of experimental data is not high, as stated in Ref. 12, the agreement is quite satisfactory. No doubt we need more of this kind of experimental data for various multicomponent systems

Table III. Predicted and Experimental Bubble-Point Pressures and Vapor Phase Compositions for R-32/R-125/POE68 Ternary Mixtures[a]

Temperature (°C)	R-32/R-125 in POE68 (mass%)	Pressure P_{obs} (kPa)	$100^*(1-P_{\text{cal}}/P_{\text{obs}})$ (%)	R-32 y_{obs} (mass%)	$y_{\text{obs}}-y_{\text{cal}}$ (mass%)
−5.10	32.77/25.10	679.19	0.43	57.73	−1.92
9.38	30.61/24.20	1056.48	−0.55	56.88	−2.14
23.43	28.72/22.64	1553.88	2.10	56.22	1.14
37.81*	24.40/20.96*	2209.27*	−5.55	59.47*	4.31
−5.71	42.31/33.62	679.58	1.66	62.26	2.70
9.07	41.95/33.52	1051.10	−0.21	61.65	2.58
23.24	41.54/33.19	1568.44	0.07	58.65	0.55
37.08	40.83/32.72	2229.86	1.04	57.71	−0.22
51.24	39.50/31.82	3120.33	−1.94	57.13	0.17

[a] The experimental data are taken from Ref. 12. The data set marked by * (37.81°C) is stated as being "probably due to poor sampling" [12].

with high accuracy. Reliable VLLE data are also critically important for the EOS model validation.

5. CONCLUSION

Solubility data of various refrigerant/lubricant oil mixtures are well correlated with a cubic type of EOS model with nonconventional mixing rules. A universal EOS valid for any kind of oil, which requires only an average molecular weight, has been developed for the refrigerant/oil solubility correlation. It is also demonstrated that predicted properties by the present EOS model are in good agreement with experimental data, indicating the validity and usefulness for solubility predictions.

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