International Journal of Thermophysics, Vol. 16, No. 1, 1995

Describing Vapor–Liquid Equilibria in Methanol + *n*-Alkane Systems by Means of an Equation of State with Association[1]

P. Voňka,[2,3] J. Lovland,[4] and T. Prokeš[2]

The ability of an equation of state incorporating association to describe vapor–liquid equilibrium of methanol + *n*-alkane systems has been tested. An equation of state with association is divided into "physical" and "chemical" parts, where the Patel–Teja cubic equation of state is used for the description of the physical part and an association term forms the chemical part. Five two- and three-parameter mixing rules were tested and compared with an equation of state without association. On the average for the first eight *n*-alkanes, the improvement in fit of pressure using association was 30–50% and the calculated vapor compositions were also much improved. In addition, there were fewer points with unstable liquid phase (false liquid–liquid split). Both with and without association, density-dependent mixing rules based on a local-composition concept gave the best result.

KEY WORDS: association; equation of state; false liquid–liquid split; methanol + *n*-alkane systems; mixing rule; vapor–liquid equilibrium.

1. INTRODUCTION

Modeling vapor–liquid equilibria (VLE) of polar + nonpolar mixtures of an alcohol and *n*-alkane is very difficult with present-day models. In addition to VLE, these mixtures have liquid–liquid equilibria at lower temperatures, and it is common to get a false liquid–liquid phase split when modeling VLE [1–3]. This phenomenon occurs because for a

---

[1] Paper presented at the Twelfth Symposium on Thermophysical Properties, June 19–24, 1994, Boulder, Colorado, U.S.A.

[2] Department of Physical Chemistry, Institute of Chemical Technology, 16628 Prague 6, Czech Republic.

[3] To whom correspondence should be addressed.

[4] Department of Chemical Engineering, Norwegian Institute of Technology, 7034 Trondheim, Norway.

0195-928X/95/0100-0227$07.50/0 © 1995 Plenum Publishing Corporation

binary system above the actual liquid–liquid region the gas mole fraction vs liquid mole fraction curve (y_1–x_1 curve) has a combination of a very steep, a very flat, and again, a very steep part. Trying to describe such a behavior typically gives an S-shape of the calculated y_1–x_1 curve, i.e., false liquid–liquid splits are predicted. The calculated upper critical points lie usually inside or above the experimental VLE region. Good description of liquid phase stability is important particularly if binary interaction parameters are used for phase behavior prediction of a multicomponent system.

In our previous work [3], we calculated VLE for methanol, ethanol, and 1-propanol with n-alkanes up through hexadecane using a modified Redlich–Kwong cubic equation of state (EOS) and a variety of mixing rules. In this paper we wish to look at fewer systems, but to focus on an EOS incorporating association and on comparison between an EOS with and an EOS without association from the point of view of fit of the experimental data and also from the point of view of description of liquid phase stability. The main goal of this paper is to show that the model considering chemical reality (association) will provide better results from both points of view.

2. EQUATION OF STATE AND MIXING RULES USED

2.1. Pure Compound

To include association, the compressibility factor is divided [4, 5] into a physical part and a chemical part,

$$z = z_{\mathrm{phys}} + z_{\mathrm{chem}} - 1 \tag{1}$$

where z_{phys} is the compressibility factor of a hypothetical compound without association and $z_{\mathrm{chem}} = n_t/n_0$, where n_t is the total number of true (real) moles (considering association) and n_0 is the total number of analytical moles (discounting association).

For the Kempter–Mecke association model [6], the chemical part is usually considered [4, 5, 7, 8] in the form

$$z_{\mathrm{chem}} = \frac{2}{1 + \sqrt{1 + (4RTK/P_{\mathrm{st}}v)}} \tag{2}$$

where P_{st} is standard pressure 0.101 MPa, R is the universal gas constant, T is the absolute temperature, $v = V/n_0$ is the volume of one analytical mole, and K is the equilibrium (association) constant of association reactions $A_1 + A_i = A_{i+1}$, $i = 1, 2, 3, \ldots$ where $A_1, A_2, A_3, \ldots$ stand for the monomer, dimer, trimer, etc. Derivation of the relation for the ratio n_t/n_0 is always based on the Heidemann and Prausnitz procedure [9]. The temperature dependence of the association constant K is expressed assuming that the standard heat capacity of association ΔC_p is independent of temperature [7, 8].

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

$$\Delta H = \Delta H_{298} + \Delta C_p(T - 298) \tag{3}$$

$$\Delta S = \Delta S_{298} + \Delta C_p \ln(T/298)$$

where ΔH_{298} and ΔS_{298} are the standard enthalpy and entropy of association at the temperature 298 K and the standard pressure P_{st}. Because these three values (ΔH_{298}, ΔS_{298}, and ΔC_p) are not known, they are used as adjustable parameters.

The Patel–Teja EOS [10]

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b) + c(v - b)} \tag{4}$$

is used in this work for the description of the physical part [see Eq. (1)]. The general relations $a = a_c f(T_r)$, $b = b_c$, and $c = c_c$ are applied, where $T_r = T/T_{c1}$. The critical values of the parameters a, b, and c are determined from the critical temperature T_{c1}, critical pressure P_{c1}, and critical compressibility factor z_{c1} of the hypothetical not self-associated monomer (denoted by subscript 1) in the usual manner. Because these values are not known we use them again as adjustable parameters. The function f is considered in the form $f = \exp\{\alpha(T_r - 1)\}$ containing only one explicit adjustable parameter α.

For the alkanes, which are nonassociating, we used a modified Redlich–Kwong EOS [3]. For this EOS, $c = 0$, and the values of the parameters a_c and b are fitted in the usual way to the experimental critical T and P. The function $f(T_r)$ in the above-mentioned general relation $a = a_c f(T_r)$ is given here by

$$f(T_r) = \exp\left[\sum_j \alpha_j (T_r^{m_j} - 1)\right] \tag{5}$$

where α_j, $j = 1, 2, \ldots$, are adjustable parameters. The Wagner's set of exponents $\{m\} = \{1, 1.5, 3, 6\}$ is used. The same EOS was used for methanol as well, for the cases without association, which were calculated for comparison.

2.2. Mixing Rules

For binary system, the compressibility factor is divided into a physical part and a chemical part just as for the pure components.

Let us first consider the physical part, Eq. (4). The classical quadratic mixing rules (which satisfy the low-density limit and are invariant to dividing a component into a number of identical subcomponents [11]) are used for parameters a, b, and c with the following general form of cross-terms

$$\begin{aligned} b_{12} &= \frac{b_{11}+b_{22}}{2}(1-k_1), \qquad c_{12}=\frac{c_{11}+c_{22}}{2} \\ a_{12} &= a_{12}^0\left(1-k_2-\frac{k_7}{T}-H(T,v,x_1,b,k_4,k_5)\right) \qquad (6) \\ a_{12}^0 &= \sqrt{a_{11}a_{22}} \end{aligned}$$

H is a nonrandom term proposed on the basis of the local-composition concept [12] and extended in [3].

$$H=\frac{1}{2}\left(\frac{k_4E_{12}}{x_1E_{12}+x_2}+\frac{k_5E_{21}}{x_1+E_{21}x_2}\right) \qquad (7)$$

where

$$E_{12}=\exp[-k_4\alpha], \qquad E_{21}=\exp[-k_5\alpha], \qquad \alpha=\frac{a_{12}^0\ln(1+\beta)}{RT(v_1-v_2)} \qquad (8)$$

In Eq. (8), $\beta=(v_1-v_2)/(v-v_1)$ and v_1, v_2 are roots of the equation $v(v+b)+c(v-b)=0$. The adjustable interaction parameters "k" are numbered in agreement with Ref. 3. An arbitrary subset of the five parameters k_1, k_2, k_4, k_5, and k_7 in Eqs. (6) and (7) can be chosen.

For the chemical part we get the following formulae when only one of the components is associating [7]:

$$z_{\mathrm{chem}}=\frac{2x_1}{1+\sqrt{1+(4RTK_{11}x_1/P_{\mathrm{st}}v)}}+x_2 \qquad (9)$$

where x_1 and x_2 are the apparent (analytical) mole fractions of the associating and nonassociating component, respectively. For this case, the chemical part z_{chem} does not contain any "chemical" binary interaction parameters. It means that the same binary interaction (adjustable) parameters are used whether we consider association or not. Therefore we can compare models with and without association containing the same set of binary interaction (adjustable) parameters.

3. METHOD OF CALCULATION

3.1. Pure Compound

3.1.1. Nonassociating (Inert) Compound

The sum of weighted squares of differences between $a_{i,\mathrm{exp}}$ and $a_{i,\mathrm{calc}}$ was used as the objective function for determination of the adjustable parameters $\{\alpha_j\}$ [see Eq. (5)], where $a_{i,\mathrm{exp}}$ is the value of the parameter "a" guaranteeing the same value of calculated and experimental vapor pressure at the experimental temperature T_i.

3.1.2. Associating Compound

As seen in Section 2.1, the model has seven parameters: T_{c1}, P_{c1}, z_{c1}, α, ΔH_{298}, ΔS_{298}, and ΔC_{p}. To reduce the number of adjustable parameters, an arbitrary but fixed value of z_{c1} was selected before the fit, since this parameter can be given a reasonable value beforehand. The remaining six parameters are determined by a nonlinear least-squares technique from vapor-pressure data, second-virial coefficient data, and gaseous PVT data. As initial values the critical values of the homomorph [5] (we used ethane as methanol's homomorph) were used and, also, the values $\alpha = -0.75$, $\Delta H_{298} = -20\ \mathrm{kJ \cdot mol^{-1}}$, $\Delta S_{298} = -80\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, and $\Delta C_{\mathrm{p}} = 0$.

3.2. Binary Mixture

For the binary system, the sum of squares of relative differences between experimental and calculated pressures was chosen as the objective function for the determination of the chosen set of adjustable parameters, and thus the percentage mean square deviation δP (%) serves as a measure of goodness of fit. Also, the absolute mean square deviation δy of the gas phase composition was determined. Since the values of the gas composition are not included in the objective function, the value of δy has a predictive character.

For each binary system and each mixing rule all VLE data were fitted together and two models were considered. In the first of them ("without association"), methanol is considered as a nonassociating (inert) compound, i.e., $K_{11} = 0$. In the second model ("with association"), methanol is considered as a self-associating compound.

To get information about the region of false liquid-liquid split, the values of G11 (the second derivative of the molar Gibbs energy with respect of liquid mole fraction x_1 at the constant temperature and pressure) were calculated from the fitted model in each experimental point (x_1, T). For each system and mixing rule the value of U (%)

$$U(\%) = 100 \frac{NUP}{N} \tag{10}$$

is calculated where NUP is the number of unstable points ($G11 < 0$) and N is the number of all experimental VLE points in the given binary system.

4. RESULTS

4.1. Pure Compound

4.1.1. Model Without Association

The use of three or four adjustable parameters in Eq. (5) gives a very good description of vapor-pressure data (less then 0.1%), but the calculated second-virial coefficient data of methanol have more than 50% systematic deviation from experimental data in the low-temperature region (300–320 K). In our opinion, the model without association gives good results for *n*-alkanes, but for methanol it is not possible to get a satisfactory simultaneous description of both vapor-pressure and gaseous PVT data.

4.1.2. Model With Association

Agreement between calculated and experimental vapor-pressure data of methanol is a little worse but still satisfactory (less than 1%). Description of the gaseous PVT data is much better than in the previous model; the second-virial data have less than 10% deviation over the whole temperature interval. The following optimal values of the adjustable parameters were determined for methanol: $T_{c1} = 437.42$ K, $P_{c1} = 7.358$ MPa, $z_{c1} = 0.291$, $\alpha = -0.6633$, $\Delta H_{298} = -19.13\ \mathrm{kJ \cdot mol^{-1}}$, $\Delta S_{298} = -86.46\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, and $\Delta C_p = -31.79\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. They are in a very good agreement with those obtained by Anderko [5] or Wenzel and Krop [8]. Anderko also compared calculated values ΔH_{298}, ΔS_{298}, and ΔC_p with calorimetric measurements.

Table I. Experimental Data for Methanol + *n*-Alkane Systems[a]

C_n	T(K)		P(MPa)		N	T_c(K)	Ref. No.
	Min	Max	Min	Max			
1	273.15	300.0	1.40	41.4	43	—	16
2	260.0	373.15	0.45	6.0	33	--	17-19
3	313.1	373.1	0.35	3.9	25	241.0	13, 20
4	273.15	373.15	0.006	1.72	34	266.5	21-23
5	303.0	422.6	0.101	2.53	28	286.9	23-25
6	322.6	492.6	0.101	6.0	36	307.2	13, 26, 27
7	332.0	531.5	0.101	6.8	26	324.5	14, 15, 27
8	335.9	539.2	0.101	6.9	48	339.3	14, 15, 27

[a] C_n = alkane number; N = number of binary experimental points; T_c = upper critical solution temperature at 0.1 MPa.

4.2. Binary Mixture

We have performed calculations for eight binary methanol + *n*-alkane systems. Information about the experimental data are presented in Table I. The value of the experimental upper critical solution temperature at atmospheric pressure, T_c, gives us information about the "distance" between the real liquid–liquid region and the experimental VLE region. We did not find any experimental data for T_c for methanol–methane and methanol–ethane systems.

The values of U (%), δP (%), and δy calculated for any given system, mixing rule, and model depend significantly on the distribution and quality of the experimental points; i.e., we cannot use such results for comparison

Table II. Results for Adjustable Parameters k_1 and k_2 [Eqs. (6) and (10)]

C_n	Without association			With association		
	U(%)	δP(%)	δy	U(%)	δP(%)	δy
1	0	20.6	0.023	0	9.5	0.008
2	3.0	16.1	0.006	0	6.6	0.008
3	20.0	14.2	0.015	12.0	7.5	0.012
4	14.7	8.3	0.032	14.7	3.8	0.023
5	10.5	11.6	0.074	10.5	6.8	0.066
6	11.1	4.4	0.105	8.3	4.3	0.087
7	19.2	6.2	0.176	15.4	4.8	0.124
8	16.7	8.9	0.138	16.7	6.6	0.088
Ave.	11.9	11.3	0.071	9.7	5.4	0.052

Table III. Results for Adjustable Parameters k_2 and k_7 [Eqs. (6) and (10)]

	Without association			With association		
C_n	U(%)	δP(%)	δy	U(%)	δP(%)	δy
1	0	7.2	0.019	0	5.8	0.004
2	0	6.0	0.020	0	9.1	0.015
3	28.0	9.3	0.025	16.0	3.7	0.018
4	5.9	11.9	0.033	2.9	4.7	0.020
5	7.9	18.2	0.089	10.5	7.4	0.069
6	8.8	7.9	0.166	2.9	5.4	0.021
7	13.6	8.2	0.182	9.1	5.8	0.090
8	26.2	9.5	0.106	19.0	7.1	0.043
Ave.	11.3	9.8	0.080	7.6	6.1	0.035

Table IV. Results for Adjustable Parameters k_4 and k_5 [Eqs. (6) and (10)]

	Without association			With association		
C_n	U(%)	δP(%)	δy	U(%)	δP(%)	δy
1	0	4.3	0.013	0	2.9	0.002
2	0	10.9	0.014	0	6.9	0.016
3	16.0	9.8	0.010	12.0	3.4	0.020
4	14.7	3.8	0.028	13.1	2.6	0.020
5	5.2	3.3	0.067	10.5	4.7	0.062
6	25.0	1.7	0.146	19.4	1.4	0.057
7	34.6	3.9	0.162	15.4	2.0	0.043
8	20.8	6.0	0.078	10.4	4.3	0.062
Ave.	14.5	5.5	0.065	10.1	3.5	0.035

Table V. Results for Adjustable Parameters k_1, k_2, and k_7 [Eqs. (6) and (10)]

	Without association			With association		
C_n	U(%)	δP(%)	δy	U(%)	δP(%)	δy
1	0	4.0	0.028	0	3.0	0.008
2	3.0	4.7	0.017	0	3.6	0.011
3	20.0	5.4	0.018	16.0	3.4	0.019
4	14.7	6.5	0.027	11.8	3.2	0.019
5	28.9	10.0	0.075	21.1	6.1	0.067
6	25.0	3.4	0.223	8.3	4.3	0.079
7	3.8	6.7	0.189	3.8	4.8	0.119
8	16.7	7.1	0.126	14.6	5.6	0.065
Ave.	14.0	6.0	0.088	9.5	4.3	0.048

Table VI. Results for Adjustable Parameters k_1, k_4, and k_5 [Eqs. (6) and (10)]

	Without association			With association		
C_n	U(%)	δP(%)	δy	U(%)	δP(%)	δy
1	0	2.6	0.017	0	2.8	0.002
2	0	5.1	0.014	0	4.3	0.013
3	12.0	5.0	0.021	0	2.5	0.020
4	11.8	2.4	0.022	2.9	1.0	0.018
5	10.5	1.2	0.065	5.3	1.2	0.064
6	41.7	1.3	0.063	11.1	0.5	0.056
7	34.6	3.2	0.081	15.4	1.8	0.045
8	10.4	3.4	0.132	8.3	1.3	0.008
Ave.	15.1	3.0	0.052	5.4	1.9	0.028

between two or more systems. But for a given system and mixing rule the calculated data can be used for comparison between the two models "without association" and "with association." The results are presented in Tables II–VI. The chosen set of binary interaction (adjustable) parameters is mentioned in the title of each table. If, for example, the mixing rule with adjustable parameters k_1 and k_2 is chosen (see Table II), then other parameters are equal to zero. The last row contains average values of U(%), δP(%), and δy for all considered n-alkanes.

5. DISCUSSION

As was expected, the model including association gave a better fit for the experimental data included in the fit, better prediction of the gas phase composition, and better representation of liquid phase stability. Considering only the average values for each mixing rule (the bottom line in each of Tables II–VI), the improvement in fit for the pressure is roughly 30–50%, with the biggest improvement for the simplest mixing rule (Table II). For the predicted vapor composition, the improvement is similar, but with no particular trend with mixing rule. For the percentage of unstable points the improvement is of the same order but, again, with no clear trend with mixing rule. The density-dependent mixing rules based on the local-composition concept (Tables IV and VI) give the best results. Even the use of three adjustable parameters, but without the local-composition concept (Table V), gives worse results for the average than the two-parameter local-composition rule does (Table IV), both with and without association. This is in accord with our previous work [3].

A number of other authors have also calculated the VLE of methanol-alkane binaries by means of an EOS but there is no case exactly comparable to ours, because of different data, mixing rules, objective functions, or other aspects. Typically, most others have fitted each isotherm separately (which may give a better fit), while we have fitted them simultaneously. Our results are fairly consistent with those of others.

Even if association is clearly a great model improvement for these alkanol–alkane systems, we still get false liquid–liquid splits. Probably it is not possible to achieve much better results with a relatively simple model for such complex system. Although false liquid–liquid split may be minimized or avoided, the price is a worse fit to the VLE data [3]. Thus, a good description of alkanol–alkane systems remains a challenge.

ACKNOWLEDGMENT

This research was funded by the SPUNG program under the Norwegian NTNF research council.

REFERENCES

1. J. Schwartzentruber, F. Galivel-Solastiouk, and H. Renon, *Fluid Phase Equil.* **38**:217 (1987).
2. P. Englezos, N. Kalogerakis, and P. R. Bishnoi, *Fluid Phase Equil.* **53**:81 (1989).
3. P. Voňka, P. Dittrich, and J. Lovland, *Fluid Phase Equil.* **88**:63 (1993).
4. G. D. Ikonomou and M. D. Donohue, *Fluid Phase Equil.* **33**:61 (1987).
5. A. Anderko, *Fluid Phase Equil.* **45**:39 (1989).
6. H. Kempter and R. Mecke, *Z. Phys. Chem.* **46**:229 (1940).
7. A. Anderko, *AIChE J.* **37**:794 (1991).
8. H. Wenzel and E. Krop, *Fluid Phase Equil.* **59**:147 (1990).
9. R. A. Heidemann and J. M. Prausnitz, *Proc. Natl. Acad. Sci.* **73**:1773 (1976).
10. N. C. Patel and A. S. Teja, *Chem. Eng. Sci.* **37**:463 (1982).
11. M. L. Michelsen and H. Kistenmacher, *Fluid Phase Equil.* **58**:229 (1990).
12. J. Mollerup, *Fluid Phase Equil.* **22**:139 (1985).
13. A. F. Francis, in *Critical Solution Temperatures* (Am. Chem. Soc., Washington, DC, 1961), p. 115.
14. L. S. Budantseva, T. M. Lesteva, and M. S. Nemtsov, *Zh. Fiz. Khim.* **49**:1844 (1975).
15. J. B. Ott, I. F. Hoelscher, and G. M. Schneider, *J. Chem. Thermodyn.* **18**:815 (1986).
16. J. H. Hong, P. Malone, M. D. Jett, and R. Kobayashi, *Fluid Phase Equil.* **38**:83 (1987).
17. S. Zeck and H. Knapp, *Fluid Phase Equil.* **25**:303 (1986).
18. K. Oghaki, F. Sano, and T. Katayama, *J. Chem. Eng. Data* **21**:55 (1976).
19. Y. H. Ma and J. P. Kohn, *J. Chem. Eng. Data* **9**:3 (1964).
20. F. Galivel-Solastiouk, S. Laugier, and D. Richon, *Fluid Phase Equil.* **28**:73 (1986).
21. C. B. Kretschmer and R. Wiebe, *J. Am. Chem. Soc.* **74**:1276 (1952).
22. A. D. Leu, C. J. Chen, and D. B. Robinson, *AIChE Symp. Ser.* **271**(85):11 (1989).
23. U. Haarhaus and G. M. Schneider, *J. Chem. Thermodyn.* **20**:1121 (1988).
24. L. S. Budantseva, T. M. Lesteva, and M. S. Nemtsov, *Zh. Fiz. Khim.* **49**:1848 (1975).
25. R. D. Wilsak, S. W. Campbell, and G. Thodos, *Fluid Phase Equil.* **33**:157 (1987).
26. L. S. Budantseva, T. M. Lesteva, and M. S. Nemtsov, *Zh. Fiz. Khim.* **49**:260 (1975).
27. Th. W. de Loos, W. Poot, and J. de Swaan Arons, *Fluid Phase Equil.* **42**:209 (1988).