Application of Electrolyte Theory to Extractive Separations Using Hydrotropes

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The use of polar hydrotropes in extractive distillation and in liquid-liquid extraction has been extensively reported in the literature. In this article, the effect of hydrotropes on increasing the effectiveness of separation is explained in terms of the effect of the dipole-induced dipole and the ion-induced dipole interactions on the activity coefficients of the neutral solutes in the aqueous phase. The self-consistent local composition theory is used to correlate quantitatively the observed behavior in systems involving liquid-liquid equilibria. The theory yields composition-dependent expressions for the effect of each independent pair interaction on the activity coefficient of a neutral solute in the aqueous phase. The ratio of the activity coefficients of the two solutes is of interest in this context. The resulting expression for the separation factor is elegant and admits simple physical interpretation. The essential features of hydrotrope-assisted extraction are correctly described by the theory. The ability of the theory to correlate data is demonstrated for two systems.

Introduction

In recent years there has been an increased interest in the use of hydrotropes in the selective aqueous extraction of close boiling organic compounds from an organic solution (Gaikar and Sharma, 1986, 1993). Hydrotropes, which are usually organic salts, increase the solubility of the organic compounds in water very selectively without emulsion formation. The subsequent recovery of the solute from the aqueous solution exploits the nonlinear dependence of the solubility of the solute on the hydrotrope concentration. Two aspects of this selective salting-in phenomenon appear to be significant: both the hydrotrope and the solutes are comparatively large, and the solubility curve for a solute is sigmoidal as a function of the hydrotrope concentration. In addition, the amounts salted-in are large beyond a certain concentration of the hydrotrope referred to as the minimum hydrotrope concentration (MHC).

The increase in solubility due to the presence of a hydrotrope is generally described by the empirical equation:

$$\ln\left(\frac{S}{S_o}\right) = K_S \times C_h \tag{1}$$

where S and S_o are the solubilities in water in the presence and absence of the hydrotrope respectively, and C_h is the concentration of the hydrotrope. K_S is the Setschenow constant. For small sized ions, K_S is generally negative representing salting-out while it is positive in the case of large ions that are of interest in the present work. Various theories have attempted to calculate this constant *a priori* (Bockris et al., 1951; McDevit and Long, 1952; Schneider, 1976; Pandit and Sharma, 1987). Electrostatic forces have been taken into account to explain the observed behavior of these systems. The McDevit and Long theory appears to predict correctly that the sign of the volume change of the hydrotrope upon dissolution determines the sign of the Setschenow constant.

The experimental work in the field of separations using hydrotrope solutions is not extensive and has been thoroughly reviewed by Gaikar and Sharma (1993). Very little experimental work on extractive separations using hydrotropes has been reported before 1986. Sharma and coworkers have studied a large number of industrially important mixtures using hydrotropes. Separation factors were remarkably high in most cases. Extraction was higher from inert/nonpolar solvents than from polar solvents. The selectivity was a strong function of the hydrotrope concentration and especially high above the MHC value of the hydrotrope.

In this article, the recently developed self-consistent local composition (SCLC) theory of electrolyte solutions (Ananth

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and Ramachandran, 1990; Narayanan, 1993) is applied to the problem of hydrotropic extraction. The experimental system of interest is one in which two closely-boiling solutes in an organic solvent are extracted using an aqueous solution of the hydrotrope. The hydrotrope is assumed to dissociate partially. The SCLC theory yields an expression for the natural logarithm of the activity coefficient of the solute in the aqueous phase in the presence of electrolytes. The expression for $\ln \gamma$ is linear in the interaction parameters. It is shown that the SCLC theory is not only in qualitative agreement with all the observed phenomena but can correlate quantitatively the observed data on separation factors with essentially four parameters.

Idealized Experimental System

The experimental system is idealized as follows: the two close-boiling solutes that are to be separated are initially present in the dissolved state in an organic solvent. This organic phase (phase *n*) is then brought into contact with an aqueous phase (phase *w*) containing the hydrotrope and allowed to equilibrate. It is assumed that water and the solvent are completely immiscible and that the hydrotrope is insoluble in the organic phase. This assumption can be relaxed if necessary with a little additional bookkeeping effort. It is also assumed that the hydrotrope dissociates partially in the aqueous phase. At equilibrium the aqueous phase thus contains six components, namely, water 1, the two solutes 2 and 3, the positive ions 4 and the negative ions 5 from the dissociation of the hydrotrope and the undissociated hydrotrope 6 while the organic phase contains only three components, namely, the solvent 7 and the two solutes 2 and 3. The thermodynamic quantity of interest is the separation factor which is defined as:

$$\alpha = \left(\frac{x_3^w}{x_2^w} \times \frac{x_2^n}{x_3^n} \right) \tag{2}$$

Classical Thermodynamic Description

Clearly the thermodynamic equilibrium of the system is governed by an equality of the chemical potentials in the two phases of the common species, namely 2 and 3. In terms of standard state fugacities and activity coefficients, this criterion can be written as:

$$\begin{gathered} f_{2ss}^w \gamma_2^w x_2^w = f_{2ss}^n \gamma_2^n x_2^n \\ f_{3ss}^w \gamma_3^w x_3^w = f_{3ss}^n \gamma_3^n x_3^n \end{gathered} \tag{3}$$

Combining these equations with the definition of α in Eq. 2 we obtain an expression for $\ln \alpha$ in terms of the activity coefficient ratios:

$$\ln \alpha = \ln \left(\frac{f_{3ss}^n}{f_{2ss}^n} \times \frac{f_{2ss}^w}{f_{3ss}^w} \right) + \ln \left(\frac{\gamma_3^n}{\gamma_2^n} \right) + \ln \left(\frac{\gamma_2^w}{\gamma_3^w} \right) \tag{4}$$

In the absence of the hydrotrope the expression for $\ln \alpha^o$ is then written as:

$$\ln \alpha^o = \ln \left(\frac{f_{3ss}^n}{f_{2ss}^n} \times \frac{f_{2ss}^{wo}}{f_{3ss}^{wo}} \right) + \ln \left(\frac{\gamma_3^n}{\gamma_2^n} \right) + \ln \left(\frac{\gamma_2^{wo}}{\gamma_3^{wo}} \right) \tag{5}$$

Equations 4 and 5 describe the separation factor in two different experiments with the same organic phase in equilibrium at the same temperature and pressure with the aqueous phase with and without the presence of the hydrotrope respectively. By subtracting $\ln \alpha^o$ from $\ln \alpha$ using Eqs. 4 and 5 we get:

$$\ln \left(\frac{\alpha}{\alpha^o} \right) = \ln \left(\frac{f_{2ss}^w \, f_{3ss}^{wo}}{f_{2ss}^{wo} \, f_{3ss}^w} \right) + \ln \left(\frac{\gamma_2^w}{\gamma_3^w} \right) + \ln \left(\frac{\gamma_3^{wo}}{\gamma_2^{wo}} \right) \tag{6}$$

The first term in Eq. 6 can be set to zero if it is assumed that the standard state fugacities of the solutes 2 and 3 in the solvent 1 are practically unaffected by the presence of the hydrotrope. Hence, we conclude that (α/α^o) is effectively the ratio of the activity coefficients of 2 and 3 in the aqueous phase in the presence of the hydrotrope plus a constant K^o which represents the logarithm of the ratio of the activity coefficients of the solutes 3 and 2 in the absence of the hydrotrope:

$$\ln \frac{\alpha}{\alpha^o} \approx \ln(\gamma_2^w / \gamma_3^w) + K^o \tag{7}$$

The constant K^o is independent of the hydrotrope concentration and is constant at specified temperature. Numerically, K^o is expected to be small. The hydrotrope has already been described as an organic salt that dissociates partially in the aqueous phase. Hence, the calculation of α involves the use of a model for the activity coefficient of a neutral solute in an electrolyte solution. It is for this purpose that the SCLC model is used.

Model

The SCLC model has been described in detail elsewhere (Ananth and Ramachandran, 1990). It assumes that the excess Gibbs free energy can be written as a sum of two contributions: one due to the long-range electrostatic interactions and the other due to the short-range interactions. The former is obtained from the Pitzer modification of the Debye-Huckel theory while the latter is described by a local-composition lattice model. The lattice model incorporates correct pair counting, accounts for like-ion repulsion, and includes the effect of the nearest as well as the second-nearest neighbor interactions. The model is then linearized in the interaction parameters by a perturbation analysis. This perturbed model has only binary interaction parameters and can predict the behavior of multicomponent mixtures from a knowledge of that of the component binary mixtures. Of particular interest in the present context is the expression for the activity coefficient of the solute in the hydrotropic solution which is expressed in terms of the local mole fractions and nearest neighbor and next nearest neighbor interaction parameters. The theory takes into account the repulsive forces between like-ions by simply assigning a zero value to x_{ij}, the local mole fraction of i in the neighborhood of a j molecule, whenever i and j are like ions. The first term in the expression for activity coefficient (Ananth and Ramachandran, 1990) arises from the nonrandom arrangement of molecules that results from this assignment. The second term is the contribution of nearest neighbor interactions while the third term is that of the second nearest neighbor interactions. In this work, the effect of the second nearest neighbor interactions is neglected partly for the sake of simplicity and partly to reduce the number of parameters that have to be determined by fitting the theory to the somewhat scanty experimental data that is available.

In order to calculate $\ln \alpha$ it is clearly necessary to evaluate the difference between $\ln \gamma_2$ and $\ln \gamma_3$ using the SCLC theory:

$$\ln \gamma_2^w = \ln \frac{x_{22}^o}{x_2} + \sum v_{kj} \frac{x_{22}^{kj}}{x_{22}^o} \tag{8}$$

$$\ln \gamma_3^w = \ln \frac{x_{33}^o}{x_3} + \sum v_{kj} \frac{x_{33}^{kj}}{x_{33}^o} \tag{9}$$

The first term in each of these equations represents the contribution to $\ln \gamma$ arising from entropic considerations in the absence of all interactions between the molecules and ions except for an infinite repulsion between nearest neighbor like-ions. Except for this constraint the mixture is a random mixture and the local mole fractions will simply be equal to the global mole fractions: $x_{ij}^o = x_i$. The summation in the second term of Eqs. 8 and 9 runs over all the 13 independent interaction pairs kj: 21, 31, 61, 32, 62, 63, 42, 52, 43, 53, 64, 65, and 54. Both x_{22}^{kj} and x_{33}^{kj} can be calculated by solving the prescribed set of simultaneous linear equations (Ananth and Ramachandran, 1990).

The ratio of the activity coefficients can be written down from Eqs. 8 and 9:

$$\ln \left(\frac{\gamma_2}{\gamma_3}\right)^w = \ln \left(\frac{x_{22}^o}{x_{33}^o} \frac{x_3}{x_2}\right) + \sum v_{kj} \left(\frac{x_{22}^{kj}}{x_{22}^o} - \frac{x_{33}^{kj}}{x_{33}^o}\right) \tag{10}$$

In this work the zero order equations are solved approximately: the "random mixture" approximation is retained for x_{ij}^o for $i<j$ except for x_{14}^o and x_{15}^o which are obtained using the normalization condition. x_{ij}^o is set to zero for like ion pairs ij. The remaining local mole fractions are calculated using the correct pair-counting equations while the x_{ii}^o for neutral species i are obtained using the normalization equations. The resulting specifications of the local mole fractions differ from those in a truly random mixture only for the ionic components, 4 and 5, and the neutral arbitrarily-chosen reference component, 1. This is illustrated in Table 1 for the specific system of interest. In this table, as well as in the rest of this article, it is assumed that the hydrotrope is a 1-1 electrolyte.

In the present case, the expression for the ratio of activity coefficients in Eq. 10 involves x_{22}^o and x_{33}^o only. It follows from the random mixture approximation and normalization condition that $x_{22}^o = x_2$ and $x_{33}^o = x_3$. Hence, the first term in Eq. 10 vanishes. For the first-order terms, the set of linear equations for the molecule-molecule local mole fractions x_{i2}^{kj} $(i \neq 2)$ and x_{i3}^{kj} $(i \neq 3)$ can be solved numerically by Gaussian elimination.

Table 1. Zero-Order Local Mole Fractions

Pair i, j	x_{ij}^o, Random Mixing	x_{ij}^o, Random Mixing and Like Ion Repulsion
1,1	0.84100	0.84090
4,1	0.00757	0.00764
5,1	0.00757	0.00764
1,4	0.84100	0.84110
1,5	0.84100	0.84110

The above values correspond to an aqueous phase containing 3 mol of component 2, 2 mol of component 3, and 5 mol of hydrotrope per kilogram water. Degree of dissociation = 0.1.

x_{22}^{kj} and x_{33}^{kj} can then be obtained from the normalization condition. This has been done and the expression $(x_{22}^{kj}/x_2 - x_{33}^{kj}/x_3)$ that appears in Eq. 10 has been numerically evaluated over the entire range of mole fractions of 2 and 3. It is found that the following analytical expression agrees exactly with the numerical evaluation:

$$\frac{x_{22}^{kj}}{x_2} - \frac{x_{33}^{kj}}{x_3} = x_k(\delta_{j3} - \delta_{j2}) + x_j(\delta_{k3} - \delta_{k2}) \tag{11}$$

The corresponding analytical expression for x_{i2}^{kj} $(i \neq 2)$ and x_{i3}^{kj} $(i \neq 3)$ are harder to determine. The simple form of Eq. 11 appears to be valid because of a fortuitous cancellation of terms.

Of the 13 terms in the sum in Eq. 10 some vanish and many are clearly interrelated, as can be verified from Eq. 11. Indeed these relations are more general and can be deduced on the basis of symmetry considerations in the case of symmetric electrolytes. The sum in Eq. 10 then reduces to a sum of just four independent terms:

$$\ln \left(\frac{\gamma_2}{\gamma_3}\right)^w = v_{21} \left(\frac{x_{22}^{21}}{x_2} - \frac{x_{33}^{21}}{x_3}\right) + v_{31} \left(\frac{x_{22}^{31}}{x_2} - \frac{x_{33}^{31}}{x_3}\right) + v_{23} \left(\frac{x_{22}^{32}}{x_2} - \frac{x_{33}^{32}}{x_3}\right) - v_{326} \left(\frac{x_{22}^{62}}{x_2} - \frac{x_{33}^{62}}{x_3}\right) \tag{12}$$

Equation 11 can be used to simplify Eq. 12 further to yield an elegant expression for $\ln (\alpha/\alpha^o)$:

$$\ln \left(\frac{\alpha}{\alpha_o}\right) = K^o + (v_{31} - v_{21})x_1 + (v_{23})(x_2 - x_3) + (v_{326})x_6 \tag{13}$$

For a 1-1 electrolyte the parameter v_{326} is defined as:

$$v_{326}(1-\epsilon) = \left(\frac{\beta z}{2}\right) [(1-\epsilon)(v_{63} - v_{62}) + \epsilon((v_{43} - v_{42}) + (v_{53} - v_{52}))] \tag{14}$$

Further x_1 can be expressed in terms of the other mole fractions. Equation 13 can be now rewritten as:

$$\ln \alpha = K_{123} - v_{213}x_2 + v_{312}x_3 + v_{3,261}x_6 \tag{15}$$

x_6 in Eq. 15 is related to x_6', the mole fraction of the hydrotrope in the aqueous phase in the absence of dissociation. For a 1-1 electrolyte $x_6 = x_6'(1-\epsilon)/(1+\epsilon x_6')$. When $\epsilon = 1$, $x_6 = 0$, but the effect of the hydrotrope is quantified through x_6' and the parameter $(1-\epsilon)\ v_{326}$ which is not zero, as is obvious from Eq. 14.

Interaction Parameters

Equation 15 has four parameters which are defined as:

$$K_{123} = K^o - (v_{21} - v_{31}) + \ln \alpha_0$$

$$v_{213} = -(v_{21} + v_{23})$$

$$v_{312} = -(v_{31} + v_{23})$$

$$v_{3,261}(1-\epsilon) = v_{326}(1-\epsilon) - (1+\epsilon)(v_{31} - v_{21}) \tag{16}$$

The parameters v_{21}, v_{31}, and v_{23} can be expressed in terms of the fundamental nearest neighbor pair interaction parameters using the definition of the v_{ij} in the SCLC theory for neutral i and j. (In the SCLC theory the potential energy of interaction is so defined that u_{ij} is positive whenever the pair interaction is attractive):

$$v_{ij} = (\beta z/2)(2u_{ij} - u_{ii} - u_{jj})$$

The expression for v_{326} can be simplified if it is observed that u_{22} and u_{33} can be assumed to be approximately equal while the 62, 63, 42, 43, 52 and 53 interactions are either of the dipole-induced dipole or the charge-induced dipole type, each of which is proportional to the polarizability of the solute (Hirschfelder et al., 1956). Similarly $(v_{31} - v_{21})$ is essentially proportional to $(u_{31} - u_{21})$. The latter is the difference between the dipole-induced dipole interactions of the two solutes with water and is therefore proportional to the difference in their polarizabilities. Hence, the parameter $(1-\epsilon)\ v_{3,261}$ can be written as:

$$v_{3,261}(1-\epsilon) = [(1+\epsilon)K_1 - K_h](\nu_2 - \nu_3) \tag{17}$$

Expressions for both K_h and K_1 can be written down for the types of interactions discussed above (Hirschfelder et al., 1954):

$$K_h = \beta z\left((1-\epsilon)\,\frac{\mu_6^2}{r_m^6} + \epsilon\,\frac{C_4^2 + C_5^2}{2\,r_m^4}\right) \tag{18}$$

$$K_1 = \beta z\left(\frac{\mu_1^2}{r_m^6}\right) \tag{19}$$

K_h is a positive constant that depends on the nature of the hydrotrope and the ions into which it dissociates as well as on the nearest neighbor distance r_m. Similarly, K_1 is a positive constant that depends only on the nature of the solvent and r_m. The polarizabilities of the solutes are approximately proportional to their respective molecular volumes. Hence, the sign of $v_{3,261}$ depends on two factors: one that depends only on the properties of water and the hydrotrope, $[K_1(1+\epsilon) - K_h]$ and a second one that depends on the difference between the polarizabilities of the two solutes, $(\nu_2\text{-}\nu_3)$. The sign of the former determines whether the effect of the salt is to salt-in or salt-out the solute. For example, for a salt like NaCl in water $\epsilon = 1$ and $[2K_1 - K_h]$ is less than zero while for a large organic salt like sodium toluate, ϵ is nearly zero and $[K_1 - K_h]$ is positive. The two salts thus have opposite effects.

In this work, we are specifically interested in describing the increase in the separation factor due the addition of hydrotropes like sodium toluate, for which the first factor in $v_{3,261}$ is positive. The second factor $(\nu_2\text{-}\nu_3)$ is positive whenever the molecular volume of 2 is more than that of 3. The theory predicts therefore that the solute with the smaller molecular volume will be preferentially extracted in the presence of the hydrotrope. This appears to be in agreement with experimental observation (Agarwal and Gaikar, 1992).

The parameter v_{ij} is a measure of the affinity of i and j for one another. Customarily, u_{ij} is expressed as the geometric mean of u_{ii} and u_{jj} and $(-v_{ij}) = (z/2)(\sqrt{u_{ii}} - \sqrt{u_{jj}})^2$ is therefore expected to be a positive quantity. Hence, the parameters v_{312} and v_{213} are expected to be positive. This means that the separation factor increases as more 3 and less 2 are extracted into the aqueous phase. This feature is responsible for the change in slope of the α vs. hydrotrope concentration curve (Figure 1).

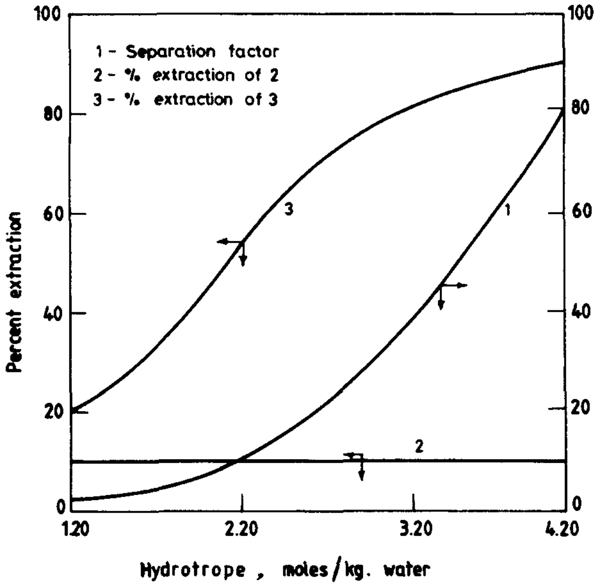

Figure 1. Simulation results indicating the variation of percent extraction and separation factor with hydrotrope concentration.

$K_{123} = -0.5$, $v_{213} = 70.0$, $v_{312} = 300.0$, $v_{3,261} = 40.0$.

Finally, the effect of the nature of the organic solvent appears only through α^0 in the present model. It is easy to extend the theory to also take into account the presence of the solvent in the aqueous phase and more directly its effect on α.

Results and Discussion

Figure 1 shows the results of the simulation of the model using typical values of the parameters. The calculations are made on the following basis. It is assumed that 3 is to be extracted preferentially. The number of moles of 2 and 3 initially present in the organic phase is taken to be 0.5 each. The aqueous phase is assumed to contain 1,000 g of water and the maximum tolerable fraction of 2 that is to be extracted at equilibrium, ϕ_2, is specified as 0.1. The degree of dissociation of the hydrotrope is assumed to be 0.1. Equation 15 is then used to calculate α iteratively for each chosen value of the hydrotrope concentration. It is simpler for the purpose of simulation to calculate the mole fraction of the hydrotrope added to the aqueous phase x_6' and α for each assumed value of ϕ_3. Both α and ϕ_3 (as a percentage) are plotted as a function of the molality of the hydrotrope in Figure 1. The ϕ_3 curve is appropriately sigmoidal while the α curve has a change in slope at a MHC of about 1.6 m. At a fixed percentage extraction of 2, viz. 10%, the percentage of 3 extracted increases with hydrotrope concentration, especially beyond MHC to as high as 80% at 3 m. Thereafter, the curve flattens out. The behavior is similar at other values of the degree of dissociation.

Figure 2 shows the effect of varying the parameters v_{213}, v_{312}, and $v_{3,261}$ on α. From the curves 2 and 3 it is clear that increasing

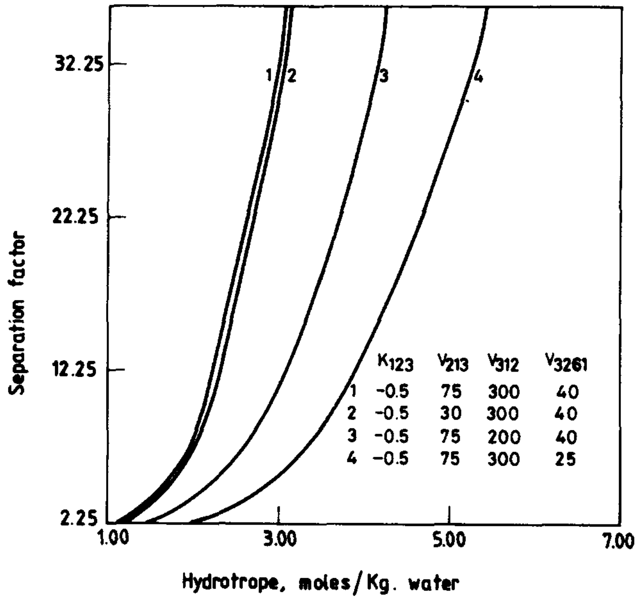

Figure 2. Simulation results indicating separation factor as function of hydrotrope concentration for different sets of parameter values.

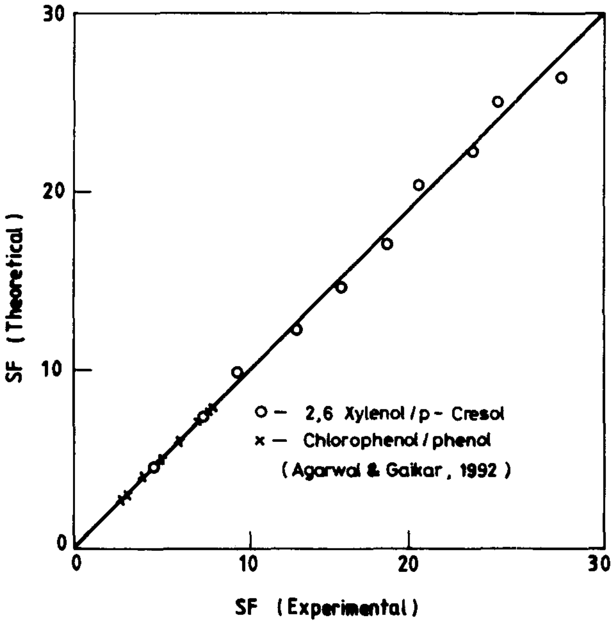

Figure 3. Comparison of the model with experimental results.

the value of v_{312} from 200 to 300 increases α for a given hydrotrope concentration. Reducing v_{213} from 75 to 30 results in an increase in the separation factor, but the effect is very small as can be seen from curves 1 and 2. More interesting is the increase in α at any given hydrotrope concentration as $v_{3,261}$ increases. From the discussion above this implies that as the difference in the polarizabilities of 2 and 3 increases, 3 is more preferentially extracted into the aqueous phase. Since the polarizability is in turn proportional to the molecular volume, this confirms the experimental observation (Agarwal and Gaikar, 1992) that the solute with the smaller molecular volume is extracted in preference to that with the larger molecular volume. It is also clear that the hydrotrope with the larger K_h (or larger v_{326}) value gives larger separation factors in aqueous extraction.

Figure 3 illustrates the correlative ability of the present model. The comparison is between experimental (Agarwal and Gaikar, 1992) and calculated values of α for two systems: extraction of 2,6-xylenol(2) and *p*-cresol(3) from *n*-heptane and *o*-chlorophenol(2), and phenol(3) from chlorobenzene with Na-toluate as the hydrotrope in both cases. In each case, the parameters K_{123}, v_{213}, v_{312}, and $v_{3,261}$ have been determined from Eq. 15 assuming α^o to be unity. The parameters K_{123}, v_{213}, v_{312}, and $v_{2,361}$ are -0.791, 81.718, 362.537, 47.527 for the xylenol/cresol system and 0.473, 148.227, 142.947, 20.238, respectively, for the chlorophenol/phenol system. The root-mean square deviation of the fit is about 3.08% for the former and 1.4% for the latter.

Conclusion

The SCLC theory of electrolyte solutions is used to successfully explain the effect of hydrotropes in increasing the separation factors in aqueous extraction of close-boiling solutes from an organic solvent. The theory predicts correctly several observed features of hydrotrope assisted extraction: the separation factor vs. concentration of hydrotrope curve has a change in slope with α increasing steeply with concentration especially beyond an identifiable MHC. In principle, *a priori* estimation of the parameters should be possible from fundamental interaction information. The present work, however, is confined to a demonstration of the ability of the theory to correlate experimental data on the separation factor as a function of hydrotrope concentration in two typical systems.

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Notation

C_h = concentration of hydrotrope in solution
C_4, C_5 = charge on ions
f_{iss} = fugacity of i in the standard state
K_h = positive constant in equation for $v_{3,261}$ related to interaction between hydrotrope and organic solute
K_1 = positive constant in equation for $v_{3,261}$ related to interaction between water and organic solute
K_S = Setschenow constant
r_m = nearest neighbor distance
S = solubility in the presence of hydrotrope
S_o = solubility in the absence of hydrotrope
x_{ij} = local mole fraction of i around j
x_{ij}^o = zero-order approximation for x_{ij}
x_{ij}^{kl} = first-order correction to x_{ij} due to v_{kl}
u_{kl} = interaction energy of pair kl
v_{kl} = nearest neighbor interaction parameter

Greek letters

α = separation factor in presence of hydrotrope
α^o = separation factor in absence of hydrotrope
β = $1/kT$
γ_i = activity coefficients of species, m

ϵ = degree of dissociation of hydrotrope
μ = dipole moment
ν_i = polarizability of i
ϕ_i = fraction of i extracted

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