An augmented hard core equation of state generalized in terms of T_c, P_c, and ω

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Abstract – A generalized Carnahan–Starling hard core equation of state perturbed by attractive forces is presented for nonpolar fluids. The information required is the critical temperature the critical pressure and Pitzer's acentric factor. Realistic predictions of the critical compressibility factor and second virial coefficients are ensured and the representation of pure compound liquid molar volumes in the reduced temperature range of 0.5 to 1.0 is improved significantly over cubic equations of state. The equation of state is then modified for 1-alkanols and extended to mixtures by augmenting the mixing rules of Arai et al.

INTRODUCTION

The use of equations of state to represent volumetric properties and to correlate phase equilibria of fluids has been very popular recently. The widely used cubic equations of state, although simple and successful in most cases, have some inherent limitations: they predict too large compressibility factors and they do not represent accurately second virial coefficients. The first of these shortcomings causes cubic equations to give significant deviations in liquid densities in the proximity of the critical point while the second shortcoming affects the representation of fugacities in the vapor phase at low reduced temperatures. A more precise representation of the volumetric properties and of phase equilibrium conditions requires the use of multiparameter equations of state. These equations are less attractive due to the large number of parameters required to describe the volumetric properties of each pure compound.

In this work a multiparameter equation of state previously developed by Orbey and Vera (ref. 1), which allows realistic estimations of critical compressibility factors and of second virial coefficients is first generalized for nonpolar substances in terms of T_c, P_c and Pitzer's acentric factor, ω. This generalized form is then modified for 1-alkanols and the equation is extended to mixtures by modifying the mixing rules of Arai et al. (ref. 2).

THE GENERALIZED AUGMENTED HARD-CORE EQUATION OF STATE

As described previously (ref. 1), the equation of state has the form

$$z = z_0 + \sum_{i=1}^{4} b_i^0/v^i \tag{1}$$

where z_0 is given by the expression proposed by Carnahan and Starling (ref. 3) for non-attracting hard spheres, that is

$$z_0 = (v^3 + v_0 v^2 + v_0^2 v - v_0^3) / (v - v_0)^3 \tag{2}$$

The above formulation follows the generalized van der Waals theory (ref. 4, 5) and thus is similar to other hard core models presented in the literature (refs. 6–8). The basic difference resides in the method used to evaluate the parameters v_0 and b_i, where i=1 to 4. In this work we basically follow a method proposed earlier (ref. 1) but with generalized terms. Based on the studies of the representation of the critical isotherms of alkanes, we propose to use the following generalized form for v_0 of nonpolar compounds

$$v_0 = 0.2272 \, z_c R \, T_c/P_c \tag{3}$$

with z_c obtained from the expression,

$$z_c = 0.291 - 0.08 \, \omega \tag{4}$$

The terms of the energetic contribution are expressed in a virial coefficient-like way as

$$b_i = b_i^o + x_i v_o^i \tag{5}$$

where the numerical constants x_i arising from the expansion of equation (2) take the values 4,10,18, and 28 for i from 1 to 4, respectively.

With the exception of b_1, which corresponds to the second virial coefficient and is directly taken from the Tsonopoulos correlation (ref. 9), the b_i terms are related to their values at the critical temperature, b_{ic}, by relations of the form

$$b_i = b_{ic}(f_i^o + \omega f_i^1) \tag{6}$$

The b_{ic} values for i=2 to 4 are obtained from the conditions of the critial point i.e.,

$$(\partial p/\partial v)_c = 0 \tag{7}$$

$$(\partial^2 p/\partial v^2)_c = 0 \tag{8}$$

combined with the condition imposed by the relation given in equation (4) as detailed elsewhere (ref. 1). The particular forms of the functions of reduced temperature f_i^o and f_i^1 proposed in this work are given in Appendix I along with expressions for b_{ic}.

By exact thermodynamics, the following relations are obtained from the present equation of state

$$\ln \phi = (z_o - 1) - \ln z + 4 v_o/(v-v_o) + v_o^2/(v-v_o)^2 + \sum_{i=1}^{4} (i+1)b_i^o/(iv^i) \tag{9}$$

and

$$(h-h^{ig})/(RT) = z-1-T \left[\sum_{i=1}^{4} (\partial b_i^o/\partial T)/(iv^i) \right] \tag{10}$$

where ϕ is the fugacity coefficient, h is the molar enthalpy and h^{ig} is the molar enthalpy in the ideal gas state.

EXTENSION TO 1-ALKANOLS

Studies of saturation data of 1-alkanols up to 1-pentanol has shown that with the modifications explained below, a reasonable representation of saturation behaviour of these alkanols could be achieved with the present form of the equation of state.

With the exception of methanol, saturation liquid volume predictions of the alcohols studied greatly improved when the z_c value of 0.265 was used instead of z_c that was calculated from equation (4).

After changing z_c, in an attempt to improve saturation pressure predictions, f_2^o and f_2^1 functions were redefined, keeping all other procedures and functions the same. New versions of f_2^o and f_2^1 functions are given in Appendix II. In the evaluation of b_1 from the Tsonopoulos (ref. 9) relation, the correction reported by Tsonopoulos for alcohols was not employed.

EXTENSION TO MIXTURES

To extend the present equation of state to mixtures, the corresponding states approach proposed by Arai et al. (ref. 2) was used with a modification to improve its flexibility. Arai et al. propose the following equations based on the van der Waals one-fluid model for the computation of pseudocritical properties:

$$v_{ci} = z_{ci} RT_{ci}/P_{ic} \tag{11}$$

$$v_{cij} = (v_{ci}^{1/3} + v_{cj}^{1/3})^3/8 \tag{12}$$

$$v_{cm} = \sum_i \sum_j x_i x_j v_{cij} \tag{13}$$

$$\omega_m = \sum_i x_i \omega_i \tag{14}$$

$$T_{cij} = (T_{ci}T_{cj})^{1/2} (1-x_i k_{ij} - x_j k_{ji}) \tag{15}$$

$$T_{cm} = \sum_i \sum_j x_i x_j T_{cij} v_{cij}^n / v_{cm}^n \qquad (16)$$

$$z_{cm} = \sum_i x_i z_i \qquad (17)$$

$$P_{cm} = z_{cm} R T_{cm} / v_{cm} \qquad (18)$$

In the original Arai approach the power n in equation (16) is unity. In the present case it was used as a constant which may assume values other than unity, and 0.75 was found to be the best. In equation (15), $k_{ij} = k_{ji}$ for alkane/alkane and for alcohol/alcohol couples.

RESULTS AND DISCUSSION

In this study, the critical constants used were those reported in TRC tables (ref. 10). For alkanes experimental saturation pressures were obtained from TRC tables and from Vargaftik (ref. 11) compilation. Saturation liquid molar volumes were obtained from the correlation of Spencer and Adler (ref. 12). For alcohols saturation pressures compiled by Boublik et al. (ref. 13) were used. For saturation liquid volumes Joffe-Zudkevitch (ref. 14) correlation was used. For internal consistency Pitzer's acentric factor values were back calculated from the data for all substances. These ω values are given in Table 1.

TABLE 1. Pitzer's acentric factor values

methane	0.011	octane	0.397
ethane	0.099	methanol	0.572
propane	0.153	ethanol	0.635
butane	0.200	1-propanol	0.624
pentane	0.252	1-butanol	0.590
hexane	0.293	1-pentanol	0.580
heptane	0.350		

In Table 2, the average absolute deviations (AAD) in saturation pressure and saturation liquid volumes for the fluids investigated in this work are summarized. For comparison results from Peng-Robinson (ref. 15) equation were also included. For alkanes there is a significant improvement in the prediction of liquid saturation volumes. For alcohols saturation volumes are comparable, whereas saturation pressure predictions are usually better with the present approach.

TABLE 2. Results for pure compounds

substance	T_R range	data points	AAD[a] in P_{sat}		AAD in v_{sat}	
			this work	PR	this work	PR
methane	.6-.95	10	0.737	1.185	0.303	8.30
ethane	.6-.95	10	0.489	0.849	0.373	5.90
propane	.6-.95	10	0.708	0.533	0.545	4.90
butane	.6-.95	10	0.610	0.969	1.173	4.00
pentane	.6-.95	10	0.652	0.929	1.102	2.70
hexane	.6-.95	10	1.100	1.860	0.750	1.90
heptane	.6-.95	10	0.399	0.500	0.586	2.70
octane	.6-.95	10	0.334	0.310	0.507	4.10
methanol	.56-.70	20	0.801	5.35	15.600	16.40
ethanol	.57-.71	25	0.510	3.48	1.700	1.55
1-propanol	.62-.70	18	2.800	4.940	0.210	0.51
1-butanol	.64-.71	19	4.201	4.490	1.040	1.01
1-pentanol	.59-.73	19	14.57	12.63	1.35	1.34

[a] $AAD = (100/n) \sum_n abs(P_{exp,i} - P_{cal,i}) / P_{exp,i}$

For binary mixtures investigated in this work, a summary of the results are given in Table 3. For three of these binary systems, the results are also depicted in Figs. 1 to 3. For comparison, some alternative methods are also shown in these figures.

TABLE 3. Results for binary systems studied

System	Temp/K	data points	k_{12}/k_{21}	AAD in P	AAD in vapor composition	data source
ethane/ hexane	449.8 394.3	5 5	0/0 0/0	7.93 11.80	2.99 1.86	ref. 16
methanol/ ethanol	373	9	-0.005/-0.005	1.68	-	ref. 19
ethanol/ 1-propanol	353	9	0.007/0.007	1.27	1.75	ref. 19
pentane/ ethanol	397.7	10	0.09945/0.05655	3.02	3.74	ref. 18
hexane/ ethanol	328.15	17	0.0890/0.0355	14.10	13.41	ref. 19
ethanol/ heptane	353.15	9	0.1124/0.0650	10.52	7.48	ref. 19
heptane/ 1-propanol	348.15	21	0.0780/0.033	12.0	20.35	ref. 19

The method works well for the alkane-alkane couples. In Fig. 1 the results for ethane+ n-hexane binary system are presented. The experimental data are from Zais and Silberberg (ref. 16). The performance of the Peng-Robinson (ref. 15) EOS is also indicated in the figure. In this case, for both methods, $k_{12}=0$. Similarly good results are obtained with alcohol/alcohol binaries with one single k_{12}. For these cases, Peng-Robinson EOS gives comparable results. For example, for ethanol+1-propanol system, AAD in P is 1.69 and AAD in vapor composition is 3.32 with a k_{12} of 0.005 for Peng-Robinson model.
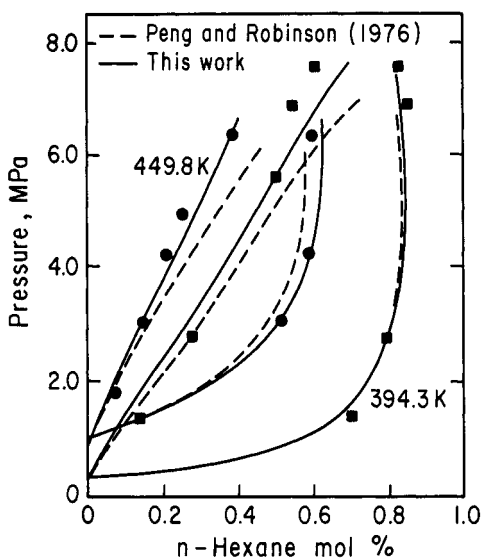

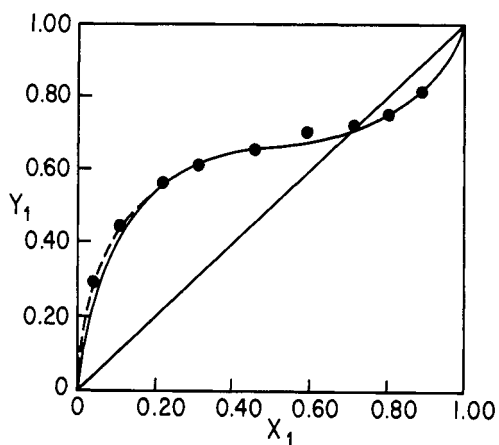Fig. 1. Predictions of ethane-hexane binary system

Fig. 2. Predictions of pentane-ethanol binary system

In the case of alcohol/alkane binary systems, it was necessary to use two different values for k_{ij} and k_{ji} following Stryjek and Vera (ref. 17). The results for n-pentane+ethanol system are depicted in Fig. 2. The dashed lines represent predictions by four suffix Margules equation as given by Campbell et al (ref. 18), the solid line represents the results obtained in the present study. Among the alcohol/alkane systems studied, the best results are obtained for this system where pressures are above atmospheric (up to 1197 kPa), the region for which the present EOS was originally developed. For other alkane/alcohol systems, in general the present model performs satisfactorily in mid-concentration regions and becomes less accurate at the limiting concentrations where pressures are subatmospheric. The results for n-heptane+1-propanol system are depicted in Fig. 3. The dashed lines represent
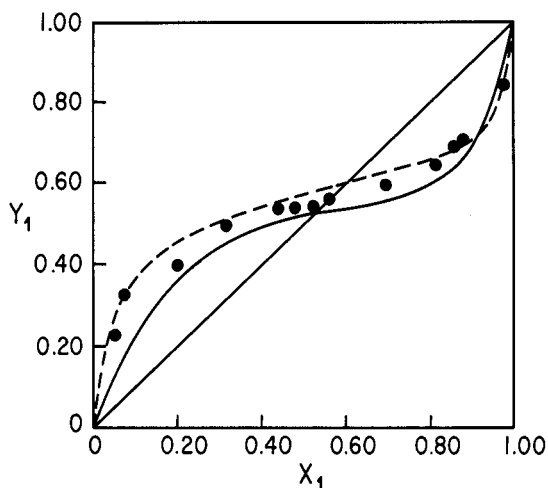

Fig. 3. Predictions of heptane-1-propanol binary system

predictions by the NRTL model, and the solid line represents predictions by the present method. The data are from Gmehling and Onken compilation (ref. 19). Since the generalized temperature functions of the present model are multipurpose functions aiming at a rather broad range of pressures, they are not particularly sensitive at subatmospheric pressures. For such low pressure applications of the model presented in this work, the temperature functions given in Appendices I and II can be further modified and upgraded using the techniques described in the text.

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APPENDIX I

$b_{1c}^{o} = b_{1c} - 4v_{o}$ where b is the second virial coefficient as obtained from the Tsonopoulos correlation.

Using equations (4), (7) and (8) of the text,

$b_{2c}^{o} = v_{c}^{2}(10F1-5F2+F3)$

$b_{3c}^{o} = v_{c}^{3}(-15F1+9F2-2F3)$

$b_{4c}^{o} = v_{c}^{4}(6F1-4F2+F3)$

where

$F1 = z_{c}-(z_{o})-b_{1c}^{o}/v_{c}$

$F2 = -(z_{o})_{c}-v_{c}(\partial z_{o}/\partial v)_{c}-2b_{1c}^{o}/v_{c}$

$F3 = F2-(1/2)v_{c}^{2}(\partial^{2}z_{o}/\partial v^{2})_{c} - b_{1c}^{o}/v_{c}$ with

$(\partial z_{o}/\partial v)_{c} = 2(v_{o}^{3} - 2v_{o}^{2}v_{c} - 2v_{o}v_{c}^{2})/(v_{c} - v_{o})^{4}$

$(\partial^{2}z_{o}/\partial v^{2})_{c} = 4(2v_{o}v_{c}^{2} + 5v_{o}^{2}v_{c} - v_{o}^{3})/(v_{c} - v_{o})^{5}$

b_{ic} values are calculated from the b_{ic}^{o} using equation(5) in the text. Functions of reduced temperature are

$f_{2}^{o} = 1.3683 - .4247/T_{R} - 4.4192/T_{R}^{2} + 7.9349/T_{R}^{3} - 4.3297/T_{R}^{4} + 0.8704/T_{R}^{5}$

$f_{2}^{1} = -1.1368 - 1.7570/T_{R} + 10.9073/T_{R}^{2} - 18.5242/T_{R}^{3} + 15.0749/T_{R}^{4} - 5.5618/T_{R}^{5} + 0.9976/T_{R}^{6}$

$f_{3}^{o} = -1.5893 + 5.0608/T_{R} - 4.1749/T_{R}^{2} + 1.7062/T_{R}^{3} - .0028/T_{R}^{8}$

$f_{3}^{1} = -.728 + 2.0237/T_{R} - 4.3467/T_{R}^{2} + 3.0193/T_{R}^{3} + .0317/T_{R}^{8}$

$f_{4}^{o} = .2328 + .2592/T_{R} + .2484/T_{R}^{2} + .2600/T_{R}^{3} - .0004/T_{R}^{8}$

$f_{4}^{1} = -.4653 - .8728/T_{R} + .5675/T_{R}^{2} + .7577/T_{R}^{3} + .0129/T_{R}^{8}$

APPENDIX II

For alcohols, f_{2}^{o} and f_{2}^{1} in the above set (APPENDIX I) should be replaced by

$f_{2}^{o} = 3.1394 - 3.0119/T_{R} - 1.1537/T_{R}^{2} + 2.0448/T_{R}^{3} - .0186/T_{R}^{8}$

$f_{2}^{1} = -3.3322 + 3.2670/T_{R} + .0652/T_{R}^{8}$