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Selective Separation of Lanthanides with Phenolic Resins: Extraction Behavior and Thermal Stability

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ABSTRACT

Catechol, resorcinol, and their admixtures with 8-hydroxyquinoline were converted into polymeric resins by alkaline polycondensation with formaldehyde. The resins were characterized by FTIR spectroscopy, moisture regain, ion-exchange capacity, and distribution coefficient (*D*) for Eu^{3+}. Thermogravimetric analysis of the polymer samples was studied, and the effect of the sorption of metal ions on their thermal stability was evaluated. Complexation of Eu^{3+} to the resins was modeled based on metal ion charge neutralization. The selective uptake of Eu^{3+} from aqueous solutions containing La^{3+} was investigated, and the ionoselectivities of the resins were compared. The incorporation of 8-hydroxyquinoline in the molecular matrix of the phenolic resins is shown to exert a significant influence upon the competitive sorption of La^{3+} and Eu^{3+}, leading to their intragroup separation. The separation factors obtained by phenolic ion-exchange resins from aqueous solutions indicate ion-specific resins can be developed for the specific separation of actinide ions from nuclear waste.

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INTRODUCTION

One of the most critical aspects of the nuclear waste-disposal problem concerns safe long-term storage. Society and the environment need protection from the hazards associated with radioactive waste. The waste products contain a variety of radioactive elements, including long-lived α-emitting actinides that require an extended period of storage. Long-term radiotoxicity of nuclear waste produced during spent nuclear fuel reprocessing can be reduced if the minor actinides (Np, Am, and Cm) contained within the wastes are separated for their subsequent transmutation into short-lived radionuclides or for separate storage. For such a strategy, it is necessary to define minor actinide separation methods. For trivalent actinides Am^{3+} and Cm^{3+}, the main obstacle is separation from the lanthanides which have similar ionic radii (1) and electronic structures (2).

The separations of the actinides ions are based on the small differences in their ionic radii across the series and/or in the stronger interaction of actinides with soft donor ligands like S, Cl, or N (3, 4). Organic ligands containing acidic phenol or carboxyl functional groups are known to complex radionuclides under a variety of conditions (5–8). Such organic ligands can form remarkably stable complexes, compete with inorganic ligands, affect the oxidation and reduction of the actinides, and alter the behavior of the actinides. An improved process for the separation of these ions requires both size-selective complexation and a ligand with the optimum mix of hard and soft donors. Numerous methods based on liquid–liquid extraction (9–11) or solid–liquid extraction (12, 13) have been described for effecting this separation (14, 15).

From the waste management point of view, the most attractive feature of solid–liquid extraction is its ability to partition radioactive elements into two separate components and produce decontaminated effluent suitable for direct disposal. Many studies have pointed out that the use of a mineral matrix (16) constitutes an additional waste. In contrast, organic resins, and especially phenolic resins, can be destroyed with nitric acid, eliminating the need to dispose of the solid separately.

Ion-exchange resins containing phenolic groups are known to possess exceptionally high affinity for Cs^{+} and Sr^{2+} in aqueous radioactive solution (8–19), and their stability to radiolysis has been shown (18). Separation procedures employing ion-exchange resins are frequently made more selective by the addition of complexing agents during sorption or elution. Although the most stable and selective complexes often involve chelating compounds, some of these, because of size and solubility characteristics, are not suitable for the usual ion-exchange techniques. To avoid these difficulties and still take advantage of the selectivity of chelating agents, some resins have been synthesized which incorporate the chelating compound in the structure of the resin itself. Resins made from 8-hydroxyquinoline and phenolic compounds contain both weakly acidic and weakly basic groups. The properties of these resins are expected to be applicable to element separations for actinide-containing waste. To test this hypothesis, initial experiments are performed with Eu^{3+} and La^{3+}. The trivalent lanthanide Eu^{3+} is suitably homologous for the trivalent actinides Am^{3+} and Cm^{3+} (20). If a selectivity is achieved between Eu^{3+} and La^{3+}, further experiments examining the separation of Am^{3+} or Cm^{3+} from lanthanides can be performed with a degree of confidence.

The present article examines Eu^{3+} uptake behavior by synthetic polymers prepared from monomers containing phenolic groups. The influence of 8-hydroxyquinoline introduction in the molecular matrix on intragroup separation is studied. The complexation constants of the resins are then determined, and the thermal behavior of the synthesized resins is studied by thermogravimetry under helium atmosphere.

EXPERIMENTAL

Materials

Chemicals and Reagents. Phenol, resorcinol, catechol, 8-hydroxyquinoline, and formaldehyde (37% aqueous solution) were obtained from Aldrich and used without further purification. The Eu and La nitrate hexahydrate salts used were from Aldrich.

Resins Synthesis. The resins were synthesized by alkaline polycondensation of formaldehyde with phenolic compounds according to Refs. 8 and 19. After curing, the resins were crushed, sieved to from 75 to 180 μm size particle, washed, and conditioned by subjecting them to two 1 N HCl/0.1 N NaOH cycles. The resins were finally converted to acid form and washed thoroughly with water until neutral.

Resins Conversion to Na^+-Form. 0.05 g of H^+-form resin was shaken for 2 hours with 10 mL of 1 M NaOH. The resin was then filtered and washed with water until neutral.

Analytical Section

FTIR Spectroscopy. FTIR spectra were recorded on a 1600 Perkin-Elmer spectrophotometer. The measurements were in the 4000–400 cm^{-1} range with samples in KBr.

Thermal Analysis. Thermogravimetric (TG) measurements were performed under helium atmosphere with a DuPont Instruments TGA 2950 instrument. Resin samples (5–15 mg) were weighted into the thermobalance, and the weight loss was determined as a function of the temperature from 30 to 500°C with a heating rate of $10°C\cdot min^{-1}$.

Resins Characterization

Moisture Regain. This was determined by heating 0.1 g of resin in an air oven at 100°C for 24 hours, the weight loss giving the percentage of water in the resin.

Ion-Exchange Capacity. For determination of total ion-exchange capacity, 0.25 g of resin in the H^+ form of known moisture regain was equilibrated overnight with 50 mL of 0.1 N NaOH solution containing 5% NaCl. The amount of NaOH consumed in the $H^+ \rightarrow Na^+$ exchange was determined by titrating the remaining NaOH in the supernatant with 0.1 M HCl solution.

Solid–Liquid Extraction

As a measure of the resin's affinity for Eu^{3+} and for a comparison between various resins, a standard procedure was followed for the measurement of distribution coefficients, D (mL/$g_{(dry)}$). Batch extraction was performed at room temperature. A known weight of resin was equilibrated 20 hours with metal ion solution. The supernatant was then removed and the concentration of metal ions in the solution was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Spectro D ICP system from Spectro Analytical Instruments). The distribution coefficient (D) was calculated by using the formula

$$D = \left(\frac{C_i - C_f}{C_f}\right)\left(\frac{V}{m}\right) \qquad (1)$$

where C_i and C_f are the initial and final concentrations of metal ion in solution, respectively, V is the volume of the equilibration solution in milliliters and m is the weight in grams of dry resin. The standard deviation was determined from six independent ion-exchange experiments.

RESULTS AND DISCUSSION

The six resins were synthesized with phenol (**a**), catechol (**b**), resorcinol (**c**), and 8-hydroxyquinoline (**d**) (Fig. 1, Table 1). Alkaline polycondensation of formaldehyde with phenolic compound gives an infusible, insoluble, amor-

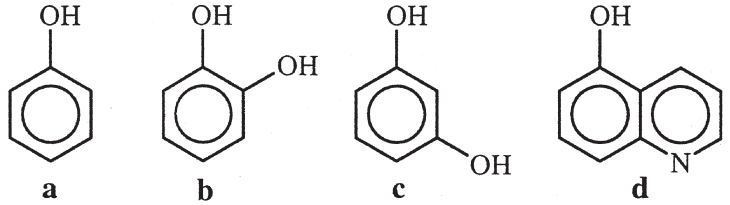

FIG. 1 Phenol (**a**), catechol (**b**), resorcinol (**c**), and 8-hydroxyquinoline (**d**) molecules.

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TABLE 1
Resins Examined

Resin	Symbol
Phenol formaldehyde	PF
Catechol formaldehyde	CF
Resorcinol formaldehyde	RF
Phenol 8-hydroxyquinoline formaldehyde	PQF
Catechol 8-hydroxyquinoline formaldehyde	CQF
Resorcinol 8-hydroxyquinoline formaldehyde	RQF

phous, crosslinked polymer. By assuming complete crosslinking, the repeating unit in such a polymer is given by the following expression (18):

$$(C_6H_{3-n})(OH)_n(CH_2)_{1.5} \tag{2}$$

where $n = 1$ for phenol and $n = 2$ for catechol and resorcinol. If all the OH groups are accessible in the polymer, the theoretically expected $H^+ \rightarrow Na^+$ ion-exchange capacity in alkaline solution would be 8.9 meq/g for phenol and 15.6 meq/g for the two dihydroxybenzene resins. The results of the characterization of the resins are presented in Table 2.

The ion-exchange capacities for the catechol and resorcinol formaldehyde resins are lower than the theoretical capacities but they are higher (17) than and comparable (8) with those of the literature. The ion-exchange capacities obtained for the resins made from 8-hydroxyquinoline and a phenolic compound are comparable with those obtained for the catechol and resorcinol resins.

Europium Sorption—H^+ Form Resins

Many ion-exchange materials based on phenol-formaldehyde condensation polymers have been described in the literature together with details of

TABLE 2
Moisture Regain and Ion-Exchange Capacities for Phenolic Resins

Resin	Moisture regain (% wt/wt)	Ion-exchange capacity (meq/g$_{(dry)}$)
CF	20	8.6
RF	40	11.5
PQF	10	5.9
CQF	20	9.6
RQF	19	9.9

their chelating behavior toward metal ions and selectivity (8, 17, 18), which is the main feature of chelating ion exchange. Weakly acidic phenolic groups of the resins showed, as expected, a low metal adsorption in the acid range (pH 4), and results obtained for the five resins are presented in Table 3.

In these conditions catechol and resorcinol resins are inefficient for Eu^{3+} sorption, whereas 8-hydroxyquinoline-based phenolic resins show Eu^{3+} sorption. A strong influence of the nature of the phenolic compounds is observed. PQF shows a low distribution coefficient for Eu^{3+} whereas CQF and RQF show synergistic extraction. The Eu^{3+} distribution coefficient is raised by the introduction of two hydroxy groups. Enhanced sorption is also noticed when resorcinol is used instead of catechol for the 8-hydroxyquinoline-containing resins.

Europium Sorption—Na^+ Form Resins

Ion-exchange sorption of the Eu^{3+} cation is controlled by deprotonation of the phenolic groups of the resin. Phenolic groups are weak acids ($pK_a = 9.9$) and are deprotonated at high pH where precipitation of the lanthanides occurs. To avoid precipitation of Eu^{3+} and still enhance its sorption, it is necessary to transform the resins in their Na^+-form before extraction, using the procedure described in the Experimental section. Typical batch distribution data for Eu^{3+} with the five resins are given in Table 4. A strong distribution coefficient for Eu^{3+} is observed with catechol and resorcinol resins. In general, the distribution coefficient for Eu^{3+} increases when the Eu concentration in solution decreases. Introduction of an 8-hydroxyquinoline group in the matrix of the polymer leads to less efficient extraction of Eu^{3+}.

TABLE 3
Distribution Coefficients (D) for the Phenol–Formaldehyde Resin in Their H^+-Form.
$[Eu] = 0.05$ M, pH 4,
$V = 10$ mL, $m = 0.05$ g,
T (shaking) = 20 hours

Resin	D (mL/$g_{(dry)}$)
CF	0
RF	0
PQF	1.3
CQF	12.6
RQF	17.8

TABLE 4
Distribution Coefficients *D* and Amount of Eu Extracted by Substituted Phenol-Formaldehyde Resin in their Na^+-Form, for Various Concentrations of Eu. $V = 10$ mL, pH 4, $m = 0.05$ g, T (shaking) = 20 hours

Resin	C_iEu (M)	*D* ($mL/g_{(dry)}$)	Eu extracted ($mmol/g_{(dry)}$)
CF	0.005	6,450,000	1.35
CF	0.010	415	1.43
CF	0.025	134	1.73
CF	0.050	64	1.72
RF	0.005	946,000	1.86
RF	0.010	824	1.93
RF	0.025	134	2.01
RF	0.050	50	1.95
PQF	0.005	157	0.50
PQF	0.010	37	0.28
PQF	0.025	21	0.43
PQF	0.050	5	0.23
CQF	0.005	216	0.63
CQF	0.010	122	0.77
CQF	0.025	32	0.72
CQF	0.050	50	2.14
RQF	0.005	411	0.84
RQF	0.010	151	0.94
RQF	0.025	25	0.59
RQF	0.050	42	1.98

Lanthanum-Europium Competitive Extraction—Na^+ Form Resins

The initial studies showed a strong influence of 8-hydroxyquinoline on the ion-exchange capacity of phenolic resins. The influence of this chelating compound on ion-exchange selectivity was then examined, yielding lower distribution coefficients for resins with the same phenolic-based functional groups. These results were used in evaluating competitive extraction between La and Eu.

Using the results obtained for Eu^{3+} extraction, the resins were converted to their Na^+-form before the extraction experiments. Europium and La extraction is expected to be somewhat slow, and kinetic experiments were performed. The resulting distribution coefficients for La and Eu with the different resins as a function of time are presented in Fig. 2 and Table 5. The results were used to evaluate the rate of metal ion sorption to the examined resins.

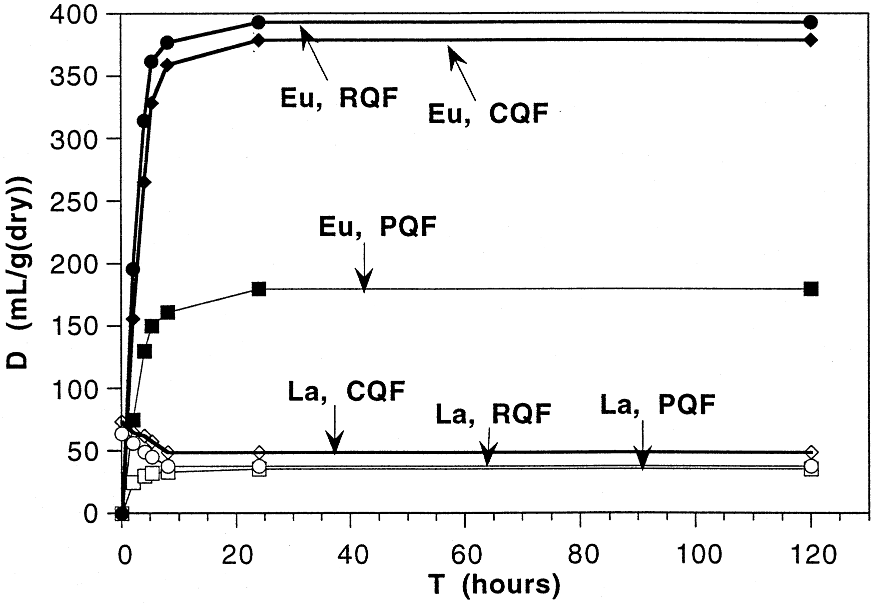

FIG. 2 Europium–lanthanum distribution coefficient profiles for the phenol–catechol– and resorcinol–8-hydroxyquinoline formaldehyde resins as a function of the time. $[La] = [Eu] = 0.0025\ mol{\cdot}L^{-1}$, pH 4, $V = 10$ mL, $m = 0.05$ g.

For each collection time presented in Table 5, the concentration of metal ion bound to the resin ($C_i - C_f$) was evaluated with Eq. (1). If presented graphically, the shape of the saturation curve is the same as Fig. 2. To evaluate the rate of metal ion sorption to resin, the concentration of metal bound to resin ([M − Res]) as a function of time is fit to

$$[\mathrm{M} - \mathrm{Res}] = A + B\exp(-kT) \qquad (3)$$

TABLE 5
Kinetic Data for Competition Experiment for Eu and La with Different Resins.
The Distribution Coefficients for Eu and La with CQF, PQF, and RQF Are Presented

Time (hours)	*D*Eu, CQF	*D*La, CQF	*D*Eu, PQF	*D*La, PQF,	*D*Eu, RQF	*D*La, RQF
0	0	73.4	0	0	0	64
2	156	65	75	25	196	56
4	265.1	62	130	30	314.5	49
5.3	328.4	57.4	150	32	362	45
8	359	48.5	161	33	377	37.7
24	378.8	48.5	180	35.4	393	37.8
120	378.8	48.5	180	35.4	393	37.8

TABLE 6
Evaluated Rates (k in hour^{-1}) for the Sorption of Eu^{3+} and La^{3+} to the Examined Resins at pH 4

Resin	Eu^{3+}	La^{3+}
CQF	0.54 ± 0.02	0.20 ± 0.05
PQF	0.44 ± 0.02	0.66 ± 0.07
RQF	0.69 ± 0.02	0.23 ± 0.04

where A and B are constants for the conditions examined, T is the time in hours, and k is the rate in hour^{-1}. The resulting values for k are presented in Table 6. The Eu^{3+} sorption rates are greater for the dihydroxy-based resins, while La^{3+} sorption is faster for PQF resin. The minimum rate from the measured values is 0.20 h^{-1} for La^{3+} sorption to CQF resin. From this value, a mixing time of 20 hours was chosen. This will result in ≈99% of the equilibrium concentration being reached in the kinetically slowest case.

After extraction with the catechol and the resorcinol formaldehyde resins, the concentrations of La^{3+} and Eu^{3+} in the aqueous solution are too low to be measured by ICP-AES. Their distribution coefficients are very high and their selectivity can not be determined with accuracy. Incorporation of 8-hydroxyquinoline in the polymeric matrix strongly reduces the distribution coefficient of La^{3+} and Eu^{3+}, but results in selective extraction of Eu^{3+}. The phenol-, catechol-, and resorcinol-8-hydroxyquinoline-formaldehyde resins sorbed Eu^{3+} with a Eu^{3+}/La^{3+} separation factor of 6.2, 6.9, and 9.9 respectively (Table 7). These results are similar to separation factors obtained from

TABLE 7
Distribution Coefficients D (mL/g$_{(dry)}$) and Separation Factors for the Competitive Extraction of Lanthanum and Europium by Phenolic Resins. Standard Deviation ± 5. $[La] = [Eu] = 0.0025\ mol{\cdot}L^{-1}$, $V = 10$ mL, pH 4, $m \approx 0.05$ g, T (shaking) = 20 hours. The Separation Factors Obtained from the Kinetic Experiments at 24 Hours Are Also Presented

Phenolic resin	Distribution coefficient (mL/g$_{(dry)}$)		Separation factor Eu/La	
	La	Eu	20 hours	Kinetic experiments (24 hours)
CF	>2,000,000	>2,000,000	~1	
RF	>2,000,000	>2,000,000	~1	
PQF	64	400	6.2	5.1
CQF	98	672	6.9	7.8
RQF	82	816	9.9	10

the kinetic experiments measured at 24 hours. Additionally, the trend for the increase in Eu^{3+}/La^{3+} separation factors for the different resins is mirrored by the evaluated sorption rates. If the ratios of the rates are compared, the trend is the same found for the separation factors: RQF $>$ CQF $>$ PQF. These results demonstrate that introduction of 8-hydroxyquinoline in phenolic resins allows a high separation factor of Eu^{3+} and La^{3}, resulting in resins with different behaviors toward Eu and La. Similar experiments with Am^{3+} are in progress.

Evaluating Complexation Constants

Determining complexation constants for the interaction of the resins with different metal ions can be extremely useful for evaluating potential applications and maximizing separation schemes. For determining the complexation constant, the resin concentration can be reported in mol/L based on the proton-exchange capacity:

$$[\mathrm{Res}(Z)]_{\mathrm{t}} = \frac{\mathrm{Res}\cdot\mathrm{PEC}}{Z} \tag{4}$$

where $[\mathrm{Res}(Z)]_{\mathrm{t}}$ is the total resin concentration in mol/L, Res is the resin concentration in g/L, PEC is the proton-exchange capacity in eq/g, and Z is the charge of the complexing metal species. In this work, $Z = 3$ since Eu^{3+} is trivalent and the experimental conditions preclude hydrolysis. The resin concentration is designated by [Res(III)].

In aqueous solutions the complexation reaction of a given metal ion is assumed to follow a charge neutralization process; the metal ion occupies the number of proton exchange sites equal to its charge (21). This concept is based on ion-exchange resins complexation and has been used to model humic acid. For Eu^{3+}, the complexation reaction is described as

$$\mathrm{Eu}^{3+} + \mathrm{Res(III)} \leftrightarrow \mathrm{EuRes(III)} \tag{5}$$

and its reaction constant is given by

$$\beta = \frac{[\mathrm{EuRes(III)}]}{[\mathrm{Eu}^{3+}]_{\mathrm{f}}[\mathrm{Res(III)}]_{\mathrm{f}}} \tag{6}$$

where [EuRes(III)] is the concentration of the metal bound to the resin, $[\mathrm{Eu}^{3+}]_{\mathrm{f}}$ is the free Eu ion concentration, and $[\mathrm{Res(III)}]_{\mathrm{f}}$ is the free resin concentration.

Depending upon the resins and experimental conditions, not all the proton-exchange sites on the resin are available for bonding. The amount of sites available for metal ion complexation changes with pH, ionic strength, and resin. This change is defined as loading capacity (LC) and is analogous to protonation constants. In this work the LC is based on $[\mathrm{EuRes(III)}]/[\mathrm{Res(III)}]_{\mathrm{t}}$ from the experimental results (Table 8).

TABLE 8
Loading Capacity Values
for the Examined Resin

Resin	LC
CF	0.622
RF	0.540
PQF	0.262
CQF	0.689
RQF	0.637

The free resin concentration in Eq. (6) can be calculated with LC by

$$[\mathrm{Res(III)}]_f = [\mathrm{Res(III)}]_t\mathrm{LC} - [\mathrm{EuRes(III)}] \tag{7}$$

This results in

$$\beta = \frac{[\mathrm{EuRes(III)}]}{[\mathrm{Eu}^{3+}]_f([\mathrm{Res(III)}]_t\mathrm{LC} - [\mathrm{EuRes(III)}])} \tag{8}$$

The equilibrium constants for the examined resins with Eu^{3+} are calculated from the speciation data in Table 9. The speciation data are evaluated from the distribution coefficients in Table 4.

The evaluated average complexation constants are similar for the examined resins. The complexation constants are used to calculate the experimental points measured in this work (Fig. 3). When the normalized mole fractions of Eu^{3+} bound to a resin are examined, acceptable agreement is generally found between experiment and calculation. However, more experimental data are truly needed, including different pH values, to fully test the utility of the complexation constants for assessing the ion-specific resins.

Changes and Thermal Behavior during Heating

When the resins are submitted to TG analysis, the resulting thermoanalytical curves are similar in shape across the same group (CF, RF or CQF, RQF). For all the resins, a first weight loss of ca. 5 to 11% occurs in the 30 to 140°C temperature range. This weight loss is due to the removal of the residual moisture from the samples prepared by powdering the air-dried resin. The CF and RF resins show one stage of decomposition whereas CQF and RQF resins show two stages of decomposition (Table 10). The thermal decomposition profile of RF resin is given in Fig. 4.

The first decomposition arises from the phenol groups at 242°C, from catechol groups at 145–149°C, and from resorcinol groups at 152–156°C. The second stage decomposition, occurring at 222 and 293°C for the CQF and RQF resins, can be attributed to the decomposition of the phenolic part of the

TABLE 9
Eu Speciation Data Used for the Complexation Constant Evaluation. The Average Stability Constant Used for Calculations Is Given in Parentheses. The Values in Italics Are Excluded in the Averages

Resin	$[Eu^{3+}]_t$ (M)	$[Res(III)]_t$ (M)	[Eu-Res(III)] (M)	$[Eu^{3+}]_f$ (M)	$[Res(III)]_f$ (M)	log β (L/mol)
CF	5.0×10^{-3}	1.06×10^{-2}	5.00×10^{-3}	2.09×10^{-7}	1.60×10^{-3}	*7.2*
CF	1.0×10^{-2}	1.31×10^{-2}	6.55×10^{-3}	3.45×10^{-3}	1.61×10^{-3}	3.1
CF	2.5×10^{-2}	2.00×10^{-2}	1.21×10^{-2}	1.29×10^{-2}	3.62×10^{-4}	3.4
CF	5.0×10^{-2}	3.85×10^{-2}	2.31×10^{-2}	2.69×10^{-2}	8.32×10^{-4}	3.0 (3.2)
RF	5.0×10^{-3}	1.03×10^{-2}	5.00×10^{-3}	1.97×10^{-6}	5.65×10^{-4}	*6.7*
RF	1.0×10^{-2}	1.52×10^{-2}	7.66×10^{-3}	2.34×10^{-3}	5.57×10^{-4}	3.8
RF	2.5×10^{-2}	1.91×10^{-2}	1.00×10^{-2}	1.50×10^{-2}	3.00×10^{-4}	3.3
RF	5.0×10^{-2}	2.16×10^{-2}	1.10×10^{-2}	3.90×10^{-2}	6.79×10^{-4}	2.6 (3.2)
PQF	5.0×10^{-3}	7.14×10^{-3}	1.82×10^{-3}	3.18×10^{-3}	5.45×10^{-5}	4.0
PQF	1.0×10^{-2}	1.71×10^{-2}	2.44×10^{-3}	7.56×10^{-3}	2.04×10^{-3}	2.2
PQF	2.5×10^{-2}	2.07×10^{-2}	4.52×10^{-3}	2.05×10^{-2}	8.94×10^{-4}	2.4
PQF	5.0×10^{-2}	3.42×10^{-2}	4.00×10^{-3}	4.60×10^{-2}	4.96×10^{-3}	1.2 (2.5)
CQF	5.0×10^{-3}	1.06×10^{-2}	2.08×10^{-3}	2.92×10^{-3}	5.21×10^{-3}	2.1
CQF	1.0×10^{-2}	1.53×10^{-2}	3.69×10^{-3}	6.31×10^{-3}	6.88×10^{-3}	1.9
CQF	2.5×10^{-2}	1.11×10^{-2}	2.50×10^{-3}	2.25×10^{-2}	5.16×10^{-3}	1.3
CQF	5.0×10^{-2}	1.08×10^{-2}	7.21×10^{-3}	4.28×10^{-2}	2.16×10^{-4}	2.9 (3.2)
RQF	5.0×10^{-3}	1.13×10^{-2}	2.96×10^{-3}	2.04×10^{-3}	4.22×10^{-3}	2.5
RQF	1.0×10^{-2}	1.29×10^{-2}	3.78×10^{-3}	6.22×10^{-3}	4.42×10^{-3}	2.1
RQF	2.5×10^{-2}	7.60×10^{-3}	1.40×10^{-3}	2.36×10^{-2}	3.44×10^{-3}	1.2
RQF	5.0×10^{-2}	4.69×10^{-3}	2.90×10^{-3}	4.71×10^{-2}	8.70×10^{-5}	2.8 (3.0)

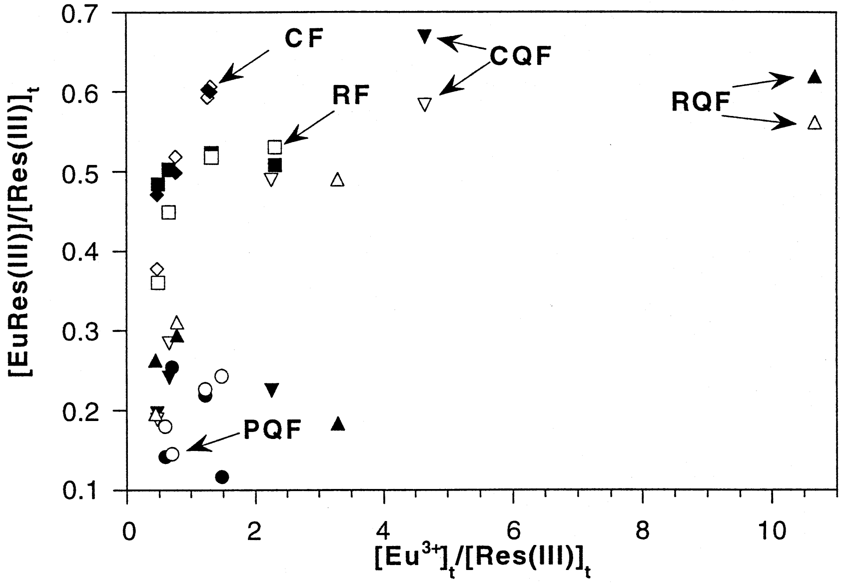

FIG. 3 Comparison of measured (filled) and calculated (open) data points. The values are normalized to the total resin concentration for intercomparison.

TABLE 10
Phenomenological Data on the Thermal Decomposition of the Phenolic Resins

Resin	T_1 (°C)	T_2 (°C)	Weight loss at 500°C (%)
PF	241.62	—	17
CF	148.84	—	40
RF	152.19	—	32
CQF	145.48	221.53	30
RQF	155.54	292.51	24

8-hydroxyquinoline groups. For a temperature of 500°C, the weight loss is from 17 to 40%, depending on the resin.

Thermogravimetric Studies of the Polymer–Metal Complexes

Thermal analysis of the polymer complexes can reveal the change in the thermal stability induced by introduction of metal ions in the polymer matrix (22–24). The thermal stability varies with the metal ion and the structure of the polymer–metal complex (23). This part of the study is concerned with the thermal decomposition behavior of Eu^{3+} complexes of the phenolic resins. The phenomenological data of the thermal decomposition of various systems are given in Table 11.

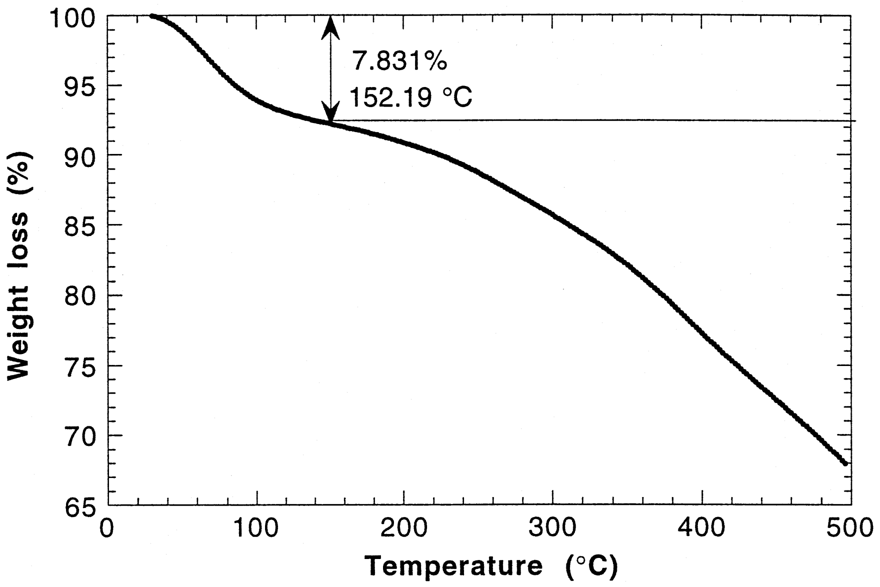

FIG. 4 TG curve of RF resin.

TABLE 11
Phenomenological Data on the Thermal Decomposition of the Metal Complexes of Phenolic Resins

Resin complex	T_1 (°C)	T_2 (°C)	T_3 (°C)	T_4 (°C)	Weight loss at 500°C (%)
PF–Eu	243.42	—	—	—	18
CF–Eu	172.31	445.06	—	—	29
RF–Eu	193.55	457.36	—	—	32
CQF–Eu	163.37	290.80	361.22	431.65	25
RQF–Eu	172.31	300.00	361.22	451.77	26

The complexation of the metal ion increases the stability of the resin. This is similar to the results for the polychelates from 8-quinolyl acrylate (25). The stabilities are in the order PF–Eu $>$ RF–Eu $>$ CF–Eu $>$ RQF–Eu $>$ CQF–Eu. The first weight loss of 5 to 8% that occurs below 140°C is attributed to the desorption of adsorbed/coordinated water molecules. In the temperature range of 30 to 500°C, the PF–Eu polymer complex degrades in one stage whereas the CF–Eu and RF–Eu polymers degrade in two stages. A four-stage decomposition is seen for CQF–Eu and RQF–Eu. The PF–Eu complex decompose at 243°C. For CF–Eu and RF–Eu complexes, the first-stage decomposition is within 149–152°C whereas the second-stage decomposition occurs in the 445–457°C temperature range. For CQF–Eu and RQF–Eu complexes, the first-stage decomposition is within 163–172°C. A second-stage decomposition occurs in the 291–300°C temperature range. The third-stage decomposition at 360°C may be due to the decomposition of the coordinated hydroxyquinoline groups. The last stage decomposition occurs in the 432–452°C temperature range. The CQF–Eu and RQF–Eu complexes have weaker thermal stabilities compared to the other complexes. The degradation temperatures for the complexes are greater than for the polymeric ligand, indicating that stability is gained on complexation with the metal ions. The greater stability of the metal complexes is probably due to the formation of stable ring-structured metal complexes.

CONCLUSION

These investigations on complexation behavior of phenolic polymers demonstrate that phenolic resins are effective in the selective removal of Eu^{3+} from an acidic aqueous medium. Conversion of the resins in their Na^{+} form markedly enhanced Eu^{3+} sorption. The incorporation of 8-hydroxyquinoline into the phenolic matrix produces important changes in the competitive sorption of La^{3+} and Eu^{3+}. Compared with resorcinol and catechol formaldehyde resins, the phenolic 8-hydroxyquinoline-based resins show low distribution coefficients for Eu^{3+} sorption, but they show a selectivity between La^{3+} and Eu^{3+}. The selectivity of competitive Eu^{3+}/La^{3+} sorption is found to be influenced by the identity of the ion-exchange phenolic matrix. The separation factors obtained for PQF, CQF, and RQF resins are $S_{PQF} = 6.2$, $S_{CQF} = 6.9$, and $S_{RQF} = 9.9$. Evaluated complexation constants showed acceptable agreement between experiment and calculation. However, further effort is needed to determined the utility of the complexation model and the evaluated terms. Phenomenological analyses of the thermal decomposition of the different resins reveal that the thermal stabilities of the polymers vary significantly by complexation with a metal ion. The thermal stabilities of the metal complexes are higher than the uncomplexed resins.

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