Thermodynamic Modeling of Hydrotrope Solutions

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A new model for the excess Gibbs energy of hydrotrope solutions is presented. This model is based on the local composition model by Chen et al. Hydrotropes are usually organic salts that can increase the solubility of organic and inorganic compounds in water. The proposed model has five adjustable parameters; one of them is related to long-range forces, and four of them are related to short-range forces. Long-range forces are modeled by the Pitzer-Debye-Huckel equation. However, in our model, the effect of the molecular solute on the dielectric constant of water has also been considered. Modeling of short-range forces is based on local composition concepts. The model parameters are obtained using experimental data for six hydrotropes with four solutes at different temperatures. The water solubility of molecular solutes in the presence of hydrotropes has been calculated for different systems. Accurate results are obtained.© 2005 American Institute of Chemical Engineers *AIChE J,* 52: 333–341, 2006
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Introduction

Modeling the excess Gibbs energy of electrolyte solutions is an important topic in the field of chemical engineering thermodynamics. In this investigation, a thermodynamic model for the excess Gibbs energy of hydrotrope solutions is proposed.

Hydrotropism is a word proposed by Neuberg[1] in 1916 to describe the large enhancement of the solubility of a variety of sparingly water-soluble organic compounds in the aqueous phase in the presence of certain organic salts. These salts, which are highly soluble in water, are termed "hydrotropes" and conventionally include alkali and alkaline earth metal salts of short-chain alkylbenzene sulfonic acids and alkylbenzene carboxylic acids. The phenomenon of hydrotropy is operative in the high concentration range of the hydrotrope, and a minimum hydrotrope concentration (MHC) is usually required to exhibit the increase in solubility.[2] Hydrotropes have been used to solubilize drugs and detergents. Recently, they have also been used in heterogeneous reactions. Hydrotropes have also been successfully used in the development of extractive separation of close boiling point components. The use of hydrotrope solutions as solvents in industrial applications is attractive because of non-flammability, high selectivity, preventing emulsification, and easy recovery of solubilized material by dilution with or without solvent extraction with a polar solvent.[3-10] Experimental work in the field of separation using hydrotrope solutions is not extensive and has been thoroughly reviewed by Gaikar and Sharma.[11] Very little experimental work on extractive separations using hydrotropes had been reported before 1986.

In the field of modeling hydrotrope solutions, we can refer to the Self Consistent Local Composition model (SCLC), which has been proposed by Ramachandran and Ananth.[12] Gaikar and Phatak[2] proposed an association model for hydrotrope solutions.

In this work a thermodynamic model is proposed for hydrotrope solutions. In this model the excess Gibbs energy of the solution is assumed to be the sum of two parts; the first part has been related to long-range forces, and the second part to short-range forces. Long-range forces are modeled by the

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Pitzer-Debye-Huckel equation,[13,14] but in our model the effect of molecular solute on the dielectric constant of water has been taken into account. Short-range forces are modeled by the Nonrandom Two Liquid Theory (NRTL)[15-17] and the local composition model of Chen et al.[18]

Theory

The system considered consists of three components and two liquid phases at equilibrium, water rich phase, and solute rich phase. The role of the hydrotrope is to increase the solubility of the molecular solute in the water-rich phase. The solubility of the hydrotrope in the solute-rich phase is negligible. We propose that the hydrotrope is dissociated completely due to either the strong electrolyte nature of the hydrotrope, or the complex formation between the hydrotrope and the molecular solute.[2]

Thermodynamic Framework

The excess Gibbs energy of an electrolyte solution is assumed to be the sum of the contribution of a long-range interaction term $g^{ex,\,lr}$, and a short-range interaction term $g^{ex,sr}$, as below

$$\frac{g^{ex}}{RT} = \frac{g^{ex,lr}}{RT} + \frac{g^{ex,sr}}{RT} \tag{1}$$

The long-range interaction term accounts for the electrostatic interactions between anions and cations. The short-range interaction term considers ion–molecular species (solvent and solute) interactions, non-electrostatic ion-ion interactions, and molecule-molecule interactions.[18]

A New Modification for Long-Range Interactions

To represent the long-range interaction term in Eq. 1, we have used the extended version of the Debye-Huckel model proposed by Pitzer[15,18,19]

$$g^{ex*,el}/RT = -\left(\sum n_k\right)\left(\frac{1000}{M_s}\right)^{1/2}\left(4A_\phi \frac{I_x}{\rho}\right) \ln\left(1 + \rho I_x^{1/2}\right) \tag{2}$$

where M_S is the molecular weight of the solvent and ρ is the closest approach parameter. In general, the value of ρ depends on the electrolyte as well as the expression used to represent the short-range forces. In order to maintain simplicity for more complex electrolyte systems, it is desirable that ρ should have the same value for a wide variety of salts. The value of 14.9 is usually assigned to it. I_x is the ionic strength in mole fraction scale and is defined as below

$$I_x = \frac{1}{2}\sum_i x_i z_i^2 \tag{3}$$

z_i is the charge number of ionic species.

A_ϕ is the Debye-Huckel constant for the osmotic coefficient and is defined as

$$A_\phi = \frac{1}{3}\left(2\pi N_o \frac{d_w}{1000}\right)^{1/2}\left(\frac{e^2}{DkT}\right)^{3/2} \tag{4}$$

N_0 is the Avogadro number, d_w is water density, e is electron charge, k is the Boltzmann constant, T is temperature, and D is relative permittivity of water.[18]

In this work, we have assumed that the molecular solute has an effect on relative permittivity of water and propose the following relation

$$D = 78.3 + ax_n \tag{5}$$

The number 78.3 is the dielectric constant of water at 25°C, x_n is the mole fraction of the molecular solute, and a is a coefficient that is obtained by fitting experimental data that is dependent on temperature and the nature of both molecular solute and hydrotrope.

To obtain the activity coefficient of the molecular solute, we combine Eqs. 2-5. After differentiation from excess Gibbs energy with respect to the mole fraction of the molecular solute, keeping the other variables constant, we obtain the activity coefficient of the molecular solute as follows

$$\ln \gamma_n^{el*} = A\cdot B\cdot\left[-\frac{3}{2}(78.3 + ax_n)^{-5/2}\cdot a(1 - x_n)\cdot I_x^{1/2} - \frac{1}{2}\rho\frac{I_x^{3/2}}{(1 + \rho I_x^{1/2})}\times(78.3 + ax_n)^{-3/2}\right] \tag{6}$$

A and B are defined as follows:

$$A = \frac{1}{3}\left(\frac{2\pi N_o d_w}{1000}\right)^{1/2}\times\left(\frac{e^2}{kT}\right)^{3/2} \tag{7}$$

$$B = -\left(\frac{1000}{M_s}\right)^{1/2}\cdot\frac{4}{\rho} \tag{8}$$

The expression for the activity coefficients of other species (water and the ions) is expressed by Eq. 9:

$$\ln \gamma_i^{el*} = A\cdot B \cdot\left[-\frac{3}{2}(78.3 + ax_n)^{-5/2}\cdot a\cdot x_n\cdot I_x + \frac{1}{2}z_i^2(78.3 + ax_n)^{-3/2}\right] ln(1 + \rho I_x^{0.5}) + \rho(78.3 + ax_n)^{-3/2}\cdot\left[\frac{\frac{1}{4}z_i^2 - \frac{1}{2}I_x^{3/2}}{(1 + \rho I_x^{0.5})}\right] \tag{9}$$

To obtain the activity coefficient of water, z_i must be set equal to zero in Eq. 9.

Short-Range Interaction Contribution

Among the various approaches used previously to develop local composition models for nonelectrolyte systems, the one used by Renon and Prausnitz[15] to develop the nonrandom two liquid (NRTL) model has been used in this work because it is algebraically simple and applicable to liquid mixtures. Furthermore, it does not require specific volume or area data, such as that required by the UNIQUAC local composition model.[20]

The local composition models for electrolyte solutions are

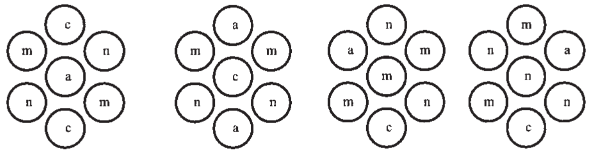

Figure 1. Four kinds of cells in a hydrotrope solution according to like-ion repulsion and local electroneutrality assumption.

based on two fundamental assumptions. The first assumption is like-ion repulsion, and the second assumption is that the distribution of cations and anions around a central solvent or solute molecule is such that the net local ionic charge is zero. The first assumption is referred to as like-ion repulsion, and the second assumption as local electroneutrality.[18,19]

There are four types of cells in hydrotrope solutions, which are demonstrated in Figure 1. The first type consists of a central solvent molecule surrounded by solvent, solute, anion, and cation species. The second type consists of a central solute molecule with solute, solvent, cation, and anion species around it. (The local-electroneutrality assumption is applied to cells of solvent and solute as central molecules.) The other two types are based on the like-ion repulsion assumption and have either an anion or a cation as the central species. Solvent and solute molecules, and the oppositely-charged ions, are located in their immediate neighborhood.

Based on NRTL[15] and Chen et al.,[18] the following relations express local mole fractions in terms of overall mole fractions

$$\frac{x_{ji}}{x_{ii}} = \frac{x_j}{x_i} G_{ji} \tag{10}$$

$$G_{ji} = \exp(-\alpha\tau_{ji}) \tag{11}$$

$$\tau_{ji} = (g_{ji} - g_{ii})/RT \tag{12}$$

In Eq. 10 quantities x_i and x_j are the overall mole fractions of components i and j in the solution, and x_{ji} and x_{ii} are local mole fractions of molecules j and i around the central molecule i, respectively.

The quantities g_{ii} and g_{ji} are interaction Gibbs energies between i-i and j-i pairs of species, respectively, which are inherently symmetric ($g_{ji} = g_{ij}$); and α is the nonrandomness factor, which is usually equal to 0.2.

For systems of more than two components, other local mole fraction ratios are defined as follows

$$\frac{x_{ji}}{x_{ki}} = \frac{x_j}{x_k} G_{ji,ki} \tag{13}$$

$$G_{ji,ki} = \exp(-\alpha\tau_{ji,ki}) \tag{14}$$

$$\tau_{ji,ki} = (g_{ji} - g_{ki})/RT \tag{15}$$

The local mole fractions are related by the mass balance equations as follows

$$x_{am} + x_{cm} + x_{mm} + x_{nm} = 1 \quad \text{(Central solvent cell)} \tag{16a}$$

$$x_{ma} + x_{na} + x_{ca} = 1 \quad \text{(Central anion cell)} \tag{16b}$$

$$x_{mc} + x_{nc} + x_{ac} = 1 \quad \text{(Central cation cell)} \tag{16c}$$

$$x_{mn} + x_{cn} + x_{an} + x_{nn} = 1 \quad \text{(Central solute cell)} \tag{16d}$$

In the above equations, subscripts m, n, a, and c refer to solvent, solute, anion, and cation, respectively.

By combining Eqs. 10, 13, and 16, the following expressions for the local mole fractions can be derived in terms of overall mole fractions

$$x_{im} = \frac{x_i G_{im,mm}}{x_a G_{am,mm} + x_c G_{cm,mm} + x_n G_{nm,mm} + x_m} \quad i = a, c, n, m \tag{17a}$$

$$x_{in} = \frac{x_i G_{in,nn}}{x_a G_{an,nn} + x_c G_{cn,nn} + x_m G_{mn,nn} + x_n} \quad i = a, c, n, m \tag{17b}$$

$$x_{ic} = \frac{x_i G_{ic,nc}}{x_m G_{mc,nc} + x_a G_{ac,nc} x_n} \quad i = a, n, m \tag{17c}$$

$$x_{ia} = \frac{x_i G_{ia,na}}{x_m G_{ma,na} + x_c G_{ca,na} x_n} \quad i = c, n, m \tag{17d}$$

In order to obtain an expression for the excess Gibbs energy, $g^{(a)}$, $g^{(c),}$ $g^{(m)}$, and $g^{(n)}$ are defined as the residual Gibbs energies per mole of cells of central anion, cation, solvent, and solute molecule, respectively. These Gibbs energies are related to the local mole fractions as follows[18]

$$g^{(a)} = z_a(x_{ma}g_{ma} + x_{ca}g_{ca} + x_{na}g_{na}) \tag{18a}$$

$$g^{(c)} = z_c(x_{mc}g_{mc} + x_{ac}g_{ac} + x_{nc}g_{nc}) \tag{18b}$$

$$g^{(m)} = x_{am}g_{am} + x_{cm}g_{cm} + x_{nm}g_{nm} + x_{mm}g_{mm} \tag{18c}$$

$$g^{(n)} = x_{an}g_{an} + x_{cn}g_{cn} + x_{mn}g_{mn} + x_{nn}g_{nn} \tag{18d}$$

In the next step, reference state Gibbs energies must be determined. The reference states are defined as below

$$g^{(a)}_{ref} = z_a g_{ca} \tag{19a}$$

$$g^{(c)}_{ref} = z_c g_{ac} \tag{19b}$$

$$g^{(m)}_{ref} = g_{mm} \tag{19c}$$

$$g^{(n)}_{ref} = g_{nn} \tag{19d}$$

It can be observed that the reference state for solvent and solute is their pure form. For cations and anions, the reference state is the pure completely dissociated liquid electrolyte form.

The reference Gibbs energy for anions and cations is multiplied by their charge numbers to represent the fact that the ratio of the coordination number of central anion cells to that of central cation cells must be equal to the corresponding ratio of their charge numbers.

In order to obtain the excess Gibbs energy of the solution, we must sum the changes in the residual Gibbs energies resulting when: x_m moles of solvent molecules are transferred from the solvent's reference state, x_n moles of solute molecules are transferred from the solute pure state, and x_a moles of anions and x_c moles of cations are transferred from the electrolyte reference state to the center of their respective cells in the mixture.

The following expression is obtained

$$g^{ex,lc} = x_m(g^{(m)} - g^{(m)}_{ref}) + x_n(g^{(n)} - g^{(n)}_{ref}) + x_a(g^{(a)} - g^{(a)}_{ref}) + x_c(g^{(c)} - g^{(c)}_{ref}) \quad (20)$$

Substituting Eqs. 18 and 19 into Eq. 20 results in:

$$g^{ex,lc}/RT = x_m(x_{am}\tau_{am} + x_{cm}\tau_{cm} + x_{nm}\tau_{nm}) + x_n(x_{an}\tau_{an} + x_{cn}\tau_{cn} + x_{mm}\tau_{mn}) + x_a z_a(x_{ma}\tau_{ma,ca} + x_{na}\tau_{na,ca}) + x_c z_c(x_{mc}\tau_{mc,ac} + x_{nc}\tau_{nc,ac}) \quad (21)$$

The assumption of local electroneutrality applied to the cells of the central solvent and central molecular solute is stated as

$$x_{am}z_a = x_{cm}z_c \quad (22)$$

$$x_{an}z_a = x_{cn}z_c \quad (23)$$

Substituting Eqs. 22 and 23 into the local composition definition expressed by Eqs. 10-15, the following equalities are derived

$$g_{am} = g_{cm} \quad (24)$$

$$g_{an} = g_{cn} \quad (25)$$

The second assumption that we propose in this work is that the interaction Gibbs energies between an ion (cation or anion) and a central molecule (solvent or solute) are equal. Our intention is to reduce the number of parameters of the model. This assumption is expressed by the following equation

$$g_{am} = g_{cm} = g_{an} = g_{cn} \quad (26)$$

Since the interaction energies are symmetric, the following relations are obtained

$$\tau_{ma,ca} = \tau_{na,ca} = \tau_{mc,ac} = \tau_{nc,ac} = \tau_1 \quad (27a)$$

$$\tau_{am} = \tau_{cm} = \tau_2 \quad (27b)$$

$$\tau_{an} = \tau_{cn} = \tau_3 \quad (27c)$$

$$\tau_{nm} = \tau_4 \quad (27d)$$

$$\tau_{mn} = \tau_5 \quad (27e)$$

Replacing the above equalities in Eq. 21, the short-range contribution to excess Gibbs energy will have five parameters. Additionally, since τ_5 is related to the other parameters by Eq. 28, the actual number of parameters reduces to four

$$\tau_5 = \tau_3 - \tau_2 + \tau_4 \quad (28)$$

In order to combine Eq. 21 with the long-range contribution, it is necessary to normalize the contribution of short-range interactions to the infinite dilution reference state for the ions. This results in Eq. 29

$$g^{\mathrm{ex}*,\mathrm{lc}}/RT = g^{ex,lc}/RT - x_c \ln \gamma_c^\infty - x_a \ln \gamma_a^\infty \quad (29)$$

The expressions $\ln \gamma_c^\infty$ and $\ln \gamma_a^\infty$ are obtained from Eq. 21. The final unsymmetrical relation is as follows

$$\begin{aligned} g^{ex*,lc}/RT ={}& \frac{x_m}{((x_a + x_c)G_2 + x_n G_4 + x_m)}((x_a + x_c)G_2\tau_2 + x_n G_4\tau_4) + \frac{x_m}{((x_a + x_c)G_3 + x_m G_4 + x_n)}((x_a + x_c)\tau_3 G_3 \\ & + x_m\tau_5 G_5) + \frac{x_a z_a \tau_1(x_n + x_m)}{(x_m + x_c G_1 + x_n)} + \frac{x_c z_c \tau_1(x_n + x_m)}{(x_m + x_a G_1 + x_n)} \\ & - x_c\left(\frac{(\tau_2 G_2 x_m(x_n G_4 + x_m) - G_2 x_m x_n \tau_4 G_4)}{(x_n G_4 + x_m)^2} + \frac{(\tau_3 G_3 x_n(x_m G_5 + x_n) - G_3 x_n x_m \tau_5 G_5)}{(x_m G_5 + x_n)^2} + \tau_1 z_c\right) \\ & - x_a\left(\frac{(\tau_2 G_2 x_m(x_n G_4 + x_m) - G_2 x_m x_n \tau_4 G_4)}{(x_n G_4 + x_m)^2} + \frac{(\tau_3 G_3 x_n(x_m G_5 + x_n) - G_3 x_n x_m \tau_5 G_5)}{(x_m G_5 + x_n)^2} + \tau_1 z_a\right) \end{aligned} \quad (30)$$

The activity coefficient of any of the four species is obtained through the following thermodynamic relation

$$\left(\frac{\partial n_T g^{ex*,lc}/RT}{\partial n_i}\right)_{T,P,n_{J\neq i}} = \ln \gamma_i^{lc*} \quad (31)$$

where n_i is the number of moles of species i, and n_T is the total number of moles of all the species present in the system.

Performing the differentiation of Eq. 31 for all the four species present in the solution, the activity coefficients of the species are obtained. These coefficients derived from Eqs. A1-A4 in Appendix A.

To obtain the complete activity coefficient of each species, the above expression based on the local composition concept

Table 1. The Names of the Systems Under Investigation

	System	Ref.
A	Effect of citric acid concentration on the solubility of butyl acetate in water	21
B	Effect of sodium benzoate concentration on the solubility of butyl acetate in water	21
C	Effect of sodium salicylate concentration on the solubility of butyl acetate in water	21
D	Effect of urea concentration on the solubility of butyl acetate in water	21
E	Solubility of *p*-chlorobenzoic acid at various concentrations of sodium *p*-toluenesulfonate in aqueous solution	7
F	Solubility of *o*-chlorobenzoic acid at various concentrations of sodium *p*-toluenesulfonate in aqueous solution	7
G	Solubility of *p*-chlorobenzoic acid at various concentrations of sodium butyl monoglycol sulfate in aqueous solution	7
H	Solubility of *o*-chlorobenzoic acid at various concentrations of sodium butyl monoglycol sulfate in aqueous solution	7
I	Effect of citric acid concentration on the solubility of methyl salicylate in water	22
J	Effect of sodium benzoate concentration on the solubility of methyl salicylate in water	22
K	Effect of sodium salicylate concentration on the solubility of methyl salicylate in water	22
L	Effect of urea concentration on the solubility of methyl salicylate in water	22

must be combined with the expression obtained for the long-range contribution

$$\ln \gamma_i = \ln \gamma_i^{LR} + \ln \gamma_i^{SR} \tag{32}$$

The final form of our model has five parameters: a, τ_1, τ_2, τ_3, and τ_4. The parameter a belongs to the long-range interaction term. The others belong to short-range interaction terms.

Calculation of the Experimental Activity Coefficient of the Molecular Solute in Water

As discussed above, we have two phases at equilibrium: the solute rich phase and the water rich phase. The equality of activity of any component present in both phases is the necessary and sufficient condition for equilibrium between them[23]

$$a_{n(n)} = a_{n(aq)} \tag{33}$$

where $a_{n\ (n)}$ is the activity of the molecular solute in the solute rich phase and $a_{n\ (aq)}$ is its activity in the water rich phase. Since the solubility of water in the solute rich phase is very small, $a_{n\ (n)}$ can be approximated by Raoult's law

$$a_{n(n)} = x_n a_n^* \tag{34}$$

where $x_{n,}$ is the mole fraction of the molecular solute in the solute-rich phase, and a_n^* is its activity in the pure state. Since x_n is approximately equal to one, the activity of the molecular solute in the solute rich phase remains nearly constant and equal to its pure state value. As a result, its activity in the water rich phase is also constant and equal to its pure state value.

The above statement results in the following equation for equilibrium between two solutions of the molecular solute in water, in the presence and in the absence of hydrotrope[23]

$$a_{n(aq)} = x_{n(aq)}\gamma_{n(aq)} = x_n^o \gamma_n^o \tag{35}$$

In Eq. 35, x_n^o and γ_n^o are, respectively, the experimental solubility and activity coefficients of the molecular solute in water in the absence of hydrotrope. Also, $x_{n(aq)}$ and $\gamma_{n(aq)}$ are, respectively, the experimental solubility and activity coefficients in the presence of hydrotrope or in the electrolyte solution. Since the solubility of the molecular solute in water (x_n^o) is very small, the value of γ_n^o is equal, with a very good approximation, to its value at infinite dilution, which is equal to one.[23] With this approximation, the activity coefficient of the molecular solute in the hydrotrope solution can be calculated by Eq. 36

$$\gamma_{n(aq)} = \frac{x_n^o}{x_{n(aq)}} \tag{36}$$

We used the solubility data of molecular solutes in water in the presence and in the absence of hydrotrope for calculating experimental activity coefficients. The systems, which we have considered in this work, are introduced in Table 1. For convenience, each system is named by a letter.

Data Regression

To obtain the model parameters, we have used the experimental activity coefficients of the molecular solute calculated by Eq. 36, together with Eq. 32 for the molecular solute. This is the sum of Eqs. A1 and 6.

An optimization software has been used to obtain the best fit of the model parameters. The parameters obtained are presented in Table 2. In this Table the root mean square relative deviation, $\sigma_{\ln\gamma}$, between the experimental and calculated activity coefficients, is defined as follows[24]

$$\sigma_{\ln \gamma_n} = \left[\frac{\Sigma(\ln \gamma_{n,\mathrm{exp}} - \ln \gamma_{n,\mathrm{cal}})^2}{N}\right]^{0.5} \tag{37}$$

N is the number of data points.

Model Parameters

In Table 2, parameters τ_1, τ_2, τ_3, τ_4, and a are presented for each system. Since these parameters are temperature dependent, different values are obtained at different temperatures. In the following discussions, it should be mentioned that all the parameters g_{ij} are inherently negative because they represent potential functions in the NRTL model.[15]

Parameter τ_1 is defined as below

$$RT\tau_1 = g_{ma} - g_{ca} = g_{na} - g_{ca} = g_{mc} - g_{ac} = g_{nc} - g_{ac} \tag{38}$$

Since the interaction between a cation and an anion is stronger than the interaction between an ion and a molecule,

Table 2. The Parameters of the Model for the Systems Considered

	T	τ_1	τ_2	τ_3	τ_4	a	N	σ
A	303	13.79	−14.14	−14.64	0.27	−11.88	19	0.07
	313	7.92	−15.19	−15.58	0.27	−10.83	19	0.07
	323	8.18	−15.97	−16.24	0.26	−12.22	19	0.08
B	303	6.84	−12.63	−12.99	0.27	−7.66	19	0.11
	313	6.45	−12.51	−12.70	0.19	−7.24	19	0.11
	323	8.06	−14.53	−14.53	0.21	−9.67	19	0.13
C	303	12.09	−10.70	−11.17	0.29	−9.87	19	0.04
	313	12.84	−11.97	−12.17	0.21	−13.61	19	0.12
	323	16.09	−13.01	−13.23	0.22	−21.69	19	0.14
D	303	8.16	−15.03	−15.26	0.27	−11.16	19	0.10
	313	10.57	−15.56	−15.80	0.25	−11.54	19	0.08
	323	9.16	−16.28	−16.52	0.25	−10.87	19	0.11
E	303	15.62	−12.13	−12.27	0.15	−16.50	16	0.07
	313	15.23	−12.15	−11.97	0.07	−13.60	16	0.07
	323	10.68	−12.70	−12.99	0.01	−20.20	16	0.08
F	303	7.04	−11.21	−11.02	−0.03	−14.40	16	0.02
	313	6.94	−11.51	−11.29	−0.02	−13.86	16	0.02
	323	7.85	−12.88	−12.98	0.21	−16.08	16	0.04
G	303	8.99	−14.73	−16.08	0.25	−23.01	17	0.15
	313	13.94	−15.28	−16.40	0.25	−29.00	17	0.13
	323	7.50	−14.57	−15.79	0.23	−17.46	17	0.06
H	303	9.96	−13.39	−13.21	0.10	−14.11	17	0.04
	313	11.61	−14.02	−14.23	0.18	−14.74	17	0.05
	323	11.48	−14.33	−14.52	0.20	−16.00	17	0.04
I	303	28.66	−13.39	−14.03	0.31	−14.20	19	0.10
	313	26.28	−14.55	−15.04	0.28	−20.71	19	0.07
	323	17.51	−15.07	−15.57	0.25	−20.10	19	0.10
J	303	6.67	−10.58	−11.24	0.39	−22.93	19	0.03
	313	6.10	−11.63	−11.99	0.26	−22.18	19	0.07
	323	6.79	−12.41	−12.66	0.22	−21.04	19	0.10
K	303	5.39	−8.97	−9.07	0.10	−15.9	19	0.07
	313	5.49	−9.84	−10.10	0.20	−16.36	19	0.09
	323	5.25	−9.47	−9.56	0.09	−17.51	19	0.09
L	303	7.22	−13.02	−13.56	0.33	−20.32	19	0.04
	313	7.94	−12.78	−13.04	0.23	−16.10	19	0.10
	323	8.21	−12.95	−13.35	0.22	−12.15	19	0.08

parameter τ_1 is dominated by g_{ca} or g_{ac}. Therefore, it must have a positive value, and it is not surprising that positive values have been obtained for all the systems under consideration.

Values of τ_2 and τ_3 are negative and of similar magnitude. They are defined below

$$RT\tau_2 = g_{am} - g_{mm} = g_{cm} - g_{mm} \tag{39}$$

$$RT\tau_3 = g_{an} - g_{nn} = g_{cn} - g_{nn} \tag{40}$$

These parameters are negative because ion-molecule interaction is stronger than molecule-molecule interaction. According to Eq. 26, the difference between these parameters is due to the difference between g_{mm} and g_{nn}. Since g_{mm} and g_{nn} represent interactions between molecules, we expect their values to

Table 3. The Parameters of the Model for Some Systems Considering Four Parameters for Them

	T	τ_1	$\tau_2 = \tau_3$	τ_4	a	σ
A	303	11.44	−10.63	−0.14	−11.20	0.26
B	323	7.97	−14.53	0.21	−6.70	0.21
C	333	9.92	−12.82	0.15	−8.85	0.20
D	323	10.53	−16.58	0.23	−15.80	0.13
E	303	13.25	−11.57	0.07	−8.33	0.08
F	313	5.06	−11.97	0.09	−8.03	0.04

Table 4. Comparison Between Experimental and Calculated Solubility for the Effect of Sodium Salicylate Concentration on the Solubility of Butyl Acetate in Water at T = 303 K

Concentration of Hydrotrope (kmol/m^3)	Solubility (exp)	Solubility (cal)	Error (%)
0.10	0.057	0.053	6.55
0.20	0.056	0.054	4.63
0.30	0.057	0.055	3.51
0.40	0.058	0.057	2.25
0.50	0.058	0.059	0.51
0.60	0.058	0.061	4.47
0.70	0.058	0.063	8.57
0.80	0.058	0.066	14.14
0.90	0.070	0.069	0.72
1.00	0.074	0.073	1.90
1.20	0.079	0.079	0.76
1.40	0.087	0.087	0.11
1.60	0.095	0.095	0.21
1.80	0.101	0.103	2.38
2.00	0.116	0.112	3.46
2.25	0.137	0.122	10.90
2.50	0.138	0.132	4.42
2.75	0.138	0.141	2.54
3.00	0.139	0.149	7.64
	Average		4.19

Table 5. Comparison Between Experimental and Calculated Solubility for Effect of Urea Concentration on the Solubility of Butyl Acetate in Water at T = 313 K

Concentration of Hydrotrope (kmol/m^3)	Solubility (exp)	Solubility (cal)	Error (%)
0.10	0.058	0.049	16.35
0.20	0.058	0.057	2.74
0.30	0.059	0.070	18.47
0.40	0.082	0.088	8.09
0.50	0.109	0.112	3.12
0.60	0.143	0.143	0.21
0.70	0.181	0.181	0.11
0.80	0.219	0.225	3.02
0.90	0.301	0.278	7.70
1.00	0.318	0.338	6.23
1.40	0.722	0.641	11.18
1.60	0.839	0.813	3.06
1.80	0.981	0.985	0.39
2.00	1.340	1.166	13.03
2.25	1.341	1.318	1.68
2.50	1.342	1.411	5.20
2.75	1.342	1.440	7.32
3.00	1.342	1.410	5.04
	Average		5.94

be of similar magnitude. Hence, the difference between the values of parameters τ_2 and τ_3 must be very small, because

$$g_{cn} = g_{cm} = g_{am} = g_{an} > g_{mm},\, g_{nn} \tag{41}$$

As we observe in Table 2, the values of parameter τ_4 are small in comparison with the other parameters. The reason is that it is defined as the difference between two molecule interactions as follows. This is weaker than the interactions between an ion and a molecule

$$RT\tau_4 = g_{nm} - g_{mm} \tag{42}$$

The fifth parameter, a, is related to long-range forces and shows the effect of the molecular solute on the dielectric constant of water. For this parameter, a small negative value is obtained for all the systems under consideration.

It must be mentioned that there is not a general law describing the effect of different materials on the dielectric constant of water. In this study, however, dielectric constant has decreased.

Table 6. Comparison Between Experimental and Calculated Solubility for Solubility of o-Chlorobenzoic Acid at Various Concentrations of Sodium p-Toluenesulfonate in Aqueous Solution at T = 313 K

Concentration of Hydrotrope (kmol/m^3)	Solubility (exp)	Solubility (cal)	Error (%)
0.10	0.012	0.012	1.23
0.20	0.013	0.013	0.56
0.30	0.014	0.013	0.08
0.40	0.015	0.015	3.18
0.50	0.016	0.016	1.49
0.60	0.017	0.017	0.78
0.70	0.019	0.019	0.25
0.80	0.021	0.022	1.43
0.85	0.022	0.023	3.49
0.90	0.024	0.024	0.97
0.95	0.026	0.026	0.38
1.00	0.027	0.027	2.16
1.20	0.035	0.035	0.22
1.40	0.046	0.045	2.83
1.60	0.059	0.057	4.01
2.00	0.090	0.092	2.86
	Average		1.62

Table 7. Comparison Between Experimental and Calculated Solubility for Effect of Sodium Salicylate Concentration on the Solubility of Methyl Salicylate in Water at T = 313 K

Concentration of Hydrotrope (kmol/m^3)	Solubility (exp)	Solubility (cal)	Error (%)
0.10	0.0043	0.0039	9.48
0.20	0.0043	0.0039	7.84
0.30	0.0043	0.0040	5.91
0.40	0.0043	0.0041	4.27
0.50	0.0043	0.0042	1.83
0.60	0.0043	0.0044	2.26
0.70	0.0044	0.0046	5.17
0.80	0.0044	0.0048	9.22
0.90	0.0044	0.0050	13.71
1.00	0.0045	0.0052	16.48
1.20	0.0052	0.0058	10.17
1.40	0.0061	0.0064	3.71
1.60	0.0071	0.0070	0.10
1.80	0.0093	0.0078	16.55
2.00	0.0088	0.0086	2.36
2.25	0.0119	0.0097	18.89
2.50	0.0114	0.0109	4.31
2.75	0.0116	0.0121	4.49
3.00	0.0117	0.0134	14.42
	Average		7.95

Decreasing the Number of Parameters

It is observed from Table 2 that the parameters τ_2 and τ_3 are nearly of similar magnitude. Hence, we can assume they are equal, especially for systems where their difference is smaller.

The results obtained by this assumption are presented in Table 3. It is observed that the root mean square deviation has increased. Consequently, we conclude that this assumption is not accurate, and we accept five parameters for this model.

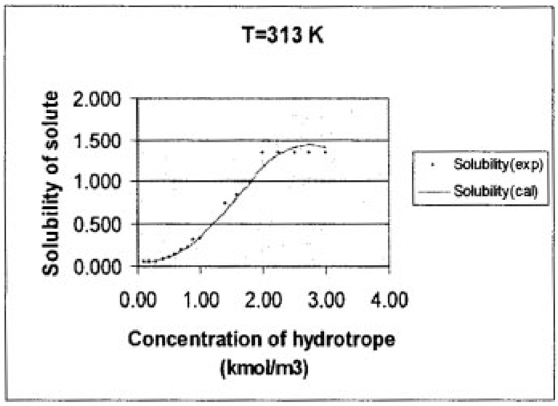

Figure 2. Solubility of butyl acetate in water at T = 313 K as a function of urea concentration.

Discussion

Data show that at constant temperature, the solubility of the solute in water increases with hydrotrope concentration. To prove the ability of the model to predict this behavior, we have performed the following calculations.

Using the parameters of our model presented in Table 2, we first calculated the activity coefficients of the molecular solutes in the electrolyte solutions by Eqs. 32, A1, and 6. This enabled us to calculate the solubility of the molecular solutes in water in the presence of hydrotrope ($x_{n(aq)}$) by Eq. 36. We performed these calculations for all the systems introduced in Table 1. The results of solubility calculations for the four systems of Table 1 are presented in Tables 4-7, together with absolute percent deviation defined by Eq. 43. The average absolute percent deviation is also presented in each Table

$$error(\%) = \frac{|x_{n\,\mathrm{exp}} - x_{n\,\mathrm{cal}}|}{x_{n\,\mathrm{exp}}} \times 100 \tag{43}$$

The variation of solubility of the solute with hydrotrope concentration for the selected four systems of Tables 4-7 are also shown in Figures 2 and 3. As is observed in these Figures, the experimental solubilities are very well represented by the model. For other systems under investigation in Table 1, only the average absolute percent deviations are presented in Table 8.

As is observed from this Table, acceptable results, which are within experimental error, are obtained.

Conclusion

In this article, a thermodynamic model for the excess Gibbs energy is proposed for hydrotrope solutions. The model consists of two contributions, a long-range term based on the Deby-Huckel theory and a short-range term based on the NRTL theory. The model has five adjustable parameters. Four of them represent short-range forces, and the other one represents long-range forces. Using these parameters, the solubility of a number of molecular solutes in water in the presence of a hydrotrope is calculated. Accurate results are obtained.

Since the thermodynamic framework is explained properly, it is an easy task to obtain the parameters of the model for any new hydrotrope solution.

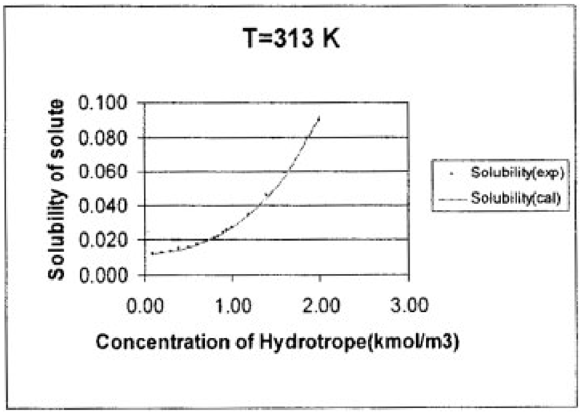

Figure 3. Solubility of o-chlorobenzoic acid in water at T = 313 K as a function of sodium p-toluenesulfonate concentration.

Table 8. Average Absolute Percent Deviations of Solubility Calculations for the Systems Considered in This Work

	T (K)	Error (%)
A	303	5.18
	313	5.52
	323	6.79
B	303	11.33
	313	12.71
	323	15.80
C	303	4.19
	313	11.50
	323	12.88
D	303	8.38
	313	5.94
	323	7.52
E	303	4.21
	313	4.75
	323	7.08
F	303	3.15
	313	1.62
	323	2.47
G	303	7.64
	313	9.17
	323	4.02
H	303	4.47
	313	4.80
	323	3.31
I	303	7.64
	313	6.57
	323	8.45
J	303	3.44
	313	7.81
	323	8.81
K	303	6.05
	313	7.95
	323	7.50
L	303	3.92
	313	9.02
	323	14.35
	Average error = 7.11	

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Appendix A

The equations for activity coefficient of the four species (molecular solute, solvent, cation, and anion) are presented below.

For molecular solute:

$$\begin{aligned}
\ln \gamma_n^{lc*} = {} & \frac{((x_a + x_c)G_2G_4x_m(\tau_4 - \tau_2) - \tau_4G_4x_m^2)}{((x_a + x_c)G_2 + x_nG_4 + x_m)^2} \\
& + \frac{((x_a + x_c)\tau_3G_3 + x_m\tau_5G_5)((x_a + x_c)G_3 + x_mG_5)}{((x_a + x_c)G_3 + x_mG_5 + x_n)^2} \\
& + \frac{\tau_1x_az_ax_cG_1}{(x_m + x_cG_1 + x_n)^2} + \frac{\tau_1x_cz_cx_aG_1}{(x_m + x_aG_1 + x_n)^2} \\
& - x_c\biggl(\frac{(-\tau_2G_2x_mG_4(x_nG_4 + x_m) + G_2x_m\tau_4G_4(x_nG_4 - x_m)}{(x_nG_4 + x_m)^3} \\
& + \frac{(\tau_3G_3x_mG_5(x_mG_5 + x_n) + G_3x_m\tau_5G_5(x_mG_5 - x_n)}{(x_mG_5 + x_n)^3}\biggr) \\
& - x_a\biggl(\frac{(-\tau_2G_2x_mG_4(x_nG_4 + x_m) + G_2x_m\tau_4G_4(x_nG_4 - x_m)}{(x_nG_4 + x_m)^3} \\
& + \frac{(\tau_3G_3x_mG_5(x_mG_5 + x_n) - G_3x_m\tau_5G_5(x_mG_5 - x_n)}{(x_mG_5 + x_n)^3}\biggr) \qquad \text{(A1)}
\end{aligned}$$

For solvent molecule:

$$\begin{aligned}
\ln \gamma_m^{lc*} = {} & \frac{((x_a + x_c)G_2 + x_nG_4)(\tau_2G_2(x_a + x_c) + x_nG_4\tau_4)}{((x_a + x_c)G_2 + x_nG_4 + x_m)^2} \\
& + \frac{(G_5x_nG_3(x_a + x_c)(\tau_5 - \tau_3) + G_5\tau_5x_n^2)}{((x_a + x_c)G_3 + x_mG_5 + x_n)^2} + \frac{\tau_1x_az_ax_cG_1}{(x_m + x_cG_1 + x_n)^2} \\
& + \frac{\tau_1x_az_cx_cG_1}{(x_m + x_aG_1 + x_n)^2} \\
& - x_c\biggl(\frac{(\tau_2G_2G_4x_n(x_nG_4 + x_m) - \tau_4G_4G_2x_n(x_nG_4 - x_m))}{(x_nG_4 + x_m)^3} \\
& + \frac{(\tau_3G_3x_nG_5(x_mG_5 + x_n) - G_3\tau_5G_5x_n(-x_mG_5 + x_n)}{(x_mG_5 + x_n)^3}\biggr) \\
& - x_a\biggl(\frac{(\tau_2G_2x_n(x_nG_4 + x_m) - G_2G_4\tau_4x_n(x_nG_4 - x_m)}{(x_nG_4 + x_m)^3} \\
& + \frac{(\tau_3G_3G_5x_n(x_mG_5 + x_n) - \tau_5G_5G_3x_n(-x_mG_5 + x_n)}{(x_mG_5 + x_n)^3}\biggr) \qquad \text{(A2)}
\end{aligned}$$

For cation:

$$\begin{aligned}
\ln \gamma_c^{lc*} = {} & \frac{(\tau_2G_2x_m(x_nG_4 + x_m) - G_2x_mx_n\tau_4G_4)}{((x_a + x_c)G_2 + x_nG_4 + x_m)^2} \\
& + \frac{(\tau_3G_3x_n(x_mG_5 + x_n) - G_3x_nx_m\tau_5G_5)}{((x_a + x_c)G_3 + x_mG_5 + x_n)^2} - \frac{G_1x_az_a\tau_1(x_m + x_n)}{(x_m + x_cG_1 + x_n)^2} \\
& + \frac{z_c\tau_1(x_m + x_n)}{(x_m + x_aG_1 + x_n)} - \frac{(\tau_2G_2x_m(x_nG_4 + x_m) - G_2x_mx_n\tau_4G_4)}{(x_nG_4 + x_m)^2} \\
& - \frac{(\tau_3G_3x_n(x_mG_5 + x_n) - G_3x_nx_mG_5\tau_5)}{(x_mG_5 + x_n)^2} - \tau_1z_c \qquad \text{(A3)}
\end{aligned}$$

For anion:

$$\begin{aligned}
\ln \gamma_a^{lc*} = {} & \frac{(\tau_2G_2x_m(x_nG_4 + x_m) - G_2x_nx_m\tau_4G_4)}{((x_a + x_c)G_2 + x_nG_4 + x_m)^2} \\
& + \frac{(\tau_3G_3x_n(x_mG_5 + x_n) - G_3x_nx_m\tau_5G_5)}{((x_a + x_c)G_3 + x_mG_5 + x_n)^2} + \frac{\tau_1z_a(x_n + x_m)}{(x_m + x_cG_1 + x_n)} \\
& - \frac{G_1x_cz_c\tau_1(x_n + x_m)}{(x_m + x_aG_1 + x_n)^2} - \frac{(\tau_2G_2x_m(x_nG_4 + x_n) - G_2x_nx_m\tau_4G_4)}{(x_nG_4 + x_m)^2} \\
& - \frac{(\tau_3G_3x_n(x_mG_5 + x_n) - G_3x_nx_m\tau_5G_5)}{(x_mG_5 + x_n)} - \tau_1z_a \qquad \text{(A4)}
\end{aligned}$$

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