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A chemical theory based equation of state for self-associating compounds

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Abstract

The Redlich–Kwong–Soave equation of state commonly used to describe the volumetric behavior of pure fluids and mixtures is modified using chemical theory to account for chain-like association occurring in self-associating compounds such as alcohols. The equation treats the pure fluid as a mixture of clusters, with parameters *a* and *b* related to the number of molecules involved in their formation and obtained by regression of vapor pressure data using hydrocarbons as homomorphs. The model is extended to mixtures of a self-associating compound and inert ones, and used to correlate the phase behavior of alcohol–hydrocarbon mixtures. The model resulted in excellent correlation of bubble point pressure experimental data and good predictions of vapor phase composition, especially at low temperatures, situation in which equations of state are usually inaccurate. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Equations of state of the form $p=p(V, T)$ constitute a powerful and widely used tool in chemical thermodynamics calculations. Many of these equations are explicit in pressure and cubic in volume, and are prototypes of the van der Waals equation [1]. These equations are simple to handle, but are not reliable to describe the behavior of polar compounds or when self-associating compounds are involved.

Self-associating compounds are constituted by molecules that undergo hydrogen bonding with other molecules. Their molecules have at least one hydrogen atom bonded to a strongly electronegative atom (F, O or N), that can bond to another electronegative atom. Although the enthalpy of hydrogen bonding (up to 40 kJ mol^{-1}) is smaller than that attributed to covalent bonding (200 kJ mol^{-1}), the clusters formed are very stable.

A possible way to thermodynamically model the behavior of self-associating compounds is to regard the clusters formed as independent chemical species. This approach is known as chemical theory approach [1].

The first work encountered in literature where chemical theory was used to modify an equation of state in order to account for self-association is that of Heidemann and Prausnitz [2]. A generalized van der Waals type equation of state was used and a closed form expression was obtained, which the authors employed along the critical isotherm.

Ikonomou and Donohue [3] extended the approach of Heidemann and Prausnitz [2] to the study of

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mixtures containing a self-associating fluid and inert compounds. The associating equation was based on perturbed anisotropic chain theory. This approach was later modified and extended [4–7]. However, the way by which phase equilibrium calculations were performed was never shown clearly.

Anderko [8] regarded the consequences of the work of Ikonomou and Donohue [3] as hypotheses, and solved the chemical equilibrium as if the self-associating fluid was a mixture of ideal gases. Other authors [9–11] used Anderko's approach without any verification of the validity of the assumptions used.

The aim of this work is to present a simple and consistent way to model the behavior of mixtures of an alcohol and inert compounds using a van der Waals type equation of state (the Soave [12] equation) modified using chemical theory. The development is based on principles first cited by Heidemann and Prausnitz [2], with no further hypotheses being necessary to perform phase equilibrium calculations.

2. Theoretical development

The development is based on four hypotheses:

Hypothesis 1. The self-associating compound is regarded as a mixture of clusters in chemical equilibrium according to the series of chemical reactions

$$A_1 + A_1 \leftrightarrow A_2 \tag{1a}$$

$$A_1 + A_2 \leftrightarrow A_3 \tag{1b}$$

$$A_i + A_1 \leftrightarrow A_{i+1} \tag{1c}$$

with equilibrium constants K_1, K_2, ..., K_i, ... for the reactions cited in Eqs. (1a), (1b) and (1c), respectively.

Hypothesis 2. The pVT behavior of the self-associating compound is represented by the Redlich–Kwong–Soave equation of state [12]:

$$p = \frac{RT}{V-b} - \frac{a}{V(V+b)}, \tag{2}$$

in which p is the pressure, T the absolute temperature, V the molar volume and R is the ideal gas constant. Parameters a (attractive) and b (repulsive) are functions of composition (clusters amount fractions), and the attractive parameter is a function of temperature (see Appendix A).

Hypothesis 3. The equation of state parameters for the clusters are given by the expressions [2]:

$$\sqrt{a_{\mathrm{A}_i}} = i\sqrt{a_{\mathrm{A}_1}}, \tag{3}$$

$$b_{\mathrm{A}_i} = ib_{\mathrm{A}_1}, \tag{4}$$

in which i is the size (number of monomers that constitute the cluster) and a_{A_i} and b_{A_i} are the parameters attributed to the multimer A_i. The following simple van der Waals mixing rules are also involved:

$$a = \sum_i \sum_j z_i z_j a_{\mathrm{A}_i\mathrm{A}_j}, \tag{5}$$

with:

$$a_{\mathrm{A}_i\mathrm{A}_j} = \sqrt{a_{\mathrm{A}_i} a_{\mathrm{A}_j}}, \tag{6}$$

$$b = \sum_j z_{\mathrm{A}_j} b_{\mathrm{A}_j}, \tag{7}$$

in which z_{A_i} is the effective amount fraction of multimer A_i.

Hypothesis 4. The standard state is the pure multimer in the ideal gas state with fugacity f^0=100 kPa, and the value of the equilibrium constant, K_i, is independent of i [2].

These hypotheses allow us to define a macroscopic (or apparent) property value, representing the situation where no self-association occur. While the amount of a given sample is that of clusters, the macroscopic amount is the number of monomers that constitute the clusters. Defining $\tilde{n}$ as the macroscopic amount and n as the effective amount, the ratio between the two numbers, ξ, is

$$\xi = \frac{\tilde{n}}{n} = \sum_j j z_{\mathrm{A}_j}. \tag{8}$$

The graphical symbol ~ is used to designate macroscopic quantities throughout this paper. ξ relates the values of effective and macroscopic quantities; for instance, in the case of macroscopic and effective molar volumes, we have

$$V = \xi\tilde{V}. \tag{9}$$

Eqs. (5) and (7) can thus be rewritten as:

$$a = a_{A_1}\xi^2, \tag{10}$$

$$b = b_{A_1}\xi. \tag{11}$$

The substitution of expressions (9)–(11) into Eq. (2) results in the following expression for the modified RKS equation, in terms of macroscopic volumes:

$$p = \frac{RT}{\xi(\tilde{V} - b_{A_1})} - \frac{a_{A_1}}{\tilde{V}(\tilde{V} + b_{A_1})}. \tag{12}$$

In order to apply Eq. (12), we need to be able to evaluate chemical equilibrium in any phase. The main steps are:

1. to obtain an expression for the multimer amount fraction through equilibrium relations,
2. to obtain an expression for the monomer amount fraction as a function of macroscopic quantities by imposing that the sum of amount fractions equal unity, and
3. to use the definition of ξ (Eq. (8)).

The implementation of these steps results in the following equations:

$$\xi = \frac{1 + \sqrt{1 + (4KRT/f^0(\tilde{V} - b_{A_1}))}}{2} \tag{13}$$

and the pressure equation can now readily be used. It is worth noting that ξ reduces to 1 if K tends to 0, as one may expect.

This development assures us that chemical equilibrium is always satisfied in any phase, whatever T and $\tilde{V}$ may be. To perform vapor–liquid phase equilibrium calculations, we must assure the equality in both phases of pressure, temperature and monomer fugacity (or chemical potential). Invoking the equality of the fugacities of each multimer in both phases is redundant, once

$$\ln\left(\frac{f_{A_i}}{p}\right) = i\ln\left(\frac{f_{A_1}}{p}\right) + (i-1)\ln\left(\frac{Kp}{f^0}\right). \tag{14}$$

Algorithms already used in phase equilibrium calculations can thus be used with the proposed model, provided slight modifications are made: the equation of state must be changed, and monomer fugacity must be used instead of pure compound fugacity, assuring that the conditions of both chemical and phase equilibria are satisfied.

2.1. Extension to mixtures

The expressions previously obtained can be extended to mixtures of a self-associating compound and inert ones (compounds that can undergo neither self-association nor cross-association with molecules of the self-associating compound). For this, it is only necessary to modify hypothesis 3: the attractive parameter must include expressions for multimer–multimer and inert–multimer interactions. A binary interaction parameter is considered independent of the multimer size. The new terms to be added for the extension of the model to mixtures are:

$$a_{D_iD_j} = \sqrt{a_{D_i}a_{D_j}}(1 - \delta_{D_iD_j}), \tag{15}$$

$$a_{A_iD_j} = \sqrt{a_{A_i}a_{D_j}}(1 - \delta_{D_j}), \tag{16}$$

in which the subscript D represents inert compounds. Using similar mixing rules to those stated in Eqs. (5) and (6), the macroscopic expressions for the parameters a and b are:

$$\tilde{b} = \sum_{j=1}^{m} \tilde{z}_{D_j} b_{D_j} + \tilde{z}_A b_{A_1}, \tag{17}$$

$$\tilde{a} = \sum_{i=1}^{m}\sum_{j=1}^{m} \tilde{z}_{D_i}\tilde{z}_{D_j}\sqrt{a_{D_i}a_{D_j}}(1 - \delta_{D_iD_j}) + 2\sum_{j=1}^{m} \tilde{z}_A\tilde{z}_{D_j}\sqrt{a_{D_j}a_{A_1}}(1 - \delta_{D_j}) + \tilde{z}_A^2 a_{A_1}. \tag{18}$$

The final form of the equation of state for the mixture is

$$p = \frac{RT}{\xi(\tilde{V} - \tilde{b})} - \frac{\tilde{a}}{\tilde{V}(\tilde{V} + \tilde{b})}. \tag{19}$$

The procedure to obtain ξ is slightly more extensive, but follows the same steps used in the development of the equation for pure self-associating compounds, and is similar, for instance, to [3]. The final expression for ξ, in this case, is

$$\xi = \frac{1 + \sqrt{1 + (4\tilde{z}_A KRT/f^0(\tilde{V} - \tilde{b}))}}{2\tilde{z}_A + (1 - \tilde{z}_A)\left(1 + \sqrt{1 + (4\tilde{z}_A KRT/f^0(\tilde{V} - \tilde{b}))}\right)}. \tag{20}$$

It is worth noting that the expression for ξ reduces, as expected, to that for pure compounds if the macroscopic amount fraction of the self-associating compound is made equal to 1.

As in the case of a pure self-associating compound, vapor–liquid phase equilibrium must be solved by the equality of monomer fugacity in the two phases.

3. Results

The model for pure substances (Eqs. (12) and (13)) was used to correlate saturation pressure data of 15 alcohols in wide temperature range up to T_r=0.9 [13]. Hydrocarbon data were used for the parameters of homomorphs (obtained by replacing the hydroxyl (OH) by a methyl (CH_3) group, for example, ethane being homomorph for methanol, propane for ethanol, etc.). Standard entropy and enthalpy of association are related to the association constant by

$$\ln K = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}. \tag{21}$$

These properties are the only parameters considered for pure alcohols. They are also considered to be independent of temperature.

Percent mean deviations in saturation pressures and saturated liquid volumes obtained with the correlation of experimental data are shown in Table 1. The acronym RKS stands for the Redlich–Kwong–Soave equation while ARKS stands for the associating model.

The correlation using the ARKS equation are clearly superior when compared to that obtained with the RKS equation. A large improvement in the prediction of saturated liquid volume is obtained with the ARKS equation.

Table 2
Standard enthalpy and entropy of association

Compound	ΔH^0 (kJ mol^{-1})	ΔS^0 (J K^{-1} mol^{-1})
Methanol	22.45	90.04
Ethanol	22.11	93.72
1-Propanol	21.11	93.17
2-Propanol	21.07	95.26
1-Butanol	19.86	90.71
1-Pentanol	19.60	90.37

Data correlation was done using two adjustable parameter, ΔH^0 and ΔS^0. The values obtained for the standard entropy and enthalpy obtained are shown in Table 2. Although dependent on the standard state, the values obtained for the association enthalpy are found to be in close agreement with those obtained through vaporization enthalpy data, using ethers as homomorphs [15].

3.1. Mixtures with inert compounds

The model developed was applied to the correlation of bubble point pressure data of mixtures of an alcohol and a hydrocarbon. The value of δ_D that resulted in the best fit of bubble point pressure data at each temperature was obtained. Vapor–liquid equilibrium data for 46 binary systems and 133 isotherms were correlated [13]. Typical results are shown in Table 3.

Table 1
Percent mean deviation[a] in saturation pressure and saturated liquid volume calculation

Compound	Mean deviation in saturation pressure calculation[b] (%)		Mean deviation in saturated liquid volume calculation[b] (%)	
	ARKS	RKS	ARKS	RKS
Methanol	2.02	5.33	5.39	36.23
Ethanol	2.68	2.70	4.40	23.75
1-Propanol	4.05	4.74	3.97	18.02
2-Propanol	3.84	4.23	3.98	18.51
1-Butanol	4.90	9.62	3.36	14.77
1-Pentanol	5.10	17.77	5.27	12.60

[a] Percent mean deviation = (100/number of data points) $\sum$ |(calculated value − experimental value)/calculated value|.

[b] Experimental data from [14].

Table 3
Bubble point calculations for binary mixtures

Alcohol	Inert	T (K)	Equation	DP (%)[a,c]	Δy[b,c]	δ_D
Methanol	Hexane	333.15	ARKS	5.55	0.040	−0.0051
			RKS	23.11	0.140	
Ethanol	Hexane	313.15	ARKS	4.47	0.026	−0.0208
			RKS	15.50	0.077	
1-Propanol	Heptane	333.15	ARKS	3.38	0.029	−0.0282
			RKS	9.62	0.069	
2-Propanol	Hexane	303.15	ARKS	5.29	0.031	−0.0712
			RKS	10.41	0.108	

[a] DP (%): percent mean deviations in bubble pressure calculation.
[b] $\Delta y = (1/\text{number of data points}) \sum |y^{\text{experimental}} - y^{\text{calculated}}|$.
[c] Experimental data from [16].

The values of δ_D are, without exception, negative and small in value. The small value indicates the validity of the developed equations. These parameters, however, while small, are necessary for good correlation of bubble pressure data.

Graphical representation of the data and model correlation of bubble point pressure and predictions of vapor phase compositions are shown in Figs. 1–4.

In both systems methanol/hexane (Fig. 1) and ethanol/hexane (Fig. 2), the use of another value of δ_D that provides a lowest value for the deviation in bubble pressure for RKS equation predicts liquid phase split, which does not actually occurs. The ARKS equation does not foresee such false phase split. We also see that the improvement in correlation is pronounced even at the alcohol infinite dilution

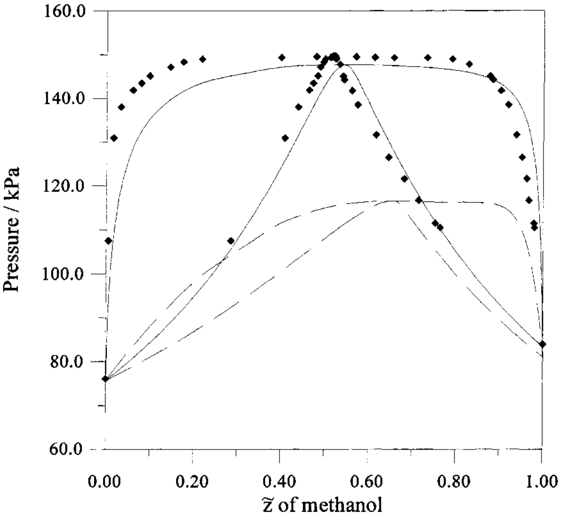

Fig. 1. p–$\tilde{x}$–$\tilde{y}$ diagram for the mixture methanol/hexane at 333.15 K: (◆) experimental data [14]; (– – –) RKS equation; (———) ARKS equation.

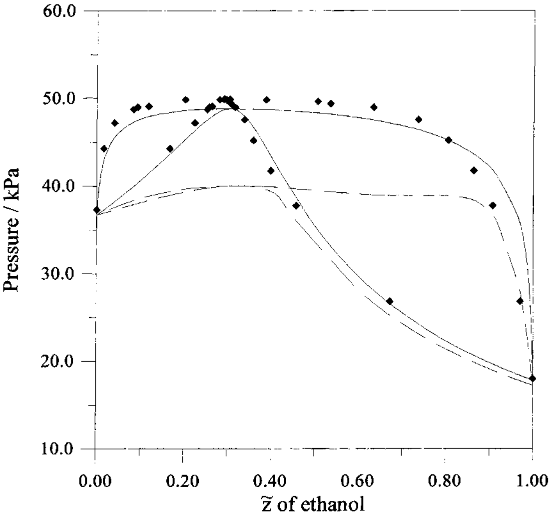

Fig. 2. p–$\tilde{x}$–$\tilde{y}$ diagram for the mixture ethanol/hexane at 313.15 K: (◆) experimental data [14]; (– – –) RKS equation; (———) ARKS equation.

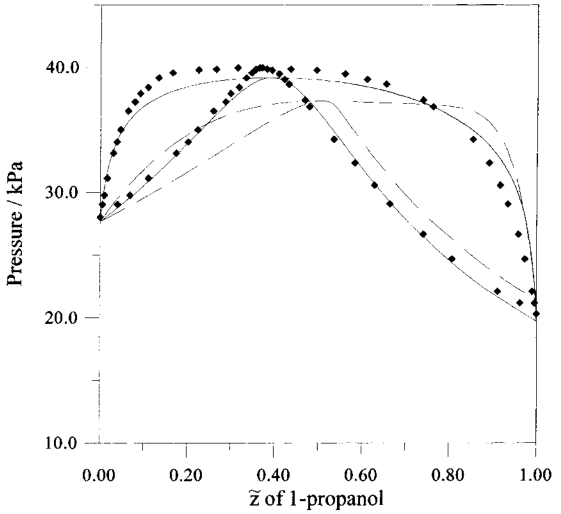

Fig. 3. p–$\tilde{x}$–$\tilde{y}$ diagram for the mixture 1-propanol/heptane at 333.15 K: (◆) experimental data [14]; (– – –) RKS equation; (———) ARKS equation.

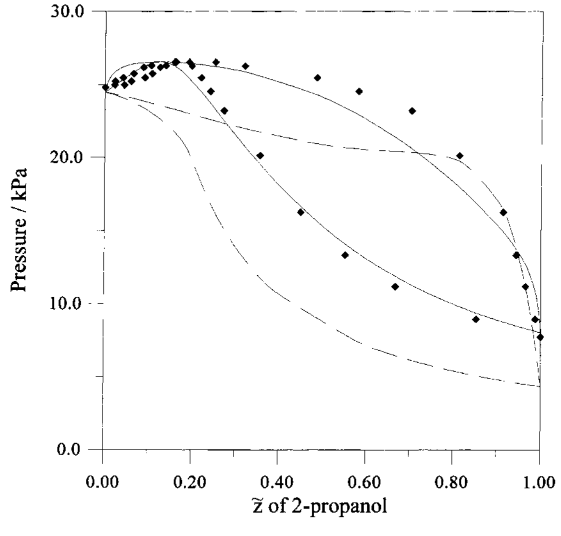

Fig. 4. p–$\tilde{x}$–$\tilde{y}$ diagram for the mixture 2-propanol/hexane at 303.15 K: (◆) experimental data [14]; (– – –) RKS equation; (———) ARKS equation.

limit. In this limit, monomers will be present in much higher concentration than other multimers, and the ARKS equation reduces to the original RKS equation, but with monomer parameters, instead of alcohol parameters.

In the case of the system 2-propanol/hexane (Fig. 4), RKS equation cannot correlate the existence of the azeotrope occurring at low concentrations of 2-propanol.

While the RKS equation applied to a pure alcohol can predict with precision its saturation pressure by correcting the temperature dependence of the attractive parameter the correlation of bubble point pressure and prediction of vapor phase compositions for binary systems would still be inaccurate. Incorporating self-association phenomenon into the equation of state does not only result in better correlation of the saturation pressure of pure alcohols, but also large improvements in pressures and predictions of vapor phase compositions brought about by the correct descriptions of the molecular structure in associating fluids.

4. Conclusions

- It was possible to incorporate the effect of linear chain self-association into the RKS equation of state, permitting the solution of phase equilibrium without introducing thermodynamic inconsistencies.
- The proposed model resulted in excellent correlation of saturation pressures and good predictions of liquid phase molar volumes.
- Using the extended model, p–$\tilde{x}$–$\tilde{y}$ diagrams for binary systems were well correlated, allowing good predictions of vapor phase compositions even at low temperatures, a situation where equations of state are usually inaccurate.

Appendix A

The Soave (or Redlich–Kwong–Soave) equation of state is given by

$$p = \frac{RT}{V-b} - \frac{a(T,\omega)}{V(V+b)}, \tag{22}$$

in which:

$$a(T,\omega) = a_{\mathrm{c}}\alpha(T,\omega), \tag{23}$$

$$a_{\mathrm{c}} = 0.42748\frac{R^2T_{\mathrm{c}}^2}{p_{\mathrm{c}}}, \tag{24}$$

$$b = 0.08664\frac{RT_c}{p_c}, \tag{25}$$

in which ω is the Pitzer acentric factor and the subscript c represents critical properties. For $\alpha(T,\omega)$ the expression of Graboski and Daubert [17] is widely used

$$\alpha(T,\omega) = \left(1 + (0.48508 - 1.55171\omega - 0.15613\omega^2)\left(1 - \sqrt{\frac{T}{T_c}}\right)\right)^2. \tag{26}$$

For mixtures, the following mixing rules are applicable:

$$a = \sum_{i=1}^{n}\sum_{j=1}^{n} z_i z_j a_{ij}, \tag{27}$$

in which

$$a_{ij} = \sqrt{a_i a_j}(1 - \delta_{ij}) \tag{28}$$

and

$$b = \sum_{i=1}^{n} z_i b_i. \tag{29}$$

References

[1] J.M. Prausnitz, Molecular Thermodynamics of Fluid-phase Equilibria, Prentice-Hall, Englewood Cliffs, NJ, 1969.

[2] R.A. Heidemann, J.M. Prausnitz, Proc. Natl. Acad. Sci. U.S.A. 73 (1976) 1773.

[3] G.D. Ikonomou, M.D. Donohue, AIChE J. 32 (1986) 1716.

[4] G.D. Ikonomou, M.D. Donohue, Fluid Phase Equilibria 33 (1987) 61.

[5] G.D. Ikonomou, M.D. Donohue, AIChE J. 39 (1988) 129.

[6] J.R. Elliott Jr., S.J. Suresh, M.D. Donohue, Ind. Eng. Chem. Res. 29 (1990) 1476.

[7] S.J. Suresh, J.R. Elliott, Ind. Eng. Chem. Res. 30 (1991) 524.

[8] A. Anderko, Fluid Phase Equilibria 45 (1989) 39.

[9] A. Anderko, Fluid Phase Equilibria 65 (1991) 89.

[10] H. Wenzel, E. Krop, Fluid Phase Equilibria 59 (1990) 147.

[11] A.A. Shinta, A. Firoozabadi, Can. J. Chem. Eng. 73 (1995) 367.

[12] G. Soave, Chem. Eng. Sci. 27 (1972) 1197.

[13] P.A. Pessôa Filho, Equações de estado para compostos autoassociativos: modificação da equação de Redlich–Kwong–Soave por meio da abordagem química, M.Sc. Thesis, Unicamp, Campinas, 1998.

[14] B.D. Smith, R. Srivastava, Thermodynamic Data for Pure Compounds. Part B: Halogenated Hydrocarbons and Alcohols, Elsevier, Amsterdam, 1986.

[15] T. Hofman, I. Nagata, Fluid Phase Equilibria 25 (1986) 113.

[16] J. Gmehling, U. Onken, W. Arlt, Vapor–liquid equilibrium data collection, Chemistry Data Series, vol. 1, Dechema, Dortmund, 1982.

[17] M.S. Graboski, T.E. Daubert, Ind. Eng. Chem. Process Des. Dev. 17 (1978) 443.