

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:

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

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

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:

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

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).

Table 3Calculation of composition (in mol%) of microemulsion phase from NRTL model (Eq. (2)) assuming $Z_{\text{diss,surf}} = 1$ for the system of Table 1.

Composition in mol% for microemulsion phase, Φ = ratio of moles of oil phase to total number of moles								
Data				Predicted from NRTL				
Oil	Water	Surfactant	100* Φ	Oil	Water	Surfactant	100* Φ	Oil (vol.%)
<i>Exp # Chev 63 T (surfactant wt.% = 0.5)</i>								
0.18	99.81	0.014	0.37	0.55	99.43	0.014	0.00	5
0.43	99.56	0.015	0.73	1.16	98.83	0.015	0.00	10
0.15	99.83	0.016	2.42	0.99	99.00	0.016	1.51	20
0.09	99.90	0.018	4.25	0.96	99.02	0.018	3.23	30
0.36	99.62	0.021	6.24	0.93	99.05	0.021	5.45	40
0.15	99.82	0.024	9.43	0.95	99.03	0.024	8.39	50
0.33	99.64	0.030	13.43	1.05	98.92	0.029	12.47	60
0.77	99.19	0.039	19.26	0.97	98.99	0.038	18.81	70
1.05	98.89	0.057	29.23	1.09	98.85	0.056	29.05	80
1.37	98.51	0.112	48.85	1.08	98.81	0.112	48.99	90
<i>Exp # Chev 64 T (surfactant wt.% = 1.0)</i>								
0.22	99.75	0.029	0.33	0.55	99.42	0.028	0.00	5
0.33	99.64	0.030	0.83	1.16	98.81	0.030	0.00	10
0.48	99.49	0.033	2.12	1.00	98.97	0.033	1.57	20
0.44	99.52	0.037	3.93	0.97	99.00	0.036	3.36	30
0.51	99.45	0.042	6.15	0.98	98.98	0.041	5.63	40
0.48	99.47	0.049	9.21	1.03	98.92	0.049	8.63	50
0.64	99.30	0.060	13.29	0.97	98.97	0.060	12.94	60
1.13	98.80	0.078	19.19	0.99	98.93	0.078	19.27	70
1.51	98.37	0.115	29.34	1.01	98.87	0.115	29.69	80
2.57	97.19	0.230	49.28	1.17	98.59	0.234	50.00	90
<i>Exp # Chev 65 T (surfactant wt.% = 2.0)</i>								
0.18	99.76	0.058	0.38	0.56	99.38	0.057	0.00	5
0.36	99.58	0.060	1.00	1.18	98.76	0.060	0.00	10
0.54	99.40	0.066	2.44	0.92	99.01	0.066	1.70	20
0.70	99.22	0.074	4.24	0.96	98.96	0.074	3.47	30
0.88	99.03	0.084	6.57	0.98	98.94	0.084	5.79	40
1.07	98.84	0.099	9.66	0.99	98.91	0.099	8.90	50
1.38	98.50	0.121	13.98	1.00	98.88	0.122	13.24	60
1.71	98.13	0.159	20.47	1.02	98.82	0.161	19.75	70
3.15	96.61	0.236	31.27	1.04	98.72	0.241	30.60	80
7.19	92.33	0.480	52.83	1.12	98.37	0.511	52.26	90

The ionic strength (I) is defined as:

$$I = \text{ionic strength} = \frac{1}{2} \sum_{i=\text{ion}} z_i^2 m_i \quad (6)$$

z_i valences of ions (i.e., for Ca^{++} , $z = +2$ and for Cl^- , $z = -1$)
 m_i molality (mol/kg of water) of ions i .

3. Experimental data

Two sets of data have been used in this work. Data set I involved a system of oil, brine and ionic surfactant (sodium dodecylsulfonate) and data set II involved oil, brine, surfactant (petroleum sulfonate) and a co-surfactant (2-methyl, 1-propanol or Isobutyl alcohol, IBA). Surfactants used for the test were obtained from Witco Corporation. Experimental data used in this work were conducted at the UT/Austin (Delshad, 2004). In the first set of experiments, the system consists of mainly two phases of oil and micro-emulsion (water + oil + surfactant). Oil has molecular weight of 134 and density (at 20 °C) of 0.78 g/cm³ while these values for the surfactant are 534.7 and 1 g/cm³, respectively. The water contained CaCl₂ salt at concentration of 500 mg/l (Ca⁺⁺) which is equivalent to salt concentration of 0.138 wt.%. Equilibrium compositions were determined visually through measuring volume of oil phase and location of oil interface with the micro-emulsion phase. The oil phase was nearly free of water or surfactant. The experiments were conducted at atmospheric pressure and room temperature of 293 K. Three sets of experiments were conducted with three surfactant concentrations (0.5, 1 and 2 wt.%). In each set, 10 different oil volumes were used at which initial volume of oil varied from 5 to 90% of total volume of system. The total number of

experiments performed was 30. In the second set of experiments, salt concentration varied from 0.1 to 0.9 wt.% and an alcohol co-surfactant was used. A co-surfactant such as IBA when involved with surfactant molecules change properties such as solubility of surfactant.

4. LLE calculation scheme

4.1. Modified NRTL model

Formulation of liquid-liquid equilibrium at low pressures is discussed by Null (1980). If the oil-rich phase is specified by "o" and

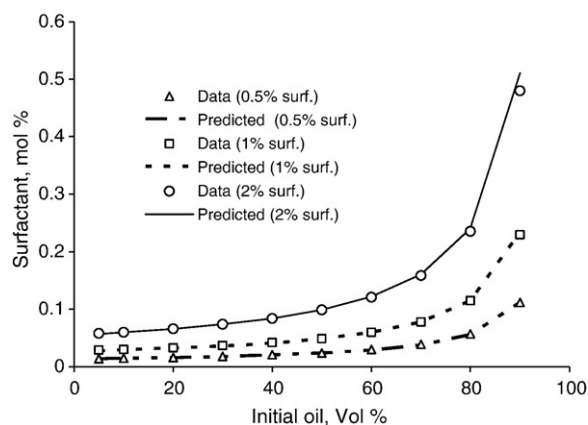


Fig. 1. Prediction of surfactant composition in the micro-emulsion phase using NRTL model for the oil/brine/surfactant system of Table 1.

Table 4
Effect of degree of dissociation of surfactant on NRTL model prediction for the system of Table 1.

Oil (vol%)	Exp. data surf. (vol.%)	Calc., $Z_{\text{diss}} = 1$	Calc., $Z_{\text{diss}} = 0$
<i>Exp # Chev 63 T (surfactant wt.% = 0.5)</i>			
5	0.51	0.50	0.50
10	0.53	0.50	0.50
20	0.59	0.56	0.56
30	0.66	0.62	0.62
40	0.74	0.71	0.70
50	0.88	0.83	0.82
60	1.06	1.00	0.99
70	1.33	1.30	1.27
80	1.91	1.89	1.81
90	3.65	3.70	3.31
<i>Exp # Chev 64 T (surfactant wt.% = 1)</i>			
5	1.02	1.00	1.00
10	1.06	1.00	1.00
20	1.15	1.11	1.11
30	1.29	1.24	1.24
40	1.47	1.41	1.41
50	1.72	1.65	1.63
60	2.07	2.02	1.98
70	2.61	2.62	2.55
80	3.71	3.83	3.64
90	6.79	7.42	6.64
<i>Exp # Chev 65 T (surfactant wt.% = 2)</i>			
5	2.05	2.00	2.00
10	2.12	2.00	2.00
20	2.30	2.24	2.23
30	2.54	2.49	2.48
40	2.86	2.84	2.81
50	3.30	3.32	3.28
60	3.95	4.05	3.97
70	5.02	5.26	5.10
80	6.74	7.69	7.33
90	10.79	14.98	13.78

Calculated values of surfactant vol.% in the microemulsion phase are compared with the actual values for two cases of full ($Z_{\text{diss}} = 1$) and no dissociation ($Z_{\text{diss}} = 0$). Note that data presented in Table 3 are in mol% calculated from original data in vol.%.

the microemulsion (water-rich) phase is specified by “w”, then the equilibrium relation for all components in the system is given by:

$$x_i^o \gamma_i^o = x_i^w \gamma_i^w \quad (7)$$

where x_i^w is the mole fraction of component i in the microemulsion (or water-rich) phase. Derivation of this equation is straightforward and by equating fugacities of each component in both phases ($f_i^o = f_i^w$) and using the definition of activity coefficient in each phase ($\gamma_i^o = x_i^o f_i$)

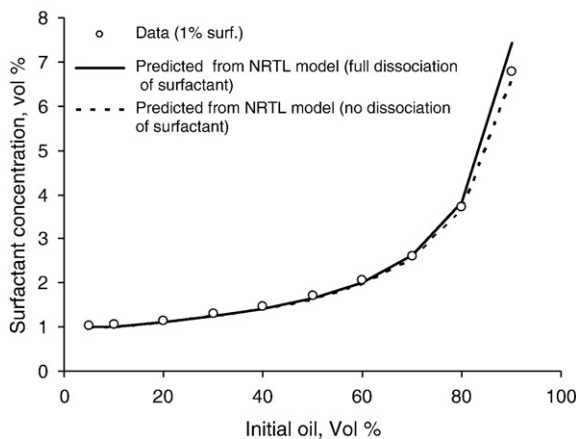


Fig. 2. Effect of degree of dissociation of surfactant on prediction of surfactant composition (vol.%) using NRTL model for the oil/brine/surfactant system of Table 1 at initial surfactant concentration of 1 wt.%.

Table 5
Calculated PR EOS parameters through optimization for the oil/brine/water system of Table 1.

Comp.	Compound	T_c (K)	P_c (MPa)	ω	a ($\text{m}^3/\text{mol} \times \text{J}/\text{mol}$)	b (m^3/mol)
1	Oil	623.7	20	0.444	0.98475	1.8978×10^{-5}
2	Water	647.1	22.06	0.345	1.056	2.01714×10^{-5}
3	Surfactant	800.0	30	0.40	1.2647	1.72488×10^{-5}

we have: $x_i^o \gamma_i^o f_i = x_i^w \gamma_i^w f_i$ in which by canceling f_i (fugacity of pure component i) Eq. (7) can be derived. If we assume Φ represents the mole ratio of oil phase to the total number of moles in the system, then through material balance between two phases we get:

$$x_i^w = z_i / [1 + \Phi(K_i - 1)] \quad (8)$$

where z_i is the mole fraction of component i in the whole mixture (both phases combined) and K_i is equilibrium ratio defined as:

$$K_i = x_i^o / x_i^w = \gamma_i^w / \gamma_i^o \quad (9)$$

When two phases of oil and microemulsion are in equilibrium, Φ is between 0 and 1 and

$$\sum_i x_i^w = 1. \quad (10)$$

To determine Φ the function $\psi = \sum_i x_i^w - 1$ must become zero. Newton–Raphson method may be used to obtain Φ (Null, 1980). In practice when $\psi < 10^{-5}$, assumed value of Φ is considered as a correct answer.

In our calculation scheme we assume salt (CaCl_2) is only dissolved in water and is considered as part of water. Assumption of brine as a single pseudocomponent is a valid assumption in the study of microemulsion phase behavior (Robertson, 1986). However, its ions affect the activity coefficients of solvents. In this system, hydrocarbon and water are considered non-ionic (solvents) while surfactant and salt are the ionic materials which may dissociate in aqueous solutions. The dissociation reaction (ionization) for the salt is:



For surfactant the dissociation reaction is:



where R is the hydrophobic tail of surfactant molecule. If the degree of dissociation (ionization) is shown by Z_{diss} , then number of moles of Na^+ produced is $Z_{\text{diss}} m_{\text{surf}}$ in which m_{surf} is the molality of surfactant. Z_{diss} can be determined from the equilibrium constant K_{diss} as the following

$$Z_{\text{diss, surf}} = \left[(K_{\text{diss, surf}} / (1 + K_{\text{diss, surf}})) \right]^{1/2}. \quad (13)$$

For full dissociation as $K_{\text{diss}} \rightarrow \infty$ then $Z_{\text{diss}} \rightarrow 1$. In our analysis we assume both reactions (11) and (12) are 100% complete ($Z_{\text{diss}} = 1$) and there is no chemical reaction between anionic surfactant (R-SO_3^-) and bivalent ions (Ca^{++}). If such a reaction exists then we have to modify our calculation procedure. Under such conditions we have:

$$m_{\text{R-SO}_3^-} = m_{\text{Na}^+} = m_{\text{surf}} \quad (14)$$

$$m_{\text{CaCl}_2} = m_{\text{Ca}^{++}} = \frac{1}{2} m_{\text{Cl}^-} \quad (15)$$

where m_{surf} is the molality of surfactant and represents moles of surfactant dissolved in each kg of water.

Table 6
Calculated k_{ij} parameters through optimization for the oil/brine/water system of Table 1.

Binary	Compound	k_{ij}
1–2	Oil–water	0.242–0.2042 (z_1)
1–3	Oil–surf.	–1.8553
2–3	Water–surf.	–1.9095

Table 7

Calculation of composition (in vol.%) of oil phase from PR EOS model for the oil/brine/surfactant system of Table 1.

Composition in vol.% for the oil phase, Φ = ratio of moles of oil phase to total number of moles								
Data ^a				Predicted from PR EOS				
Oil	Water	Surfactant	100* Φ	Oil	Water	Surfactant	100* Φ	Oil (vol.%)
<i>Exp # Chev 63 T (surfactant wt.% = 0.5)</i>								
100.00	0.00	0.00	3.36	99.93	0.07	0.01	2.58	5
100.00	0.00	0.00	6.31	99.93	0.07	0.01	7.69	10
100.00	0.00	0.00	18.86	99.92	0.07	0.01	17.82	20
100.00	0.00	0.00	29.31	99.91	0.08	0.01	27.97	30
100.00	0.00	0.00	37.96	99.90	0.09	0.01	38.10	40
100.00	0.00	0.00	49.31	99.89	0.10	0.01	48.15	50
100.00	0.00	0.00	58.77	99.86	0.13	0.01	58.24	60
100.00	0.00	0.00	67.83	99.81	0.17	0.02	68.20	70
100.00	0.00	0.00	78.02	99.68	0.29	0.02	78.03	80
100.00	0.00	0.00	88.73	99.07	0.88	0.06	87.46	90
<i>Exp # Chev 64 T</i>								
100.00	0.00	0.00	2.98	99.92	0.07	0.01	2.57	5
100.00	0.00	0.00	7.14	99.92	0.07	0.01	7.65	10
100.00	0.00	0.00	16.41	99.91	0.07	0.01	17.81	20
100.00	0.00	0.00	27.10	99.91	0.08	0.01	27.96	30
100.00	0.00	0.00	37.14	99.89	0.09	0.02	38.08	40
100.00	0.00	0.00	47.77	99.88	0.10	0.02	48.13	50
100.00	0.00	0.00	57.62	99.85	0.13	0.03	58.18	60
100.00	0.00	0.00	66.84	99.79	0.17	0.03	68.20	70
100.00	0.00	0.00	77.21	99.65	0.30	0.05	78.05	80
100.00	0.00	0.00	87.68	98.93	0.93	0.14	87.47	90
<i>Exp # Chev 65 T</i>								
100.00	0.00	0.00	3.31	99.91	0.07	0.02	2.63	5
100.00	0.00	0.00	6.25	99.91	0.07	0.02	7.75	10
100.00	0.00	0.00	18.12	99.90	0.07	0.03	17.83	20
100.00	0.00	0.00	28.06	99.89	0.08	0.03	27.98	30
100.00	0.00	0.00	36.50	99.88	0.09	0.04	38.10	40
100.00	0.00	0.00	46.88	99.86	0.10	0.04	48.22	50
100.00	0.00	0.00	56.04	99.82	0.13	0.05	58.26	60
100.00	0.00	0.00	65.43	99.75	0.18	0.07	68.24	70
100.00	0.00	0.00	74.44	99.57	0.31	0.12	78.07	80
100.00	0.00	0.00	83.63	98.58	1.06	0.36	87.58	90

^a Data are based on visual observation in which the oil phase is nearly pure with insignificant amount of water and surfactant.

For our system we assume there are three components in the system: oil (component 1), water (component 2) and surfactant (component 3). As mentioned earlier salt is considered as part of water (brine as a pseudocomponent) and the whole oil is also considered as a single carbon number (SCN) pseudocomponent. Assumption of single component for oil and brine is widely used in such analyses (Robertson, 1986). The oil density is 0.781 g/cm³ which is equivalent to SCN of C₁₀ group with molecular weight of 134 (Riazi, 2005). Properties of components involved in the system are given in Table 1. Value of dielectric constant of water is taken from CRC Handbook (Weast and Astle, 1981). For oil, value of ϵ is calculated from refractive index at 20 °C (n_{20}) as for hydrocarbons we have $\epsilon \approx n^2$ (Speight, 1999). Value of n_{20} for C₁₀ hydrocarbon group is taken from ASTM Manual 50 (Riazi, 2005).

For all three components involved in the system values of γ_i are calculated from Eqs. (2) and (3). However, only for surfactant, Eq. (3) for calculation of ionic effects, $\ln \gamma^{D-H}$ is modified in the following form:

$$\ln \gamma_n^{D-H} = \left(2AM_n d_s / b^3 d_n \right) \left[1 + bl^{1/2} - 1 / (1 + bl^{1/2}) \right] - 2 \ln(1 + bl^{1/2}) + \delta l \quad (16)$$

where the term δl is a correction term to consider the interaction that may exist between surfactant ions and salt ions. This interaction term is in fact a simplified version of interaction between different ions as suggested by Christensen et al. (1983). Parameter δ in the above

relation is an adjustable parameter that can be determined from experimental data. We found that addition of this term greatly improves model capability to predict surfactant composition. In calculation of A and b special unit of kg/m³ must be used for density while in the above equation M_n is in kg/mol. Eq. (5) is used to calculate dielectric constant of solvent mixture (hydrocarbon + water). Parameter l should be calculated from Eq. (6). For a mixture

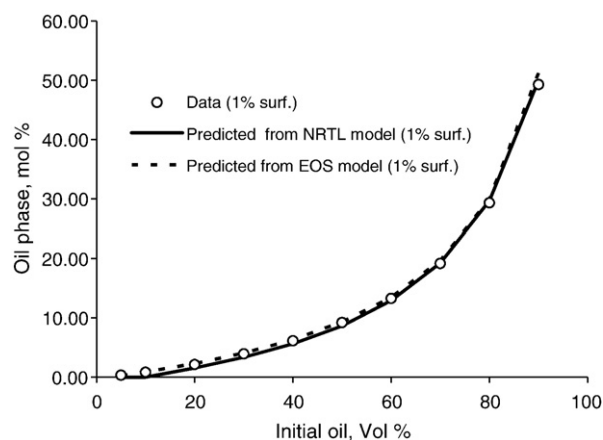


Fig. 3. Prediction of amount of oil phase (mol%, 100 Φ) using NRTL and EOS models for the oil/brine/surfactant system of Table 1 at surfactant concentration of 1 wt.%.

Table 8
Physical properties of compounds in the system of oil/brine/surfactant/co-surfactant.

Comp.	Compound	M (g/mol)	d_{20} (g/cm ³)	V_{20} (cm ³ /mol)
1	Oil	142.3	0.73	194.9
2	Water	18.01	0.998	18
3	Surfactant	420	1	420
4	Alcohol, IBA	74.12	0.802	92.4

d_{20} and V_{20} are liquid density and molar volume at 20 °C.

of anionic surfactant and CaCl₂, Eq. (6) gives the following relation in terms of molality of compounds:

$$I = 3Z_{\text{diss.salt}}m_{\text{salt}} + Z_{\text{diss.surf}}m_{\text{surf}} \quad (17)$$

where m_{salt} is the molality of salt (CaCl₂) and m_{surf} is the molality of surfactant in mol/kg of water. In order to obtain various adjustable parameters for the activity coefficient model, the following objective (OF) function is defined:

$$\text{OF} = \left\{ \sum_j \theta_j^{\text{calc}} / (\theta \exp - 1)^2 \right\}^{1/2} / N_j \quad (18)$$

where N_j is the number of data points (in our case $N_j = 30$).

4.2. EOS model

For the EOS model we use the original PR EOS as given (Riazi, 2005):

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b) + b(V-b)} \quad (19)$$

$$a = \frac{0.45724R^2T_c^2}{P_c} \left[1 + f_\omega (1 - T_r^{0.5}) \right]^2$$

$$b = 0.0778RT_c / P_c$$

$$f_\omega = 0.37464 + 1.54226\omega - 0.26992\omega^2.$$

For defined mixtures a and b are calculated as:

$$\begin{aligned} a_{\text{mix}} &= \sum \sum x_i x_j (a_i a_j)^{1/2} (1 - k_{ij}) \\ b_{\text{mix}} &= \sum x_i b_i. \end{aligned} \quad (20)$$

For two phases of oil and microemulsion, the equilibrium ratios, K_i , are defined as:

$$K_i = \frac{x_i^{\text{OIL}}}{x_i^{\text{ME}}} = \frac{\varphi_i^{\text{ME}}}{\varphi_i^{\text{OIL}}} \quad (21)$$

where i is oil, water and surfactant. ME stands for microemulsion phase and φ is fugacity coefficient determined from PR EOS through standard relations (Riazi, 2005; Riazi and Moshfeghian, 2007).

4.3. Empirical Hand's method

The Hand's rule is an empirical method which assumes the bionodal curve to be the same in various LLE systems and is based on the observation that equilibrium phase concentration ratios follow a straight line on a log–log graph (Hand, 1939). Then the bimodal curve can be calculated from the following relation:

$$\frac{x_3}{x_1} = A \left(\frac{x_3}{x_2} \right)^B \quad (22)$$

in which A and B are empirical constants specific for each system and x_1, x_2 and x_3 are mole fractions of oil, water and surfactant, respectively ($x_1 + x_2 + x_3 = 1$). For a symmetric bimodal curve with $B = -1$, surfactant concentration can be calculated from oil concentration (x_1) in the following form (Alban and Gabitto, 1999):

$$x_3 = 0.5 \left[-Ax_1 + \sqrt{(Ax_1)^2 + 4A(1 - x_1)} \right]. \quad (23)$$

The Hand's rule has no theoretical basis and can represent systems with three components, thus one cannot use it when a co-surfactant is present in addition to surfactant, oil and water. Although the method has been used in some simulators such as UTCHEM (Nelson and Pope, 1978) but a more accurate and fundamentally based approach would be an attractive alternate for such methods. Especially use of a cubic EOS is attractive because it already exists in all simulators developed for PVT and VLE phase behavior calculations.

5. Calculation results and discussion

5.1. NRTL model

Due to simplicity, the first model evaluated was the Hildebrand model (Eq. (1)). The solubility parameter for oil is 7.7 (cal/cm³)^{1/2} and for water is 23.4 (cal/cm³)^{1/2} (Riazi, 2005). Solubility parameter of surfactant was considered as an adjustable parameter. Simply this model did not work for our system. This was mainly expected as the Hildebrand activity coefficient model is usually used for non-polar systems.

The second model that was used for calculation of LLE in surfactant–water–oil system is a modified version of NRTL model as expressed by Eqs. (2)–(6). For surfactant, Eq. (17) was used instead of Eq. (6). Parameter δ in Eq. (16) was determined by minimizing the following objective function:

$$\xi = \left\{ \sum_j \left[\left(x_{\text{surf}}^{\text{jacalc}} - x_{\text{surf}} \exp \right)^2 \right] \right\}^{1/2} / N_j \quad (24)$$

for our data set, $N_j = 30$.

Mixture composition in terms of mole fraction is given in Table 2.

Table 9
General properties and initial composition in mol, vol. and wt.% for one set of experiment (salt concentration of 0.1 wt.%) for the oil/brine/surfactant/co-surfactant system of Table 8 at 1 atm.

Component	Name	Initial volume (cm ³)	Mol (wt.)	Density (g/cm ³)	Initial feed composition in %		
					mol%	vol.%	wt.%
1	Oil (n-C ₁₀)	50.41	142.3	0.73	8.98	42.61	50.23
2	Water	46.95	18.01	0.998	90.33	54.26	46.78
3	Surfactant	1.5	420	1	0.12	1.74	1.49
4	Alcohol	1.5	74.12	0.802	0.56	1.39	1.49
Total		100.36			100.00	100.00	100.00

Table 10

Calculated PR EOS parameters through optimization for the oil/brine/surfactant/co-surfactant system of Table 8.

Comp.	Compound	T_c (K)	P_c (MPa)	ω	a ($\text{m}^3/\text{mol} \times \text{J}/\text{mol}$)	b (m^3/mol)
1	Oil	932.4 – 459.56 × salt wt.%	20	0.444	From 1.90503 to 0.64956	From 2.5652×10^{-5} to 1.6764×10^{-5}
2	Water	647.3	22.055	0.345	0.97720	1.8978×10^{-5}
3	Surfactant	800.0	30	0.400	1.25576	1.7249×10^{-5}
4	Alcohol	547.8	4.3	0.592	3.76066	8.2403×10^{-5}

The NRTL parameters (A_{ij} and α_{ij}) in Eq. (2) were determined by minimizing OF in Eq. (18). The results are given as:

$$A_{\text{oil-water}} = A_{12} = 10$$

$$A_{\text{water-oil}} = A_{21} = 1$$

All other A_{ij} s are zero; $A_{ij} = 0$ (for $A_{13}, A_{31}, A_{23}, A_{32}$) where component 3 is surfactant.

$$\alpha_{ij} = 0.1 \text{ (for all values of } i \text{ and } j\text{)}$$

$$\delta = -50.$$

Parameter δ for use in Eq. (16) was found by minimizing objective function ξ in Eq. (24). It was found that the interaction parameters A_{ij} for oil-surfactant and water-surfactant pairs are all zero. Thus there was no need to determine α_{ij} for such pairs. Parameter δ in Eq. (16) had a good impact on calculation of surfactant composition x_{surf}^w . By ignoring the interaction term in Eq. (16) [i.e., $\delta = 0$], it was not possible to obtain a good match between experimental and calculated surfactant mole fractions.

Required data for our calculations is the overall mixture composition (Z_1, Z_2 and Z_3) in addition to temperature and pressure. Calculated values of mixture composition based on data of Table 1 are given in Table 2. Calculated composition of microemulsion (ME) phase in terms of mole percentage is given in Table 3. Predicted values of Φ (oil phase fraction) are also given in this table. Predicted weight percent of surfactant is also shown in Fig. 1. The model also predicts composition of oil phase as nearly as a pure oil ($x_{\text{oil}}^o \approx 1$). However, as shown in Table 3, predicted values of Φ for the first and last two data points deviate from experimental values. Predicted values of x_{oil}^o for such points also deviate significantly from expected value of unity. As it is seen from Table 3, the first and last two points in each data set represent the extreme cases of very low or very high oil ratios (5 or 90%). For the first data point value of Φ is so small that a trivial solution of zero was obtained in satisfying Eq. (10). However, in practical applications values of Φ are not at these limiting cases. It is believed that a large difference in molecular weights of water and surfactant in the system has also contributed to this difficulty when Φ is very small or large. Moreover assumption of pure oil phase is theoretically invalid.

In our calculations ionic strength (parameter I) was calculated from Eq. (17) assuming Z_{diss} for both salt and surfactant as unity. This is to assume full ionization for both components. However, by keeping the degree of dissociation of surfactant ($Z_{\text{diss,surf}}$) variable, it is possible to predict better values for surfactant mol or vol.%. Calculated values of surfactant vol.% in the microemulsion (ME) phase for two extreme cases of $Z_{\text{diss,surf}} = 1$ (100% dissociation) and $Z_{\text{diss,surf}} = 0$ (no surfactant dissociation) are given in Table 4 as well as Fig. 2. As we can see from these results, parameter Z_{diss} has some effects on model predictions. While assumption of full dissociation for salt is reasonable but for surfactant may not be valid. Many factors such as pH, temperature, salinity, etc. can affect the degree of ionization of surfactant.

5.2. Evaluation of EOS model

In this model PR EOS in the form of Eqs. (19)–(21) is used to calculate the phase split. For the components shown in Table 1 for the

oil/brine/surfactant system, PR EOS parameters have been obtained through optimization and are given in Table 5. Calculated binary interaction parameters (BIPs), k_{ij} are given in Table 6. In this table BIP of oil–water pair is given in terms of a linear function of Z_i which is the mole fraction of oil in the original fluid (initial mixture). All data given in Table 2 have been used for the optimization of BIP's. The critical properties of water given in Table 5 are true value while for oil are predicted from its molecular weight through the method given in ASTM Manual 50 (Riazi, 2005) and assuming the oil is similar to a n-alkane hydrocarbon. For the surfactant the critical values are calculated based on the molecular weight and are fixed for any ionic-surfactant of similar nature (i.e., petroleum based sulfonate) as calculations showed the results are not very sensitive to such data for the surfactant. For both surfactants that were used in this study critical properties of 800 K and 30 bar (and acentric factor of 0.400) were used in which they are recommended for all future calculations without any changes. Calculated composition in terms of vol.% for the system of Table 1 when PR EOS model is used is given in Table 7. For the third sample of data presented in this table the Hand's rule (Eq. (22)) was also used for calculation of surfactant composition in the oil phase in which resulted an average error of 14% while calculated surfactant composition through NRTL method (as shown in Table 4) has average error of 1.3% and for PR EOS as presented in Table 7 gives an average error of 1.7%.

Phase behavior prediction from PR EOS model for the system of Table 1 is generally as good as NRTL model. For example for predicting water mol% for all 30 data points of Table 3, the modified NRTL model gives an average error (%AAD) of 0.8% while the PR EOS model gives an error of 0.9%. A comparison between the two models for the amount of oil phase (100 Φ) is shown in Fig. 3. In this figure the ratio of oil phase to total mixture is shown by Φ which is defined as

$$\Phi(\text{mole basis}) = \frac{\text{moles of oil phase}}{\text{moles of oil phase and moles of ME phase}} \quad (25)$$

The second data set that was used for evaluation purposes is based on a system consisting a co-surfactant (iso-butyl-alcohol, IBA), water, oil and surfactant. Surfactant is a petroleum sulfonate with molecular weight of 420, oil is simply n-decane and salt is NaCl. The initial composition in terms of vol.% is: 1.5 vol.% surfactant, 1.5 vol.% IBA, 50 vol.% n-decane (oil) and the rest (47 vol.%) is water. Total volume of 100 cm^3 was used in each experiment. In this set of experiments temperature and pressure were kept constant (30 °C and 1 atm) while salt concentration varied from 0.1 to 1 wt.%. It was observed that at salt concentrations below 1 wt.% the system formed two phases of oil and

Table 11Calculated k_{ij} parameters for PR EOS through optimization for the oil/brine/surfactant/co-surfactant system of this table.

Binary	Compound	k_{ij}
1–2	Oil–water	0.2483
1–3	Oil–surf.	2.000
1–4	Oil–alcohol	1.4661
2–3	Water–surf	1.8015
2–4	Water–alcohol	1.2231
3–4	Surf–alcohol	–2.000

Table 12
Prediction of composition (in mol%) of microemulsion (ME) phase from PR EOS for the oil/brine/surfactant/co-surfactant system of Table 10.

Salt wt. %	Data for the ME composition, mole fraction				Predicted composition of ME, mole fract. ^a				
	Oil	Water	Surfact	Alcohol	Oil	Water	Surfact	Alcohol	% AD
0.1	0.000000	0.992242	0.001362	0.006396	8.79E-05	0.992353	0.001362	0.006197	0.00
0.196	0.000118	0.992158	0.001363	0.006361	0.000164	0.992278	0.001362	0.006196	0.07
0.303	0.000877	0.991490	0.001373	0.006259	0.000323	0.992119	0.001362	0.006196	0.81
0.402	0.000373	0.992011	0.001366	0.006250	0.000597	0.991847	0.001362	0.006194	0.29
0.496	0.006755	0.985539	0.001350	0.006356	0.001057	0.99139	0.001361	0.006192	0.81
0.598	0.008778	0.983550	0.001360	0.006313	0.001932	0.990521	0.00136	0.006186	0.00
0.7	0.014420	0.977745	0.001354	0.006481	0.00347	0.988995	0.001358	0.006177	0.29
0.798	0.010764	0.981304	0.001349	0.006584	0.005969	0.986516	0.001353	0.006162	0.30
0.901	0.021447	0.970956	0.001343	0.006254	0.010281	0.982276	0.001337	0.006107	0.45

^a % AD is % relative absolute deviation error calculated for surfactant composition and for all data the overall average error of 0.34%.

microemulsion (ME), while at salt concentrations of 1 to 1.1 wt.%, three phases of oil, ME and water were formed and for salt concentrations ranging from 1.2 to 1.5 wt.% two phases of ME and water were observed. General properties of the components for this system are given in Tables 8 and 9. Experimental data were converted into mole fraction as shown in Table 9. For this data set only two phases of oil and microemulsion (ME) were observed.

Calculated value of PR EOS parameters for this system including BIPs are given in Tables 10 and 11. Value of T_c in Table 10 for oil is given as a function of salt concentration determined only for this data set and for the condition of $T=303.2$ K and $P=0.10325$ MPa. A non-linear optimization program was developed for this purpose (Marquardt, 1963). Predicted composition of ME phase from PR EOS is given in Table 12. A comparison between predicted values of water concentration in the ME phase with actual data is also shown in Fig. 4 for this system. The oil phase was nearly pure with little water and surfactant in it for all 9 salt concentration. The overall average error for calculation of surfactant concentration from this method is 0.34% as shown in the last column of Table 12.

Results presented in this paper indicate that both modified version of NRTL and a modified PR EOS model are capable of predicting phase behavior of oil/brine/surfactant or oil/brine/surfactant/co-surfactant systems with acceptable accuracies. Although the NRTL model is slightly more accurate than PR EOS but the advantage of a cubic EOS is that it already exists in nearly all reservoir simulators and with appropriate modification and optimized values of input parameters liquid–liquid phase behavior can be estimated with good accuracy. Use of EOS is particularly attractive over empirical Hand's rule as it can be used simultaneously for gas–liquid–liquid systems present in petroleum reservoirs. All data used in this study have been in the two-phase region in which only two phases of oil and microemulsion coexist

together. However, as high brine salinity reduces the surfactant solubility an excess brine phase can be formed at such high salinity concentration of brines (Hirasaki, 1981). Usually when salt concentration in brine reaches about 1 wt.% three phases may form. In such cases the proposed model should be expanded to present three-phase systems (oil, microemulsion and brine phases). This can be a future phase of this study as more experimental data become available for ionic surfactant/oil/brine/co-surfactant systems.

6. Conclusions

In this paper liquid–liquid–equilibrium data on two types of oil/brine/ionic surfactant, and co-surfactant systems have been used to propose modified NRTL and cubic equation of state models. Generally the NRTL model calculates phase composition with AAD of 0.8% and for the EOS model with AAD of 0.9%. The advantage of NRTL model is that it does not require critical properties while the advantage of cubic EOS is that it can be used at the same time for vapor–liquid–equilibrium calculations for cases that gas phase exists in the system. The effects of surfactant and salt dissociations were also studied and it was found that the degree of surfactant dissociation affects phase split and composition calculations.

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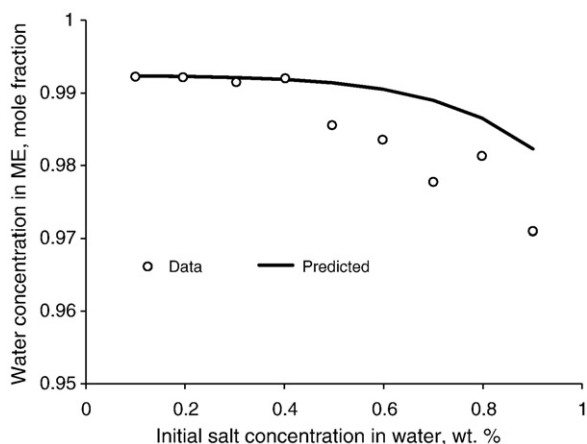


Fig. 4. Prediction of water concentration in microemulsion (ME) phase from PR EOS for the oil/brine/surfactant/co-surfactant system of Table 10.

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