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PREDICTION OF REFRIGERANT THERMODYNAMIC PROPERTIES BY EQUATIONS OF STATE: VAPOR LIQUID EQUILIBRIUM BEHAVIOR OF BINARY MIXTURES

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ABSTRACT

The ability of three equations of state (EOS) for describing the vapor-liquid equilibria of refrigerants has been studied for several binary mixtures. The three uations of state studied were the Soave-Redlich-Kwong (SRK), Peng-Robinson (PR) and Parameters From Molecule Contribution (PFMC). For azeotropic mixtures, the bubble point pressure, vapor molar volume, saturated liquid density, and heat of vaporization were calculated and compared with the values reported in the ASHRAE hand- book. Binary interaction parameters for each equation of state were optimized to achieve better agreement between calculated values and the reported experimental data. The optimized binary interaction parameters for several binary mixtures are presented. Sample graphical error analyses are shown.

INTRODUCTION

Mixtures of halogenated compounds are becoming popular as heat transfer agents for use in domestic and industrial heat-pumps and refrigeration units. For selection of a thermodynamic model, the thermodynamic properties play an important role. Equations of state have been shown to be effective tools for calculating thermodynamic properties and describing the VLE behavior of binary refrigerant mixtures (Mesle-Lesavre, et al., 1982; Moshfeghian, et al., 1989; Shariat, et al., 1989; Asselineau, et al., 1978).

The ability of three equations of state (EOS) to predict the thermodynamic properties of pure refrigerant compounds was discussed in the first paper (Moshfeghian, et al., 1991). In this paper, the capability of the same three equations [SRK (Soave, 1972),PR (Peng and Robinson, 1976), and PFMC (Moshfeghian and Maddox, 1991)] in describing the vapor-liquid equilibria of binary refrigerant mixtures is discussed.

The objective of this paper was to evaluate the ability and, if necessary, improve the accuracy of three equations of state in predicting the thermodynamic properties and VLE behavior of binary refrigerant mixtures. A data bank composed of the data reported in the ASHRAE handbook (ASHRAE, 1988) and other literature was used as the basis for this work. A computer program, EOS*TAILOR (Fathi- Kalahaji, et al., 1991) with graphics capability was used for evaluating and upgrading each of the equations of state under study. With the aid of EOS*TAILOR the following tasks were performed for eighteen refrigerant mixtures.

1. The binary interaction coefficients for the Peng Robinson, Soave-Redlich-Kwong, and PFMC EOS were optimized to give the best prediction of bubble point pressure and vapor phase composition for each refrigerant mixture.

2. For four azeotropic mixtures where experimental data were available, the bubble point pressure, saturated vapor molar volume, saturated liquid density and heat of vaporization were predicted and compared with reported values.

3. The predicted results of part 2 were compared with the results of calculations in which each of the azeotropic mixtures was treated as a pure compound (Moshfeghian, et al., 1991).

THE EQUATIONS OF STATE

The three equations of state selected for evaluation were the Peng-Robinson (Peng and Robinson, 1976), the Soave-Redlich-Kwong (Soave, 1972), and the Moshfeghian and Maddox adaptation of the Parameters From Group Contribution (Cunningham, 1974) which they described as PFMC (Moshfeghian and Maddox, 1990a).

Appendix A shows the mixing rules for the PFMC equation of state. Mixing rules for the PR and SRK equations are readily available in any thermodynamics textbook (Prausnitz, et al., 1986). Quadratic mixing rules as suggested by Moshfeghian and Maddox (1990a) were used for PFMC in the present evaluation.

BINARY INTERACTION PARAMETER OPTIMIZATION

One way of improving the accuracy of an equation of state in describing the VLE behavior of a binary mixture is through the use of a binary interaction parameter. For example, bubble point pressure calculated by the PR, SRK or PFMC is very sensitive to the value of binary interaction parameter used. Unfortunately, there is no theoretical method available to determine a binary interaction parameter. For an "ideal system", the binary interaction parameter is either zero or unity depending how it is defined. For a non-ideal system experimental vapor-liquid equilibrium data must be available if the interaction parameter is to be determined. Nonlinear regression techniques are used to determine the value of the binary interaction parameter that will minimize the objective error function for the given set of experimental data. Moshfeghian and Maddox (1990b) reported the sensitivity of binary interaction parameter determination to the type of VLE calculation performed and the objective error function defined.

In this work, optimization of binary interaction parameters was achieved through the use of EOS*TAILOR (Fathi-Kalahaji, et al., 1990) which permits the user to choose among several combinations of VLE options and objective functions. The objective function selected was to minimize the sum of errors in bubble point pressure and vapor- liquid equilibrium ratio (vapor phase composition) at a fixed temperature and liquid phase composition. The form of objective function used was:

$$OF=\sum_{i=1}^{ND}\left[A\left(\frac{P_E-P_C}{P_E}\right)^2+B\left(\frac{K_{1E}-K_{1C}}{K_{1E}}\right)^2+C\left(\frac{K_{2E}-K_{2C}}{K_{2E}}\right)^2\right]_i \qquad (1)$$

Weighting factors A through C can be used to emphasize accuracy in calculating a specific property. In this study each of them was set to 100, there being no basis for considering one property more reliably determined than the others.

Using this optimization technique, the binary interaction parameters for 18 binary mixtures were determined. Table 1 shows the temperature and pressure range, and source of experimental data for each system. For selected systems the optimized interaction parameters for the SRK, PR, and PFMC are presented in Table 2. For the SRK and PR EOS only one interaction parameter, k_{ij}, was used. PFMC requires that a four-term binary interaction parameter be used. The four parameter terms are k_{ij}, l_{ij}, p_{ij}, and q_{ij}. Both p_{ij} and l_{ij} describe the temperature dependency of a_{ij} . For a fair evaluation and comparison of the three EOS, PFMC was also used with only a one-term interaction parameter. In this case, q_{ij} was set equal to zero, and both k_{ij} and l_{ij} were set equal to unity. In order to distinguish between the two cases, PFMC with the one-term interaction parameter is referred to as PFMC1 and PFMC4 indicates a four-term interaction parameter.

The SRK and PR interaction parameter, by definition, is 1.0 minus the single PFMC interaction parameter.

EVALUATIONS

Based on the optimized interaction parameters like those presented in Table 2, bubble point pressure, saturated vapor molar volume, saturated liquid molar density and heat of vaporization for four azeotropic mixture refrigerants were calculated and compared with values reported in the ASHRAE Handbook of Fundamentals (ASHRAE, 1988). For each temperature, the percent error defined by equation 2 was calculated.

TABLE 1

List of binary systems

System Number	Components 1 2	Pressure Range, psia	Temperature Range, °F	Number of Points	Reference Number
1	CF_4 + $CClF_3$	29 - 200	-100 to 100	10	Stein and Proust, 1979
2	CF_4 + H_2	592 - 1763	-243 to -162	24	Shiau and Ziegler, 1980
3	$CBrF_3$ + $C_2H_4F_2$	22 - 558	8 to 152	33	Morrison and Ziegler, 1980
4	C_2H_6 + iC_4H_{10}	155 - 657	100 to 220	23	Besserer and Robinson,1973a
5	$CClF_3$ + H_2	296 - 1170	-216 to -64	23	Stein and Proust, 1971
6	$CClF_3$ + iC_4H_{10}	79 - 642	100 to 260	35	Weber, 1989
7	$CClF_3$ + nC_4H_{10}	62 - 660	100 to 260	49	Weber, 1989
8	CHF_3 + $CClF_3$	25 - 400	-100 to 32	60	Besserer and Robinson,1973b
9	CCl_2F_2 + $C_2Cl_2F_4$	50 - 210	40 to 210	40	Storm, et al., 1989
10	$C_2H_4F_2$ + CCl_2F_2	42 - 52	32 to 32	17	Stein and Proust, 1971
11	$CHClF_2$ + $C_2Cl_2F_4$	142 - 195	73 to 218	17	Stein and Proust, 1979
12	$CHClF_2$ + CCl_2F_2	142 - 202	72 to 132	20	Stein and Proust, 1979
13	CH_2F_2 + CO_2	16 - 616	-60 to 50	48	Adams and Stein, 1971
14	CCl_2F_2 + $C_2H_4F_2$	3 - 569	-90 to 200	31	ASHRAE, 1988
15	$CHClF_2$ + C_2ClF_5	7 - 474	-75 to 160	25	ASHRAE, 1988
16	CHF_3 + $CClF_3$	1 - 505	-190 to 50	25	ASHRAE, 1988
17	CH_2F_2 + C_2ClF_5	3 - 618	-120 to 140	27	ASHRAE, 1988
18	NH_3 + H_2O	0.34 - 502	32 to 250	100	Perry and Chilton, 1973

TABLE 2

Optimized binary interaction coefficients.

Components	SRK	PR	PFMC1		PFMC4		
1 2	k_{ij}	k_{ij}	p_{ij}	p_{ij}	q_{ij}	k_{ij}	l_{ij}
CF_4+H_2	0.2356	0.2422	0.3980	0.7357	0.3301	1.3413	1.2761
C_2H_6+iC_4H_{10}	-0.0084	-0.0102	0.9711	0.9904	-0.0263	1.0083	1.0156
$CClF_3$+H_2	0.2139	0.2170	0.4234	0.7697	0.0528	1.3311	1.3311
$CClF_3$+nC_4H_{10}	0.0733	0.0735	0.9260	0.9478	-0.0413	1.0005	1.0094
CH_2F_2+CO_2	0.0129	0.0127	0.9735	0.9979	-0.0813	0.9752	0.9946
NH_3+H_2O	-0.2846	-0.2694	0.9666	0.8580	0.0543	0.6770	0.8784

$$\text{Percent Error} = \left[\frac{(\text{Experimental Value}) - (\text{Calculated Value})}{(\text{Experimental Value})}\right] \times 100 \qquad (2)$$

For each binary mixture, the average absolute percent deviation (AAPD) defined by equation 3 was also calculated.

$$\text{AAPD} = \frac{1}{\text{ND}} \sum_{i=1}^{ND} \left[\left|\frac{(\text{Experimental Value}) - (\text{Calculated Value})}{(\text{Experimental Value})}\right|\right]_i \times 100 \qquad (3)$$

Tables 3 through 6 show the summary of average errors for predicting the bubble point pressure, heat of vaporization, saturated vapor molar volume and saturated liquid molar density of the four azeotropic mixtures using the SRK, PR and PFMC, respectively. The Tables show the errors for two different techniques for calculating the mixture properties. In the first case the azeotropic mixture is considered as a single component with equation of state parameters determined from reported property values for the azeotrope. In the second case the azeotrope was considered a binary of azeotrope composition, but the equation of state parameters were determined from reported property values for the two pure components. The three equations do equally well at predicting mixture properties, and there is little difference in the error of values calculated using the two different techniques for representing the azeotropic composition mixture. With the exception of high reduced temperature (i.e. $T_r > 0.97$) all three EOS handle the azeotropic as a binary mixture as well as if the mixture were treated as a pure a compound. In fact, the calculated bubble point pressure for the mixture is much better than the predicted vapor pressure of the pure component. The fourteen remaining systems in Table 1 were then evaluated over the temperature and pressure range for which data were available. Table 7 summarizes the error in calculated bubblepoint pressure and vapor-liquid equilibrium constants for the eighteen systems.

CONCLUSIONS

The capability and accuracy of the PR, SRK and PFMC EOS for calculation of thermodynamic properties of refrigerant mixtures have been

TABLE 3

Calculated PVT data by four EOS for an azeotropic mixture of 60.61 mol% CCl_2F_2 + 39.39 mol% $C_2H_4F_2$ (R500).

	Average Absolute Percent Deviation							
	Treated As A Pure Compound				Treated As A Binary Mixture			
EOS	Vapor Pressure	Vapor Volume	Liquid Density	Latent Heat	Bubble Pressure	Vapor Volume	Liquid Density	Latent Heat
SRK	1.65	1.20	7.68	2.70	1.10	5.49	13.38	7.68
PR	1.00	0.53	6.27	2.07	0.60	2.97	3.64	5.25
PFMC1	1.00	1.37	4.42	1.46	0.60	2.73	4.09	1.48
PFMC4	-	-	-	-	0.30	2.74	4.21	1.06

TABLE 4

Calculated PVT data by four EOS for an azeotropic mixture of 63.0 mol% $CHClF_2$ + 37.0 mol% C_2ClF_5 (R502).

	Average Absolute Percent Deviation							
	Treated As A Pure Compound				Treated As A Binary Mixture			
EOS	Vapor Pressure	Vapor Volume	Liquid Density	Latent Heat	Bubble Pressure	Vapor Volume	Liquid Density	Latent Heat
SRK	1.00	0.84	9.50	2.34	0.90	1.23	9.79	2.34
PR	1.00	1.02	5.29	1.90	1.40	2.30	4.57	2.10
PFMC1	1.00	0.55	5.79	1.34	1.80	3.34	8.46	5.97
PFMC4	-	-	-	-	0.40	3.86	8.01	5.26

TABLE 5

Calculated PVT data by four EOS for an azeotropic mixture of 49.97 mol% CHF_3 + 50.03 mol% $CClF_3$ (R503).

	Average Absolute Percent Deviation							
	Treated As A Pure Compound				Treated As A Binary Mixture			
EOS	Vapor Pressure	Vapor Volume	Liquid Density	Latent Heat	Bubble Pressure	Vapor Volume	Liquid Density	Latent Heat
SRK	2.04	5.77	11.39	1.59	1.00	2.74	11.00	1.55
PR	4.41	6.93	4.08	1.84	2.40	3.17	4.20	1.76
PFMC1	1.00	0.84	6.64	0.85	1.40	3.26	4.45	0.90
PFMC4	-	-	-	-	0.70	3.78	4.22	0.76

TABLE 6

Calculated PVT data by four EOS for an azeotropic mixture of 73.43 mol% CH_2F_2 + 26.57 mol% C_2ClF_5 (R504).

	Average Absolute Percent Deviation							
	Treated As A Pure Compound				Treated As A Binary Mixture			
EOS	Vapor Pressure	Vapor Volume	Liquid Density	Latent Heat	Bubble Pressure	Vapor Volume	Liquid Density	Latent Heat
SRK	1.01	1.98	14.26	2.00	0.70	2.87	17.99	3.30
PR	1.19	2.17	3.32	1.49	0.70	1.97	7.40	2.63
PFMC1	1.00	3.36	3.62	4.78	1.80	7.22	9.12	9.98
PFMC4	-	-	-	-	0.20	8.17	6.42	6.02

TABLE 7

Comparison of Calculated and Experimental Bubble Point Pressures and Equilibrium Constants

	Average Absolute Percent Deviation											
	SRK			PR			PFMC1			PFMC4		
Sys No.	K_1	K_2	P	K_1	K_2	P	K_1	K_2	P	K_1	K_2	P
1	1.0	1.8	1.3	1.0	1.9	1.3	0.7	1.3	1.0	0.6	1.2	1.3
2	8.1	0.4	8.2	4.4	0.3	6.0	41.0	1.9	40.6	11.2	0.6	8.4
3	1.6	2.7	2.6	0.4	1.0	0.7	1.3	2.0	1.3	0.3	0.4	0.8
4	3.7	4.6	1.6	3.7	4.7	1.4	3.3	5.1	2.9	1.9	2.7	2.5
5	5.5	0.7	10.7	6.0	0.6	8.0	46.5	3.6	37.0	15.9	1.6	7.6
6	6.5	3.1	3.4	3.8	1.6	2.3	7.8	9.1	2.5	3.0	3.0	2.8
7	2.5	2.7	1.2	2.1	2.1	0.9	6.5	10.8	1.3	5.5	8.3	1.2
8	2.3	2.2	1.3	1.9	1.8	1.3	2.4	2.6	2.4	1.4	1.5	1.3
9	3.0	7.9	3.0	3.0	7.8	2.6	3.2	8.5	3.5	3.9	6.8	5.2
10	4.9	4.0	2.2	5.7	7.3	1.2	4.6	6.8	1.1	4.3	6.5	1.1
11	13.6	19.4	12.9	13.6	19.2	13.7	12.8	17.0	9.8	11.7	14.7	5.6
12	7.0	1.7	1.3	7.0	11.6	2.5	6.7	11.4	1.2	7.8	9.4	2.1
13	2.8	1.8	0.9	2.9	1.7	1.2	2.5	1.5	1.1	2.9	1.3	0.9
14	3.7	5.7	1.1	4.6	7.0	0.6	5.8	8.9	0.6	3.0	4.6	0.3
15	1.9	3.2	0.9	1.4	2.4	1.2	2.3	3.9	1.8	2.6	4.4	0.4
16	6.6	6.6	1.0	6.9	6.9	2.4	7.0	7.0	1.4	7.0	7.0	0.7
17	4.5	12.3	0.7	3.0	8.5	0.7	4.8	13.3	1.8	5.9	16.2	0.2
18	1.5	21.4	10.0	1.6	20.1	9.5	2.3	22.3	16.8	1.9	19.4	9.5
AAA	4.5	5.7	3.6	4.1	5.9	3.2	9.0	7.6	7.1	5.0	6.1	2.9

AAA = Average of Average Absolute Percent Deviation for all of the systems studied.

evaluated. A data bank based on the saturated properties of refrigerants as reported in the ASHRAE handbook of Fundamentals and experimental data reported in the literature were used as the basis for this evaluation. In order to increase the accuracy of each equation of state, specific binary interaction parameters were optimized for each equation of state. Typical optimized binary interaction parameters for several binary refrigerants are presented. The saturated properties of four different azeotropic refrigerant mixtures were calculated and compared with the values reported in the ASHRAE handbook. For each property the percent error over a wide temperature range was calculated and plotted as a function of reduced temperature. Typical variations of percent error with reduced temperature for several mixture are presented. In addition, the average absolute percent error for the bubble point pressure and vapor liquid equilibrium ratios using each equation of state were calculated and presented.

The summary of the errors indicates that all three EOS considered perform well when applied to predict bubble point pressure, saturated vapor volume, and heat of vaporization. However, their accuracy for prediction of saturated liquid density is not as good as one would desire. The lack of accuracy for prediction of liquid density is more pronounced in the case of the SRK and PR.

Of the three EOS considered, the PR gave better performance in predicting the properties of refrigerant mixtures. Based on this evaluation, application of the PR for calculating thermodynamic properties of refrigerants is recommended. However, for saturated liquid density, a method such as that proposed by Hankinson and Thomson (1979) is recommended.

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NOMENCLATURE

A, B, and C = weighting factors

a_{jn} = binary interaction coefficient of energy term between molecules j and n
b = molecular volume of system, m^3/k mole
b_i = molecular volume of component i, m^3/k mole
C = calculated property
E = experimental property
E_j = energy term for group j
E_{jn} = interaction energy term between groups j and n
g = total number of groups in system
i = experimental data point
K_1 = vapor-liquid equilibrium ratio for component 1
K_2 = vapor-liquid equilibrium ratio for component 2
k_{ij} = binary interaction coefficient between molecules i and j
l_{ij} = binary interaction coefficient between molecules i and j
m_{ij} = number of groups j in molecule i
ND = number of data points
P = bubble point pressure
p_{jn} = binary parameter between groups j and n
q_{jn} = binary parameter between groups j and n
s_i = degrees of freedom of component i
v = volume of system, m^3/k mole
$x = b/v$
y_i = mole fraction of component i
Z = compressibility factor
Γ_j = fraction of volume for group j
Θ_{jn} = energy parameter between groups j and n

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APPENDIX A

Parameters From Molecule Contribution Equation of State

The dimensionless form compressibility factor is

$$Z = 1 - (s/x) - s + 12bx \sum_{n}^{g} \Gamma_n \left[\frac{1 - \sum_j \Gamma_j \Theta_{nj}}{1 - x + x \sum_j \Gamma_j \Theta_{nj}} \right]$$

$$b = \sum_{j}^{c} \sum_{i}^{c} y_i y_j \left(b_i b_j \right)^{0.5} k_{ij}$$

$$b = \sum_{j}^{c} \sum_{i}^{c} y_i y_j \left(b_i b_j \right)^{0.5} k_{ij}$$

$$s = \sum_{j}^{c} \sum_{i}^{c} y_i y_j \left(s_i s_j \right)^{0.5} l_{ij}$$

The fraction of molecular volume for group j is

$$\Gamma_j = \left(\sum_{i}^{c} y_i m_{ij} b_j \right) / b$$

The interaction energy function between groups j and n is

$$\Theta_{jn} = \exp\left(-E_{jn} / RT \right)$$

The interaction energy parameter between groups j and n is given by

$$E_{jn} = a_{jn} \left(E_j + E_n \right) / 2$$

The binary interaction coefficient, a_{jn} is defined as a linear function of temperature

$$a_{jn} = p_{jn} + q_{jn} T / 1000$$