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Saturated Liquid Densities for 33 Binary Refrigerant Mixtures Based on the ISM Equation of State

Z. Sharafi[1, 2] **and A. Boushehri**[1]

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In this work, the ISM equation of state based on statistical-mechanical perturbation theory has been extended to liquid refrigerant mixtures by using correlations of Boushehri and Mason. 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 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 equation of state was tested on 33 liquid mixtures from 12 refrigerants. The results indicate that the liquid densities can be predicted to at most 2.8% over a wide range of temperatures, 170–369 K.

KEY WORDS: correlation; equation of state; heat of vaporization; refrigerants; saturation liquid density of mixtures.

1. INTRODUCTION

The equation of state plays a central role in the treatment of the thermodynamic properties of fluids, particularly of mixtures. For this purpose, an analytical equation having a statistical–mechanical basis in molecular theory is very desirable. The most fundamental tool in providing a basis to predict the thermophysical properties of matter is the equation of state. Equations of state attempt to describe the relationship between temperature, pressure, and volume for fluids or mixtures of substances. Once the

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[1] Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran.
[2] To whom correspondence should be addressed. E-mail: zahra_sharafi@yahoo.com

EOS of a system is established, all thermodynamic behavior of the system can be calculated by means of statistical mechanical tools. Unfortunately, among the equations of state available, only a few are on a sound analytical basis and are proper for this purpose. Regarding the vast applicability of different refrigerants, a precise knowledge of the pressure–density relation of these refrigerants over an extended range of temperature and pressure is extremely useful in predicting 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 a useful reference state for perturbation theories.

An analytical EOS, which has a sound basis in statistical–mechanical perturbation theory was proposed by Song and Mason [1] for pure fluids. This equation of state produces very accurate results for fluids up to the critical temperature. One of the most powerful features of this equation of state is the presence of only one adjustable parameter related to the structure of the substance. The only initial information needed for this equation of state is the intermolecular potential function of the systems. But there are no exact intermolecular potential energies (except for some simple compounds) for real fluids. Ihm et al. [2] presented a new corresponding-states method that reduces the entire pressure–volume–temperature (PVT) surface of a pure nonpolar fluid to a single curve. This reduction of a surface to a curve is based on statistical–mechanical theory, which also furnishes the algorithms for calculating, from the intermolecular pair potential, the three temperature-dependent parameters needed for the reduction. If the pair potential is not known, data on the second virial coefficient as a function of temperature can be used instead. The ISM equation of state is not accurate enough in the critical and two-phase regions, but otherwise describes the volumetric behavior of real fluids well over the entire range from the dilute gas to the dense liquid. It has considerable predictive power, since it permits the construction of the entire PVT surface from just the second virial coefficient plus a few liquid densities.

In 1992, Ihm et al. [3] 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-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. A knowledge of the binary intermolecular potential energy between atomic and molecular constituents of the systems [3, 4] 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 [4–11] 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 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. We tested the ISM equation of state [3] for mixtures of fluids, by applying correlations of Boushehri and Mason [11] over a wide range of temperatures from 170 to 369 K with good agreement with refrigerant mixture densities of Refs. 12 and 13. The purpose of this paper is to develop a method [11] for predicting the equation of state of saturated mixtures from properties that are readily available at ordinary pressures and temperatures. In particular, we used the latent heat of vaporization and the liquid density at the normal boiling point as two properties that can be used to correlate and predict the behavior of saturated liquids. These two properties, if not directly available, can be obtained with sufficient accuracy from two measured vapor pressures and liquid densities [11].

2. EOS FOR PURE SUBSTANCES

In this section, we summarize the results of the derivation of the statistical mechanical equation of state for pure fluids, which was derived by Ihm et al. [2], from statistical–mechanical perturbation theory. This equation of state is

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

where P is the pressure, ρ is the molar 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. The strong principle of corresponding states contained in Eq. (1) has led to an appreciable improvement in both accuracy and simplicity [2]. The basic idea is that the form of $G(b\rho)$ does not need to be specified according to some model of a fluid composed of hard convex bodies, but Eq. (1) can be solved for $G(b\rho)$ in terms of $Z = P/(\rho \mathrm{RT}), \rho, B$, and α, and this particular combination of quantities can then be predicted as a function of the single variable $b\rho$. The whole PVT surface is thereby collapsed to a single curve by plotting the data in this way. The new corresponding states principle has the form [2],

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

where $Z = P/(\rho kT)$ is the compressibility factor and $G(b\rho)$ is the average pair distribution function for hard convex bodies at contact. It is shown that $[G(b\rho)]^{-1}$ vs. $b\rho$ is very nearly a straight line whose slope defines the constant, λ [2]. The foregoing results culminate in the equation of state that is the starting point for the present work:

$$\frac{P}{\rho kT} = 1 + \frac{(B_2 - \alpha)\rho}{1 + 0.22\lambda b\rho} + \frac{\alpha\rho}{1 - \lambda b\rho} \tag{3}$$

where λ is equal to 0.454 for noble-gas fluids and less for more complex fluids, and it was found that δ in Eq. (2) can be taken equal to 0.22λ with sufficient accuracy [2, 3]. Because the theoretical foundation of this EOS involves a mean-field approximation, it can be applied to predict PVT data at any pressure and temperature, except the critical and two-phase regions. If the values of B_2, α, and b are known, the free parameter λ can be determined experimentally from high-density PVT data such as a saturated liquid density. The major problem now is to find the parameters B_2, α 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. (3). 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]:

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

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]:

$$\alpha\rho_{nb} = a_1 \exp[-c_1(RT/\Delta H_{\text{vap}})] + a_2 \left\{1 - \exp[-c_2(\Delta H_{\text{vap}}/RT)^{1/4}]\right\} \tag{5}$$

$$\begin{aligned} b\rho_{nb} = {} & a_1[1 - c_1(RT/\Delta H_{\text{vap}})]\exp[-c_1(RT/\Delta H_{\text{vap}})] \\ & + a_2 \left\{1 - [1 + 0.25c_2(\Delta H_{\text{vap}}/RT)^{1/4}]\exp[-c_2(\Delta H_{\text{vap}}/RT)^{1/4}]\right\} \end{aligned} \tag{6}$$

$$\begin{aligned} a_1 &= -0.1053 \quad & c_1 &= 5.7862 \\ a_2 &= 2.9359 \quad & c_2 &= 0.7966 \end{aligned}$$

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.

The remaining problem is to find λ from PVT data. This adjustable parameter is determined from Eq. (3) using normal boiling point data. Once the value of the constant λ is determined, the entire volumetric behavior is established. The values of λ for each fluid are given in Table I. When the temperature-dependent parameters together with the values of λ are known, Eq. (3) can been applied to calculate the PVT properties.

4. EXTENSION TO MIXTURES

A formal extension of Eq. (1) to mixtures can be written as [3]

$$\frac{P}{\rho kT} = 1 + \rho \sum_{ij} x_i x_j [(B_2)_{ij} - \alpha_{ij} F_{ij})] + \rho \sum_{ij} x_i x_j G_{ij} \alpha_{ij} \tag{7}$$

where x_i and x_j are the mole fractions.

Table I. Parameters for 12 Refrigerants

Refrig.	Chemical formula	T_{nb}(K)[a]	ρ_{nb} (kg·m^{-3})[a]	$\Delta H_{\text{vap}}/R$(K)[a]	λ
R12	CCl_2F_2	243.35	1486	2414.1	0.3911
R13	$CClF_3$	191.75	1522	1884.7	0.3890
R22	$CHClF_2$	232.35	1412	2438.9	0.4027
R23	CHF_3	191.05	1460	2021.0	0.4042
R32	CH_2F_2	221.35	1215	2396.4	0.4085
R115	C_2ClF_5	234.21[b]	1558[c]	2334.5[b]	0.3921
R116	C_2F_6	194.95	1605	1942.2	0.3920
R125	C_2HF_5	224.95	1516	2382.1	0.4044
R134a	$CF_3–CH_2F$	247.05	1378	2663.0	0.4077
R143a	$CF_3–CH_3$	225.55	1166	2324.9	0.3991
R152a	$CHF_2–CH_3$	248.45	1011	2581.9	0.4008
R218	$CF_3–CF_2–CF_3$	236.45	1603	2351.9	0.3917

[a] From Ref. 14.
[b] From Ref. 15.
[c] From Ref. 12.

For mixtures, the quantities G_{ij} and F_{ij} are given by [3]

$$F_{ij} = \frac{1}{1-\xi_3} - \left(\frac{d_i d_j}{d_{ij}}\right) \frac{\frac{1}{6}\pi\rho \sum_k x_k d_k^2 (4\delta_k + 1)}{(1-\xi_3)(1+\frac{2}{3}\pi\rho\sum_k x_k d_k^3 \delta_k)} \tag{8}$$

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

$$\xi_3 = \frac{1}{6}\pi\rho\sum_k x_k d_k^3 \tag{10}$$

with $\delta_k = 0.22\ \lambda_k$.

The equation for calculating d_k is

$$b_k = \tfrac{2}{3}\pi d_k^3 \tag{11}$$

The single summations run over all the components. The only interaction parameter in these expansions is b_{ij}. G_{ij} and F_{ij} depend on all the components of the mixtures. The simplest combining rules for predicting unlike molecule interactions from like-molecule interactions are an arithmetic mean for $\rho_{nb}^{-1/3}$ and a geometric mean for ΔH_{vap}.

$$(\rho_{nb})_{ij}^{\frac{-1}{3}} = \frac{1}{2}\left[(\rho_{nb})_i^{\frac{-1}{3}} + (\rho_{nb})_j^{\frac{-1}{3}}\right] \tag{12}$$

Table II. Comparisons between Calculated and Experimental Values [12] of Saturated Liquid Densities for 33 Mixtures

T(K)	P(bar)	ρ_{exp}(kg·m^{-3})^{a}	NP^{b}	AAD (%)^{c}
	0.186 R12 + 0.814 R152a			
183.15–358.65	0.03–29.30	1246.2–738.1	14.0	0.852
	0.340 R12 + 0.660 R152a			
183.15–358.15	0.03–30.23	1328.9–772.9	15.0	1.316
	0.606 R12 + 0.394 R152a			
183.15–359.95	0.61–31.28	1463.6–833.9	14.0	1.105
	0.824 R12 + 0.176 R152a			
183.15–352.15	0.03–25.19	1569.5–982.35	14.0	1.871
	0.176 R22 + 0.824 R12			
223.15–333.15	0.05–17.76	1523.7–1134.0	12.0	2.057
	0.279 R22 + 0.721 R12			
213.15–351.15	0.03–27.34	1540.1–1008.1	13.0	1.800
	0.633 R22 + 0.367 R12			
198.15–369.65	0.01–38.58	1543.5–848.5	14.0	1.223
	0.807 R22 + 0.193 R12			
187.15–353.15	0.01–35.26	1555.0–904.2	15.0	0.767
	0.118 R22 + 0.882 R115			
198.55–339.34	0.02–25.78	1662.1–959.2	14.0	0.784
	0.241 R22 + 0.759 R115			
204.85–334.45	0.03–24.79	1621.2–997.15	13.0	1.322
	0.630 R22 + 0.370 R115			
198.15–337.35	0.02–28.41	1579.0–969.8	13.0	1.700
	0.818 R22 + 0.182 R115			
205.15–349.45	0.03–35.73	1524.3–881.0	14.0	0.993
	0.226 R32 + 0.774 R134a			
194.75–322.35	0.01–16.57	1488.5–1062.5	12.0	1.465
	0.500 R32 + 0.500 R134a			
198.35–324.35	0.02–22.20	1423.6–989.2	11.0	1.538
	0.782 R32 + 0.218 R134a			
183.15–323.55	0.01–27.11	1389.8–913.1	14.0	1.438
	0.844 R32 + 0.156 R 134a			
192.55–317.95	0.02–24.91	1345.6–923.1	12.0	1.191
	0.221 R32 + 0.779 R125			
183.15–311.55	0.01–20.89	1612.9–1073.9	13.0	1.397
	0.431 R32 + 0.569 R125			
193.15–313.15	0.02–23.04	1527.2–1029.2	13.0	1.664
	0.654 R32 + 0.346 R125			
173.15–317.15	0.01–26.52	1512.1–958.8	13.0	1.788
	0.836 R32 + 0.164 R125			
193.15–314.15	0.02–25.23	1376.1–935.7	12.0	1.535
	0.247 R23 + 0.753 R13			
173.15–289.35	0.05–36.40	1586.3–875.7	15.0	1.891
	0.500 R23 + 0.500 R13			

Table II. Continued

T(K)	P(bar)	$\rho_{\mathrm{exp}}(\mathrm{kg{\cdot}m^{-3}})^a$	NP^b	AAD (%)^c
189.15–283.15	0.12–35.10	1511.6–917.3	14.0	0.885
	0.745 R23 + 0.255 R13			
193.45–281.65	0.15–34.30	1472.7–936.59	15.0	0.802
	0.849 R23 + 0.151 R13			
173.15–281.05	0.04–33.07	1537.7–952.8	14.0	0.882
	0.138 R32 + 0.862 R115			
230.15–320.35	0.17–22.03	1523.1–1074.6	12.0	2.586
	0.174 R125 + 0.826 R143a			
220.15–328.05	0.07–25.92	1248.7–808.7	14.0	0.609
	0.369 R125 + 0.631 R143a			
209.15–324.35	0.04–24.18	1353.7–879.4	13.0	0.598
	0.616 R125 + 0.384 R143a			
188.15–321.95	0.01–23.43	1508.3–948.4	13.0	0.976
	0.805 R125 + 0.195 R143a			
221.15–315.95	0.08–20.86	1466.4–1031.5	13.0	1.132
	0.828 R23 + 0.172 R116			
172.65–256.65	0.04–17.26	1549.9–1143.6	11.0	2.674
	0.290 R22 + 0.710 R218			
167.55–317.15	0.01–20.11	1780.8–1084.1	12.0	2.769
	0.430 R22 + 0.570 R218			
167.23–274.03	0.01–6.86	1751.6–1344.7	11.0	2.554
	0.810 R22 + 0.190 R218			
239.15–325.28	0.19–24.07	1432.7–1044.1	12.0	2.705

[a] From Ref. 12.

[b] NP: Number of data points.

[c] AAD (%) $= 100(|\rho_{\mathrm{exp}} - \rho_{\mathrm{cal}}|/\rho_{\mathrm{exp}})_{\mathrm{av}}$.

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

Once $(\rho_{nb})_{ij}$ and $(\Delta H_{\mathrm{vap}})_{ij}$ are known, the values of α_{ij}, b_{ij}, and $(B_2)_{ij}$ follow from Eqs. (4)–(6) as was done for pure substances.

5. RESULTS AND DISCUSSION

In this paper, 33 mixtures from 12 pure refrigerants were studied with the ISM equation of state, and our essential result is that the ISM equation of state, Eq. (7) with the correlations of Boushehri and Mason, Eqs. (4)–(6), for liquid mixtures can be used to predict property values over the entire liquid range without the need for any high-pressure measurements. 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 we obtained them from Refs. 12, 14, and 15. There is seldom any difficulty in determining them; only simple measurements are needed if values cannot be found in the literature. The temperature-dependent parameters of the equation of state are calculated with Eqs. (4)–(6). The free parameter λ of Eqs. (8) and (9) for each component is calculated by using boiling-point data by means of Eq. (3). This method for determining λ makes the whole procedure self-correcting, because if the input values ΔH_{vap} and liquid density ρ_{nb} at the normal boiling point are not accurate, the effects will be largely compensated by this adjustable parameter. Apparently the "shape" effects describe by ω affects ΔH_{vap} and ρ_{nb} in such a way as to tend to compensate for their influence on B. 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 heats of vaporization and liquid densities at the normal boiling point for 12 refrigerants are given in Table I.

The present calculations for these saturated liquid refrigerant mixtures were made for many thermodynamic points, and the results are given in Table II, along with the AAD (average absolute deviation). All of the comparisons in this table are with NIST Standard Reference Database 23

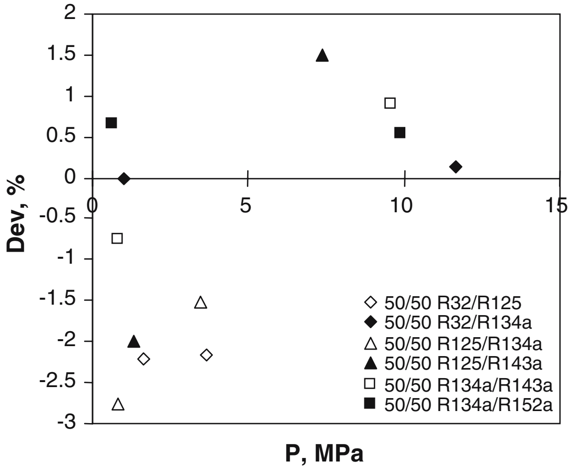

Fig. 1. Deviations of liquid densities of mixtures form Ref. 13 as a function of pressure, P, at $T = 300\,\text{K}$, 50/50 R32/R125 (◇), 50/50 R32/R134a (◆), 50/50 R125/R134a (△), 50/50 R125/R143a (▲), 50/50 R134a/R143a (□), 50/50 R134a/R152a(■).

[12], and also there are comparisons with the refrigerant mixture densities of Ref. 13 in Fig. 1. As shown in Table II and Fig. 1, there is good agreement between the calculated values and results of Refs. 12 and 13 over a wide range of temperatures, $170\,\mathrm{K} < T < 369\,\mathrm{K}$.

In summary, statistical–mechanical theory now allows the development of equations of state for saturated liquid mixtures from simple measurements at ordinary pressures and temperatures.

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