Journal of Fluorine Chemistry, *37* (1987) 103–112

Received: February 10, 1987; accepted: May 8, 1987

PREDICTION OF THE CRITICAL LOCUS OF BINARY MIXTURES OF FLUOROCOMPOUNDS WITH HYDROCARBONS

T.A. AL-SAHHAF*, A.H.N. MOUSA
Chemical Engineering Department
P.O.Box 5969, Kuwait University
13060 Safat (Kuwait)

SUMMARY

The critical temperatures and pressures for 14 binary mixtures of fluorocompounds with hydrocarbons were correlated using an iteration procedure based on a cubic equation of state. The predicted values were compared with previously measured values, the agreement being very good.

INTRODUCTION

Since their discovery, fluorine-compounds [1] are finding increasing use in industry. Some studies about vapor-liquid equilibria and critical properties [2,3] for pure fluoro-compounds have been reported. As for binary systems very little work has been done.

Many empirical and semiempirical procedures have been developed for the prediction of critical properties of mixtures. Spencer et al. [4] made an extensive evaluation of available correlations for predicting properties of binary mixture. They recommended Li's method [5] for critical temperature prediction and the method of Kreglewski and Kay [6]

0022-1139/87/$3.50

for critical pressure measurement. Peng and Robinson [7] proposed the application of an equation of state in conjunction with the rigorous critical criteria in the prediction of critical states for binary and multicomponent mixtures. More recent methods of Heidermann and Khalil [8] and Michelsen and Heidermann [9] which utilize the Gibbs criteria for criticality with a cubic equation of state, have reduced the number of mathematical operations needed. Teja *et al.* [10] and Peng [11] correlated the critical temperatures and critical pressures of binary mixtures by use of a modified two-parameter Wilson equation.

None of these methods was used for fluoro-compounds. Mousa [12] used a method based on the acentric factor and a compensating factor. In this work, the method of Heidermann and Khalil [8] with the Soave-Redlich-Kwong equation of state [13] is used to correlate the binary critical locus for binary systems containing fluoro-compounds.

THEORY

Based on Gibbs criteria for the critical state of a mixture, Heidermann and Khalil [8] derived equations which must be satisfied at the critical point of a mixture of n components:

$$d^2 A = \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} \left(\frac{\partial^2 A}{\partial N_i \, \partial N_j} \right) \Delta N_i \, \Delta N_j = 0 \qquad (1)$$

$$d^3 A = \sum_{i} \sum_{j} \sum_{k} \left(\frac{\delta^3 A}{\partial N_i \, \partial N_j \, \partial N_k} \right) \Delta N_i \, \Delta N_j \, \Delta N_k = 0 \qquad (2)$$

it can be shown that

$$\frac{\partial^2 A}{\partial N_i \; \partial N_j} = RT \left(\frac{\partial \ln f_i}{\partial N_i} \right)_{T,V} \qquad (3)$$

$$\frac{\partial^3 A}{\partial N_i \; \partial N_j \; \partial N_k} = \left(\frac{\partial^2 \ln f_i}{\partial N_j \; \partial N_k} \right) \qquad (4)$$

The fugacity derivatives are evaluated using an equation of state. In this work the Soave-Redlich-Kwong equation (SRK) is implemented. The SRK is given by

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)} \qquad (5)$$

The parameters a and b for the pure components are given by:

$$a_i = a_{c_i} \; \alpha_i \qquad (6)$$

$$a_{c_i} = 0.42747 \; R^2 \; T^2_{ci}/P_{ci} \qquad (7)$$

$$\alpha_i^{1/2} = 1 + K \left[1-(T/T_{c_i})^{1/2} \right] \qquad (8)$$

$$K = 0.48 + 1.574 \; \omega_i - 0.176 \; \omega^2_i \qquad (9)$$

and $$b_i = 0.08646 \; R \; T_{c_i}/P_{c_i} \qquad (10)$$

The following mixing rules are used for mixtures

$$a = \sum_i^n \sum_j^n x_i \; x_j \; a_{ij} \qquad (11)$$

where $$a_{ij} = (1- k_{ij}) \; a_i^{1/2} \; a_j^{1/2} \qquad (12)$$

and k_{ij} is a binary interaction coefficient specific to each binary pair in the mixture.

$$b = \sum_i^n x_i \; b_i \qquad (15)$$

The expression for the fugacities of the different components in the mixture is given by Soave. The derivatives of the fugacities with respect to mole numbers were obtained and inserted in the previous equations. The critical temperatures and volumes were calculated using nested iterations of equations [3] and [4] as given by Heidemann and Khalil [8]. Then the critical pressures were calculated fro equation (5).

RESULTS AND DISCUSSION

The critical properties for 14 binary systems were calculated and compared with the experimental data of Mousa [12] and [14]. The critical properties for the pure components were taken from [12] and [14], whereas the acentric factors were taken from [6].

For each binary system, the binary interaction coefficient k_{ij}, was adjusted to obtain the best correlation between the experimental and calculated critical pressures and temperatures. The optimum value of k_{ij} was found by minimizing the following objective function (15):

$$\min \quad \sum \left[\frac{(T_{c\,exp} - T_{c\ calc.})^2}{\sigma_T^2} + \frac{(P_{c\ exp} - P_{c\ calc.})^2}{\sigma_P^2} \right]$$

where σ_T and σ_P are the standard deviation of temperature and pressure in the experimental data. The estimated values of σ_T and σ_P are 0.2 K and 0.034 bars respectively. The critical volumes of the mixture were also calculated, but no comparison was made because no experimental values are available.

A summary of the results for the 14 systems studied are presented in Table 1 which presents the optimum k_{ij} along with the percent average absolute deviations (AAD%) in pressures and temperatures for each system. Comparisons between the experimental and calculated critical temperatures and pressures and the calculated critical volumes are shown in Table 2.

The calculated critical temperatures and pressures agree very well with experimental values. The deviations of the calculated pressures are higher than those of the critical temperatures. The best fit is obtained for the [C_3H_8 + n-C_6F_{14}] system. While the systems [C_3H_8 + n-C_7F_{16}] gave the lowest fit. The optimum values for k_{ij} lies between 0.128 and 0.175 except for the systems [C_3H_8 + C_6F_6] and [n-C_6H_{14} + C_6F_6] and [C_3H_8 + n-C_7F_{16}]. For the two systems with [C_6F_6], k_{ij} has the lowest values. It is evident that the value of k_{ij} is specific to each hydrocarbon-fluorocarbon pair.

The parameters used in the SRK equation of state were developed using mostly data for hydrocarbons. As demonstrated by several authors [7], the prediction of the critical temperature and pressure is generally good, but use of the cubic equation of state to predict critical volumes is expected to cause higher errors. This work

TABLE 1

Binary interaction coefficients and average absolute deviations in T_c and P_c

Systems	k_{ij}	AAD% $\Delta T/T$	AAD% $\Delta P/P$
$C_3H_8 + CF_3CN$	0.128	0.17	2.15
$C_3H_8 + CF_3COCF_3$	0.145	0.125	1.17
$C_3H_8 + n\text{-}C_6F_{14}$	0.136	0.32	0.66
$C_3H_8 + C_3F_8$	0.165	0.13	1.91
$C_3H_8 + C_6F_6$	0.08	0.96	4.06
$C_3H_8 + n\text{-}C_7F_{16}$	0.195	1.08	5.05
$n\text{-}C_4H_{10} + n\text{-}C_7F_{16}$	0.165	0.516	2.33
$n\text{-}C_5H_{12} + C_4F_8$	0.165	0.45	3.63
$n\text{-}C_5H_{12} + n\text{-}C_7F_{16}$	0.125	0.66	2.89
$n\text{-}C_6H_{14} + C_6F_6$	0.08	0.17	2.27
$n\text{-}C_6H_{14} + n\text{-}C_6F_{14}$	0.17	0.14	2.97
$n\text{-}C_6H_{14} + n\text{-}C_7F_{16}$	0.148	0.31	1.91
$n\text{-}C_7H_{16} + n\text{-}C_7F_{16}$	0.165	0.25	1.62
$n\text{-}C_8H_{18} + n\text{-}C_7F_{16}$	0.175	0.49	3.10

$$\text{AAD\% } \Delta T/T = \frac{1}{m} \sum_{i=1}^{m} \left| \frac{T_{c_{exp}} - T_{c_{calc.}}}{T_{c_{exp}}} \right| . (100)$$

$$\text{AAD\% } \Delta P/P = \frac{1}{m} \sum_{i=1}^{m} \left| \frac{P_{c_{exp}} - P_{c_{calc.}}}{P_{c_{exp}}} \right| . (100)$$

where m is the number of experimental points

demonstrates the applicability of the SRK equation of state

TABLE 2

Comparison between experimental and calculated critical properties

System	Mole Fraction of Hydrocarbon	Crit. Temp. K		Crit. Press MPa		Crit. Volume m^3/kg mole
		Exp.	Calc.	Exp.	Calc.	Calc.
C_3H_8 + CF_3CN						
	.1188	311.94	312.24	3.61	3.68	.2352
	.3340	318.59	319.43	3.77	3.84	.2312
	.5504	332.53	333.12	4.07	4.16	.2243
	.7130	345.00	346.08	4.25	4.36	.2243
	.8435	357.17	357.02	4.31	4.41	.2288
C_3H_8 + CF_3COCF_3						
	.1240	353.57	353.55	2.97	3.00	.3308
	.3194	349.05	348.76	3.12	3.16	.3109
	.4437	346.90	347.02	3.21	3.26	.2988
	.7047	351.38	350.47	3.58	3.61	.2683
	.8573	359.48	358.59	3.91	3.95	.2495
C_3H_8 + $n-C_6F_{14}$						
	.1225	443.20	443.00	2.21	2.23	.5996
	.3287	430.19	430.55	2.83	2.83	.5041
	.5781	405.50	408.82	3.56	3.53	.3958
	.7345	388.50	390.86	3.79	3.77	.3381
	.8695	375.67	375.18	3.88	3.86	.2950
	.9088	372.57	371.77	3.95	3.91	.2806
C_3H_8 + C_3F_8						
	.1162	341.73	341.82	2.77	2.82	.3405
	.3233	337.77	337.51	2.93	2.99	.3178
	.4263	337.38	336.78	3.03	3.08	.3066
	.5232	338.37	337.58	3.13	3.19	.2945
	.7060	345.28	344.49	3.45	3.53	.2670
	.9074	360.40	360.48	3.99	4.08	.2427
C_3H_8 + C_6F_6						
	.1008	508.13	509.11	3.67	3.75	.3986
	.3027	488.66	490.81	4.35	4.55	.3453
	.5319	454.53	461.92	5.06	5.30	.2890
	.7314	420.39	427.45	5.10	5.39	.2510
C_3H_8 + $n-C_7F_{16}$						
	.0940	468.09	470.47	2.20	1.95	.7333
	.3120	450.41	457.00	3.03	2.74	.5935
	.5150	430.91	437.58	3.66	3.58	.4664
	.7200	404.62	406.38	4.10	4.14	.3521
	.8090	394.23	389.60	4.12	4.07	.3186
	.9080	377.63	372.60	4.11	3.89	.2920
$n-C_4H_{10}$ + $n-C_7F_{16}$						
	.1300	467.26	468.77	1.97	1.94	.7224
	.3090	455.57	458.45	2.39	2.33	.6285
	.4620	444.21	447.45	2.68	2.64	.5526
	.6770	428.26	429.12	2.99	2.94	.4594
	.9160	420.80	417.88	3.36	3.21	.3613

(Continued)

TABLE 2 (cont.)

System	Mole Fraction of Hydrocarbon	Crit. Temp. °K		Crit . Press MPa		Crit. Volume m^3/kg mole
		Exp.	Calc.	Exp.	Calc.	Calc.
n-C_5H_{12}	+ C_4F_8					
	.1601	388.98	389.19	2.81	2.86	.3771
	.2850	393.24	393.28	2.89	2.95	.3695
	.5076	406.43	409.34	3.12	3.28	.3447
	.6901	423.77	428.70	3.39	3.60	.3342
	.9141	453.10	454.46	3.58	3.68	.3474
n-C_5H_{12}	+ n-C_7F_{16}					
	.2910	460.29	463.52	2.16	2.08	.6660
	.5350	451.36	453.20	2.45	2.40	.5662
	.6100	449.42	450.55	2.51	2.49	.5361
	.7770	452.09	448.31	2.81	2.77	.4638
	.9130	459.54	454.42	3.04	3.19	.3958
n-C_6H_{14}	+ C_6F_6					
	.0813	513.79	512.96	3.24	3.33	.4271
	.2961	506.65	505.49	3.14	3.23	.4338
	.5071	502.80	501.64	3.08	3.15	.4418
	.6541	502.31	501.35	3.05	3.11	.4466
	.8875	505.00	504.71	3.04	3.09	.4535
n-C_6H_{14}	+ n-C_6F_{14}					
	.1012	447.16	446.8	1.89	1.96	.6372
	.3352	446.66	446.09	2.02	2.10	.5915
	.5018	451.68	451.80	2.20	2.26	.5480
	.6242	461.49	460.75	2.40	2.46	.5087
	.9020	492.57	493.99	2.92	2.98	.4565
n-C_6H_{14}	+ C_7F_{16}					
	.2940	464.80	467.72	1.96	1.90	.6984
	.3790	464.74	466.57	1.97	1.97	.6717
	.5260	467.03	466.90	2.18	2.11	.6223
	.6620	472.67	471.53	2.33	2.29	.5684
	.8340	486.98	2.69	2.66	.4974	
n-C_7H_{16}	+ C_7F_{16}					
	.1000	471.82	473.29	1.75	1.72	.7680
	.1430	471.68	472.86	1.78	1.74	.7577
	.1780	471.87	472.64	1.81	1.76	.7493
	.2320	472.93	472.59	1.83	1.79	.7361
	.3620	474.92	474.40	1.88	1.88	.7009
	.4700	478.50	478.71	1.97	1.98	.6645
	.9040	522.07	526.07	2.63	2.69	.5384
n-C_8H_{14}	+ n-C_7F_{16}					
	.0540	474.79	474.72	1.75	1.69	.7830
	.2760	482.28	479.77	1.83	1.79	.7378
	.4740	493.50	495.04	1.98	2.02	.6629
	.5300	501.10	501.29	2.08	2.12	.6392
	.5760	502.37	506.98	2.09	2.20	.6218
	.9010	548.83	555.11	2.50	2.57	.6056

to thermodynamic calculation for hydrocarbon-flourocarbon systems. The critical loci (T_c and P_c vs x) for the systems studied have simple continuous curves, and no problems were encountered in correlating their behavior using SRK equation of state.

ACKNOWLEDGEMENT

The authors would like to thank Dr. S. Hamam for his assistance and valuable suggestions.

NOMENCLATURE

a and b = parameters in equation of state

A = Helmoltz per energy

k_{ij} = binary interaction parameter

N = mole number

n = number of components

p = pressure

P_c = critical pressure

R = gas constant

T = temperature

T_c = critical temperature

v = molar volume

x = mole fraction

ω = acentric factor

REFERENCES

1 J.H. Simons and L.P. Block, J. Am. Chem. Soc. (1939) 2962.

2 A.H.N. Mousa, J. Fluorine Chem., 30 (1985) 29.

3 A.H.N. Mousa, J. Fluorine Chem., 25 (1984) 165.

4 C.F. Spencer, T.E. Danbert and D.F. Danner, AIChE J., 19 (1973) 522.

5 C.C. Li, J. Chem. Eng., 19 (1971) 709.

6 A. Kreglewski, and W.B. Kay, J. Phys. Chem., 73 (1969) 3359.

7 D.-Y. Peng, and D.B. Robinson, AIChE J., 23 (1977) 137.

8 R.A. Heidemann and A.M. Khalil, AIChE J., 26 (1980) 769.

9 M.L. Michelsen and R.A. Heidemann, AIChE J., 27 (1981) 521.

10 A.S. Teja, K.B. Garg and R.L. Smith, Ind. Eng. Chem. Process Des. Dev., 22 (1983) 672.

11 D.-Y. Peng, Can. J. Chem. Eng., 64 (1986) 827.

12 A.H.N. Mousa, W.B. Kay and A. Kreglewski, J. Chem. Thermodynamics, 4 (1972) 301.

13 G. Soave, Chem. Eng. Sci., 27 (1972) 1197.

14 L.W. Jordan and W.B. Kay, Chem. Eng. Sym. Series, 50 (1963) No.44.

15 C.R. Reid, J.M. Prausnitz and T.K. Sherwood, Properties of gases and liquids, Third Edition, McGraw-Hill (1977) 314.