THE KINETICS OF EXCHANGE OF TRIVALENT ACTINIDE IONS WITH EUROPIUM ETHYLENEDIAMINETETRAACETATE

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While the kinetics of the exchange of lanthanide aminopolycarboxylate complexes with free lanthanide ions have been investigated for several different aminopolycarboxylate ligands, the three reports (1,2,3) on analogous exchange reactions with actinide ions have been concerned only with Am(III) and EDTA. In this paper we report an extension of our previous work with the $Am(III)/EuEDTA^-$ exchange reaction to include the exchange of $EuEDTA^-$ with Cm(III), Bk(III), and Cf(III). The isotopic exchange system $Eu(III)/EuEDTA^-$ was also investigated, so that results for the actinide and lanthanide ions could be compared.

Previously (3) we reported that the exchange of Am(III) with $EuEDTA^-$ is a first-order reversible reaction and that the forward and reverse rate constants each contain an acid-dependent and an acid-independent term:

$$k_F = k_A' \frac{[EuEDTA^-][Am^{3+}][H^+]}{[Eu^{3+}]} + k_B' [EuEDTA^-][Am^{3+}] \qquad [1]$$

$$k_R = k_C[H^+][AmEDTA^-] + k_D' [Eu^{3+}][AmEDTA^-] \qquad [2]$$

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The acid-independent terms were found to correlate with a mechanism in which the free metal ion approaches the complex to form a dinuclear intermediate $Eu(EDTA)Am^{2+}$. This acid-independent mechanism may be represented schematically as follows (where EDTA = Y):

$$EuY + Am \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Eu{\equiv}Y{-}Am \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} Eu{=}Y{=}Am \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} Eu{-}Y{\equiv}Am \qquad [3]$$

$$k_{-4} \uparrow\downarrow k_4$$

$$AmY + Eu$$

The lines between Y and the cations indicate the number of carboxylate groups which are bonded to each metal ion (ionic charges have been omitted). From this treatment the acid-independent rate constants k_B' and k_D' are given by:

$$k_B' = \frac{K_1 k_2 k_3}{k_3 + k_{-2}} \qquad [4]$$

$$k_D' = \frac{K_{-4} k_{-3} k_{-2}}{k_3 + k_{-2}} \qquad [5]$$

$$(K_i = \frac{k_i}{k_{-i}};\ K_{-i} = \frac{k_{-i}}{k_i}$$

For the acid-catalyzed mechanism we have proposed that the first step is a rapid equilibrium in which one of the carboxylate groups of the EDTA complex is protonated. The slow step is either (1) the dissociation of a second carboxylate group from the metal ion or (2) the transfer of a proton from the carboxylate oxygen to the nitrogen. The ligand is then able to dissociate rapidly from the metal ion. In either case the free europium and actinide ions compete for the free protonated EDTA. Schematically this mechanism is given by:

$$\mathrm{EuY} + \mathrm{H} \underset{k_{1E}}{\overset{k_{-1E}}{\rightleftharpoons}} \mathrm{HEuY} \underset{k_{2E}}{\overset{k_{-2E}}{\rightleftharpoons}} {}^{*}\mathrm{HEuY} \underset{k_{3E}}{\overset{k_{-3E}}{\rightleftharpoons}} \mathrm{Eu} + \mathrm{H}_x\mathrm{Y} + \mathrm{Am}$$

$$k_{3A} \; + \; k_{-3A}$$

$$\mathrm{AmY} + \mathrm{H} \underset{k_{-1A}}{\overset{k_{1A}}{\rightleftharpoons}} \mathrm{HAmY} \underset{k_{-2A}}{\overset{k_{2A}}{\rightleftharpoons}} {}^{*}\mathrm{HAmY} \qquad [6]$$

*HEuEDTA and *HAmEDTA represent the intermediates formed. The forward and reverse rate constants by the acid-dependent pathway are given by:

$$k_A' = K_{-1E}K_{-2E}K_{-3E}K_{3A}k_{2A} \qquad [7]$$

$$k_C = K_{-1A}k_{-2A} \qquad [8]$$

EXPERIMENTAL PROCEDURE

The preparation of the solutions, the procedure for the kinetics runs, and the measurement of pH were described earlier.[3] The radioactive tracers were ^{244}Cm, ^{249}Bk, ^{252}Cf and $^{152\text{-}4}Eu$, all obtained from Oak Ridge National Laboratory.

The counting was performed on a Packard #3320 Liquid Scintillation Counter. The scintillation cocktail described earlier[3] was used for all tracers except the ^{249}Bk. For the low energy beta decay of ^{249}Bk Preblended Liquid Scintillation Cocktail 3a40 was used as obtained from Research Products International Corporation. For ^{252}Cf only the alpha peak was counted to avoid contributions from fission products. For ^{249}Bk the small alpha contribution from the

^{249}Cf daughter was monitored on a separate channel and subtracted from the total activity.

RESULTS

Figure 1 indicates that the exchange reaction obeys a first-order reversible rate law with respect to each of the tracer ions studied. The Am(III) data from reference (3) are included for purposes of comparison. The slope of each of these lines gives the first-order rate constant k_1 ($k_1 = k_F + k_R$). The plots in Figure 2 of k_F versus $[H^+]$ for each of the tracer ions are linear with non-zero intercepts indicating that equations [1] and [2] are valid for the Cm, Bk and Cf as well as the Eu and Am systems. Calculations based on these equations are given in Tables 1 and 2 where it can be seen that the agreement of the results for different solution concentrations is good.

DISCUSSION

Figure 3 is a plot of the logarithms of the rate constants in Tables 1 and 2 as a function of the reciprocal of the ionic radii. For Am(III), Cm(III), Bk(III) and Cf(III) the estimated radii of Jones and Choppin were used.[4] Curves d and f of the forward reaction rate constants include the values for the Eu(III) isotope exchange reaction.

Included for comparative purposes are the acid dependent rate constants for lanthanide-DCTA[5] formation (k_M^{HCY}) and dissociation (k_H^{MCY}) and the rate constants for lanthanide-murexide formation[6].

Both k_C (the rate constant for the acid dependent dissociation of the actinide-EDTA complex) and k_D (the rate constant for the direct attack dissociation) follow a 1/r dependence which parallels the lanthanide-DCTA dissociation curve. Similarly, the formation rate constants k_A' and k_B' show a non-linear pattern resembling the patterns of the formation rate constants of the DCTA and murexide systems. In an attempt to understand these trends, let us consider in more detail the terms in the forward and reverse rate constants of the EDTA system.

The acid dependent forward sequence has a rate constant k_A' given in equation 7. In this equation $K_{-1E}K_{-2E}K_{-3E}$ is constant in all of our exchange reactions since these terms relate to the dissociation of the $EuEDTA^-$ complex into Eu^{3+} and H_xEDTA^{4-x}. At the pH values of our experiments (pH 5-6) H_2EDTA^{2-} is predominant species of H_xEDTA^{4-x} which establishes the relationship

$$K_{-1E}K_{-2E}K_{-3E} = (K_{SC}K_{A_3}K_{A_4})^{-1} \qquad [9]$$

where K_{SC} is the stability constant for $EuEDTA^-$ and K_{A_3} and K_{A_4} are the acid dissociation constants for H_2EDTA^{2-} and $HEDTA^{3-}$. Using the known values for these three constants[7], we obtain a value of 37.2 for $K_{-1E}K_{-2E}K_{-3E}$ which from equation 7 gives the values of log $K_{3A}k_{2A}$ listed in Table 3. From the reactions in [6] we see that K_{3A} is the equilibrium constant for the reaction between H_xEDTA^{4-x} and An^{3+} to form *HAnEDTA while k_{2A} is the rate constant for the conversion of *HAnEDTA to HAnEDTA. We can, then, conclude that the variation of log k_A' with 1/r must be related to processes involving *HAnEDTA, HAnEDTA and/or An^{3+}.

Now consider the reverse rate constant k_C for the acid dependent mechanism. Equation [8] shows that k_C is dependent on K_{-1A}, the equilibrium constant for the protonation reaction of $AnEDTA^-$ to form HAnEDTA and on k_{-2A}, the rate constant for the conversion of HAnEDTA to *HAnEDTA. Based on data for the analogous lanthanide reactions[8,9], the value of K_{-1A} is expected to be relatively independent of the actinide ionic radii and can be estimated to have a value of about 350. The values of log k_{-2A} obtained by dividing k_C by 350 are listed in Table 3. Obviously, if our assumption of a relatively constant K_{-1A} term is valid, log k_{-2A} is inversely related to 1/r. The rate constant k_{-2A} measures the rate of conversion of HAnEDTA to *HAnEDTA so it would seem likely that the rate constant for reverse process, k_{2A}, would have a similar dependence on 1/r. If this assumption is valid, the non-monotonic variation of the log k_A' term reflects the variation of log K_{3A} with 1/r.

For the acid-independent mechanism, log k_D' follows the 1/r relationship. This rate constant involves K_{-4}. k_{-3} and k_{-2} (since the denominators in equations 4 and 5 are identical, they cannot be responsible for the different variations with 1/r). These constants all involve processes in which An-EDTA bonds are broken to form Eu-EDTA bonds. Since the bonding is primarily ionic, it is reasonable that these processes exhibit a monotonic 1/r dependence. By the same reasoning the pattern exhibited by the formation rate constant k_B' in Figure 3 should not be related to processes involving replacement of Eu-EDTA bonds by An-EDTA

bonds (k_2 and k_3 terms) since these would also be expected to have a simple 1/r dependence. Consequently, the dependence of log k_B' on 1/r would seem to reflect the variation of log K_1 with 1/r.

To summarize, then, it would seem that the simple relationship between log k_C and log k_D' with 1/r reflects the ionic nature of the metal-ligand bonding. This same explanation can explain the similar pattern for the Ln-DCTA dissociation rate constants. By contrast, the formation rate constants show a complex variation with 1/r for both the acid dependent and acid independent processes with EDTA as well as for the Ln-DCTA and Ln-murexide systems. In the EDTA systems we have seen that this is seemingly related to the variation of log K_{3A} (for the acid dependent path) with log K_1 (for the acid independent path) with 1/r.

K_{3A} involves $An^{+3}_{(aq)}$ and *HAnEDTA while K_1 involves $An^{+3}_{(aq)}$ and Eu≡EDTA-An. The appearance of $An^{+3}_{(aq)}$ in both constants and the similarity of the dependence on 1/r would suggest the radius effect is related to the hydrated actinide ion. By analogy the dependency of the formation rate constants for the Ln-DCTA and Ln-murexide systems reflect a radius effect due to the hydrated lanthanide ion. It has been suggested previously that the hydrated radii of the trivalent lanthanide[10,11] and actinide[4] ions may not have a simple inverse relationship to the ionic radii.

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TABLE 1

Forward Reaction Data

Exchange of $EuEDTA^-$ with Cm^{3+}, Bk^{3+}, Cf^{3+}, and Eu^{3+}

$[OAc^-]$ = 0.02M; μ = 0.1M; 25°C

Metal	$[Eu^{3+}]$ $(Mx10^3)$	$[Eu(EDTA)^-]$ $(Mx10^3)$	ratio = $\frac{[Eu^{3+}]}{[Eu(EDTA)^-]}$	Slope $(M^{-1}s^{-1}x10^{-2})$	$k'_A = \frac{slope}{ratio}$ $(M^{-1}s^{-1}x10^{-2})$	Intercept $(s^{-1}x10^5)$	$k'_B = \frac{intercept}{[Eu(EDTA)^-]}$ $(M^{-1}s^{-1}x10^2)$
Cm	1.20	1.04	1.15	1.57 ± 0.01	1.81 ± 0.02	4.80 ± 0.14	4.620 ± 0.131
Cm	1.57	1.49	1.05	1.66 ± 0.05	1.74 ± 0.05	6.89 ± 0.78	4.625 ± 0.520
			Average Values		1.78 ± 0.05		4.623 ± 0.003
Bk	1.20	1.04	1.15	1.94 ± 0.06	2.23 ± 0.07	9.53 ± 0.67	9.16 ± 0.65
Bk	1.85	0.595	3.11	0.827± 0.03	2.57 ± 0.10	5.04 ± 0.46	8.46 ± 0.78
			Average Values		2.40 ± 0.24		8.81 ± 0.50
Cf	1.57	1.49	1.05	2.40 ± 0.07	2.52 ± 0.07	12.9 ± 1.1	8.68 ± 0.73
Cf	1.85	0.595	3.11	0.944± 0.029	2.94 ± 0.09	4.10 ± 0.49	6.90 ± 0.82
			Average Values		2.73 ± 0.30		7.79 ± 1.26
Eu	1.57	1.49	1.05	2.17 ± 0.05	2.28 ± 0.05	6.48 ± 1.00	4.35 ± 0.67
Am[3]					1.87 ± 0.19		4.54 ± 0.65

TABLE 2

Reverse Reaction Data

Exchange of $EuEDTA^-$ with Cm^{3+}, Bk^{3+}, Cf^{3+}, and Eu^{3+}

$[OAc^-]$ = 0.02M; μ = 0.1M; 25°C

Metal	$[Eu^{3+}]$ $(Mx10^3)$	$[Eu(EDTA)^-]$ $(Mx10^3)$	k_C=slope $(M^{-1}s^{-1}x10^{-2})$	k_D=intercept $(s^{-1}x10^5)$	$k_D' = \frac{\text{intercept}}{[Eu^{3+}]}$ $(M^{-1}s^{-1}x10^2)$
Cm	1.20	1.04	1.22 ± 0.02	3.17 ± 0.25	2.64 ± 0.21
Cm	1.57	1.49	1.16 ± 0.05	4.38 ± 0.79	2.79 ± 0.50
	Average Values		1.19 ± 0.04		2.72 ± 0.11
Bk	1.20	1.04	0.549± 0.075	1.85 ± 0.88	1.54 ± 0.73
Bk	1.85	0.595	0.582± 0.028	3.34 ± 0.39	1.80 ± 0.21
	Average Values		0.566± 0.023		1.67 ± 0.18
Cf	1.57	1.49	0.249± 0.012	1.24 ± 0.19	0.788± 0.122
Cf	1.85	0.595	0.259± 0.013	1.40 ± 0.22	0.759± 0.120
	Average Values		0.254± 0.007		0.774± 0.02
Eu	1.57	1.49	2.28 ± 0.05	6.83 ± 1.05	4.35 ± 0.67
Am[3]			1.39 ± 0.13		3.19 ± 0.53

TABLE 3

CALCULATED VALUES OF LOG $K_{3A}\ k_{2A}$ AND k_{-2A}

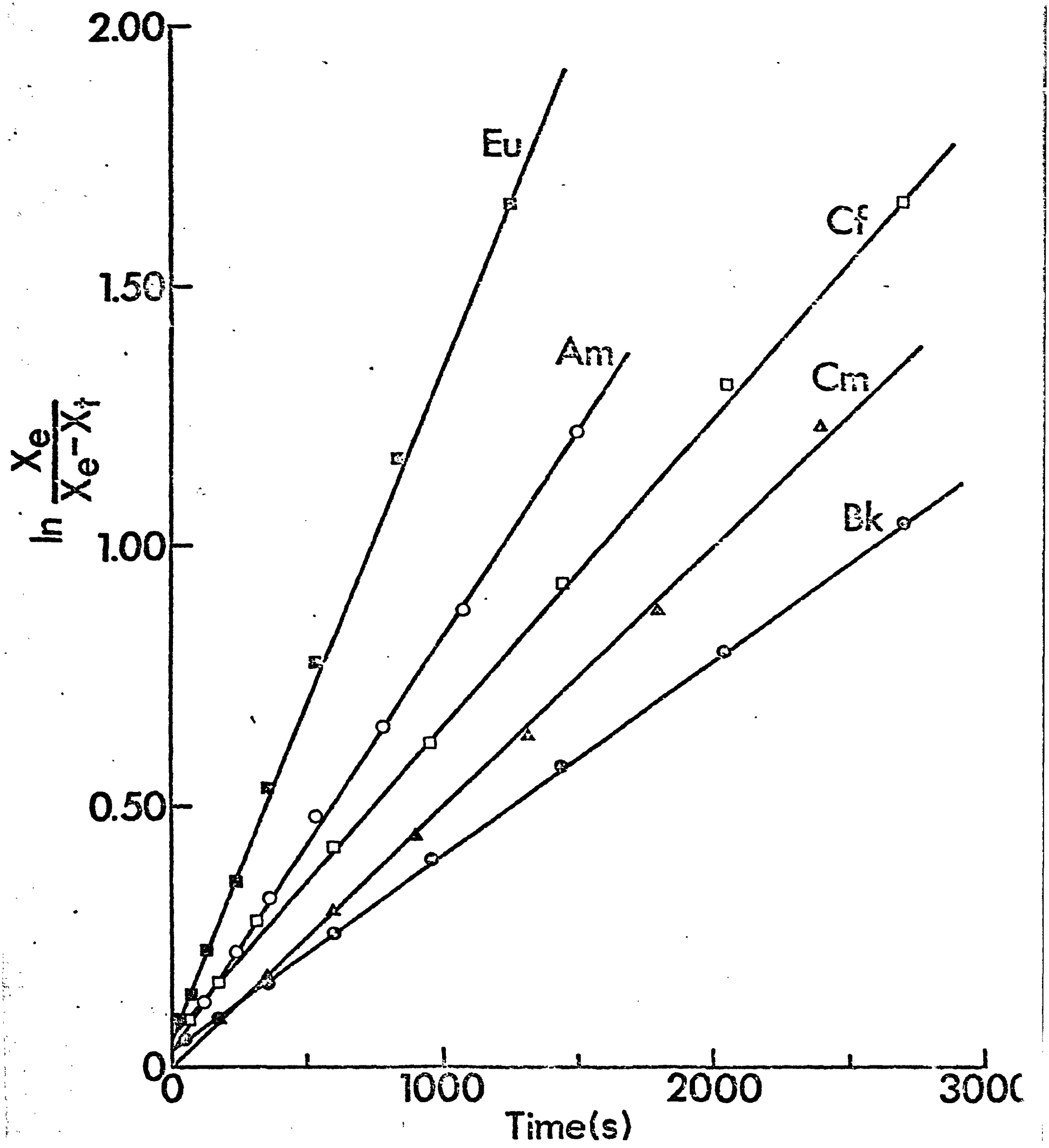
Actinide	log $K_{3A}k_{2A}$	log k_{-2A}
Am	0.70	-0.40
Cm	0.68	-0.47
Bk	0.81	-0.79
Cf	0.87	-1.14

CAPTIONS

Figure 1. Plots of $\ln \frac{x_e}{x_e - x_t}$ versus time for exchange of $Eu(EDTA)^-$ with Am^{3+}, Cm^{3+}, Bk^{3+}, Cf^{3+}, and Eu^{3+} at 25°C, μ=0.1M and [acetate]=0.02M. Reaction conditions are:
Am--1.20×10^{-3}M Eu^{3+}, 1.04×10^{-3}M $Eu(EDTA)^-$, 2.51×10^{-6}M H^+;
Cm--1.20×10^{-3}M Eu^{3+}, 1.04×10^{-3}M $Eu(EDTA)^-$, 1.51×10^{-6}M H^+;
Bk--1.85×10^{-3}M Eu^{3+}, 5.95×10^{-4}M $Eu(EDTA)^-$, 2.09×10^{-6}M H^+;
Cf--1.57×10^{-3}M Eu^{3+}, 1.49×10^{-3}M $Eu(EDTA)^-$, 1.78×10^{-6}M H^+;
Eu--1.57×10^{-3}M Eu^{3+}, 1.49×10^{-3}M $Eu(EDTA)^-$, 2.57×10^{-6}M H^+.
x_e = specific activity of $M(EDTA)^-$ at equilibrium;
x_t = specific activity of $M(EDTA)^-$ at time t.

Figure 2. Plots of k_F versus $[H^+]$ for exchange of $Eu(EDTA)^-$ with Am^{3+}, Cm^{3+}, Bk^{3+}, Cf^{3+}, and Eu^{3+} at μ=0.01M, [acetate]=0.02M, and 25°C. Reaction conditions are: Cm--1.57×10^{-3}M Eu^{3+}, 1.49×10^{-3}M $Eu(EDTA)^-$; Bk--1.85×10^{-3}M Eu^{3+}, 5.95×10^{-4}M $Eu(EDTA)^-$; Cf--1.85×10^{-3}M Eu^{3+}, 5.95×10^{-4}M $Eu(EDTA)^-$; Eu--1.57×10^{-3}M Eu^{3+}, 1.49×10^{-3}M $Eu(EDTA)^-$.
Am--1.27×10^{-3}M Eu^{3+}, 7.14×10^{-4}M $Eu(EDTA)^-$.

Figure 3. Relationship of the log of rate constants for lanthanide and actinide complexes and the reciprocal of the ionic radii: a - log k_M^{HCy}, the formation rate constant for LnDCTA[5]; b- log k_H^{MCy}, the acid catalyzed dissociation rate constant for LnDCTA[5]; c- log of the formation constant of the lanthanide-murexide complexes;[6] d- log k'_A; e- log k_C; f- log k'_B; g- log k'_D.


2.00
1.50
1.00
0.50
0
$\ln \frac{X_e}{X_e - X_t}$
Eu
Am
Cf
Cm
Bk
0
1000
2000
3000
Time(s)

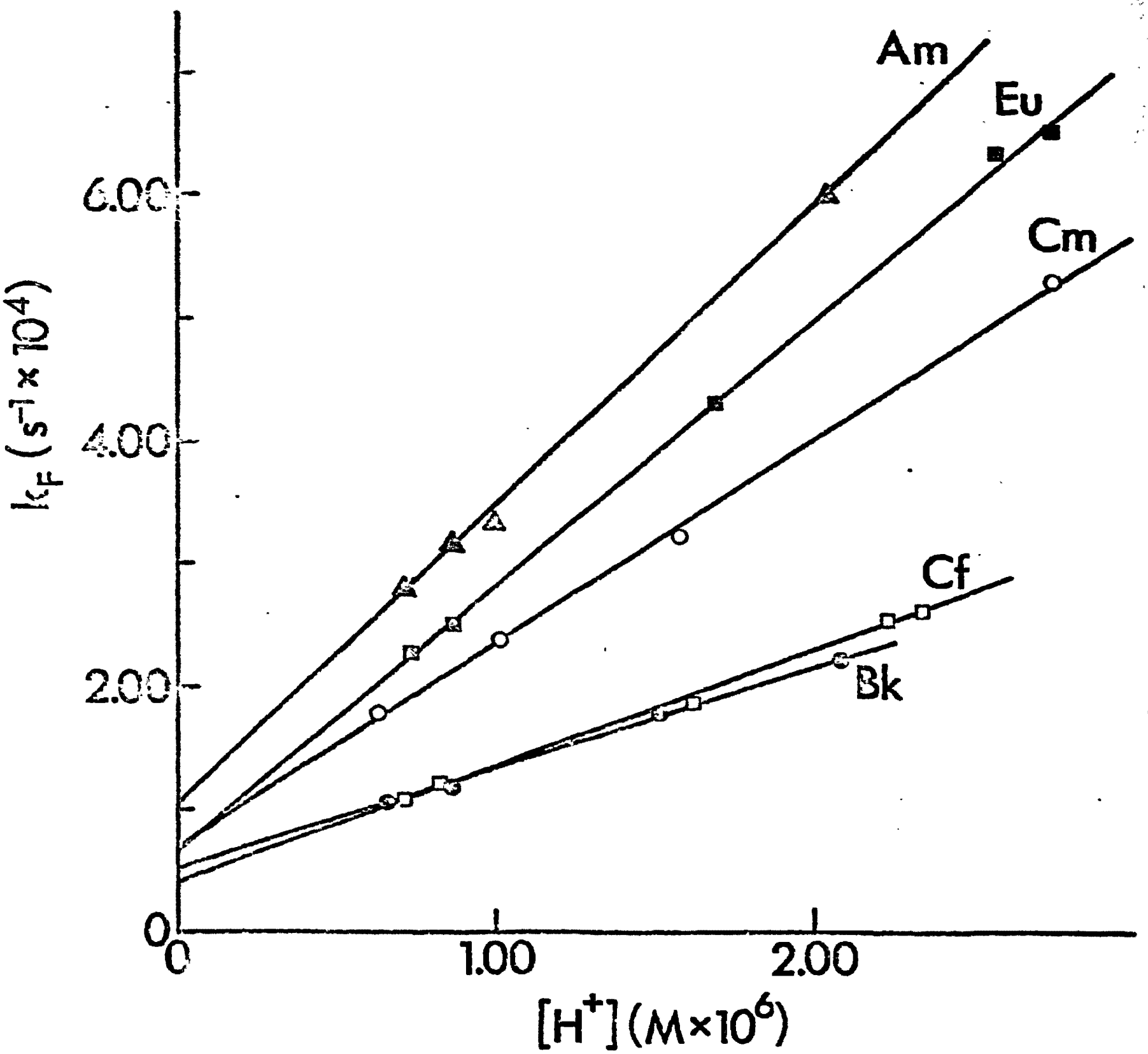


FIG 2

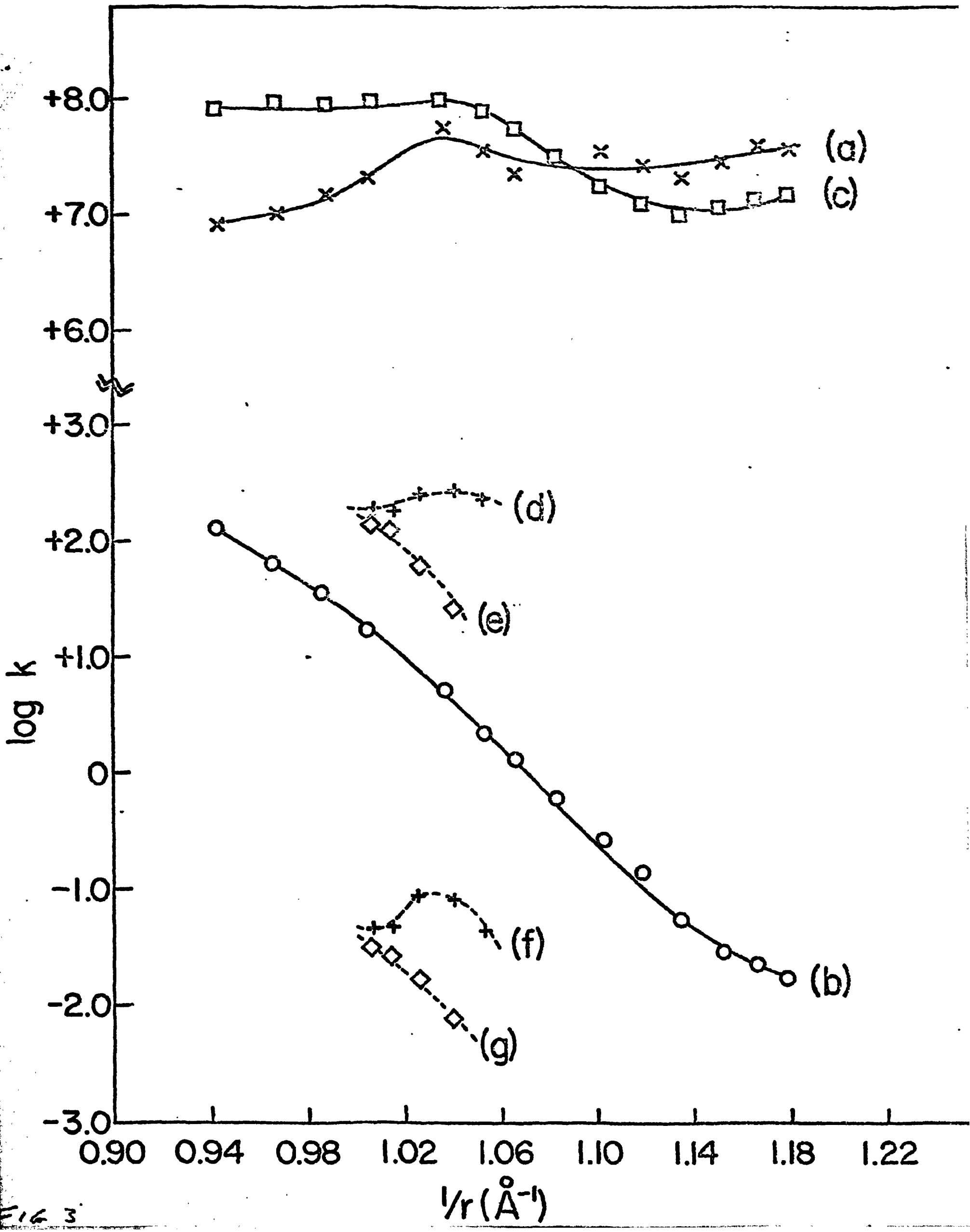

+8.0
+7.0
+6.0
+3.0
+2.0
+1.0
0
-1.0
-2.0
-3.0
log k
0.90
0.94
0.98
1.02
1.06
1.10
1.14
1.18
1.22
1/r (Å⁻¹)
(a)
(c)
(d)
(e)
(b)
(f)
(g)

FIG 3