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RECOVERY OF AMINO ACIDS FROM AQUEOUS SOLUTION BY REVERSIBLE COMPLEXATION WITH MIXED ORGANIC EXTRACTANTS

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RECOVERY OF AMINO ACIDS FROM AQUEOUS SOLUTION BY REVERSIBLE COMPLEXATION WITH MIXED ORGANIC EXTRACTANTS

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ABSTRACT

Extraction equilibria are presented for reversible complexation of L-phenylalanine by the liquid ion-exchange extractants, Aliquat 336 and di-2-(ethylhexyl) phosphoric acid (DEHPA), in the diluent, methyl isobutyl ketone. Results are compared for extraction by each of the single extractants and a mixed extractant system composed of equimolar amounts of Aliquat 336 and DEHPA. The mixed system displayed lower loading values by a factor of 3 than the single-extractant systems; however, it was able to sustain uptake capacity for pH values 1.8 to 9.2. A simple complexation model, based on the Law of Mass Action, was employed to describe the experimental results.

INTRODUCTION

Amino acids are valuable bioproducts and important chemicals in the food, pharmaceutical, and chemical industries. Recent advances in fermentation technology have led to more affordable production of amino acids. Accompanying

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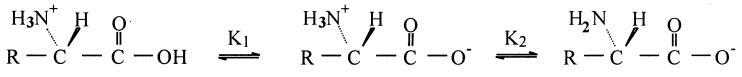
these more affordable production methods has been an interest to extend the uses of amino acids to include their use as raw materials in the production of various industrial chemicals. Examples of chemicals that can be derived from amino acids include amino acid-based surfactants used as oil gelating agents to recover effluent oil in seas and rivers, and poly(amino acids), which are attracting attention for biodegradable plastics manufacture [1].

Amino acids have both acidic carboxyl groups and basic amino groups. At high enough pH, amino acids behave as anions, and at low enough pH, they behave as cations. Over an intermediate pH range, amino acids are zwitterionic, i.e., ionized both positively at the basic amino sites and negatively at the acidic carboxyl groups. These features make amino acids hydrophilic at all values of pH and complicate their recovery.



Present separation techniques for removal and recovery of amino acids from dilute aqueous solutions typically employ ion exchange [2-10]; cation-exchange agents are most typical. For ion exchange to be effective, the amino acid must be present in the correct ionic form. A cation-exchange agent, for example, would be ineffective at high pH values where there are essentially no positively charged amino acid molecules. Similarly, an anion-exchange agent would be ineffective at low pH where there are essentially no negatively charged amino acid molecules. Controlling the solution pH to ensure that the amino acid is present in the correct ionic form may therefore require the addition of an acid or a base. Addition of another base or acid may then be required to regenerate the amino acid-laden ion-exchange agent, thereby consuming chemicals and producing a waste salt by-product. A separation process is needed that recovers the amino acid over a broad range of pH values, including under conditions where the amino acid exists primarily in its zwitterion form. Combined with an appropriate method of regeneration, e.g., temperature or diluent swing [11,12], leaching with a solution of a volatile base or acid [13-16], or precipitation by stripping of coextracted water [17-19], such a process could accomplish the separation without chemical consumption and waste-salt generation.

A number of researchers have used liquid ion-exchange extractants in the recovery of amino acids from dilute aqueous solutions. Among the extractants employed have been anion-exchange extractants [20-25], cation-exchange extractants [26-28], and chelative extractants [29,30]. Methods for their use include conventional extraction [20-26], liquid-membrane extraction [27,30-36], and micellar extraction [19, 37-42]. In extraction of amino acids from aqueous solution, the ion-exchange extractant recovers the amino acid by reacting with it to form an ion-pair complex that is solubilized into the organic phase. Once the organic phase has

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been phase-separated from the aqueous amino acid solution, the reaction is reversed in a step referred to as regeneration to recover the amino acid into a product phase and the amino acid-free extractant, available for recycle.

An advantage to liquid extractants over solid ion-exchange resins is that they offer more control over the reaction environment. Typically, the extractants are employed as organic solutions in a suitable organic solvent (referred to as the diluent) that controls physical properties such as density, viscosity, interfacial tension, water uptake, and boiling point of the extractant phase. Additionally, the diluent can dramatically affect the extraction equilibria. There is increased extraction power with a diluent that stabilizes the ion-pair complex effectively. Such diluents are referred to as 'active' diluents. Relatively nonpolar aprotic diluents provide no such stabilization of the ion-pair complex. Such diluents are referred to as 'inert' diluents. Furthermore, a liquid extraction system has the flexibility to work with mixed extractants.

Mixed extractant systems have been described previously for the recovery of inorganic salts from aqueous solutions. Grinstead et al. [43-45] introduced a type of solvent extraction system for recovering salts such as NaCl and $MgCl_2$ that has elements common to both cation and anion exchange. This system employs a combination of cationic and anionic extractants and is referred to as a mixed ionic extractant. These researchers recognized that it would be advantageous for the regeneration step to recover these salts as neutral compounds, rather than as individual ions. Their work showed that the positive and negative ions could be removed from an aqueous salt solution in a stoichiometric ratio by mixed extractants, so that the result is extraction of a neutral compound. The reverse reaction was favorable, allowing regeneration of the salt-laden extractant by water stripping.

The separation method under consideration uses mixed cationic and anionic extractants to recover amino acids from aqueous solutions. The idea for this process stems from the work by Grinstead et al. [43-45] on extraction of inorganic salts. The intent here is for the cationic and anionic extractants to associate with the protonated amine group and negatively charged carboxylate group, respectively, of a zwitterionic amino acid molecule. Thus, the "neutral" zwitterion replaces the "neutral" inorganic salt. Under conditions of low and high pH, the individual cationic and anionic extractants should provide extraction capacity for the cationic and anionic forms, respectively, of the amino acid.

An objective of this research was to provide information and insight concerning the recovery of amino acids from dilute aqueous solution by mixed cationic and anionic extractants. Results are presented for recovery of the amino acid, L-phenylalanine, over a broad pH range by a mixed extractant composed of the phosphoric acid ester, di-2-(ethylhexyl) phosphoric acid, and the alkylammonium chloride extractant, Aliquat 336, in methyl isobutyl ketone. These results are compared with those for extraction by the single-extractant systems. A simple model based on the Law of Mass Action was used to describe the experimental data.

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EXPERIMENTAL MATERIALS AND METHODS

Materials

Chemical Reagents

Methyl isobutyl ketone (MiBK; Sigma, HPLC grade) and L-phenylalanine (Sigma, 99+% SigmaUltra) were used as received. All aqueous solutions were prepared from distilled water that had been passed through a Milli-Q water purification system (Millipore Corp.).

Extractants

The liquid extractants, di-(2-ethylhexyl) phosphoric acid (DEHPA; Alfa Aesar) and tricaprylmethylammonium chloride (Aliquat 336; Aldrich), were also used as received. Aliquat 336 has aliphatic C_8 and C_{10} side chains with C_8 predominating. The manufacturer reports an average molecular weight of 404.17 g/mol for this extractant.

Methods

Stock aqueous solutions of L-phenylalanine were prepared at 0.06 M concentration. These solutions were adjusted to various initial pH values using sodium hydroxide solution (1.0-1.1 M). Known volumes (typically 50-100 mL) of the amino acid stock solution were then contacted with equal volumes of extractant solutions. All organic solutions used MiBK as the diluent; they differed only in the concentration and type of extractant used. The extractant systems studied were (1) 0.3 M Aliquat 336, (2) 0.3 M DEHPA, and (3) 0.15 M Aliquat 336 and 0.15 M DEHPA employed as dual extractants.

The two-phase solutions were shaken vigorously for 15 seconds and then allowed to equilibrate for at least 3 hours in a constant-temperature reciprocating shaker bath operating at 90 RPM and 25 °C. Equilibrium aqueous-phase L-phenylalanine concentrations were determined by high-performance liquid chromatography (HPLC) using a Hewlett-Packard, Series 1100 modular chromatography system. A Hewlett-Packard ZORBAX SB-C18 column was used for all concentration measurements. Measurements were performed at 40 °C using 0.01 N H_2SO_4 mobile phase at a flow rate of 0.4 mL/min and UV detection at 210 nm. The correlation of UV absorbance to concentration was found to be linear over the

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experimental concentration range, and allowed the determination of L-phenylalanine concentration with a relative error of ± 3.3 %.

DESCRIBING AND MODELING THE EXTRACTANT SYSTEMS

Reaction Equilibria

Extraction of amino acids by DEHPA and Aliquat 336 occurs by ion-pair formation. For this extraction mechanism, the Law of Mass Action can be a useful tool for describing extraction equilibria. A mass-action-law description of equilibrium postulates the formation of one or more stoichiometric complexes of amino acid and extractant. An equilibrium description of the system comprises reactions of p amino acid (AA) molecules and q extractant (E) molecules to form a set of (p,q) complexes along with overall equilibrium constants, $K_{pq,true}$:

$$K_{pq,true} = \frac{\gamma_{(AAp-Eq)}}{\gamma_{AA}^{p}\gamma_{E}^{q}} \frac{[AA_p - E_q]}{[AA]^p[E]^q} \tag{1}$$

For dilute liquid solutions, the ratio of activity coefficients in Equation 1 can typically be assumed to be constant over the experimental concentration range [46]. With this assumption, the ratio of activity coefficients can be incorporated into an apparent equilibrium constant, K_{pq}. Loading of the extractant, defined as the concentration of amino acid in all forms in the organic phase, divided by the concentration of extractant in all forms in the organic phase, is then given as [46]

$$Z = \frac{\sum_{p}\sum_{q} pK_{pq}[AA]^p[E]^{(q-1)}}{1 + \sum_{p}\sum_{q} qK_{pq}[AA]^p[E]^{(q-1)}} \tag{2}$$

Factors that influence the values of the equilibrium constants, and therefore the extractant loading, include the natures of the amino acid, extractant, and diluent.

Physical Extraction

In addition to extraction of the amino acid by ion exchange, there exists the possibility of "physical" extraction of the amino acid by the extractant and the diluent(s). Conventional organic solvents realize low distribution coefficients for

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amino acids due to their hydrophilic, ionizing functional groups. In this work, physical extraction by the extractant and diluent was therefore neglected.

Amino Acid Solution Chemistry

L-Phenylalanine is a neutral amino acid; it has only one amino group and only one carboxyl group. Its net charge varies in magnitude and sign with changes in solution pH. The degree of ionization of the two functional groups on L-phenylalanine is governed by the association-dissociation equilibria in solution. L-Phenylalanine exhibits the following equilibria in solution:

$$AA^+ \xleftrightarrow{K_1} AA^{\pm} + H^+ \tag{3}$$

$$AA^{\pm} \xleftrightarrow{K_2} AA^- + H^+ \tag{4}$$

where AA^+, $AA^{\pm}$, and AA^- represent the cation, zwitterion, and anion forms of L-phenylalanine. The equilibrium constants, K_1 and K_2, are the first and second ionization constants, respectively; they are $pK_1 = 1.83$ and $pK_2 = 9.13$ for L-phenylalanine at 25 °C [1]. For extraction by ion exchange to be effective, the amino acid must be present in an ionic form that is amenable to extraction. Equations 3 and 4, combined with an overall aqueous-phase amino acid mass balance, lead to concentration expressions for the three ionic forms as a function of solution pH:

$$[AA^+] = \frac{[AA]_T}{1 + 10^{pH-pK_1} + 10^{2\cdot pH-pK_1-pK_2}} \tag{5}$$

$$[AA^{\pm}] = \frac{[AA]_T \cdot 10^{pH-pK_1}}{1 + 10^{pH-pK_1} + 10^{2\cdot pH-pK_1-pK_2}} \tag{6}$$

$$[AA^-] = \frac{[AA]_T}{1 + 10^{pK_2-pH} + 10^{pK_1+pK_2-2\cdot pH}} \tag{7}$$

Here, $[AA]_T$ represents the total concentration of amino acid in all forms in the aqueous solution. Species concentrations are denoted by square brackets and are generally expressed in units of molarity.

If the amino acid is dissolved in water in the absence of other ionizing solutes, the predominant form is zwitterionic and the molecule has no net charge. The pH where the amino acid has no net charge is called the isoelectric point, pI; it is pI = 5.48 for L-phenylalanine at 25 °C [1]. For solutions at pH < pI, the amino acid is positively charged; for solutions at pH > pI, the amino acid is negatively charged.

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RESULTS AND DISCUSSION

Experimental results and model predictions are presented as loading-pH curves. All models represent the simplest model that gave low residuals between the experimental and model loading values. If inclusion of a postulated complex did not reduce the residuals significantly, then they were not included in the simplest model. Finally, all postulated complexes are believed to represent physically reasonable complexes. No attempt was made in this work to confirm the existence (or lack thereof) of the postulated complex stoichiometries.

Extraction by Aliquat 336

Figure 1 shows the equilibrium loading-pH data for extraction of L-phenylalanine from a 0.06 M aqueous solution into 0.3 M Aliquat 336 in MiBK at 25 °C. Experimental data are represented by symbols. The dashed curve represents the mathematical model to describe loading equilibria for this system. Extractant loading decreased with decreasing values of pH. This result is consistent with the notion that uptake of amino acids by alkylammonium chloride extractants occurs

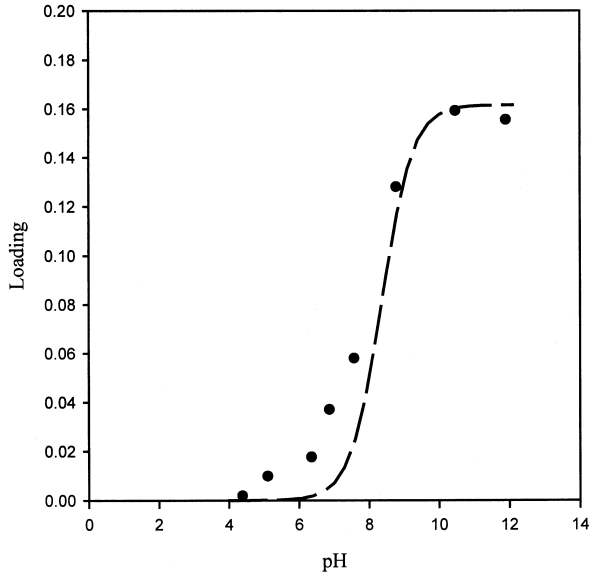

Figure 1. Equilibrium loading-pH data for extraction of L-phenylalanine from a 0.06 M aqueous solution into 0.3 M Aliquat 336 in MiBK at 25 °C. (● represents experimental data; dashed curve represents model fit with (1:1) complexation.)

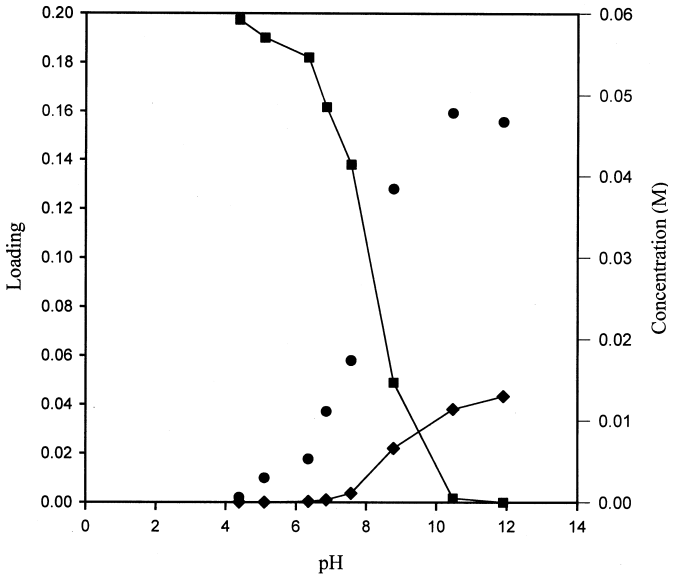

Figure 2. Relationship among equilibrium L-phenylalanine loading, anion, and zwitterion concentrations for extraction into Aliquat 336 in MiBK at 25 °C. (● represents experimental data; ■ represents zwitterion concentration; ◆ represents anion concentration.)

by ion exchange of the chloride ion with the anion form of the amino acid [20,21,47].

In order to describe the data, they were fit to Equation 2, postulating the formation of (1,1) amino acid anion-extractant complexes. A best-fit value of the apparent equilibrium constant K_{11} was determined by a nonlinear, least-squares regression of the experimental data; the best-fit value was $K_{11} = 16.71$ L/mol. The equilibrium constant is about 35-fold higher than that reported by Uddin et al. [47] for extraction of L-phenylalanine by Aliquat 336 in xylene. This result is encouraging because it suggests that the polar, or "active", MiBK diluent provides better solvation of the amino acid-extractant complex than does the nonpolar, or "inert", xylene diluent.

The model to describe the experimental data in Fig. 1 describes the high pH (> 8) data reasonably well; however, it fails to describe the data at lower values of pH. In order to understand why this model breaks down at values of pH < 8, the experimental loading data were plotted along with anion and zwitterion concentration versus pH. Figure 2 shows these plots, where the y-axis represents loading or aqueous-phase concentration (M). This figure reveals the fact that below pH $= 8$, the zwitterion form of L-phenylalanine begins to dominate over the anion form. This fact suggests that loading may depend on the zwitterion form of the

amino acid. However, at pH = 4, where the zwitterion concentration is high, loading values are near zero. To account for these two observations, a complex was postulated that involves both the anion and zwitterion forms of the amino acid. It was postulated that overloading of the extractant, i.e., formation of complexes that contain more than one amino acid molecule per extractant molecule, occurred by hydrogen bonding of a charge-neutral amino acid zwitterion with the amino acid anion-extractant complex to form a (2,1) complex.

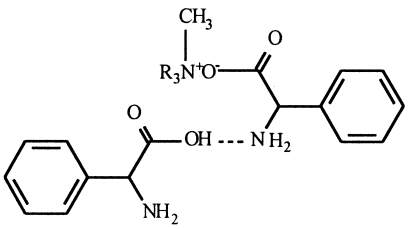

Figure 3 shows the model fit to the data for a model that postulates the formation of both (1,1) and (2,1) complexes. In order to describe the data in Fig. 3, they were fit to Equation 2. A best-fit value of the apparent equilibrium constant

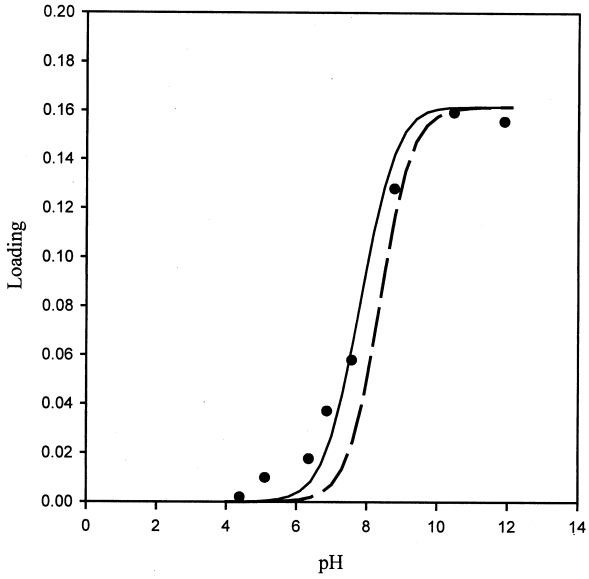

Figure 3. Model fit to L-phenylalanine loading-pH data for extraction into Aliquat 336 in MiBK at 25 °C. (● represents experimental data; dashed curve represents model fit with (1:1) complexation; solid curve represents model fit with (1:1) and (2:1) complexation.)

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K_{21} was determined by a nonlinear least-squares regression of the data; its value was K_{21} = 31.93 L/mol. The solid curve in Fig. 3 represents the model fit. The dashed curve reproduces the model that includes only (1,1) complexes for comparison. Inclusion of (2,1) complexes improved the model fit at lower values of pH.

Examining the above schematic representation of a (2,1) complex, one could envision additional overloading by hydrogen bonding of a third amino acid molecule to the (2,1) complex. Inclusion of a (3,1) complex had only a minor effect on the model loading-pH curve; therefore, complexes with stoichiometries above (2,1) were not included. Overall, inclusion of overloading by the zwitterion form of the amino acid improved significantly the model description of the experimental data for this system.

Extraction by DEHPA

Figure 4 shows the equilibrium loading-pH data for extraction of L-phenylalanine from a 0.06 M aqueous solution into 0.3 M DEHPA in MiBK at 25 °C.

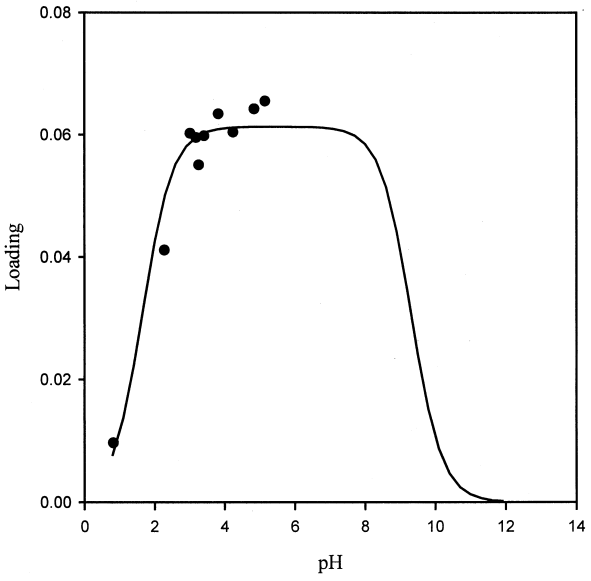

Figure 4. Equilibrium loading-pH data for extraction of L-phenylalanine from a 0.06 M aqueous solution into 0.3 M DEHPA in MiBK at 25 °C. (● represents experimental data; solid curve represents model fit with (1,1) complexes.)

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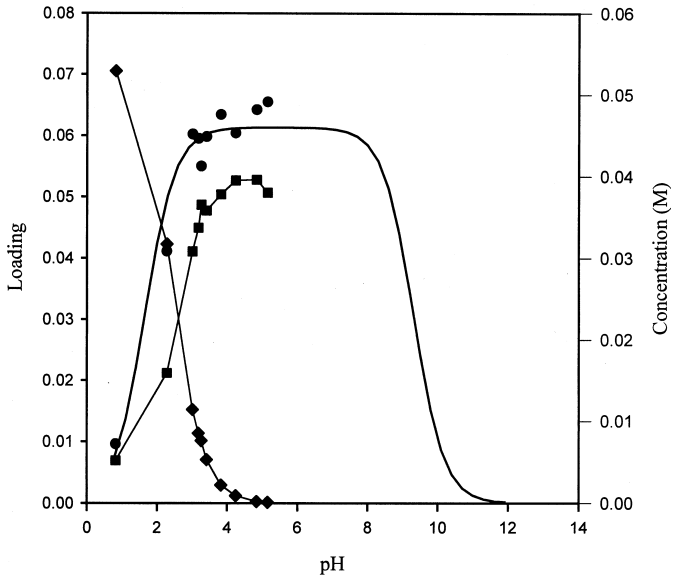
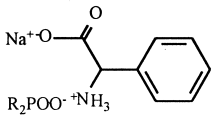


Figure 5. Relationship among equilibrium L-phenylalanine loading, cation, and zwitterion concentrations for extraction into DEHPA in MiBK at 25 °C. (● represents experimental data; ■ represents zwitterion concentration; ◆ represents anion concentration.)

Experimental data are represented by symbols. The solid curve represents the mathematical model to describe loading equilibria for this system. Extractant loading increased initially with increasing values of pH before reaching a plateau value of about 0.066. Intuitively, this result is inconsistent with what might be expected for uptake of amino acids by ion exchange with this cation exchange extractant, since amino acid cation concentration decreases with increasing pH. However, these results are consistent with previous studies [26,28] of amino acid extraction by cation exchange extractants.

In order to understand what extraction mechanism might explain this behavior, the experimental loading data were plotted along with plots of cation and zwitterion concentration versus pH. Figure 5 shows these plots, where the y-axis represents loading or aqueous-phase concentration (M). This figure reveals the fact that the zwitterion concentration is nonnegligible and increasing with increasing pH up to a pH value of about 3.5 where it reaches a plateau value of about 0.04 M. This fact suggests that loading likely depends on the zwitterion form of the amino acid. A zwitterion molecule might be taken up by DEHPA, with electroneutrality maintained by the extractant counterion, i.e., H^+ or Na^+.



In order to describe the data, they were fit to Equation 2, postulating the formation of (1,1) amino acid zwitterion-extractant complexes. A best-fit value of the apparent equilibrium constant K_{11} was determined by a nonlinear, least-squares regression of the experimental data; the best-fit value was $K_{11} = 1.54$ L/mol. The model provides a suitable description of the experimental data.

Extraction by a Mixed Extractant of Aliquat 336 and DEHPA

Figure 6 shows the equilibrium loading-pH data for extraction of L-phenylalanine from a 0.06 M aqueous solution into a mixed extractant comprising 0.15 M Aliquat 336 and 0.15 M DEHPA in MiBK at 25 °C. This system was able to sustain uptake of amino acid for pH values 1.8 to 9.2. Figure 7 compares the loading-pH data for all three systems. The mixed extractant system shows lower load-

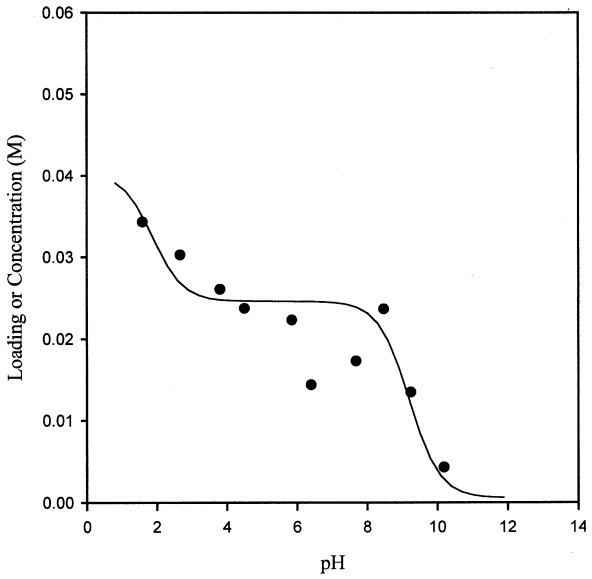


Figure 6. Model fit to L-phenylalanine loading-pH data for extraction into a mixed extractant comprising 0.15 M Aliquat 336 and 0.15 M DEHPA in MiBK at 25 °C. (● represents experimental data; solid curve represents model fit.)

ing values than either single extractant system. This result is likely due to association between the anionic and cationic extractant molecules.

Despite the lower loadings for the mixed extractant system, two advantages might exist for such a system. Lower extraction capacity for forward extraction in the mixed extractant system suggests that regeneration of amino acid-laden extractant might be accomplished more easily than in the single extractant systems. Competition between the amino acid molecule and a second extractant drives the reverse reaction. An additional, subtle advantage to the mixed extractant system relates to extractant losses into the aqueous process stream. The two extractants have charged, hydrophilic head groups that give these extractants low measurable solubilities in water. The mixed extractant system might afford still lower solubilities by association of the two extractants in the organic phase. This organic-phase association will likely lower the activity coefficients for both species in the organic phase relative to the single-extractant cases.

Examination of the slopes of the loading versus pH data at pH < 4 in Fig. 7 suggests that uptake by the mixed extractant system occurs perhaps by a different mechanism than that by DEHPA alone. The decrease in loading with increasing pH for the mixed system suggests that uptake of the amino acid cation is nonneg-

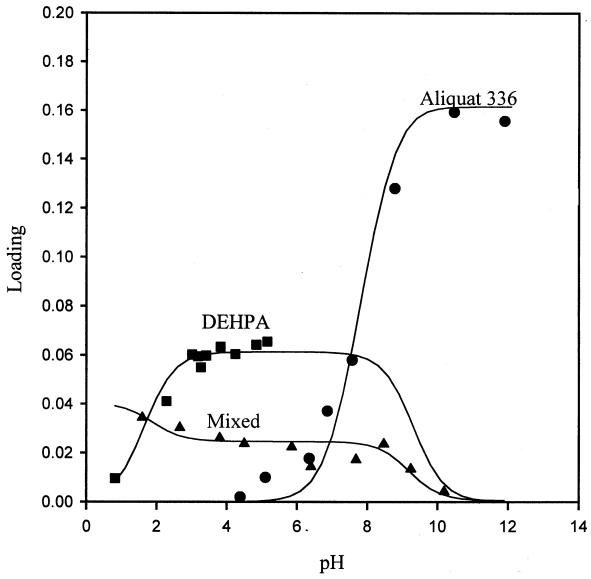
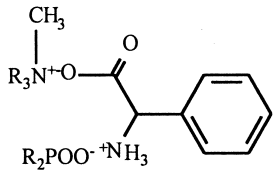


Figure 7. Comparison among the loading-pH L-phenylalanine extraction isotherms for extraction by 0.3 M Aliquat 336, 0.3 M DEHPA, and a mixture of 0.15/0.15 M Aliquat 336/DEHPA in MiBK at 25 °C. (Symbols represent experimental data; solid curves represent model fits.)

ligible. As the cation concentration drops to zero at about pH = 4.5, loading reaches a plateau region associated with uptake of the amino acid zwitterion. Below this pH, loading is influenced by cation concentration. This result does not hold for the single-extractant system. What might be the difference that allows significant uptake of the cation in the mixed extractant system over the single extractant system? One postulate is that the Aliquat 336 molecule in the mixed extractant system stabilizes the complex formed between the DEHPA molecule and the amino acid cation. This stabilization may occur by exchange of the proton on the carboxyl group of the complexed amino acid with the ammonium group on the Aliquat 336.



No such stabilization is afforded in the single extractant system.

Secondly, the low loading values at pH > 9 in Fig. 7 suggest that the mixed extractant system affords negligible uptake capacity for amino acid anion. One postulate for this result is that DEHPA is not able to stabilize uptake of the anion in an analogous manner to Aliquat 336 for the amino acid cation. The amino group on the amino acid anion is not available for ion exchange with DEHPA. Thus, association between the anionic and cationic extractants alone dominates the high pH region.

A model description of this mixed extractant system was developed based on the assumption that both extractants are involved in the complexation reaction. In the absence of other species, the anionic and cationic extractant molecules are expected to associate to form an ion-pair complex. Uptake of amino acid by this system would result from association with this ion-pair complex. Therefore, the DEHPA-Aliquat 336 ion-pair complex represents the "extractant" for this mixed extractant system. The solid curve in Fig. 6 represents the model to describe the mixed extractant system. This model was based on the postulates above that describe the availability of amino acid cation and zwitterion for extraction and the unavailability of amino acid anion for extraction. In order to describe the data in Figure 6, they were fit to Equation 2. Best-fit values of the apparent equilibrium constants for (1,1) uptake of amino acid cation K_{11}^{+} and amino acid zwitterion $K_{11}^{\pm}$ were determined by a nonlinear least-squares regression of the data; their values were $K_{11}^{+} = 0.94$ L/mol and $K_{11}^{\pm} = 0.42$ L/mol.

A number of questions still remain as to the reaction stoichiometries that truly exist for extraction of L-phenylalanine by these mixed extractant systems. The postulated stoichiometries serve as best estimates that provide sufficiently well a description of the observed experimental data.

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CONCLUSIONS

A mixed extractant system composed of the cation-exchange extractant DEHPA, the anion-exchange extractant Aliquat 336, and MiBK was investigated for its ability to extractant L-phenylalanine from dilute aqueous solution over a broad range of pH. The extraction capacity of this mixed extractant system was lower by a factor of 3 than the corresponding single extractant systems likely as a result of association between the two extractants in the former.

Uptake of L-phenylalanine by Aliquat 336 alone in MiBK appeared to occur by ion exchange of the chloride ion of the extractant with the anion form of the amino acid. Overloading of this extractant was also postulated by hydrogen bonding of a charge-neutral amino acid zwitterion with the amino acid anion-extractant complex to form a (2,1) complex. For uptake of L-phenylalanine by DEHPA alone in MiBK, loading likely occurred by formation of a (1:1) zwitterion-extractant complex. Uptake of the cation form of the amino acid by DEHPA alone appeared to be negligible.

For the mixed extractant system, unlike the single extractant system with DEHPA, loading values below pH = 4.5 appears to be influenced by the amino acid cation concentration. Here, Aliquat 336 in the mixed extractant system might stabilize the complex formed between the DEHPA molecule and the amino acid cation by exchange of the proton on the carboxyl group of the complexed amino acid with the ammonium group on the Aliquat 336. Loading values above pH = 9 suggest that the mixed extractant system affords negligible uptake capacity for amino acid anion. One postulate for this result is that DEHPA is not able to stabilize uptake of the anion in an analogous manner to Aliquat 336 for the amino acid cation. The amino group on the amino acid anion is not available for ion exchange with DEHPA. Thus, association between the anionic and cationic extractants alone dominates the high pH region.

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