Determination by Ion Exchange of the Complexation of Europium by a Stibine, an Arsine, and Perchlorate in Anhydrous Aprotic Organic Solvents

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It has been shown for the first time that a lanthanide (Eu^{3+}) can be complexed by a stibine or a neutral arsine. In benzonitrile (PhCN) as the solvent the predominant complexes were (1) $[Eu(Ph_3Sb)_z]^{3+}$ with triphenylstibine at a concentration of 0.003 mol dm^{-3}, (2) $[Eu(Ph_3As)_y(ClO_4)]^{2+}$ with triphenylarsine at 0.07 mol dm^{-3}, and (3) $[Eu(Ph_3As)_x(ClO_4)_2]^+$ with Ph_3As at 0.003 mol dm^{-3}. In pure PhCN, neutral and/or negative complexes of Eu^{3+} with ClO_4^- were found, but in pure dimethyl sulphoxide no complexation was detected. All complexes were determined by an ion-exchange technique employing the macroreticular resin Amberlyst 15.

Schumann and co-workers[1,2] have prepared salts of $AsPh_2H$ and $AsBu^t_2H$ with lanthanide–arsenic bonds, but complexes of the neutral trialkyl- or triaryl-arsines have not been reported nor have any complexes with monodentate stibines. In a preliminary account of the present work[3] the first complexes of a lanthanide, Eu^{3+}, with a monodentate stibine (triphenylantimony) and with a neutral arsine (triphenylarsine) were reported.

Higher oxidation states of transition metals (such as Ni^{III}) are known to complex arsines better than stibines.[4] In contrast, we have found that triphenyl*antimony* (Ph_3Sb) complexes more strongly than triphenyl*arsine* (Ph_3As) to Eu^{3+}. Also, in general, lanthanides prefer oxygen and nitrogen donors to those of arsenic and antimony;[5] but, under our experimental conditions, Eu^{3+} prefers Ph_3As and Ph_3Sb bonding over that of benzonitrile (PhCN) or of perchlorate. On the other hand, we found Eu^{3+} does not complex with ClO_4^- in dimethyl sulphoxide (Me_2SO). This difference in behaviour in the two solvents is not unexpected, since Me_2SO solvates[6–8] cations more strongly than water, whereas PhCN solvates them more weakly.

Experimental

Anhydrous PhCN (>99%, water <0.005%), Me_2SO (>99%, water <0.005%), Ph_3As (97%), Ph_3Sb (97%), and $Ba(ClO_4)_2$ (99%) were obtained from Aldrich. Caesium perchlorate (99.9%) was obtained from Alpha. Amberlyst 15 resin in the hydrogen form was supplied by Rohm and Haas. The resin was converted into the caesium form by washing with caesium hydroxide until the washings were alkaline and then with water until the washings were neutral. As a final test for total displacement of the H^+ ions by Cs^+, a solution of caesium chloride was run through the resin. These washings were also neutral. The barium form of the resin was made by washing with a basic solution of the chloride ($NH_4OH–BaCl_2$) until the washings were alkaline, then with water until neutral. Finally a solution of $BaCl_2$ was run through the resin to test that all H^+ ions had been displaced by Ba^{2+}. These washings were also neutral. The barium and caesium forms of the resin were dried in a vacuum at ≈50 °C prior to use. Amberlyst 15 is a sulphonic acid-type macroreticular resin. It has a rigid, non-swelling, styrene–divinylbenzene structure with a large average pore[9] diameter of 288 Å. Because of the large pore size coupled with a rigid network structure, we assume in our experimental procedures and calculations that the solution 'inside' the resin is identical to the solution 'outside' the resin.† This assumption is supported by the results of Pfrepper[10] on macroporous resins. The tracer employed, a mixture of ^{152}Eu ($T_{\frac{1}{2}}$ = 13.2 a) and ^{154}Eu ($T_{\frac{1}{2}}$ = 8.55 a), was produced in the Oak Ridge High Flux Isotope Reactor. All experiments were carried out at room temperature under an argon atmosphere with moisture content of less than 10 p.p.m.

In all experiments the $Ba(ClO_4)_2$ or $CsClO_4$ concentration was varied between ≈0.03 and ≈0.06 mol dm^{-3}. Solutions (750 μl) containing the solvent (PhCN or Me_2SO), tracer, barium or caesium perchlorate, and (where noted) Ph_3As or Ph_3Sb were first equilibrated by vibrating vigorously with a Thermolyne Maxi Mix for several hours. Then the solutions were shaken in the same manner with a weighed (≈50 mg) amount of Amberlyst 15 resin. For $Ba(ClO_4)_2$ solutions in Me_2SO, our shaking tests with the resin show the same slope and log D_{Eu} values for equilibration times of 17 [Figure 1(*a*)], 25, and 45 h. Seventeen hours are therefore sufficient for the europium tracer to reach equilibrium in the resin with $Ba(ClO_4)_2$ as the bulk electrolyte in Me_2SO. A similar time was found to be sufficient for $CsClO_4$ in Me_2SO. Checks with the europium tracer *vs.* $Ba(ClO_4)_2$ in PhCN solutions showed that a resin equilibration time of 24 h for the complexation studies with Ph_3As and Ph_3Sb was more than sufficient. After equilibration, aliquots of 500 μl of the solution phase were counted. Also the original tube containing the remaining 250 μl of solution and the equilibrated resin was counted. The counts attributable to the 250 μl of solution remaining in the original tube with the resin were subtracted from the total to obtain the counts attributable to the Eu^{3+} actually bound to the sulphonate sites of the macroporous resin itself. All samples were counted on a Hewlett-Packard 500C auto-gamma counter to 1% statistical accuracy. The parameter D_{Eu}, as calculated from these measurements, is defined[11] as (counts Eu per gram of dry resin)/(counts Eu per cm^3 of solution).

Results and Discussion

Ion Exchange.—Theory. The ion-exchange equilibrium[3,12–14] between a bulk displaceable ion, A^{a+}, and a radioactive tracer

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† Our model for macroreticular resins differs from the one usually applied to gel-type resins where a non-porous, elastic matrix contains the imbibed internal solution in equilibrium with the external solution.[8]

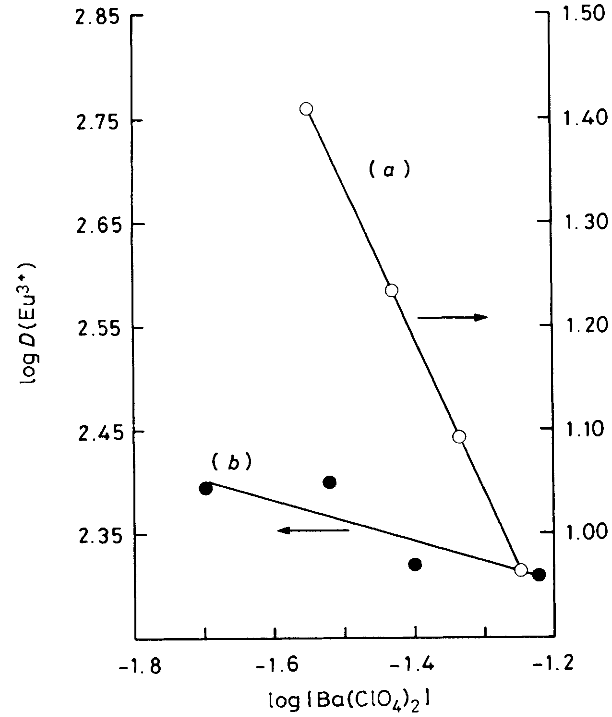

Figure 1. Exchange of Eu^{3+} *vs.* Ba^{2+} in (*a*) Me_2SO and (*b*) PhCN

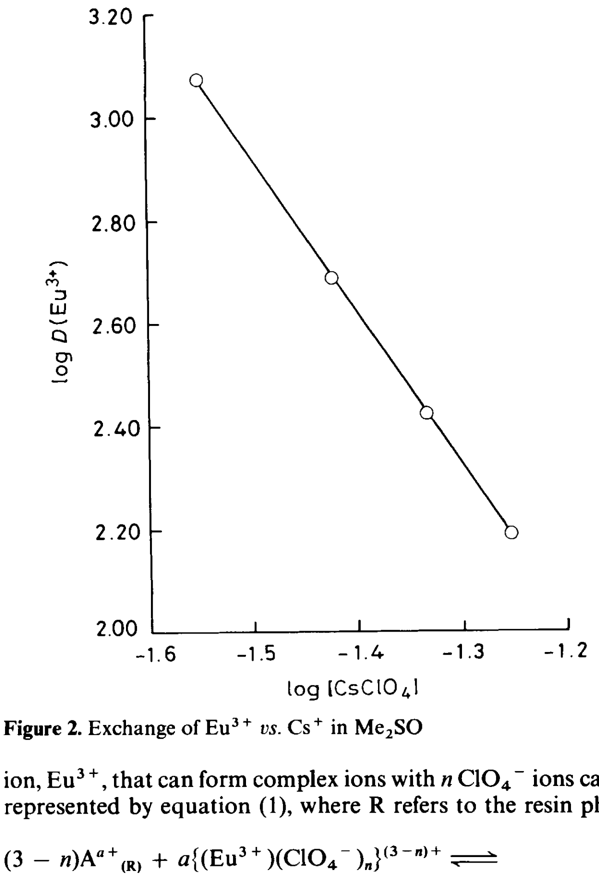

Figure 2. Exchange of Eu^{3+} *vs.* Cs^+ in Me_2SO

ion, Eu^{3+}, that can form complex ions with n ClO_4^- ions can be represented by equation (1), where R refers to the resin phase.

$$(3-n)A^{a+}_{(R)} + a\{(Eu^{3+})(ClO_4^-)_n\}^{(3-n)+} \rightleftharpoons a\{(Eu^{3+})(ClO_4^-)_n\}^{(3-n)+}_{(R)} + \cdots + (3-n)A^{a+} \qquad (1)$$

For convenience, we rewrite equation (1) as (2) where $b = 3 - n$

$$bA^{a+}_{(R)} + aB^{b+} \rightleftharpoons aB^{b+}_{(R)} + bA^{a+} \qquad (2)$$

and $B = \{(Eu^{3+})(ClO_4^-)_n\}$. From the law of mass action, the equilibrium constant for the reaction written in terms of molarities and activity coefficients is $K_{AB} = [(c_{B(R)})^a(c_A)^b/(c_B)^a(c_{A(R)})^b](\gamma^a_{B(R)}\gamma^b_A/\gamma^a_B\gamma^b_{A(R)})$. Following the usual conventions,[13] we define $D_B = c_{B(R)}/c_B$ and $\Gamma_{AB} = (\gamma_{B(R)}/\gamma_B)^a(\gamma_A/\gamma_{A(R)})^b$. Then $D^a_B = K_{AB}(\Gamma_{AB})^{-1}(c_{A(R)})^b(c_A)^{-b}$ or equation (3)

$$(d \log D_B)/(d \log c_A) = -(b/a) \qquad (3)$$

can be written if Γ_{AB} and $c_{A(R)}$ are constants. Since B is present only in trace concentrations, the displacement of the bulk ion, A, from the resin is negligible; so $c_{A(R)}$ is a constant. The question of the constancy of Γ_{AB} is determined as part of each experiment.

Returning to equation (1) and specifying for our work that the slope of log D_{Eu} *vs.* log c_A will be $-(3 - n)/a$ if Eu^{3+} is present as a tracer, the bulk displaceable ion (Cs^+ or Ba^{2+}) is uncomplexed by perchlorate, the applicable activity coefficient ratios, Γ_{AB}, are constant, and the formula of the europium complex (of positive charge) is the same on the resin and in the solution.

Results. (*a*) *Dimethyl sulphoxide as solvent.* Our searches in the literature have located no references using equation (3) to study complexation in anhydrous aprotic organic solutions of electrolytes. It was, therefore, desirable to test the applicability of equation (3) in a solvent that inhibits complexation of perchlorate before going on to more complicated cases. Since Me_2SO solvates more strongly than water, europium is unlikely to complex with perchlorate in it and equation (3) should be easy to test. For our first work, then, we exchanged Eu^{3+} with Ba^{2+} [Figure 1(*a*)] and with Cs^+ (Figure 2) in Me_2SO as the solvent. We found, as expected, that equation (3) was applicable.* The plot of log D_{Eu} *vs.* log $[Ba^{2+}]$ [Figure 1(*a*)] gave a slope of -1.49 ($-3/2$) with[15] an R^2 of 0.9986 and *vs.* log $[Cs^+]$ (Figure 2) gave a slope of -2.95 (-3) ($R^2 = 0.9984$), the values expected from equation (3) for an uncomplexed Eu^{3+} ion.

The ideality of these results might be considered unexpected. For example, a 'constant ionic medium' is commonly used in studies[11] of complexation in aqueous solutions in an attempt to keep the activity coefficients of the reacting ions constant. This technique requires a constant concentration of a bulk electrolyte whose concentration is high relative to the reacting ions (whose concentrations vary). Even in aqueous solutions the use of a constant ionic medium is difficult for ion-exchange studies.[11] The 'constant ionic medium' technique is, in general, not applicable to electrolyte solutions in aprotic organic solvents because of solubility limitations. Fortunately, in our work there was no need for it because, in the exchange of Eu^{3+} *vs.* Ba^{2+} and Cs^+ in Me_2SO, the slopes [Figures 1(*a*) and 2] are unaffected by the large changes in ionic strength associated with switching from the 2+ to the 1+ ion as the bulk displaceable electrolyte. The activity coefficient ratios, Γ_{AB}, are constant. Otherwise, the results expected theoretically from equation (3) could not appear in both plots. It is interesting to speculate that this experimentally determined constancy of Γ_{AB} may be connected with the stronger solvation of cations in Me_2SO than in water.[6] Also Me_2SO is larger than the H_2O molecule. Thus electrostatic interactions between the Eu^{3+} and ClO_4^- ions could be smaller and less variable than in water even though the bulk dielectric constant of Me_2SO is not as large. These results, showing no complexation of Eu^{3+} with perchlorate, are encouraging for the use of Me_2SO as an aprotic solvent in searching for new oxidation states of elements available only in trace quantities such as the heavy actinides and light transactinides.[16]

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* The line fitted to the data in all plots was obtained by least squares. As a test of the goodness of fit, we give in the text the coefficient[15] of determination, R^2, for each plot.

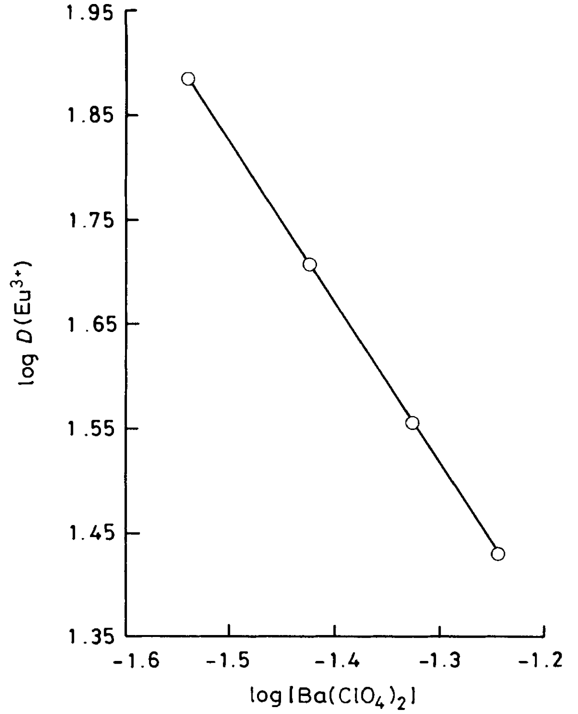

Figure 3. Exchange of Eu^{3+} *vs.* Ba^{2+} in benzonitrile with triphenylstibine added to a concentration of 0.003 mol dm^{-3}

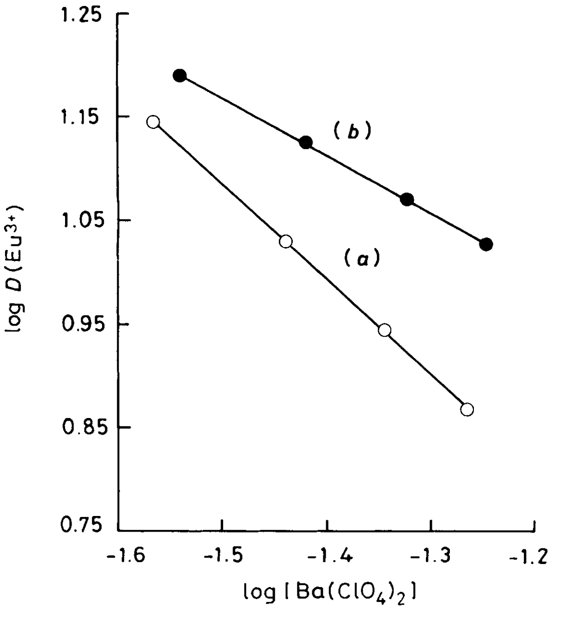

Figure 4. Exchange of Eu^{3+} *vs.* Ba^{2+} in benzonitrile with triphenylarsine added to a concentration of (*a*) 0.07 and (*b*) 0.003 mol dm^{-3}

(*b*) *Triphenylantimony and triphenylarsenic in* PhCN *as solvent.* We next studied the bonding of Ph$_3$Sb and Ph$_3$As to Eu^{3+}. The basic idea was to use PhCN, a solvent in which Eu^{3+} would complex with some number, n, of perchlorate ions to give a complex of charge $3 - n$, where the charge might be positive, neutral, or negative. Then, through the addition of Ph$_3$Sb and Ph$_3$As to the PhCN solvent, the ClO$_4^-$ ions could be displaced with these neutral molecules thus changing n and the charge. The changes in charge would be detected by ion exchange using equation (3). The choice of PhCN as the solvent for these experiments was based on spectroscopic evidence that Eu^{3+} forms inner-sphere complexes with ClO$_4^-$ ions in acetonitrile,[17,18] (MeCN), but not[19] in Me$_2$SO. We also made use of the order of cation solvation developed by Parker[6] from a survey of thermodynamic and kinetic studies of electrolyte solutions in a number of solvents. In Parker's list the strength of solvation decreases from Me$_2$SO (highest) to water (about 1/3 down) to MeCN > PhCN (next to lowest). Since MeCN allows complexation of ClO$_4^-$ with Eu^{3+}, the similar PhCN will also. We chose PhCN over MeCN as a solvent for ClO$_4^-$ complexation because its high boiling point makes the experiments more precise and convenient to carry out.

Bonding of triphenylantimony and triphenylarsenic to Eu^{3+}. On the basis of Parker's survey,[6] as noted above, we know that ClO$_4^-$ ions will bond to Eu^{3+} in pure MeCN and therefore in pure PhCN. But, as seen in Figure 3, a slope of -1.53 ($-3/2$) ($R^2 = 0.9986$) was obtained for log D_{Eu} *vs.* log[Ba^{2+}] in a 0.003 mol dm^{-3} solution of Ph$_3$Sb in PhCN. In this solvent, as in Me$_2$SO, the slope indicates the full 3+ charge of Eu^{3+}, so no ClO$_4^-$ ions are bound to it. The Ph$_3$Sb must have displaced all of the ClO$_4^-$ ions and be bound to the Eu^{3+} in their places. We therefore propose that the predominant ion in this medium is [Eu(Ph$_3$Sb)$_Z$]$^{3+}$. This explanation is confirmed by the results of experiments using PhCN solutions of two different concentrations of Ph$_3$As instead of Ph$_3$Sb. The Ph$_3$As bonds less strongly than the stibine, so it is not able to displace all of the ClO$_4^-$ ions from the Eu^{3+} and a charge different from 3+ is left on the complex ion. This effect is seen in Figure 4(*a*), where the slope for the exchange of europium *vs.* Ba^{2+} in a 0.07 mol dm^{-3} Ph$_3$As solution in PhCN is -0.92 ($\approx -2/2$) ($R^2 = 0.9984$). The slope of close to -1 shows that the Eu^{3+} complexes with about one perchlorate ion on the average in this solvent to give predominantly a complex of charge 2+. We propose that the predominant ion in this medium is [Eu(Ph$_3$As)$_Y$(ClO$_4$)]$^{2+}$. The correctness of the interpretation that Ph$_3$As is bonding in preference to ClO$_4^-$ was confirmed by reducing the Ph$_3$As concentration to 0.003 mol dm^{-3}. The slope for the exchange of europium *vs.* Ba^{2+} [Figure 4(*b*)] is reduced in this medium to -0.55 ($\approx -1/2$) ($R^2 = 0.9994$). The lower concentration of Ph$_3$As allows two rather than one ClO$_4^-$ ion to be retained on the Eu^{3+} to give predominantly a complex of total charge 1+. We propose in this medium that the predominant complex is [Eu(Ph$_3$As)$_X$(ClO$_4$)$_2$]$^+$.

The above explanation interprets the changes in slope as reflecting changes in the charge of europium complex ions as Ph$_3$As and Ph$_3$Sb displace ClO$_4^-$ ions from the Eu^{3+} central ion. Possible interferences with this explanation could be (1) changes in the activity coefficient ratio, Γ_{AB}, and (2) changes of the charge on the Ba^{2+} bulk displaceable ion through complexation with ClO$_4^-$. Changes in activity coefficients cannot be causing the changes in slope from one experiment to another (Figures 3 and 4), because the solutions only differ by the addition in low concentration of the molecular reagents Ph$_3$As and Ph$_3$Sb which cannot significantly alter either the ionic strength or the bulk dielectric constant of the system. Thus, if any activity coefficient changes occur due to the varying concentration of Ba(ClO$_4$)$_2$ in the plots of Figures 3 and 4 they are the same in all experiments, and the variations in the observed slopes cannot arise from this source. Also it is known that the alkali and alkaline-earth metals do not complex with arsines and stibines.[20] In the experiments in 0.003 mol dm^{-3} Ph$_3$Sb in PhCN the slope is $-3/2$ showing that neither the europium nor the barium ions are complexing with ClO$_4^-$ ions. (It would be fortuitous indeed to have both the europium and barium complex with ClO$_4^-$ in just the right amounts to give the theoretical slope for the bare ions.) Since the arsines and stibines have no effect on the Ba^{2+}, the fact that barium is not complexed by ClO$_4^-$ in 0.003 mol dm^{-3} Ph$_3$Sb means that it is not complexed by ClO$_4^-$ in any of the above experiments in PhCN and thus retains a charge of 2+ throughout. These explanations demonstrate that ion-exchange techniques have a high enough resolution to show unequivocally that Eu^{3+} bonds with the arsine and the stibine. On the other hand, the resolution may not be high enough to determine all the species that are present. In two of the three cases we have proposed simplistically that the Eu^{3+} was present predominantly in a species indicated by a theoretical slope that is near but is not exactly equal to the experimental one. In reality the solutions may be more complicated. Other species possibly present in lesser amounts can be sought by spectroscopic methods capable of supplying greater detail than ion exchange such as those applied by Bünzli and co-workers.[17,18] Unlike ion-exchange, such methods cannot, in general, be applied at the few atoms level required in certain areas of interest such as transeinsteinium chemistry.

(*c*) *Benzonitrile as the solvent.* We also carried out exchange of europium *vs.* Ba^{2+} in pure PhCN. The complexation number, *n*, of ClO_4^- with europium should equal at least two in the pure solvent since that is the value achieved with 0.003 mol dm^{-3} Ph_3As present. Additional ClO_4^- ions could bind to the Eu^{3+} in pure PhCN, however, yielding neutral or even negatively charged complexes. The results of the ion exchange of europium *vs.* barium perchlorate in pure PhCN are given in Figure 1(*b*). Although the least-squares fit is not good ($R^2 = 0.7240$) the slope of near zero makes it tempting to suggest that the europium is complexed by nearly three ClO_4^- ions[3] giving a nearly neutral complex. This interpretation, based on the idea that europium is exchanging with barium according to equation (1), does not appear to be correct, however, because the distribution coefficient is around 200 (over 90% of the europium went into the resin). Since the exchange of europium complexes with a positive charge *vs.* barium results in much lower distribution coefficients (of around 8—80), we must look to a mechanism other than ion exchange to explain the presence of europium in the resin. This mechanism can be seen in a discovery made by Kraus *et al.*[21]

Work of Kraus *et al.*[21] leads us to the conclusion that in pure PhCN neutral and/or negatively charged complex ions of europium with perchlorate are invading the Amberlyst 15 ion exchanger by interacting with the organic network of the resin. In aqueous solutions, using a gel type, strongly acidic, *cation*-exchange resin with a polystyrene–divinylbenzene network (Dowex-50), Kraus *et al.*[21] found that *anionic* complexes of Au^{III}, Fe^{III}, and Ga^{III} had distribution coefficients of approximately 10^2 in HCl solutions and approximately 10^5 in LiCl solutions. They explained these large distribution coefficients for the seeming exchange of anions into a cation exchanger as actually arising from interactions of the anions with the organic network of the ion exchanger leading to their invasion. Their interpretation was subsequently proven in extensive studies by Pfrepper[10,22,23] who used several different ion exchangers including macroporous polystyrene–divinylbenzene-based resins without functional groups. The discovery of anion invasion into cation exchangers by Kraus *et al.* has been employed over the years in a number of practical applications[24,25] with several resins including Nafion 117.[26]

Since anions can invade the polystyrene–divinylbenzene matrix of cation exchangers in aqueous electrolyte solutions, it is even more likely that neutral and anionic species can invade in organic electrolyte solutions. The correspondence between our results [Figure 1(*b*)] and those of Kraus suggests strongly that neutral and/or anionic complexes of europium with perchlorate that are present in the PhCN–$Ba(ClO_4)_2$ solutions invade the organic network of the Amberlyst 15 to give a distribution coefficient of around 200. We therefore propose that the principal species present are $[Eu(ClO_4)_n]^{3-n}$ where $n \geqslant 3$.

Acknowledgements

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