



An Analytical Equation of State for Saturated Liquid Refrigerant Ternary Mixtures

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Abstract

In this work an analytical equation of state has been employed to calculate the PVT properties of ternary refrigerant mixtures. The theoretical EoS is that of Ihm, Song and Mason, which is based on statistical-mechanical perturbation theory, and the two constants are enthalpy of vaporization ΔH_{vap} and molar density ρ_{nb} , both at the normal boiling temperature. The following three temperature-dependent parameters are needed to use the EoS: 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 scaling rules. This procedure predicts liquid densities of ternary mixtures at saturated state with a temperature range from 173 K to 373 K and pressure up to 4.0 MPa, with very good results.

Keywords: Equation of State, Liquid Densities, Ternary Mixtures, Heat of Vaporization.

Introduction

In the previous work [1] we have described the method for calculation saturated liquid densities of refrigerant binary mixtures. This work applies the procedure to a number of ternary mixtures. Information about thermodynamic properties is important initially to qualify potential candidates for working fluids in refrigeration machinery. It is also very useful in calculating the thermodynamic properties necessary for the design of that machinery. In this respect, 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. In general, thermodynamic and physical properties such as enthalpy, vapor

pressure, and density of fluids can be estimated through an equation of state. The applicability of an equation of state to a given system is reliable if in the first place, accurate input data are available. In practice, the input data may not be available for a given system or it may not be possible to measure these data accurately for some systems. Hence, there is a need to extend the method by using of alternative procedures. An analytical EoS, which has a sound basis in statistical-mechanical perturbation theory, was proposed by Song and Mason [2] for pure fluids. 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. Ihm, Song and Mason [3] presented a new strong principle of corresponding states method that reduces the entire pressure-volume-temperature (P-V-T)

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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 has considerable predictive power, since it permits the construction of the entire P-V-T surface from just the second virial coefficient plus a few liquid densities. In 1992, Ihm, Song and Mason [4] 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. Knowledge of the binary intermolecular potential energy between atomic and molecular constituents of the systems [4,5], 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 [5-12] 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. The purpose of this paper is to develop a method [12] for predicting the equation of state of saturated ternary 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 correlate and predict the behavior of saturated liquid mixtures. These two values, if not directly available, can be obtained with sufficient accuracy from two measured vapor pressures and liquid densities [12].

Theoretical Equation of State

An alternative to empirical representation of the PVT behavior is to develop theoretical model, starting from an understanding of the forces that exist between molecules. In principle, these forces could be calculated from quantum mechanics, however, since the true potential energy function is not known exactly, one usually assumes that those forces obey an empirical potential law such as the hard-sphere or Lennard-Jones 12-6 potential. The use of statistical mechanics bridges the gap between quantum and continuum mechanics, allowing one to take statistical averages using molecular variable to obtain macroscopically observable quantities.

Here, we consider the statistical-mechanical equation of state derived by Song and Mason [2], which is based on the Week-Chandler-Anderson (WCA) [13], including the division of the intermolecular potential at its minimum into regions of attractive and repulsive forces, but differs in two significant respects. The first is that the second virial coefficient is treated by a perturbation theory. The second is choice of an algorithm for calculating the effective hard-sphere diameter as a function of temperature.

The derivation begins with the equation relating the pressure to the pair distribution function, $g(r)$ [14]

$$\frac{P}{\rho kT} = 1 - \frac{2\pi}{3} \frac{\rho}{kT} \int_0^{\infty} \frac{du}{dr} g(r) r^3 dr \quad (1)$$

where P is the pressure, ρ is the density, kT is the thermal energy per molecule, and du/dr is the derivative of the intermolecular potential function with respect to the distance r . Upon applying the perturbation scheme of the WCA method to the potential function and working out a correction for attractive forces, the equation of state reads [3]

$$\frac{P}{\rho kT} = 1 - \frac{(\alpha - B_2)\rho}{1 + 0.22\lambda b\rho} + \frac{\alpha\rho}{1 - \lambda b\rho} \quad (2)$$

where, the new corresponding-state principle for $G(b\rho)$ has the form

$$G(b\rho)^{-1} \equiv \alpha\rho \left[Z - 1 + \frac{(\alpha - B_2)\rho}{(1 + 0.22\lambda b\rho)} \right]^{-1} = 1 - \lambda b\rho \quad (3)$$

where $Z = P/\rho kT$ 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 as in $g(r)$. The many-body nature of the system may be contained in $G(b\rho)$ [3]. The parameters $B_2(T)$, $b(T)$ and $\alpha(T)$ can be obtained by integration if the intermolecular potential is accurately known, but we do not have any potential model here. Song and Mason [15] showed that $B_2(T)$ can be found experimentally and $\alpha(T)$ and $b(T)$ can be calculated from $B_2(T)$ by means of simple two-constant scaling rules, because $\alpha(T)$ and $b(T)$ depend only on the intermolecular repulsive forces and are insensitive to the details of the shape of the intermolecular potential. $G(b\rho)^{-1}$ is a function of $b\rho$ only and satisfies corresponding states, varying linearly with slope λ over the whole range of temperatures from the freezing line up to the critical point. The functional form of $G(b\rho)^{-1}$ implies that, according to corresponding states, all the PVT data collapse to a single line. The value of λ , determined from PVT data by iteration, along with $B_2(T)$, $\alpha(T)$ and $b(T)$, characterizes the thermodynamic properties of particular systems.

Ihm et al. [4] have extended the theory for pure cases to mixture of any number of components as follows:

$$\frac{P}{\rho kT} = 1 + \rho \sum_{ij} x_i x_j (B_{ij} - \alpha_{ij}) F_{ij} + \rho \sum_{ij} x_i x_j G_{ij} \alpha_{ij} \quad (4)$$

where x_i and x_j are mole fractions, and summations run over all components of the mixture and subscripts ij refer to the i - j interactions. The parameters F_{ij} and G_{ij} are defined as:

$$F_{ij} = \frac{1}{1 - \xi_3} - \left(\frac{d_i d_j}{d_{ij}} \right) \frac{\frac{1}{6} \pi \rho \sum_k x_k d_k^2 (4\delta_k + 1)}{(1 - \xi_3) \left(1 + \frac{2}{3} \pi \rho \sum_k x_k d_k^3 \lambda_k \right)} \quad (5)$$

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

$$\xi_3 = \frac{1}{6} \pi \rho \sum_k x_k d_k^3 \quad (7)$$

where ξ_3 is packing fraction for the mixture with $\delta_k = 0.22 \lambda_k$ and λ is an adjustable parameter.

The equation for calculating d_k is:

$$b_k = \frac{2}{3} \pi d_k^3 \quad (8)$$

B_{ij} , b_{ij} and α_{ij} are well defined in terms of i - j intermolecular potential and are evaluated in the same way as the corresponding quantities for single substances, either from the potential model or from experimental data on second virial coefficient. In the following section, we describe the procedure for the determination of these temperature-dependent parameters using a macroscopic corresponding state correlation.

Correlation Procedure

The second virial coefficient $B_2(T)$ plays a central role in the application of Eq. (2). 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 [12]:

$$B\rho_{nb} = 0.403891 - 0.076484(\Delta H_{vap} / RT)^2 - 0.0002504(\Delta H_{vap} / RT)^4 \quad (9)$$

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 [12]:

$$a\rho_{nb} = a_1 \exp[-c_1(RT / \Delta H_{vap})] + a_2 \{1 - \exp[-c_2(\Delta H_{vap} / RT)^{1/4}]\} \quad (10)$$

$$b\rho_{nb} = a_1[1 - c_1(RT / \Delta H_{vap})] \exp[-c_1(RT / \Delta H_{vap})] + a_2 \{1 - [1 + 0.25c_2(\Delta H_{vap} / RT)^{1/4}] \exp[-c_2(\Delta H_{vap} / RT)^{1/4}]\} \quad (11)$$

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

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} .

$$(\rho_{nb})_{ij}^{-1/3} = (1/2) [(\rho_{nb})_i^{-1/3} + (\rho_{nb})_j^{-1/3}] \quad (12)$$

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

Once $(\rho_{nb})_{ij}$ and $(\Delta H_{vap})_{ij}$ are known, the values of α_{ij} , b_{ij} and $(B_2)_{ij}$ follow from Eqs. (9)-(11) as was done for pure substances, where ρ_{nb} and ΔH_{vap} are liquid density and heat of vaporization at normal boiling point respectively.

The remaining problem is to find λ from PVT data. This adjustable parameter is determined

from Eq. (2) at normal boiling point data. Once the value of the constant λ is determined, the entire volumetric behavior of the given fluids is established. The obtained values of λ for each fluid, are given in Table 1. If the correlation Eq. (9) produces values of B_2 that are somewhat in error, or if the input values of ρ_{nb} and ΔH_{vap} are not accurate, the defects will be largely compensated by the determination of λ .

Results and Discussions

This study was undertaken to predict the PVT behavior of saturated ternary refrigerant mixtures, over the whole range of available temperatures and pressures. Our essential result is that the equation of state for saturated liquid mixtures can be predicted over the entire liquid range without the need for any high-pressure measurements. Two constants are needed for each pure component, ρ_{nb} and ΔH_{vap} , that are available easily. In this respect, 16 saturated ternary mixtures from 10 pure refrigerants are studied. These pure refrigerants are: R22 (chlorodifluoromethane), R32 (difluoromethane), R124 (1-chloro-1,2,2,2-tetrafluoroethane), R125 (pentafluoroethane), R134a (1,1,1,2-tetrafluoroethane), R142b (1-chloro-1,1-difluoroethane), R143a (1,1,1-trifluoroethane), R152a (1,1-difluoroethane), R290 (propane), R1270 (propene).

Calculated saturated liquid densities at different temperatures and pressures and our comparisons with experimental data [16] have been reported in Tables 2, 3 as well as percent deviations (Dev %) and average absolute deviations (AAD %).

As Tables show, agreement between calculated liquid densities and literature values are quite good and all deviations are within 3%. No fitting was done for these systems other than combining rule by using of the parameters of the pure refrigerants without proposing any mixing rule.

Conclusion

Our procedure successfully predicts a statistical-mechanical equation of state for density of saturated liquid ternary mixtures over a wide range temperatures and pressures. This work indicates that the physical

properties can be predicted from just two scaling constants, the enthalpy of vaporization and the liquid density at normal boiling point, which can readily be measured.

The present work demonstrated that the mixture version of the ISM EoS is able to provide reliable information on the PVT properties of ternary mixtures as well as pure systems without using any fitting parameter.

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Table 1. Parameters for pure refrigerants.

Refrigerant	Chemical Formula	T_{nb} (K) ^a	ρ_{nb} (kg/m ³) ^a	$\Delta H_{vap}/R$ (K) ^a	λ
R22	CHClF ₂	232.35	1412	2438.9	0.4027
R32	CH ₂ F ₂	221.35	1215	2396.4	0.4085
R124	CHClF-CF ₃	261.05	1474	2677.4	0.3981
R125	C ₂ HF ₅	224.95	1516	2382.1	0.4044
R134a	CF ₃ -CH ₂ F	247.05	1378	2663.0	0.4077
R152a	CHF ₂ -CH ₃	248.45	1011	2581.9	0.4008
R142b	CClF ₂ -CH ₃	263.95	1195	2671.5	0.3954
R143a	CF ₃ -CH ₃	225.55	1116	2324.9	0.3991
R290	C ₃ H ₈	231.15	582	2280.7	0.3899
R1270	C ₃ H ₆	225.45	611	2221.93	0.3896

^a from Ref. [17]

Table 2. Calculated saturated densities of mixture 0.60 R22+ 0.25 R124+ 0.15 R142b for computer code verification.

T (K)	P (MPa)	$\rho_{exp.}$ (kg/m ³) ^a	$\rho_{cal.}$ (kg/m ³)	Dev % ^b
173.15	0.001	1581.2	1553.4	1.758
185.25	0.004	1550.7	1534.8	1.025
197.35	0.009	1519.8	1512.9	0.454
209.45	0.020	1488.4	1478.8	0.040
221.25	0.040	1456.5	1459.8	-0.227
233.65	0.074	1423.8	1428.9	-0.358
245.75	0.127	1390.1	1395.3	-0.374
257.85	0.206	1355.2	1359.0	-0.280
269.95	0.317	1318.8	1320.1	-0.099
282.05	0.470	1280.6	1278.5	0.164
294.15	0.671	1240.3	1234.3	0.484
306.25	0.930	1197.3	1187.2	0.844
318.35	1.257	1150.9	1137.1	1.199
330.35	1.659	1100.0	1084.4	1.418
342.55	2.147	1042.5	1027.2	1.468
354.65	2.732	975.0	966.7	0.849
366.75	3.423	889.0	902.1	-1.477

^a from Ref [16].

$${}^b Dev\% = \frac{\rho_{exp.} - \rho_{cal.}}{\rho_{exp.}} \times 100$$

Table 3. Comparison between calculated and experimental values [16] of saturated liquid densities for 15 ternary mixtures.

T(K)	P (MPa)	ρ_{exp} (kg/m ³) ^a	NP ^b	AAD % ^c
0.530R22 + 0.130R152a + 0.340R124 178.15-367.55	0.002-3.487	1574.9-864.8	16	0.809
0.655R22 + 0.155R152a + 0.190R124 173.15-365.15	0.001-3.697	1554.8-838.5	16	0.922
0.331R22 + 0.149R152a + 0.520R124 173.15-362.15	0.001-2.715	1609.6-954.0	16	0.637
0.508R125 + 0.046R290 + 0.446R22 173.15-314.75	0.004-2.029	1586.4-1054.9	13	1.280
0.380R125 + 0.020R290 + 0.600R22 173.15-320.75	0.003-2.200	1599.0-1050.3	13	0.872
0.358R125 + 0.604R143a + 0.038R134a 173.15-323.95	0.003-2.353	1465.9-893.1	14	0.831
0.346R32 + 0.300R125 + 0.354R134a 173.15-314.75	0.002-1.908	1570.2-1062.0	13	1.711
0.198R32 + 0.600R125 + 0.202R134a 173.15-308.35	0.003-1.716	1630.3-1114.5	14	1.511
0.262R32 + 0.113R125 + 0.625R134a 173.15-324.35	0.002-1.954	1558.0-964.9	13	1.859
0.404R32 + 0.104R125 + 0.492R134a 173.15-318.35	0.002-1.919	1529.5-1038.8	13	1.730
0.050R125 + 0.476R143a + 0.474R22 173.15-336.95	0.003-2.899	1440.6-853.2	15	0.570
0.727R22 + 0.177R124 + 0.096R142b 173.15-360.35	0.001-3.380	1580.7-909.2	16	0.733
0.029R1270 + 0.833R22 + 0.138R152a 173.15-352.35	0.002-3.400	1492.9-866.8	17	1.126
0.030R1270 + 0.940R22 + 0.030R152a 173.15-358.45	0.002-4.049	1497.0-797.8	18	1.582

^a From Ref. [16].^b NP: Number of Data Point.^c $AAD \% = 100(|\rho_{exp} - \rho_{cal}| / \rho_{exp})_{av}$

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