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ABSTRACT

Because there are fewer tools available to probe the interactions therein, the effect of the fundamental chemistry of the organic diluent on solvent extraction equilibria has been under-characterized relative to the aqueous. As a result, diluents for solvent extraction are often selected for an application not for their utility as a medium for reaction, but for other (often equally) important reasons (like low flammability). To begin to improve this imbalance in the science, twenty different diluents have been used in a study of the extraction of radiotracer $^{152/154}Eu^{3+}$ from dilute nitric acid solutions using the extractant 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]). To increase the utility of the study and to honor the memory of Professor Jan Rydberg, this investigation was conducted by a cadre of comparatively inexperienced separation scientists (who are as a result no longer inexperienced separation scientists) as a radioanalytical chemistry and solvent extraction educational exercise. Slope analysis was used to determine the apparent stoichiometry of the extracted metal complex. The results discussed in the following indicate that, while the pH dependence exhibits the expected three H^+ exchanged per metal ion extracted, the extractant dependence suggests that the number of protonated extractant molecules in the extracted complex changes with the organic diluent. The experimentally observed "extractant dependency" ranges from 2.5 to 3.0 dimer equivalent molecules per extracted metal ion. Ironically, in the diluents exhibiting the highest apparent $M:(HA)_3$ stoichiometry, HEH[EHP] extracts Eu^{3+} less efficiently. Europium luminescence spectroscopy was used to probe for changes in the first coordination sphere of the complex in different diluents. A model and conceptual framework for understanding these observations is described.

KEYWORDS
Europium; diluent effect; stoichiometry; HEH[EHP]; solvent extraction

Introduction

Solvent extraction/Rydberg dedication

Dr. Jan Rydberg was a leading scientist in the field of solvent extraction and was dedicated to developing new techniques for the characterization of solvent extraction systems as well as training young scientists in the method. His textbooks are considered among some of the greatest sources of basic solvent extraction knowledge and are a vital tool for aspiring solvent extraction chemists.[1] This work details the results of a relatively simple slope analysis experiment utilized by first year graduate students to train on solvent extraction and radiochemical methods, and is offered in memory of Professor Rydberg (who was also a renowned nuclear/radiochemist). This simple exercise has since ballooned into several graduate student Ph.D. projects that encompass many different aspects of solvent extraction chemistry and different methodologies for the investigation and characterization of solution composition and structure.

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/lsei.

Diluent effect

While solvent extraction methods have been used extensively to study aqueous phase equilibria, organic phase equilibria (though integral to the solvent extraction process) have been the subject of far fewer studies. In particular, the effect of the "inert" diluent on metal ion extraction has been touched upon by a small number of authors. Mason and Peppard investigated the influence of the diluent on numerous organophosphorus extractants through slope analysis and observed that the "inert" diluent had a significant effect on the efficiency of the extraction.[2–4] They also observed that some diluents appeared to decrease the number of extractant molecules in the final extracted metal complex, i.e., lanthanide extraction stoichiometry decreased from the nominal 3.0 ratio of extractant dimers to metal ion expected. The diluent did not seem to affect the apparent amount of H^+ exchanged for the metal when cation exchanging extractants were used, as a slope of three was observed.

Similar results on the extraction of Eu^{3+} and Tb^{3+} were also reported by Kolarik using the extractant di-n-octyl phosphoric acid (DOP).[5] Kolarik tested sixteen different diluents with a wide range of properties and theorized that the stoichiometry of the extracted metal complex varied with diluent. He proposed that the number of deprotonated extractants in the complex must equal the charge on the metal center while additional unionized extractant molecules acted to solvate the complex. He concluded that the preferred Eu^{3+} complex in aromatic diluents was $EuA_3 \cdot (HA)_3$ while aliphatic diluents favored an apparently lower stoichiometry species ($EuA_3 \cdot (HA)_2$). The alternate approach of explaining the apparent variable stoichiometry (favored for cation exchanging extractants by Danesi) is to attribute the apparent stoichiometry change to bulk activity effects.[6] Either approach can provide useful characterization of extraction equilibria, but the variable stoichiometry approach is the more intriguing, hence has become the focus of this report.

With the Kolarik, Mason, and Danesi reports (and a few others) for guidance, the effect that the diluent has on dialkyl phosphoric acid extractants has been determined (though perhaps not completely explained). To consider the effect of Brønsted acidity of the extractant on this question, herein the discussion is applied to the phosphonic acid extractant 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]). This extractant has recently become relevant in f-element solvent extraction in the Advanced TALSPEAK[7] and ALSEP[8,9] processes for separating trivalent actinides from lanthanides. In Advanced TALSPEAK, the more basic HEH[EHP] provides a flatter pH dependence and more predictable chemistry than the traditional TALSPEAK extractant bis-(2-ethyl(hexyl)) phosphoric acid (HDEHP) when matched with a suitable holdback reagent.[10]

In this report, the results of slope analysis studies on Eu(III) extraction by HEH[EHP] in a variety of different diluents from dilute nitric acid/sodium nitrate solutions are reported. These analyses were completed using radiotracer [152/154]Eu to train new scientists in the proper methods of handling radioactivity while also introducing them to solvent extraction techniques. Twenty diluents with different hydrogen donor/acceptor behavior, polarity, polarizability, and molecular dimensions were used in this study. The results of the analysis of pH dependence and extractant dependence were compared based on various diluent parameters. The luminescence spectra of the Eu^{3+} metal center in selected systems were also examined to characterize the primary coordination sphere in the extracted complex.

Experimental

Materials

Organic diluents were obtained from Alfa Aesar, Sigma-Aldrich, Fisher Scientific, J. T. Baker, and Aldrich, and were of analytical grade so were used without further purification. HEH[EHP] was obtained from Yick/Vic Chemicals and Pharmaceuticals with low purity. A third phase formation procedure was used to purify the material to >99% (purity verified by phosphorus NMR spectroscopy).[11]

The aqueous phases were prepared using $Eu(NO_3)_3$ stocks (prepared by dissolving 99.999% Eu_2O_3 from Arris International Co. in nitric acid). The solutions were standardized to determine the metal, nitrate and proton concentrations using inductively coupled plasma mass spectrometry (ICP-MS), ion exchange chromatography (Dowex 50W/X8 bead, 100–200 mesh), and potentiometric titrations. Radioactive $^{152/154}Eu$ was produced by neutron activation of solid 99.999% Eu_2O_3 using a Teaching, Research, Isotopes General Atomics (TRIGA) reactor with a neutron flux of 5×10^{12} neutrons·cm^{-2}·s^{-1} at the Nuclear Radiation Center at Washington State University, subsequently dissolved in HNO_3. The $NaNO_3$ solution was prepared from $NaNO_3$ crystal dissolution in deionized H_2O (GFS Chemical), filtered through a fine/glass/frit filter, and then recrystallized from hot H_2O. All aqueous solutions were prepared with 18 MΩ H_2O.

Slope analysis

The organic phase samples were prepared gravimetrically and aqueous solutions were prepared by volume. All experiments were conducted at a 1:1 ($V_{aqueous}$:$V_{organic}$) phase ratio with variations in the pH and the ligand concentration in 20 different organic diluents (see Table 1 for list of diluents). The aqueous phase ionic strength was fixed at 0.1 mol·L^{-1} by the addition of $NaNO_3$. Radiotracer experiments using $^{152/154}Eu$ were analyzed on a Packard Cobra II Auto Gamma counter. All extractions were done at room temperature (23 ± 2°C) and run in triplicate. A 5 µL spike of the $^{152/154}Eu$ radiotracer aqueous working solution was added to the two-phase mixture (0.5 mL of each phase). This produced a total specific activity of approximately 2.5×10^4 cpm (γ)·mL^{-1}. The phases were mixed on a vortex mixer for 15 minutes and the phases separated after centrifugation at 1600 rpm for 10 minutes. Equal volume (200 µL) aliquots of each phase were then taken and assayed for total gamma activity. The distribution ratios are defined by the quotient of specific radioactivity A (Bq·mL^{-1}) of the europium radiotracer in the organic and aqueous phases.

Table 1. Slopes of the pH and extractant log-log plots (Equation 5) of the extraction of Eu^{3+} from HNO_3, (µ = 0.1 mol·L^{-1} $NaNO_3$) by HEH[EHP] into various organic diluents. Errors represent ±1σ uncertainty.

|		pH dependencies						Extractant dependencies					
	[(HA)$_2$] mol.L^{-1}	pH range			slope		pH	[(HA)$_2$] range mol.L^{-1}			slope		
tetralin	0.103	1.00	-	2.00	3.09	±	0.07	2.00	0.010	-	0.100	3.14	±	0.03
xylene	0.106	1.22	-	2.60	3.10	±	0.01	2.09	0.006	-	0.050	2.99	±	0.06
toluene	0.126	1.22	-	2.60	3.10	±	0.02	2.00	0.025	-	0.075	2.97	±	0.02
bromobenzene	0.100	1.22	-	2.60	2.92	±	0.09	2.00	0.069	-	0.153	2.97	±	0.07
benzene	0.077	1.22	-	2.29	3.10	±	0.05	2.01	0.063	-	0.100	2.95	±	0.08
carbon tetrachloride	0.018	1.61	-	2.60	2.91	±	0.02	2.00	0.010	-	0.111	2.91	±	0.02
chloroform	0.075	0.97	-	1.68	3.16	±	0.13	2.00	0.033	-	0.129	2.84	±	0.05
o-dichlorobenzene	0.073	1.00	-	2.00	3.07	±	0.03	2.00	0.010	-	0.100	2.84	±	0.03
cyclohexene	0.100	0.97	-	1.93	2.84	±	0.14	1.40	0.014	-	0.075	2.83	±	0.03
chlorobenzene	0.076	1.22	-	2.60	3.04	±	0.04	2.00	0.053	-	0.161	2.83	±	0.05
fluorobenzene	0.078	1.22	-	2.60	3.04	±	0.04	2.00	0.053	-	0.161	2.82	±	0.06
tetrachloroethylene	0.078	1.22	-	2.60	2.99	±	0.04	2.00	0.010	-	0.100	2.80	±	0.03
1,3-diisopropylbenzene	0.052	1.22	-	2.60	2.94	±	0.04	2.00	0.013	-	0.063	2.78	±	0.05
cyclohexane	0.025	0.97	-	1.96	3.13	±	0.07	1.40	0.008	-	0.079	2.78	±	0.03
decalin	0.012	1.01	-	2.03	3.05	±	0.16	2.01	0.010	-	0.030	2.72	±	0.09
nitrobenzene	0.010	1.25	-	2.75	3.07	±	0.07	2.00	0.005	-	0.050	2.68	±	0.04
isooctane	0.014	1.61	-	2.30	3.00	±	0.09	1.50	0.006	-	0.050	2.66	±	0.03
n-dodecane	0.025	1.22	-	2.60	2.93	±	0.09	1.46	0.024	-	0.074	2.63	±	0.03
n-octane	0.010	1.00	-	1.90	3.09	±	0.12	1.43	0.005	-	0.051	2.63	±	0.03
n-decane	0.025	1.22	-	2.60	2.97	±	0.04	1.46	0.026	-	0.075	2.62	±	0.04

Luminescence

Europium luminescence experiments were conducted to develop spectroscopic evidence of changes in the extracted complex structure in two different diluents (toluene and *n*-octane). In these experiments an organic solution of 0.1 mol·L^{-1} HEH[EHP] was prepared in the required diluent and contacted with a 6 mmol·L^{-1} Eu(NO$_3$)$_3$ solution (pH = 2 in HNO$_3$). To accommodate the requirements of the fluorimeter, the post-extraction organic solution was diluted by a factor of five (to ~1.2 mmol·L^{-1} Eu) with the appropriate diluent and then analyzed in a one cm. quartz cuvette. The luminescence spectra were taken on a HORIBA Scientific FluoroMax-4 fluorimeter. The excitation monochromator wavelength was 393 nm with a 14 μm slit width and the emission monochromator was scanned from 550–650 nm with 0.25 nm steps and a 1 μm slit width.

Results

Slope analysis

Extraction of trivalent metals (here Eu^{3+}) by lipophilic acidic organophosphorus extractants (HA) is conventionally written as follows (with the overbar indicating species in the organic phase and adopting the MA$_3$·3HA shorthand of Kolarik to describe the extracted complex):

$$Eu^{3+} + 3\overline{(HA)_2} \leftrightharpoons \overline{(EuA_3 \cdot 3HA)} + 3H^+ \tag{1}$$
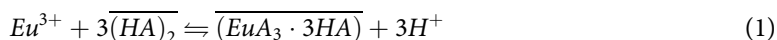
$$K_{ex}^o = \frac{\left[\overline{(EuA_3 \cdot 3HA)}\right][H]^3}{\left[\overline{(HA)_2}\right]^3 [Eu^{3+}]} \tag{2}$$

$$D = \frac{A_{\text{org,eq}}}{A_{\text{aq,eq}}} = \frac{\Sigma\left[\overline{Eu}\right]_{\text{eq}}}{\Sigma[Eu]_{\text{eq}}} = \frac{\left[\overline{(EuA_3 \cdot 3HA)}\right]}{[Eu^{3+}]} \tag{3}$$

where (HA)$_2$ is the presumed dominant dimer of the free extractant, K$_{ex}^o$ the extraction equilibrium constant, and D the distribution ratio of metal between the organic phase and the aqueous phase. Equations (2) and (3) can be combined as in Equation (4) to relate the dependent variable D to the independent variables [H$^+$] and [(HA)$_2$]:

$$K_{ex}^o = D\frac{[H]^3}{[\overline{(HA)_2}]^3} \tag{4}$$

Separating the dependent and independent variables and converting to a log-based format produces Equation (5):

$$\log D = \log K_{ex}^o + 3 \cdot \log\left[\overline{(HA)_2}\right] - 3 \cdot \log[H^+] \tag{5}$$

Though it is expected for Eu^{3+} extraction by HEH[EHP] that a 1:3 stoichiometry will govern the system, the stoichiometric coefficients in the slope analysis experiments are considered as variable coefficients, thus Equation (5) becomes Equation (6):

$$\log D = \log K_{ex}^* + n \cdot \log\left[\overline{(HA)_2}\right] - m \cdot \log[H^+] \tag{6}$$

with the revised extraction equilibrium constant K$_{ex}^o$ a slope analysis experiment is defined therefore by the characterization of the relationships between the dependent and each independent variable in

Equation (5) with the measurement of the stoichiometric coefficients as the desired parameters. With the complete data set, the extraction equilibrium constant corrected for the apparent variable stoichiometry of the overall extraction reaction can be calculated.

Studying the distribution of metal between the organic and the aqueous phase at different $\log [H^+]$ (holding $[(HA)_2]$ constant – acid dependence) and different $\log [(HA)_2]$ (holding $[H^+]$ constant – extractant dependence), it is possible to investigate the apparent stoichiometry of the extraction reaction, Equation (6). It should be noted that in all calculations, the aqueous activity coefficients (γ) are taken as 1.0 (fixed ionic strength of the aqueous medium). The organic phase activity coefficients also are taken as 1.0 for two reasons; one being the lack of Hildebrand solubility parameters for the constituents in the organic phase and the other being the recently reported inability of Hildebrand's theory to match the extent of the diluent effect in similar solvent extraction systems.[12]

Examples of the $[H^+]$ dependent and extractant ($[(HA)_2]$) dependent slope analysis in xylene and n-decane are shown in Figure 1. In addition, a plot of the $\log D$ vs. $\log K_{ex}^o$ (similar to the one used by Rydberg[1]) has been prepared to establish the internal consistency of the results from the pH and the extractant dependencies, Figure 2 (the m value has been fixed to 3 for the charge balance of the cation exchange and the n value has been taken from Table 1). The acid dependence of the Eu/0.1 mol·L^{-1} NaNO$_3$/HEH[EHP]/diluent system was determined and the results for all 20 diluents are shown in Table 1. The $[H^+]$ dependent slope in nearly all systems was within ±3σ of the expected Eu:H$^+$ stoichiometry of 1:(–3). These $[H^+]$ dependence results also establish that the extracted metal species in all diluents is Eu^{3+} and that Eu(NO$_3$$^{2+}$) (a minor species in 0.1 mol·L^{-1} NaNO$_3$ media) does not participate in the phase transfer reaction.

Unlike the $\log [H^+]$ dependence, the extractant dependence did not produce a slope of 3 in all diluents. If the equilibrium reaction occurs as proposed in Equation (1), then the slope would correspond to the average number of dimeric extractant species in the metal complex (as long as the $\gamma = 1.0$ assumption is valid). The experimental metal:extractant apparent stoichiometry changes from the
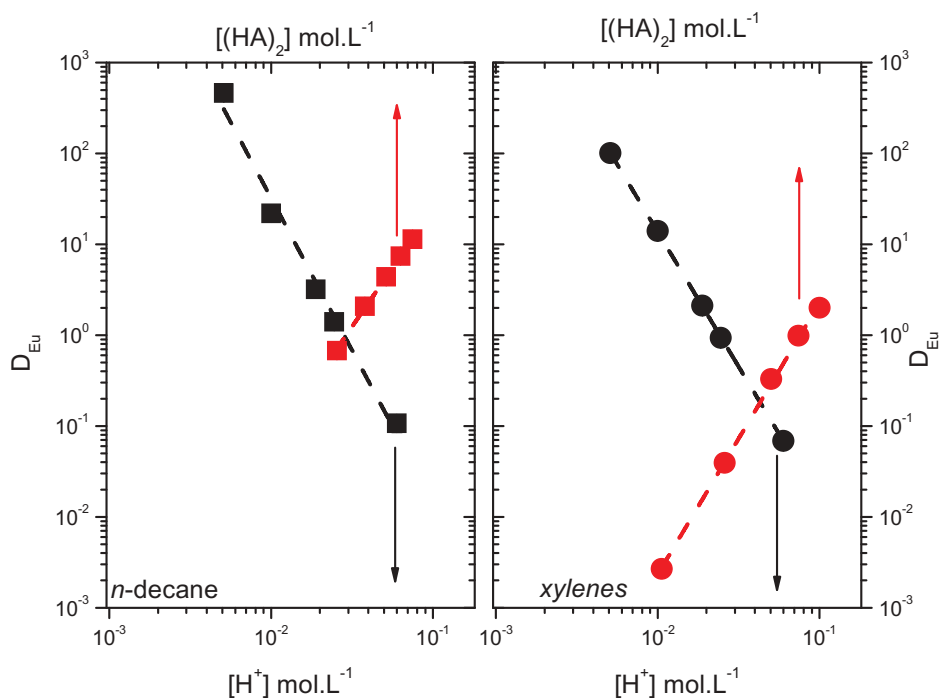

Figure 1. Slope analysis sample plots for xylenes (right) and n-decane (left). Unweighted fit of $\log D$ vs. $\log [H^+]$ and $\log [(HA)_2]$.
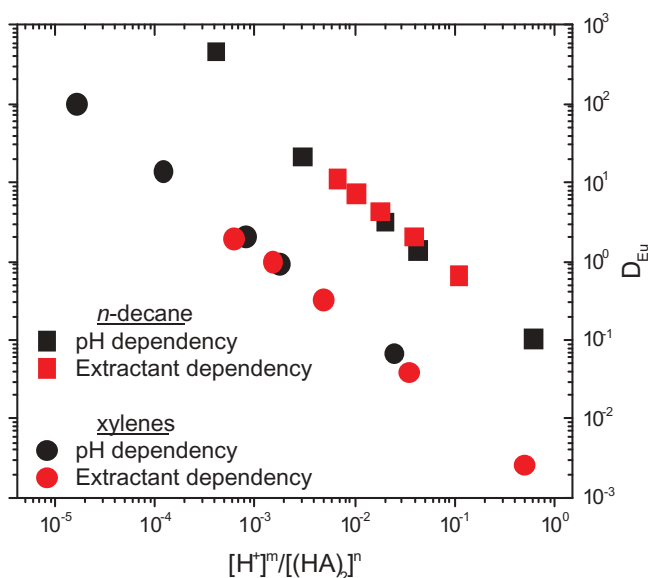
Figure 2. Sample plots from Figure 1 used to determine K_{ex}^* and to verify the consistencies of the results between the pH and extractant dependencies for a diluent.

expected value of 3 in toluene to approximately 2.6 in *n*-octane, *n*-decane and *n*-dodecane. Rather than Kolarik's observation suggesting either Eu(A)$_3$·(HA)$_3$ or Eu(A)$_3$·(HA)$_2$ species dominate (in aromatic and aliphatic diluents, respectively), the results in Table 1 suggest a continuous variation between these limits for a varied selection of classes of diluents.

As the dimers of HEH[EHP] exist as a result of the inter-molecular (head-to-head) hydrogen bonding between monomers, the apparent defect in the M:A stoichiometry would seem to require some degree of de-dimerization of the free extractant (perhaps induced by the metal ion) to satisfy the need for 3 H$^+$ ions to be released to balance the charge of the extracted Eu^{3+} cation. This apparent dichotomy is often resolved by invoking organic phase activity effects. In the following, an alternative explanation is explored, building on the earlier Kolarik model.

Extraction equilibrium constant calculations

The overall K$_{ex}^o$ was calculated according to Equation (4), assuming the complex EuA$_3$·(HA)$_3$ is the only extracted species. The values of log K$_{ex}^o$ calculated in this manner are reported in the first column of Table 2. Because the slope analysis data suggests that there may be a reduction in stoichiometry in several (particularly aliphatic) diluents, the K$_{ex}^o$ was re-calculated according to Equation (7) using the results of the slope analysis to refine K$_{ex}^o$ according to the stoichiometric coefficients determined in slope analysis.

$$K_{ex}^* = D \frac{[H]^m}{[(\overline{HA})_2]^n} \tag{7}$$

It is assumed in the calculation that there is 100% dimerization of the free extractant, and the values n and m denote the [H$^+$] dependent and extractant dependent log-log slopes respectively. Introduction of the experimental stoichiometries modifies the absolute values of K$_{ex}^o$ slightly, but improves the precision of the derived extraction equilibrium constants notably.

Table 2. Equilibrium constant values calculated using Equations (4), (7) and (14). The reported uncertainties are at ±1σ.

	log K_{ex}°			log K_{ex}^{*}			log K_3			log $K_{2.5} \cdot \sqrt{K_2}$		
tetralin	−1.87	±	0.02	−1.61	±	0.02	−1.67	±	0.01	-	±	-
xylene	−2.01	±	0.02	−2.04	±	0.02	−2.01	±	0.01	-	±	-
toluene	−1.93	±	0.01	−1.98	±	0.01	−1.97	±	0.02	−3.87	±	0.26
bromobenzene	−2.10	±	0.07	−2.17	±	0.07	−2.17	±	0.06	−3.75	±	0.73
benzene	−2.28	±	0.12	−2.38	±	0.12	−2.61	±	0.12	-	±	-
carbon tetrachloride	−1.53	±	0.02	−1.72	±	0.02	−1.65	±	0.02	−3.13	±	0.12
chloroform	−4.54	±	0.05	−4.85	±	0.06	−4.78	±	0.06	−5.85	±	0.18
o-dichlorobenzene	−1.70	±	0.02	−2.02	±	0.02	−1.91	±	0.03	−3.11	±	0.08
cyclohexene	−0.82	±	0.01	−1.05	±	0.01	−0.11	±	0.05	−0.84	±	0.07
chlorobenzene	−2.09	±	0.06	−2.44	±	0.06	−2.57	±	0.08	−3.05	±	0.07
fluorobenzene	−2.24	±	0.07	−2.31	±	0.07	−2.30	±	0.02	−4.00	±	0.31
tetrachloroethylene	−1.07	±	0.02	−1.46	±	0.03	−1.38	±	0.05	−2.35	±	0.07
1,3-diisopropylbenzene	−0.61	±	0.01	−1.05	±	0.01	−0.82	±	0.02	−2.02	±	0.06
cyclohexane	0.35	±	0.01	0.01	±	0.01	−0.33	±	0.07	−0.61	±	0.03
decalin	0.13	±	0.03	−0.43	±	0.05	−0.33	±	0.02	−1.06	±	0.01
nitrobenzene	−1.20	±	0.01	−1.82	±	0.01	−2.70	±	0.11	−2.26	±	0.01
isooctane	0.30	±	0.02	−0.20	±	0.01	−0.13	±	0.09	−0.68	±	0.03
n-dodecane	0.25	±	0.01	−0.28	±	0.01	−0.33	±	0.08	−0.61	±	0.03
n-octane	0.15	±	0.02	−0.37	±	0.01	−0.36	±	0.11	−0.73	±	0.03
n-decane	0.19	±	0.01	−0.38	±	0.02	−0.44	±	0.15	−0.66	±	0.05

The results of the extractant slope analysis could be interpreted to indicate that there is a change in the number of extractant molecules solvating the Eu^{3+} metal center in different diluents. Kolarik theorized that two principal species were forming in the DOP study, $EuA_3 \cdot (HA)_3$ and $EuA_3 \cdot (HA)_2$, depending on the nature of the diluent. As noted above, it appears that extractant dependence exhibits an almost continuously variable range of M:A stoichiometries between 2.5 and 3.0 over the range of diluents in the Eu-HEH[EHP] system as the diluent is changed. As has been demonstrated in an earlier study of lanthanide thiocyanate extraction by trioctylphosphine oxide,[13] non-integer slopes may be interpreted to indicate the presence of multiple extracted complexes. In this system, a mixture of $Eu(A)_3 \cdot (HA)_3$ and $Eu(A)_3 \cdot (HA)_2$ could account for a non-integer slope between 3 and 2.5 in the slope analysis experiment. If such a system is operable here, the following extraction equilibrium constants and dimerization constant are relevant:

$$K_3 = \left[\overline{Eu(A)_3 \cdot (HA)_3} \right] \cdot \frac{[H^+]^3}{[Eu^{3+}] \cdot \left[\overline{(HA)_2} \right]^3} \tag{8}$$

$$K_{2.5} = \left[\overline{Eu(A)_3 \cdot (HA)_2} \right] \cdot \frac{[H^+]^3 \cdot \overline{[HA]}}{[Eu^{3+}] \cdot \left[\overline{(HA)_2} \right]^3} \tag{9}$$

$$K_2 = \frac{\left[\overline{(HA)_2} \right]}{\overline{[HA]}^2} \tag{10}$$

where K_3 is the extraction equilibrium constant of the 1:3 metal to extractant dimer species, $K_{2.5}$ is the corresponding constant of the 1:2.5 metal to extractant dimer species, and K_2 is the dimerization constant of HEH[EHP]. If both equilibria contribute to the overall extraction reaction, the measured distribution ratio (D) would be as in Equation (11).

$$D = \frac{\left[\overline{Eu(A)_3(HA)_2}\right] + \left[\overline{Eu(A)_3(HA)_3}\right]}{[Eu^{3+}]} \tag{11}$$

Equations (8) and (9) can be substituted for the organic phase metal species and the equation can be rearranged as follows:

$$D = \frac{1}{[Eu^{3+}]} \cdot \left(\frac{K_{2.5} \cdot [Eu^{3+}] \cdot [\overline{(HA)_2}]^3}{[H^+]^3 \cdot \overline{HA}} + \frac{K_3 \cdot [Eu^{3+}] \cdot [\overline{(HA)_2}]^3}{[H^+]^3} \right) \tag{12}$$

The $[Eu^{3+}]$ terms cancel and Equation (10) can be substituted for the monomer K_{ex}^o to yield Equation (13).

$$D = \left(\frac{K_{2.5} \cdot [\overline{(HA)_2}]^3}{[H^+]^3} \cdot \sqrt{\frac{K_2}{[\overline{(HA)_2}]}} \right) + \frac{K_3 \cdot [\overline{(HA)_2}]^3}{[H^+]^3} \tag{13}$$

This equation can be rearranged to form the following linear expression relating D to the square root of the free dimer concentration:

$$D \cdot \frac{[H^+]^3}{[\overline{(HA)_2}]^3} = K_{2.5} \cdot \sqrt{K_2} \cdot \frac{1}{\sqrt{[\overline{(HA)_2}]}} + K_3 \tag{14}$$

A plot of $[(HEH[EHP])_2]^{-1/2}$ vs. $D \cdot [H^+]^3 \cdot [(HEH[EHP])_2]^{-3}$ should produce a straight line with a slope of K_{ex}^o and a y-intercept of K_3. The dimerization constants for HEH[EHP] are unknown for a majority of the diluents tested, as discussed by Kolarik in a recent review of biphasic equilibria on organophosphorus acid extractants.[14] Therefore, this analysis assumes that the extractant is 100% dimerized. To resolve $K_{2.5}$ and K_2 will require an independent method for determining K_2; for the purposes of this report, it is adequate to consider K_{ex}^o as a composite equilibrium constant. The resolved values of K_3 and the combined constant K_{ex}^o are shown in columns 3 and 4 of Table 2.

Europium luminescence

The europium (III) luminescence spectra of the Eu-HEH[EHP] complexes in *n*-octane and toluene are shown in Figure 3. These spectra are nearly identical and therefore do not provide clear evidence for a change in the first coordination environment of the Eu^{3+} with diluent. If there was a significant variation in the symmetry within the primary coordination sphere, it would be expected that the hypersensitive transition at 618 nm would be altered ($D_0 \rightarrow F_2$).[15] Notably however, the $D_0 \rightarrow F_0$ transition for the Eu-HEH[EHP] complex, shown in the upper-left of Figure 3, has been observed for the first time. To increase the signal to noise ratio, the data shown are the average of ~30 spectra. There appear to be at least three distinct (but very weak) peaks; at 575.0 nm, 577.5 nm and 581.0 nm. Because the $D_0 \rightarrow F_0$ transition is non-degenerate, each peak corresponds to a separate symmetry group around the metal center.[15] Additionally, due to the low intensity of the peaks, it can be argued that the ligands are arranging themselves such that the Eu^{3+} metal ion is probably located at an inversion center.

Discussion

Linear Gibbs energy correlations

It is often instructive to establish a relationship between assemblies of thermodynamic data through a comparison of the Gibbs energy that describes the overall reaction. Such "Linear Free Energy Relationships" have been employed with useful results in several correlations of lanthanide data.[1,16]
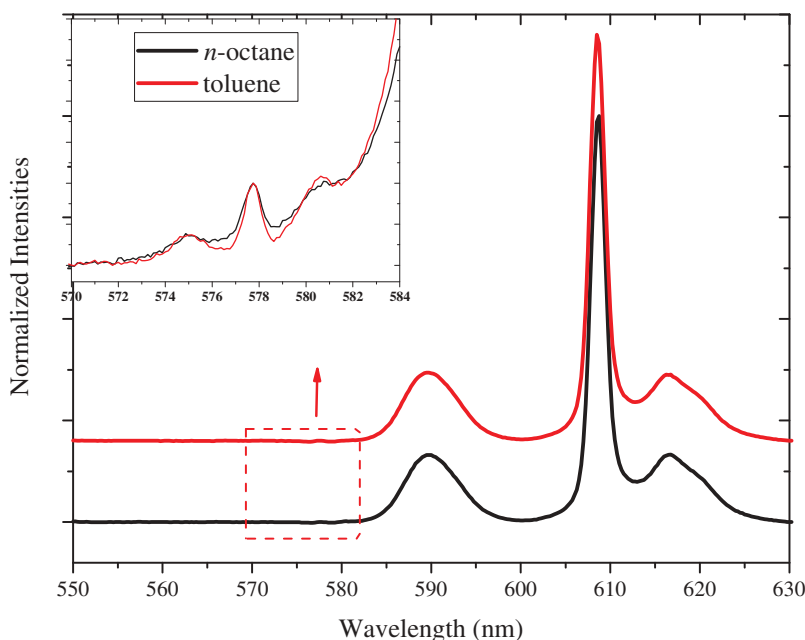
Figure 3. Normalized (at 590 nm) luminescence spectra of approx. 1.2 mmol.L^{-1} Eu^{3+} extracted by 0.05 mol.L^{-1} HEH[EHP] in two diluents (octane-black and toluene-red). Insert depicts the $^5D_0 \rightarrow {}^7F_0$ transition, normalized to the peak at 577 nm.

In this investigation, it is of interest to compare the present results with the results reported by Kolarik on dioctyl phosphoric acid extraction into various diluents. The DOP results overlap with this study on the eleven diluents common to the two studies (the aqueous media differ somewhat: 0.1 mol·L^{-1} vs. 1.0 mol·L^{-1} nitrate media). The linear correlation is acceptable for the more common diluents, deviating most significantly for chloroform and nitrobenzene (Figure 4(a)). Overall, the general consistency between these similar systems suggests that indeed the diluent is not "inert", but rather has a more-or-less predictable effect on the thermodynamics of europium extraction from nitrate media by organophosphorus cation exchanging extractants. In Figure 4(b) a linear correlation between the extraction equilibrium constants describing the extraction of Eu^{3+} as Eu(A)$_3$·(HA)$_3$ and Eu(A)$_3$·(HA)$_2$ by HEH[EHP] in 13 diluents establishes probable kinship between the complexes and again the integral role played by the diluent in the extraction strength. In each plot, the strongest extraction is into the aliphatic diluents, weakest into aromatic diluents.

In Figure 5, the correlation between the free energy of extraction (based on K$_{ex}^o$) and the average HEH[EHP]:Eu apparent stoichiometry in the average extracted complex can be seen. With a few exceptions, the relationship between the increase in the average number of coordinated extractant "dimer equivalents" and the decreasing overall favorability of the phase transfer equilibrium (increasingly positive ΔG$_{ex}$) is generally inversely proportional. Chloroform is notably the weakest system; extracted complexes in nitrobenzene and chlorobenzene exhibit reduced extraction strength relative to the average trend while the tetralin system may exhibit enhanced extraction relative to the average.

Correlation with Hildebrand Solubility Parameter

An investigation of diluent effects in solvent extraction would not be complete without considering the intrinsic "solvating properties" of the diluent. Hildebrand parameters taken from the literature[17] or calculated based on information from the CRC Handbook[18] are compared with log K$_{ex}^o$ data (Table 2) and the average extractant stoichiometry (Table 1) in Figure 6. Panel (a) reveals a systematic inverse trend between the Hildebrand parameter and the extraction
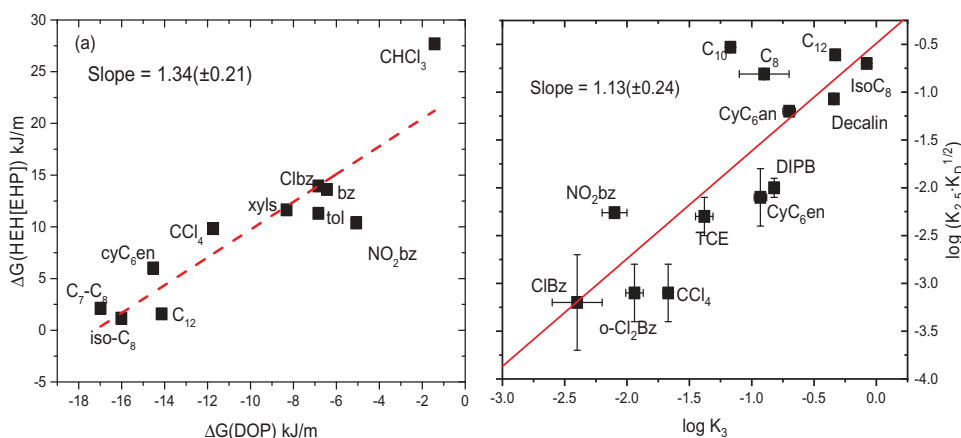
Figure 4. Linear Gibbs energy plots of Eu^{3+} extraction equilibrium data. a) Correlation between the Gibbs energy of extraction of Eu^{3+} by dioctyl phosphoric acid (DOP) and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) in various diluents. b) Correlation between the extraction equilibrium constants describing partitioning of $Eu(A)_3 \cdot (HA)_3$ and $Eu(A)_3 \cdot (HA)_2$ (where HA is HEH[EHP]) into various diluents.
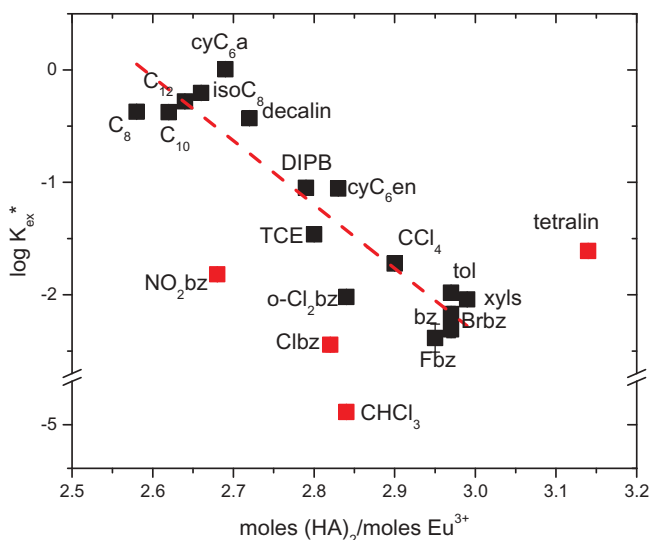
Figure 5. Correlation of average extractant dimer:metal ion stoichiometry with the Gibbs energy of extraction.

equilibrium constant, i.e., stronger solvation parameter correlated with weaker extraction of Eu^{3+}. Panel (b) appears to demonstrate a somewhat complex pattern of stoichiometry with the solubility parameter and a differentiation between two "families" of diluents. Chloroform, decalin, tetralin and nitrobenzene tend to exhibit independent patterns of behavior. It is clear that the Hildebrand parameters correlate in a complex fashion with the thermodynamic parameters and extracted complex stoichiometry, but the nature of the correlation is not clear at this time.
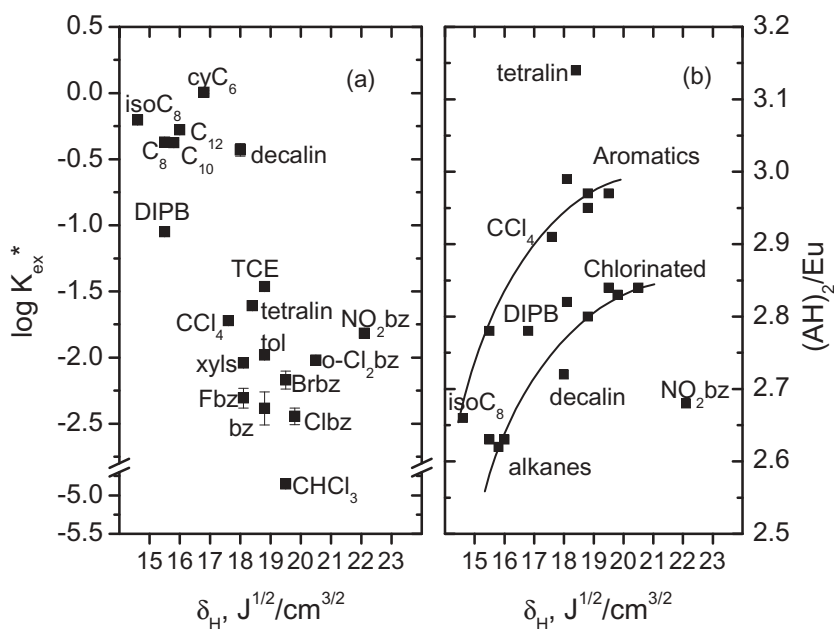
Figure 6. Correlations of Eu-HEH[EHP] extraction equilibrium constants (a) and apparent extracted complex stoichiometry with Hildebrand solubility parameters (b) (lines are to guide the eye).

Interpretation of the luminescence data

The luminescence spectra of Eu-HEH[EHP] complexes in the two extremes of the diluent effect, toluene and *n*-octane, were taken to assess potential variation in the Eu-O bonding stoichiometry of the first coordination sphere of the europium. The spectra were identical suggesting that the diluent does not directly influence the primary coordination sphere of the metal center. However, these spectra do not eliminate the possibility of changes in the extractant dependency/stoichiometry further from the metal center, for example, in the "outer" coordination sphere. To accomplish such a variation of stoichiometry, a protonated HA can hydrogen bond through the hydroxyl proton to the unpaired electrons of any oxygen atom in the metal complex.

Because the $D_0 \rightarrow F_0$ is a non-degenerate transition, the number of peaks in the transition should correspond to the number of individual symmetry environments in the metal-ligand complex. This transition should be disallowed in a formally octahedral environment, which is near to the predicted symmetry of the Eu-HEH[EHP] 1:3 dimers complex. One possible explanation for the appearance of these weak peaks is that only the Eu-O contact in EuA_3 has an influence on the spectra through a pseudo-octahedral environment. To achieve a pseudo-octahedral environment, two different binding modes of the HEH[EHP] can be considered.

The first is the ionic binding of Eu^{3+}–O-P. The second one is an ion-dipole interaction between Eu^{3+} and the phosphoryl group (Eu–:O = P). This binding mode is theoretically possible with both *Eu-A*$^-$ and *Eu-HA*, as depicted in Figure 7. In this case, the metal ion acts as a Lewis acid and the phosphoryl oxygen as Lewis base, which induces localized polarity in the bond. The suggested highly symmetrical environment is consistent with the low intensity (~ 0.1% of the 620 nm peak) of the $D_0 \rightarrow F_0$ transition. Assuming the two binding methods are inequivalent, there are three possible symmetry environments in the first coordination sphere, the *fac, Δ-mer* and *Λ-mer* orientations.
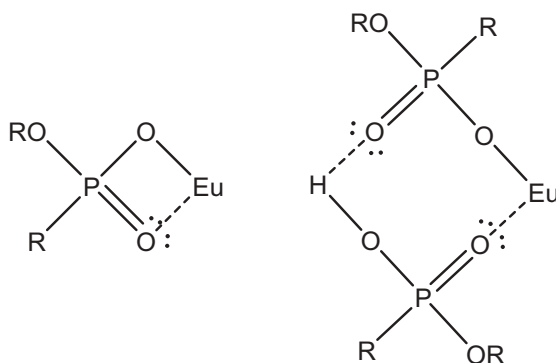
Figure 7. Possible Lewis interactions to achieve a pseudo-octahedral symmetry around the Eu^{3+} center. In the left structure, the phosphoryl oxygen of the deprotonated ligand act as a Lewis base. In the right the phosphoryl oxygen of the protonated ligand in the hydrogen bonded dimer acts as a Lewis base.

Conclusions

The effect of the organic diluent on the extraction of Eu^{3+} by HEH[EHP] has been characterized in 20 organic diluents with various functional groups, dielectric constant, polarizability, shape, and size. It appears that the number of extractant molecules in the complex changes, while the number of protons exchanged for the Eu^{3+} remains constant at three. This suggests that the number of protonated "adduct" ligands in the complex varies with diluent, from 2 in aliphatic diluents to 3 in aromatic diluents, but apparently exhibiting continuous variation in the two stoichiometries. The Eu^{3+} luminescence spectra do not show clear evidence for a change in the first coordination sphere of the metal center, which suggests that any change in stoichiometry may not involve the primary solvation sphere of the metal ion. The K_{ex} value generally decreases as the number of protonated extractants in the complex increases, suggesting reduced metal-ligand complex strength with increased inter-extractant hydrogen bonding.

There are many aspects of solvent extraction chemistry that were not taken into account in this work. For example, the dimerization of the extractant likely changes with the diluent. The interfacial behavior, pK_a, and the amount of water solubilized in the organic phase are all diluent-dependent and potentially will affect the extraction and dimerization equilibria. More studies to determine these and other organic phase parameters in a large variety of diluents and in other classes of extractants would greatly assist in defining more precisely the origins of the diluent effect.

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