



A thermodynamic model for LLE behavior of oil/brine/ionic-surfactant/alcohol co-surfactant systems for EOR processes

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ABSTRACT

In this paper application of a thermodynamic model based on NRTL method combined with Debye–Hückel activity coefficient model for electrolyte solutions to represent liquid–liquid-equilibrium (LLE) behavior of systems containing oil, brine and ionic surfactants is investigated. Results are presented in terms of phase split and compositional analysis and compared with experimental data. The effect of degree of dissociation of salt and surfactant in water on the model prediction is also examined. Parameters of Peng–Robinson Equation of State are also determined for such LLE calculations and the methods have been compared with two sets of experimental data. In the second data set, the system contains alcohol co-surfactant in addition to oil, brine and a petroleum sulfonate anionic surfactant. Investigated models may be suitable for evaluation and simulation of chemical EOR projects.

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1. Introduction

After water flooding due to capillary forces large amount of oil may remain in reservoirs and chemical surfactant injection may be the most effective method of enhanced oil recovery to reduce oil saturation in the reservoir. Through chemical (surfactants) method the interfacial tension (IFT) between the oil and water phases can be reduced. With lowering IFT additional oil can be released through lowering capillary forces. Indeed surfactants alone may not be able to significantly enhance the recovery due to the interactions between surfactant and soil and use of other chemicals such as co-surfactant (usually an alcohol) and water-soluble polymer may be needed (Lake, 1989).

Formulation and phase behavior prediction of surfactant–oil–brine systems are important in optimizing the performance of microemulsion systems for enhanced oil recovery (EOR) of reservoirs containing heavy oil (Healy and Reed, 1974; Bourrel and Schechter, 1980). Most of research work reported in the literature on formulation of phase behavior of micro-emulsion systems deal with non-ionic surfactants. In this work based on a set of experimental data on liquid–liquid-equilibrium (LLE) of an ionic-surfactant/oil, brine and co-surfactant a thermodynamic model has been proposed.

Thermodynamic approaches for such systems usually involve use of the following two methods: (1) φ_i -method and (2) γ_i -method. In the first method fugacity coefficients for each component (φ_i) in each phase are calculated through an equation of state (i.e., a cubic EOS) while in the second method an appropriate model for excess Gibbs energy (G^E) is assumed and accordingly a relation for the activity coefficient in the liquid phase (γ_i) can be used.

Generally cubic EOSs (such as Peng–Robinson) are used for high pressure VLE calculations in non-polar (i.e., hydrocarbons) and non-electrolyte (ion-free) systems. Possibility of use of a cubic EOS in predicting phase behavior of microemulsion systems with ionic surfactants and a co-surfactant is also investigated. γ_i -method is generally used for non-ideal liquid systems at low and moderate pressures. There are several widely used models for calculation of γ_i in multicomponent systems which include Scatchard–Hildebrand, NRTL and group contribution methods (i.e., UNIQUAC) methods for non-electrolyte solutions (Sandler, 1998).

In this paper we show applications of γ_i - and φ_i -methods for such systems and propose appropriate modifications with model parameters for prediction purposes. After reviewing several thermodynamic models a modified version of NRTL method is introduced which considers presence of ionic materials due to ionization of salt and surfactant in an aqueous environment. Based on a set of experimental data model parameters have been determined which can be used for LLE calculation of similar systems. Since in most reservoir simulators Peng–Robinson EOS is used for vapor–liquid-equilibrium and PVT calculations (Nelson and Pope, 1978), it has been used in this work for

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Table 1
Physical properties of compounds in the system of oil/brine/surfactant.

Comp.	Compound	M (g/mol)	d_{20} (g/cm ³)	V_{20} (cm ³ /mol)	ϵ
1	Oil	134	0.78	171.8	2.074
2	Water	18.0	1.0	18.0	78.54
3	Surfactant	534.7	1.0	534.7	
	CaCl ₂	110.9			

d_{20} and V_{20} are liquid density and molar volume at 20 °C. ϵ is the dielectric constant.

LLE calculations and method of optimization of its parameters is shown for future applications. Furthermore, proposed models have been compared with Hand's empirical method developed for LLE calculation of water–surfactant–oil systems (Hand, 1939).

2. Thermodynamic models

One of the simplest activity coefficient models is the Scatchard–Hildebrand of regular solution theory and is given as:

$$\ln \gamma_i = V_i(\delta_i - \delta_m)^2 / RT \quad (1)$$

where

$$\delta_m = \sum \Phi_i \delta_i$$

$$\Phi_i = x_i V_i / \sum x_i V_i.$$

x_i is the mole fraction of component i , V_i is the liquid molar volume and δ_i is the solubility parameter.

This model usually works well for non-polar systems whose components are similar in structure but may differ in molecular size. However, because of its simplicity and convenience some people have used it with limited degree of success for polar systems.

The other model investigated in this work was the non-random two liquid (NRTL) model which was developed mainly for systems that their components vary in molecular size and energy and considers local composition factor and has the following form:

$$\ln \gamma_i = \sum_{j=1} A_{ij} G_{ji} x_j / \sum_{j=1} G_{ji} x_j \sum_{j=1} \left[x_j G_{ji} / \sum_{k=1} x_k G_{kj} \right]$$

$$\times \left(A_{ij} - \sum_{k=1} x_k A_{kj} G_{kj} / \sum_{k=1} x_k G_{kj} \right) \quad (2)$$

where

$$G_{ij} = \exp(-\alpha_{ij} A_{ij}) \quad \alpha_{ij} = \alpha_{ji}.$$

This model has three parameters of A_{ij} , A_{ji} and α_{ij} for each pair of species. Values of α_{ij} usually vary from 0.1 to 0.6. However, γ_i calculated from Eq. (2) needs to be modified for the effect of ions present in the system.

Salts (i.e., NaCl, CaCl₂, etc.) in aqueous solutions are ionized to cations (i.e., Na⁺) and anions (i.e., Cl⁻). Presence of such ions complicates behavior of molecules and activity coefficient models as Eq. (1) cannot describe phase behavior of such systems. Debye and Huckel (1923) developed an activity coefficient model (γ^{D-H}) for electrolyte solutions. Their model is widely used in the literature for VLE calculations in mixed solvent–salt systems (Christensen et al., 1983; Hirasaki and Lawson, 1986; Sander et al., 1986; Macedo et al., 1990; Kikic et al., 1991). Electrolyte solutions are considered mixtures of ionic materials (i.e., salt, surfactant, etc.) and non-ionic solvent (water, alcohol, hydrocarbon, etc.). For solvents (indicated by n) the activity coefficients are calculated from the following relation:

$$\ln \gamma_n = \ln \gamma_n^{ne} + \ln \gamma_n^{D-H} \quad (3)$$

where γ_n is the activity coefficient of solvent in ionic solutions, and γ_n^{ne} is the activity coefficient of non-electrolyte solution in the absence of salt or ions and may be calculated from one of the models described above. γ_n^{D-H} is the Debye–Huckel activity coefficient modification due to presence of ions and may be calculated from the following relation:

$$\ln \gamma_n^{D-H} = \left(2AM_n d_s / b^3 d_n \right) \left[1 + bl^{1/2} - 1 / \left(1 + bl^{1/2} \right) - 2 \ln \left(1 + bl^{1/2} \right) \right] \quad (4)$$

M_n	molecular weight of solvent, kg/mol
d_s	density of ion-free solvent solution = $\sum_n x_n' M_n / \sum_n x_n' M_n d_n$
d_n	density of pure solvent n in kg/m ³
x_n'	ion-free mole fraction of solvent n
A	$1.327757 \times 10^5 d_s^{1/2} / (\epsilon T)^{3/2}$ where d_s is in kg/m ³
b	$6.359696 d_s^{1/2} / (\epsilon T)^{1/2}$ where d_s is in kg/m ³
ϵ	dielectric constant of the solvent mixture.

Mixture dielectric constant can be calculated from Osetr's mixing rule (Franks, 1973) which for a binary system is given as:

$$\epsilon_m \approx \epsilon_1 + [(\epsilon_2 - 1)(2\epsilon_2 + 1) / 2\epsilon_2 - (\epsilon_1 - 1)] + x_2' V_2 / V \quad (5)$$

V	$x_1' V_1 + x_2' V_2$
V_1	liquid molar volume of pure solvent 1
x_1'	ion-free mole fraction of solvent 1 in a binary mixture of solvents 1 and 2.

Table 2
Mixture composition (mole fraction) for the whole system of Table 1.

J	z_i (oil)	z_i (water)	z_i (surfactant)
1	0.0055	0.9943	0.0001
2	0.0116	0.9883	0.0001
3	0.0257	0.9741	0.0002
4	0.0433	0.9565	0.0002
5	0.0658	0.9340	0.0002
6	0.0957	0.9041	0.0002
7	0.1372	0.8626	0.0003
8	0.1988	0.8009	0.0003
9	0.2997	0.6999	0.0004
10	0.4955	0.5039	0.0006
11	0.0055	0.9942	0.0003
12	0.0116	0.9881	0.0003
13	0.0258	0.9738	0.0003
14	0.0436	0.9561	0.0004
15	0.0663	0.9333	0.0004
16	0.0964	0.9031	0.0004
17	0.1384	0.8610	0.0005
18	0.2010	0.7984	0.0006
19	0.3041	0.6951	0.0008
20	0.5058	0.4930	0.0012
21	0.0056	0.9938	0.0006
22	0.0118	0.9876	0.0006
23	0.0261	0.9732	0.0006
24	0.0441	0.9552	0.0007
25	0.0672	0.9320	0.0008
26	0.0980	0.9011	0.0009
27	0.1411	0.8579	0.0011
28	0.2057	0.7931	0.0013
29	0.3132	0.6851	0.0017
30	0.5279	0.4696	0.0024

For mixtures 1–10, Exp # Chev 63 T (surfactant wt.% = 0.5); for mixtures 11–20, Exp # Chev 64 T (surfactant wt.% = 1.0); for mixtures 21–30, Exp # Chev 65 T (surfactant wt.% = 2.0).

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