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W. Wang[a]; J. H. Vera[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, McGILL UNIVERSITY MONTREAL, QUEBEC, CANADA

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A Thermodynamic Model for the Partition of All Ionic Species in Reverse Micellar Extraction of Amino Acids with a Cationic Surfactant

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W. WANG and J. H. VERA*
DEPARTMENT OF CHEMICAL ENGINEERING
McGILL UNIVERSITY
MONTREAL, QUEBEC H3A 2A7, CANADA

ABSTRACT

Cationic surfactants normally need an alcohol as cosurfactant to form reverse micelles. A thermodynamic model has been developed to predict the concentrations of all ionic species, including the cationic surfactant, in the aqueous and the reverse micellar phases as a function of the concentration of cationic surfactant and of cosurfactant for the extraction of amino acids by reverse micelles. The model has been tested by performing flash calculations for the system of DODMAC, 1-decanol, isooctane, NaCl, and water, containing three different amino acids. The calculated results are in good agreement with the experimental data.

Key Words. Amino acids; Cationic surfactant; Extraction; Reverse micelles; Thermodynamics

INTRODUCTION

An ionic surfactant is formed by a hydrocarbon part, which may contain branched chains, and an anionic or cationic head, which may partly dissociate in water. One interesting property of some ionic surfactants is the formation of reverse micelles. Reverse micelles are aggregates of surfactant molecules which contain microscopic polar cores of solubilized water (water pools) in an apolar solvent. Solute molecules can be extracted from

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* To whom correspondence should be addressed.

an aqueous solution into the water pools. Two types of surfactants have been commonly employed to form reverse micelles for studies of amino acid and protein extraction from aqueous solutions. Aerosol-OT, an anionic surfactant, has been used in the low pH range for the extraction of proteins in their cationic state (10, 21) and of amino acids (1, 9, 19). Trioctylmethyl ammonium chloride (abbreviated TOMAC), a cationic surfactant, has been used in the high pH range for the extraction of proteins in their anionic state (12, 15) and of amino acids (11, 26). Wang et al. (31) reported the formation of reverse micelles with the two-tailed cationic surfactant dioctyldimethyl ammonium chloride (DODMAC) in isooctane, using 1-decanol as a cosurfactant. For these reverse micelles, Wang et al. (32, 33) showed that the charge of an amino acid is an important factor for its extraction. The main mechanism for the extraction of amino acids from the aqueous phase is by ion exchange with the Cl^- counterions of DODMAC in the reverse micelles.

For future applications it is desirable to have a thermodynamic model which can calculate the concentrations of all ionic species present in the extraction system. Osseo-Asare (22) proposed a mass action model based on an two-step ion exchange process but no results were presented. Leodidis and Hatton (18) proposed a model for the extraction of metallic ions by AOT/isooctane reverse micelles. They considered an electrostatic double layer in the water pool of the anionic reverse micelles and, as stated in their work, they could not find a "satisfactory phenomenological treatment of ion-ion interactions." Vijayalakshmi and Gulari (27) developed an electrostatic model for metallic ion extraction by reverse micelles using a one-dimension Stern double layer model for the adsorption of the ions onto the interface of the reverse micelles. Ashrafizadeh et al. (3) treated cation exchange with anionic reverse micelles as an ion exchange process, and proposed a model similar to the one used by Allen and Addison (2). Bratko et al. (4) qualitatively described the protein solubilization in anionic reverse micelles by a shell-and-core model, which solved the nonlinear Poisson–Boltzmann equation for the electrostatic contribution to the free energy of transfer of the protein. Woll and Hatton (35) proposed a model for protein partitioning in anionic reversed micellar systems which assumes a pseudo-chemical equilibrium between proteins in solution and a protein–micelle complex. Bruno et al. (5) proposed a model for protein extraction by anionic reverse micelles in which the free energy change of the protein extraction was expressed as a sum of electrostatic and ideal solution terms. This model gives qualitative predictions for the effect of protein concentration on the transfer efficiency.

All models considered above are oriented to the calculation of the partition coefficient of the target extractant species only and, since they deal with anionic surfactants, they do not consider the effect of a cosurfactant in the distribution. In the present work, based on the equality of the electrochemical potential of the ionic species in the bulk aqueous and in the reverse micellar phases, a thermodynamic model is proposed to predict the concentrations of all ionic species in both phases for the extraction of an amino acid using cationic reverse micelles formed with the aid of a cosurfactant.

DEVELOPMENT OF THE MODEL

We consider here the extraction of a charged amino acid from an aqueous phase containing salts into the water pool of reverse micelles formed by a cationic surfactant and a cosurfactant in an apolar solvent. We make the following simplifying assumptions.

1. The organic phase is considered to be formed: the bulk organic phase and the reverse micelles which are water pools surrounded by cationic surfactant and cosurfactant molecules (18, 22). The nonpolar solvent and the cosurfactant are assumed to be totally immiscible with water. The cosurfactant is assumed to partly dissolve in the bulk organic phase and to partition on the interface of the reverse micelles. The ionic surfactant molecules are assumed to be fully dissociated, and located on the interface of the reverse micelles only.
2. The reverse micelles are assumed to be equal size (monodisperse) rigid spheres. Since the size of the reverse micelles increases with water uptake (8, 17, 33), as an ad hoc simplification, we assume that only the size (not the number) of the reverse micelles increases when the water uptake increases.
3. Since the number of amino acid molecules in a reverse micelle is much higher than the number of protein molecules (9), it is assumed that each reverse micelle is loaded with amino acid. The charged amino acid is assumed to locate in the water pools of the reverse micelles due to electrostatic interactions (1).
4. The ions and the charged amino acids are considered to obey Donnan equilibrium for their distribution between the reverse micellar water pools and bulk aqueous phase.
5. The charges of the ionic species in a reverse micelle meet the condition of electrical neutrality.

Basic Thermodynamic Relations

Due to the electrostatic potential generated by the charged interface of the reverse micelles, the water inside the reverse micelles has different properties than bulk water and these properties change with the water uptake (24, 33, 36, 37). Thus, the water uptake affects the partitioning behavior of the ionic species between the reverse micellar water pool and the bulk aqueous phase. The thermodynamic model proposed here is based on the equality of the electrochemical potential of ionic species i in the bulk aqueous phase and in the reverse micellar water pool:

$$\gamma_i^{aq} x_i = \gamma_i^{wp} y_i \exp\left(\frac{z_i e}{kT} \psi_{wp}\right) \tag{1}$$

where γ_i^{aq} and γ_i^{wp} are the the activity coefficient of the ionic species i in the bulk aqueous phase and in the water pool of the reverse micelles, respectively, and x_i and y_i are the corresponding mole fractions. The infinite dilution of the ionic species i in the bulk water phase is chosen as the reference state for the activity coefficients in both the bulk aqueous phase and the reverse micellar water pool. The charge of the ionic species i, z_i, is negative for anions and positive for cations, e is an electronic charge, k is the Boltzmann constant, and T is the absolute temperature. The symbol ψ_{wp} represents the electrostatic potential at the reverse micellar interface of the water pool. For the bulk aqueous phase, the electrostatic potential is negligible (18). The mole fractions can be written as

$$x_i = \frac{C_i^{aq}}{\sum_{j=1}^{N} C_j^{aq} + C_{H_2O}^{aq}} \tag{2}$$

$$y_i = \frac{C_i^{wp}}{\sum_{j=1}^{N} C_j^{wp} + C_{H_2O}^{wp}} \tag{3}$$

where C_i^{aq} and C_i^{wp} are the molar concentration of ionic species i in the bulk aqueous phase and in the water pool inside the reverse micelles, respectively. Equation (1) provides the basic thermodynamic relation necessary for the calculation of the concentrations of all ionic species in both the bulk aqueous phase and the reverse micellar water pool. The partition coefficient, K_i, is defined as

$$K_i \equiv C_i^{wp}/C_i^{aq} \tag{4}$$

In what follows, we develop the equations necessary to calculate all terms of Eq. (1).

Electrostatic Potential at the Reverse Micellar Interface of the Water Pool, ψ_{wp}

Curry et al. (7) studied the electrostatic potential profile in a spherical cavity containing an aqueous electrolyte solution, and obtained an analytical solution for the linear Poisson–Boltzmann equation. They proposed a rational function to correct the analytical solution for the nonlinear Poisson–Boltzmann equation. As shown in their work, the solution for the electrostatic potential ψ at the surface of the spherical cavity is the same for both the linear and the nonlinear Poisson–Boltzmann equations due to the need to satisfy the boundary conditions. Hence, an analytical solution for ψ_{wp} can be obtained by solving the linear Poisson–Boltzmann equation (7, 20) with the following two boundary conditions (4, 13):

$$\left(\frac{d\psi}{dr}\right)_{r=0} = 0 \tag{5}$$

$$\left(\frac{d\psi}{dr}\right)_{r=R_{wp}} = \frac{z_s n_s e}{D R_{wp}^2} \tag{6}$$

where r is the radial distance from the center of a reverse micelle, z_s represents the charge of the ionic surfactant, n_s stands for the aggregation number of the surfactant in a reverse micelle, and R_{wp} and D are the radius and the dielectric constant of the water pool of a reverse micelle, respectively. Thus, the electrostatic potential generated by the interface of reverse micelles, ψ_{wp}, can be obtained as

$$\psi_{wp} = \frac{z_s n_s e}{D} \frac{[e^{-KR_{wp}} - e^{KR_{wp}}]/R_{wp}}{[1 - KR_{wp}]e^{KR_{wp}} - [1 + KR_{wp}]e^{-KR_{wp}}} \tag{7}$$

Following Lewis and Randall (20), K is defined as

$$K^2 \equiv \frac{4\pi e^2}{DkT} \frac{N_A}{1000} \sum C_i^{wp} z_i^2 \tag{8}$$

where N_A is Avogadro's number. The electrostatic potential calculated by Eq. (7) satisfies the limit that ψ_{wp} should be zero for the case of "reverse micelles" with infinitely large size of the water pool. Although no experimental data are available, it is reasonable to assume that the dielectric constant D of water in the water pool changes with the size of reverse micelles (14, 18). Since the dielectric constant does not vary significantly with the electric field strength and with the ionic concentrations, as a first approximation the dielectric constant D of the water pool can be assumed to have a fixed value which is lower than that of bulk water (5, 13). The radius of the water pool, R_{wp}, and the aggregation number of the surfactant, n_s, can be determined by a geometrical model based on a suggestion of Weber (34) and detailed in the Appendix.

The Activity Coefficient of the Ionic Species *i* in the Bulk Aqueous Phase

The Pitzer model (23) is used to calculate the activity coefficient of the ionic species *i* in the bulk aqueous phase. Since the ionic strength of the bulk aqueous phase is less than 0.50 M, the short-range interaction can be neglected and we write

$$\ln \gamma_i^{aq} = -A_x \left[\frac{2z_i^2}{\rho} \ln(1 + \rho I_x^{0.5}) + \frac{z_i^2 I_x^{0.5} - 2I_x^{1.5}}{1 + \rho I_x^{0.5}} \right] \tag{9}$$

with

$$A_x = \frac{1}{3} \left(\frac{2\pi N_A d_{H_2O}}{M_{H_2O}} \right)^{0.5} \left(\frac{e^2}{DkT} \right)^{1.5} \tag{10}$$

$$\rho = 2150 \left(\frac{d_{H_2O}}{DT} \right)^{0.5} \tag{11}$$

where d_{H_2O} and M_{H_2O} are the density and molecular weight of water, respectively. Here, the ionic strength, I_x, is defined as

$$I_x = \frac{1}{2} \sum z_i^2 x_i \tag{12}$$

The Activity Coefficient of the Ionic Species *i* in the Reverse Micellar Phase

Ashrafizadeh et al. (3), following the work of Allen and Addison (2), expressed the activity coefficients of metal ions in the reverse micellar phase by the Wilson equation. In previous work (29, 30) we demonstrated the link between Guggenheim's configurational partition function and semiempirical activity coefficient equations, such as UNIQUAC and the Wilson equation. Experimental results (33) indicate that the ionic species inside reverse micelles tend toward their undissociated states and that the concentrations of all ionic species inside the reverse micelles are much higher than those in the bulk aqueous phase. In this work we assume that long-range interaction contributions to the activity coefficient can be neglected, and that the state of the ionic species inside the reverse micelles is similar to a lattice-solid state. Hence, only the term of configurational energy contributes to the partition function, and the final expression for the activity coefficient of ionic species i can be obtained as (30)

$$\ln \gamma_i^{\mathrm{wp}} = \frac{zq_i}{2} \sum_{k \neq l}^{N} \chi_{ik}\theta_k - \frac{zq_i}{2} \sum_{k=1}^{N} \sum_{l>k}^{N} \chi_{kl}\theta_k\theta_l - \frac{zq_i}{2} \chi_{i,\mathrm{H_2O}} \tag{13}$$

with

$$\chi_{kl} = \frac{\epsilon_{kk} + \epsilon_{ll} - 2\epsilon_{kl}}{RT} \tag{14}$$

$$\theta_k = \frac{q_k x_k}{\sum_m q_m x_m} \tag{15}$$

where χ_{kl} and ϵ_{kl} represent the dimensionless interaction parameter and the characteristic interaction energy between species k and l, respectively; θ_k and q_k stand for the surface area fraction and the surface area parameter of the species k, respectively; and z is the coordination number. The last term on the right-hand side of Eq. (13) appears from the normalization of the activity coefficient to the infinite dilution reference state.

USE OF THE MODEL TO REPRESENT EXPERIMENTAL DATA

In this work we test the capabilities of the model using the only experimental data reported in the literature for cationic reverse micelles which give the distribution of all ionic species (28). The amino acids DL-glutamic acid (Glu), DL-aspartic acid (Asp), and DL-threonine (Thr) were extracted from an aqueous solution with reverse micelles formed by the cationic surfactant DODMAC in isooctane using 1-decanol as cosurfactant at 23°C. The data reported are at pH near 12.5 at which aspartic acid and glutamic acid have two negative charges and threonine has one negative charge. The extraction systems contained three anions (amino acid, Cl^-, and OH^-) and two cations (Na^+ and DODMAC; H^+ ions are negligible).

For such systems there are the following practical difficulties for the calculation of reverse micellar extraction.

1. Since the molar concentrations of Na^+, OH^-, and amino acid in the reverse micellar phase are much lower than those of Cl^- and DODMAC, it is difficult to get the same calculation sensitivity for all ionic species.

2. Due to the interfacial curvature generated by the microscopic size of the reverse micelles and the charged interface, the physicochemical properties of the water pool change with the size of the reverse micelles (24). Hence, binary parameters estimated from experimental data of bulk water systems cannot be used for calculations inside the water pool of the reverse micelles.
3. Even assuming that the binary interaction parameters in Eq. (11) are symmetric ($\chi_{kl} = \chi_{lk}$), at least 15 binary interaction parameters are needed for the calculation of the concentrations of five ionic species, plus the water uptake, in the extraction system.

These problems are addressed below.

Considering that Eq. (13) corresponds to the form used by the Regular Solution theory (30) to reduce the number of the binary interaction parameters, χ_{kl}, in Eq. (14), we use

$$\chi_{kl} = \left(\sqrt{\frac{\epsilon_{kk}}{RT}} - \sqrt{\frac{\epsilon_{ll}}{RT}}\right)^2 \tag{16}$$

This assumption is equivalent to considering that ϵ_{kl} is the geometric mean of ϵ_{kk} and ϵ_{ll} in Eq. (14). Thus, only six energy parameters for the pure species k, ϵ_{kk}, remain in Eq. (13) for this extraction system. After some preliminary calculations, the energy parameter of water, ϵ_{H_2O}, was fixed at $9RT$. The following nonlinear equations were used to obtain the five energy parameters for the five ionic species at each experimental point:

$$\{F_{i,j}\}_{5,M} = \left\{x_{ij}\gamma_{ij}^{aq} - y_{ij}\gamma_{ij}^{wp} \exp\left(\frac{z_i e}{kT}\psi_{wp}\right)\right\}_{5,M} = 0 \tag{17}$$

where M is the number of experimental points.

The values of q_i for all five ionic species in the reverse micellar water pool were set at 1.00 in order to get the same sensitivity of the calculation for different ionic species, especially for amino acids. The convergence of the calculations was very sensitive to the value of q_{H_2O}, and we used $q_{H_2O} = 0.01$. The very low value required can only be justified by the special properties of the small number of water molecules inside the reverse micelles. As suggested by Bruno et al. (5), for the dielectric constant of the water in the water pool a value $D = 50$ was chosen in this work.

Since the size of the reverse micelles increases with water uptake (8, 17, 33) and the nature of the water in the water pool changes with the size of the reverse micelles (24), changes of the interaction energy ϵ_{kk} in the reverse micellar phase are expected. The interaction energy ϵ_{kk} can be correlated to the volume fraction of water f_{H_2O} and the molality of 1-decanol m_{dec} in the organic phase by the following equation:

$$\frac{\epsilon_{kk}}{RT} = [\alpha_1 + \alpha_2 \ln(f_{H_2O}) + \alpha_3 \ln(m_{dec})]^2 \tag{18}$$

where α_1, α_2, and α_3 are constants, and their values are listed in Table 1. The correlation coefficient, R^2, is more than 0.93 for all the ionic species.

In this work we calculate the change of the concentrations of all ionic species in both bulk aqueous and reverse micellar phases by a flash calculation using parameters evaluated from limited experimental data. To perform the flash calculations, two pieces of information are needed: (a) a correlation of the volume fraction of water in the organic phase, f_{H_2O}, with a specific operation variable, C_I, which can be the initial concentration of DODMAC or 1-decanol. In this work we have used a correlation of the form

$$f_{H_2O} = [\beta_1 + \beta_2 C_I^{\beta_3}]^2 \tag{19}$$

where the β_i are constants listed in Table 2. The variable C_I stands for the initial concentration of DODMAC in the organic phase (mM) for systems in which the concentration of 1-decanol is kept constant (250 mM was used in this work). For systems in which the concentration of DODMAC is kept constant (200 mM was used in this work), C_I stands for the initial concentration of 1-decanol. The correlation coefficient, R^2, is more than 0.97 for both cases. It should be noted that this correlation is independent of the thermodynamic model. (b) The concentrations of all ionic species in both aqueous phase and reverse micellar water pool for as few as five experimental points. With this limited information the interaction energy parameters, ϵ_{kk}, are evaluated by optimization using Eq. (17) and then they are correlated with the volume fraction of water f_{H_2O} and the molality of 1-decanol m_{dec} in the organic phase by Eq. (18).

TABLE 1
Constants in Eq. (18) for Different Ionic Species

	Amino acid	Cl^-	OH^-	Na^+	DODMAC
α_1	3.151892	2.782945	3.005278	2.179145	1.405168
α_2	0.145248	0.127600	0.131723	0.060869	−0.017412
α_3	0.069928	−0.012368	−0.050375	−0.168459	−0.196052
R^2	0.963	0.985	0.941	0.930	0.941

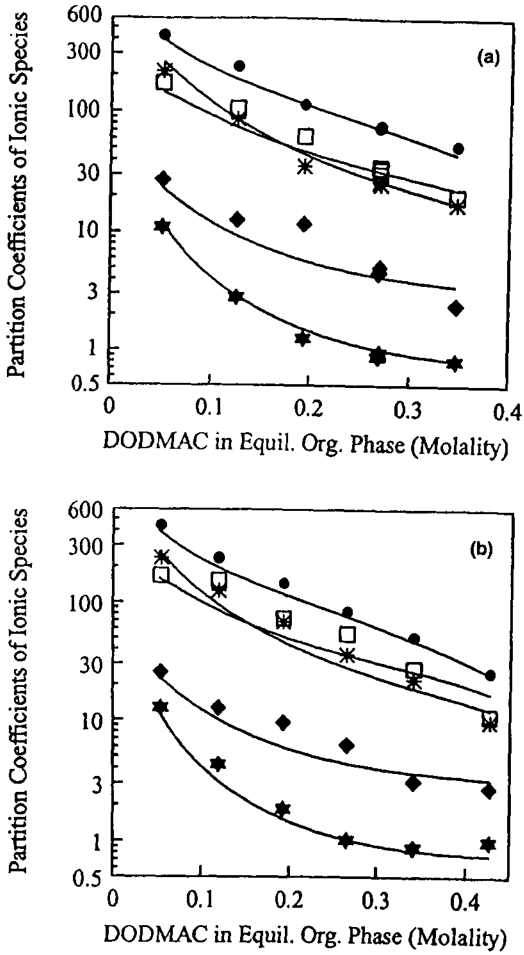

FIG. 1 Effect of DODMAC concentration in the equilibrium organic phase on the partition coefficients of ionic species for the extractions of (a) Asp, (b) Glu, and (c) Thr. Initial organic: 50–300 mM DODMAC, 250 mM 1-decanol; initial aqueous: 5 mM amino acid, no NaCl, pH 12.6 for (a) aspartic acid (Asp) and (c) threonine (Thr), pH 12.5 for (b) glutamic acid (Glu); (□) amino acid, (∗) Cl, (◆) OH, (✱) Na, (●) DODMAC.

For a given composition of the initial organic and aqueous phases, a flash calculation of the concentration of all ionic species in both bulk aqueous phase and reverse micellar water pool is performed as follows: (a) a value is assumed for the molar concentration of each of the ionic species in the bulk aqueous phase; (b) the water uptake is calculated by

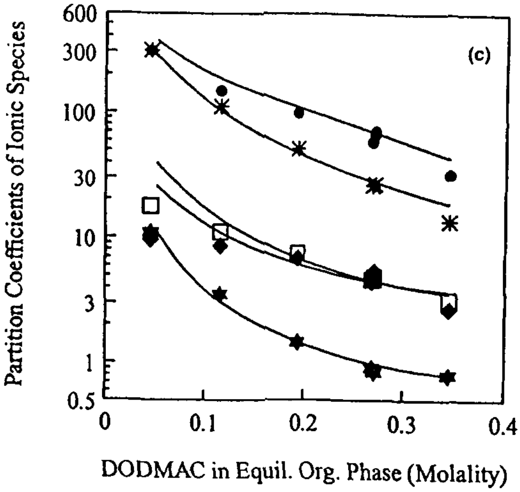

FIG. 1 Continued

Eq. (19); (c) the molar concentrations of all the ionic species in the reverse micellar water pool are calculated by material balances and the condition of electrical neutrality; (d) the two sides of Eq. (1) are compared for all ionic species; (e) the calculations are repeated until Eq. (1) is satisfied for all ionic species. In principle there are five unknowns and five nonlinear equations, and any method of solution of nonlinear equations can be used for this purpose.

RESULTS AND DISCUSSION

Figures 1 and 2 show the results of flash calculations for the extraction of three amino acids by the DODMAC reverse micelles. These figures

TABLE 2
Constants for Eq. (19) for the Different Systems

β_1	β_2	β_3
	Effect of DODMAC on Water Uptake	
3.90894×10^{-2}	1.13961×10^{-4}	1.5
	Effect of 1-Decanol on Water Uptake	
1.21354×10^{-1}	1.46382×10^{4}	−2

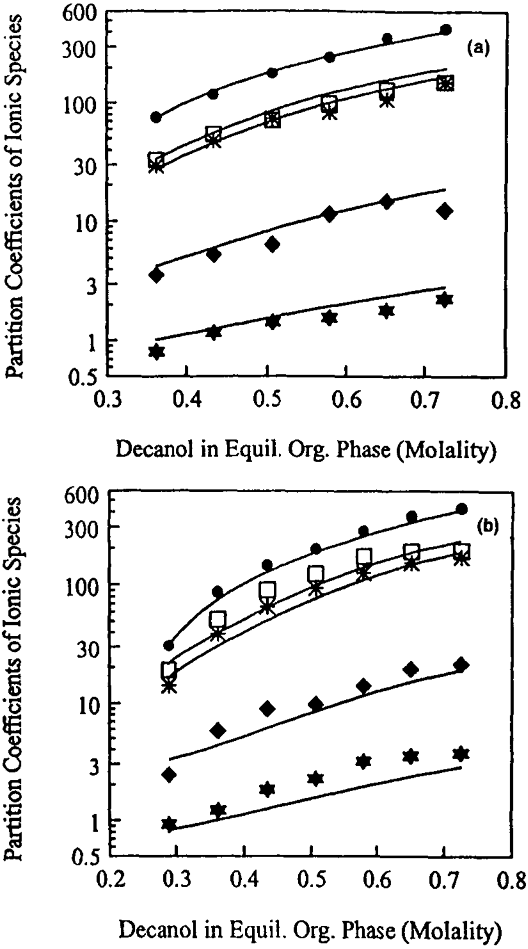

FIG. 2 Effect of 1-decanol concentration in the equilibrium organic phase on the partition coefficients of ionic species for the extractions of (a) Asp, (b) Glu, and (c) Thr. Initial organic: 200 mM DODMAC, 200–500 mM 1-decanol; initial aqueous: 5 mM amino acid, no NaCl, pH 12.6 for (a) aspartic acid (Asp) and (c) threonine (Thr), pH 12.5 for (b) glutamic acid (Glu); (□) amino acid, (*) Cl, (◆) OH, (✱) Na, (●) DODMAC.

present the effect of changes in the concentrations of DODMAC and 1-decanol, respectively. The solid lines represent the results of the flash calculations, and the points with labels are the experimental results (28). The values of the parameters used for the calculations are listed in Tables 1 and 2. Some representative results of the flash calculations for the extraction of aspartic acid are listed in Tables 3 and 4. The results of the calculations shown in Fig. 1 are slightly inferior to those shown in Fig.

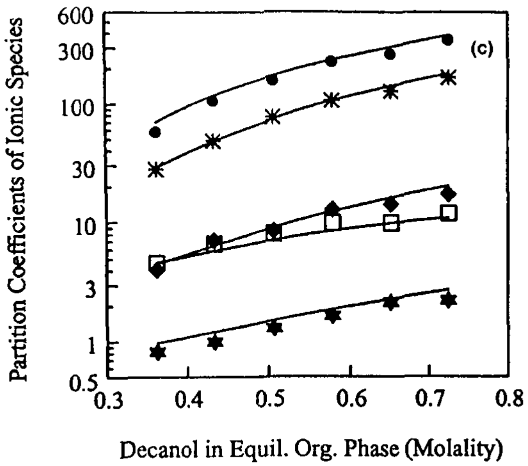

FIG. 2 Continued

TABLE 3

Results of Flash Calculations for the Extraction of DL-Aspartic Acid with Changes of the Initial DODMAC Concentration in the Organic Phase (the data in parentheses are the experimental values)[a]

DODMAC (mM)	f_{H_2O} (% vol)	Ionic species in bulk aqueous phase (mM)					Ionic species in reverse micellar phase (mM)				
		Asp	Cl	OH	Na	D	Asp	Cl	OH	Na	D
50	0.63	2.64	19.1	28.	55.2	14.3	375	4890	660	655	5640
	(0.56)	(2.55)	(22.7)	(33.9)	(55.9)	(14.6)	(435)	(4840)	(1160)	(613)	(6260)
100	2.34	1.76	31.4	45.3	56.1	17.9	137	2890	450	175	3440
	(2.66)	(1.30)	(30.0)	(33.1)	(56.2)	(13.6)	(137)	(2590)	(460)	(157)	(3170)
150	6.17	1.24	38.8	46.6	57.1	17.7	58	1730	270	87	2030
	(6.34)	(0.97)	(45.0)	(32.4)	(57.9)	(17.4)	(61)	(1600)	(330)	(73)	(1980)
200	13.06	0.88	41.3	33.5	58.8	16.9	28	1110	140	60	1240
	(12.61)[b]	(0.85)	(43.1)	(30.9)	(59.9)	(17.3)	(30)	(1130)	(140)	(53)	(1280)
	(13.04)[b]	(0.92)	(43.0)	(30.9)	(59.9)	(16.5)	(28)	(1090)	(150)	(54)	(1240)
	(12.89)[b]	(0.86)	(43.5)	(31.6)	(59.3)	(16.3)	(29)	(1100)	(160)	(57)	(1260)
250	23.97	0.63	40.2	20.9	62.4	16.8	15	710	70	52	760
	(23.35)	(0.74)	(41.6)	(30.2)	(62.2)	(14.9)	(15)	(730)	(80)	(51)	(790)

[a] Initial organic (30 mL): 50–250 mM DODMAC; 250 mM 1-decanol. Initial aqueous (30 mL): 5 mM Asp; pH 12.6 (59.0 mM NaOH).

[b] Experimental replicates.

TABLE 4

Results of Flash Calculations for the Extraction of DL-Aspartic Acid with Changes of the Initial 1-Decanol Concentration in the Organic Phase (the data in parentheses are the experimental values)[a]

Decanol	f_{H_2O}	Ionic species in bulk aqueous phase (mM)					Ionic species in reverse micellar phase (mM)				
(mM)	(% vol)	Asp	Cl	OH	Na	D	Asp	Cl	OH	Na	D
250	12.64	0.87	41.3	33.4	58.9	17.2	29	1140	140	60	1280
	(12.28)	(0.92)	(40.3)	(34.7)	(60.7)	(17.5)	(30)	(1180)	(130)	(49)	(1320)
300	8.07	0.86	40.5	36.7	57.7	16.8	48	1860	220	73	2110
	(8.20)	(0.87)	(38.6)	(35.5)	(58.2)	(17.5)	(47)	(1850)	(200)	(68)	(2060)
350	5.80	0.81	38.0	33.2	57.0	16.4	69	2670	280	89	3000
	(6.10)	(0.91)	(35.3)	(36.3)	(57.3)	(16.1)	(64)	(2570)	(250)	(82)	(2850)
400	4.53	0.75	35.2	28.0	56.5	15.7	90	3510	320	110	3900
	(4.88)	(0.84)	(38.6)	(36.3)	(57.3)	(14.9)	(82)	(3180)	(400)	(89)	(3620)
450	3.75	0.70	32.6	23.6	56.0	14.8	111	4330	350	133	4770
	(4.00)	(0.79)	(36.8)	(37.2)	(57.0)	(12.6)	(102)	(3950)	(500)	(103)	(4510)
500	3.24	0.66	30.3	20.3	55.6	13.7	130	5100	380	159	5580
	(3.38)	(0.80)	(32.3)	(36.3)	(56.4)	(12.5)	(121)	(4820)	(400)	(128)	(5370)

[a] Initial organic (30 mL): 200 mM DODMAC; 250–500 mM 1-decanol. Initial aqueous (30 mL): 5 mM Asp; pH 12.6 (59.0 mM NaOH).

2. This may be caused by the fact that the simplifying assumption (II) of this model gives a poor approximation to reality, especially when the concentration of DODMAC changes. As it can be seen in the Appendix, the simplifying assumption (2) affects the value of R_{wp} and n_s, which in turn affect the value of ψ_{wp} given by Eq. (7). When the concentration of DODMAC increases, the water uptake is greatly increased (33), and the changes in the number of reverse micelles and in the number of the surfactant molecules dissolved in the bulk organic phase become significant. On the other hand, increases in the concentration of 1-decanol cause relatively minor decreases in the water uptake (32, 33).

CONCLUSIONS

A thermodynamic model has been developed based on the equality of the electrochemical potential of the ionic species between the bulk aqueous phase and the reverse micellar water pool. With this model it is possible to predict the concentrations of all ionic species, including the surfactant, in both the bulk aqueous phase and the reverse micellar water pool as a function of the extraction variables, such as the concentration of surfactant or cosurfactant. For a system with N ionic species, only N interaction energy parameters, which can be evaluated from as few as five experimental points, are needed. It should be noted that for each experimental point five compositions are calculated for each of the two phases. Thus, for 30 experimental points, for example, the model reproduces well 300 compositions using a limited number of parameters. The differentiation between amino acids is done through their charge number only. No specific parameters are introduced for each particular amino acid. For the extraction by DODMAC reverse micelles of aspartic acid, glutamic acid, and threonine, the prediction results of the flash calculations are in good agreement with the experimental data.

APPENDIX: DETERMINATION OF THE RADIUS OF THE WATER POOL, R_{wp}, AND THE AGGREGATION NUMBER OF THE SURFACTANT, n_s, BY A GEOMETRICAL MODEL

Geometrical relations have been used in the literature (13, 18) to determine the radius of the water pool and the aggregation number of the surfactant. In this work, as a starting point, we use a geometrical model proposed by Weber (34) which is based on the assumption of hexagonal close packing of spherical reverse micelles in the organic apolar solvent at the state of maximum water uptake. In this case,

$$\frac{V_M^*}{V_o} = \frac{\pi\sqrt{2}}{6} = 0.7405 \tag{A-1}$$

where V_M and V_o are the volume of the reverse micelles and of the equilibrium organic phase, respectively. The superscript $*$ refers to the state of close packing. Assuming that the maximum volume fraction of water in the organic phase, $f_{H_2O}^*$, is obtained at the state of close packing,

$$f_{H_2O}^* = 0.7405\left(\frac{V_{wp}^*}{V_M^*}\right) = 0.7405\left(\frac{d_{wp}^*}{d_{wp}^* + 2l_s}\right)^3 \tag{A-2}$$

where V_{wp} and d_{wp} are the volume and diameter of the water pool of a reverse micelle, respectively, and l_s is the length of surfactant molecule. Equation (A-2) is conveniently rearranged as

$$d_{wp}^* = \frac{2l_s}{(0.7405/f_{H_2O}^*)^{1/3} - 1} \tag{A-3}$$

When the reverse micelles are not in the case of close packing, we propose here an extension of Weber's treatment (34) based on the assumption that only the size (not the number) of the reverse micelles changes with the water uptake. In this case we can write

$$\frac{V_M}{V_o} = \frac{V_{wp}}{V_o}\frac{V_M}{V_{wp}} = f_{H_2O}\left(\frac{d_{wp} + 2l_s}{d_{wp}}\right)^3 = \frac{V_M^*}{V_o}\frac{V_M}{V_M^*} = 0.7405\left(\frac{d_{wp} + 2l_s}{d_{wp}^* + 2l_s}\right)^3 \tag{A-4}$$

From Eq. (A-4) the diameter of the water pool, d_{wp}, can be estimated by

$$d_{wp} = 2R_{wp} = (d_{wp}^* + 2l_s)\left(\frac{f_{H_2O}}{0.7405}\right)^{1/3} \tag{A-5}$$

The number of reverse micelles per unit volume of the equilibrium organic phase, N_M, is then given by

$$N_M = \frac{V_M}{\frac{1}{6}\pi\,(d_{wp} + 2l_s)^3 V_o} = \frac{6f_{H_2O}}{\pi d_{wp}^3} = \frac{(C_s - C_o)(1 - f_{H_2O})N_A}{n_s} \tag{A-6}$$

where C_s is the total number of moles of surfactant per unit volume of organic solvent, and C_o is the number of moles of surfactant monomer dissolved in the organic solvent (at equilibrium) per unit volume of organic solvent. By neglecting C_o, the aggregation number of surfactant in a reverse micelle, n_s, can be calculated from Eq. (A-7) as

$$n_s = \frac{\pi d_{wp}^3 C_s(1 - f_{H_2O})N_A}{6f_{H_2O}} \tag{A-7}$$

For the case of DODMAC, for example, according to Tanford's work (25), the length of DODMAC molecule is calculated as $l_s = 1.5 + 1.265 \times 8 = 11.6$ Å. The maximum volume fraction of water was found from experiment to be 0.40 (28). The value of d_{wp}^* obtained from Eq. (A-5) is then 101.8 Å. This value seems reasonable when compared with the experimental data of the diameter of the water pool in other reverse micellar systems ranging from 40 to 130 Å (6, 16, 17).

SYMBOLS

C_l	dummy concentration variable
C_i	molar concentration of ionic species i
C_o	number of moles of surfactant monomer dissolved in the organic solvent per unit volume of organic solvent
C_s	number of moles of surfactant per unit volume of organic solvent
D	dielectric constant

d_{H_2O}	density of water
d_{wp}	diameter of the water pool inside a reverse micelle
e	electronic charge
f_{H_2O}	volume fraction of water in the organic phase
I_x	ionic strength in the unit of mole fraction
k	Boltzmann constant
K_i	partition coefficient of ionic species i
l_s	length of surfactant molecule
M	number of experimental points
M_{H_2O}	molecular weight of water
m_{dec}	molality of 1-decanol in organic phase
N	number of ionic species
N_A	Avogadro constant
N_M	number of reverse micelles per unit volume of the organic phase
n_s	aggregation number of the surfactant in a reverse micelle
q_i	surface area parameter of species i
r	radial distance from the center of a reverse micelle
R_{wp}	radius of the water pool of a reverse micelle
T	absolute temperature
V_M	total volume of reverse micelles in the organic phase
V_o	volume of the organic phase
V_{wp}	total volume of the water pool inside reverse micelles
x_i	mole fraction of species i in the bulk aqueous phase
y_i	mole fraction of species i in the reverse micellar phase
z	coordination number
z_i	charge of the ionic species i

Greek Letters

α	fitting constant in Eq. (18)
β	fitting constant in Eq. (19)
γ	activity coefficient
ϵ	characteristic interaction energy
θ	surface area fraction
K	constant defined by Eq. (8)
ρ	parameter defined by Eq. (11)
χ	dimensionless interaction parameter
ψ	electrochemical potential

Superscripts

*	pertaining to close-packing state of the reverse micelles

aq	bulk aqueous phase
wp	water pool inside the reverse micelles

Subscripts

i, j, k, l	types of ionic species
aq	bulk aqueous phase
s	surfactant
wp	water pool inside the reverse micelles

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