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SEPARATION OF AMERICIUM FROM EUROPIUM
BY SOLVENT EXTRACTION FROM AQUEOUS
PHOSPHONATE MEDIA

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ABSTRACT

The stoichiometry and stability constants for americium and europium complexes with phosphonoacetic acid ($\text{HO}_2\text{CCH}_2\text{PO}_3\text{H}_2$ - PAA) in dilute acid solutions (0.005 to 0.02 M) have been determined by distribution methods at 0.5 M ionic strength and 25.0°C. The identified Am and Eu complexes and log β_{mhl} values are $\text{Am}(\text{H}_2\text{L})_2^{2+}$ - 13.82(±0.04), $\text{Am}(\text{HL})^+$ - 11.62(±0.04), $\text{Am}(\text{H}_2\text{L})_2^+$ - 27.35(±0.01), $\text{Eu}(\text{HL})^+$ - 12.10(±0.05), $\text{Eu}(\text{H}_2\text{L})_2^+$ - 27.81(±0.01), $\text{Eu}(\text{HL})_2^-$ - 23.08(±0.05). The Eu complexes are stronger than Am complexes of comparable stoichiometry, in accord with the electrostatic nature of the metal-ligand interaction. PAA was tested as a potential agent of enhanced Am/Eu separation in solvent extraction systems by examining Am and Eu extraction using different extractants. For extraction into bis(2-ethylhexyl)phosphoric acid (HDEHP), PAA slightly reduces the Am/Eu separation factor. With dinonylnaphthalenesulfonic acid (HDNNS), or octyl(phenyl)-N,N-diisobutyl-carbamoylmethylphosphine oxide (CMPO)-nitrate extraction systems, $S_{\text{Eu}}^{\text{Am}}$ is slightly enhanced by PAA. A three fold increase in $S_{\text{Eu}}^{\text{Am}}$ is observed in CMPO extraction from 0.5 M KSCN/PAA media (over extraction from 0.5 M KSCN) suggesting an improved method for lanthanide/trivalent actinide separation.

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INTRODUCTION

The intra- and intergroup separation of trivalent actinide and lanthanide elements remains one of the most challenging and important problems in separation science. These elements play a significant role in the development of methods for cleanup and decommissioning of nuclear facilities and the long-term storage of high-level waste. Advanced concepts for actinide burnup either in reactors or by accelerator transmutation demand efficient methods for separation of lanthanides from actinides. A recent review article on trivalent f-element separations (1) noted that most of the successful group separations were based on systems combining lipophilic extractants with aqueous complexing reagents.

Both polycarboxylic and aminocarboxylic acids have been used in f-element separations. Recent work at Argonne has focussed on the thermodynamics of lanthanide and actinide complexes with phosphonic acid complexants. One of the objectives of this work has been to assess the potential of these reagents for use in lanthanide/actinide separations. Stability constants for Eu(III) (2), Th(IV) (3), and U(VI) (4) complexes with a wide variety of substituted diphosphonic acids have been measured. These reagents show a significant increase in complexing strength over their carboxylate analogs. The relative stability of the metal complexes is consistent with an electrostatic bonding model for these elements. It has been demonstrated that substituted methanediphosphonic acids are particularly efficient for stripping radioactivity from loaded organic phases in solvent extraction (5).

Little data is available on the complexation of the trivalent actinide ions with these phosphonate ligands. Elesin et al (6) report stability constants for the $M(H_2L)^{2+}$, MHL^+ , and $M(HL)_2^-$ complexes of Pm(III), Am(III), and Cm(III) with phosphonoacetic acid (PAA). Their reported constants exhibit little difference in complex stability between the three metals. However, aspects of their methodology cast doubt on the absolute value of the constants.

In this work we report the stoichiometry and stability constants for Eu(III) and Am(III) complexes with PAA. Subsequently, the ability of PAA to enhance group separation of lanthanides and actinides was investigated by determining the distribution of Am(III) and Eu(III) from aqueous solutions of PAA into extractant solutions containing an acidic extractant (bis(2-ethylhexyl) phosphoric acid - HDEHP), a micellar extractant (dinonylnaphthalene sulfonic acid - HDNNS), and a neutral bifunctional extractant (octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide - CMPO) from nitrate and thiocyanate media.

EXPERIMENTAL

Reagents

PAA, 99%, was obtained from the Aldrich Chemical Company and used without further

purification. The extractants HDEHP, HDNNS, and CMPO were purified before use by well-known methods taken from the literature. Reagent grade toluene was used to prepare most of the extractant solutions. Diethyl benzene was the diluent for the CMPO solutions. All other reagents used were analytical reagent grade or better.

Procedures

Potentiometry. Stock solutions of PAA were prepared and standardized by potentiometric titration using NaOH. Ionic strength was controlled at 0.5 M using NaNO_3 as the supporting electrolyte. A Ross combination electrode was used as the pH probe. The electrode was calibrated by titrating 0.01 M HNO_3 , 0.49 M NaNO_3 with 0.10 M NaOH, 0.40 M NaNO_3 . The data provided a pH -p[H] calibration curve for conversion of the measured hydrogen ion activity to hydrogen ion concentration. Titrimetric analyses were performed using a Mettler DL21 titrator with associated TS² software for data acquisition. Gran plots were made to determine titration endpoints. Protonation constants for PAA were calculated as reported previously (2).

Distribution Measurements. The ^{241}Am and $^{152-154}\text{Eu}$ stock solutions were prepared from lab stocks by repeated evaporations to dryness in concentrated HNO_3 followed by final dissolution in 0.01M HNO_3 , 0.49 M NaNO_3 . Radiotracers were assayed using Packard Cobra Auto Gamma counter. The experiments for determination of Am-PAA stability constants were run in dual-label experiments with both ^{241}Am and $^{152-4}\text{Eu}$ present simultaneously using HDEHP as the extractant. The Am(III) counting channel covered the 60 keV γ -ray emission. The Eu channel included the Eu γ -rays between 100-700 keV. Each isotope's count rate was corrected for spill-over from the other based on prepared standards. Because the $D_o(\text{Eu})$ values were too high in the dual label experiments for accurate stability constant determination, Eu-PAA stability constants were determined in single label experiments. Separation factors with HDNNS and CMPO extraction systems were measured in dual-labeled experiments.

All distribution experiments were done at 25°C and 0.50 M ionic strength (adjusted with $\text{HNO}_3/\text{NaNO}_3$). For the determination of stability constants, PAA concentrations were varied between 0 and 0.40 M. This procedure was repeated at $[\text{H}^+] = 0.005, 0.01, \text{ and } 0.02 \text{ M}$. Under each set of experimental conditions at least two replicate experiments were performed with freshly prepared solutions. To maximize precision in the resolved stability constants, the concentration of HDEHP was varied with acidity to maintain the measured D_o ($[\text{PAA}]=0$) between 5 and 20. All PAA solutions were prepared by volumetric dilution of a stock solution which had been standardized by potentiometric titration. Eu/Am separation factors with different extractants were measured at PAA concentrations between 0 and 0.34 M. The aqueous phase ionic strength was 0.5 M ($\text{HNO}_3/\text{NaNO}_3$) in the HDNNS experiments while $[\text{NaNO}_3]$ or $[\text{KSCN}]$ was maintained at 0.5 M in the CMPO experiments.

RESULTS AND DISCUSSION

Ligand Protonation and Metal Complex Stability

The protonation constants of PAA were calculated using the program PKAS (7). The results of the potentiometric titrations of free PAA shown in Table 1 are the average of five determinations at various PAA concentrations. Earlier reports at 2 M ionic strength (3) and infinite dilution (8) are consistent with the present results. The first and third protonation reactions describe association of hydrogen ions with the phosphonate group, the second hydrogen ion associates with the carboxylate. This sequence has been previously confirmed by Heubel and Popov (8) based on ^{31}P and ^{13}C NMR spectroscopy. Comparison of the acidity of the $-\text{CO}_2^-$ and $-\text{PO}_3^-$ groups in PAA with the $\text{pK}'\text{s}$ of analogous monoacids suggests that each group has minimal effect on the relative basicity of the other or perhaps that the sharing of

Table 1. Protonation Constants for PAA and related ligands at 25°C.

Ligand	pK_1	pK_2	pK_3	Conditions	Reference
PAA	1.12 (0.15)	4.66 (0.02)	7.69 (0.02)	I=0.5 M, NaNO ₃	present work
PAA	0.92 (0.10)	4.57 (0.01)	7.23 (0.01)	I=2.0 M NaClO ₄	3
PAA	2.0	5.11	8.69	I=0	8
$\text{CH}_3\text{CH}_2\text{PO}_3^{2-}$	2.29	7.79		I=0.1 M	9
$\text{CH}_3\text{CH}_2\text{CO}_2^-$	4.69			I=0.1 M	9

hydrogen ions by the two functional groups offsets the inductive effect.

To calculate the stability constants for the Am and Eu PAA complexes, it is first necessary to correct the distribution data for the presence of nitrate complexes. The stability constant for EuNO_3^{2+} at 0.5 M ionic strength ($\log \beta_{\text{EuNO}_3} = 0.44$) was taken from Martell (9). Appropriate stability constants for AmNO_3^{2+} ($\log \beta_{\text{AmNO}_3} = 0.38$) were extrapolated from existing data at higher ionic strength by comparing the Am β 's with more extensive data on EuNO_3^{2+} . The distribution data as a function of [PAA] and $[\text{H}^+]$ were reduced to the form $D_0/D-1-\beta_{\text{MNO}_3}[\text{NO}_3^-]$. Averaged distribution data used to determine stoichiometry and stability of the Am-PAA and Eu-PAA complexes are shown in Figures 1 and 2 respectively. In Table 2 we have included the complete data set for Am.

Preliminary analysis of the data consisted of plots of $D_0/D-1-\beta_{\text{MNO}_3}[\text{NO}_3^-]$ ($D_0/D-1-C$ for simplicity) vs. $[\text{PAA}^3]$ at constant acidity. These plots were fit by a quadratic expression,

Table 2. Distribution data for Am^{3+} + PAA at 25°C, $I=0.5$ M (NaNO_3).

$[\text{PAA}]_t$	$[\text{H}^+]$	D_o	D	$D_o/D-1-C$	$\sigma(D_o/D-1-C)$
0.01	0.005	6.942	2.320	0.7923	0.0658
0.01	0.005	6.942	2.426	0.6615	0.0540
0.02	0.005	6.942	1.973	1.319	0.109
0.02	0.005	6.942	2.118	1.078	0.089
0.04	0.005	6.942	1.354	2.926	0.235
0.04	0.005	6.942	1.332	3.013	0.268
0.07	0.005	6.942	0.793	6.558	0.538
0.07	0.005	6.942	0.815	6.317	0.518
0.1	0.005	6.942	0.574	9.900	0.780
0.1	0.005	6.942	0.586	9.643	0.867
0.15	0.005	6.942	0.330	18.86	1.49
0.15	0.005	6.942	0.350	17.63	1.42
0.2	0.005	6.942	0.233	27.58	2.26
0.2	0.005	6.942	0.223	28.88	2.34
0.01	0.01	10.17	3.518	0.6902	0.0550
0.01	0.01	10.17	3.935	0.3840	0.0339
0.02	0.01	10.17	2.354	2.120	0.808
0.02	0.01	10.17	3.502	0.7038	0.0600
0.04	0.01	10.17	2.168	2.489	0.213
0.04	0.01	10.17	2.329	2.167	0.175
0.07	0.01	10.17	1.399	5.070	0.440
0.07	0.01	10.17	1.438	4.872	0.404
0.1	0.01	10.17	1.085	7.170	0.759
0.1	0.01	10.17	1.051	7.471	0.619
0.15	0.01	10.17	0.597	14.83	1.29
0.15	0.01	10.17	0.599	14.76	1.25
0.2	0.01	10.17	0.412	22.47	1.78
0.2	0.01	10.17	0.433	21.29	1.76
0.0194	0.02	19.78	6.592	0.8001	0.0474
0.0194	0.02	19.78	6.302	0.9384	0.0530
0.0485	0.02	19.78	4.598	2.102	0.135
0.0485	0.02	19.78	4.618	2.082	0.137
0.0727	0.02	19.78	3.220	3.942	0.223
0.0727	0.02	19.78	3.088	4.204	0.254
0.0921	0.02	19.78	2.560	5.527	0.283
0.0921	0.02	19.78	2.553	5.547	0.360
0.145	0.02	19.78	1.672	9.632	0.654
0.145	0.02	19.78	1.662	9.700	0.617
0.242	0.02	19.78	0.830	21.64	1.252
0.242	0.02	19.78	0.841	21.31	1.192
0.339	0.02	19.78	0.422	44.61	2.309
0.339	0.02	19.78	0.427	44.13	2.716

Figure 1 Distribution data and least-squares fit for Am-PAA system. Extraction into various

Figure 2 Distribution data and least-squares fit for Eu-PAA system. Extraction into various concentrations of HDEHP in toluene. The term C on the y axis label represents $\beta_{\text{MNO}_3}[\text{NO}_3]$.

indicating M:L stoichiometries of 1:1 and 1:2. The resolved conditional constants varied with the acidity to indicate the stoichiometry of the 1:1 and 1:2 complexes with respect to $[H^+]$. The hydrogen ion dependence for the 1:1 and 1:2 complexes of Am were $1.66(\pm 0.01)$ and $3.92(\pm 0.01)$ respectively, suggesting the presence of the species MH_2L^{2+} , MHL^+ , and $M(H_2L)_2^+$. The corresponding values for Eu were $0.92(\pm 0.54)$ and $3.59(\pm 0.03)$ indicating the dominant species were MHL^+ , $M(H_2L)_2^+$, and $M(HL)_2^-$. Data files like those represented in Table 2 were fit using a nonlinear least-squares program described previously (2). The following fit equation was used to adjust the data:

$$D_o/D-1-C = \beta_{121}[H^+]^2[L^{3-}] + \beta_{111}[H^+][L^{3-}] + \beta_{142}[H^+]^4[L^{3-}]^2 + \beta_{122}[H^+]^2[L^{3-}]^2 \quad (1)$$

The σ 's in Table 2 are based primarily on radioactivity counting statistics for the determination of distribution ratios D and D_o . All other sources of error were considered to contribute equally to the uncertainty of the individual points. The data were fit using $1/\sigma$ as the weighting factor.

Neither set of data supported all four of the model parameters in equation 1 (β_{121} , β_{111} , β_{142} , β_{122}), but each system was best described by a different three parameter equation. The best fit parameters are given in Table 3. The solid lines in Figures 1 and 2 are the least squares fit lines calculated using the stability constants in Table 3. Stepwise constants for $Am(H_2L)/Am(H_2L)_2$ ($\log K_{121} = 13.82(\pm 0.04)$, $\log K_{142} = 13.53(\pm 0.04)$) show only a factor of 2 decrease for addition of the second H_2L^- ligand to the 1:1 complex implying that the strength of interaction of the second ligand with Am^{3+} is effected little by the presence of the first. For europium, the step-wise constants for $Eu(HL)^+/Eu(HL)_2^-$ are $12.10(\pm 0.05)$ and $10.98(\pm 0.07)$ respectively. Here, the 1:2 complex is an order of magnitude weaker than the 1:1 complex, perhaps reflecting the greater perturbation of the inner coordination sphere of Eu by the doubly ionized $H(PAA)^{2-}$ anion. The relatively greater importance of $H(PAA)^{2-}$ in the Eu system

Table 3. Stability constants for americium and europium complexes with phosphonoacetic acid at 25°C^a.

Metal	$\log \beta_{121}$	$\log \beta_{111}$	$\log \beta_{142}$	$\log \beta_{122}$	I, ref
Am^{3+}	13.82(0.04)	11.62(0.04)	27.35(0.01)	-	0.5 M, p.w.
Eu^{3+}	-	12.10(0.05)	27.81(0.01)	23.08(0.05)	0.5 M, p.w.
UO_2^{2+}	15.42	13.91	29.87	26.50	0.1 M, 4
Th^{4+}	15.73	-	30.51	-	2.0 M, 3

reflects stronger electrostatic attraction of the smaller Eu^{3+} cation for the ligand.

Besides the present results, earlier data on UO_2^{2+} (4) and Th^{4+} (3) are included in Table 3. Only the $M(H_2L)_2$ complex is common to all four systems. The relative order of complex

stability for this series is $\text{Am}^{3+} < \text{Eu}^{3+} < \text{UO}_2^{2+} < \text{Th}^{4+}$. This order is consistent with expectation, though the uranyl complexes appear to be exceptionally strong, perhaps reflecting a favorable contribution to overall complex stability by hydrogen bonding interactions between the protonated phosphonate group and the uranyl oxygens. The stepwise constants for both uranyl and thorium show an order-of-magnitude dropoff for addition of the second ligand, similar to the Eu-PAA system.

Am/Eu Separation Factors

The net separation factor for metal ions in a solvent extraction process which uses

$$S_a^A = \frac{D^A}{D^B} = \frac{D_o^A(1+\sum \beta_i^A [L]^i)}{D_o^B(1+\sum \beta_i^B [L]^i)} \quad (2)$$

aqueous complexes is described by equation 2:

where D_o represents the distribution of the respective metal ions in the absence of aqueous complexes and β 's are the stability constants of the respective metal ions. It is clear from this equation that the separation factors of A from B are directly dependent on their relative extraction but inversely dependent on the relative stability of their aqueous complexes. For the most efficient separation, both the extractant and the aqueous complexant must have appropriate properties.

In the case of HDEHP, literature reports and the D_o values determined herein indicate that Eu is extracted about 30 times more efficiently than Am ($\log K_{\text{ex}}^{\text{Eu}} = -1.06$, $\log K_{\text{ex}}^{\text{Am}} = -2.61$, after correction for nitrate complexes). Since the Eu-PAA complexes are more stable than those of Am, the extractant and complexant ligands in this system work in the opposite sense resulting in lower separation factors when the complexant is present than when it is absent. At 0.01 M acid and $[\text{HDEHP}] = 0.15$ M, the distribution ratios and separation factors are $D_{\text{Am}} = 4.49$, $D_{\text{Eu}} = 140$, and $S_{\text{Eu}}^{\text{Am}} = 0.032$. For extraction from 0.2 M PAA solutions under the same conditions, the corresponding values are $D_{\text{Am}} = 0.42$, $D_{\text{Eu}} = 8.22$, and $S_{\text{Eu}}^{\text{Am}} = 0.051$. Calculations based on the resolved stability constants as applied in equation 2 reproduce the latter results. Similar results were obtained at 0.005 M acid.

Sulfonic acid extractants like HDNNS are known to exhibit little selectivity when extracting metal ions of the same charge (1). Because the D_o^A/D_o^B term in equation 2 is near 1, the aqueous complexant should enhance Am/Eu separation efficiency in this system. In dual-label experiments using 0.0112 M HDNNS in toluene as the extractant, the following results were obtained at 0.02 M acid, 0.5 M NaNO_3 : $D_{\text{Am}} = 16.1$, $D_{\text{Eu}} = 19.4$, and $S_{\text{Eu}}^{\text{Am}} = 0.83$. For extraction from 0.34 M PAA at $[\text{H}^+] = 0.02$ M and 0.5 M NaNO_3 , the observed distribution ratios and separation factors are: $D_{\text{Am}} = 1.70$, $D_{\text{Eu}} = 0.94$, and $S_{\text{Eu}}^{\text{Am}} = 1.81$. Corresponding values calculated from the experimental D_o values and the resolved stability constants are: $D_{\text{Am}} = 0.79$, $D_{\text{Eu}} = 0.42$, and $S_{\text{Eu}}^{\text{Am}} = 1.88$. While the separation factor is consistent, the distribution ratios are lower than the experimental values suggesting the possible partial extraction of both

the Eu and Am-PAA complexes by HDNNS.

Neutral bifunctional extractants like CMPO also exhibit little lanthanide/actinide selectivity when extracting these metal ions from nitrate media (1). When thiocyanate is the counter ion, actinide/lanthanide separation factors average about 7 (10, 11). This result is related to the stronger interaction between actinides and the soft donor SCN^- . Since actinides are more strongly extracted from this system and the europium complexes with PAA are more stable, both the $D_0^{\text{Am}}/D_0^{\text{Eu}}$ and $(1+\Sigma\beta_{mhl}[\text{H}^+]^h[\text{L}^{3-}]^l)_{\text{Eu}}/(1+\Sigma\beta_{mhl}[\text{H}^+]^h[\text{L}^{3-}]^l)_{\text{Am}}$ terms of equation 2 are favorable. The separation factors in both the nitrate and thiocyanate systems could be improved by the addition of an aqueous complexant like PAA. Because the systems offer additional parameters for adjustment of the relative D's, we have examined only a few selected sets of conditions. These conditions do not necessarily represent the optimized configuration for these systems.

The distribution ratios and separation factors for Am and Eu extraction by 0.5 M CMPO-diethylbenzene from 0.5 M NaNO_3 at pH 1.88 are $D_{\text{Am}} = 110$, $D_{\text{Eu}} = 107$, and $S_{\text{Eu}}^{\text{Am}} = 1.03$. When 0.2 M PAA is introduced into the aqueous phase, the corresponding values are $D_{\text{Am}} = 4.57$, $D_{\text{Eu}} = 2.21$, and $S_{\text{Eu}}^{\text{Am}} = 2.07$. Distribution ratios calculated from the experimental D_0 values (corrected for the mononitrate complex in the aqueous phase) and the stability constants reported in Table 3 are $D_{\text{Am}} = 10.7$ and $D_{\text{Eu}} = 5.00$ ($S_{\text{Eu}}^{\text{Am}} = 2.14$). The experimental separation factor is well described by the calculation, but the distribution ratios are lower than the calculated values. At 0.3 M PAA, the discrepancy between experimental and calculated distribution ratios is larger while the separation factors are still consistent. We cannot at present explain this observation, but it may be related to the procedures used to preequilibrate the extractant phase or perhaps to the extraction of mixed ligand complexes.

The CMPO - thiocyanate system was investigated at pH 1.88-2.00, 0.05 M CMPO-diethylbenzene, 0.5 M KSCN, and [PAA] between 0 and 0.3 M. The D_0 values were corrected for AmSCN^{2+} ($\beta = 4.0$) and EuSCN^{2+} ($\beta = 2.4$) complexes in the aqueous phase using the stability constants of Kinard and Choppin (12). Their constants were determined at 5.0 M ionic strength and so may not be appropriate for 0.5 M media. The average distribution ratios for replicate experiments done with slightly different extractant preconditioning procedures are $D_{\text{Am}} = 25.8$, $D_{\text{Eu}} = 4.30$, and $S_{\text{Eu}}^{\text{Am}} = 6.00$, consistent with literature reports for similar conditions. At both 0.1 M and 0.2 M PAA, the Am/Eu separation potential is enhanced: 0.1 M PAA, $D_{\text{Am}} = 4.82$, $D_{\text{Eu}} = 0.42$, and $S_{\text{Eu}}^{\text{Am}} = 11.6$; 0.2 M PAA, $D_{\text{Am}} = 1.24$, $D_{\text{Eu}} = 0.084$, and $S_{\text{Eu}}^{\text{Am}} = 14.7$. Calculations based on the experimental D_0 's and β 's in Table 3 again reproduce the separation factors, but predict higher distribution ratios. Further experiments are planned to optimize and further test and optimize this system for actinide/lanthanide separations.

CONCLUSION

Complexes between Am^{3+} or Eu^{3+} and phosphonoacetic acid differ in relative stability

in accord with the electrostatic model of cation binding. The smaller Eu^{3+} cation forms stronger complexes with PAA than the larger Am^{3+} cation. The observed metal complexes in the acid range from 0.005 M to 0.02 M (at $I = 0.5$ M) are $\text{Eu}(\text{HL})^+$, $\text{Eu}(\text{H}_2\text{L})_2^+$, $\text{Eu}(\text{HL})_2^-$ and $\text{Am}(\text{H}_2\text{L})_2^+$, $\text{Am}(\text{HL})^+$, $\text{Am}(\text{H}_2\text{L})_2^+$. When used as a holdback reagent, PAA slightly enhances the separation of Am/Eu when used with sulfonic acids or CMPO/nitrate, but reduces separation efficiency with HDEHP. In a CMPO/ SCN^- extraction system which favors extraction of Am over Eu, addition of PAA increases the separation efficiency by a factor of 2-3 at 0.3 M PAA/0.5 M SCN^- . The calculated stability constants can be used to explain the separation factors, but do not always accurately predict metal distribution ratios in the CMPO systems, implying that there are details of this system which have not been fully elucidated.

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