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Prediction of PVT Properties of Pure Refrigerants Using ISM Equation of State

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Abstract

A three-parameter cubic equation of state has been proposed for predicting PVT of pure refrigerants such as R236ea, R236fa, R245fa, R245ca, R218, R227ea, and R717, from freezing point up to critical point temperature and pressures up 650 atm. We explore the theory of the equation of state from the view point of Ihm–Song–Mason (ISM) equation of state, which has been derived on the basis of statistical mechanical perturbation theory, and is characterized by three temperature dependent parameters, a, b, B_2 , and a free parameter λ. The second virial coefficients are calculated from a correlation based on the heat of vaporization, ∆Hvap, and the liquid density at the normal boiling point, ρ_{nb}. $\alpha(T)$ and $b(T)$ can also be calculated from second virial coefficients by a scaling rule. The theory has considerable predictive power, since it permits the construction of the *PVT* surface from the heat of vaporization and the liquid density at the normal boiling point. The results indicate that the liquid densities can be predicted with very good agreement over a wide range of temperatures, 100–400 K.

1. Introduction

Accurate knowledge and prediction of the thermophysical properties of refrigerants, is of great importance to evaluate the performance of refrigeration cycles and to determine the optimum composition of new working fluids in pure and mixture states. The development of models for representation and prediction of physical properties and phase equilibria as well as the improvement of current equations of state (EOS) is of particular interest for the refrigeration industry. Thermodynamic properties of the long-known refrigerants and the new refrigerants are the key data needed for the calculation of refrigeration cycles and for designing refrigeration and air-conditioning equipment.

In 1992, Ihm, Song and Mason [1] presented an EOS based on statistical-mechanical perturbation theory for mixtures of fluids. The second virial coefficient, which characterizes binary interactions between atoms and molecules, plays an important role in the EOS, as a source of a scaling factor for calculating the other two temperature-

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dependant parameters, $\alpha(T)$ and $b(T)$. It will be shown that by knowing the second virial coefficient, the prediction of the entire pressure-volume-temperature (PVT) surface of fluids can be achieved at least for state points less than the critical temperature. Knowledge of the binary intermolecular potential energy between atomic and molecular constituents of the systems [1, 2] makes it possible to calculate second virial coefficients. Unfortunately, there are no exact intermolecular potential energies (except for some simple gases) for real fluids.

Therefore it seems reasonable to find other methods to evaluate the second virial coefficient. Of course, the experimental second virial coefficient is another good source for using the EOS. But experimental second virial coefficients have not been derived for all systems over a wide range of temperatures. The most generally useful method for prediction of the volumetric properties of fluids, such as the second virial coefficient, is the use of the hypothesis of corresponding states, which came originally from van der Waals in his well-known EOS.

Many investigations have attempted to extend the applicability of equations of state for pure and liquid mixtures [2-12] with even more readily available parameters to cover a wide range of substances, even for those which experimental data such as the second virial coefficient or the intermolecular potential energy are not yet available . In the absence of the accurate values of the second virial coefficients, there are several correlation methods, usually based on a principle of corresponding states, by which $B_2(T)$ can be estimated with reasonable accuracy.

2. Theory

Starting from the pressure equation [13] and applying the Weeks–Chandler–Andersen [14] decomposition of the potential energy function, Song and Mason [15, 16] obtained

an analytical equation of state of the form

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

for nonpolar and slightly polar fluids. Here P is the pressure, ρ is the molar (number) density, B_2 is the second virial coefficient, α is the contribution of the repulsive forces to the second virial coefficient, b is a temperature dependent parameter analogous to the van der Waals covolume, kT is the thermal energy of one molecule, and λ is an adjustable parameter. The parameters $B2$, α, and b are all temperature dependent and can be evaluated by knowing the intermolecular forces. However, such forces are almost never known with sufficient accuracy, except for noble gases [17]. If the values of the three parameters are known, the free parameter λ can be determined experimentally from high-density PVT data such as a saturated liquid density. Also the major problem now is to find the three dependent parameters $B2, \alpha$ and b. In the following, we describe a procedure for the determination of these temperature-dependent parameters using a macroscopic corresponding-states-correlation.

3. Correlation procedure

The second virial coefficient $B_2(T)$ plays a central role in the application of Eq. (1). It is used both directly and as the source of scaling constants for the calculation of $\alpha(T)$ and $b(T)$. The minimum input information needed to use Eq. (1) consists of the value of $B_2(T)$ plus some high-density data to fix the value of an adjustable shape constant in $G(b\rho)$. For many fluids, neither accurate potential functions nor experimental values of $B_2(T)$ over the whole range of temperature are available. In the absence of accurate values of $B_2(T)$, there are several correlation schemes, usually based on the principle of corresponding states, by which $B_2(T)$ can be estimated with reasonable

accuracy. To determine the parameter $B_2(T)$, we have used the following correlation [11]:

$$B\rho_{nb} = 0.403891 - 0.076484(\Delta H_{vap}/RT)^2 - 0.0002504(\Delta H_{vap}/RT)^4 \quad (2)$$

Once the $B_2(T)$ values are known, the parameters $\alpha(T)$ and $b(T)$ of the equation of state are derived from the second virial coefficient [11]:

$$\alpha\rho_{nb} = a_1\exp[-c_1(RT/\Delta H_{vap})] + a_2\{1 - \exp[-c_2(\Delta H_{vap}/RT)^{1/4}]\} \quad (3)$$

$$b\rho_{nb} = a_1[1 - c_1(RT/\Delta H_{vap})]\exp[-c_1(RT/\Delta H_{vap})] + \\ a_2\{1 - [1 + 0.25c_2(\Delta H_{vap}/RT)^{1/4}]\exp[-c_2(\Delta H_{vap}/RT)^{1/4}]\} \quad (4)$$

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

where ρ_{nb} and ΔH_{vap} are the liquid density and heat of vaporization at the normal boiling point respectively. The correlations cover a wide range of temperatures.

4. Results and Discussion

In this work Ihm-Song-Mason equation of state (ISM EOS) for pure refrigerants [18] is applied to calculate saturated liquid densities. Actually the purpose of this work is to show how the ISM equation of state can be used with even less input information for refrigerants. Two constants are needed for each pure component, ΔH_{vap} and ρ_{nb}, which are readily available, and there is seldom any difficulty in determining them; only simple measurements are needed if values cannot be found in the literature.

Three temperature-dependent parameters of the ISM EOS are calculated with Eqs. (2)-(4). The free parameter λ of Eq. (1) for each pure refrigerant is calculated by using boiling-point data. This method for determining λ makes the whole procedure self-correcting, because if the input values ΔH_{vap} and ρ_{nb} at the normal boiling point are not accurate, the effects will be largely compensated by this adjustable parameter. Once the value of the constant λ is determined, the entire volumetric behavior of the given fluids is established. Values obtained for λ as well as the heat of vaporizations and liquid densities at the normal boiling point for refrigerants are given in Table 1.
We considered the refrigerants that widely used currently and also substitutions of harmful refrigerant such as R12, R114, R22 and R502.

In the search fluids for potential applications as refrigerants in high-temperature heat pumps, centrifugal chillers, and chemical blowing agents, two new refrigerants, namely, 1,1,1,2,3,3-hexafluoropropane (R236ea), and 1,1,1,3,3,3-hexafluoropropane (R236fa), are among the most promising. The refrigerants have virtually zero potential to deplete the stratospheric ozone, low global warming

Table 1. Parameters used for pure refrigerants.

Refrigerant	Formula	T_{nb} (K)	ρ_{nb} (kg.m⁻³)	$\Delta H_{vap}/R$ (K)	λ
R236ea [a]	$CF_3CHFCHF_2$	279.3	1482.6	3020.5	0.408
R236fa [a]	$CF_3CH_2CF_3$	271.7	1444.7	2931.8	0.408
R245fa [a]	$CF_3CH_2CHF_2$	288.1	1365.7	3171.3	0.411
R245ca [a]	$CHF_2CF_2CH_2F$	298.3	1386.0	3240.2	0.409
R218 [b]	C_3F_8	236.4	1603.0	2351.9	0.392
R227ea [b]	CF_3CHFCF_3	256.7	1535.0	2695.4	0.403
R717 [b]	NH_3	239.9	682.0	2804.2	0.421

[a] from Ref. [19].
[b] from Ref. [20].

potential, and are completely nonflammable over a wide range of concentrations in air at temperatures up to 323 K, and no unusual toxicity has been indicated in limited toxicity testing. Through thermodynamic evaluation and experimental tests, R236ea has been demonstrated to have high potential as an alternative for R-114 [21]. Calculated of saturated liquid densities for R236ea and R236fa is shown in Figures 1 and 2.
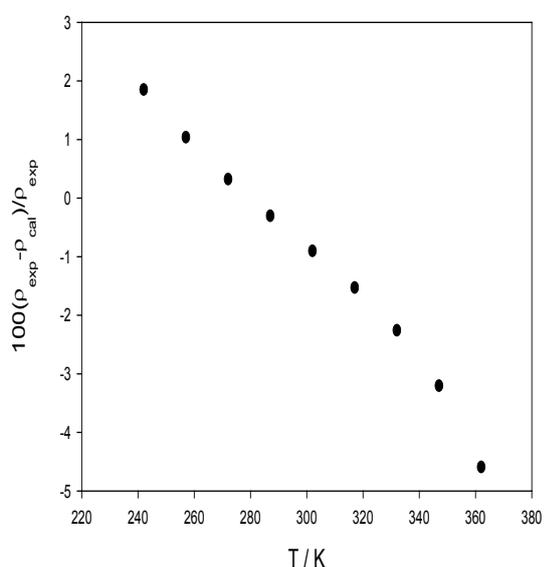
1,1,2,2,3-pentafluoropropane (R245ca) is currently considered as a potential replacement for chlorine-containing compounds used in chillers, such as R-11 [22].

1,1,1,3,3-pentafluoropropane (R245fa), a non-flammable, low-pressure (relative to R-134a) HFC refrigerant has been introduced for the foam blowing industry [23, 24]. The relatively high critical temperature of this fluid means that it would be an efficient working fluid for air-conditioning equipments [25]. The results for R245ca and R245fa are shown in Figures 3 and 4.
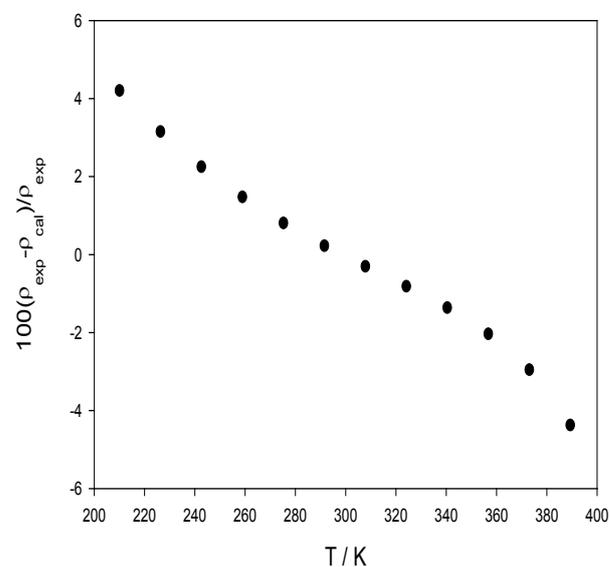

Fig. 1. Deviation plot for calculated saturated liquid densities by ISM EOS as a function of temperature, for R236ea and compared with Ref. [19].

Fig. 3. The same as figure 1. for R245ca.

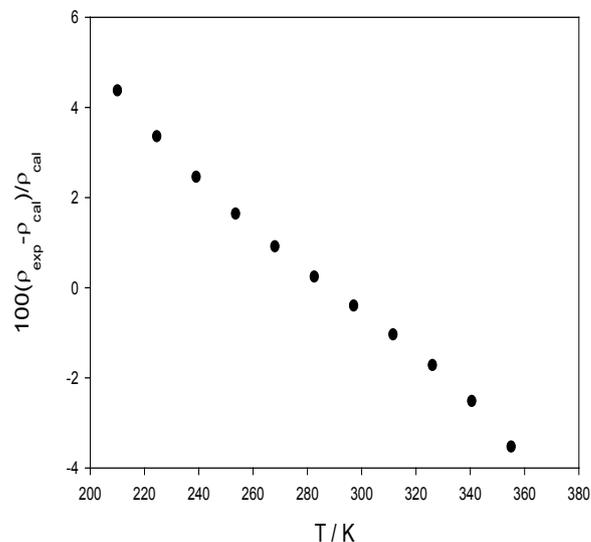
Fig. 2. The same as fig.1. for R236fa.

Fig. 4. The same as figure 1. for R245fa.

1,1,1,2,3,3,3-heptatafluoropropane (R227ea), which is chlorine-free, can be considered as a possible alternative refrigerant. It is intended as a potential alternative for R12 and R114 for units with high condensing temperatures, and also blends containing R227ea are potential alternatives to R22 and R502. It can be used in fire suppression, sterilization, and propellant applications [26].

Octafluoropropane (R218) is used in mixture with oxygen in semiconductor applications as an etching material for SiO_2 layers, and also is a component in refrigeration mixtures.

Ammonia (R717) is perhaps most well recognized as a household cleaner, and makes another important contribution to daily life as an industrial refrigerant. More recently, ammonia refrigeration systems have been used for air conditioning in publicly accessed buildings and increasing output efficiencies for power generation facilities.

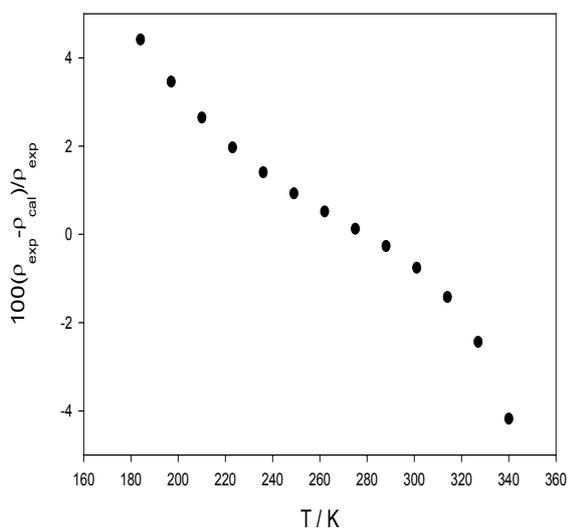Figures.5-7 are deviation plots for R227ea, R218, and R717.

Fig. 5. The same as fig. 1. R227ea.

As shown in Figures 1-7, the trend of percent deviation, from positive to about zero then becoming negative is due to the particular choice of λ. All of measurements are from freezing point up to critical temperature

and at the boiling temperature at which λ is determined the deviation is around zero.
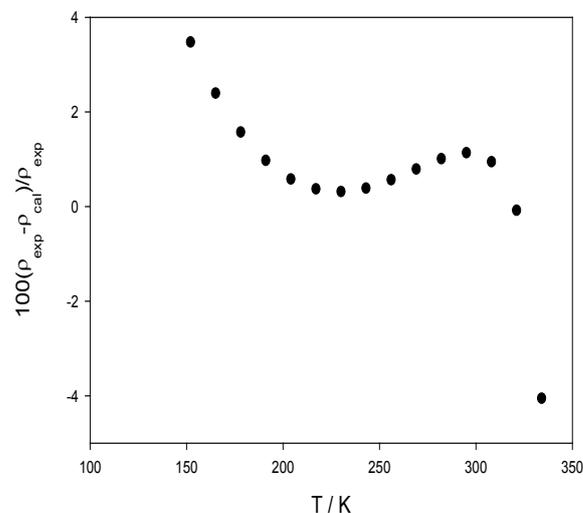

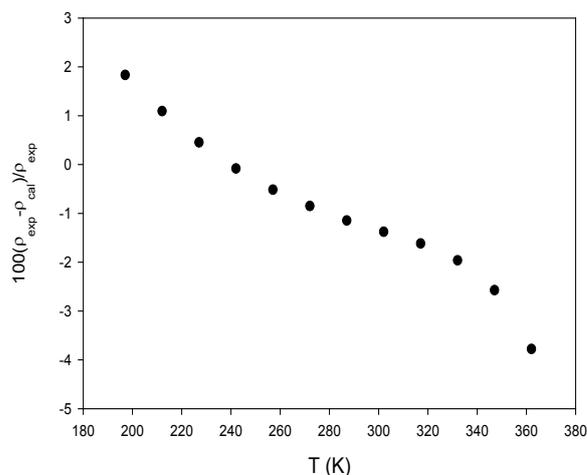**Fig. 6.** The same as fig. 1. for R218.

Fig. 7. The same as fig. 1. for R717.

As the figures show there is very good agreement between the calculated values by ISM equation of state and experimental results [19] for pure refrigerants over a wide range of temperatures and pressures.

5.Conclusions

A cubic-perturbed equation of state has been proposed that can predict PVT properties for pure refrigerants over a wide range of

temperatures and pressures. An important problem in the thermodynamics of fluids is to derive analytical EoS for real substances, i.e., to obtain explicit relations for the thermodynamic variables in terms of relevant molecular features. Such relations allow us to understand the specific behavior of a real substance in terms of its molecular features and, on practical terms, to use efficiently the usually limited knowledge of the properties of a substance to predict their values in other states. So far, this goal has been partially attained by the ISM EoS. Hence, a conclusion central to our study is that it seems to describe an interesting example of the application of ISM EoS to calculate the molar volume pure refrigerants. The second virial coefficients are calculated from a correlation based on the heat of vaporization, ΔHvap, and the liquid density at the normal boiling point, ρ_{nb}. $\alpha(T)$ and $b(T)$ can also be calculated from second virial coefficients by a scaling rule.

Acknowledgements

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