

A MODIFIED PERTURBED HARD-SPHERE EQUATION USING SOAVE'S ATTRACTIVE TERM

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ABSTRACT

A modified perturbed hard-sphere equation of state, represented by the Carnahan-Starling equation with the Soave's attractive part, has been investigated using the Mollerup approach for the energy parameter a for pure substances. The equation has been extended to mixtures, for both vapor-liquid equilibria and solid-supercritical fluid equilibria, using the Boublik-Mansoori equation with the same Soave's attractive part. The vapor pressure, density, second virial coefficient, specific heat capacity and enthalpy were examined for pure substances. The new equation was also able to predict accurately the vapor pressure of fatty acids. The predictions of both vapor-liquid equilibria and solid-supercritical fluid equilibria, using the one fluid van der Waals mixing rules with one binary interaction parameter, are significantly better than those obtained by cubic equation of state, especially for large molecules. The predictions for solid-supercritical fluid systems were improved by incorporating solute-solute interaction parameters. Density dependent mixing rules were also examined.

Keywords: Equation of state, Mixing rules, Perturbed hard-sphere, Solid-supercritical fluid, Vapor-liquid equilibria.

INTRODUCTION

Since van der Waals (VDW) proposed his Equation of state (EOS) more than 120 years ago, numerous attempts have been made to develop an analytical model of the EOS using either an empirical or theoretical approach. Empirical EOSs have been based partly on the VDW repulsive term while theoretical EOSs have been based on repulsive terms described by theoretical expressions. The Carnahan-Starling equation (CS-EOS) for hard sphere [1] and its extension to mixtures by Boublik [2] and Mansoori *et al.* [3] represents a considerable improvement in this area. In order to be applicable to real fluids, Carnahan and Starling [4] suggested two perturbation terms: the VDW perturbation term used by van der Waals [5] in 1873 and perturbation term used by Redlich and Kwong [6] in 1949.

Different perturbation terms were proposed by several authors (e.g. Beret and Prausnitz [7], Chen and Kreglewski [8], Donohue and Prausnitz [9], Brandani and Prausnitz [10], Aim and Nezbeda [11], Cotterman and Prausnitz [12], Gernzheuser and Gmeling [13], Cotterman *et al.* [14], Dohrn and Prausnitz [15]). Despite its so far limited empirical success, the Carnahan-Starling equation provides a better basis for developments broadly applicable EOS than does the popular hard-sphere reference equation used by van der Waals, Redlich-Kwong, Peng-Rubinson and many other. These common equations have been remarkable successful for numerous VLE calculations for hydrocarbon systems but their extension to more complex system has encountered severe difficulties.

Some studies on the use of empirical EOS's based on theoretical models such as a repulsive term, instead of the VDW repulsive term, have been published (Dimitrelis and Prausnitz [16], Bertucco *et al.* [17], Mathias *et al.* [18], Wu *et al.* [19], Wogalzki and Gutsche [20], Ashour [21]. Bertucco *et al.* [17] investigated the modified Carnahan-Starling-van der Waals EOS (CSV-EOS) and compared it with the Redlich-Kwong EOS (RK-EOS) in correlation of binary solid and liquid data in a supercritical fluid phase. In some cases, the CSV-EOS was slightly better than the RK-EOS, especially in terms of the physical meaning of the parameters.

Adachi *et al.* [22] evaluated 16 two-term (repulsive + attractive) three-parameter EOSs for the representation of saturation properties and the high liquid density region (reduced density < 3) of pure compounds. They concluded that the VDW repulsive term yielded the lower deviation in liquid compressibility factor and that the Redlich-Kwong attractive term was considered the best because of its flexibility. In a comprehensive review, Han *et al.* [23] evaluated seven EOSs, cubic and non-cubic, for the calculation of the VLE of non-polar and slightly polar substances over a range of pressures, temperatures and molecular variety. They concluded that the quality of EOS representation of VLE was in general the best symmetric mixtures composed of similar molecules and the worst for hydrogen mixtures. The other mixture categories investigated were generally in between the two extremes according to the similarity (or diversity) of the mixture components. They also reached the same conclusion of Adachi *et al.* [22], which states that several cubic EOSs are found to be effective and, in many instances, better than more complex equations. However, the usefulness of EOSs for polar substances is still limited.

Kolasinska [24] covered advances in the field of empirical EOSs for the correlation and prediction of fluid phase equilibria during the period 1980-1985. Anderko [25] discussed the different EOSs, based on either the VDW repulsive term or theoretical term. He elaborated on the importance of an accurate representation of pure component

vapor pressure by an EOS. The equation must be accurate for pure component vapor pressures in order to be accurate in VLE calculations. However, this alone is not sufficient. It is the mixing rules that are important for phase equilibria calculations, in addition to pure component properties. He also concluded that in spite of the progress made in the field of EOSs, no equation can simultaneously represent all pure components and mixtures with satisfactory accuracy.

Mathias *et al.* [18] presented an empirical EOS containing a theoretically realistic repulsive term (Percus-Yevick EOS), for the representation of VLE for high-pressure CO₂-lemon oil and CO₂-triglyceride systems. Their equation resulted in somewhat better predictions compared with Peng-Robinson EOS. Dimitrelis and Prausnitz [16] presented a comparison between the modified CSV-EOS and another EOS based on the scale particle theory proposed by Boublik [2] and Mansoori *et al.* [3] with the same VDW attractive term (BMV-EOS) for VLE calculations. The Boublik-Mansoori EOS proved to be superior, especially in the diluted region. Wu *et al.* [19] used the BMV-EOS, but the pure component parameters were estimated as a function of VDW volume for fatty acid methyl esters. The determination of whether the BMV-EOS is accurate or not is dependent mainly on the accuracy of solubility data. Malanowski and Anderko [26] covered the most of EOSs either cubic or noncubic and other model used for phase equilibrium calculations. Their merits and limitations were presented. Aly and Ashour [27] examined perturbed hard-sphere EOS. For pure substances, Carnahan-Starling equation with van der Waals attractive term and this equation extended to mixtures using Mansoori *et al.* [3] as a repulsive term with the same attractive term. Wogalzki and Gutsche [20] used the BMV-EOS for the prediction of VLE data; the attractive parameter a for pure component being into two parts:

Where ρ_r and p_r are the reduced density and pressure, respectively.

$$a(T, \rho) = [\alpha^{(0)}(T) - \alpha^{(1)}(T)] \exp\left(-\frac{\rho r}{p_r}\right) + \alpha^{(1)}(T) \quad (1)$$

Parameter $\alpha^{(0)}$ is determined from low-density data, e.g. second virial coefficient, while the parameter $\alpha^{(1)}$ can be calculated from vapor pressure data and high-density PVT data. The prediction of VLE phase behavior for ternary systems was good.

In spite of the fact that many researchers have pointed out the major weaknesses of most empirical EOSs in terms of the use of VDW repulsive term (Henderson [28], Rowlinson and Swinton [29], Vidal [30], Dimitrelis and Prausnitz [16], Cuadros *et al.* [31], the majority of researchers are still working on the development of the attractive term of the model of the empirical EOSs. This problem is vividly illustrated by the words of Dimitrelis and Prausnitz [16], who were of the opinion that "most recent literature has focused on the tail rather than the dog". Furthermore, some work is being done to develop different mixing rules (e.g. Dahl and Michelsen [32], Wong and Sandler [33]. Also, Sheng *et al.* [34] suggested a mixing rule for the energy parameter, similar to that developed by Wong and Sandler [33], together with a new mixing rule for the excluded volume parameter b and a generalized correlation for that parameter was presented. Satisfactory solid-supercritical fluid equilibrium (SFE) predictions were obtained for polycyclic aromatics solids in carbon dioxide. Their results were however comparable with those obtained by the van der Waals mixing rules with multiple unlike pair parameters. Furthermore, a comprehensive comparison was recently published of five different mixing rules for the calculation of phase equilibria for complex systems [35]. Ashour and Aly (27) and Ashour *et al.* [37] concluded that the weakness of phase-equilibria predictions using EOSs is not only a result of the weakness of the equations themselves but may also be a result of the computation techniques applied. The main objective of this work was to investigate the validity of a modified perturbed hard-sphere EOS, in which the repulsive term is represented by the Carnahan-Starling equation and the attractive term is represented by the Soave's

attractive term. This equation is referred to as the MCSS-EOS and was applied to pure substances. It was extended to mixtures using the Boublik—Mansoori equation as the repulsive term and keeping the Soave's term as the attractive term. This equation is referred to as the BMMS-EOS. The temperature-dependent function describing the energy parameter a , which was originally developed by Mollerup [38], is used in this work.

THE EQUATION OF STATE

Pure components

The perturbed hard sphere EOS studied in this work is commonly known as MCSS-EOS and consists of the Carnahan-Starling Equation [1] a repulsive term and VDW's term as an attractive term. It can be written as follows:

$$p = RT\rho \frac{(1 + y + y^2 - y^3)}{(1 - y)^3} - \frac{a(T) \rho^2}{1 + b\rho} \quad (2)$$

where $y = (b\rho/4)$ and $a(T) = a_c \alpha(T)$

The co-volume parameter b is taken as a temperature independent. Equation 6, which was, derived from the critical point constraints, namely that the first and second derivatives of pressure with respect to density are equal to zero, as given in Equations 3 and 4:

$$\frac{\partial P}{\partial \rho} = 0.0 \quad (3)$$

$$\frac{\partial^2 P}{\partial \rho^2} = 0.0 \quad (4)$$

For temperature-dependent energy parameter $a(T)$ in Equation 2, the corresponding parameters a , and b , can also be derived from the above critical point constraints:

$$a_c = 0.61883 \left(\frac{R^2 T_c^2}{P_c} \right) \quad (5)$$

$$b_c = 0.104899 \left(\frac{R T_c}{P_c} \right) \quad (6)$$

An expression for $\alpha(T_{r,i})$ was developed by Mollerup [38] for Soave's EOS:

$$\alpha(T_{r,i}) = 1 + \beta(1/T_{r,i} - 1) + \gamma_i T_{r,i} \ln T_{r,i} + \delta_i(T_{r,i} - 1) \quad T_{r,i} \leq 1 \quad (7)$$

In order to avoid negative values at higher reduced temperatures, extrapolation of $\alpha(T_{r,i})$ in Equation 7 can be performed using the following expression at T_r greater than one (i.e. above the critical temperature):

$$h(x) = \frac{1}{(1 + d_1 x_i + d_2 x_i^2)} \quad (8)$$

where $x_i = (T_{r,i} - 1)$. The constants d_1 and d_2 are calculated from the following constraints [38]:

$$\begin{aligned} \alpha'(1) &= h'(0) \\ \alpha''(1) &= h''(0) \end{aligned}$$

from which

$$d_1 = \beta_1 - \gamma_1 - \delta_1 \quad (9)$$

and

$$d_2 = d_1^2 - \beta_1 - \gamma_2/2 \quad (10)$$

The pure component parameters (β , γ and δ) are fitted to vapor pressure data by minimizing the objective function represented by the following equation:

$$Q = \sum_{i=1}^m \left[\frac{(T^{\text{exp}} - T^{\text{calc}})^2}{\sigma_T^2} + \frac{(P^{\text{exp}} - P^{\text{calc}})^2}{\sigma_P^2} \right]_i \quad (11)$$

where T and P are temperature and vapor pressure and σ is the standard deviation. The vapor pressure data fitting was

performed subjected to the following phase equilibrium constraints, including minimum free energy:

$$f_i^I = f_i^{II} \quad i = 1, nc$$

where f is the fugacity of the component i in phase I, either liquid or solid and phase II, either supercritical fluid or vapor.

Table 1 gives, for 51 components, the pure component parameters (β , γ and δ) of the MCSS-EOS, together with the absolute average relative deviation between the experimental and calculated vapor pressures, ΔP . The references for the experimental data of vapor pressure data are given in Ashour [21]. For oleic acid and fatty acid methyl esters, the experimental vapor pressure data are available at temperatures greater than 373 K. These vapor pressures were extrapolated to 313 K using a two-parameter equation based on the kinetic theory of gases [39]. The critical data are either taken from Reid *et al.* [40] or estimated. The impact of extrapolation vapor pressures affects the accuracy of predictions as shown in Table 1. It should be pointed out that the minimum vapor pressure is 1.0 Pa (10^{-5} bar). As can be seen, the MCSS-EOS has successfully predicted the vapor pressures for simple molecules as well as for strongly non-polar molecules. For instance, it gives excellent prediction for all fatty acids as demonstrated in Table 1 and Figures 1 and 2 for both caproic acid and palmitic acid. The results of predicting the vapor pressures using the MCSS-EOS are significantly better than those obtained using cubic EOSs and the GVW-EOS [21] and slightly better than modified perturbed hard sphere using van der Waal's attractive term [27].

Figures 3-5 show the experimental [41-43] and calculated density for pure carbon dioxide and ammonia and the second virial coefficient for pure methane, respectively.

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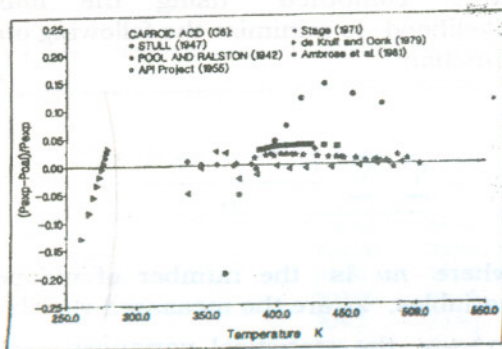


Figure 1 Relative deviation of experimental vapor pressure from calculated values at different temperature for caproic acid

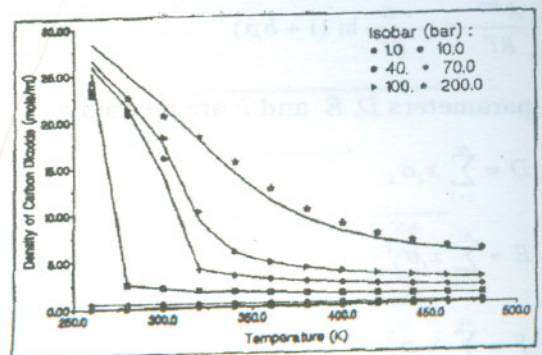


Figure 3 Density prediction for carbon dioxide

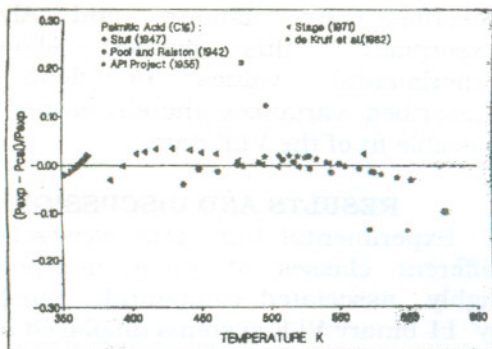


Figure 2 Relative deviation of experimental vapor pressure from calculated values at different temperature for palmitic acid

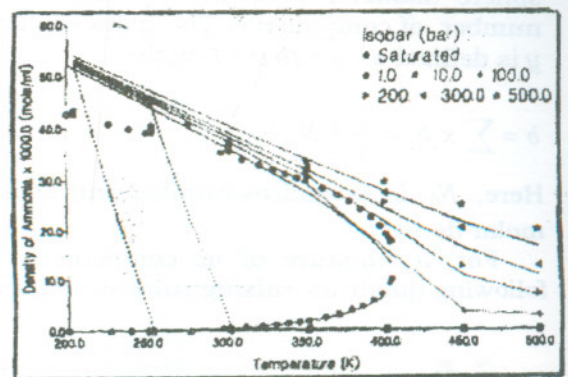


Figure 4 Density prediction for ammonia

The density prediction, as displayed in Figure 3 and 4, show the same trend as that obtained using the same EOS but with different attractive term as was presented by Aly and Ashour [2]. As can be observed, the prediction is accurate except at low temperatures and high pressures in the liquid region. Similarly, Figure 5 demonstrates accurate predictions for the second virial coefficient of methane. Furthermore, the MCSS-EOS predicted accurately the enthalpy of methane even in the saturated areas. It also succeeded in predicting the specific saturated ammonia and the results are physically meaningful. The last results are not shown because of space limitations.

Mixtures

The MCSS-EOS (Equation 2), was extended to mixtures using Boublik-Mansoori Equation [2,3] as a repulsive term plus the same VDW's attractive term. The resulting equation is referred to as the BMMS-EOS. It has the general form for the reduced Helmholtz free energy as given below

$$A^r = A^{rep} + A^{pert} \quad (13)$$

The expressions for A^{rep} and A^{pert} are:

$$\frac{A^{rep}}{RT} = \frac{\left(\frac{3}{F}\right)y - \left(\frac{E^3}{F^2}\right)}{(1-y)} + \frac{\left(\frac{E^3}{F^2}\right)}{(1-y)^2} + \left(\frac{E^3}{F^2} - 1\right) \ln(1-y) \quad (14)$$

and

$$\frac{A^{pert}}{RT} = -\frac{a}{RT} \ln(1 + b\rho) \quad (15)$$

parameters D , E and F are defined as :

$$D = \sum_{i=1}^{nc} x_i \sigma_i \quad (16)$$

$$E = \sum_{i=1}^{nc} x_i \sigma_i^2 \quad (17)$$

$$F = \sum_{i=1}^{nc} x_i \sigma_i^3 \quad (18)$$

where x_i is the mole fraction, σ_i is the hard-sphere diameter of molecule i and nc is the number of components. The reduced density y is defined as $y = (b\rho/4)$ with

$$b = \sum x_i b_i = \frac{2}{3} \pi N_A F \quad (19)$$

Here, N_A is Avogadro's number and ρ is the molar density.

For a mixture of nc components, the following quadratic mixing rules were used:

$$a = \sum_{i=1}^{nc} \sum_{j=1}^{nc} x_i x_j \sqrt{a_i a_j} (1 - k_{ij}) \quad (20)$$

where k_{ij} are dimensionless interaction parameters.

The following density-dependent mixing rules, according to Mohamed and Holder [44], were also examined:

$$a = \sum_{i=1}^{nc} \sum_{j=1}^{nc} x_i x_j \sqrt{a_i a_j} [1 - (k_{ij}^{(0)} - k_{ij}^{(1)} \rho)] \quad (21)$$

The pure component parameters are taken from Table 1. The one fluid van der Waals mixing rules, represented by Equation 20, both with and without the solute-solute interaction parameter, k_{22} and the density-dependent mixing rules, represented by Equation 21 were evaluated in this study to extend the pure component parameters to mixtures. The binary interaction parameters

were computed using the maximum likelihood to minimize the following objective function:

$$Q = \sum_{i=1}^m \sum_{j=1}^{nv} \frac{\{z_{i,j}^{\text{exp}} - z_{i,j}^{\text{cal}}\}^2}{\sigma_{i,j}^2} \quad (22)$$

where nv is the number of independent variables, $z_{i,j}$ are the measured variables and $\sigma_{i,j}^2$ are the statistical variances associated with the measured variables. In this method, the objective function was minimized subject to the phase equilibrium constraints including the minimum Gibbs free energy as described by Ashour and Aly [27]. Essentially, this method allows all experimental values to float within prescribed variances, thereby giving the best possible fit of the VLE data.

RESULTS AND DISCUSSION

Experimental VLE data were selected in different classes of polar, non-polar and highly associated compounds, represented by 11 binary VLE systems displayed in Table 2. As can be seen, the test systems consist of one symmetric mixture, four symmetric mixtures (starting with argon-neopentane and ending with CO_2 -fatty acid methyl esters), four alcohol-containing mixtures and one acetone-containing mixture. It may also be observed that the experimental data covers a wide range of temperature, pressure and molecular variety.

The values of binary interaction parameters were calculated for each binary mixture by minimizing the above objective function. The optimum interaction parameters determined in this way were used in the final computation for comparison with the experimental data. The maximum likelihood method together with this objective function was adapted in this study.

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Table 1 Physical property data and pure component parameters

Component	T _c (K)	P _c (bar)	ω	BMMS-EOS			
				β	γ	δ	
Argon	150.86	48.98	-0.004	0.169933	-0.815779	0.644741	0.068
Nitrogen	126.20	33.90	0.040	0.139186	-0.676380	0.424375	0.067
Hydrogen	33.20	12.96	-0.220	-0.047605	-0.283239	0.215852	0.062
Feorn 13	302.00	39.08	0.177	0.178241	-0.792695	0.367754	0.350
CO ₂	304.2	73.80	0.225	0.807143	-2.327906	2.485760	0.08
Methane	190.58	46.04	0.008	0.065342	-0.492557	0.203597	0.12
Ethane	305.42	48.80	0.098	0.067002	-0.419757	0.013781	0.24
Propane	369.82	42.49	0.152	0.049767	-0.315561	-0.182152	1.2
Butane	425.17	37.97	0.193	0.113297	-0.538735	-0.182152	0.65
Pentane	469.65	33.69	0.251	0.173915	-0.714285	0.188416	0.32
n-Hexane	507.85	30.31	0.296	0.216646	-0.774582	0.241057	0.58
n-Octane	568.83	24.86	0.394	0.037882	-0.042056	-0.774659	0.12
n-Decane	618.45	21.23	0.485	-0.137321	-0.898483	-1.926068	0.74
Neopentane	433.75	31.67	0.197	0.504369	-1.675053	1.546222	0.107
Ethylene	282.40	50.40	0.085	0.065597	-0.365465	-0.012725	0.21
Benzene	562.16	48.98	0.212	0.228680	-0.838657	0.437134	0.14
Water	647.13	220.6	0.344	0.049360	-0.355375	-0.413792	0.29
Ammonia	405.5	113.5	0.250	0.052936	-0.276368	-0.344947	0.12
Methanol	512.60	80.89	0.559	0.249803	-1.705417	0.670079	5.4
Ethanol	513.90	61.40	0.644	0.521236	-1.155901	0.508484	0.84
Acetone	508.20	47.01	0.309	0.537561	-1.534193	1.566949	0.6
Toluene	591.80	40.99	0.263	0.998651	-0.386651	-0.207320	0.43
Tetraline	719.00	35.10	0.303	0.132119	-0.705417	0.670079	.053
1-Methylnaphthalene	772.00	36.00	0.310	0.124141	-0.864916	0.333674	1.01
Decanediol	778.89	25.15	1.330	4.536569	-4.142514	10.00000	1.70
Biphenyl	789.00	38.50	0.364	0.099199	-0.629793	0.094678	0.16
Naphthalene	748.40	40.53	0.303	0.379455	-51.59370	54.04078	0.31
Anthracene	883.00	28.90	0.455	-0.917720	2.862873	-4.381589	0.29
Phenanthrene	890.00	33.33	0.429	0.130242	-1.000470	0.320616	0.27
Pyrene	748.78	26.06	0.835	1.023883	-6.320192	5.700318	2.12
Fluorene	820.80	29.93	0.406	-0.144763	0.643659	-1.353962	0.11
Benzoic acid	752.00	45.59	0.620	-0.377905	1.632783	-2.771551	0.28
2,3-Dimethylnaphthalene	773.45	30.05	0.500	0.285970	-1.573850	1.017834	0.29
2,6-Dimethylnaphthalene	781.78	30.05	0.510	0.811644	-4.13394	3.927127	0.03
Fatty acids							
Caproic	663.00	32.00	0.608	-0.243011	1.967241	-3.257069	1.38
Caprylic	694.00	27.00	0.754	-0.124999	1.614992	-2.88969	0.61
Capric	726.00	21.00	0.854	-0.285939	2.911129	-4.157564	0.82
Lauric	733.50	19.10	0.934	-0.617930	4.276001	-5.912916	9.7
Myristic	755.30	16.70	1.018	3.272296	-12.793271	13.56259	20.67
Palmitic	774.22	14.27	1.027	0.46989	-0.6041369	-0.618016	0.41
Stearic	801.40	13.60	1.079	0.611817	-1.022456	-0.064067	0.84
Oleic	817.75	13.85	1.085	-2.624749	8.426664	-10.85156	11.9
Methyl esters							
Caproate	583.50	27.80	0.481	-0.41345	1.359237	-2.883789	0.41
Caprylate	632.50	23.10	0.569	1.247775	-5.354548	5.001222	1.9
Caprate	670.50	19.80	0.654	0.104992	-0.0545048	-1.038174	1.3
Laurate	714.70	17.30	0.731	-0.049563	0.5542274	-1.732778	6.89
Myristate	730.70	15.40	0.816	0.079592	-0.3298532	-1.104194	1.7
Palmitate	792.00	13.80	0.891	0.710930	-0.7109301	-0.729652	0.69
Stearate	788.60	12.60	0.963	0.388799	-1.758314	0.436649	1.7
Oleate	810.10	12.80	0.953	0.012765	-0.1312525	-1.24095	3.9
Linoleate	813.90	13.10	0.943	0.135076	-0.8214317	-0.508175	2.9

Table 2 Binary VLE systems

System ID	Binary system	Temperature (K)	Pressure range (bar)	Reference
I	Argon - neopentane	323.15	11.09-250.62	45
II	Hydrogen - n-hexane	277.59	68.90-689.40	46
III	CO ₂ - benzene	298.15	8.90-57.34	47
IV a	CO ₂ - n-decane	344.3	68.85-164.50	48
IV b	CO ₂ - n-decane	377.60	103.40-127.30	48
V a	CO ₂ - methanol	298.15	2.18-61.26	49
V b	CO ₂ - methanol	313.15	5.77-80.58	49
VI	CO ₂ - ethanol	304.20	37.50-72.20	50
VII a	Methanol - ethanol	373.15	2.46-3.53	51
VII b	Methanol - ethanol	414.15	8.87-10.83	51
VIII	Ethanol - water	363.15	0.73-1.58	52
IX a	CO ₂ - propane	310.93	13.01-69.12	27
IX b	CO ₂ - propane	344.26	26.46-67.29	27
X a	Propane - methanol	313.10	3.50-13.23	27
X b	Propane - methanol	343.10	4.20-25.30	49
X c	Propane - methanol	373.10	8.80-42.80	27
XI	CO ₂ - acetone	313.15	10.05-74.13	27
XII a	Acetone - water	308.15	0.18-0.45	27
XII b	Acetone - water	373.15	1.11-3.68	36
XIII a	CO ₂ - methyl stearate	313.15	94.50-134.40	36
XIII b	CO ₂ - methyl stearate	323.15	81.30-163.20	36
XIII c	CO ₂ - methyl stearate	333.15	89.90-178.80	36
XIII d	CO ₂ - methyl stearate	343.15	127.50-197.30	36
XIV a	CO ₂ - methyl oleate	313.15	72.10-116.50	36
XIV b	CO ₂ - methyl oleate	323.15	79.80-130.00	36
XIV c	CO ₂ - methyl oleate	333.15	87.30-148.80	36
XIV d	CO ₂ - methyl oleate	343.15	100.50-200.00	36
XV a	CO ₂ - methyl linoleate	313.15	48.70-125.26	53
XV b	CO ₂ - methyl linoleate	343.15	41.38-200.41	53

The performance of the BMMS-EOS presented in Table 3 and Figures 5-11. For each binary mixture, we present the binary interaction parameters, using both the quadratic one fluid mixing rules and the density-dependent mixing rules and the root mean square (rms) average relative deviation between experimental and calculated pressure, ΔP , liquid composition, Δx , and vapor composition Δy . The temperature predictions are not shown in Table 3 since

very accurate predication were obtained for all systems investigated. The rms average relative deviation is defined as:

$$\Delta z = \sqrt{\left(\frac{1}{np}\right) \left[\sum_{i=1}^{np} \left(\frac{z_i^{\text{cal}} - z_i^{\text{exp}}}{z_i^{\text{exp}}} \right)^2 \right]} \quad (23)$$

where np is the number of experimental data, z is the measured variable (P , T , x and y).

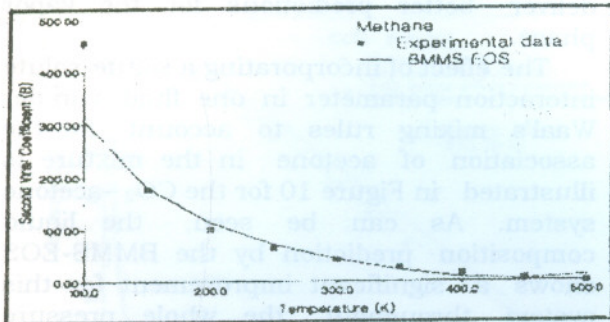


Figure 5 Second virial coefficient for methane

Figure 6 shows the predication of VLE for the argon-neopentane system, which consists of molecules of different sizes. As can be seen, the BMMS-EOS accurately predicts both vapor and liquid compositions.

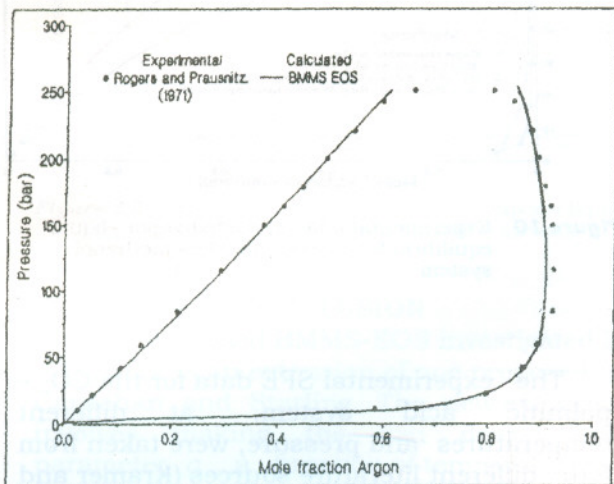


Figure 6 Calculated and experimental VLE for argon / neopentane at 32.15 K

Studies of VLE for mixtures containing hydrogen have been intensive in recent years, due to the development of coal liquefaction and other sinful processes. New experimental data have become available at high temperatures and high pressures.

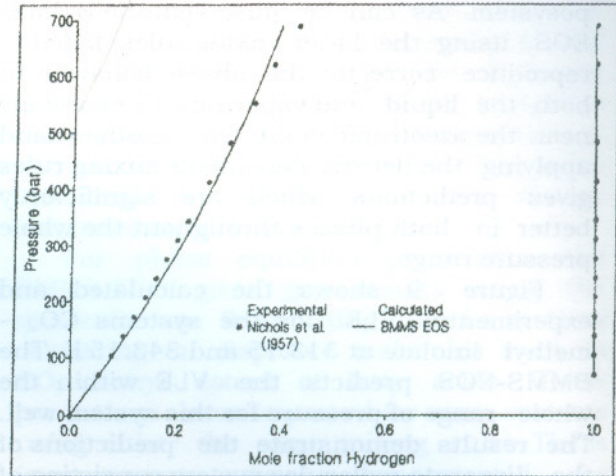


Figure 7 Calculated and experimental VLE for Hydrogen n-hexane at 277.59 K

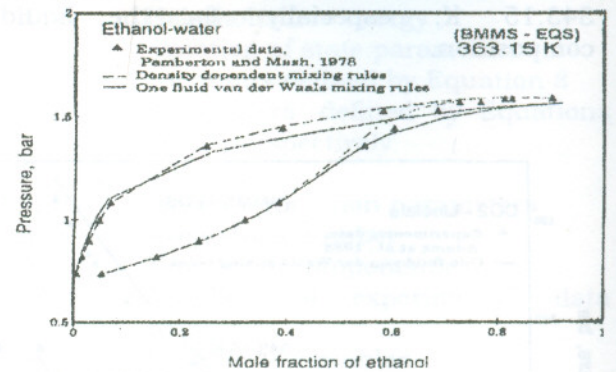


Figure 8 Experimental and calculated vapor - liquid equilibria for ethanol - water system

Representation of the equilibrium behavior of these asymmetric systems poses a challenge on account of the significant difference of hydrogen from the other component in the mixture in terms of molecular size, energy and other properties. The results of predicting VLE phase behavior for the hydrogen -n-hexane asymmetric system significantly better than the other published equation of state [36].

The results displayed in both Table 3 and Figure 8, for the ethanol-water system at 363.15 K, clearly show the advantage of using the density-dependent mixing rules, compared with the traditional quadratic one fluid mixing rules for such a strong

posystem. As can be observed, the BMMS-EOS, using the latter mixing rules, failed to reproduce correctly the phase behavior in both the liquid and vapor phases especially near the azeotropic point. On the other hand applying the density-dependent mixing rules gives predictions which are significantly better in both phases throughout the whole pressure range.

Figure 9 shows the calculated and experimental VLE for the systems CO_2 - methyl linolate at 313.15 and 343.15 K. The BMMS-EOS predicts the VLE within the whole range of pressure for this system well. The results demonstrate the predictions of the disparate molecules system consisting of carbon dioxide and of methyl esters acids. As can be seen, the equation predicts quite well the VLE at 313.15 K, but the predictions are less accurate at higher temperature of 343.15 K, especially for the liquid composition.

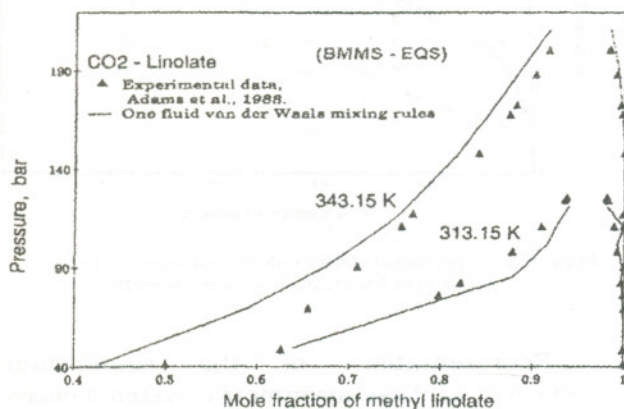


Figure 9 Experimental and calculated vapor - liquid equilibria for carbon dioxide - methyl linolate system

Figure 10 shows the VLE predictions for the CO_2 -methanol system using both quadratic and density-dependent mixing rules. This system is one which demonstrates the advantage of the density-dependent mixing rules as shown in Table 3. It may be noted that the liquid composition predictions are similar for both mixing rules, but the density-dependent mixing rules

deliver better predictions for the vapor phase.

The effect of incorporating a solute-solute interaction parameter in one fluid van der Waal's mixing rules to account for the association of acetone in the mixture is illustrated in Figure 10 for the CO_2 -acetone system. As can be seen, the liquid composition prediction by the BMMS-EOS shows a significant improvement for this system throughout the whole pressure range. However, this behavior did not hold for other highly associated systems, such as propane-methanol and CO_2 -methanol, as demonstrated by Ashour and Wennersten [54].

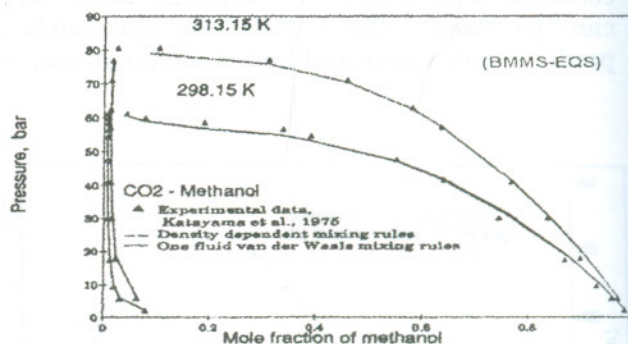


Figure 10 Experimental and calculated vapor -liquid equilibria for carbon dioxide - methanol system

The experimental SFE data for the CO_2 - palmitic acid system, at different temperatures and pressure, were taken from four different literature sources (Kramer and Thodos [55], Bamberger *et al.* [56], Ashour [21], Ohgaki *et al.* [56]). It should be noted that the variability in solubility data obtained by different research groups underscores the importance of some experimental variables such as the sample purity, build-up and clogging of lines and values with heavy solid or liquid, density inversion or failure to achieve equilibrium in the system and entrainment of the solute in the supercritical fluid phase (Ashour [21], Dimitrelis and Prausnitz [57], Maheswari *et al.* [58]).

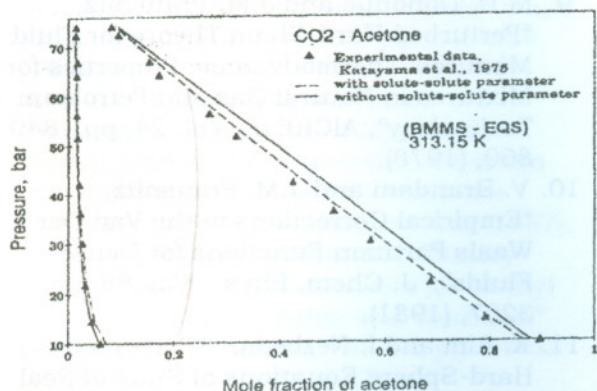


Figure 11 Experimental and calculated vapor - liquid equilibria for carbon dioxide - acetone system

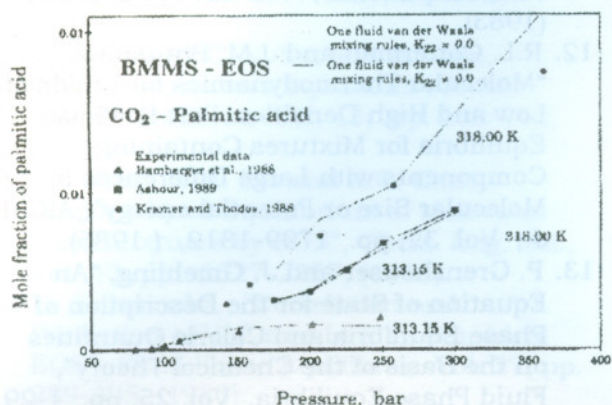


Figure 12 Experimental and calculated vapor - liquid equilibria for carbon dioxide - acetone system

CONCLUSION

The proposed BMMS-EOS investigated in this work is an extension of one proposed by Carnahan and Starling. The new extension involves making the van der Waals parameter a a function of temperature. In doing so, a number of new substance specific parameters are introduced, leading to improved accuracy of the equation. It did yield excellent results for vapor pressure predictions as well as phase equilibria at high pressures. The equation failed, however, to predict phase equilibria at low pressure. This result supports the conclusion of Anderko [21] that a better representation of pure component properties does not necessarily ensure an improvement in prediction the phase equilibria for mixtures. The result also resembles the conclusion of Han et al. (23) that the quality of the EOS

representation of VLE was best, in general for asymmetric mixtures composed of similar molecules and the worst for hydrogen mixtures. The other mixture categories investigated in their work were generally in between the two extremes, according to the similarity (or diversity) of the mixture components.

For phase equilibria predication, the BMMS-EOS gives good results using the quadratic one fluid mixing rules for systems consisting of disparate molecules such as CO₂-methyl esters of fatty acids. These predictions were improved for some systems using either the same mixing rules. These improvements were demonstrated for systems such as CO₂-acetone (VLE) and CO₂-palmitic acid (SFE), respectively.

NOMENCLATURE

A	Helmholtz free energy
a, b	equation of state parameters
d	constants defined by Equation 8
D, E, F	parameters defined by Equations 16-18, respectively
F	fugacity
k, l	binary interaction parameters
N_A	Avogadro's number
N_c	Number of components
np	Number of experimental data points
nv	Number of variables
P	Pressure
Q	Objective function
R	Universal gas constant
T	Temperature
v	Volume
x	mole fraction of liquid phase
y	mole fraction of vapor phase and reduced density
z	measured variable
Z	compressibility factor

Greek letters

α	parameter in Equation 7
β, γ, δ	pure component parameters
Δ	root mean square average relative deviation, Equation 23 molar density
σ	standard deviation in Equation 11 and hard-sphere diameter in Equations 16-18

ϕ	fugacity coefficient
ω	acentric factor of pure component

Superscripts

cal	calculated value
exp	experimental value
L	liquid state
Pert	perturbed
R	reduced
Rep	repulsive
S	solid stat
V	vapor

Subscripts

C	critical property
ij	components o mixture
r	reduced

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معادلة بيرتويبريد المحسنة للكرات الصلبة باستخدام حد سواف للتجاذب

ابراهيم عبد السلام عاشور و ابراهيم اسماعيل ابراهيم

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ملخص البحث

تم دراسة معادلة بيرتويبريد المحسنة للكرات الصلبة (باستخدام سواف للتجاذب) والمثلة بمعادلة كارناهان - ستارلنج بإدخال معامل موللراب للطاقة a للمادة النقية. المعادلة وسعت لتشمل المخاليط عند الاتزان لكل من البخار - السائل والصلب - المائع السوبر حرج باستخدام معادلة بوبليك - منصورى بالإضافة الى حد سواف للتجاذب. للمواد النقية تم اختبار الضغط البخارى، الكثافة، معامل فيرجل الثنائى، السعة الحرارية والإنثاللى. المعادلة الجديدة قادرة أيضا على تقدير الضغط البخارى للأحماض الدهنية بدقة. تقدير لكل من البخار - السائل والصلب - المائع السوبر حرج باستخدام قانون در فالز للخلط مع معامل التجاذب الثنائى كان أفضل من تقديره باستخدام معادلة الحالة التكميية خاصة للجزينات الكبيرة. لقد تحسن تقدير أنظمة الصلب - المائع السوبر حر بإدخال عوامل التجاذب للمذاب - المذاب. تم أيضا اختبار قانون الخلط المعتمد على الكثافة.