Segment-Based Excess Gibbs Energy Model for Aqueous Organic Electrolytes

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The aqueous electrolyte nonrandom two-liquid (NRTL) model of Chen et al. is extended to represent the excess Gibbs energy of aqueous organic electrolytes. These organic electrolytes exhibit very different solution nonideality from typical aqueous electrolytes with elemental ions. The proposed extension is an integration of the electrolyte NRTL model for aqueous electrolytes and the polymer NRTL model (Chen, 1993) for oligomers and polymers. Organic ions are treated as oligomers that consist of hydrocarbon segments and ionic segments that each exhibit distinctive physical interactions with neighboring species. This integrated NRTL model captures the nonideal phase behavior of aqueous organic electrolytes, including micelle formation. The model further provides a versatile thermodynamic framework to correlate solution nonideality of electrolyte systems, organic or inorganic, and complex systems containing both electrolytes and polymers.

Introduction

There are many industrially important organic electrolytes, such as salts of carboxylic acids, amines, ionic surfactants, and so on. These organic electrolytes exhibit very different solution nonideality from typical aqueous electrolytes with elemental ions. While aqueous electrolytes have been well described by various semi-empirical excess Gibbs energy models such as Meissner and Tester (1972), Pitzer (1973), and Chen et al. (1982, 1986, 1999), these engineering models do not capture the solution nonideality of aqueous organic electrolytes.

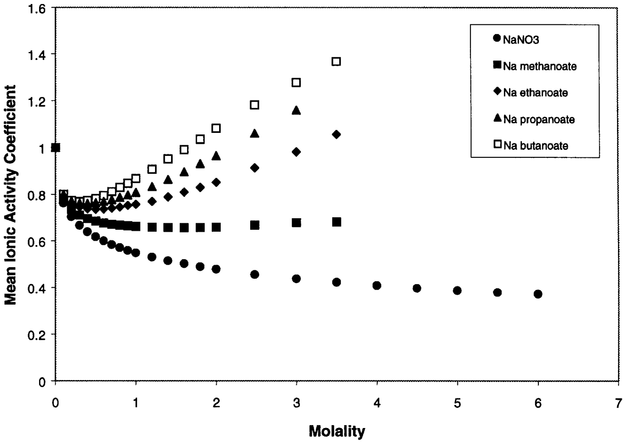

Figure 1. Molality scale mean ionic activity coefficients for short sodium carboxylates.

Data from Robinson and Stokes (1970).

Robinson and Stokes (1970) reported extensive data on mean ionic activity coefficient of sodium carboxylates. More recent data are available for sodium octanoate and decanoate (Ekwall et al., 1967; Stenius, 1973; Vikingstad, 1979; de Lisi et al., 1981). Figure 1 plots molality scale mean ionic activity coefficient data of Robinson and Stokes (1970) for some small sodium carboxylates vs. molalities along with those of sodium nitrate. With small carboxylates, such as methanoate and ethanoate, the general trends in mean ionic activity coefficients as a function of electrolyte concentration are similar to those of inorganic electrolytes, such as sodium nitrate. With the increasing size of the organic acids, such as propanoate and butanoate, the nonideality of organic electrolytes increases. When the organic acid reaches a certain size, say, pentanoate, hexanoate, and higher, the mean ionic activity coefficients exhibit a peculiar downturn at certain electrolyte concentrations, as shown in Figure 2. This pecu-

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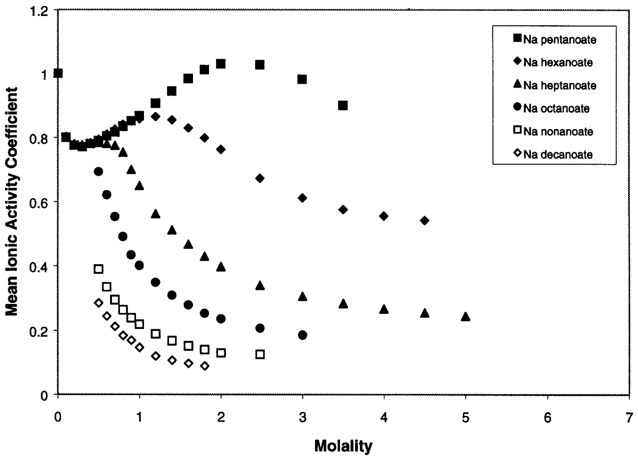

Figure 2. Molality scale mean ionic activity coefficients for long sodium carboxylates.

Data from Robinson and Stokes (1970).

liar nonideal behavior is a result of the tendency of the larger organic electrolytes to form micelles at higher electrolyte concentrations (Smith and Robinson, 1942).

The increase in solution nonideality due to the increasing size of the organic acids cannot be explained by either the long-range ion-ion interactions or the short-range ion-molecule interactions that are characteristic of aqueous electrolytes with elemental ions. Indeed, the molecular structure of organic electrolytes is distinctively different from that of other aqueous electrolytes. First, the organic ions are larger in their molecular size in comparison to elemental ions. Second, the organic ions are composed of an ionic head group and a hydrocarbon tail group. The two different moieties of the same ion exhibit completely different characteristics of physical interactions toward their neighboring solvent molecules. Specifically, the ionic head group is hydrophilic in nature, while the hydrocarbon tail group is hydrophobic in nature. This dual nature of organic ions toward their neighboring species leads to the formation of micelles at high electrolyte concentrations. It is this fundamental molecular characteristic of aqueous organic electrolytes that must be properly accounted for in the thermodynamic representation of aqueous organic electrolytes. Figure 3 shows the molecular makeup of organic electrolytes (as ionic surfactants) in micelles along with that of nonionic surfactants.

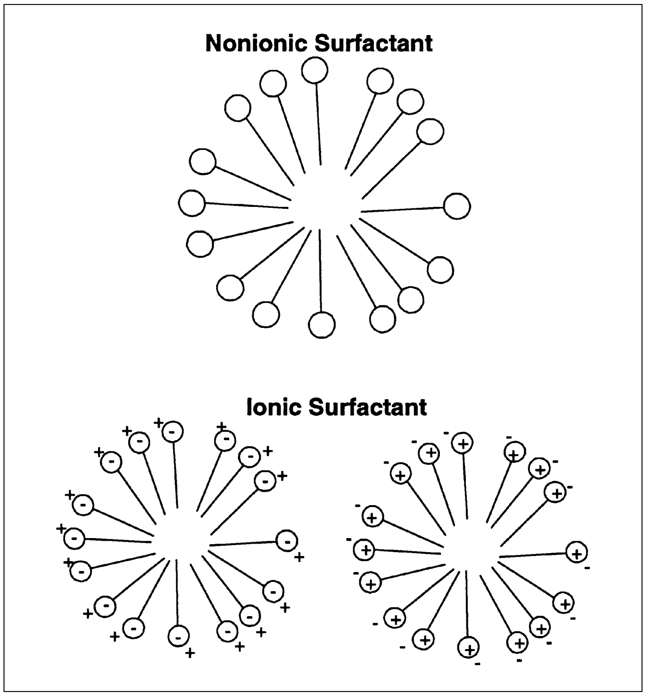

Figure 3. Molecular makeup of organic electrolytes (as ionic surfactants) in micelles with that of nonionic surfactants.

There have been several theoretical studies that did focus on the solution nonideality of ionic surfactants. For the mean ionic activity coefficients of sodium carboxylates, Douheret and Viallard (1982) proposed a mass action law model with a two-parameter polynomial expression for activity coefficients of ionic species. Burchfield and Woolley (1984) proposed equations for activity coefficients of aqueous ionic surfactant solutions. The Burchfield-Woolley model is a synthesis of the Guggenheim equation for activity coefficients of ionic species and a mass-action model involving a single surfactant aggregate species. However, these theoretical studies have not been aimed at understanding the origins of the solution nonideality of organic electrolytes.

A comprehensive molecular thermodynamic model for aqueous organic electrolytes requires proper representation of several key characteristics: (1), presence of ion-ion interactions, ion-molecule interactions, and molecule-molecule interactions; (2) presence of ionic and molecular species of various sizes; and (3) presence of hydrophilic ionic moiety and hydrophobic organic moiety for amphiphilic species. In this work, we extend the electrolyte NRTL model for aqueous electrolytes (Chen et al., 1982, 1999; Chen and Evans, 1986) to represent the excess Gibbs energy of aqueous organic electrolytes. The extension is in fact an integration of the electrolyte NRTL model and the polymer NRTL model (Chen, 1993). Specifically, we treat the organic ions as oligomers that consist of hydrocarbon segments and ionic segments, each with distinctively different physical interactions with surrounding species. With increasing size of the organic ions, the repulsive hydrophobic interaction between the hydrocarbon segments and the neighboring water molecules increases. This results in the increasing tendency for the electrolytes to form micelles.

Although the work primarily focuses on binary aqueous organic electrolytes, the model provides a versatile and proven thermodynamic framework to study multicomponent electrolyte systems, organic or inorganic, and complex chemical systems containing both electrolytes and polymers. This integrated NRTL model reduces to the multicomponent electrolyte NRTL model if there are no oligomers or polymers present, and it reduces to the multicomponent polymer NRTL model if there are no electrolytes present.

Note that this study does not address the solution nonideality of polyelectrolytes, which are further characterized by counterion condensation (Manning, 1979), an intramolecular phenomenon that closely resembles micelle formation.

Electrolyte NRTL Model

The electrolyte NRTL model has been summarized in the literature (Chen et al., 1982; Chen and Evans, 1986). For the purpose of better understanding the extension of the model to organic electrolytes, a brief review of the electrolyte NRTL model is given here.

The excess Gibbs energy expression for aqueous electrolytes contains two contributions: one from the long-range ion-ion interactions that exist beyond the immediate neighborhood of an ionic species, and the other related to the local interactions that exist at the immediate neighborhood of any species. The model uses pure liquid at the system temperature and pressure as the reference state for water. For ions, the reference state is at infinite dilution in water at the system temperature and pressure.

To account for the long-range ion-ion interactions, the model uses the unsymmetric Pitzer-Debye-Hückel (PDH) expression. To account for the local interactions, the model uses the local composition (lc) concept as given by the NRTL expression. This local composition term is first developed as a symmetric expression that envisions a hypothetical reference state of pure, completely dissociated, liquid electrolyte. It is then normalized using "infinite-dilution activity coefficient in water" terms for each ion, in order to obtain an expression based on the unsymmetric convention.

Equation 1 is the excess Gibbs energy expression for aqueous electrolytes

$$\frac{g^{*\,\mathrm{ex}}}{\mathrm{RT}} = \frac{g^{*\,\mathrm{ex,PDH}}}{\mathrm{RT}} + \frac{g^{*\,\mathrm{ex,lc}}}{\mathrm{RT}} \tag{1}$$

Here, the asterisk denotes the unsymmetric convention.

The PDH term in Eq. 1, normalized to mol fractions of unity for solvent and zero for electrolytes, is shown in Eq. 2.

$$\frac{g^{*\,\mathrm{ex,PDH}}}{RT} = -\left(\frac{1{,}000}{M_s}\right)^{1/2}\left(\frac{4A_\varphi I_x}{\rho}\right)\ln\left(1+\rho I_x^{1/2}\right) \tag{2}$$

In applying the NRTL theory to the local interaction contribution, two fundamental assumptions were introduced to elucidate the local composition of electrolyte solutions:

(1) The like-ion repulsion assumption: this states that the local composition of cations around cations is zero (and likewise for anions around anions). This assumption is based on the hypothesis that the repulsive forces between ions of like charge are extremely large.

(2) The local electroneutrality assumption: this states that the distribution of cations and anions around a central molecular species is such that the net local ionic charge is zero. Local electroneutrality has been observed for interstitial molecules in salt crystals.

Following the model, the effective local mol fractions X_{ji} and X_{ii} of species j and i, respectively, in the neighborhood of i are related by

$$\frac{X_{ji}}{X_{ii}} = \left(\frac{X_j}{X_i}\right)G_{ji} \tag{3}$$

where

$X_j = x_j C_j$ ($C_j = z_j$ for ions and $C_j =$ unity for molecules)

$G_{ji} = e^{(-\alpha_{ji}\tau_{ji})}$

$\tau_{ji} = \dfrac{g_{ji} - g_{ii}}{RT}$

α_{ji} is the nonrandomness factor. g_{ji} and g_{ii} are energies of interaction between species j and i, and i and i, respectively. Both g_{ij} and α_{ij} are inherently symmetric ($g_{ji} = g_{ij}$ and $\alpha_{ji} = \alpha_{ij}$).

Similarly,

$$\frac{X_{ji}}{X_{ki}} = \left(\frac{X_j}{X_k}\right)G_{ji,ki} \tag{4}$$

where

$G_{ji,ki} = \mathrm{e}^{(-\alpha_{\mathrm{ji,ki}}\tau_{\mathrm{ji,ki}})}$

$\tau_{ji,ki} = \dfrac{g_{ji} - g_{ki}}{RT}$

$\alpha_{ji,ki}$ is the nonrandomness factor.

The NRTL term to account for the local interaction contribution is given in Eq. 5. The NRTL term should be normalized to the infinite dilution reference state for ions and solutes before it can be combined with the PDH term in Eq. 1

$$\begin{aligned}\frac{g^{\mathrm{ex,lc}}}{\mathrm{RT}} &= \sum_m X_m \frac{\sum_j X_j G_{jm}\tau_{jm}}{\sum_k X_k G_{km}} \\ &+ \sum_c X_c \sum_{a'}\left(\frac{X_a}{\sum_{a''} X_{a''}}\right)\frac{\sum_j X_j G_{jc,a'c}\tau_{jc,a'c}}{\sum_k X_k G_{kc,a'c}} \\ &+ \sum_a X_a \sum_{c'}\left(\frac{X_{c'}}{\sum_{c''} X_{c''}}\right)\frac{\sum_j X_j G_{ja,c'a}\tau_{ja,c'a}}{\sum_k X_k G_{ka,c'a}}\end{aligned} \tag{5}$$

where j and k can be any species, and the quantities G_{cm}, G_{am}, α_{mc} and α_{ma} are defined as follows

$$G_{cm} = \frac{\sum_a X_a G_{ca,m}}{\sum_{a'} X_{a'}} \tag{6}$$

$$G_{am} = \frac{\sum_c X_c G_{ca,m}}{\sum_{c'} X_{c'}} \tag{7}$$

$$\alpha_{mc} = \alpha_{cm} = \frac{\sum_a X_a \alpha_{m,ca}}{\sum_{a'} X_{a'}} \tag{8}$$

$$\alpha_{ma} = \alpha_{am} = \frac{\sum_c X_c \alpha_{m,ca}}{\sum_{c'} X_{c'}} \tag{9}$$

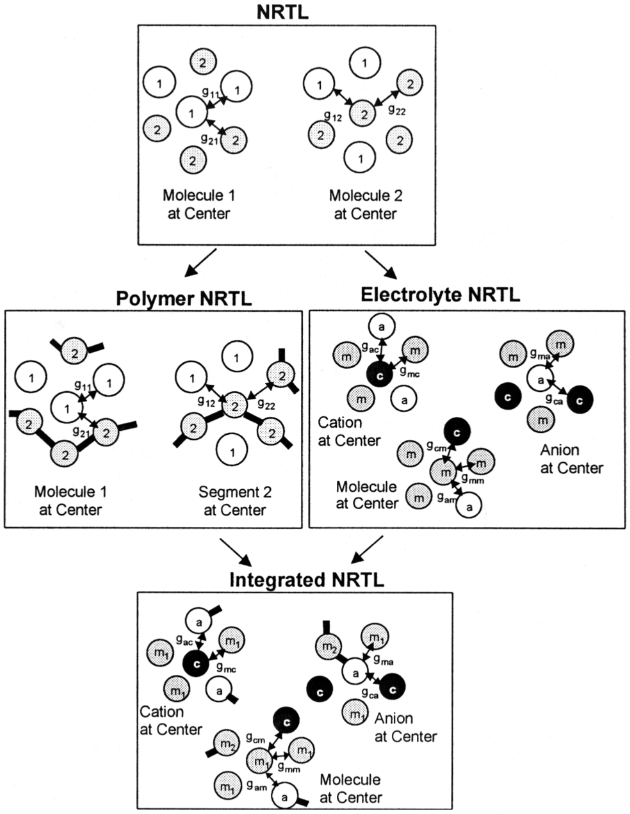

Figure 4. Various physical interactions contributing to the nonideality of small molecule systems (NRTL model), electrolyte systems (Electrolyte NRTL model), polymer systems (Polymer NRTL model), and organic electrolyte systems (integrated NRTL model).

Extension for Organic Electrolytes

The extension of the electrolyte NRTL model for organic electrolytes integrates into the model the segment-based local composition concept proposed for the polymer NRTL model (Chen, 1993). The polymer NRTL model has proven to be a successful Gibbs energy expression for oligomers and polymers (Chen, 1993), biopolymers (Chen et al., 1992a,b, 1995) and nonionic surfactants (Chen, 1996). The segment-based local composition concept assumes that the unique physical interactions of each segment with its neighboring segments and species determines the local composition around the segment. In other words, the local composition concept should be applied to the individual segments of polymeric chains, not the polymeric chain as a whole.

Figure 4 shows the various physical interactions contributing to the nonideality of small molecule systems (NRTL model), electrolyte systems (electrolyte NRTL model), polymer systems (polymer NRTL model), and organic electrolyte systems (integrated NRTL model). With the integrated NRTL model, we apply the segment-based local composition concept to the individual segments of the organic electrolyte. These segments can include cationic segments c, anionic segments a, and molecular segments m.

The integrated model has three terms: the Pitzer-Debye-Hückel term (Eq. 2), the local composition term (Eq. 11), and the Flory-Huggins term (Eq. 12). Here, the local composition term is re-derived according to the segment-based local composition concept of Chen (1993)

$$\frac{g^{*\,\mathrm{ex}}}{RT} = \frac{g^{*\,\mathrm{ex,PDH}}}{RT} + \frac{g^{*\,\mathrm{ex,lc}}}{RT} + \frac{g^{*\,\mathrm{ex,FH}}}{RT} \tag{10}$$

$$\begin{aligned}\frac{g^{\mathrm{ex,lc}}}{RT} = {}& \sum_I \sum_m r_{m,I} X_m \frac{\sum\limits_j X_j G_{jm} \tau_{jm}}{\sum\limits_k X_k G_{km}} \\ & + \sum_I \sum_c r_{c,I} X_c \sum_{a'} \left(\frac{X_a}{\sum\limits_{a''} X_{a''}} \right) \frac{\sum\limits_j X_j G_{jc,a'c} \tau_{jc,a'c}}{\sum\limits_k X_k G_{kc,a'c}} \\ & + \sum_I \sum_a r_{a,I} X_a \sum_{c'} \left(\frac{X_{c'}}{\sum\limits_{c''} X_{c''}} \right) \frac{\sum\limits_j X_j G_{ja,c'a} \tau_{ja,c'a}}{\sum\limits_k X_k G_{ka,c'a}}\end{aligned} \tag{11}$$

$$\frac{g^{\mathrm{ex,FH}}}{RT} = \sum_I x_I \ln\left(\frac{\phi_I}{x_I} \right) \left(\sum_I n_I m_I \right) \tag{12}$$

Taking the appropriate derivative of Eq. 2, an expression for the PDH term to the activity coefficient can be derived

$$\ln \gamma_i^{*\,\mathrm{PDH}} = -\left(\frac{1{,}000}{M_s} \right)^{1/2} A_\varphi \left[\left(\frac{2 z_i^2}{\rho} \right) \ln\left(1 + \rho I_x^{1/2}\right) + \frac{z_i^2 I_x^{1/2} - 2 I_x^{3/2}}{1 + \rho I_x^{1/2}} \right] \tag{13}$$

To compute the local composition term for the activity coefficients of organic electrolytes, we first compute local composition contributions for each of the segments. The segment contributions to the activity coefficients from molecular segments, cationic segments, and anionic segments are given in the next three equations

$$\begin{aligned}\ln \gamma_{m,I}^{lc} = {}& \frac{\sum\limits_j X_j G_{jm} \tau_{jm}}{\sum\limits_k X_k G_{km}} \\ & + \sum_{m'} \frac{X_{m'} G_{mm'}}{\sum\limits_k X_k G_{km'}} \left(\tau_{mm'} - \frac{\sum\limits_k X_k G_{km'} \tau_{km'}}{\sum\limits_k X_k G_{km'}} \right) \\ & + \sum_c \sum_{a'} \frac{X_a}{\sum\limits_{a''} X_{a''}} \frac{X_c G_{mc,a'c}}{\sum\limits_k X_k G_{kc,a'c}} \left(\tau_{mc,a'c} - \frac{\sum\limits_k X_k G_{kc,a'c} \tau_{kc,a'c}}{\sum\limits_k X_k G_{kc,a'c}} \right) \\ & + \sum_a \sum_{c'} \frac{X_{c'}}{\sum\limits_{c''} X_{c''}} \frac{X_a G_{ma,c'a}}{\sum\limits_k X_k G_{ka,c'a}}\end{aligned}$$

$$\times \left(\tau_{ma,c'a} - \frac{\sum\limits_k X_k G_{ka,c'a} \tau_{ka,c'a}}{\sum\limits_k X_k G_{ka,c'a}} \right) \quad (14)$$

$$\frac{1}{z_c} \ln \gamma_{c,I}^{lc} = \sum_{a'} \left(\frac{X_{a'}}{\sum\limits_{a''} X_{a''}} \right) \frac{\sum\limits_k X_k G_{kc,a'c} \tau_{kc,a'c}}{\sum\limits_k X_k G_{kc,a'c}}$$

$$+ \sum_{m'} \frac{X_m G_{cm}}{\sum\limits_k X_k G_{km}} \left(\tau_{cm} - \frac{\sum\limits_k X_k G_{km} \tau_{km}}{\sum\limits_k X_k G_{km}} \right)$$

$$+ \sum_a \sum_{c'} \left(\frac{X_{c'}}{\sum\limits_{c''} X_{c''}} \right) \frac{X_a G_{ca,c'a}}{\sum\limits_k X_k G_{ka,c'a}}$$

$$\left(\tau_{ca,c'a} - \frac{\sum\limits_k X_k G_{km,c'a} \tau_{ka,c'a}}{\sum\limits_k X_k G_{ka,c'a}} \right) \quad (15)$$

$$\frac{1}{z_a} \ln \gamma_{a,I}^{lc} = \sum_{c'} \left(\frac{X_{c'}}{\sum\limits_{c} X_{c''}} \right) \frac{\sum\limits_k X_k G_{ka,c'a} \tau_{ka,c'a}}{\sum\limits_k X_k G_{ka,c'a}}$$

$$+ \sum_{m} \frac{X_m G_{am}}{\sum\limits_k X_k G_{km}} \left(\tau_{am} - \frac{\sum\limits_k X_k G_{km} \tau_{km}}{\sum\limits_k X_k G_{km}} \right)$$

$$+ \sum_c \sum_{a'} \left(\frac{X_{a'}}{\sum\limits_{a''} X_{a''}} \right) \frac{X_c G_{ac,a'c}}{\sum\limits_k X_k G_{kc,a'c}}$$

$$\times \left(\tau_{ac,a'c} - \frac{\sum\limits_k X_k G_{kc,a'c} \tau_{kc,a'c}}{\sum\limits_k X_k G_{kc,a'c}} \right) \quad (16)$$

The local composition term for the activity coefficient of a species I is then computed as the sum of the individual segment contributions

$$\ln \gamma_I^{lc} = \sum_c r_{c,I} \ln \gamma_{c,I}^{lc} + \sum_a r_{a,I} \ln \gamma_{a,I}^{lc} + \sum_m r_{m,I} \ln \gamma_{m,I}^{lc} \quad (17)$$

For electrolytes, we are interested in unsymmetric convention activity coefficients. Therefore, we need to compute "infinite dilution activity coefficients" for ionic segments and molecular segments. They are then used to compute the unsymmetric activity coefficients of organic ions.

Taking the limit of the expressions for the activity coefficients at infinite dilution and summing over all segments, one obtains

$$\ln \gamma_{m,I}^{\infty lc} = \tau_{wm} + G_{mw} \tau_{mw} \quad (18)$$

$$\frac{1}{Z_c} \ln \gamma_{c,I}^{\infty lc} = \tau_{w,ca} + G_{cw} \tau_{ca,w} \quad (19)$$

$$\frac{1}{Z_a} \ln \gamma_{a,I}^{\infty lc} = \tau_{w,ca} + G_{aw} \tau_{ca,w} \quad (20)$$

$$\ln \gamma_I^{\infty lc} = \sum_c r_{c,I} \ln \gamma_{c,I}^{\infty lc} + \sum_a r_{a,I} \ln \gamma_{a,I}^{\infty lc} + \sum_m r_{m,I} \ln \gamma_{m,I}^{\infty lc} \quad (21)$$

where $r_{j,I}$ is the number of segments of type j in species I.

Table 1. Molecular Representation of Sodium Carboxylate Organic Electrolytes

Sodium Carboxylate	Name	Cation	Anion	Segments
CHO_2Na	Sodium Methanoate	Na^+	CHO_2^-	0.0 C_2, 1 CO_2^-
$C_2H_3O_2Na$	Sodium Ethanoate	Na^+	$C_2H_3O_2^-$	0.5 C_2, 1 CO_2^-
$C_3H_5O_2Na$	Sodium Propanoate	Na^+	$C_3H_5O_2^-$	1.0 C_2, 1 CO_2^-
$C_4H_7O_2Na$	Sodium Butanoate	Na^+	$C_4H_7O_2^-$	1.5 C_2, 1 CO_2^-
$C_5H_9O_2Na$	Sodium Pentanoate	Na^+	$C_5H_9O_2^-$	2.0 C_2, 1 CO_2^-
$C_6H_{11}O_2Na$	Sodium Hexanoate	Na^+	$C_6H_{11}O_2^-$	2.5 C_2, 1 CO_2^-
$C_7H_{13}O_2Na$	Sodium Heptanoate	Na^+	$C_7H_{13}O_2^-$	3.0 C_2, 1 CO_2^-
$C_8H_{15}O_2Na$	Sodium Octanoate	Na^+	$C_8H_{15}O_2^-$	3.5 C_2, 1 CO_2^-
$C_9H_{17}O_2Na$	Sodium Nonanoate	Na^+	$C_9H_{17}O_2^-$	4.0 C_2, 1 CO_2^-
$C_{10}H_{19}O_2Na$	Sodium Decanoate	Na^+	$C_{10}H_{19}O_2^-$	4.5 C_2, 1 CO_2^-

Then, by definition

$$\ln \gamma_I^{*lc} = \ln \gamma_I^{lc} - \ln \gamma_I^{\infty lc} \tag{22}$$

Similarly, for the PDH term, we sum up the contributions from various ionic segments of species I.

$$\ln \gamma_I^{*\mathrm{PDH}} = \sum_c r_{c,I} \ln \gamma_{c,I}^{*\mathrm{PDH}} + \sum_a r_{a,I} \ln \gamma_{a,I}^{*\mathrm{PDH}} \tag{23}$$

We also compute the unsymmetric activity coefficients from the Flory-Huggins term as follows

$$\ln \gamma_I^{FH} = \ln\left(\frac{\phi_I}{x_I}\right) + 1 - m_I \sum_J \left(\frac{\phi_J}{m_J}\right). \tag{24a}$$

$$\ln \gamma_I^{\infty FH} = \ln m_I + 1 - m_I \tag{24b}$$

$$\ln \gamma_I^{*FH} = \ln \gamma_I^{FH} - \ln \gamma_I^{\infty FH} \tag{25}$$

Following Eq. 10, the ionic activity coefficient is the sum of three terms: the Pitzer-Debye-Hückel term (Eq. 23), the local composition term (Eq. 22), and the Flory-Huggins term (Eq. 25)

$$\ln \gamma_I^{*} = \ln \gamma_I^{*\mathrm{PDH}} + \ln \gamma_I^{*lc} + \ln \gamma_I^{*\mathrm{FH}} \tag{26}$$

Mean ionic activity coefficients and molality scale mean ionic activity coefficients can then be computed by the following expressions

$$\ln \gamma_{\pm}^{*} = \frac{1}{\nu_c + \nu_a}\left(\nu_c \ln \gamma_c^{*} + \nu_a \ln \gamma_a^{*}\right) \tag{27}$$

$$\ln \gamma_{\pm m}^{*} = \ln \gamma_{\pm}^{*} - \ln\left(1 + M_s(\nu_c + \nu_a)m/1{,}000\right) \tag{28}$$

Application to Organic Electrolytes

The integrated NRTL model allows us to compute unsymmetric activity coefficients for organic electrolytes as functions of molecular structure of electrolytes, electrolyte concentrations, and so on.

As an illustration, the model is applied to the sodium salts of carboxylic acids. Following our earlier treatment (Chen, 1996), we chose ethylene (C_2H_4) hydrocarbon segment and carboxylate ionic segment as building blocks for the carboxylates. Table 1 shows representation of these organic electrolytes in terms of sodium cation, various numbers of C_2H_4 segment, and the carboxylate anionic segment.

We successfully correlated the literature data (Robinson and Stokes, 1970) on molality scale mean ionic activity coefficients and water activity of the sodium salts of lower carboxylic acids (up to pentanoate) simultaneously. Here, the water activity data were actually computed from the osmotic coefficient data. Table 2 shows the identified values of the segment-based NRTL binary parameters for sodium carboxylates. These values were obtained with the nonrandomness factor fixed at 0.2, as suggested in an earlier work (Chen et al., 1982). Figure 5 shows the excellent representation of the molality scale mean ionic activity coefficients of lower sodium carboxylates with the segment-based adjustable NRTL binary parameters. A much larger set of NRTL binary parameters would be required if we were to correlate data for each sodium carboxylate individually with the electrolyte NRTL model. The integrated model successfully accounts for the upward trend of the mean ionic activity coefficients for larger organic electrolytes as a result of the greater contributions to the solution nonideality from the longer hydrocarbon tail. Figure 6 shows the excellent representation of the corresponding water activity data.

Table 2. NRTL Binary Interaction Parameters for Sodium Carboxylates

Interacting Pair		Parameter	Standard
I	*J*	Estimate	Deviation
H_2O	(Na^+, $-CO_2^-$)	7.827	0.098
(Na^+, $-CO_2^-$)	H_2O	−4.104	0.040
$-C_2H_4$	(Na^+, $-CO_2^-$)	6.783	0.499
(Na^+, $-CO_2^-$)	$-C_2H_4$	12.000	n.a.*
H_2O	$-C_2H_4$	2.844	0.077
$-C_2H_4$	H_2O	0.292	0.170

*Upper bound.

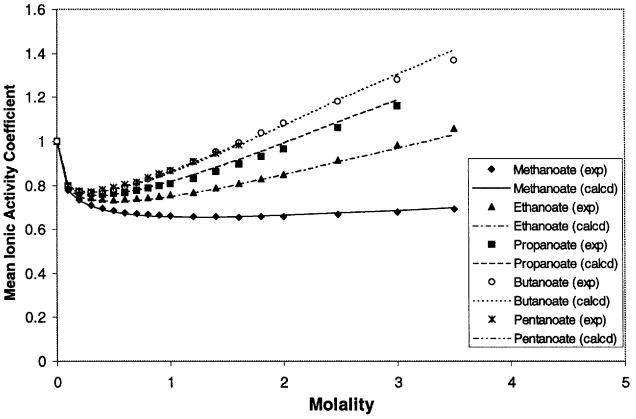

Figure 5. Model representation of molality scale mean ionic activity coefficients of lower sodium carboxylates.

Data from Robinson and Stokes (1970).

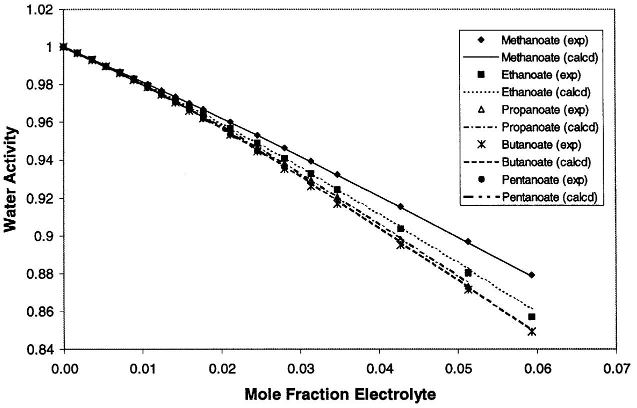

Figure 6. Model representation of water activity data for lower sodium carboxylates.

Data computed from Robinson and Stokes (1970).

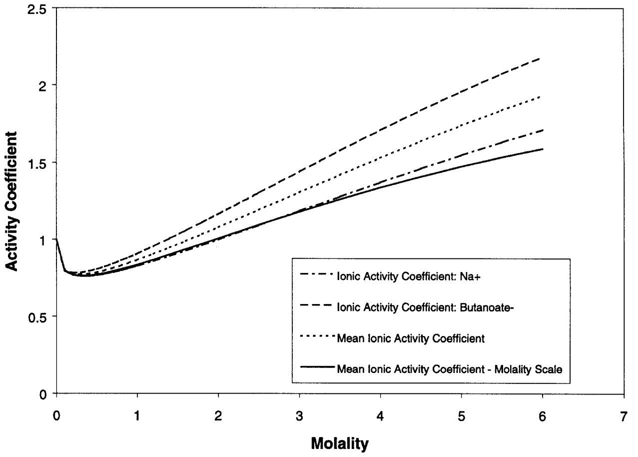

Figure 7. Model representation of activity coefficients for sodium butanoate.

Figure 7 shows the computed mean ionic activity coefficients of sodium butanoate in mol fraction scale and in molality scale. Also shown are the computed ionic activity coefficients of the sodium ion and the butanoate ion. These two ionic activity coefficients have different values primarily due to the unique water-hydrocarbon (that is, C_2H_4 segment) interaction contribution for the butanoate ion. For these small oligomeric ions, the Flory-Huggins contribution is negligible.

Critical Micelle Concentrations

When the size of the hydrocarbon tail reaches a certain threshold, organic electrolytes exhibit characteristics of ionic surfactants. At and above "critical micellar concentration (cmc)," that is, the surfactant concentration at the onset of micelle formation, ionic surfactants exist in two different forms: monomeric surfactants in the aqueous phase and aggregated surfactants in the micellar phase (Figure 8). Having proper representation of various contributions to the liquid-phase nonideality, the integrated NRTL model should predict cmc and the formation of micelles.

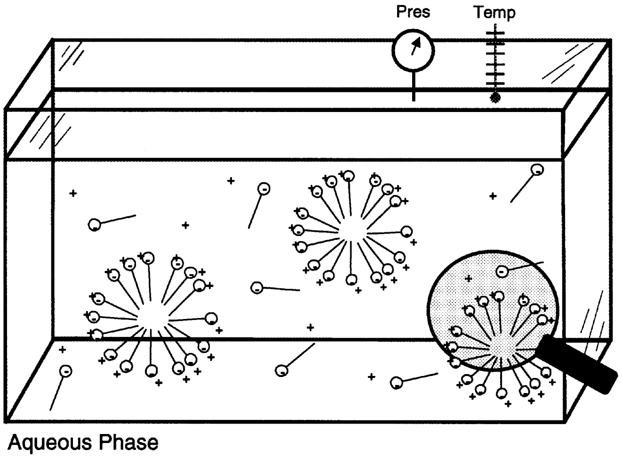

Figure 8. Micelle formation of organic electrolytes in the aqueous phase.

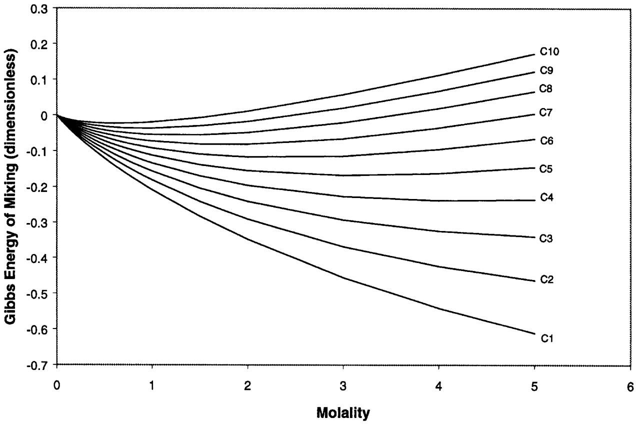

Figure 9. Gibbs energy of mixing as function of carbon number for sodium carboxylates.

Figure 9 shows the Gibbs energy of mixing as computed from the NRTL parameters reported in Table 2 for small sodium carboxylates. The model predicts a local minimum in the Gibbs energy of mixing, indicative of phase instability, as the carbon number of sodium carboxylates exceeds 4 (or C_2H_4 segment number exceeds 2). Indeed, starting from pentanoate, that is, C5, formation of micelles is reported for aqueous sodium carboxylates (Smith and Robinson, 1942).

For nonionic surfactants, the activities of two forms of surfactants (monomeric and micellar) should be the same at and above cmc and their activities should be unity, since the micellar form is essentially the reference state (Chen, 1996)

$$a = x_{aq}^{cmc}\gamma_{aq} = x_{\text{micellar}}\gamma_{\text{micellar}} = 1 \tag{29}$$

where both x_{micellar} and γ_{micellar} are unity.

For ionic surfactants, we use unsymmetric activity coefficients

$$a = x_{\text{aq}}^{cmc}\gamma^*_{\pm,\text{aq}} = x_{\text{micellar}}\gamma^*_{\pm,\text{micellar}} = \gamma^*_{\pm,\text{micellar}}(\text{at } x_{\text{micellar}} = 1) \tag{30}$$

In the micellar phase, hydrocarbon segments are in their corresponding reference states where all hydrocarbon segments are surrounded by hydrocarbon segments. The ionic segments, together with their counter ions, remain immersed in the aqueous phase at the micelle-aqueous phase interface.

The unsymmetric activity coefficients of micellar carboxylate ions can be computed with Eqs. 31 to 34

$$\ln\gamma^*_{I,\text{micellar}} = \ln\gamma^{*\text{PDH}}_{I,\text{micellar}} + \ln^{*lc}_{I,\text{micellar}} + \ln\gamma^{*\text{FH}}_{I,\text{micellar}} \tag{31}$$

$$\ln\gamma^{*\text{PDH}}_{I,\text{micellar}} \equiv -0.9571 \tag{32}$$

$$\ln\gamma^{*lc}_{I,\text{micellar}} = -\ln\gamma_I^{\infty lc} \tag{33}$$

$$\ln\gamma^{*FH}_{I,\text{micellar}} = -\ln\gamma_I^{\infty FH} \tag{34}$$

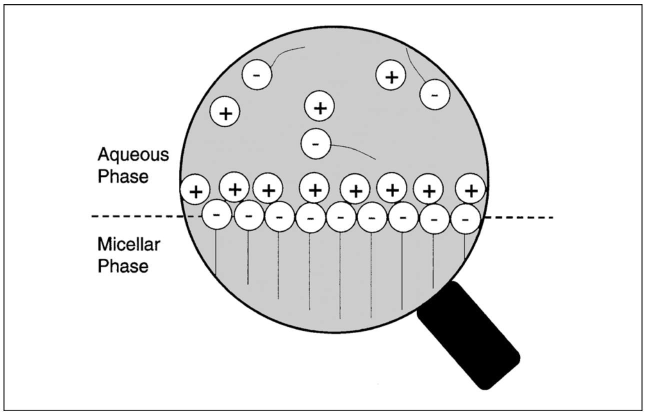

Figure 10. Ions assemble at the micelle-aqueous solution interface.

Here, we set γ^{*PDH} to 0.384 (or -0.9571 for ln γ^{*PDH}), the limiting value of the PDH term for univalent ions as the electrolyte concentration approaches unity. As shown in Figure 10, ions assemble and concentrate at the micelle-aqueous solution interface to maintain local electroneutrality around micellar particles. Note that the same value is used for γ^{*PDH} of sodium cation.

With increase in the size of the hydrocarbon tail (or carbon number), the local composition term will have an increasingly larger negative contribution to ln $\gamma^{*}_{I,\mathrm{micellar}}$ due to the hydrophobicity of the hydrocarbon tail. On the other hand, the corresponding FH term will have a larger positive contribution to ln $\gamma^{*}_{I,\mathrm{micellar}}$.

Figure 11 shows the activities of aqueous phase sodium carboxylates at the cmc vs. the carbon number. These activities were computed from the literature cmc data (Brandrup and Immergut, 1975) and the literature mean ionic activity coefficient data (Robinson and Stokes, 1970). Also shown are the activities of micellar sodium carboxylates as computed by the model with Eq. 31. For completeness, the literature data on cmc and the molality scale mean ionic activity coefficients are summarized in Table 3.

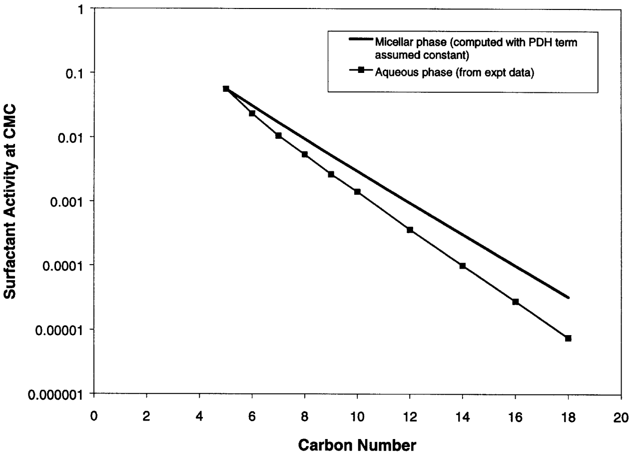

Figure 11. Surfactant activities at cmc for the aqueous phase and the micellar phase sodium carboxylates.

Table 3. CMC and Mean Ionic Activity Coefficient Data at CMC for Sodium Carboxylates

Sodium Carboxylate	*CMC (Molality)*	$\gamma_{\pm m}$
$C_5H_9O_2Na$	3	0.982
$C_6H_{11}O_2Na$	1.5	0.84
$C_7H_{13}O_2Na$	0.77	0.75
$C_8H_{15}O_2Na$	0.39	0.75
$C_9H_{17}O_2Na$	0.195	0.75
$C_{10}H_{19}O_2Na$	0.1	0.78
$C_{12}H_{23}O_2Na$	0.025	0.8
$C_{14}H_{27}O_2Na$	0.0065	0.85
$C_{16}H_{31}O_2Na$	0.0017	0.9
$C_{18}H_{35}O_2Na$	0.00044	0.95

The computed activities of micellar sodium carboxylates from Eq. 31 are reasonably close to the experimental values, especially for lower sodium carboxylates. The computed activities of micellar sodium carboxylates show a slightly weaker dependency with respect to the increase in carbon number than those of aqueous phase sodium carboxylates. This suggests that either the NRTL parameters in Table 2 slightly underestimate the local composition term to ln $\gamma^{*}_{I,\mathrm{micellar}}$ or the Flory-Huggins term is slightly overestimated. Nevertheless, the results clearly show that the model captures the broad trend of the dependency of micellar sodium carboxylate activity with respect to the increase in carbon number with a single set of binary interaction parameters.

Above Critical Micelle Concentrations

Dissolved micelles in the aqueous phase have their hydrophilic head groups, that is, carboxylate ionic segments and their counter ions, dissolved in the aqueous phase. These structured interfacial ion pairs exert certain physical interactions with surrounding aqueous phase water molecules, while the hydrocarbon tail buried inside micelles stays hidden from interacting with aqueous phase species.

Figure 12 shows water activity data for various aqueous sodium carboxylates as converted from the osmotic coefficient data of Robinson and Stokes (1970). The corresponding molality scale mean ionic activity coefficient data for the sodium carboxylates have been shown in Figure 2. Below cmc, water activity is decreasing linearly as the electrolyte concentrations increase. At and above cmc, the slope of the change in water activity with respect to the electrolyte concentration shows an abrupt upward change indicating a shift in the nature of the water-electrolyte interaction. The water-interfacial ion pair interaction accounts for the further drop in water activity as the electrolyte concentration increases beyond cmc and the micelle concentration and the micelle-aqueous phase interface area increase in the aqueous phase. The formation of structured ion pairs at the micelle-aqueous phase interface presents a water-electrolyte interaction that is very different from the water-ion interaction in the aqueous phase. In this work, we treat the interfacial ion pairs as a distinctive nondissociating interacting species different from the dissolved ions in the aqueous phase. Also shown in Figure 12 are the excellent representations with the model for the wa-

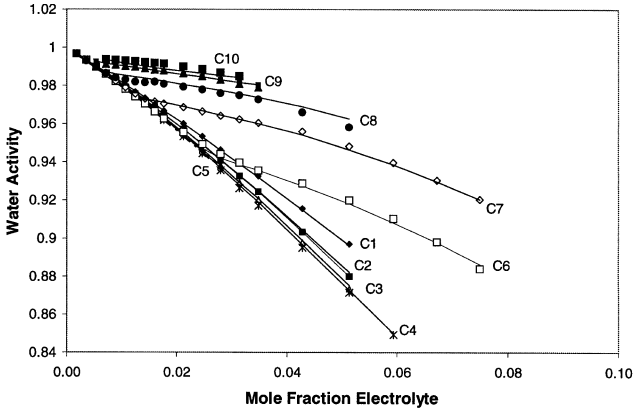

Figure 12. Water activity vs. electrolyte concentration for various aqueous sodium carboxylates and model representation.

Data computed from Robinson and Stokes (1970).

ter activity data both below and above cmc. Figure 13 shows water activity vs. carbon number for the sodium carboxylates at two electrolyte concentrations. At a given electrolyte concentration, water activity would initially decrease with increasing carbon number of the carboxylates. Water activity would then jump once micelles are formed due to the increase in carbon number. Table 4 summarizes the values of the NRTL binary interaction parameters for micellar sodium carboxylates.

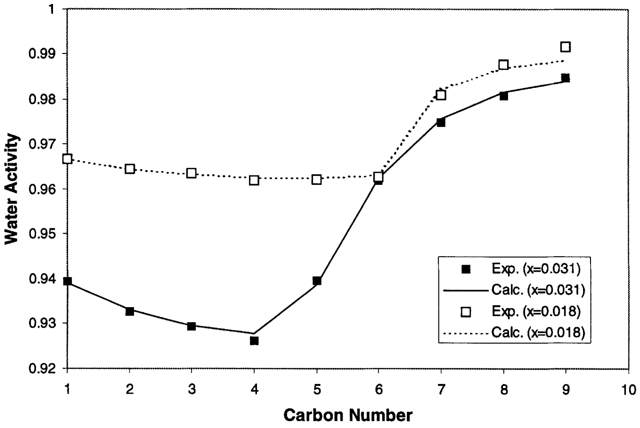

Figure 13. Water activity vs. carbon number for aqueous sodium carboxylates at two electrolyte concentrations.

Data computed from Robinson and Stokes (1970).

Conclusions

We have presented a thermodynamically consistent excess Gibbs energy expression for aqueous organic electrolytes. The nonrandom two-liquid theory, together with the like-ion repulsion assumption, the local electroneutrality assumption, the segment-based local composition concept, the Pitzer-Debye-Hückel equation, and the Flory-Huggins equation, provides a versatile mathematical framework to correlate and predict solution nonideality of aqueous organic electrolytes and systems with electrolytes and polymers.

The model satisfactorily accounts for the highly nonideal phase behavior of aqueous organic electrolytes, including formation of micelles, with a minimal set of segment-based binary interaction parameters. Our next study will focus on aqueous two-phase polymer solutions with electrolytes.

Acknowledgment

We dedicate this work to our beloved colleague, Dr. Hasan Orbey. Hasan shared our love and devotion to molecular thermodynamics and process modeling. This work would have benefited from Hasan's creativity, insights, and hard work if he had returned to AspenTech after his tragic August 1999 vacation.

Notation

A_φ = Debye-Hückel parameter
I_x = ionic strength (mol fraction scale): $1/2\ \sum_i x_i z_i^2$
M_s = solvent molecular weight, kg/kmol
R = gas constant
T = temperature, K
X = effective liquid-phase mol fraction (based on number of mols of segments and solvents)
a = activity
g = interaction energy
g^{ex} = molar excess Gibbs energy
m = ratio of polymer volume to segment volume (approximated as segment number (in Eq. 12)
m = molality (in Eq. 28)
n = number of moles
r = number of segments per oligomeric species
x = liquid phase mol fraction
z = charge number
α = NRTL nonrandomness factor
γ = activity coefficient
$\gamma_\pm$ = mean ionic activity coefficient
$\gamma_{\pm m}$ = molality scale mean ionic activity coefficient
ν = stoichiometric coefficient
ρ = the "closest approach" parameter of the Pitzer-Debye-Hückel equation (= 14.9)
τ = NRTL binary interaction energy parameter
ϕ = segment fraction (in Eq. 12)

Table 4. NRTL Binary Interaction Parameters for Micellar Sodium Carboxylates

Interacting Pair			
I	*J*	*Parameter Estimate*	*Standard Deviation*
H_2O	$(Na^+, \text{-}CO_2^-)_{\text{interfacial}}$	6.596	0.073
$(Na^+, \text{-}CO_2^-)_{\text{interfacial}}$	H_2O	−3.012	0.027
$(Na^+, \text{-}CO_2^-)$	$(Na^+, \text{-}CO_2^-)_{\text{interfacial}}$	0.787	0.572
$(Na^+, \text{-}CO_2^-)_{\text{interfacial}}$	$(Na^+, \text{-}CO_2^-)$	12.000	n.a.*

*Upper bound.

Superscripts

$*$ = unsymmetric convention
∞ = infinite dilution
FH = Flory-Huggins
NRTL = Nonrandom two-liquid
PDH = Pitzer-Debye-Hückel
cmc = critical micelle concentration
lc = local composition

Subscripts

C = cationic species (molecule-based)
A = anionic species (molecule-based)
I = any species (molecule-based)
a, a', a'' = anionic species (segment-based)
c, c', c'' = cationic species (segment-based)
i, j, k = any species (segment-based)
m, m' = molecular species (segment-based)
s = solvent
w = water

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