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The ISM Equation of State Applied to Refrigerants

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In this work, we apply an equation of state based on statistical–mechanical perturbation theory to liquid refrigerants and their mixtures. Three temperature-dependent parameters are needed to use the equation of state: the second virial coefficient, $B_2(T)$, an effective van der Waals covolume, $b(T)$, and a scaling factor, $\alpha(T)$. The second virial coefficients are calculated from a correlation based on the heat of vaporization, ΔH_{vap}, and the liquid density at the freezing point, ρ_{fp}. $\alpha(T)$ and $b(T)$ can also be calculated from the second virial coefficient by a scaling rule. Based on the theory, these two temperature-dependent parameters depend only on the repulsive branch of the potential function, and therefore, by our procedure, can be found from ΔH_{vap} and ρ_{fp}. The theory has considerable predictive power, since it permits the construction of the p–v–T surface from the heat of vaporization plus the triple-point density. The equation of state is tested for pure, two- and three-component liquid refrigerant mixtures.

KEY WORDS: cohesive energy; equation of state; non-polar fluids; refrigerants.

1. INTRODUCTION

The equation of state provides a basis for accurate thermophysical properties. Theories of liquids have been developed over the past years based on the recognition that the structure of a liquid is determined primarily by repulsive forces, so that fluids of hard bodies can serve as useful reference states for perturbation theories. Song and Mason [1] extended these results to obtain a simple analytical equation of state for real fluids, which includes the low-density vapor and the super-critical fluids as well as the true liquid.

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All temperature–dependent parameters can be determined by knowing the intermolecular potential, but the equation of sate can be used with much less input information than the intermolecular potential. Because the parameters of the equation of state that depend only on the repulsion are insensitive to the detailed shape of the potential, a knowledge of just the second virial coefficient as a function of temperature is sufficient to construct the p–v–T surface, as shown by Ihm et al. [2].

The purpose of this paper is to elucidate how the equation of state of Ihm, Song, and Mason (ISM EOS) can be used with even less input information for refrigerants and refrigerant mixtures. In particular, a knowledge of only two constants, the heat of vaporization and the liquid density at the triple point, is sufficient to determine the p–v–T surface of these fluids [3].

2. THEORY

Theory yields for molecular fluids [2]:

$$\frac{p}{\rho kT}=1+\frac{(B_2-\alpha)\,\rho}{(1+0.22\lambda b\rho)}+\alpha\rho G(b\rho) \tag{1}$$

where p is the pressure, ρ is the molar (number) density, B_2 is the second virial coefficient, α is the contribution of repulsive forces to the second virial coefficient, b is the van der Waals covolume, and kT is the thermal energy. A new corresponding-states principle has the form [2]:

$$G(b\rho)^{-1}=\alpha\rho\left[Z-1-\frac{(B_2-\alpha)\,\rho}{(1+0.22\lambda b\rho)}\right]^{-1}=1-\lambda b\rho \tag{2}$$

where $Z=p/\rho RT$ is the compressibility factor and $G(b\rho)$ is the average pair distribution function at contact for equivalent hard convex bodies that still have pairwise additivity of the intermolecular forces. The many–body nature of the system may be contained in $G(b\rho)$. λ is the magnitude of the slope of G^{-1} vs. $b\rho$, a constant that must be determined empirically.

The equation of state can be expressed in terms of the Helmholtz energy A, which is composed of an ideal part A^0 and a residual part A^{r}, i.e.,

$$A=A^0+A^{\mathrm{r}} \tag{3}$$

where

$$\frac{A^{\mathrm{r}}}{kT}=\frac{(B_2-\alpha)}{0.22\lambda b}\ln(1+0.22\lambda b\rho)-\frac{\alpha}{\lambda b}\ln(1-\lambda b\rho) \tag{4}$$

and the ideal part does not concern us here. The residual Helmholtz free energy is the free energy compared to the ideal gas at the same temperature and pressure.

The minimum input information needed for using Eq. (1) are the values of B_2, α, and b. All three parameters are related to the potential energy function by means of three integrals [1]. If the intermolecular potential does not exist, a knowledge of experimental second virial coefficient data is sufficient to calculate values of the other two temperature-dependent parameters [2]. When the intermolecular potential and the experimental B_2 values are not available, there are several correlation schemes, usually based on the corresponding-states principle, by which second virial coefficients can be calculated [3, 4]. Boushehri and Mason [5] used the heat of vaporization and the liquid density at the triple point as two scaling constants for correlating B_2. Their resulting correlation for the second virial coefficient is

$$B_2^* = B_2(T)\,\rho_{\text{tp}} = A + B\left(\frac{\Delta H_{\text{vap}}}{RT}\right)^2 + C\left(\frac{\Delta H_{\text{vap}}}{RT}\right)^4 \qquad (5)$$

with

$$A = 0.403891, \qquad B = -0.076484, \qquad \text{and} \qquad C = -0.0002504$$

The other two parameters, α and b, can be calculated by scaling using

$$\alpha\rho_{\text{tp}} = a_1\left\{\exp\left[-c_1\left(\frac{RT}{\Delta H_{\text{vap}}}\right)\right]\right\} + a_2\left\{1 - \exp\left[-c_2\left(\frac{\Delta H_{\text{vap}}}{RT}\right)^{1/4}\right]\right\} \qquad (6)$$

$$b\rho_{\text{tp}} = a_1\left[1 - c_1\left(\frac{RT}{\Delta H_{\text{vap}}}\right)\right]\exp\left[-c_1\left(\frac{RT}{\Delta H_{\text{vap}}}\right)\right] + a_2\left\{1 - \left[1 + 0.25c_2\left(\frac{\Delta H_{\text{vap}}}{RT}\right)^{1/4}\right]\right\}\exp\left[-c_2\left(\frac{\Delta H_{\text{vap}}}{RT}\right)^{1/4}\right] \qquad (7)$$

with

$$a_1 = -0.1053 \qquad c_1 = 5.7862$$
$$a_2 = 2.9359 \qquad c_2 = 0.7966$$

The correlations cover the temperature range $T_{\text{tp}} < T < T_{\text{c}}$. In addition, we need the constant λ, the free parameter of the equation of state, in order to use Eq. (1). Once B_2, α, and b are known, it takes only one experimental point, the triple point [5] or the freezing point [6] to calculate λ from Eq. (1). For this purpose, we can use saturation vapor pressure data to find ΔH_{vap} and the liquid density at the freezing point. This method for determining λ makes the entire procedure self correcting. If the correlation, Eq. (5), produces values of B_2 that are somewhat in error, or if the input values of ΔH_{vap} and ρ_{tp} are not accurate, the defects will be largely compensated by the determination of λ.

A formal extension of Eq. (1) to mixtures can be written as [7]

$$\frac{p}{\rho kT} = 1 + \rho \sum_{ij} x_i x_j [(B_2)_{ij} - \alpha_{ij} F_{ij})] + \rho \sum_{ij} x_i x_j G_{ij} \alpha_{ij} \tag{8}$$

where x_i and x_j are the mole fractions.

For mixtures, the quantities G_{ij} and F_{ij} are given by [7]

$$F_{ij} = \frac{1}{1-\xi_3} - \left(\frac{d_i d_j}{d_{ij}}\right) \frac{\frac{1}{6}\pi\rho \sum_k x_k d_k^2 (4\delta_k + 1)}{(1-\xi_3)(1 + \frac{2}{3}\pi\rho \sum_k x_k d_k^3 \delta_k)} \tag{9}$$

$$G_{ij} = \frac{1}{1-\xi_3} + \left(\frac{d_i d_j}{d_{ij}}\right) \frac{\frac{1}{6}\pi\rho \sum_k x_k d_k^2 (4\lambda_k - 1)}{(1-\xi_3)(1 - \frac{2}{3}\pi\rho \sum_k x_k d_k^3 \lambda_k)} \tag{10}$$

$$\xi_3 = \frac{1}{6}\pi\rho \sum_k x_k d_k^3 \tag{11}$$

with $\delta_k \approx 0.22\lambda_k$.

The algorithm for calculating d_k is

$$b_k = \tfrac{2}{3}\pi\rho_k^3 \tag{12}$$

Here the single summations run over all the components. Notice that the only interaction parameter in these expressions is b_{ij}, but G_{ij} and F_{ij} depend on all the components of the mixture.

The simplest combining rules for predicting unlike molecule interactions from like-molecule interactions are an arithmetic mean for $\rho_{\text{tp}}^{-1/3}$ and a geometric mean for ΔH_{vap}. Thus, our combining rules would be [5]

$$(\Delta H_{\text{vap}})_{ij} = [(\Delta H_{\text{vap}})_i \, (\Delta H_{\text{vap}})_j]^{1/2} \tag{13}$$

and

$$(\rho_{\text{tp}})_{ij}^{-1/3} = \tfrac{1}{2}[(\rho_{\text{tp}})_i^{-1/3} + (\rho_{\text{tp}})_j^{-1/3}] \tag{14}$$

Once $(\rho_{\text{tp}})_{ij}$ and $\Delta(H_{\text{vap}})_{ij}$ are known, the values of α_{ij}, b_{ij}, and $(B_2)_{ij}$ follow from Eqs. (5)–(7) as for pure substances, respectively.

Table I. Parameters for Refrigerants

Substance	CF_2Cl_2	C_4F_8	Biphenyl	R-134a	R-32
λ	0.473	0.433	0.496	0.491	0.497
ρ_{fp} $(mol \cdot l^{-1})^a$	14.91	8.66	6.44		
ρ_{bp} $(mol \cdot l^{-1})^b$				13.50	23.31
$\Delta H_{vap}/R$ (K)	2451.79	2859.92	6295.20	2990.82	2625.20
ω^c	0.1699	0.3918	0.5026		
v^{*c}	0.2147	0.3284	0.5099		
T_c $(K)^a$	384.95	388.15	801.15		
p_c $(bar)^a$	41.32	27.83	41.8		

[a] These values are taken from Ref. 8.

[b] These values are taken from Refs. 9 and 10.

[c] These values are calculated from the equation in Ref. 12.

3. COMPARISON WITH EXPERIMENT

Using the tabulations of Vargaftik [8] for vapor pressure, we have calculated the heat of vaporization of CF_2Cl_2, C_4F_8, and biphenyl by using the Clausius–Clapeyron equation. The temperature-dependent parameters of the equation of state are calculated with Eqs. (5)–(7). The free parameter of the equation of state λ is calculated by using freezing point or boiling point data, ρ_{fp} and ρ_{bp}, respectively [8–11]. The results are given in Table I. The liquid density of CF_2Cl_2, C_4F_8, and biphenyl at saturation states has been calculated and compared with data in Ref. 8. The

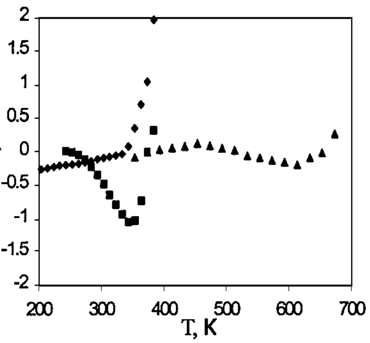

Fig. 1. Deviation plot for the liquid density of (◆) CF_2Cl_2, (■) C_4F_8, and (▲) biphenyl at their saturation pressures compared with experiment [8].

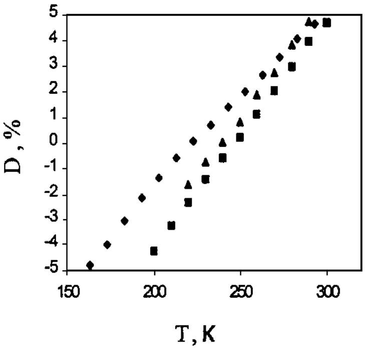

Fig. 2. Same as Fig. 1 for (■) R-134a, (◆) R-32, and (▲) 0.3953 R-32 + 0.6047 R-134a compared with experiment [9–11].

deviation plots are shown in Fig. 1. The deviation plots for the liquid density of difluoromethane (R-32), 1,1,1,2-tetrafluoroethane (R-134a), and their mixtures at saturation and for compressed states, and their comparison with experiment [9–11] are shown in Figs. 2 and 3, respectively. Also, the liquid density of CF_2Cl_2, C_4F_8, and biphenyl and their equimolar binary and ternary mixtures in the temperature range of 203 to 673 K and the pressure range of 10 to 500 bar, has been calculated and compared with the corresponding-states liquid densities (COSTALD) [12]. The deviation

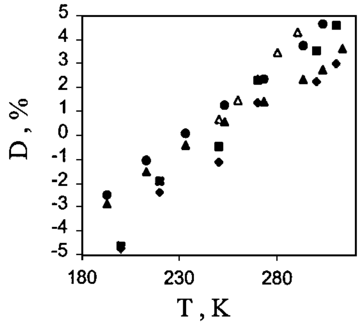

Fig. 3. Deviation plot for the density of R-134a at (■) 50 bar and (◆) 100 bar, R-32 at (●) 50 bar and (▲) 100 bar, and 0.3953 R-32 + 0.6047 R-134a at (△) 20 bar compared with experiment [9–11].

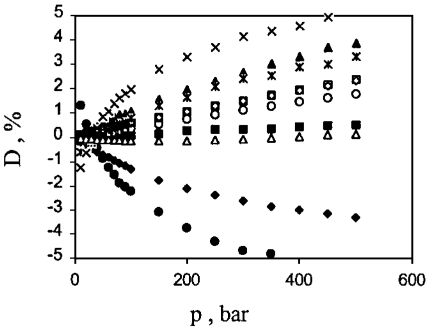

Fig. 4. Deviation plot for the density of CF_2Cl_2 at (■) 273.15 K, (◆) 323.15 K, (●) 353.15 K, C_4F_8 at (▲) 273.15 K, (∗) 323.15 K, (×) 353.15 K, and biphenyl at (□) 373.15 K, (◇) 473.15 K, (○) 573.15 K, (△) 673.15 K compared with COSTALD [12].

plots are shown in Figs. 4–6. The Clausius–Clapeyron plot of ln P vs. $1/T$ is shown in Fig. 7 and is compared with COSTALD. Saturation vapor-pressure data are computed by solving the equation of state simultaneously with the Maxwell equal-area construction. Analytical computation is not straightforward; hence, we have proceeded numerically.

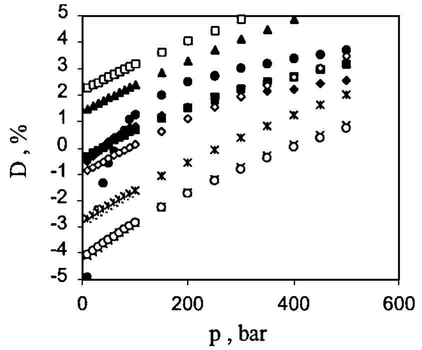

Fig. 5. Same as Fig. 4 for equimolar mixtures of CF_2Cl_2-C_4F_8 at (■) 273.15 K, (◆) 323.15 K, (●) 363.15 K, CF_2Cl_2-biphenyl at (▲) 323.15 K, (∗) 373.15 K, (×) 423.15 K, and C_4F_8-biphenyl at (□) 323.15 K, (◇) 373.15 K, (○) 423.15 K.

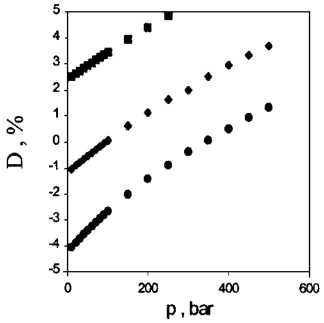

Fig. 6. Same as Fig. 4 for equimolar mixture of CF_2Cl_2-C_4F_8-biphenyl at (■) 273.15 K, (◆) 323.15 K, and (●) 373.15 K.

4. CONCLUSION

The present work shows how the equation of state can be used with just two scaling constants that are readily available at ordinary temperatures and pressures. The scaling constants are the heat of vaporization and the liquid density at the freezing or boiling point. Two vapor-pressure data points are sufficient to calculate the heat of vaporization.

The other two temperature-dependent parameters are calculated with the Lennard-Jones (12-6) potential together with a scaling rule. In fact α

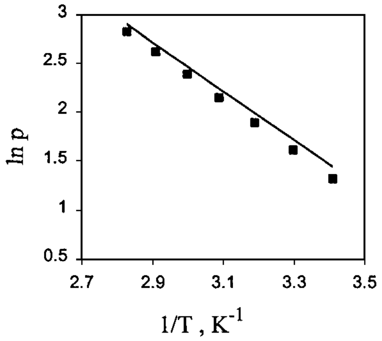

Fig. 7. Clausius–Clapeyron plot of $\ln p$ vs. $1/T$ for equimolar mixture of CF_2Cl_2-C_4F_8. The curve is from the equation of state, and dots are from COSTALD [12].

and b do not depend on the details of the potential function. In addition, the free parameter of the equation of state compensates for any inaccuracies in the temperature-dependent parameters of the equation of state.

Comparison of our results with experiment and the COSTALD method, which is claimed to be the best method for predicting the density of hydrocarbons [13], show that these two scaling constants play their role very well for estimating the second virial coefficient of refrigerants.

Although in the case of real liquids, we have made a comparison with experiment and COSTALD for single, binary, and equimolar ternary systems, some significant conclusions can be drawn. The results for mixtures are as accurate as those for single liquids. In other words, the equation of state applied to mixtures studied maintains nearly the same accuracy when the energy and size parameters of the components are varied. This feature distinguishes the theory from most existing theories, for which the accuracy is generally good only when the component parameters are not very different. Even in the steep liquid branch the agreement of calculated and COSTALD values as well as experimental data (at fixed pressure) is within 5%.

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