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Lactic Acid Partitioning in TALSPEAK Extraction Systems

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The TALSPEAK process, developed in the 1960s at the Oak Ridge National Laboratory and demonstrated in various forms up to pilot scale elsewhere, has emerged as a primary method for partitioning of trivalent transplutonium actinides from fission product lanthanides in advanced nuclear fuel cycles. The baseline process relies on the monoacidic dialkyl phosphoric acid extractant bis-(2-ethylhexyl)phosphoric acid (HDEHP), the aqueous complexant diethylenetriamine-N,N,N′,N″,N″-pentaacetic acid (DTPA), and high concentrations of a pH 3.5 buffer, usually 1-2 M lactic acid (HL). Previous reports have established that HL not only buffers the pH, but also increases phase transfer kinetics, improves the radiation stability of DTPA, and has been implicated as a possible participant in the formation of ternary complexes in both the aqueous and organic phases. One feature central to the interpretation of these results is the extent of partitioning of HL between the phases. In this study, ^{14}C-labeled HL has been used to examine the details of its partitioning between aqueous solutions and organic solutions relevant to the possible deployment of TALSPEAK. It is found that, contrary to previous reports, HL partitions into the organic phase independently of the amount and identity of the metal ions that are present.

Keywords actinide-lanthanide separations; DTPA; HDEHP; lactic acid; TALSPEAK

INTRODUCTION

Responding to demands for low-emission energy sources, it is likely that additional nuclear generating capacity will be installed in the U.S. in the coming years. Motivated by the need to secure adequate supplies of fissile materials into the future and to improve waste management options, recycling of used nuclear fuel in the U.S. is again being considered. Beyond the comparatively simple option of present day recycling of plutonium using PUREX, advanced separation systems could include options for transmutation of minor actinides in fast neutron spectrum reactors. In this limit, separating the minor actinides (predominately Am and Cm) from the fission product lanthanides (Ln^{3+}) is a necessary step.

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In recent years the fuel cycle research effort in the U.S. has developed a suite of processes for partitioning of fission byproducts, the UREX+ process. Within this conceptual framework, the currently favored process for separating the trivalent lanthanides from the trivalent actinides (An^{3+}) is the TALSPEAK (Trivalent Actinide-Lanthanide Separations by Phosphorus reagent Extraction from Aqueous Komplexes) process. TALSPEAK was developed at the Oak Ridge National Laboratory in the 1960s by B. Weaver and F. A. Kappelman (1,2). Though there have been several demonstrations of process development (up to the pilot scale) based on TALSPEAK, its fundamental chemistry is still incompletely understood.

The separation is achieved by extraction of Ln^{3+} into an organic solvent containing di(2-ethylhexyl) phosphoric acid (HDEHP) from an aqueous medium that selectively retains the An^{3+}. The extraction behavior of HDEHP from mineral acid solutions is well established. In the pH range of TALSPEAK, the standard extraction reaction for the Ln^{3+} and/or An^{3+} is as shown in Eq. (1) (3–6).

$$M^{3+} + \overline{3(HA)_2} \leftrightarrows \overline{M(AHA)_3} + 3H^+ \qquad (1)$$

$(HA)_2$ denotes the dimeric HDEHP and the line above the species indicates its presence in the organic phase. HDEHP is a liquid cation exchanger; during extraction of M^{3+} it binds the metal ion with three hydrogen-bonded dimers forming three eight member rings, simultaneously releasing 3 H^+ to the aqueous phase. In TALSPEAK the extractability of the An^{3+} is suppressed by the addition of the polyaminopolycarboxylate complexing agent diethylenetriamine-N,N,N′,N″,N″-pentaacidic acid (DTPA). The "soft" donor nitrogen atoms in DTPA bind more strongly to the trivalent actinides than to lanthanides, thus are primarily responsible for the group separation. The exact cause for the preferential binding of the actinides with soft donors is still being debated, but it is known that the 5f electron shell of actinide ions extends further into the valence region (7) making the actinides slightly softer than the lanthanides. The DTPA molecule surrounds the metal, and creates a charged complex ($AnDTPA^{2-}$, probably

most typically as a monohydrate species), holding it in the aqueous phase rendering it virtually unextractable. The formation of this actinide/DTPA complex in the aqueous phase allows the trivalent species (An^{3+}/Ln^{3+}) with similar chemistries to be separated.

Previous work has shown that TALSPEAK is very sensitive to pH changes (8,9). Lactic acid is added to the aqueous phase primarily to control pH. However, literature reports indicate that lactic acid plays other roles, including enhancing phase compatibility, improving phase-transfer kinetics, extending the radiation stability of DTPA, and possibly partitioning between phases (1,2,8,10). The concentration of the lactate in TALSPEAK ranges between 0.5 and 2 M. At these concentrations the affinity of lactate for Ln^{3+}/An^{3+} is high enough to allow the possibility of mixed complexes (e.g., Am-DTPA-L, $ML(AHA)_2$). Kosyakov and Yerin (6) investigated the effect of varying the lactate concentration on the distribution ratio of Cm. These authors hypothesized the presence of mixed $CmL(AHA)_2$ complex in the organic phase. The proposed equilibrium expression for the extraction of the mixed complex is as shown in Eq. (2) (6,11)

$$M^{3+} + \overline{2(HA)_2} + HL \leftrightarrows \overline{ML(AHA)_2} + 3H^+ \qquad (2)$$

where HL is protonated lactic acid.

The purpose of this study is to investigate the specific role of lactic acid, its behavior in this extraction system (e.g., if and/or how it partitions during extraction), and to address the question of a mixed extracted complex. This investigation has been accomplished using ^{14}C labeled lactic acid, which allowed the direct monitoring of the lactate/lactic acid species during the extraction experiments.

EXPERIMENTAL

Reagents

The extractant di(2-ethylhexyl)phosphoric acid (97%) was purchased from Aldrich and purified by the copper precipitation method (12). The purified HDEHP was determined to be 99.8% pure by titration. The organic diluents, 1,4-diisopropylbenzene (99%, Alfa Aesar) and *n*-dodecane (99+ %) were used without further purification. The organic phases were prepared by dissolving weighed amounts of the purified HDEHP into the 1,4-diisopropylbenzene. The aqueous phases were prepared using lanthanide nitrate stocks from lab supplies (prepared from 99.999% lanthanide oxides or carbonates from Arris International Co.). The solutions were standardized to determine metal concentration, nitrate concentration, and H^+ concentration. The 85% (w/w) lactic acid (Baker) was used to prepare a 3 M lactic acid solution with a pH of 3.6, neutralizing with standardized NaOH. Sodium lactate was purchased as a 60% (w/w) aqueous solution from Alpha Aesar and standardized by titration after exchanging Na^+ for H^+ by cation exchange. All aqueous solutions were prepared in 18 MΩ water.

Solvent Extraction

To prepare the various lactate solutions, lactic acid and sodium lactate were combined in different ratios to create media at varying pH and $[lactate]_{tot}$. Total added lactate in a system (C_L) is defined by the expression:

$$C_L = [HL] + [\overline{HL}] + [L^-] + \sum_{n=1}^{m} n \cdot [Complex] \qquad (3)$$

where HL is free protonated lactic acid either in the aqueous phase or the organic phase, L^- is free lactate ion in the aqueous phase and [Complex] is the concentration of any lactate complexes in either aqueous or organic phase. This term includes metal complexes and any species involving interactions between HL and HDEHP; where n is the number of lactate and/or lactic acid molecules involved in the complex. At high concentrations of C_L and low concentration of potential complexes and low distribution of HL into the extractant phase C_L can be considered equal to the sum of lactic acid and lactate in the aqueous phase. The ratio of free to protonated lactate ($[L^-]/[HL]$) is governed by the pK_a of lactic acid and the $p[H^+]$ of the solution.

The experiments performed in this study were done as a function of lactic acid concentration, with and without metal present, and as a function of [HDEHP]. For the C_L dependencies in experiments with metals present, the nitrate concentrations in the aqueous phases were maintained constant at 1 M by addition of $NaNO_3$ and the phases were pre-equilibrated with the organic diluent 1,4-diisopropylbenzene (DIPB). The organic phases contained 0.2 M HDEHP for all extractions (with exception to the HDEHP dependence) and were pre-equilibrated with 1 M $NaNO_3$. Thirty minutes of vortex mixing followed by 15 min. of centrifugation were considered adequate for the pre-equilibration.

Experiments investigating the partitioning of HL from an aqueous phase into the extractant phase were conducted in the concentration range 0–2 M at constant metal concentration of 1 mM. The acidity was adjusted for all extractions to the pH range of 3.6–3.9. All experiments were carried out in triplicate and in two parallel sets, with and without a 10 μL spike of ^{14}C labeled lactic acid added to each aqueous phase.

To better control the pH, the aqueous phase samples for extractions without metal were prepared in a different manner. The pH was controlled using a lactate buffer solution. The $C_L = 2$ M buffer solutions were prepared by adding sodium lactate, Na^+L^- and nitric acid in the appropriate amounts to achieve a pH of 3.6, the solution was then diluted with degassed, deionized 18 MΩ water

to obtain the desired concentrations of lactate. The advantage of using this approach is the absence of the lactones, lactides, and polylactate esters (in NaLac) that can be present in lactic acid solutions. The total lactate concentrations, C_L, ranged from 0–2 M. The ionic strength was held constant at 2 M during these extractions by the addition of $NaNO_3$. The experiments were carried out in triplicate with a 10 μL spike of ^{14}C labeled lactic acid added to each aqueous phase.

The ^{24}Na isotope used to study the sodium distribution was generated by neutron activation of solid $NaNO_3$ in the 1 megawatt TRIGA reactor located on the Washington State University campus.

Solvent Extraction Procedures

Experiments were performed to determine a K_d for HL by contacting a prepared aqueous phase with a pure organic diluent (no metal ions or HDEHP present in the system). Two diluents were used in the K_d studies, 1,4-DIPB and *n*-dodecane, the former used in the original TALSPEAK studies and the latter favored in more recent process development. The concentration of HL in the aqueous phase varied from 0–1 M for the experiments. The aqueous phase contained 1 M HNO_3 to ensure that the lactic acid was fully protonated.

The extraction procedure was identical for all experiments. However, the extraction volumes differed for the two different types of extractions. The nonradioactive extractions contained 700 μL total volume for each phase, while the radiotracer experiments utilized 500 μL total sample size. The extractions were carried out by vigorous shaking on the vortex mixer for 30 min., followed by 15 min. centrifugation. For extractions done in the absence of the radioactive tracers, the organic phase was removed and a 300 μL sample of the aqueous phase was taken and diluted to 3 mL with 2% HNO_3 for analysis (of lanthanide content) by Inductively Coupled Plasma Optical Emission Spectroscopy (Perkin Elmer Optima 3200 RL). For the radiotracer experiments a 300 μL sample was taken from both phases and analyzed by liquid scintillation counting (Beckman LS6500) for the beta events of ^{14}C and solid scintillation counting using a NaI(Tl) detector (Packard Cobra 5003) monitoring γ-radiation from ^{24}Na. Hydrogen ion concentration was measured at equilibrium using a glass electrode. The $p[H^+]$ of the solution was determined directly, based on a strong acid-strong base titration used as an electrode calibration curve.

RESULTS AND DISCUSSION

The extraction reactions were investigated within limits relevant to TALSPEAK conditions (aside from the exclusion of DTPA). Quantitative extraction of the trivalent lanthanides was seen in the acid dependency studies. This was a desired effect since the purpose of the study was to learn more about the behavior of the lactic acid in TALSPEAK. Table 1 shows the percent extraction of trivalent lanthanides into the organic phase. With the exception of yttrium, metal extraction remains quantitative until C_L increases above 1 M.

The percent extraction fell measurably at 2 M C_L for La^{3+}, and Nd^{3+}, generally consistent with expectations of the relative strength of their extraction by HDEHP vs. lactate complexing in the aqueous phase; a similar effect is not seen with Eu^{3+} or Y^{3+} because these cations are more strongly extracted than La^{3+} or Nd^{3+} relative to their respective lactate complexes. A speciation diagram for the complexation of Nd^{3+} with lactate has been constructed using a set of internally consistent thermodynamic data (13) (Fig. 1). It is seen that ML_3 is the dominant aqueous species at all lactate concentrations above 0.2 M; at 2.0 M this species represents about 95% of aqueous Nd^{3+} species. The extraction results indicate that the overall predominating species is that present in the organic phase, presumed as a first approximation to be $M(AHA)_3$. The slight decrease in percent extraction for the metals at the higher lactate concentrations is not accounted for by these calculations. Given the composition of the medium, it is conceivable that this is a limitation of the modeling (which was done using constants at a fixed ionic strength of 2.0 M). It also could indicate the presence of a previously reported (14,15) ML_4^- species at high lactate concentrations. In TALSPEAK, the strength of the DTPA complexes would

TABLE 1
Percent extraction of the Ln^{3+} in the lactic acid dependency studies. The experiments were conducted with a 0.2 M HDEHP/1,4-diisopropylbenzene extractant phase and an aqueous phase of 0–2 M lactate, 1 mM Ln^{3+}, 1 M $NaNO_3$ (Eu^{3+} extractions were done using 2 M $NaNO_3$), and a fixed pH ~ 3.6–3.9

Ln^{3+}	0.01	0.05	0.1	0.2	0.5	0.7	1	1.5	2
Y^{3+}	99.9	99.9	100.0	99.9	100.0	100.0	100.0	100.0	99.9
La^{3+}	99.7	99.9	99.8	99.7	99.9	99.8	99.5	96.7	85.3
Nd^{3+}	99.9	99.9	99.8	99.9	99.9	99.9	99.8	97.6	91.2
Eu^{3+}	99.8	99.9	99.9	99.9	99.9	99.9	99.9	99.6	98.0

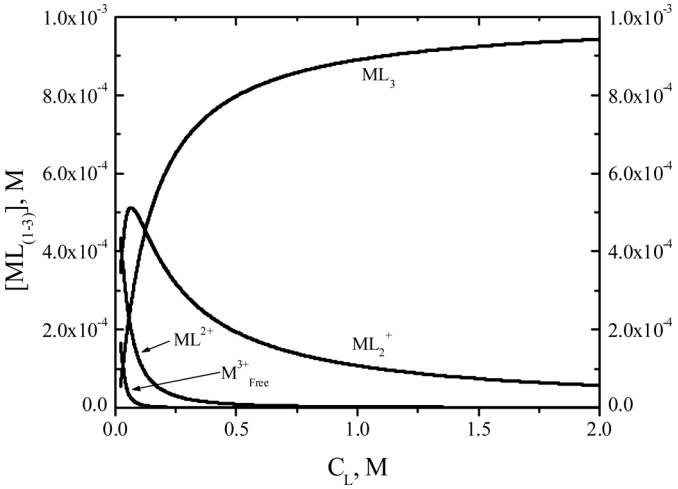

FIG. 1. Predicted speciation of Nd^{3+} in lactate media as a function of total lactate concentration at pH 3.6. The diagram shows the predominant species to be ML_3 at high concentrations of C_L. The calculations were performed using experimental conditions as described for the extraction experiments; 0.001 M M^{3+}, 0–2.0 M lactate, no considerations for ionic strength were given for the calculations. Equilibrium constants were as defined by the Martell and Smith database (reference 13), I = 2.0 M, 25°C.

be expected to overwhelm the effect of all ML_n^{3-n} species, i.e., $MDTPA^{2-}$ or $MH(DTPA)^{-}$ are likely to be the predominant species present.

Lactate partitioning was monitored in parallel with the metal ion distribution; Fig. 2 shows the partitioning of lactate in the presence of metal ions. The extraction data showed that ^{14}C partitioning to the extractant phase increased with increasing C_L. Between 0.01–0.2 M C_L the D_{Lac} increases slightly; the increase is somewhat more pronounced in the presence of Nd^{3+} than the other metal ions. At C_L above 0.5 M, lactic acid distribution ratios increase more dramatically in the presence of any metal ion.

In Fig. 3 the concentration of both lanthanide and lactate in the organic phase at equilibrium are shown. The concentration of the metal in the organic phase remained constant at 0.001 M until C_L reached 1 M where a slight decrease is observed. The concentration of ^{14}C labeled lactic acid in the organic phase increased steadily as the concentration of C_L was increased. For the systems containing Y^{3+}, La^{3+}, and Nd^{3+} at 2 M C_L, up to 3% of the total lactate partitioned; for Eu^{3+} it was slightly lower at 2%. At 2 M C_L the ratio of lactate to metal in the organic phase is about 75 for Y^{3+}, La^{3+}, and Nd^{3+} and 40 for Eu^{3+}, respectively. These high concentrations of lactate in the organic phase cannot be explained by partitioning of $LnL(AHA)_2$ (Eq. 2) alone, as has been suggested in the prior literature. Lactate must be partitioning by some means other than just the hypothetical mixed complex with the lanthanide and HDEHP.

To further probe the tendency of lactate to partition between these phases, additional studies were done in the absence of Ln^{3+} in the aqueous phase. The K_d values remained constant for both diluents over the concentration range of C_L. The K_d for HL in 1,4-DIPB was 0.0042 ± 0.0009 (as compared with the 0.033 value of the distribution ratio of lactic acid observed at 2 M C_L with

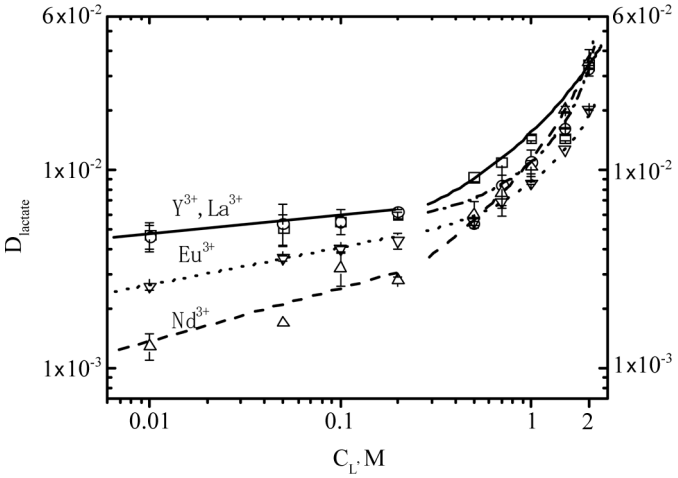

FIG. 2. Partitioning of lactate between 0.2 M HDEHP in 1,4-diisopropylbenzene and an aqueous phase of 0–2 M lactate, 1 mM Ln^{3+}, 1 M $NaNO_3$ (Eu^{3+} extractions were carried out with 2 M $NaNO_3$), and a fixed pH ~3.6–3.9 as a function of total lactate concentration (□ yttrium, ○ lanthanum, △ neodymium, ▽ europium). The lines are shown only to "guide the eye".

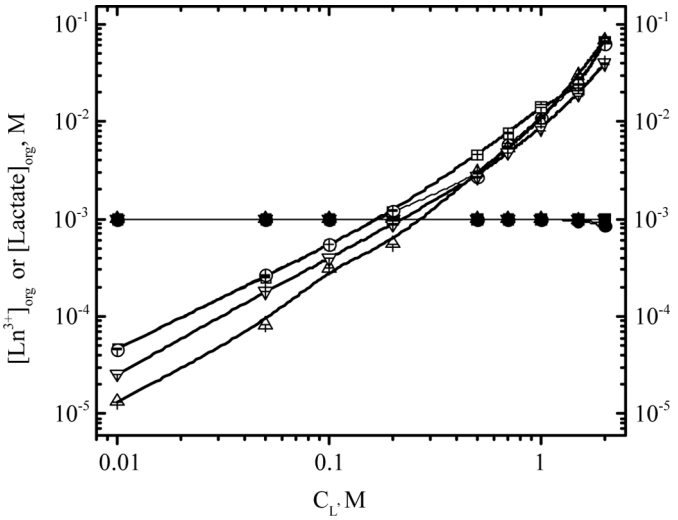

FIG. 3. Concentration of the Ln^{3+} and lactate in the organic phase at equilibrium. The metals are represented by the following symbols, ■ Y^{3+}, ● La^{3+}, ▲ Nd^{3+}, ▼ Eu^{3+}; the lactate and the accompanying extraction system containing metals are denoted with □lac_Y^{3+}, ○lac_{La}^{3+}, △ lac_{Nd}^{3+}, ▽lac_{Eu}^{3+}. The experiments were carried out with an organic phase which consisted of 0.2 M HDEHP in 1,4-diisopropylbenzene and an aqueous phase of 0–2 M lactate, 1 mM Ln^{3+}, 1 M $NaNO_3$ (Eu^{3+} extractions were carried out with 2 M $NaNO_3$), and a fixed pH ~ 3.6–3.9.

HDEHP present). The K_d for HL in *n*-dodecane was 0.0012 ± 0.0005. The K_d is much lower in the aliphatic diluent than the aromatic diluent. The experimental evidence indicates that HL partitions into the organic diluents used in TALSPEAK (absent HDEHP) only slightly. The increased partitioning could indicate a specific interaction between lactate and HDEHP, or it may be considered simply a result of the increased polarity of the extractant phase (relative to the pure diluent).

The distribution of lactate into the organic phase is also seen to be altered by the degree of neutralization of lactate in the aqueous phase (Fig. 4). It is seen that the distribution of lactate into the organic phase steadily increases as the concentration of the total lactate, C_L, increases, but also that lactate partitioning increases as the pH increases. As pH rises, the ratio of $[L^-]/[HL]$ in the aqueous phase increases ($[L^-]/[HL]) = 0.25$, 1.0, and 4 at pH 3.0, 3.6, and 4.2 respectively, though there will be subtle variations superimposed on these estimates as C_L increases as the composition of the medium is in flux). In this context, it is noteworthy that lactate distribution ratios are higher across the range of C_L in proportion to the pH value. Since the relative concentrations of lactic acid increase with decreasing pH, this result seems upon first examination to be counterintuitive.

Two effects could account for the pattern of increasing D_{Lac} values at higher pH. First, the sodium salt of lactate (Na^+L^-) could be extracted as well as the HL since at pH 4.2 the aqueous phase contained approximately 77% Na^+L^- (23% HL). Alternatively, the increasing partitioning might indicate a salting out effect, making the HL more extractable as the concentration of Na^+L^- increases in the aqueous phase. It is also interesting to note the behavior of the lactate partitioning over the C_L concentration range. The lower concentrations of C_L indicated slightly increasing extraction behavior on the log-log scale. At around 0.5 M C_L, the extraction sharply increased approaching a similar limiting slope for all 3 pH values as C_L reached 2 M. Similar behavior for lactate was observed for the extraction systems when lanthanide ions were present. Such a dramatic shift in the partitioning of any species often indicates a change in the nature of the phase transfer reaction. In this system a change from discrete association complexes to a higher degree of aggregation of solute molecules in the organic phase can be postulated. Further examination of this possibility is needed.

To address the question of Na^+L^- vs. HL extraction, sodium ion extraction experiments were examined using ^{24}Na produced by neutron activation. If D_{Na} is seen to increase with D_{Lac}, it is reasonable to assume that Na^+L^- is partitioning, otherwise lactic acid must be the primary species transported to the organic phase. It is seen in Fig. 5 that lactate partitioning increases with the C_L while D_{Na+} remains constant (within $\pm 2\sigma$) over the full range of C_L. As Na^+ does not partition in parallel with lactate, it appears that Na^+L^- is not the principal lactate species partitioning into the organic phase.

As $[Na^+]_{org}$ is constant with increasing C_L, it is reasonable to assume that its extraction indicates partial neutralization of $(HDEHP)_2$. It has been reported previously that Na^+ ion can be extracted by HDEHP (16,17), displacing one

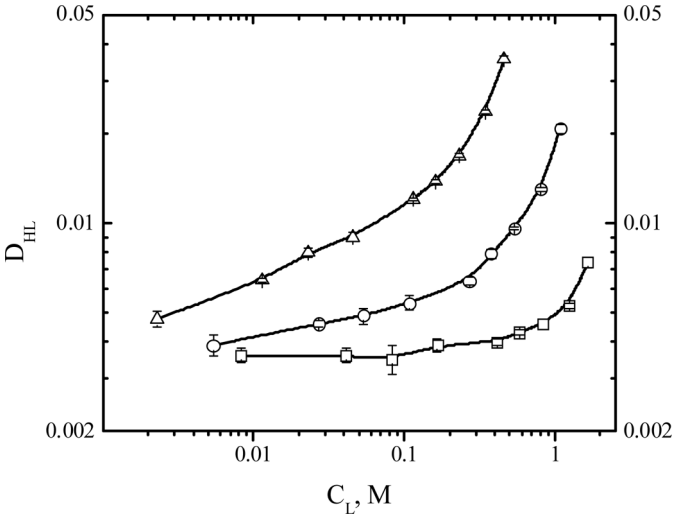

FIG. 4. The extraction of lactate into 0.2 M HDEHP in 1,4-diisopropylbenzene from aqueous solutions of 0–2 M lactic acid, constant 2 M ionic strength (adjusted with $NaNO_3$) as a function of increasing total lactate (C_L) at different pHs (□ pH 3.0, ○ pH 3.6, △pH 4.2).

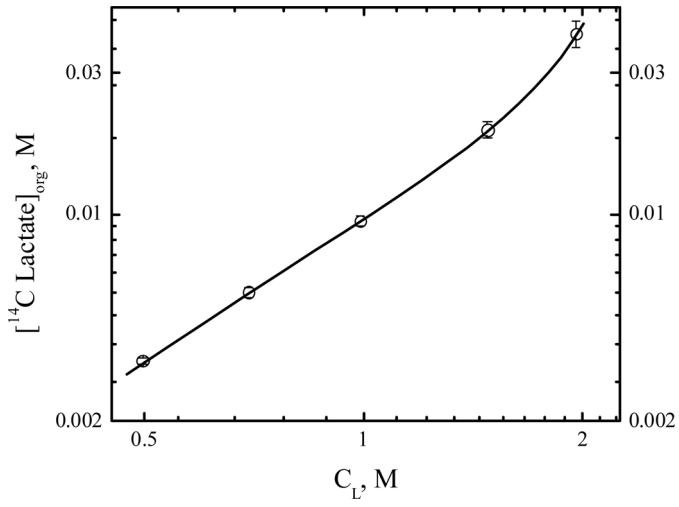

FIG. 5. Concentration of ^{14}C-labeled lactate in the organic phase as a function of total lactate (C_L). The average $[Na^+]_{org}$ was 0.035 ± 0.007 M across the C_L range. The experiments were conducted using 0.2 M HDEHP in 1,4-diisopropylbenzene in contact with aqueous solutions of 0–2 M lactate, constant 2 M ionic strength (adjusted with $NaNO_3$) and a fixed pH 3.6.

H^+ from the normal HDEHP dimer forming a 1:4 complex ion in the organic phase,

$$Na^+ + 2\overline{(HDEHP)_2} \leftrightarrows \overline{NaDEHP(HDEHP)_3} + H^+ \quad (4)$$

The present results do not rule out partitioning of NaL, but it appears far more likely that the reaction defined in Eq. (4) represents the most probable explanation for the comparatively high (and constant) $[Na^+]_{org}$. Though lactic acid is extracted into the HDEHP-DIPB organic solution, preliminary results of NMR experiments offer no indication of a specific interaction between HDEHP and lactic acid, hence we are not prepared to interpret these results further at present. It appears probable that sodium ion is associated with HDEHP, but we likewise cannot determine whether this interaction impacts the progress of lactic acid (or lanthanide) extraction in a predictable fashion. Additional experiments are underway.

To address further the possibility of a salting out effect on HL partitioning, additional experiments were carried out using different background electrolyte salts to determine if changing radius of the counter cation would affect the distribution ratios. Figure 6 shows lactate partitioning in the presence of $NaNO_3$, $LiNO_3$, NH_4NO_3, and KNO_3 supporting electrolytes. The experimental results are grouped according to the size of the cationic radius. Figure 6a shows the extraction of lactate from Li^+ (0.60 Å) and Na^+ (0.95 Å), while in Fig. 6b extraction from K^+ (1.33 Å) and NH_4^+ (1.48 Å) (18) is shown. The extraction data demonstrate suppression in the distribution ratios when lactate is extracted from $LiNO_3$ at high C_L and NH_4NO_3 relative to KNO_3. This pattern could be attributed to ion-pairing between Lac^- and the Li^+ or NH_4^+. Since ion-pairing is driven by electrostatic attraction, the results shown in Fig. 6 indicate more complex behavior. If the electrostatic parameter (z^2/r) is to be considered to explain the possible ion-pairing occurring in the extractions systems at the higher C_L concentrations, the observed suppression of the distribution ratios should be greater for the systems containing the Li^+ and the Na^+ cations. The weakest ion-pairing (and subsequent lesser affect on the distribution ratios) should be present in the systems containing the K^+ and the NH_4^+ cations. The extraction system containing the KNO_3 is the only one showing the expected trend (unaffected D ratio for lactate) based on the electrostatic argument. At this time it is felt that ion pairing arguments are inadequate for describing the observed lactate partitioning trends. Neither are the increased partitioning of lactate at the low C_L concentrations for the $LiNO_3$ and the KNO_3 systems easily explained. Further examination of ion hydration/solvation and extraction effects may yield an explanation.

To better understand the possible reorganization of the organic extractant after contact with high concentrations of lactic acid (0.5–2 M), Karl Fischer titrations were employed to determine the H_2O content in the organic phase. The results of the Karl Fischer titrations are compared with lactic acid partitioning in Fig. 7. The H_2O content of the organic phase remains constant at 40.5 mM until C_L reaches 0.5 M. When C_L is increased to 2 M the H_2O concentration in the organic phase triples to 124 mM. This observation occurs in parallel with the rapid uptake of lactic acid into the organic phase when C_L reaches 0.5 M; at $C_L = 2$ M the organic phase lactic acid concentration is about 41 mM, resulting in a H_2O/lactic acid ratio of about 3 in the upper range of lactate concentration. The ratio of $[H_2O]_{org}/[HDEHP]$ is about 0.6 at the upper limit of C_L. The discontinuity seen in the solubility of a component often indicates a change in solute ordering

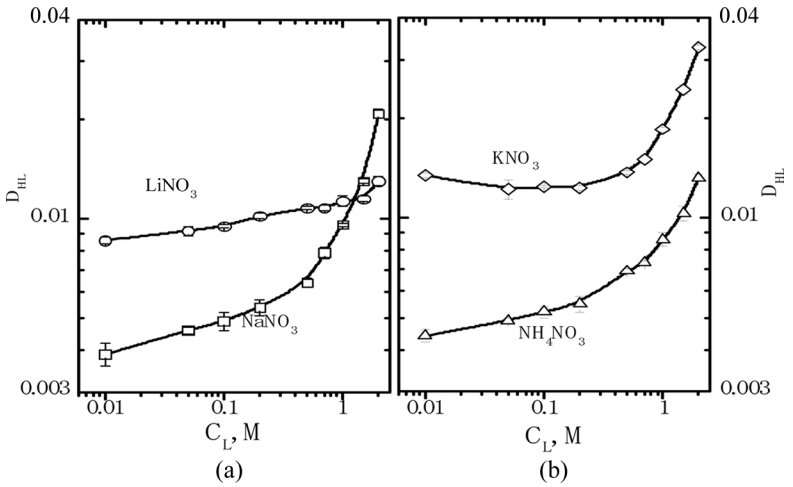

FIG. 6. (a) Distribution of lactic acid into 0.2 M HDEHP in 1,4-diisopropylbenzene from (○) $LiNO_3$ and (□) $NaNO_3$. (b) Distribution of lactic acid from (◇) KNO_3 and (△) NH_4NO_3. Aqueous phases were 0–2 M lactic acid, constant 2 M ionic strength (adjusted with MNO_3) and a fixed pH 3.6.

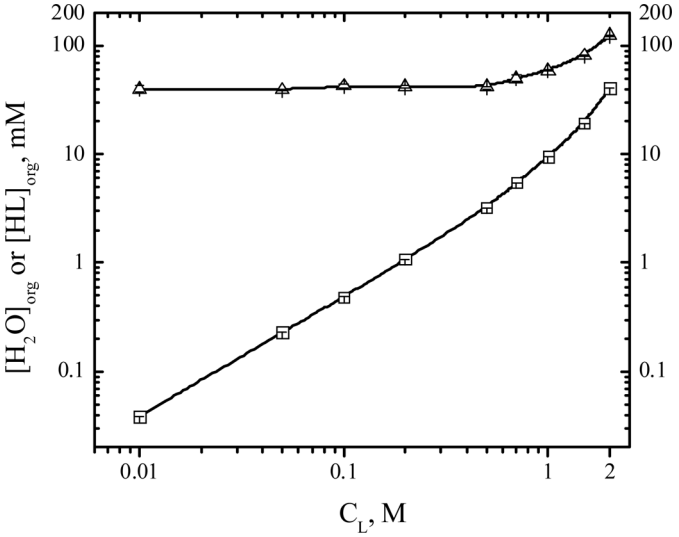

FIG. 7. Comparison of the organic phase concentration of (△) H_2O (determined by Karl Fischer titration) compared to (□) lactic acid concentration in 0.2 M HDEHP in 1,4-diisopropylbenzene after contact with aqueous phases of 0–2 M lactic acid and C_L, constant 2 M ionic strength (adjusted with $NaNO_3$) and a fixed pH 3.6.

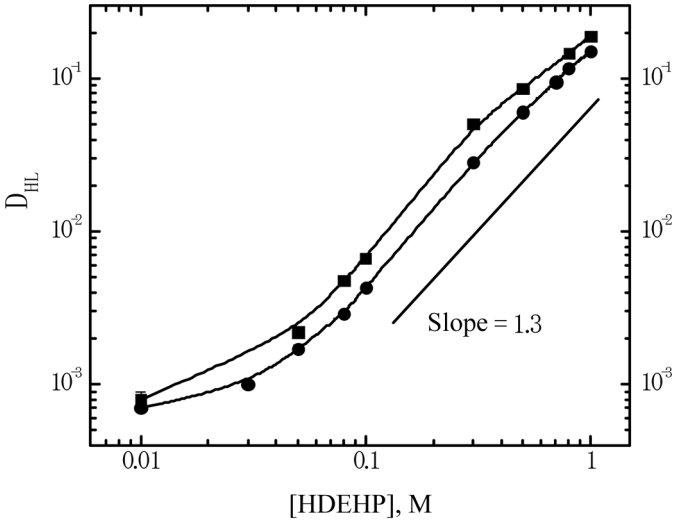

FIG. 8. Comparison of the extraction behavior of HL at 1 M (●) and 2 M (■) C_L as a function of HDEHP concentration in 1,4-diisopropylbenzene. The aqueous phase was 1 or 2 M C_L, constant 2 M ionic strength (adjusted with $NaNO_3$) and a fixed pH 3.6.

in the extractant phase. These data do not allow a more profound statement to be made concerning the ordering of solute and solvent molecules in the extractant phase. Combined with other observations on the kinetics of lanthanide extraction as a function of lactate concentration, they suggest the need for more careful examination of the supramolecular organization of solute and solvent molecules in the loaded TALSPEAK extractant phase.

These experimental results also do not explicitly reveal the stoichiometry of the association between HL_{org} and HDEHP. It is tempting to speculate on the presence of new species containing multiple HDEHP molecules with HL:H_2O species also incorporated at a 1:3 ratio. Preliminary results of an NMR investigation reveal no explicit evidence for direct association between lactic acid/HDEHP/H_2O in the organic phase (no substantial line broadening of the ^{31}P signal of HDEHP is seen) hence direct replacement or insertion of HL into the HDEHP dimeric structure cannot be confirmed. Additional experiments are underway to address this question.

To extend the understanding of HL/HDEHP interactions occurring in the organic phase, additional experiments were performed examining the partitioning of radiotracer lactate at different C_L concentrations (1 and 2 M) as a function of HDEHP. The results in Fig. 8 show that lactate partitioning at 1 M and 2 M total lactate increases with C_L and [HDEHP]. Between 0.1 and 1 M HDEHP, D_{HL} is seen to be proportional to $[HDEHP]^{1.3}$, though the stoichiometry of this relationship is seen to vary with [HDEHP]. As concentrations of HDEHP and HL are of similar magnitude, simple slope analysis to determine the stoichiometry cannot be utilized. However, the observed slope shows some proportionality between HL and HDEHP at the higher concentrations of HDEHP, and may suggest that multiple equilibria are needed to explain the interaction of HL with HDEHP. At 1 M HDEHP the 2 M C_L system shows a HL/HDEHP ratio of 0.32, this represents 16% of the total C_L partitioning to the organic phase possible acid adduct forming in the organic phase. Though the data in Fig. 7 suggest a proportionality between HL and HDEHP is seen, there is no evidence of any explicit interaction between these solute species at this time. Further experiments are underway to address this possible interaction between HL and HDEHP in the organic phase.

CONCLUSIONS

The experiments performed in this study have provided new insights into the extraction behavior of lactic acid in TALSPEAK solvents. It is clear that lactate partitions into the extractant phase independently of the lanthanide metal ion, in contrast with previous literature reports. The results suggest that lactate partitions primarily as the lactic acid (HL) and probably not as sodium lactate. The work of McDowell on the extraction of Na^+ by HDEHP has been confirmed. For analytical considerations, the losses of lactic acid to the organic phase were not extreme but at 2 M about 3% of the C_L did partition into the organic phase. This loss of lactic acid into the organic phase with one contact will be important upon scale up of this process since careful pH control in TALSPEAK is crucial. Experimental evidence does not rule out the possibility of the mixed $ML(AHA)_2$ complex in the organic phase; however, positive identification of a mixed complex is not confirmed.

The concentrations of HL in the organic phase is seen to increase both at higher pH and at higher total lactate concentrations, indicating that while HL partitions, Na^+-Lac^- salts out the lactic acid increasing the partitioning of HL into the extractant phase. The implicit continuous change in ion activity of these lactate solutions hinders any attempts to accurately model this system using available thermodynamic equilibrium data.

At total lactate concentrations above 0.5 M, it appears that the basic nature of the extractant phase changes. At the lower concentrations of C_L, lactate partitioning steadily increases as the C_L concentration increases. When the concentration of C_L reaches 0.5 M, the partitioning of the lactic acid increases sharply, suggesting a change in the mode of transport for lactic acid into the organic phase. This change may be caused by an interaction between HDEHP and HL in the extractant phase, high concentrations of HL in the aqueous phase forming acid catalyzed cyclic polyesters that partition to the organic phase, or reorganization of the organic extractant into tetramers or some other ring structure and partitioning of HL into the polar core. In the extreme, the extraction pathway may shift toward a micellar organizational structure. Under these conditions the ratio of H_2O:HL:HDEHP in the extractant phase is approximately 3:1:5. Given that this metal ion extraction system exhibits slow metal ion phase transfer kinetics at lower concentrations of total lactate, the implicit supramolecular ordering of solute and solvent molecules at high lactate concentrations might in fact be essential to system performance. More work is needed in particular to address this question.

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