

Solubility of Methane, Ethane, and Propane in Pure Water Using New Binary Interaction Parameters

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Abstract

Solubility of hydrocarbons in water is important due to ecological concerns and new restrictions on the existence of organic pollutants in water streams. Also, the creation of a thermodynamic model has required an advanced study of the phase equilibrium between water (as a basis for the widest spread muds and amines) and gas hydrocarbon phases in wide temperature and pressure ranges. Therefore, it is of great interest to develop semi-empirical correlations, charts, or thermodynamic models for estimating the solubility of hydrocarbons in liquid water. In this work, a thermodynamic model based on Mathias modification of Sova-Redlich-Kwong (SRK) equation of state is suggested using classical mixing rules with new binary interaction parameters which were used for two-component systems of hydrocarbons and water. Finally, the model results and their deviations in comparison with the experimental data are presented; these deviations were equal to 5.27, 6.06, and 4.1% for methane, ethane, and propane respectively.

Keywords: Methane, Ethane, Propane, Light Hydrocarbons, Solubility

1. Introduction

The knowledge of phase equilibrium data on water-hydrocarbon systems is fundamental in the environmental sciences, in petroleum, and in chemical engineering industries. For example, gas solubility in water is an important issue from an environmental aspect due to new legislation on the restriction of hydrocarbon content in disposed water (Chapoy, 2006). However, it has been challenging to accurately describe the phase behavior of such systems by using theoretical approaches due to complicated non-idealities from the strong hydrogen bonding of water molecules (Li and Firoozabadi, 2009). Moreover, the creation of a thermodynamic model has required an advanced study of the phase equilibrium between water (as a basis for the widest spread muds) as well as liquid and gas hydrocarbon phases in wide temperature and pressure ranges from reservoir to atmospheric conditions (Liège, 2006). Thus the prediction of the extent, composition, and other equilibrium properties of the phases in equilibrium is the objective of thermodynamic calculations. Cubic equations of state (EOS) are the most widely used thermodynamic calculation and physical property estimation in petroleum engineering. The two most famous ones are Sova-Redlich-Kwong (SRK) EOS and the Peng-Robinson (PR) EOS (Yan et al., 2007). Using an equation of state requires several input parameters. For pure component inputs, these equations require the critical temperature, critical pressure, and an acentric factor; some of the popular classic equations of state, such as the SRK- and

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PR-EOS, have traditionally had problems in handling polar components like water. The traditional way of fixing this limitation of modeling polar components correctly has been to use a modified attractive term in the equation of state to reproduce the vapor pressure of the polar components more accurately (Mathias et al., 1983). Furthermore, most modern equations of state are developed by fitting parameters (e.g. binary interaction parameters) to experimental data for both pure components and mixtures (Althaus, 1999).

2. Thermodynamic model

There are mainly two different approaches toward modeling phase equilibrium, Φ - Φ approach and γ - Φ approach. The two approaches are based on the fact that at thermodynamic equilibrium, fugacity values are equal in both vapor and liquid phases.

$$f_i^L(P, T) = f_i^V(P, T) \quad (1)$$

The Φ - Φ approach uses an equation of state for each phase of the system. Thus the thermodynamic equilibrium can be written as:

$$x_i \phi_i^L(T, P, x_i) = y_i \phi_i^V(T, P, y_i) \quad (2)$$

For each approach toward the calculation of the fugacity coefficient in the vapor phase and liquid phase, the use of an equation of state is necessary.

Fugacities and/or fugacity-coefficients in mixtures are easily evaluated from all kinds of equation-of-state models. Most equation-of-state models have temperature and volume as the independent variables. In that case, the following, generally valid, expression can be used for the evaluation of the fugacity and/or fugacity-coefficient in mixtures at a constant temperature and composition:

$$RT \ln \phi_i^\lambda = RT \ln \left(\frac{f_i^\lambda}{y_i p} \right) = \int_V^\infty \left(\left(\frac{\partial p}{\partial n_i} \right)_{T, V, n_i^\lambda} - \frac{RT}{V} \right) dV - RT \ln Z \quad (3)$$

2.1. Mathias equation of state

The Mathias equation of state is a modification of the Soave equation, which is of the Redlich-Kwong type:

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

where, for pure fluid i , one may obtain:

$$a_i(T) = 0.42747 \frac{R^2 T_{c_i}^2}{P_{c_i}} \alpha_i(T_{r_i}) \quad (5)$$

$$b_i = 0.08664 \frac{RT_{c_i}}{P_{c_i}} \quad (6)$$

$\alpha_i(T_{r_i})$ is a dimensionless function of the reduced temperature (T_{r_i}) defined as follows:

$$\alpha_i(T_{r_i})^{0.5} = 1 + m_i(1 - T_{r_i}^{0.5}) - p_i(1 - T_{r_i})(0.7 - T_{r_i}) \quad (7)$$

Below the critical temperature and for supercritical components one may obtain:

$$\alpha_i(T_{r_i})^{0.5} = \exp(c_i(1 - T_{r_i}^{d_i})) \quad (8)$$

where, m_i is correlated to the acentric factor:

$$m_i = 0.48508 + 1.55171\omega_i - 0.15613\omega_i^2 \quad (9)$$

The supercritical parameters c_i and d_i are then given by following relations:

$$d_i = 1 + \frac{m_i}{2} + 0.3p_i \quad (10)$$

$$c_i = \frac{d_i - 1}{d_i} \quad (11)$$

The so-called “polar parameter” (p_i) was introduced by Mathias to improve the representation of pure component vapor pressures and is especially effective for polar compounds (Table 1) (Schwartzentruber et al., 1986).

Table 1
Polar parameters.

Compound	p_i
Acetone	0.115100
Acetonitrile	0.186300
Aniline	0.083350
Benzene	0.027090
1-butanol	-0.066952
2-butanol	-0.090424
Dimethyl ether	0.009383
Ethane	0.037690
Ethanol	0.087450
n-heptane	0.068940
n-hexane	0.049050
Methanol	0.168700
Methyl acetate	0.059340
Methyl ethyl ketone	0.102430
Methyl-n propyl ketone	0.075940
n-pentane	0.041290
Propane	0.031580
1-propanol	-0.009389
Isopropyl alcohol	0.064087
Water	0.142200

It should be noted that these parameters were deduced from the generalized Antoine law parameters of the Aspen Plus Pure Component Data Bank.

ϕ_i is the fugacity coefficient of component i in the mixture and can easily be derived from the equation of state using the following relation:

$$RT \ln \phi_i = \int_V^{\infty} \left(\frac{\partial P}{\partial N_i} - \frac{RT}{V} \right) dV - RT \ln Z \quad (12)$$

Considering that Z is the compressibility factor of the mixture, one obtains:

$$\ln \phi_i = -\ln \frac{P(v-b)}{RT} - \frac{a}{bRT} \ln \frac{v+b}{v} + Z - 1 + \left(\sum_{j \neq i} x_j \frac{\partial a}{\partial x_j} \right) \frac{1}{bRT} \ln \frac{v+b}{v} \left(\sum_{j \neq i} x_j \frac{\partial b}{\partial x_j} \right) \left(1 - Z - \frac{a}{bRT} \ln \frac{v+b}{v} \right) \quad (13)$$

2.2. Mixing rules

For mixtures, quadratic mixing rules for both coefficients a and b are assumed to be given by:

$$a = \sum_{i,j} a_{ij} x_i x_j \quad (14)$$

$$b = \sum_{i,j} b_{ij} x_i x_j \quad (15)$$

$$a_{ij} = (a_i a_j)^{0.5} (1 - k_{ij}^a) \quad (16)$$

$$b_{ij} = \frac{b_i + b_j}{2} (1 - k_{ij}^b) \quad (17)$$

3. Results and discussion

k_{ij}^a is used as the adjusting parameter for a_{ij} (attraction term) but because of liquids molecular structure, the repulsive term has effective influence on the correct prediction of system properties especially at high pressures in liquid phase. Therefore, the solubility of hydrocarbons in water is sensitive to b_{ij} (repulsive term) and k_{ij}^b is used to adjust its amount. 25 data points of methane solubility data were used to tune k_{ij}^a and k_{ij}^b through a simplex algorithm in order to minimize average absolute deviation (AAD) of the calculated data toward the experimental data (Culberson and McKetta, 1951).

$$AAD = \frac{1}{N} \sum_1^N \left| \frac{x_{i,exp} - x_{i,cal}}{x_{i,exp}} \right| \quad (18)$$

where, N is the number of data points; x_{exp} is the experimental methane solubility and x_{cal} stands for the calculated methane solubility in water. The same work was done for ethane-water and propane-water systems; 16 data points were used for ethane-water from the work of Culberson and McKetta (1951) and 37 data points were used for propane-water systems (Chapoy, 2004). Finally, two

polynomial cubic type equations were suggested for each system the coefficients of which are tabulated in Tables 2 and 3.

As can be seen in Table 4, different groups of the experimental methane solubility data were used in order to study the ability of the suggested thermodynamic model and corresponding binary interaction parameters in the prediction of methane solubility in water. Finally, the absolute average deviation of each data group plus average error of the whole data are presented; an average error equal to 5.27% was obtained.

Table 2
New suggested binary interaction parameters (k_{ij}^a) for Mathias EOS and classic mixing rules.

	$k_{ij}^a = c_0 + c_1 \times T + c_2 \times T^2 + c_3 \times T^3 \quad T(^{\circ}\text{C})$			
	c_0	c_1	c_2	c_3
Methane	0.46	0.0021	-2.16e-005	8.51e-008
Ethane	0.54			
Propane	0.53			

Table 3
New suggested binary interaction parameters (k_{ij}^b) for Mathias EOS and classic mixing rules.

	$k_{ij}^b = c_0 + c_1 \times T + c_2 \times T^2 + c_3 \times T^3 \quad T(^{\circ}\text{C})$			
	c_0	c_1	c_2	c_3
Methane	-0.356	-0.0615	0.0002	-1.08e-006
Ethane	3.922	-0.133	0.0009	-3.33e-006
Propane	-2.59	-0.087	0.000142	-2.355e-006

Table 4
List of experimental methane solubility data in water studied in this work.

Ref.	T (K)	P (MPa)	No. of Experimental points	AAD (%) This work
Culberson and McKetta (1951)	283.15-444.26	1.04-9.38	35	3.22
Chapoy (2004)	298.15-333.15	1.04-18	12	5.64
Davis and McKetta (1960)	310.9-394.3	0.689-2.758	37	6.66
Yang et al.(2001)	298.1	4.11-12.68	17	5.62
Yarym et al. (1985)	298.15-338.15	2.5-12.5	15	4.72
Lekvam and Bishnoi (1997)	274.48-285.37	1.005-7.058	14	6.7
Gillepsie and Wilson (1982)	323.2-423.2	1.379-13.79	9	6.03
Crovetto et al. (1982)	297.5-430.6	1.327-2.131	5	3.71
Average Error				5.27

Like methane, the same tables of data are presented for ethane (Table 5) and propane (Table 6); the average errors equal to 6.06% for ethane-water and 4.1% for propane-water systems show that our

model, using the suggested binary interaction parameters, has the enough capability of the prediction of these hydrocarbons solubility in water.

Table 5

List of experimental ethane solubility data in water studied in this work.

Ref.	T (K)	P (MPa)	No. of Experimental points	AAD (%) This work
Culberson and McKetta (1951)	310.93-444.26	0.401-8.38	27	6.06

Table 6

List of experimental propane solubility data in water studied in this work.

Ref.	T (K)	P (MPa)	No. of Experimental points	AAD (%) This work
Chapoy (2004)	277.62-368.16	0.357-3.915	61	1.89
Azarnoosh and McKetta (1958)	310.9-394.3	0.362-3.528	52	6.66
Claussen and Polglase (1952)	288.7-377.6	0.5516-3.4474	17	5.62
Kobayashi and Katz (1953)	310.93-383.15	0.496-5.585	14	3.57
Wehe and McKetta (1961)	344.3	0.5114-1.247	8	1.98
Average Error				4.10

Figures 1-3 show of the calculated results of our model for methane-water, ethane-water, and propane-water systems respectively in comparison with the experimental data. As can be seen, there is good agreement between the calculated results and the experimental data.

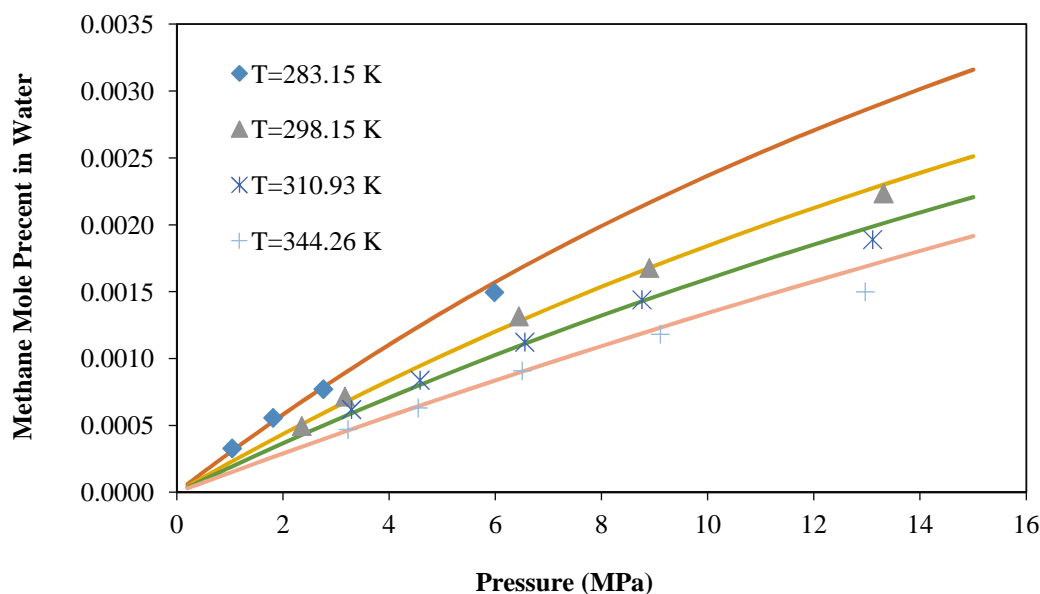
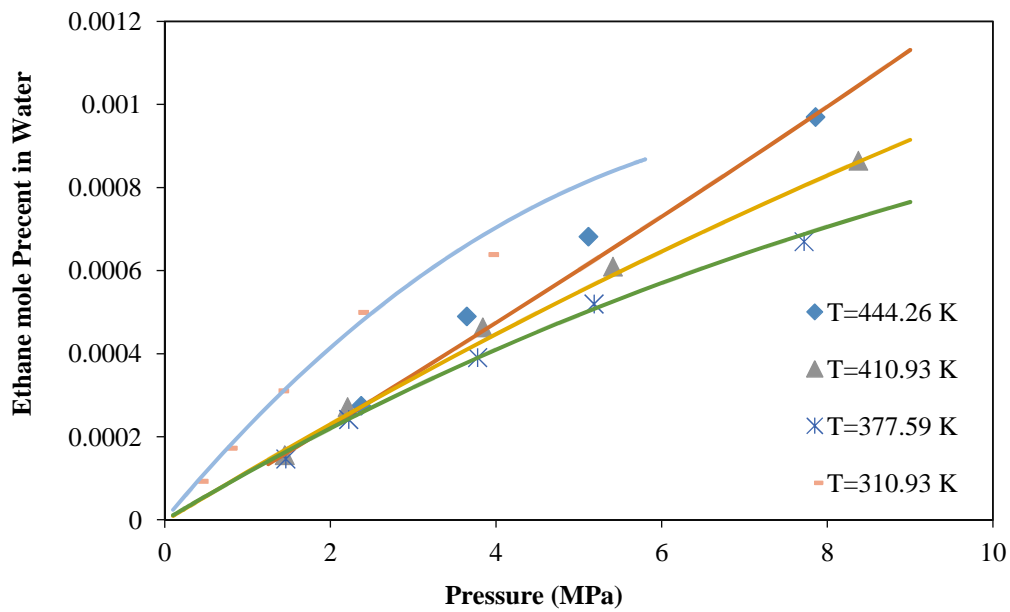
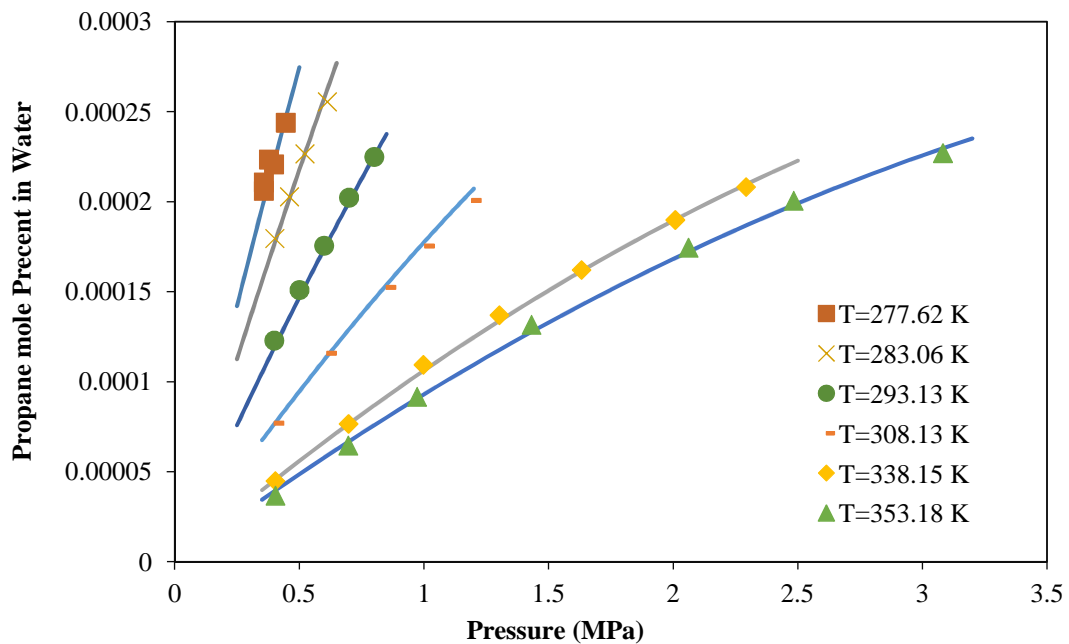


Figure 1

Methane solubility in liquid phase (water); experimental data are from Culberson and McKetta.

**Figure 2**

Ethane solubility in liquid phase (water); experimental data are from Culberson et al.

**Figure 3**

Propane solubility in liquid phase (water); experimental data are from Chapoy.

4. Conclusions

For methane solubility in pure water, suitable relations for k_{ij}^a and k_{ij}^b as binary interaction parameters were suggested and for the temperature range of 274.47 K to 444.26 K and pressures up to 18 MPa, the absolute average error was equal to 5.27%. Furthermore, for ethane solubility in water, in addition to the presentation of relations for k_{ij}^a and k_{ij}^b for a working temperature range of 310.93 K to 444.26

K and pressures up to 8.4 MPa, the absolute average error was equal to 6.06%. Finally, k_{ij}^a and k_{ij}^b binary interaction parameters were developed for propane solubility in water in a temperature range of 277.62 K to 394.3 K and pressures up to 5.6 MPa and the absolute average error was 1.89%.

5. Nomenclature

a	: Parameter of the equation of state (Co-volume parameter) [$\text{m}^3 \cdot \text{Mole}^{-1}$]
b	: Binary interaction parameter for the classical mixing rules
k	: Binary interaction parameter for the classical mixing rules
m	: Parameter of the equation
P	: Pressure (MPa/psia)
T	: Temperature (K)
V	: Volume
X	: Liquid mole fraction
Z	: Compressibility factor
c	: Supercritical parameter
d	: Supercritical parameter
p	: Polar parameter
f	: Fugacity
\emptyset	: Fugacity coefficient
ω	: Acentric factor
α	: Alpha function of the equation of state
g	: Gas
i	: Component i
j	: Component j
cal	: Calculation
exp	: Experimental

References

- Althaus, K., Messung und Berechnung von Wassergehalten kohlenwasserstoffhaltiger Gasgemische, Dissertation, Fortschritt-Berichte VDI Reihe 3, Nr. 590, VDI Verlag, 1999.
- Azarnoosh, A. and McKetta Jr., J. J., The Solubility of Propane in Water: (Experimental and Smoothed Data are Given here for Pressures from Atmospheric to 500 psia and for Temperatures from 60 to 280 °F, Petrol, Vol. 37, p. 275-278, 1958.
- Chapoy, A., Phase Behavior in Water/Hydrocarbon Mixtures Involved in Gas Production Systems, Ph.D. Thesis, Mines Paris Tech, November 2004.
- Claussen, W. F. and Polglase, M. F., Solubilities and Structures in Aqueous Aliphatic Hydrocarbon Solutions, J. Ame. Chem. Soc, Vol. 74, p. 4817-4819, 1952.
- Crovetto, R., Fernandez-Prini, R., and Japas, M. L., Solubilities of Inert Gases and Methane in H₂O and in D₂O in the Temperature Range of 300 to 600 K, J. Chem. Phys. Vol. 76, p. 1077-1086, 1982.
- Culberson, O. L. and McKetta Jr., J. J., Phase Equilibria in Hydrocarbon-water Systems, IV-Vapor-liquid Equilibrium Constants in the Methane-water and Ethane-water Systems, Trans AIME, Pet. Div. 192, p. 297-300, 1951.
- Davis, J. E. and McKetta, J. J., Solubility of Methane in Water, Petroleum Refiner, Vol. 39, p. 205-206, 1960.

- Gillepsie, P. C. and Wilson, G. M., Vapor-liquid and liquid-liquid Equilibria: Water-methane, Water Carbon Dioxide, Water-hydrogen Sulfide, Water-n-pentane, Water-methane-n-pentane, Gas Processors Association Research Report RR-48, Provo, Utah, April, 1982.
- Kobayashi, R. and Katz, D. L., Vapor-liquid Equilibria for Binary Hydrocarbon-water Systems, *Ind. Eng. Chem.*, Vol. 452, p. 440-446, 1953.
- Lekvam, K. and Bishnoi, P. R., Dissolution of Methane in Water at Low Temperatures and Intermediate Pressures, *Fluid Phase Equilibria*, Vol. 131, p. 297-309, 1997.
- Li, Z. and Firoozabadi, A, Cubic-plus-Association Equation of State for Water-containing Mixtures: is "Cross Association" Necessary?, *AIChE J.*, Vol. 55, p. 1803-1813, 2009.
- Liège, C. X., Dissolution of Light Hydrocarbons in Drilling Muds, Prediction of the Nature of a Reservoir Fluid based on Gas Shows, Ph.D. Dissertation, Technical University of Denmark, May 2006.
- Mathias, P. M. and Copeman, T., Extension of the Peng-Robinson Equation of State to Complex Mixtures: Evaluation of the Various Forms of the Local Composition Concept, *Fluid Phase Equilibria*, Vol. 13, p. 91-108, 1983.
- Schwartrentuber, J., Ramlrez, L. P., and Renon, H., Prediction of the Binary Parameters of a Cubic Equation of State from a Group-contribution Method, *Ind. Eng. Chem. Process Des. Dev.*, Vol. 25, p. 804-809, 1986.
- Wehe, A. H. and McKetta, J. J., Method for Determining Total Hydrocarbons Dissolved in Water, *Anal. Chem.*, Vol. 33, p. 291-293, 1961.
- Yan, W., Kontogeorgis, G. M., and Stenby, E. H., Application of the CPA Equation of State to Reservoir Fluids in the Presence of Water and Polar Chemicals, Paper SPE 110006 Presented at the 2007 SPE/Annual Technical Conference and Exhibition held in Anaheim, California, p. 11-14, 2007.
- Yang, S. O., Cho, S. H., Lee, H., and Lee, C. S., Measurement and Prediction of Phase Equilibria for Water + methane in Hydrate Forming Conditions, *Fluid Phase Eq.*, Vol. 185, p. 53-63, 2001.
- Yarym-Agaev, N. L., Sinyavskaya, R. P., Koliushko, I. L., and Levinton, L. Y., Phase Equilibria in the Water Methane and Methanol Methane Binary Systems under High Pressures, *J. Appl. Chem.*, Vol. 58, p. 154-157, 1985.