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The Use of an MHV-2 Equation of State for Modeling the Thermodynamic Properties of Refrigerant Mixtures[1]

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This paper reports on the development and application of a thermodynamic model based on the second-order Modified Huron Vidal equation of state (MHV-2) to predict the properties of ternary mixtures of the refrigerants R32, R125, and R134a. The mixing rules of this equation of state have been used to incorporate directly an activity-coefficient model for the excess Gibbs free energy. The parameters for the activity-coefficient model have been derived from experimental VLE data for binary mixtures. This methodology has enabled the production of a thermodynamically consistent model which can be used to predict the phase equilibria of R32/R125/R134a mixtures. The input data used in the model are presented in the paper and the predictions of the model are compared with available experimental data. The model has been used to predict the behavior of ternary refrigerant blends of R32/R125/R134a in fractionation scenarios, such as liquid charging and vapor leakage, which are of direct interest to the refrigeration industry. Details of these applications and comparisons with experimental data are discussed, along with other general uses of the thermodynamic model.

KEY WORDS: activity coefficient; equation of state; MHV-2; refrigerants; R32; R134a; R125; vapor–liquid equilibria.

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1. INTRODUCTION

Specific compositions of the ternary mixture comprising R32, R125, and R134a are now becoming established as leading candidates to replace R22 and R502 in the refrigeration industry. The ability to predict vapor–liquid equilibria (VLE) and vapor-phase properties of such zeotropic fluid mixtures within the operating ranges generally relevant to refrigeration and air-conditioning (−60 to +60°C) is of great interest. The modeling of the liquid phase of nonideal fluids has generated much interest and effort in the literature [1] and it is evident that a category of models based on the local-composition concept [2] has led to many useful representations of the liquid phase behavior and is therefore an attractive feature. It has been shown that incorporating such models into an equation of state in a thermodynamically consistent way, via the excess Gibbs free energy, implicitly determines the mixing rules for the equation of state [3]. The excess Gibbs free energy as calculated via the equation of state is matched at specific conditions to that predicted by the local-composition model. The original matching procedure was performed for cubic equations at infinite pressure. More recent work, however, has shown that a more suitable match is at $P=0$, as it is closer to the region covered experimentally [4]. It was from these concepts that the first- and second-order modified Huron Vidal models, MHV-1 and MHV-2, were developed.

The aim of the work reported in this paper was to develop an MHV-2 mixture model for new refrigerants which incorporates the Wilson model [5], a local composition model, in the matching procedure for the excess Gibbs free energy.

2. THERMODYNAMIC MODEL

A summary of the MHV-2 methodology is given below. Further details are available in Ref. 6. The calculations are based on a modified Redlich–Kwong equation of state:

$$P=\frac{RT}{v-b_{\mathrm{mix}}}-\frac{a_{\mathrm{mix}}}{v(v+b_{\mathrm{mix}})} \tag{1}$$

The mixture parameters a_{mix} and b_{mix} are defined below.

The mixture b_{mix} is derived from conventional linear mixing rules:

$$b_{\mathrm{mix}}=\sum_{i=1}^{n} z_i b_{ii} \tag{2}$$

with

$$b_{ii} = 0.08664 \frac{RT_{ci}}{P_{ci}} \tag{3}$$

where b_{ii} are the pure component parameters, and z_i is the mole fraction of component i in the mixture comprising n components.

The a parameters for the pure fluids are given by

$$a_{ii} = 0.4286 \frac{R^2 T_{ci}^2}{P_{ci}} [f(T_{ri})^2] \tag{4}$$

where T_{ri} is the reduced temperature (T/T_{ci}) for the ith component and where

$$f(T_{ri}) = 1 + C_1(1 - \sqrt{T_{ri}}) + C_2(1 - \sqrt{T_{ri}})^2 + C_3(1 - \sqrt{T_{ri}})^3 \qquad \text{for} \quad T_{ri} < 1 \tag{5}$$

and

$$f(T_{ri}) = 1 + C_1(1 - \sqrt{T_{ri}}) \qquad \text{for} \quad T_{ri} > 1 \tag{6}$$

C_1, C_2, and C_3 are the Mathias–Copeman parameters [7], determined by fitting an expression for the saturated vapor pressures to experimental data of the pure fluids. The values obtained for these parameters for the fluids R32, R125, and R134a are given in Table I.

By matching the excess Gibbs free energy, g^{E}, of the mixture as predicted by the equation of state with that from any independent model at zero pressure (g^{E}), the implicit equation, shown below, is obtained for the mixture parameter a_{mix} [6]:

$$q(\alpha_{\mathrm{mix}}) = \sum_{i=1}^{c} z_i q(\alpha_{ii}) + \sum_{i=1}^{c} z_i \ln \left\{ \frac{b_{\mathrm{mix}}}{b_{ii}} \right\} + \frac{g^E}{RT} \tag{7}$$

where $\alpha_{\mathrm{mix}} = a_{\mathrm{mix}}/b_{\mathrm{mix}} RT$, $\alpha_{ii} = a_{ii}/b_{ii} RT$, and z_i is the mole fraction of component i and where, for the second-order modified Huron Vidal model (MHV-2), $q(\alpha_{\mathrm{mix}})$ is approximated well by the quadratic equation:

$$q(\alpha_{\mathrm{mix}}) = q_0 + q_1 \alpha_{\mathrm{mix}} + q_2 \alpha_{\mathrm{mix}}^2 \tag{8}$$

The values for the constants q_1 and q_2 have been derived empirically to be -0.478 and -0.0047, respectively, for the MHV-2 model based on a Redlich–Kwong equation of state [8]. Equation (8) also holds for a pure fluid if α_{ii} is substituted for α_{mix}.

Table I. Values for the Pure Fluids R32, R125, and R134a Inputted into the Blend Model

Variable	R32	R125	R134a
Critical properties			
T_c (K)	351.50	339.45	374.15
P_c (bar)	58.16	36.43	40.55
Mathias Copeman parameters			
C_1	0.993253	1.018740	1.076200
C_2	−0.773470	−0.807016	−1.010070
C_3	1.287190	1.786820	2.332010
Ideal-gas enthalpy coefficients ($J \cdot kmol^{-1}$)			
A	−5.01599E6	−1.75953E7	−1.5780E7
B	0.000000	1.56026E4	1.46818E4
C	78.820180	174.235550	153.300100
D	−3.2131E-2	−9.85768E-2	−9.74810E-2
E	5.53664E-6	2.26108E-5	4.5434E-5
F	−3.52644E8	−3.31163E7	0.000000
Liquid density coefficients ($kg \cdot m^{-3}$)			
A'	429.76	571.00	509.15
B'	610.36	979.40	902.40
C'	1372.04	768.93	637.10
D'	−1962.64	−750.58	−504.31
E'	1370.34	607.14	415.77

Combining Eqs. (7) and (8) for the MHV-2 model [8] gives

$$\frac{g^E}{RT} = q_1\left(\alpha_{\text{mix}} - \sum_{i=1}^{c} z_i \alpha_{ii}\right) + q_2\left(\alpha_{\text{mix}}^2 - \sum_{i=1}^{c} z_i \alpha_{ii}^2\right) - \sum_{i=1}^{c} z_i \ln\left\{\frac{b_{\text{mix}}}{b_{ii}}\right\} \tag{9}$$

Equation (9) is a quadratic in which the only unknown is α_{mix}, the mixture parameter. Once the value for α_{mix} is determined for a given set of conditions, the mixture parameter, a_{mix}, is readily calculated, as described above.

The excess Gibbs free energy, g^E, required to solve Eq. (9) is predetermined directly from calculated activity coefficients, γ_i, for each of the pure fluids, R32, R125, and R134a via the relation

$$\frac{g^E}{RT} = \sum_{i=1}^{3} z_i \ln(\gamma_i) \tag{10}$$

The activity coefficients have been determined from Wilson values, fitted by means of experimental VLE data for the three binary pairs, i.e., R32/R134a, R32/R125, and R125/R134a. The VLE data have been measured by Brown and McDonnell [9] and cover a temperature range of

Table II. Wilson E Values Obtained from Fitting Experimental VLE Data for the Binary Mixtures

Refrigerants	E_{12}	E_{21}
1 = R32, 2 = R125	1763479	−1317615
1 = R125, 2 = R134a	−433426	770442
1 = R32, 2 = R134a	699490	−597357

−40 to +50°C. These results will be reported in full elsewhere [10]. Table II shows the Wilson E values obtained by fitting the VLE data.

The Wilson E values for each pair of fluids (i and j) are related to the Wilson A values via the relation

$$A_{ij} = \frac{V_j}{V_i} \cdot \exp\left\{-\frac{E_{ij}}{RT}\right\} \tag{11}$$

where V_i and V_j are the liquid molar values at 25°C (values of 0.04839, 0.10754, and 0.0825 $\text{m}^3 \cdot \text{kmol}^{-1}$ were used for R32, R125, and R134a, respectively, in the current work). E_{ij} is the Wilson E value in $\text{J} \cdot \text{kmol}^{-1}$ (Table II). T is the temperature in K and R is the gas constant ($8314.34\ \text{J} \cdot \text{kmol}^{-1} \cdot \text{K}^{-1}$).

The critical properties used for R32, R125, and R134a as input into the MHV-2 model are given in Table I and have been obtained from internal data and recently published papers [11–13]. In common with standard equation-of-state methods, the ideal-gas mixture enthalpy is required to evaluate the mixture enthalpies via departure functions that are calculated from the MHV-2 model. The mixture ideal-gas enthalpy was determined from the ideal mixing rule:

$$H_{\text{mix}}^{\text{id}} = \sum_{i=1}^{3} z_i H_i^{\text{id}} \tag{12}$$

The ideal-gas enthalpies of the pure fluids, H_i^{id}, were given by

$$H_i^{\text{id}} = A_i + B_i T + C_i T^2 + D_i T^3 + E_i T^4 + \frac{F_i}{T} \tag{13}$$

where T is in K. The ideal-gas enthalpy coefficients obtained are given in Table I and were determined from correlations fitted to experimental ideal-gas specific heat data for R32 [14], R125 [15], and R134a [16].

The liquid densities for the R32/R125/R134a mixtures were calculated in two ways, first, via the MHV-2 equation of state and, second, via a temperature correlation for the pure fluids and a standard linear mixing rule.

The temperature correlation used for the pure fluid liquid densities is given by

$$\rho_i^L = A_i' + B_i'X + C_i'X^2 + D_i'X^3 + E_i'X^4 \tag{14}$$

where $X = [1 - (T/T_C)]^{1/3}$.

The coefficients calculated for the pure fluid liquid densities are shown in Table I and were determined from experimental data available in the literature for R32 [11], R125 [13], and R134a [17]. The predictions of the temperature correlation method were compared with those of a correlation fitted by Defibaugh and Morrison [18] to experimental liquid density data for an R32/R134a blend of composition 33.4/66.6 wt%. Over the applicable temperature range of the latter, −20 to 60°C, the agreement is better than 0.6%. The saturated liquid density predicted directly via the MHV-2 model show much poorer agreement, with deviations of up to 20% at the higher temperatures. For this reason the temperature correlation method was used when specifically calculating the saturated liquid density. It was not used to fit the experimental VLE data or in subsequent vapor pressure calculations.

3. MODEL PREDICTIONS

Experimental VLE data have been viewed as being central to the capability of the MHV-2 model for describing the VLE properties. This is exemplified in Fig. 1, which shows the deviations of the MHV-2 model

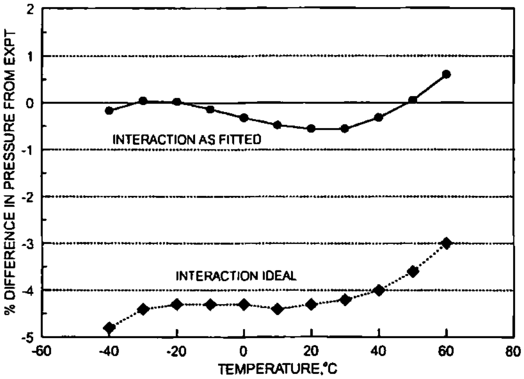

Fig. 1. The deviations of the MHV-2 model predictions from the experimental VLE data for the vapor pressure as a function of temperature for an R32/R125 blend of composition 50/50% (wt/wt) as charged.

predictions from the experimental VLE data for vapor pressure as a function of temperature for an R32/R125 blend of composition 50/50 wt% as charged. The results obtained, assuming that binary fluid interactions are zero, i.e., an ideal mixture, are compared with those obtained using the values for the interactions derived from the experimental VLE. The improvement in using the latter is clearly shown, moving the agreement with the experimental data from less than 5 to less than 1%.

In general, for the nine VLE data sets available for binary blends [9], the MHV-2 model can reproduce the measured vapor pressures to around the 1% level or less. It can predict the vapor pressures for a 33.4/66.6 wt% R32/R134a blend to within 2% of those measured experimentally from an independent source [18] over the temperature range of −40 to +60°C. The largest discrepancies are at low temperatures and are due partially to differences in the values measured experimentally. In the vapor phase region, very limited experimental *PVT* data are currently available for blends with which to evaluate the MHV-2 model. Some comparisons with *PVT* data for a 50/50 wt% R32/R134a blend [19] have shown that the MHV-2 model can predict the vapor density to within 1% for isotherms between 65 and 100°C and for pressures within the range of 3 to 40 bar. The model predictions for a 20/80 R32/R134a blend have been compared with a correlation fitted directly to experimental *PVT* data [20] recently reported over the pressure range of 0.5–25 bar and for temperatures close to the dew-point temperature up to 100°C. The agreement ranges from 0.5 to 4.5%, with the greatest discrepancies occurring at the lower temperatures. More experimental *PVT* data are required to assess fully the accuracy of the MHV-2 model in the vapor phase region, although it is recognized that its accuracy will ultimately be limited by the fact that none of the model parameters have been fitted to such data and that it is based only on the cubic equation of state.

4. FURTHER APPLICATIONS OF THE MHV-2 MODEL

The effects of fractionation on liquid and vapor compositions are an important facet of using zeotropic refrigerant blends as it may occur in many areas, both at certain points within refrigeration and air-conditioning systems and even in containers, such as cylinders and drums in which they are transported. The primary factors that influence the liquid and vapor compositions in fractionation scenarios for a given bulk composition are the mass of refrigerant within a given volume and the temperature. The MHV-2 thermodynamic model developed for R32/R125/R134a blends has been used to predict the behavior of these blends in containers under various conditions and compared directly with experimental measurements, performed using gas chromatography. Table III shows the results obtained from two bulk compositions of R32/R125/R134a of 18.3/41.3/40.4 and 9.1/72.3/18.6 wt%, which were charged into a container to a liquid level that was 90% of the total internal volume. The measurements were performed at 25°C. Table III shows a comparison of the vapor compositions measured experimentally and those predicted by the MHV-2 model. The agreement is better than 0.7 and 0.1 wt%, respectively. The MHV-2 model has also been used as a basis for simulating liquid and vapor leakages from containers, which is again important to understand in the context of using zeotropic refrigerants for refrigeration and air-conditioning. Experimental measurements of the vapor composition that leaks from containers at flow rates of 20–50 ml · min^{-1} have been recorded at temperatures ranging from −35 to 55°C. The containers were initially 85% liquid-filled by volume. For the temperature and flow rates studied, the variation in the leaked composition as a functon of the mass lost in the container can be predicted to within 1 wt% by using a series of successive VLE calculations to simulate this process, as shown in Fig. 2. This work illustrates the capability of the MHV-2 model that has been developed to predict the VLE compositions of the ternary blends for fractionation conditions in which the mass fraction of refrigerant in the liquid phase varies from 98 to 15% (85% to approximately 2%, by volume).

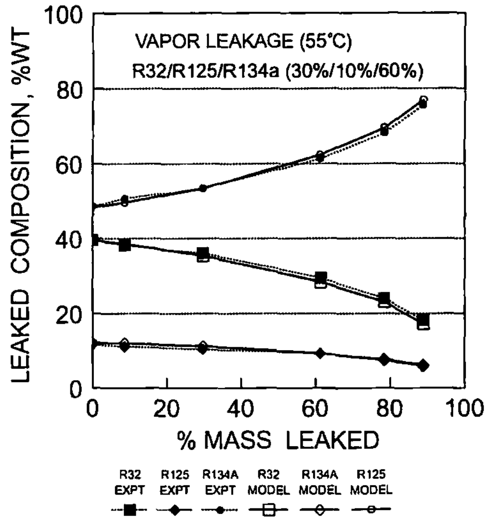

Fig. 2. Comparison of the experimental and theoretical vapor compositions as a function of the mass lost in the container, during vapor leakage (20–50 ml · min^{-1}) at 55°C for a blend initially charged as 30/10/60 R32/R125/R134a (wt%).

Table III. A Comparison of the Measured and Calculated Vapor Compositions for Two Ternary Blends of R32/R125/R134a Charged into a Container to 90% Liquid Fill at 25°C

Charge composition (wt%)			Vapor composition (wt%)					
			Measured			Calculated		
R32	R125	R134a	R32	R125	R134a	R32	R125	R134a
18.3	41.3	40.4	24.5	49.2	26.3	25.2	48.5	26.3
9.1	72.3	18.6	11.5	76.6	11.9	11.6	76.5	11.9

5. CONCLUSIONS

A thermodynamic model based on the MHV-2 equation of state has been developed to predict the thermodynamic properties of ternary mixtures of the refrigerants R32/R125/R134a. The incorporation of an independent activity-coefficient model, the Wilson model, in which the interaction coefficients have been determined from experimental VLE data is a central feature of the model. Comparisons of the predictions of the model with experimental thermodynamic data for vapor pressures that are currently available indicate that, over the temperature range of −40 to 60°C and pressure range of 1–30 bar in the VLE region, it is accurate to within 1–2% or better. It has been show that the model is capable of predicting liquid and vapor compositions within this region to an accuracy of 1 wt% or better.

Given the fact that the thermodynamic model is based on a cubic equation of state and therefore has few model parameters, and that it has been developed using a limited quantity of thermodynamic data, its capability is good and our studies have shown that it offers an attractive comprise between an overcomplex model and its accuracy for predicting thermodynamic properties of refrigerant blends. It is particularly useful for predicting compositional shifts in systems [21] and the VLE properties of blends in containers. Another attractive feature of the methodology described in this work is that it can be extended readily to systems containing any number of fluids if the appropriate VLE data are available.

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