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Mixed Complexes in the System Eu^{3+}–8-Quinolinol–Phenanthroline

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ABSTRACT

The extraction of Eu^{3+} from an aqueous perchlorate medium of constant ionic strength (0.1 M $NaClO_4$) was studied at different temperatures by 8-quinolinol (HQ) in benzene, carbon tetrachloride, and chloroform, and by a mixture of 8-quinolinol and 1,10-phenanthroline (Phen), allowing for elucidation of the thermodynamic parameters and the mechanism of extraction of the species formed. The results indicated that the extraction is enhanced by adduct formation in the organic phase, and that the main extracted species were $EuQ_3 \cdot 2HQ$, $EuQ_3 \cdot 2HQ \cdot Phen$, and $EuQ_3 \cdot 2HQ \cdot 2Phen$.

INTRODUCTION

8-Hydroxyquinoline and its derivatives have long been established as potential antimicrobial agents and drugs. It is a well-established fact that the activity of a drug increases when it is administered in the form of a metal complex. The role of mixed ligand complexes in biological processes has been well recognized, and many attempts have been made to correlate the stability of metal ligand complexes with their antimicrobial activity (1). Besides its importance in medicine, 8-hydroxyquinoline has proved to be an effective ex-

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tractant for various metal ions and can be used in the nuclear fuel industry for the separation of several metal ions (2–4).

The separation of individual lanthanides and the separation of lanthanides from thorium and uranium are still very interesting and formidable problems. The solvent extraction of Gd(III) and Tb(III) by 8-hydroxyquinoline in chloroform from the aqueous phase has been investigated. The equilibrium constants and stability constants of $GdOx_3$, $GdOx_3 \cdot HOx$, and $TbOx_3$ have been evaluated (5). Studies on the extraction of lanthanide complexes with 8-hydroxyquinoline in chloroform from the aqueous methanol phase have been carried out (6, 7). Equilibrium constants have been evaluated, and the separation factors between adjacent lanthanides as a function of the atomic number in the Sm–Yb range were discussed (6). In the presence of methanol, lanthanides were extracted as solvates $LnOx_3 \cdot 2MeOH$ whereas La(III) was the self-adduct $LaOx_3 \cdot HOx$ (7). A synergic effect was observed in the case of the extraction of Dy(III), Er(III), and Yb(III) from the aqueous methanol phase with 8-quinolinol in chloroform. The formation of solvates $LnOx_3 \cdot (MeOH)_2$ was probably the main reason for the synergic effect (8). The solvent extraction of Pr(III) and Gd(III) by 8-quinolinol in chloroform from the water–ethanol phase has been studied as a function of the pH of the polar phase and the concentration of HOx or ethanol in the organic phase. It was stated that the presence of ethanol in the polar phase also evokes a synergistic effect (9).

Freiser and others (10, 11) studied the mixed ligand chelate extraction of lanthanide ions with some 8-quinolinol derivatives combined with 1,10-phenanthroline (Phen). A detailed study on the equilibrium extraction behavior of a series of representative trivalent lanthanide ions, La, Pr, Eu, Ho, and Yb, into chloroform solutions containing either 8-quinolinol (HQ) alone or mixed with Phen was carried out (12). The results demonstrated that except for La, which was extracted as a simple chelate LaQ_3, the lanthanides extracted in the form of self-adduct complexes $LnQ_3 \cdot 2HQ$ and at higher HQ concentrations $LnQ_3 \cdot 3HQ$. In the presence of Phen, mixed ligand complexes of the type $LnQ_3 \cdot 2HQ \cdot Phen$ were formed. The extraction of mixed ligand complexes of Pr(III) with 8-quinolinol and Phen or 2,2-dipyridyl into molten naphthalene was investigated in terms of various parameters. Enhancement in the extractability of Pr(III) due to the formation of mixed ligand complexes was noticed (13). The extraction of Eu(III) by HQ, diethylhexyl phosphoric acid (HDEHP), and their mixture in benzene from phosphoric acid solutions was investigated. The stoichiometry of the extracted species was found to be $Eu(DEHP)_3 \cdot (HDEHP)_3$, $EuH_2PO_4(Q)_2$, and $EuH_2PO_4(Q)_2 \cdot 3(HDEHP)_2$ (14).

Temperature is the most important factor in exploring the mechanism of the formation and structure of the synergistic adduct. For this work a thermody-

namic study of the Eu–HQ–Phen system was performed in order to elucidate the chemical formula and the mechanism of formation of the extracted species.

EXPERIMENTAL

8-Hydroxyquinoline (HQ) 1,10-phenanthroline (Phen), and other chemicals and reagents used in this work were of A.R. grade. The radioactive tracer $^{152,154}Eu$ was prepared by thermal neutron irradiation of the oxide which was then dissolved in HCl and transferred to the perchlorate form by successive evaporation and dissolution in dilute $HClO_4$.

The solvent extraction experiments were performed by shaking an aqueous solution (0.1 M $NaClO_4$, pH 3.9) containing the radioactive tracer with an equal volume of the organic solution in a thermostated water bath until equilibrium was attained. After phase separation, equal volumes, 2 mL, were carefully withdrawn from each phase for radiometric assay.

$$\text{Distribution ratio } D = [M]_{org}/[M]_{aq}$$

The metal concentration [M] is expressed in terms of the radioactivity of the isotope per 2 mL of each phase. The error in D does not exceed $\pm$ 3%.

Thermodynamic studies were carried out by making use of the temperature gradient method in which the equilibrium constant, K, of the reaction is measured at various temperatures.

The enthalpy change, ΔH, is measured from the slope of the plot of log K versus $1/T$ where

$$\log K = -\Delta H/2.303RT$$

The change in free energy, ΔG, is measured in terms of the equilibrium constant K:

$$\Delta G = -RT \ln K$$

where R is the gas constant

T is the absolute temperature (standard state = 298 K)

The relation between ΔG and ΔH is given by

$$\Delta G = \Delta H - T\Delta S$$

where ΔS is the entropy change of the reaction.

RESULTS AND DISCUSSION

A study of the extraction of Eu^{3+} by 0.1 M HQ in benzene from an aqueous phase of 0.1 M $NaClO_4$ at varying pH values gave a slope of 3, indicating the release of 3 hydrogen ions during the chelation process.

Figure 1 shows the results of the extraction of Eu^{3+} from an aqueous phase of 0.1 M $NaClO_4$, pH 3.9 by HQ in CCl_4 at temperatures of 12, 25, 35, and 45°C. Figures 2 and 3 are similar studies using benzene and chloroform, respectively. The slope of the straight line is 5, indicating an extraction equilibrium of the type

$$Eu^{3+}_{(a)} + 5HQ_{(o)} \overset{K_1}{\rightleftharpoons} EuQ_3 \cdot 2HQ_{(o)} + 3H^+_{(a)} \qquad (1)$$

where (a) and (o) stand for the aqueous and organic phases, respectively.

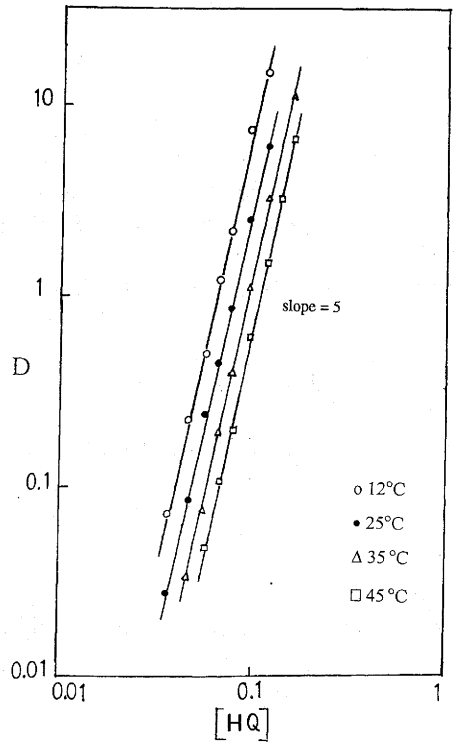

FIG. 1 The extraction of Eu^{3+} by HQ in CCl_4 from 0.1 M $NaClO_4$, pH 3.9 at different temperatures.

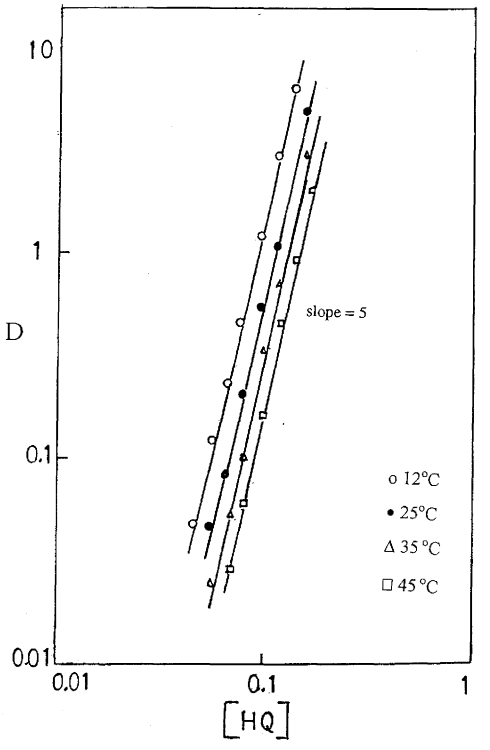

FIG. 2 The extraction of Eu^{3+} by HQ in benzene from 0.1 M $NaClO_4$, pH 3.9 at different temperatures.

Table 1 gives the log K_1 values and the calculated thermodynamic parameters of the free energy, enthalpy, and the entropy changes for the chelation reactions in the three solvents. The bond energies of the $EuQ_3 \cdot 2HQ$ are seen to be stronger than the H_2O—Eu^{3+} bonds because the reaction is exothermic. Breaking of Eu^{3+}—H_2O bonds and the release of water molecules in the dehydration step is an endothermic reaction (+ve ΔH) while formation of Eu^{3+}—HQ bonds is an exothermic reaction (−ve ΔH). The negative enthalpy change, ΔH, of the exothermic reaction indicates that the bonds formed between Eu^{3+} and HQ are stronger than the Eu^{3+}—H_2O bonds. The negative enthalpy thus favors the reaction while the formation of the ordered complex structure leads to the loss of entropy and a negative value for ΔS. It is also obvious that the bond strengths are about equal in the nonpolar solvents benzene and carbon tetrachloride, but are less so with a polar solvent such as chloroform, as is to be expected (15). Comparison with a previous work on the extraction of Eu by HTTA (16) indicates that where a species such as $EuQ_3 \cdot 2HQ$

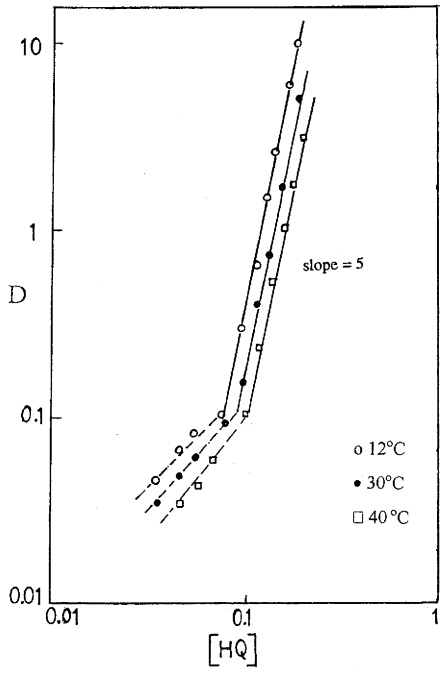

FIG. 3 The extraction of Eu^{3+} by HQ in chloroform from 0.1 M $NaClO_4$, pH 3.9 at different temperatures.

is extracted in benzene, the species $Eu(TTA)_3$ is formed under identical conditions. This means that it is easy for HQ to displace more water from the coordination sphere of the lanthanides than HTTA.

The addition of Phen as a base forms mixed complexes as follows:

$$Eu^{3+}_{(a)} + 5HQ_{(o)} + Phen_{(o)} \overset{K_2}{\rightleftharpoons} EuQ_3 \cdot 2HQ \cdot Phen_{(o)} + 3H^+_{(a)} \qquad (2)$$

TABLE 1
Formation Constants and Thermodynamic Parameters of the Reaction

$$Eu^{3+}_{(a)} + 5HQ_{(o)} \overset{K_1}{\rightleftharpoons} EuQ_3 \cdot 2HQ_{(o)} + 3H^+_{(a)}$$

Solvent	log K_1	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/deg/mol)
CCL_4	-6.14 ± 0.06	35.24	-57.77	-312.10
Benzene	-6.88 ± 0.08	39.46	-48.11	-293.85
Chloroform	-7.38 ± 0.03	42.30	-25.58	-227.77

and

$$Eu^{3+}_{(a)} + 5HQ_{(o)} + 2Phen_{(o)} \overset{K_3}{\rightleftharpoons} EuQ_3 \cdot 2HQ \cdot 2Phen_{(o)} + 3H^+_{(a)} \quad (3)$$

The log D–log[Phen] relations in Figs. 4, 5, and 6 show the distribution of the species formed in the above reactions at various temperatures in the three solvents studied. The log D–pH plot in the presence of constant concentrations of HQ and Phen gave a slope of 3, indicating the release of 3 hydrogen ions. The addition of Phen does not lead to the release of any HQ molecules as is evident from Fig. 7 where a plot of log D versus log[HQ] at constant Phen concentration leads to a slope of 5.

Tables 2 and 3 contain the log K_2 and log K_3 values and the thermodynamic parameters of the above reactions. Log K_3 for chloroform could not be calculated because the dependence at a high Phen concentration is a nonintegral value due to solvent effects (15).

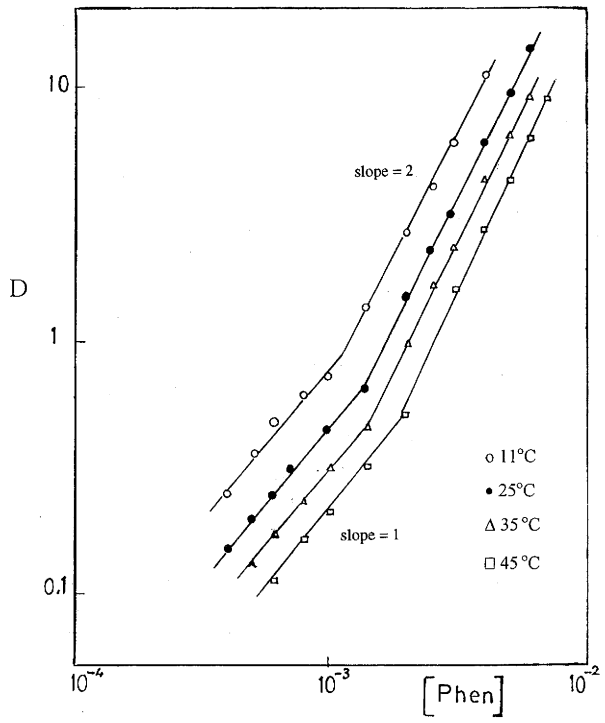

FIG. 4 The effect of Phen concentration on the extraction of Eu^{3+} at constant 0.0464 M HQ in CCl_4 from 0.1 M $NaClO_4$, pH 3.9 at different temperatures.

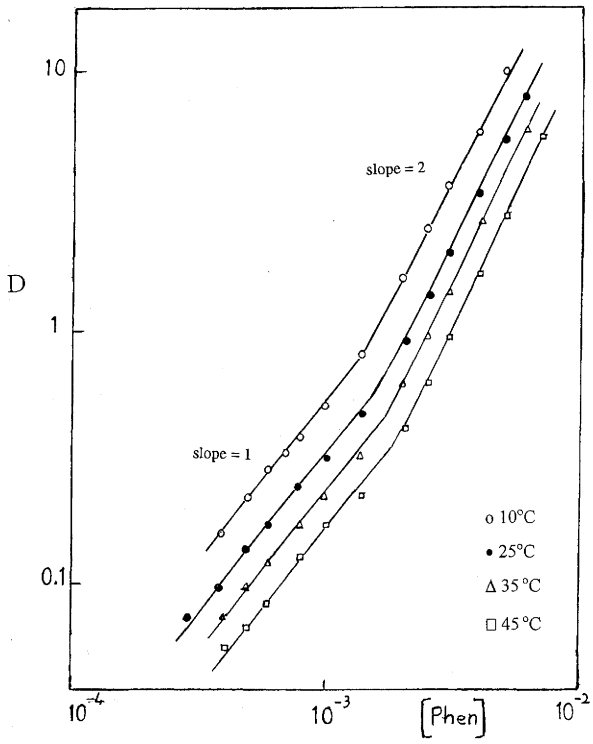

FIG. 5 The effect of Phen concentration on the extraction of Eu^{3+} at constant 0.056 M HQ in benzene from 0.1 M $NaClO_4$, pH 3.9 at different temperatures.

TABLE 2
Formation Constants and Thermodynamic Parameters of the Reaction

$$Eu^{3+}_{(a)} + 5HQ_{(o)} + Phen_{(o)} \overset{K_2}{\rightleftharpoons} EuQ_3 \cdot 2HQ \cdot Phen_{(o)} + 3H^{+}_{(a)}$$

Solvent	log K_2	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/deg/mol)
CCl_4	-2.42 ± 0.03	13.88	-28.28	-143.50
Benzene	-3.00 ± 0.05	17.22	-25.00	-141.66
Chloroform	-5.23 ± 0.04	30.01	-10.20	-134.93

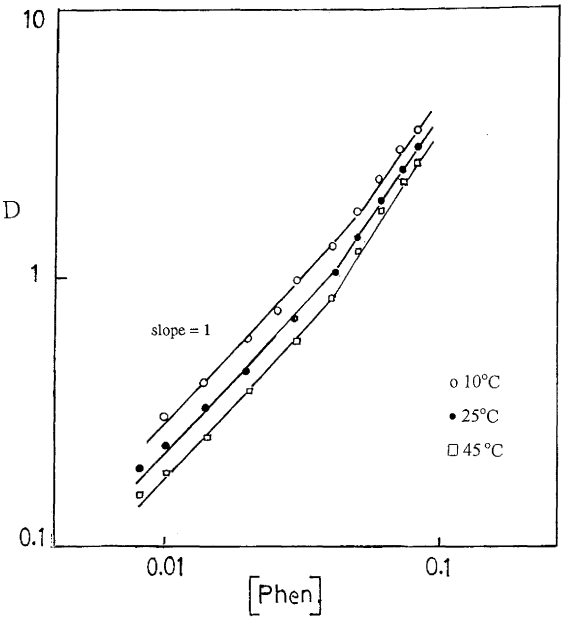

FIG. 6 The effect of Phen concentration on the extraction of Eu^{3+} at constant 0.0964 M HQ in chloroform from 0.1 M $NaClO_4$, pH 3.9 at different temperatures.

The synergistic reactions that occur in the organic phase lead to the formation of $EuQ_3 \cdot 2HQ \cdot Phen$ and $EuQ_3 \cdot 2HQ \cdot 2Phen$:

$$EuQ_3 \cdot 2HQ_{(o)} + Phen_{(o)} \overset{\beta_1}{\rightleftharpoons} EuQ_3 \cdot 2HQ \cdot Phen_{(o)} \tag{4}$$

and

$$EuQ_3 \cdot 2HQ_{(o)} + 2Phen_{(o)} \overset{\beta_2}{\rightleftharpoons} EuQ_3 \cdot 2HQ \cdot 2Phen_{(o)} \tag{5}$$

with $\beta_1 = K_2/K_1$ and $\beta_2 = K_3/K_1$.

TABLE 3
Formation Constants and Thermodynamic Parameters of the Reaction

$$Eu^{3+}_{(a)} + 5HQ_{(o)} + 2Phen_{(o)} \overset{K_3}{\rightleftharpoons} EuQ_3 \cdot 2HQ \cdot 2Phen_{(o)} + 3H^+_{(a)}$$

Solvent	log K_3	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/deg/mol)
CCl_4	0.52 ± 0.03	−2.97	−31.39	−95.39
Benzene	-0.10 ± 0.03	+0.59	−29.09	−99.57

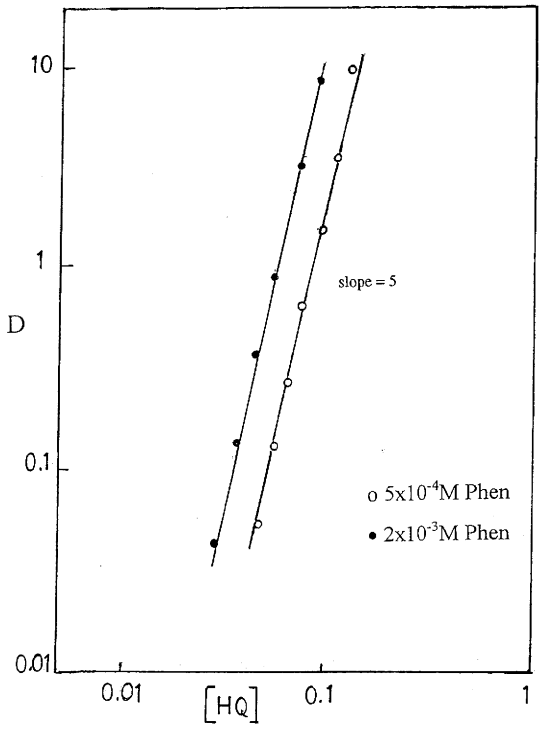

FIG. 7 The extraction of Eu^{3+} by HQ in constant Phen concentration from 0.1 M $NaClO_4$, pH 3.9 at 25°C.

Log β_1, log β_2 values, and the thermodynamic parameters of the above reactions are listed in Table 4.

The extraction of Eu^{3+} by either HTTA or Phen alone was quite low, while the mixture of the two extractants led to a large increase in extraction due to the formation of synergistic adducts between the metal chelate and the neutral donor. The formation of the mixed complex $EuQ_3 \cdot 2HQ \cdot Phen$ corresponds to an enhancement of the extraction by approximately 10^2 ($CHCl_3$) and 10^4 (benzene). This enhancement is increased largely in the formation of $EuQ_3 \cdot 2HQ \cdot 2Phen$.

Thermodynamic studies on the synergistic extraction of lanthanide ions have shown that the mechanism of synergism in this class of ions is replacement of the water molecules in the coordination sphere of the metal, existing as a chelate in the organic phase by a corresponding number of base molecules (17). In benzene and CCl_4 (Figs. 4 and 5) both $EuQ_3 \cdot 2HQ \cdot Phen$ and

TABLE 4
Formation Constants and Thermodynamic Parameters of the Reactions

$$EuQ_3 \cdot 2HQ_{(o)} + Phen_{(o)} \overset{\beta_1}{\rightleftharpoons} EuQ_3 \cdot 2HQ \cdot Phen_{(o)}$$

$$EuQ_3 \cdot 2HQ_{(o)} + 2Phen_{(o)} \overset{\beta_2}{\rightleftharpoons} EuQ_3 \cdot 2HQ \cdot 2Phen_{(o)}$$

Solvent	$\log \beta_1$	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/deg/mol)
CCl_4	3.72 ± 0.07	−21.36	28.89	168.60
Benzene	3.88 ± 0.09	−22.24	23.11	152.19
Chloroform	2.15 ± 0.05	−12.29	15.38	92.84
Solvent	$\log \beta_2$	ΔG	ΔH	ΔS
CCl_4	6.66 ± 0.07	−38.21	26.38	216.71
Benzene	6.78 ± 0.08	−38.87	19.02	194.28

$EuQ_3 \cdot 2HQ \cdot 2Phen$ mixed complexes are formed. The extraction increases with an increase of Phen concentration at low values, and straight lines of slope 1 are obtained, indicating the formation of 1:1 synergistic adducts between the Eu^{3+} chelates and Phen. At higher Phen concentrations, a slope of 2 is obtained, indicating the formation of 1:2 adducts. In chloroform, the species formed is $EuQ_3 \cdot 2HQ \cdot Phen$. At higher Phen concentrations, a slight increase in the slope is observed which does not correspond to slope 2, possibly indicating the formation of a mixture of two adducts. The relatively large solubility of chloroform in H_2O and the difficulty of the dehydration of the species $EuQ_3 \cdot 2HQ \cdot Phen(H_2O)_x$ in the organic phase makes it unfavorable for a species such as $EuQ_3 \cdot 2HQ \cdot 2Phen$ to be formed under the experimental conditions of its formation in other solvents that dissolve H_2O less (15). Complex formation is favored by a negative enthalpy change and a positive entropy change because they both act to decrease the free energy ($\Delta G = \Delta H - T\Delta S$). The formation of both the Phen and 2Phen mixed complexes is seen to be entropy driven and enthalpy opposed. Steric hindrance is seen to play an important role in the formation of Phen mixed complexes. This fact is clear when a comparison is made between ΔS and ΔH in Tables 1 and 4.

Investigation of the Co–HQ–Phen system (18) has shown that the addition of Phen causes destruction of synergism since the coordination number of Co is smaller than that of Eu where Phen has caused synergism when combined with HQ. The undissociated HQ molecule which is not directly bonded to the cobalt ion hindered further addition of Phen.

CONCLUSION

It can be concluded from this work that 8-quinolinol is an effective extractant for Eu^{3+} ions and can displace more water from the coordination sphere of the lanthanide ions than can HTTA. It forms self-adducts of the type $LnQ_3 \cdot 2HQ$ in an exothermic reaction. The addition of phenanthroline enhances the extraction by adduct formation in the organic phase, and the species $EuQ_3 \cdot 2HQ \cdot Phen$ and $EuQ_3 \cdot 2HQ \cdot 2Phen$ are formed is CCl_4 and benzene whereas $EuQ_3 \cdot 2HQ \cdot Phen$ is formed in chloroform due to its large solubility in H_2O.

REFERENCES

1. Y. Anjanyulu, R. Y. Swamy, and R. Prabhakara, *J. Indian Chem. Soc.*, *62*, 346 (1985).
2. D. Czakis-Sulikowska, A. Malinowska, and B. Kuznik, *Chem. Anal. (Warsaw)*, *39*, 475 (1994).
3. M. Borkowski and G. R. Choppin, 5th International Conference on the Chemistry and Migration of Actinides and Fission Products in the Geosphere, Saint-Malo, 10–15 September 1995.
4. S. G. Beheir, M. Aziz, and K. Shakir, *J. Radioanal. Nucl. Chem.*, *207*, 117 (1996).
5. N. Pustelnik and D. Czakis-Sulikowska, *Chem. Anal. (Warsaw)*, *36*, 727 (1991).
6. N. Pustelnik and D. Czakis-Sulikowska, *Ibid.*, *37*, 273 (1992).
7. D. Czakis-Sulikowska, B. Kuznik, A. Malinowska, and U. Kjanowicz, *Ibid.*, *38*, 53 (1993).
8. D. Czakis-Sulikowska, J. Radwanska-Doczekalska, B. Kuznik, and N. Pustelnik, *Ibid.*, *35*, 529 (1990).
9. D. Czakis-Sulikowska and N. Pustelnik, *Ibid.*, *38*, 63 (1993).
10. O. Tochiyama and H. Freiser, *Anal. Chem.*, *53*(6), 874 (1981).
11. E. Yamada and H. Freiser, *Ibid.*, *53*(13), 2115 (1981).
12. T. Hori, M. Kawashima, and H. Freiser, *Sep. Sci. Technol.*, *15*(4), 861 (1980).
13. V. P. Mittal and P. C. Vyas, *Asian J. Chem.*, *4*, 202 (1992).
14. N. Zakareia, S. M. Khalifa, M. Nofal, and H. F. Aly, *Radiochim. Acta*, *47*, 229 (1989).
15. A. T. Kandil and K. Farah, *Ibid.*, *29*, 149 (1981).
16. A. T. Kandil and K. Farah, *J. Inorg. Nucl. Chem.*, *42*, 1491 (1980).
17. A. T. Kandil and K. Farah, *Radiochim. Acta*, *28*, 165 (1981).
18. K. Farah and A. T. Kandil, *J. Radioanal. Nucl. Chem.*, *152*, 461 (1991).

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