Optical Spectroscopy Study of Organic-Phase Lanthanide Complexes in the TALSPEAK Separations Process

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ABSTRACT: Time-resolved fluorescence spectroscopy and Fourier transform IR spectroscopy have been applied to characterize the coordination environment of lipophilic complexes of Eu^{3+} with bis(2-ethylhexyl)phosphoric acid (HDEHP) and (2-ethylhexyl)phosphonic acid mono(2-ethylhexyl) ester (HEH[EHP]) in 1,4-diisopropylbenzene (DIPB). The primary focus is on understanding the role of lactate (HL) in lanthanide partitioning into DIPB solutions of HDEHP or HEH[EHP] as it is employed in the TALSPEAK solvent extraction process for lanthanide separations from trivalent actinides. The broader purpose of this study is to characterize the changes that can occur in the coordination environment of lanthanide ions as metal-ion concentrations increase in nonpolar media. The optical spectroscopy studies reported here complement an earlier investigation of similar solutions using NMR spectroscopy and electrospray ionization mass spectrometry. Emission spectra of Eu^{3+} complexes with HDEHP/HEH[EHP] demonstrate that, as long as the Eu^{3+} concentration is maintained well below saturation of the organic extractant solution, the Eu^{3+} coordination environment remains constant as both $[HL]_{org}$ and $[H_2O]_{org}$ are increased. If the total organic-phase lanthanide concentration is increased (by extraction of moderate amounts of La^{3+}), the $^5D_0 \rightarrow {}^7F_1$ transition singlet splits into a doublet with a notable increase in the intensity of both $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ electronic transitions. The increased multiplicity in the emission spectra indicates that Eu^{3+} ions are present in multiple coordination environments. The increased emission intensity of the 614 nm band implies an overall reduction in symmetry of the extracted Eu^{3+} complex in the presence of macroscopic La^{3+}. Although $[H_2O]_{org}$ increases to above 1 M at high $[HL]_{tot}$, this water is not associated with the Eu^{3+} metal center. IR spectroscopy results confirm a direct Ln^{3+}−lactate interaction at high concentrations of lanthanide and lactate in the extractant phase. At low organic-phase lanthanide concentrations, the predominant complex is almost certainly the well-known $Ln(DEHP \cdot HDEHP)_3$. As lanthanide concentrations in the organic phase increase, mixed-ligand complexes with the general stoichiometry $Ln(L)_n(DEHP)_{3-n}$ or $Ln(L)_n(DEHP \cdot HDEHP)_{3-n}$ become the dominant species.
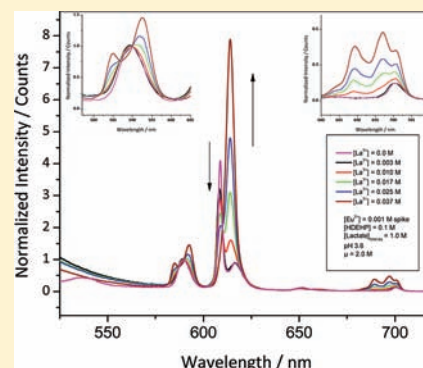
1. INTRODUCTION

It is estimated that 90% of the minor actinides (MAs = Am, Np, and Cm) found in used nuclear fuel could be transformed into shorter-lived fission products after 5−10 years if the transmutation option is utilized in an advanced nuclear fuel cycle. Completing this task would greatly reduce the long-term hazards associated with radioactive wastes from nuclear reactors.[1] A major challenge facing the development of such a nuclear fuel cycle is the need to separate the lanthanides (nearly 30% of the fission products) from the MAs Am^{3+} and Cm^{3+}. The separation is necessary because several lanthanides (particularly Nd^{3+}, Sm^{3+}, Eu^{3+}, and Gd^{3+}) have high-neutron-capture cross sections; thus, they compete with MAs for the neutrons needed to transmute the actinides.

Separation of the groups (which, aside from Np, prefer the trivalent oxidation state and are of similar ionic size) relies on the slightly greater covalency that is seen in actinide bonding with ligand-donor atoms softer than O. One strategy for exploiting this chemistry to separate the groups is to rely on the difference in complexing strength of lanthanide and actinide ions with aminopolycarboxylic acids like diethylenetriamine-

N,N,N',N'',N''-pentaacetic acid (DTPA). The TALSPEAK (Trivalent Actinide Lanthanide Separation by Phosphorus-reagent Extraction from Aqueous Komplexes) process is a liquid/liquid extraction process that exploits this chemistry to achieve the separation.[2,3] In TALSPEAK, an aqueous medium of 0.5−2.0 M lactate buffer (pH 2.5−4.0) containing DTPA is contacted with an immiscible organic phase containing the liquid-cation-exchanging reagent bis(2-ethylhexyl)phosphoric acid (HDEHP). Actinides are retained in the aqueous phase as DTPA complexes, while lanthanides are extracted as complexes with HDEHP. Since its conception, research on TALSPEAK has focused mainly on optimizing the efficiency of the separation.[4,5] Because of its potential utility in advanced fuel cycle development and the present emphasis on a science-based approach to solving this problem, studies of the fundamental chemistry of TALSPEAK have become increasingly important.[6−13]

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Studies of the partitioning of lactic acid (HL) and water (H_2O) into 0.2 M HDEHP dissolved in 1,4-diisopropylbenzene (DIPB in the presence or absence of 0.001 M lanthanide cations) have revealed complex patterns of interactions as the aqueous HL concentration ($[HL]_{aq}$) increases.[11] While the H_2O content of the extractant phase is constant in organic phases prepared by contact with 0−0.5 M lactate, lactate partitioning steadily increases. At higher $[HL]_{aq}$ (0.5−2.0 M), partitioning of both H_2O and lactate increases more steeply. Such a change in the slope could indicate (1) a change in the state of aggregation of solute molecules in the organic solution, (2) a change in the principle reaction governing biphasic transport processes, or (3) a nonsystematic change in solute activity coefficients.

A study applying ^{31}P NMR spectroscopy and electrospray ionization mass spectrometry (ESI-MS) to TALSPEAK-relevant solutions containing higher concentrations of lanthanide cations has established that the apparent stoichiometry of the extracted complexes changes with increased concentrations of both lactate and lanthanides.[14] At low concentrations of lanthanides and lactate, a discrete mononuclear species $[Ln(H(DEHP)_2)_3]$ involving coordination of the lanthanide ion by three DEHP·HDEHP dimers of the extractant in a hexacoordinate arrangement of O-donor atoms[15−20] is the predominant extracted complex. At high lactate and lanthanide concentrations, a binuclear complex with an apparent $Ln_2(Lac)_2(DEHP)_4$ stoichiometry is indicated. This change in the stoichiometry of the extracted complex was unexpected, and it may have profound implications for the application of TALSPEAK under process-relevant conditions (that will typically include high concentrations of both metal ions and lactate). In fact, the indicated change in the stoichiometry of the extracted complexes at high metal-ion concentrations may be an issue of broad concern for hydrometallurgical applications of solvent extraction. The NMR/ESI-MS experiments have probed the system by examining the behavior of lactate/H_2O/HDEHP; they do not directly address the coordination environment around the metal center.

The objective of the present study is to probe these interactions using optical spectroscopic methods that focus on the metal center. This study is the first to make fundamental observations of TALSPEAK-relevant organic-phase samples by probing the coordination environment of Eu^{3+} using time-resolved fluorescence (TRFS) and IR spectroscopies. TRFS can provide direct information about the inner coordination environment of selected lanthanides and curium.[21−23] To assess the possible influence of the basicity of the liquid-cation exchanger on this chemistry, studies of HDEHP-containing organic solutions have been complemented by parallel studies with the isostructural, but more basic, phosphonic acid extractant (2-ethylhexyl)phosphonic acid mono(2-ethylhexyl) ester (HEH[EHP]). Structures of the extractant molecules are shown in Figure 1.

2. EXPERIMENTAL SECTION

2.1. Materials. HDEHP (97%) was purchased from Aldrich. HEH[EHP] was graciously donated by EichromNPO Technologies. Each was purified by the copper precipitation method.[24] The purified HDEHP and HEH[EHP] were determined to be 99.8% and 99.7% pure (respectively) by titration. The organic diluents DIPB (99%, Alfa Aesar) and benzene (99.8%, Sigma-Aldrich) were used without further purification.
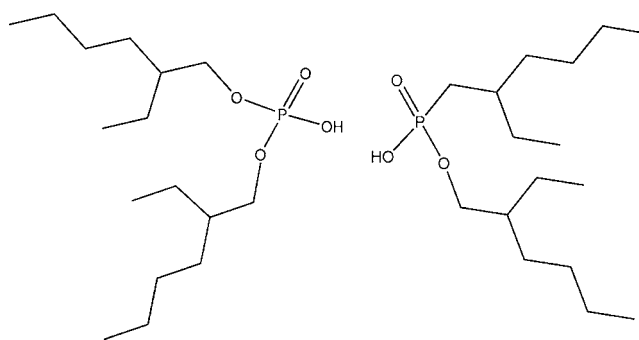

Figure 1. Structures of the phosphoric acid extractant HDEHP (left) and the phosphonic acid extractant HEH[EHP] (right).

The organic-phase samples were prepared by dissolving weighed amounts of the purified HDEHP or HEH[EHP] in DIPB or benzene. The aqueous phases were prepared using lanthanide nitrate stocks (prepared from 99.999% lanthanide oxides from Arris International Co.). The solutions were standardized to determine the metal, nitrate, and H^+ concentrations using inductively coupled plasma mass spectrometry (ICP-MS) and ion-exchange chromatography (Dowex 50W-8X beads, H^+ form, 100−200 mesh) and potentiometric titrations. HL solutions were prepared fresh on the day of experimentation to minimize acid-catalyzed ester formation (e.g., polyesters, lactones, or lactides). Sodium lactate was neutralized with nitric acid to the desired pH of 3.6. 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 (as above). $NaNO_3$ (ACS reagent grade) was purchased from GFS Chemicals; the crystals were dissolved in deionized H_2O, filtered through a fine-glass-frit filter, and then recrystallized from hot H_2O. The $NaNO_3$ solutions were then standardized using ion-exchange chromatography and potentiometric titrations. All aqueous solutions were prepared in 18 MΩ H_2O.

2.2. Solvent Extraction. All solvent extraction experiments were completed using the same procedure. Equal volumes of organic and aqueous phases were contacted by vigorous shaking for 15 min at room temperature (approximately 21 °C), followed by 15 min of centrifugation. Samples were preequilibrated with appropriate neat DIPB, benzene, or 2.0 M $NaNO_3$ phases. All solvent extraction experiments were carried out in triplicate.

2.3. HL and H_2O Partitioning. Aqueous-phase HL concentrations were varied between 0.01 and 2.0 M for all partitioning experiments. The aqueous-phase acidity was adjusted to pH 3.6. The ionic strength was adjusted to 2.0 M using $NaNO_3$. A 10 μL spike of ^{14}C-labeled HL was added to each sample aqueous phase after preequilibration. Partitioning experiments were carried out at three different [HDEHP], 0.2, 0.5, and 1.0 M. The concentration of HEH[EHP] was fixed at 0.2 M. To determine the distribution ratios, a 300 μL sample was taken from both phases and analyzed by liquid scintillation counting (Beckman LS6500). The H_2O content of the organic phase after mixing was determined by Karl Fischer titration.

2.4. Extracted Eu^{3+} Complexes. For one series of extraction experiments, the aqueous-phase Eu^{3+} concentration was held constant at 0.001 M, while $[HL]_{tot}$ was varied between 0 and 2.0 M. The aqueous-phase acidity was adjusted to pH 3.6, and the ionic strength was held constant at 2.0 M using $NaNO_3$. Eu^{3+} was quantitatively extracted into the organic phase in all samples.

As noted above, it has been established in the earlier NMR/ESI-MS study[14] that extraction of high concentrations of La^{3+} into the organic phase promotes reorganization of the organic phase with the probable formation of polynuclear metal/HDEHP/Lac complexes. To study the effect of metal loading on the extractant structure without overloading the fluorescence spectrometer, metal-loading experiments were conducted using 0.001 M Eu^{3+} in solutions containing 5−50 times higher concentrations of La^{3+}. In these samples, the HDEHP concentration was fixed at 0.1 M; the aqueous-phase La^{3+}

concentrations were adjusted to 0.005, 0.015, 0.025, 0.035, and 0.055 M. After equilibration, the corresponding $[La^{3+}]_{org}$ values were determined by analysis to be 0.003, 0.010, 0.017, 0.025, and 0.037 M. As the metal-ion concentration in the organic phase increases, the corresponding ratios of $[HDEHP]_{org}/[La^{3+} + Eu^{3+}]_{org}$ decrease (25, 9, 5.6, 3.8, and 2.6). It is assumed in the analysis of the spectroscopic data that La^{3+} and Eu^{3+} occupy similar coordination environments in samples containing both metal ions, i.e., that the metal ions mix isotropically. Distribution ratios for metal-ion extraction were determined by inductively coupled plasma optical emission spectroscopy (Perkin-Elmer Optima 3200 RL).

2.5. Fluorescence Measurements. Emission spectra and lifetime studies of Eu^{3+} in aqueous and organic phases were collected using a HORIBA Jobin Yvon IBH FluoroLog-3 fluorometer adapted for time-resolved measurements. Samples were analyzed at 25 °C using 1 cm cells. The light source used was a submicrosecond xenon flash lamp (Jobin Yvon, 5000XeF) coupled to a double-grating excitation monochromator for spectral selection. The detector, a single-photon detection module (HORIBA Jobin Yvon IBH, TBX-04-D), incorporates a fast-rise-time photomultiplier tube, a wide-bandwidth preamplifier, and a picosecond constant fraction discriminator. Data were collected using an IBH Data Station Hub and analyzed using the DAS 6 decay analysis software package from HORIBA Jobin Yvon IBH. The lifetime data were fit using a single-exponential decay curve for samples without excess La^{3+} but a double-exponential function in the mixed-metal samples. χ^2 values between 0.985 and 1.07 were observed for the entire range of samples.

2.6. IR Studies. To further assess the role of HL in the high-metal-concentration samples, additional extraction experiments were conducted and organic-phase samples were analyzed using IR spectroscopy (Nicolet 6700 FT-IR by the Thermo Corp.). All spectra were collected between 400 and 4000 cm^{-1} using 100 scans and a resolution of either 16 or 32 cm^{-1}. The samples were prepared using solvent extraction methods. One set of samples was prepared using $HNO_3/NaNO_3$ as the aqueous electrolyte (i.e., no lactate). To eliminate the need for heating and possible decomposition of the organic extractant complex, benzene was used as the organic diluent rather than DIPB. After equilibration with the aqueous phase, the samples were placed in a fume hood and benzene was allowed to evaporate. As in the fluorescence studies, the aqueous-phase La^{3+} concentrations were adjusted to 0.005, 0.015, 0.025, 0.035, and 0.055 M. The 0.055 M samples were not analyzed because a waxy precipitation formed in the organic phase after contact.

3. RESULTS

The solute/solvent partitioning isotherms for HL and the correlation of $[H_2O]_{org}$ with HL partitioning are shown in Figure 2; the 0.2 M HDEHP results reported previously have been reproduced here.[11] Both $[HL]_{org}$ and $[H_2O]_{org}$ are seen to increase with increasing $[HDEHP]_{tot}$ and $[HL]_{aq}$, although the increases are not correlated one-for-one throughout the range of conditions. The system does not reach saturation with respect to either $[H_2O]_{org}$ or $[HL]_{org}$ at $[HL]_{tot}$ = 2.0 M at any $[HDEHP]$. In 0.2, 0.5, and 1.0 M HDEHP/DIPB at $[HL]_{tot}$ = 0.01 M, $[H_2O]_{org}$ increases from 0.04 to 0.06 to 0.15 M, maintaining a $[H_2O]_{org}/[HL]_{org}$ ratio of 600−1000. In the low-lactate limit, the H_2O content is independent of $[HL]_{aq}$, so it must be considered representative of the miscibility of H_2O in the HDEHP/DIPB solution in contact with a 2 M ionic strength aqueous nitrate/lactate medium. For comparison, considering xylene (ρ = 0.857 g/mL, H_2O solubility = 0.0156 wt %[25]) as an analogue for 1,4-DIPB, the expected $[H_2O]_{org}$ in the pure diluent equilibrated with pure H_2O would be about 0.01 M.

Lactate partitioning into the organic phase increases with increasing $[HDEHP]$. Correlations of lactate distribution ratios at the lowest concentrations of lactate and HDEHP suggest a

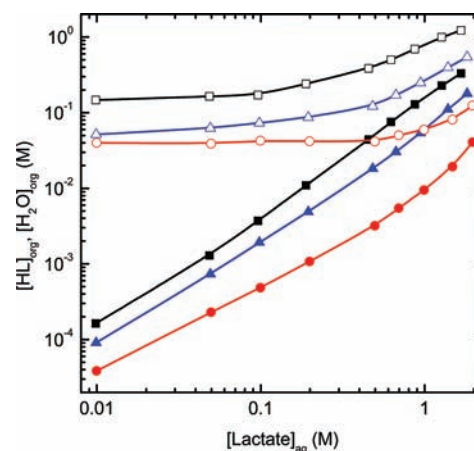**Figure 2.** Lactate and H_2O partitioning: Comparison of organic-phase $[H_2O]_{org}$ (open symbols) and $[HL]_{org}$ (closed symbols) with $[HL]_{aq}$ at different HDEHP concentrations: (■, HL; □, H_2O) 1.0 M; (▲, HL; △, H_2O) 0.5 M; (◆, HL; ◇, H_2O) 0.2 M. The trend lines in the graph are only to guide the eye.

1:1 stoichiometry for the association of these species. Results from an earlier study[11] indicate a 1:3 (HL/HDEHP) stoichiometry in the high concentration limit. It is reasonable to expect that at intermediate concentrations an HL·HDEHP$_2$ species may be important.

Emission spectra for the extracted Eu^{3+} complexes of HDEHP and HEH[EHP] are shown in Figure 3. The excitation wavelength used to collect spectra for the extracted Eu^{3+} complexes was 464 nm. The Eu^{3+} ions are excited to the $^5D_2$ excited state at this wavelength. They undergo a rapid nonradiative relaxation to the $^5D_0$ state; emission occurs during relaxation from the $^5D_0 \rightarrow \, ^7F$ ground-state manifold.[22] Changes occurring in the inner coordination sphere of Eu^{3+} result in differing intensities for the 616 nm peak, which represents the $^5D_0 \rightarrow \, ^7F_2$ electronic transition. The relaxation pathway is assumed to be the same for all extracted Eu^{3+} complexes described in this section.

As noted above, metal-loading experiments were carried out using La^{3+}, which is more soluble in the HDEHP phase than Eu^{3+} (although the extraction equilibrium constant for La^{3+} is lower than that of Eu^{3+}). Assuming that La^{3+} and Eu^{3+} have similar coordination environments in the organic phase, the Eu^{3+} spectra are assumed to also provide an image of the La^{3+} coordination environment(s). The emission spectra for the mixed-metal samples are shown in Figure 4. The emission spectra for the cation-saturation experiments indicate splitting of the $^5D_0 \rightarrow \, ^7F_1$ magnetic-dipole transition (585−600 nm) from a singlet to a doublet as $[Ln^{3+}]$ was increased. The hypersensitive electric-dipole transition $^5D_0 \rightarrow \, ^7F_2$ (605−620 nm) showed a decrease in the 608 nm transition as a 614 nm emission increased with increasing $[Ln^{3+}]$. The $^5D_0 \rightarrow \, ^7F_4$ (680−710 nm) magnetic-dipole transition showed a splitting of a singlet into a triplet as $[Ln^{3+}]$ was increased, indicating the presence of multiple electronic species. The $^5D_0 \rightarrow \, ^7F_{1,2}$ electronic transitions both contained isosbestic points, suggesting the presence of at least two species (different coordination environments) in solution.

Horrocks and Sudnick established a method for calculating hydration numbers for the various lanthanides and actinides with fluorescent emission properties.[22] They developed an empirical relationship connecting decay lifetimes to hydration
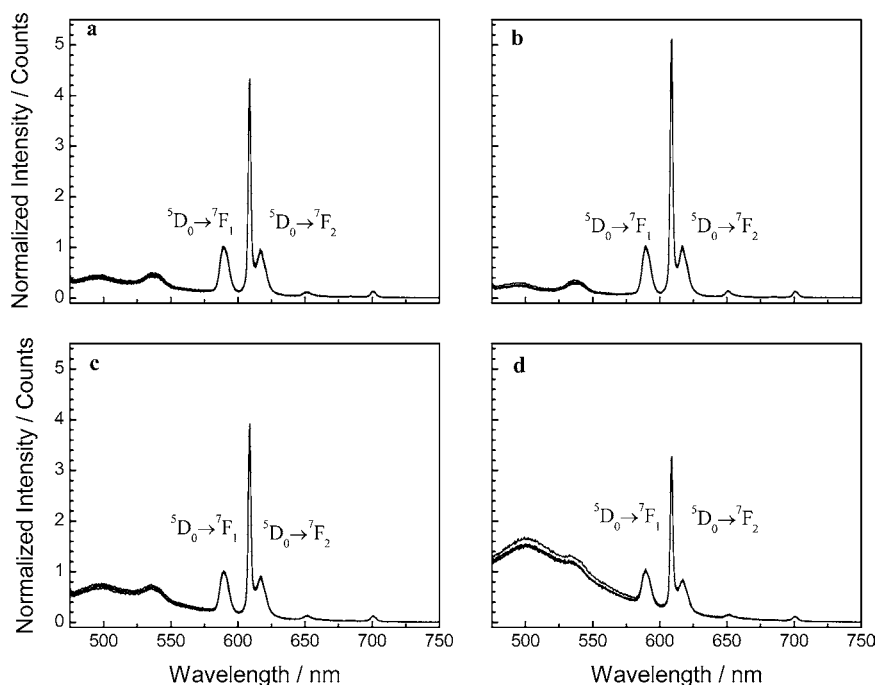
Figure 3. Emission spectra for the extracted Eu^{3+} complexes ($[Eu]_{org}$ = 0.001 M) of HDEHP and HEH[EHP] at different extractant concentrations: (a) 0.2 M HDEHP; (b) 0.2 M HEH[EHP]; (c) 0.5 M HDEHP; (d) 1.0 M HDEHP. The excitation wavelength for these experiments was 464 nm. The aqueous phases were the same for all extractions: 0−2.0 M HL, pH 3.6, ionic strength 2.0 M, adjusted with $NaNO_3$.
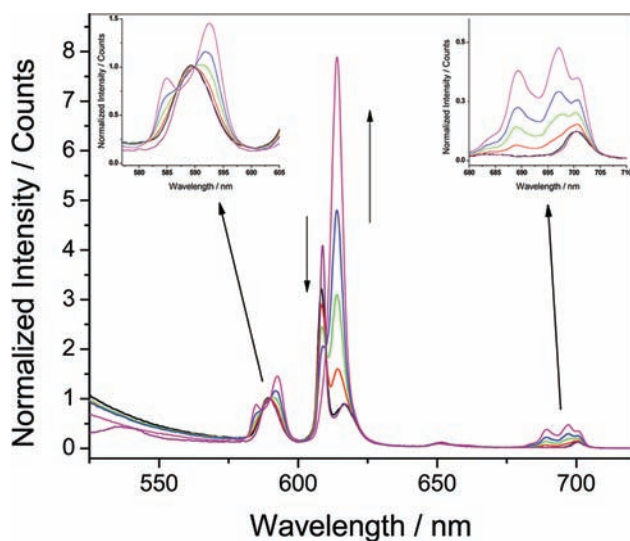

Figure 4. Emission spectra for extracted Eu^{3+} complexes under loading conditions. La^{3+} was used to load the organic phase with a 0.001 M Eu^{3+} spike to promote fluorescence. The excitation wavelength for these experiments was 464 nm. The aqueous conditions are as previously described. $[La^{3+}]$ for metal loading were 0.001, 0.003, 0.010, 0.017, 0.025, and 0.037 M.

numbers by exploiting the differences between k_{obs}'s for solutions containing H_2O and D_2O. Since this groundbreaking work, others have reported a simpler relationship between nH_2O and k_{obs} (s^{-1}) in H_2O solutions only and have utilized this relationship to develop empirical equations for calculating waters of hydration in the inner coordination sphere.[26−31] The following equation reported by Kimura and Choppin[26,27] was used to calculate the waters of hydration for this work.

$$N_{H_2O} = 1.05 \times 10^{-3} k_{obs}(Eu) - 0.44 \quad (1)$$

The empirical equation is based on the assumption that no deexcitation energy is lost through the complexing ligand, i.e., that all energy lost is through vibration of the O−H group(s). In this system, potential OH oscillators include coordinated H_2O molecules and the α-hydroxy group of a coordinated lactate ion.

Fluorescence decay rate constants for the extracted Eu^{3+} complexes from lactate media using HDEHP and HEH[EHP] as organic extractants are shown in Table 1. Uncertainties

Table 1. Fluorescence Decay Constants for Eu^{3+} Extracted into the Organic Phase from Lactate Media Using Both HDEHP and HEH[EHP][a]

	k_{obs}, s^{-1}			
[lactate], M	0.2 M HDEHP	0.5 M HDEHP	1.0 M HDEHP	0.2 M HEH[EHP]
0	339 ± 10	364 ± 9	382 ± 8	340 ± 10
0.005	338 ± 9	359 ± 10	376 ± 9	336 ± 11
0.1	337 ± 7			
0.5	347 ± 11	359 ± 9	378 ± 9	331 ± 12
1	345 ± 12			
1.5	355 ± 10			
2	367 ± 11	389 ± 10	402 ± 7	331 ± 11

[a] $[Eu^{3+}]_{org}$ = 0.001 M for all experiments; [HDEHP] and [HEH-[EHP]] = 0.2 M. Hydration numbers calculated based on eq 1: k_{obs} = 339, n_{H_2O} = −0.08; k_{obs} = 402, n_{H_2O} = −0.02.

associated with the above equation equal those of Horrock's work (±0.5 waters of hydration). The results shown in Table 1 establish that the Eu^{3+} species have (within the constraints of eq 1) no coordinated H_2O molecules because even a single coordinated H_2O molecule would produce fluorescence decay rates of approximately 1300 s^{-1}. A lactate molecule coordinated in a bidentate manner that includes the protonated α-hydroxy

group would modify the Eu^{3+} fluorescence decay rate by the equivalent of half of a H_2O molecule, producing a decay rate of about 900 s^{-1}. Within these constraints, the results in Table 1 indicate a low probability of lactate or H_2O coordination to Eu^{3+} under these conditions. This is consistent with previous literature results that reported no residual hydration for extracted Eu^{3+} complexes using HDEHP.[17,18] No literature reports are available describing the state of hydration for extracted Eu^{3+} complexes with HEH[EHP]; these results indicate that $Eu[H(EH[EHP])_2]_3$ is also anhydrous.

The observed slight increase in the decay rates for the Eu^{3+} center with increases in both the lactate and HDEHP concentrations appears to be statistically significant in the experiments involving HDEHP but not for HEH[EHP]. An increased interaction with OH-oscillating moieties (probably lactate) could account for this, but the size of the effect indicates that a mixed species containing both lactate and HDEHP is not an important contributor to the Eu^{3+} species in these solutions. On the basis of results from the prior literature, it is believed that the predominant extracted complexes under these conditions are $Eu[H(DEHP)_2]_3$ and $Eu[H(EH-[EHP])_2]_3$.

The IR spectra for La^{3+} metal-loaded organic phases are reported in Figure 5. The major features for all of the spectra

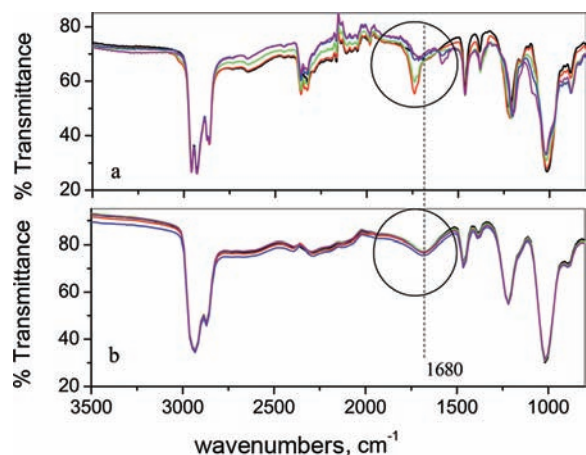**Figure 5.** IR spectra for evaporated residues of HDEHP organic phases loaded with $[La^{3+}]$ = 0.0, 0.003, 0.010, 0.017, and 0.025 M. Panel a shows the effect of metal loading with lactate buffer present in the aqueous phase at 1.0 M. The acidity of the aqueous phase was adjusted to pH 3.6. Panel b shows the effect of metal loading (same as lactate systems) with no lactate present in the aqueous phase. HNO_3 was used to adjust the acidity to pH 3.0. The ionic strength was adjusted to 2.0 M for both extraction systems.

are summarized in Table 2. Samples created by extraction of Eu^{3+} from lactate media result in changing features in the spectrum throughout the range of observation, but the most pronounced changes occur in the C−H stretching, O−H stretching, and O−H deformation regions of the spectrum, with more subtle variations occurring in the P−O stretching regions.

4. DISCUSSION

4.1. HL Partitioning. Building upon the previously reported information,[11] the HL partitioning experiments were conducted using different [HDEHP] with the intent to develop a thermodynamic model describing HL partitioning in TALSPEAK-relevant solutions. The expectation was that at

high loading a terminal complex (e.g., $HDEHP_x \cdot HL_y \cdot zH_2O$) with the same ratios of HDEHP, HL, and H_2O at the different [HDEHP] might be identified. If the terminal ratios were consistent at different [HDEHP], it would be valid to assume that the system behaves the same for all extractant concentrations. Variations in the ratios either would suggest the need for more complex equilibrium expressions or would indicate the presence of hydrogen-bonded aggregates of HL, HDEHP, and H_2O (in some combination) in the organic phase. With a fixed stoichiometry, experimental data could be used to calculate K_{ex} for HL using the following equilibrium expression (beccause the concentrations of all components, aqueous or organic, would be known).

$$x HDEHP_{(org)} + y HL_{(aq)} + z H_2O_{(aq)}$$

$$\rightleftarrows HDEHP_x HL_y (H_2O)_{z \, (org)} \qquad (2)$$
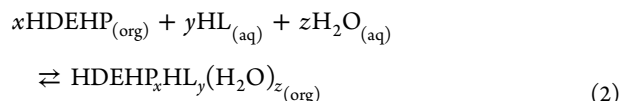
The data in Figure 2 show that both $[HL]_{org}$ and $[H_2O]_{org}$ increase as [HDEHP] is increased. The isotherms for HL at 0.5 and 1.0 M HDEHP do not show a sharp increase when $[HL]_{tot}$ reaches 0.5 M, as was observed for the 0.2 M HDEHP system. In fact, the gradient increases with increasing [HDEHP]. The equilibrium ratios of $[Lac]_{org}/[HDEHP]_{org}$ are 0.20, 0.40, and 0.34 for 0.2, 0.5, and 1.0 M HDEHP at 2.0 M $[HL]_{tot}$.

The partitioning of H_2O into 0.2 M HDEHP shows constant $[H_2O]_{org}$ up to 0.5 M HL, above which concentration a notable increase is observed. The $[H_2O]_{org}$ versus $[HL]_{aq}$ plots for the 0.5 and 1.0 M HDEHP systems show a change in the gradient across the aqueous lactate concentration range. At 2.0 M $[HL]_{tot}$, $[H_2O]_{org}$ for the 0.5 and 1.0 M HDEHP systems is increased by a factor of 4 and 10, respectively, compared to $[H_2O]_{org}$ in the 0.2 M HDEHP system. After equilibration with a 2.0 M lactate buffer, $[H_2O]_{org}$ reaches 63% [HDEHP] in 0.2 M HDEHP, 108% in 0.5 M HDEHP, and 124% in 1.0 M HDEHP. The marked increase in the slope of this relationship implies changes in the organization of solute molecules at high lactate concentrations. In a previous report,[11] it was noted that HL partitioning into 0.2 M HDEHP also increased with increasing pH. This is noteworthy because as the pH increases the fractional concentrations of [HL] ($[HL]/[HL] + [L^-]$) actually decrease. This implies a specific ion salting effect arising from the changing lactate-ion concentration.

Because the organic phase does not achieve saturation with respect to either H_2O or HL, the identity of a terminal species was not established. This analysis does not take into account extraction of Na^+ [as $NaDEHP(HDEHP)_3$],[33] which is known to occur but appears to be independent of $[HL]_{tot}$. When $[HL]_{tot}$ reaches 2.0 M, the ratios for the HDEHP/HL/H_2O species at 0.2, 0.5, and 1.0 M HDEHP were calculated to be 5:1:3 (as previously reported[11]), 3:1:3, and 3:1:4, respectively. The results at higher concentrations of HDEHP appear to indicate a terminal complex of $HL(HA)_3$ with some variation in the numbers of H_2O molecules dissolved in the HL-loaded extractant phase. These observations, of course, do not directly address the molecular associations that account for increased solubility of lactate and H_2O in the organic phase. However, given the low polarity of DIPB, it is reasonable to expect that the polar solute molecules are mutually associated in this solution and that this association is moderated by the HDEHP amphiphile.

**4.2. Eu^{3+} Fluorescence.** *4.2.a. Low Metal-Loading Conditions.* Under ideal conditions (i.e., minimal mixing of

Table 2. Summary of the IR Spectra for La Metal-Loaded Organic Phases at Equilibrium after Contact with Aqueous Phases Containing Lactate or HNO_3[a]

	wavenumber, cm^{-1}						
	1.0 M lactate, pH 3.6						0.001 M HNO_3
stretching assignments	neat HDEHP[b] in previous work	neat HDEHP in this work	0.003 M La^{3+}	0.010 M La^{3+}	0.017 M La^{3+}	0.025 M La^{3+}	0.003−0.037 M La^{3+}
methyl, methylene C−H stretching (sym and antisym)	2965	2958	2958	2958	2958	2958	
	2930	2927	2927	2927	2927	2927	2931
	2870	2858	2858	2858	2858	2858	2869
O−H st bonded	2750−2250	2638	2638	2638	2638	2638	2638
	2280	2283	2283	2283	2283	2283	2283
O−H deformation	1680	1673					1650
new peak formation			1740	1736	1700	1690	
					1570	1570	
P−O stretching	1225	1214	1210	1203	1200	1200	1218
P−O st (antisym)	1040	1006	1010	1010	1010	1010	1018

[a]$[La^{3+}]$ in the table are the actual concentrations determined by ICP-MS. It is assumed that $[La^{3+}]$ of HNO_3 is the same as for the lactate systems. [b]Peak assignments from previous work done by Peppard and Ferraro.[32]

aqueous solute molecules into the organic phase), the biphasic extraction of Ln^{3+} using HDEHP as the extractant[16,34] is considered to obey the following equilibrium expression:

$$Ln^{3+}_{(aq)} + 3(HA)_{2(org)} \rightleftarrows Ln[H(DEHP)_2]_{3(org)} + 3H^+_{(aq)} \quad (3)$$
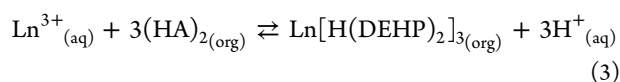
In this reaction, three molecules of the predominantly dimeric extractant molecule complex the lanthanide ion with exchange of three H^+ to the aqueous phase. Prior reports from the literature have established that the characteristic coordination mode for these complexes involves the monodentate coordination of six dialkyl phosphate ligands in which adjacent ligands are linked by hydrogen bonding between protonated and ionized HDEHP ligands.[15−20] Extended X-ray absorption fine structure studies have clearly established a coordination number of 6 for this complex (and similar species) in nonpolar organic solvents. Because directed valence effects are absent in lanthanide coordination compounds, it is reasonable to assume that the coordination environment around the metal center will be approximately octahedral, as determined by the balance of electrostatic interactions. The dimers are believed to remain intact in the extracted complex, although the rate of H^+ exchange in the coordinated dimers has not been determined. A previous report established that the rate of ligand exchange in $Eu(H(DEHP)_2)_3$ is slow (as measured on the NMR time scale[14]); thus, it is reasonable to conclude that H^+ exchange in the dimeric extractant is likely also slow in this medium.

In Figure 3, panels a, c, and d show the emission spectra for the extracted Eu^{3+} complex in 0.2, 0.5, and 1.0 M HDEHP, respectively. In each panel, features of the Eu-centered emission [$^5D_0 \rightarrow {}^7F_1$ magnetic-dipole transition (590−600 nm) and hypersensitive electric-dipole transition $^5D_0 \rightarrow {}^7F_2$ (605−620 nm) peaks] are invariant with increasing $[HL]_{org}$. The broad emission below 580 nm that increases as [HDEHP] increases is believed to arise from Raman scattering of H_2O in the organic phase.[35] As noted above, $[H_2O]_{org}$ increases with [HDEHP], in particular at elevated organic-phase lactate. The most intense emission band at 608 nm slightly decreases in intensity as [HDEHP] increases, which may indicate a shift toward slightly higher site symmetry. These results seem to indicate that the species $Eu(H(DEHP)_2)_3$ is the dominant species even in the

presence of significant concentrations of lactate in the extractant phase.

It could be argued that substitution of a bidentate lactate for one $H(DEHP)_2^-$ dimer extractant moiety would maintain a hexacoordinate environment around Eu^{3+}; it is also possible that a lactate could substitute for one HDEHP molecule [$Eu(H(DEHP)_2)_2(DEHP)(HL)$ or $Eu(H(DEHP)_2)_2$-$(HDEHP)(L)$], which also maintains a hexacoordinate environment. Although these specific species cannot be ruled out based on these results, the symmetry argument and constancy of the spectra with increasing $[HL]_{org}$ argue for $Eu(H(DEHP)_2)_3$ as the dominant complex.

Panel b in Figure 3 shows the emission spectra for the extracted Eu^{3+} complex using 0.2 M HEH[EHP]. There are no intensity changes for the $^5D_0 \rightarrow {}^7F_1$ magnetic-dipole transition (590−600 nm) or the hypersensitive electric-dipole transition $^5D_0 \rightarrow {}^7F_2$ (605−620 nm) peaks seen as $[HL]_{aq}$ is increased from 0 to 2.0 M. It has been reported previously[12] that, under the same aqueous conditions as those in this report, the partitioning of HL into HEH[EHP]/n-dodecane is 3−10 times lower than that into HDEHP/n-dodecane; H_2O partitioning is 40−100 times lower. The fluorescence results suggest a similarly extracted Eu^{3+} coordination sphere for the HDEHP and HEH[EHP] extractants under TALSPEAK conditions at low lanthanide concentrations, probably a species without inner-sphere lactate coordination. The emission intensity is highest in 0.2 M HEH[EHP] with a steadily decreasing overall emission intensity from 0.2 to 0.5 M to 1.0 M HDEHP; in this series, the HEH[EHP] solution is cleanest, having the lowest $[HL]_{org}$ and $[H_2O]_{org}$.

As was noted above, there is a slight increase noted in the decay rate for each of the HDEHP systems that correlates with increasing $[HL]_{tot}$ in the equilibrating aqueous phase. A similar trend is not seen in the HEH[EHP] system, confirming a weaker interaction between lactate and HEH[EHP] than is seen for HDEHP. The consistencies between these new results and the previous literature and the analogous nature of the phosphonic acid/phosphoric acid results confirm the predominance of the $Eu(H(DEHP)_2)_3$ and $Eu(H(EH[EHP])_2)_3$ extracted complexes when $[Eu^{3+}]_{org}$ is held at 0.001 M. These limits correspond to less than 2% of the "loading capacity" of

the organic phase (assuming that an extracted complex as defined in eq 3).

4.2.b. High Metal-Loading Conditions. As the total organic phase metal concentration is increased by coextraction of La^{3+} and of the spectroscopic probe Eu^{3+}, the intensity of the hypersensitive electric-dipole transition $^5D_0 \rightarrow {}^7F_2$ at 608 and 616 nm is seen to decrease with the coincident appearance of a band of greater intensity at 614 nm. The development of an apparent isosbestic point indicates the presence of two Eu^{3+} species, probably in equilibrium. The splitting of the $^5D_0 \rightarrow {}^7F_1$ magnetic-dipole transition (590−600 nm) from a singlet to a doublet and the increase in the intensity of the $^5D_0 \rightarrow {}^7F_2$ electronic-dipole transition are consistent with a reduction of the symmetry of the Eu^{3+} center in the extracted complex as the total lanthanide concentration increases. The hexacoordinate complex that dominates at low metal-ion concentrations is expected to have a distorted octahedral symmetry, thus exhibiting low intensity in the $^5D_0 \rightarrow {}^7F_2$ electronic-dipole transition. A reduction of the symmetry around the metal center could arise from a mixture of monomer/dimer HDEHP coordination, substitution of a lactate ion, or a shift to a bridging phosphate coordination mode. A similar observation was made in the earlier NMR/ESI-MS investigation.[14]

In solvent extraction, metal-ion partitioning into the organic phase is possible only when the extracted complex is charge neutral. Under the high metal-loading conditions in this study, there is too little extractant available for HDEHP to form the discrete 1:6 (three dimer) metal-to-ligand complex necessary for charge neutrality. To support the high concentrations of extracted metal ions that have been observed, HDEHP must (at least partially) de-dimerize and extract the metal ions as the monomeric species forming the Ln(A)$_3$ complex. At the highest [HL]$_{org}$, the [HDEHP]/[M]$_{tot}$ value drops to 2.6, requiring participation of at least 0.4 equiv of either nitrate or lactate in the extracted complex. The lactate ion is a much stronger aqueous complexant than NO$_3^-$; the log β values for the 1:1 aqueous complexes Eu(Lac)$^{2-}$ and Eu(NO$_3$)$^{2-}$ are 2.51 and 0.26, respectively.[36] Lactate is also likely to be more lipophilic than nitrate and, hence, more likely to be transported into the organic phase.

Fluorescence emission spectra in the 0.003 M La^{3+}/0.001 M Eu^{3+} system were fit using a single first-order decay. These results indicated a completely dehydrated extracted metal ion, consistent with the 0.001 M Eu^{3+} system. The remainder of the high metal-loaded data (0.010, 0.017, 0.025, and 0.037 M La^{3+}/ 0.001 M Eu^{3+}) were fit using a double-exponential model, indicating the presence of two Eu^{3+} coordination environments. The fluorescence lifetime measurements are consistent with the emission spectra because both indicate the presence of at least two extracted Eu^{3+} complexes (or, more properly, two distinct Eu^{3+} coordination environments) in the metal-loaded systems.

On the basis of the amount of aqueous solute partitioning seen in TALSPEAK, it is easy to imagine that there might be many possible species present in the organic phase. These species could include a mixture of Eu^{3+}/La^{3+} HDEHP dimer and HDEHP monomer complexes, or Eu^{3+}/La^{3+} complexes coordinated with one or two lactate molecules. Macro-concentrations of metal ion also have an impact on the extracted species. Jensen et al.[37] have reported small-angle neutron scattering measurements, indicating that a dinuclear Nd$_2$DEHP$_6$ species was present in an organic phase when 0.1 M HDEHP (in toluene) was loaded with 0.01 M Nd^{3+}. Considering these results, it seems reasonable to project the

assembly of metal-bridged polymers to support 0.037 M metal ion present in the 0.1 M HDEHP organic phases in this study. A similar species containing lactate has been suggested in the earlier ^{31}P NMR/ESI-MS study conducted on this system.[14]

4.3. IR Spectra. To establish a benchmark for IR spectra comparisons, a neat HDEHP sample (HDEHP dissolved in benzene with no further treatment) was analyzed and peak assignments were compared to those previously identified by Peppard and Ferraro.[32] The IR spectra for neat HDEHP in this work were consistent with the previous literature results. For the organic-phase samples extracted from HL buffer, when [La^{3+}] was at 0.003 and 0.010 M, the 1680 cm^{-1} absorption band shifted to around 1740 cm^{-1}, is much sharper, and displays greater intensity than the broad 1680 cm^{-1} band observed for the neat HDEHP sample. As the metal concentration increases to 0.017 and 0.025 M, the 1740 cm^{-1} band decreases and a new absorption band is observed at around 1570 cm^{-1}. The new band grows in intensity as a function of the metal concentration. The appearance of the two new peaks creates an isosbestic point, indicating the presence of two species in the La^{3+} metal-loaded organic phases. Simultaneous with the appearance of the 1570 cm^{-1} band, the intensity in the P−O stretching (around 1200 cm^{-1}) and asymmetric stretching (around 1010 cm^{-1}) bands decreases. These data combined clearly indicate the probable exchange of one or more HDEHP molecules for a lactate ion in the extracted metal complex. The IR spectra in Figure 5, panel b (La^{3+} loaded into HDEHP from an aqueous phase containing nitric acid), do not show any changes to the major absorption bands over the entire range of extracted La^{3+} metal to the organic phase. The 1680 cm^{-1} band was slightly shifted to 1650 cm^{-1}; the P−O and asymmetric stretching bands are unaffected by the increased organic-phase metal concentrations.

The IR spectra indicate that the lactate ion is directly involved with the change of the 1680 cm^{-1} absorption band and the reduction of the P−O and asymmetric stretching bands. The isosbestic point created by increasing metal concentration in the organic phase may represent the shift of the discrete hexacoordinate La(H(DEHP)$_2$)$_3$ complex to the mixed extracted complex that is tentatively proposed to be La$_2$(Lac)$_2$(DEHP)$_4$.[14] The IR spectral results agree in general terms with previous solvent extraction/slope analysis work done by Kosyakov and Yerin.[38] Those authors postulated the presence of the mixed extracted complex Ln(Lac)[H-(DEHP)$_2$]$_2$ for both Eu^{3+} and Cm^{3+}. However, their postulation was based on a negative second power hydrogen-ion dependence from slope analysis of solvent extraction data using radiotracer concentrations of metal ion and so are not strictly comparable to these results.

The IR data support the premise that, as [HDEHP]$_{org}$/ [La^{3+}]$_{org}$ drops below the 6:1 ratio required for the formation of the La(H(DEHP)$_2$)$_{3(org)}$ complex, it is likely that the lactate ion becomes a part of the extracted complex. In this species, HL provides the third H$^+$ ion needed to neutralize the charge of La^{3+} while maintaining the dimeric (HA)$_2$ structure of the coordinated extractant. From the perspective of the thermodynamics of the phase-transfer reaction, it matters not whether La(Lac)$^{2+}$ is formed in the aqueous phase then extracted by two (HA)$_{2(org)}$ dimers or some species of HL$_{(org)}$ complexes La(H(DEHP)$_2$)$_2^+$ in the interface with the coordinated release of H$^+$ to the aqueous phase. The concept that La(NO$_3$)$^{2+}$ is extracted, forming the La(NO$_3$)(H(DEHP)$_2$)$_2$ extracted complex, can be dismissed because it is present at high

concentrations in both the lactate and sans-lactate samples but nitrate has no effect on the IR spectra when lactate is absent.

5. CONCLUSIONS

Spectroscopic measurements of organic extractant solutions relevant to the TALSPEAK process have revealed that all extracted complexes are, as expected, completely dehydrated. HL partitioning experiments point to a possible terminal 3:1 HDEHP/HL ratio, suggesting a possible direct interaction between the two molecules; H_2O is also present in the organic phase at significant concentration, although the mode of its interaction is not clear. More experiments and data analysis are needed to confirm this possible interaction. It can definitely be concluded from this study that HDEHP extracts HL independently of the presence of a lanthanide under TAL-SPEAK conditions.

Under most conditions, the dominant extracted species is the well-known 1:6 complex $Ln(H(DEHP)_2)_3$ in which the Ln^{3+} ion is coordinated with three HDEHP (or HEH[EHP]) dimers. As $[HL]_{tot}$ increases, the fluorescence emission reveals that the Eu^{3+} inner coordination sphere does not change, suggesting that the dominant extracted species at low $[Ln^{3+}]$ is present in the organic phase as previously described. When the ratio of extractant to Ln^{3+} drops below the conventional stoichiometric limit of 6:1, it appears that the lactate becomes directly involved in the extracted complex. The previous ^{31}P NMR/ESI-MS study has identified a bimetallic complex species, $La_2(Lac)_2(DEHP)_4$, as the dominant species in HDEHP samples created from high lactate media and containing high lanthanide concentrations. The present results are consistent with the earlier reported speciation.

It is also important to note that the probable change of the stoichiometry of the predominant extracted complex that is indicated by these results may be a consistent feature of lanthanide coordination chemistry in hydrometallurgical applications of solvent extraction. Further investigation of such systems promises to improve the predictability of hydrometallurgical separations systems in general. The present investigation of a nuclear waste processing system could find utility in the development of similar separations of strategic metal ions like the rare earths.

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Notes
The authors declare no competing financial interest.

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