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ARTICLE

Extraction Properties of Glycine-Based Amic-Acid-Type Extractants for Minor Actinides and Rare-Earth Elements

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Herein, the extraction properties of three glycine-based amic-acid-type extractants for minor actinides and rare-earth elements were investigated using a single-stage batch method. These extractants exhibited selectivity for the Am/rare-earth elements.

KEYWORDS: solvent extraction, separation, minor actinides, Glycine-based Amic-acid-type Extractants, partitioning and transmutation

I. Introduction

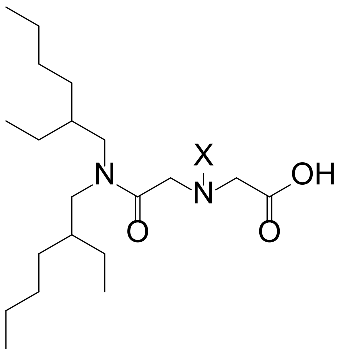
In Japan, the high-level radioactive waste (HLW) generated from the reprocessing of spent nuclear fuel is geologically disposed of in vitrified form. To reduce the volume and radiotoxicity of HLW, researchers have proposed the extraction of minor actinides (MAs) having high potential radiotoxicity, such as Np, Am, and Cm, from HLW and their transmutation to short-lived or stable nuclides using power reactors or accelerator-driven systems.[1)] The concentration of rare-earth elements (REs) in HLW is higher than that of MAs, and some REs have a large neutron-capture cross-section that interferes with the transmutation of MA. Therefore, the mutual separation of MAs and REs by the hydrometallurgical method has been investigated. However, separating trivalent MAs (MA(III)), such as Am and Cm, from trivalent REs (RE(III)) is challenging because of their similar chemical properties including ionic potential and ionic radii. Many extractants for hydrometallurgical processes have been developed for MA(III)/RE(III) mutual separation. Recently, the following extractants having N and O as donor atoms were explored: hexaoctylnitrilotriacetamide (HONTA),[2)] 1,10-phenanth- roline-2,9-dicarbox-amides (PTDA),[3)] *N*,*N*-di-2-ethylhexyl- 6-amide-pyridine-2-carboxylic acid (DEHAPA)[4)], and *N*,*N*, *N'*,*N'*-tetra(2-ethylhexyl)-3,6-(*N''*,*N'''*-dibutyl)di-aza-octane-1,8-diamide (DADA).[5)] In these extractants, each O atom works as a hard donor to extract MA(III) and RE(III) and each N atom works as a soft donor to enhance the extraction efficiency of MA(III) over RE(III).

Herein, we examined the extraction properties of MA(III) and RE(III) using glycine-based amic-acid-type extractants[6–10)], which have N and O donors in each ligand. The study investigated the extraction properties of three ligands, *N*-[*N*,*N*-di(2-ethylhexyl)aminocarbonylmethyl]methylglycine (D2EHAMG) and *N*-[*N*,*N*-di(2-ethylhexyl)amino carbonyl-methyl]ethylglycine (D2EHAEG), based on *N*- [*N*,*N*-di(2-ethyl-hexyl)aminocarbonylmethyl]glycine (D2EHAG), with the secondary amine N at the center of the chemical structure changed to a tertiary amine (CH_3 and CH_2CH_3) for MA(III) and RE(III) separation.

II. Experimental

1. Reagents

The D2EHAG, D2EHAMG, and D2EHAEG extractants (**Fig. 1**) were obtained from Kishida Chemical Co., Ltd (Osaka, Japan). The radioactive isotopes (^{152}Eu, ^{241}Am, and ^{244}Cm) were purchased from the Japan Radioisotope Association (Tokyo, Japan). All other reagents were of analytical grade and were used without further purification.



D2EHAG, X = H
D2EHAMG, X = CH_3
D2EHAEG, X = CH_2CH_3

Fig. 1 Chemical structures of glycine-based amic-acid-type extractants

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2. Procedure of the Batch Extraction Tests

Each extractant was dissolved in *n*-dodecane and employed as the organic phase. For the preparation of D2EHAMG and D2EHAEG, 2-ethyl-1-hexanol was added to the organic phase as a solubilizer at a concentration of 5%. Each organic phase was pre-equilibrated several times with the aqueous phase at its target pH for each extraction experiment. The aqueous phases comprised of 1 mg dm^{-3} of RE (Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) ions and trace concentrations of ^{152}Eu, ^{241}Am, and ^{244}Cm ions having different pH values. A 0.1 mol dm^{-3} (M) NH_4NO_3 solution was employed to maintain the ionic strength of each aqueous phase. Equal volumes of the organic and aqueous phases were mixed in a test tube with a screw cap, followed by mechanical shaking at room temperature (ca. 293 ± 2 K) for over 10 min to achieve extraction equilibrium. After separating the two phases by centrifugation, the pH value of aqueous phase was measured. The concentrations of the RE ions in the aqueous phases were measured by inductively coupled plasma mass spectrometry (7500, Agilent). The radioactivities of the aqueous and organic phases after extraction were evaluated by α-ray spectrometry (ENS-U450, ORTEC) and γ-ray spectrometry (GCD-20180X , BSI).

The distribution ratio (D) and separation factor of M1 from M2 ($SF_{\mathrm{M1/M2}}$) are defined by Eqs. (1) and (2), respectively:

$$D = \frac{A_{\mathrm{org}}}{A_{\mathrm{aq}}} = \frac{(C_{\mathrm{init}} - C_{\mathrm{eq}})}{C_{\mathrm{eq}}} \tag{1}$$

$$SF_{\mathrm{M1/M2}} = \frac{D_{\mathrm{M1}}}{D_{\mathrm{M2}}} \tag{2}$$

where A and C represent the radioactivity concentration and metal ion concentration, respectively. Subscripts org, aq, init, and eq represent the organic phase, aqueous phase, initial condition of the aqueous phase, and equilibrated condition of the aqueous phase respectively.

3. Potentiometric Measurement of the Extractants and Acetic Acid

The values of the cosolvent dissociation constants ($\mathrm{p_s}K_\mathrm{a}$) of the extractants and acetic acid were determined by potentiometric titration according to the method described in previous reports.[10,11] All potentiometric measurements were performed in a jacketed titration cell thermostated at 298 K. The extractants and acetic acid were dissolved in an ethanol–water mixture (50% ethanol) containing 0.1 M NaCl. The combined pH electrodes were calibrated by Gran's method,[12] which determined the standard potential. The $\mathrm{p_s}K_\mathrm{a}$ values were measured in solutions using an automatic potentiometric titrator. The measurements were performed three times in the pH range of approximately 2.4–11, and the average values were calculated.

III. Results and Discussion

1. pH Dependency

Figure 2 shows the dependence of the equilibrium pH on the D with the D2EHAG, D2EHAMG, and D2EHAEG. Each extractant was diluted to 0.05 M. The distribution ratios of all metal ions increased with the equilibrium pH. The slopes for all metal ions were approximately 2.5, 2, and 2 for D2EHAG, D2EHAMG, and D2EHAEG, respectively. The order of the extractability toward Am, Cm, and RE was D2EHAG > D2EHAMG > D2EHAEG. The extractability of the ligands increased with increasing pH values and with shortening carbon chains (CH_2CH_3, CH_3, and H) bonded to the central nitrogen atom. This suggests that D2EHAEG (N–CH_2CH_3) has a lower extraction performance for these metal ions compared to D2EHAG (N–H). Since, 2-ethyl-1-hexanol was added as a solubilizer to the organic phase in the experimental D2EHAMG and D2EHAEG, difference in the diluents possibly influenced on the extraction behavior [3,5]. Further investigations are necessary for the comprehensive understanding of the effects of the carbon chain bonded to the

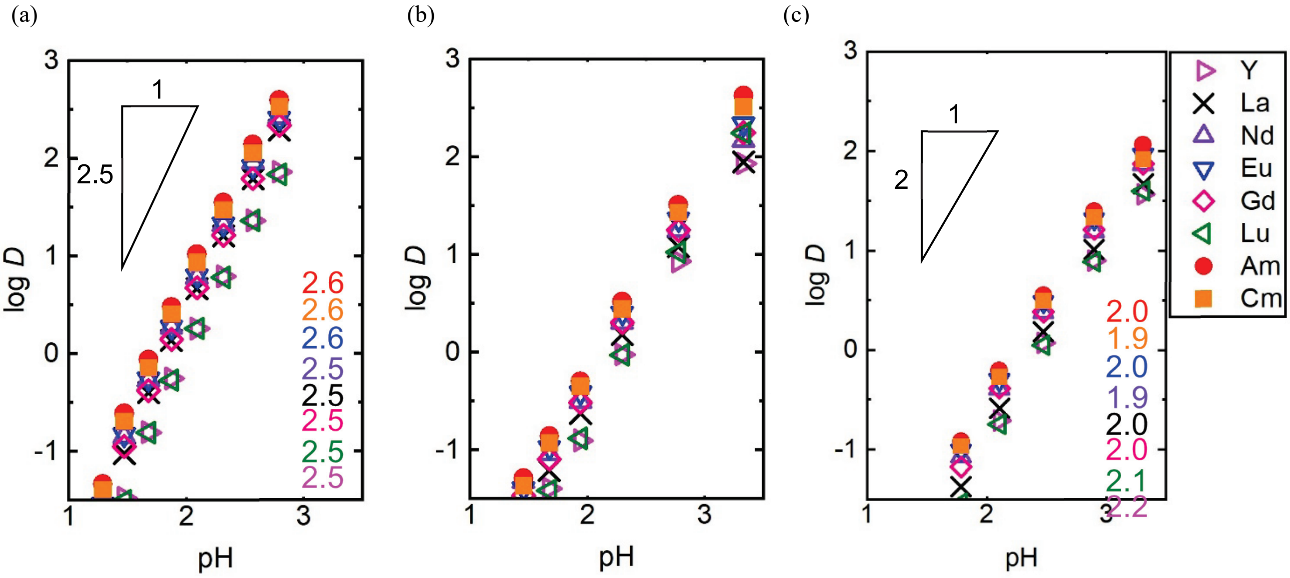

Fig. 2 Dependence of the equilibrium pH on D with (a) D2EHAG, (b) D2EHAMG, and (c) D2EHAEG. The numbers in the figures represent the slopes

central N atom and the composition of the diluents on the extraction behavior.

Figure 3 shows a profile of the *D* of MA(III) and RE(III) for each extractant. All extractants exhibited higher *D* values for Am than for RE. The *D* of Cm was similar to that of Sm, which exhibited the highest *D* values among REs. The $SF_{\mathrm{Cm/Sm}}$ values of the extractants were 1.3, 1.1, and 1.0 for D2EHAG, D2EHAMG, and D2EHAEG, respectively. This result suggests that the central N–X bond of the ligands decreases the $SF_{\mathrm{MA/RE}}$ value by lengthening the carbon chain (H, CH_3, and CH_2CH_3). Additionally, the *D* of Am was higher than that of Cm, and the lanthanide pattern exhibited selectivity toward light and medium lanthanides. Similar extraction properties have been reported for other soft donor ligands, such as HONTA2) and PTDA,3) and it can be suggested that these extractants coordinate the amine N atom to the metal ions. Interestingly, DEHAPA,4) which is a glycine-based amic-acid-type extractant having pyridine nitrogen as the central N atom, exhibited a higher distribution ratio for Eu than for Am. A more detailed investigation is required to clarify its properties.

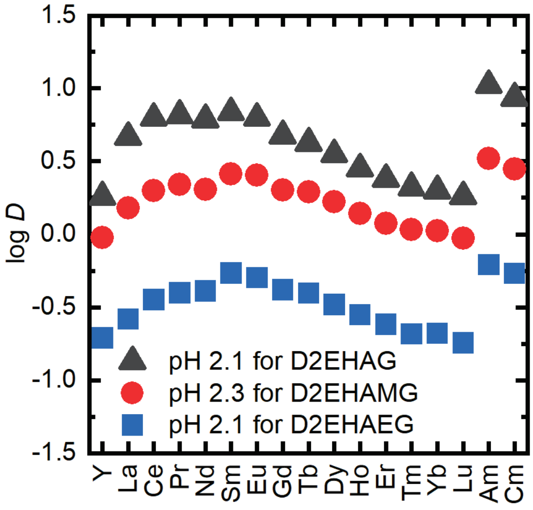

Fig. 3 Profile of the D of MA(III) and RE(III) for each extractant. pH 2.1 for D2EHAG, pH 2.3 for D2EHAMG, pH 2.1 for D2EHAEG

2. Extractant Concentration Dependency

Figure 4 shows the dependence of the extractant concentration on the *D* for D2EHAG, D2EHAMG, and D2EHAEG. The equilibrium acid concentration of the aqueous phase was attained at pH 2.1 for D2EHAG and pH 2.4 for D2EHAMG and D2EHAEG. The values of *D* increased with the extractant concentration. A slope analysis was carried out the effect of the extractant concentration on the *D* to estimate the number of ligands involved in the complexation of the metal ions. The order of the slopes was D2EHAEG > D2EHAMG > D2EHAG. This result suggests that the number of ligands coordinated to the metal ion increases with the length of the carbon chain in the central N–X bond. Contrarily, studies have indicated that D2EHAG forms a dimer in *n*-dodecane6-9) because general acid extractants are known to exist as dimers in solvents of low polarity, such as *n*-dodecane13-15). In the present study, the ligands might similarly form dimers in the organic phase. However, note that the experiments involving D2EHAMG and D2EHAEG were performed with 2-ethyl-1-hexanol as a solubilizer, and its effect must be considered. Further studies will be conducted to elucidate the extraction equilibrium state.

3. Interaction of the Extractants with H^+

To support the results of the pH dependency tests, we investigated the interaction of the extractants with H^+. **Figure 5** shows the relation between the initial pH and extraction equilibrium pH in the aqueous phase. All extractants exhibited an upward convex behavior, suggesting the extraction of the acid in the aqueous phase into the organic phase by the extractants. The H^+-extraction order was D2EHAMG > D2EHAEG > D2EHAG. The acid extraction decreases the concentration of free extractant and competes with the extraction of metal ions. Therefore, extractants that

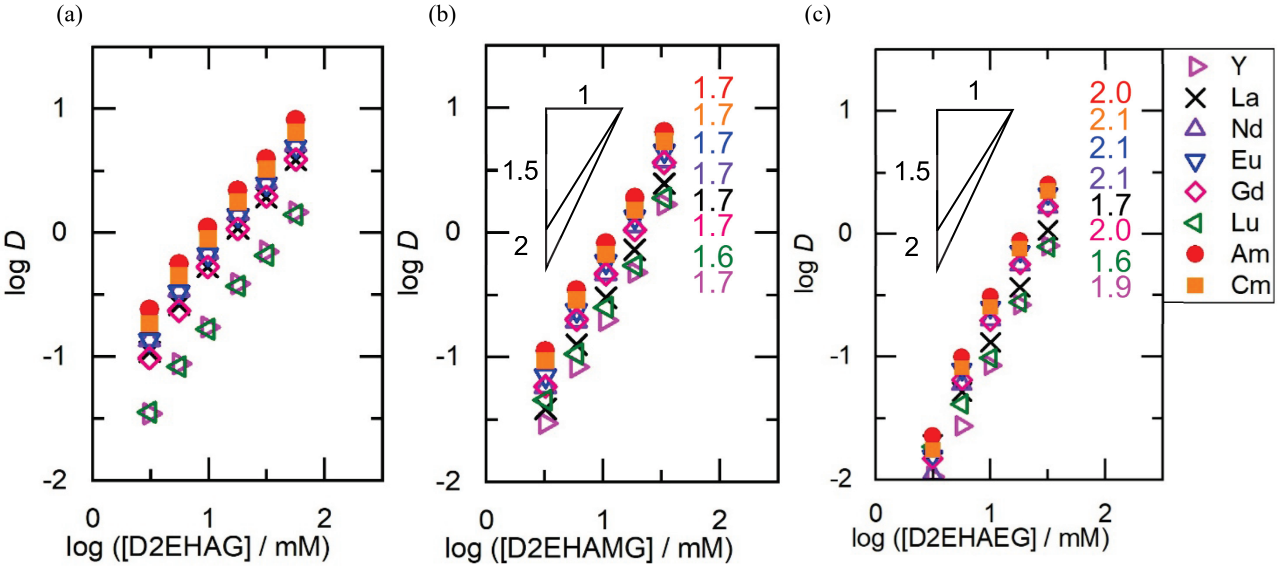

Fig. 4 Dependence of the extractant concentration on *D* with (a) D2EHAG, (b) D2EHAMG, and (c) D2EHAEG. The numbers in the figures represent the slopes

are less likely to extract acids are considered to deliver a high extraction efficiency.

The acidity constant is generally employed to compare the acidity of acidic extractants. However, the extractants are hardly soluble in water, making it difficult to obtain the acidity contestant ($\mathrm{p}K_a$). As a solution, the extractants were dissolved in a water–ethanol cosolvent, and the $\mathrm{p_s}K_\mathrm{a}$ was determined by potentiometric titration. This measurement was conducted not to obtain the exact values of the $\mathrm{p}K_a$ but to compare the acidities of the extractants and acetic acid. **Table 1** shows the $\mathrm{p_s}K_\mathrm{a}$ values of the extractants and acetic acid. The order of the $\mathrm{p_s}K_\mathrm{a}$ was D2EHAEG > D2EHAMG ≈ D2EHAG. These results suggest that the extractant with a comparatively low $\mathrm{p_s}K_\mathrm{a}$ value readily undergoes acid dissociation in the acid concentration range and that the metal ions are more easily extracted. The $\mathrm{p_s}K_\mathrm{a}$ of acetic acid was determined to be 5.41 ± 0.03, higher than the acidity constant in water ($\mathrm{p}K_a = 4.56$ in water with an ionic strength of 0.1 M at 298 K). Given that the $\mathrm{p}K_a$ varies in response to different solvents, it seems unlikely that the $\mathrm{p_s}K_\mathrm{a}$ values of the extractants obtained in this study represent the conventional acid dissociation of the carboxylic groups. This result suggests that the titration measurements were performed when the ligands were already in an acid-dissociated state or when the hydrogen of the carboxylic group was stabilized by the formation of a chelate ring with the central nitrogen atom of the ligand through intramolecular hydrogen bonding.

Based on these findings, D2EHAG, which is less likely to extract acids and has a lower $\mathrm{p_s}K_\mathrm{a}$ value, appears to have the best extraction performance among the three ligands. This result is consistent with the pH-dependency test. Therefore, extractability order in pH dependency can be explained by the acid extraction results and the $\mathrm{p_s}K_\mathrm{a}$ values of the extractants.

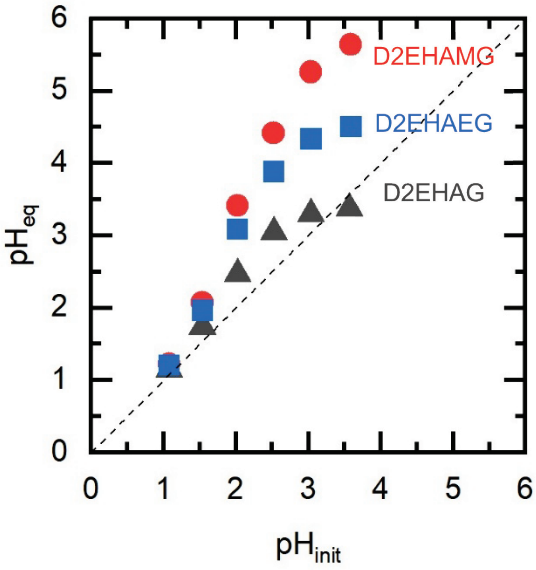

Fig. 5 pH values of the initial and equilibrium extractions in the aqueous phase

Table 1 $\mathrm{p_s}K_\mathrm{a}$ values of the extractants and acetic acid

Sample	$\mathrm{p_s}K_\mathrm{a}$
Acetic acid	5.41±0.03
D2EHAG	7.69±0.05
D2EHAMG	7.70±0.01
D2EHAEG	8.03±0.02

IV. Conclusion

Herein, we investigated the extraction properties of glycine-based amic-acid-type extractants for MAs and REs. These extractants exhibited selectivity for the Am/RE, and the central N–X bond of the ligands affected their extraction efficiency for MAs and REs. These observations were consistent with the pH-dependency test results, which can be explained by the results of the acid extraction and $\mathrm{p_s}K_\mathrm{a}$ of the extractants. To improve our understanding, we will investigate the extraction mechanism of the extractants.

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References

1) K. Minato, Y. Morita, T. Kimura, et al., “Recent research and development on partitioning and transmutation by "double-strata fuel cycle concept" in JAEA,” *Proceedings of GLOBAL 2009*, Paris, Japan, Sep. 6-11, 2009, 504 (2009).
2) Y. Ban, H. Suzuki, S. Hotoku, et al., “Minor actinides separation by *N,N,N’,N’,N”,N”*-hexaoctyl nitrilotriacetamide (HONTA) using mixer-settler extractors in a hot cell,” *Solvent Extr. Ion Exch.*, **37**[7], 489 (2019).
3) N. Tsutsui, Y. Ban, H. Suzuki, et al., “Effects of diluents on the separation of minor actinides from lanthanides with tetradodecyl-1,10-phenanthroline-2,9-diamide from nitric acid medium,” *Anal. Sci.*, **36**[2], 241 (2020).
4) C. Xu, T. Liu, Q. Liu, et al., “Complexation of Am(III) and Eu(III) with DRAPA (*N,N*-dialkyl-6-amide-pyridine-2-carboxylic acid),” *Dalton Trans.*, **52**[43], 15669 (2023).
5) P. Sinharoy, A. K. Singha Deb, Sk. M. Ali, et al., “Ligand architectural effect on coordination, bonding, interaction, and selectivity of Am(III) and Ln(III) ions with bitopic ligands: synthesis, solvent extraction, and DFT studies,” *Phys. Chem. Chem. Phys.*, **22**[27], 15448 (2020).
6) Y. Baba, F. Kubota, N. Kamiya, et al., “Development of novel extractants with amino acid structure for efficient separation of nickel and cobalt from manganese ions,” *Ind. Eng. Chem. Res.*, **53**[2], 812 (2014).
7) W. Yoshida, F. Kubota, Y. Baba, et al., “Separation and recovery of scandium from sulfate media by solvent extraction and polymer inclusion membranes with amic acid extractants,“ *ACS Omega*, **4**[25], 21122 (2019).
8) Y. Baba, A. Fukami, F. Kubota, et al., „Selective extraction of scandium from yttrium and lanthanides with amic acid-type extractant containing alkylamide and glycine moieties,“ *RSC Adv.*, **4**[92], 50726 (2014).

9) T. Hanada, K. Seo, W. Yoshida, et al., “DFT-based investigation of amic–acid extractants and their application to the recovery of Ni and Co from spent automotive lithium–ion batteries,“ *Sep. Purif. Technol.*, **281**, 119898 (2022).
10) W. Yoshida, Y. Baba, F. Kubota, et al., “Selective transport of scandium(III) across polymer inclusion membranes with improved stability which contain an amic acid carrier,” *J. Memb. Sci.*, **572**, 219 (2019).
11) Y. Sasaki, T. Oshima, Y. Baba, “Mutual separation of indium(III), gallium(III) and zinc(II) with alkylated aminophosphonic acids with different basicities of amine moiety,” *Sep. Purif. Technol.*, **173**, 37 (2017).
12) G. Gran, “Determination of the equivalence point in potentiometric titrations. Part II,” *Analyst*, **77**[920], 661 (1952).
13) D. Pouillon, F.M. Doyle, „Solvent extraction of metals with carboxylic acids — theoretical analysis of extraction behaviour,“ *Hydrometallurgy*, **19**[3], 269–288 (1988).
14) K. Inoue, Y. Baba. K. Yoshizuka, „Equilibria in the solvent extraction of indium (III) from nitric acid with acidic organophosphorus compounds,“ *Hydrometallurgy*, **19**[3], 393–399 (1988).
15) W. Tao, Y. Nagaosa, „Solvent extraction of copper (II) with di ‐ 2 ‐ methylnonylphosphoric acid in some organic diluents,“ *Solvent Extr. Ion Exch.*, **21**[2], 273–290 (2003).