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The Chemistry of Americium. I. A Study of the Preparation of Am (V) and Its Behavior by Means of TTA Extraction

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The method for preparing Am(V) in various solutions was investigated by utilizing the difference in extractability between Am(V) and Am(III) in an TTA-isobutanol extraction system; Am(III) was quantitatively extracted with 0.1M TTA in isobutanol from a 1M acetate buffer solution at a pH greater than 3, while the percentage of Am(V) extracted into the organic phase was increased substantially with an increase in the pH from 3 to 5. When the organic phase containing Am(V) was shaken with an aqueous phase having a proper pH value and composition, Am(V) was selectively stripped into the aqueous phase. The stability of the valency state of Am(V) in the perchlorate, the acetate, and the sulfate solutions was then studied by examining the variation in the percentage of americium extracted as a function of the standing time. The rate of change in the valency state in the acetate and the perchlorate media is very slow, while it is rather rapid in the sulfate medium. This difference may be attributable to the faster rate of the disproportionation reaction of Am(V) in the last medium than in the former two. By applying the above results, the chemical behavior of Am(V) in the aqueous solution was investigated by TTA extraction; it was found that Am(V) would be in the form of AmO_2^+ in the absence of a complexing reagent. By the addition of acetate ions, the step-by-step formation of the acetate complex of Am(V) was observed. The stability constants of $[AmO_2Ac]$ and $[AmO_2Ac_2]^-$ were determined to be (25.0 ± 3.1) $(\mathrm{mol}/l)^{-1}$ and (12.8 ± 1.2) $(\mathrm{mol}/l)^{-2}$ respectively.

Although many papers on the chemical behavior of Am(III), which is the most stable oxidation state of americium in aqueous solutions, have been published, the knowledge concerning that of americium in higher oxidation states in rather poor, especially when a tracer concentration is involved. Investigations of americium in higher oxidation states have been limited to work on the absorption spectra of Am(V) and Am(VI) in various solutions,[1-5] the disproportionation reaction of Am(V),[1-3,6-9] and the self-reductions of both Am(V) and Am(VI).[1-3,6,10,11] The backwardness in this study is primarily due to the technical difficulty involved in the experimentation and does not reflect any lack of importance in these valency states. Americium is the heaviest of the actinide elements which are known to have pentavalent and hexavalent

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[1] G. R. Hall and P. D. Herniman, *J. Chem. Soc.*, **1954**, 2214.

[2] G. R. Hall and T. L. Markin, *J. Inorg. Nucl. Chem.*, **4**, 296 (1957).

[3] G. N. Yakovlev and V. N. Kosyakov, Proc. Intern. Conf. Peaceful Uses of Atomic Energy, **7**, 363 (1956).

[4] S. E. Stepanou, J. P. Nigon and R. A. Penneman, *J. Chem. Phys.*, **21**, 42 (1953).

[5] S. R. Gunn, UCRL-2541 (1954).

[6] S. R. Gunn and B. B. Cunningham, *J. Amer. Chem. Soc.*, **79**, 1563 (1957).

[7] J. S. Coleman, *Inorg. Chem.*, **2**, 53 (1963).

[8] A. A. Zaitsev, V. N. Kosyakov, A. G. Rykov, Yu. D. Sobolev, and G. N. Yakovlev, *Radiokhimiya*, **2**, 339 (1960).

[9] S. E. Stepanou, L. B. Asprey and R. A. Penneman, AECU-925 (1950).

[10] L. B. Asprey, S. E. Stepanou, and R. A. Penneman, *J. Amer. Chem. Soc.*, **73**, 5715 (1951).

[11] L. B. Asprey and S. E. Stepanou, AECU-924 (1950).

oxidation states. In contrast to americium, the chemical properties of uranium, neptunium, and plutonium at higher oxidation states have been established comparatively well; therefore, a complete understanding of the properties of Am(V) or of Am(VI) is especially important for us if we are to understand the properties of the actinide series as a whole. Furthermore, for the separation and recovery of americium it is very effective to utilize the chemical properties of the higher oxidation states of americium.

It is well known that lanthanide(III,IV) and actinide(III,IV,V) ions coprecipitate with lanthanum fluoride under selected conditions.[12] However, Moore found that Am(VI) did not coprecipitate with lanthanum fluoride; he used this unique property of Am(VI) toward coprecipitation in separating and purifying americium.[13] Stokely and Moore developed a method for the purification of americium based on TTA-xylene extraction.[14] They suggested that Am(VI) was readily reduced to Am(V) when the pH was adjusted to 4—5 by the addition of an acetate buffer to Am(VI) solutions. In this pH range lanthanide(III,IV) and actinide(III,IV,VI) ions had been known to be extracted into a 0.5M solution of TTA,[15] but they found that Am(V) remained in the aqueous phase and was efficiently separated from the other metal ions. In order to study the chemistry of Am(V), it is necessary to establish a simple method for the preparation of a Am(V) solution and to find the conditions in which the oxidation state will continue as long as possible. Stokely and Moore's method is helpful for the preparation of Am(V). By their method, however, Am(V) is obtained only in an acetate buffer solution which contains many foreign materials, such as the peroxysulfate and sulfate ions; therefore, their method is not sufficient for general use.

The purpose of the present investigation is to establish a method for the production of Am(V) in various solutions and to get some idea of the stability of the valency state in these media. Furthermore, the usefulness of the method has been confirmed by showing its practical application to the determination of the stability constant of the acetate complex of Am(V), although the accuracy is limited because of the technical difficulty involved in the experiment due to the instability of Am(V).

Experimental

Reagents. $^{241}AmO_2$ which had been obtained from the Oak Ridge National Laboratory was dissolved in conc. nitric acid. The solution was then evaporated to dryness, and the residue was dissolved with 2N nitric acid and diluted to 1N in a nitric acid concentration. This solution served as the stock solution of americium. Before use, an aliquot of the stock solution was diluted to about 10^{-6}M with respect to americium with a nitric acid solution of a suitable concentration, thus making the acidity 0.1N. The radiochemical purity of ^{241}Am was confirmed by α- and γ-ray spectrometry. The xylene and isobutanol were purified by distillation, and the other chemicals, such as 2-thenoyltrifluoroacetone (TTA), ammonium persulfate and silver nitrate, were of the highest purity.

Apparatus. In order to check the radiochemical purity, the γ-ray spectra were measured with a 1¾″×1″ NaI(Tl) detector coupled with a Kobe-Kogyo 100-channel pulse-height analyzer, Model AN-100, while the α-ray spectra were measured with an Osaka-Denpa gridded ionization chamber coupled with a TMC-400 channel pulse-height analyzer. For the determination of the distribution ratio, the γ-activity was counted with the above-mentioned scintillator coupled with a Kobe-Kogyo scaler, Model SA-250. For the solvent extraction, an Iwaki universal mechanical shaker, Model V-S, was used. A Toa-Denpa-Kogyo pH-meter, Model PE-2, was used for the pH measurements.

Procedure. The experiments were carried out by the following procedure except as otherwise noted.

Procedure for the Preparation of an Am(V) Solution. To 20 m*l* of a sample solution of americium in a beaker, 5 m*l* of a 0.5M ammonium persulfate solution and 1 m*l* of a 0.2% silver nitrate solution were added. The mixture was heated for 10 min in a water bath at 90—95°C. Then 1 m*l* more of the ammonium persulfate solution was added and the solution was heated for a few more minutes. Immediately after its removal from the hot water bath, the beaker was placed in an ice bath and left standing for at least 10 min. Then 5 m*l* of a 1M ammonium acetate solution which had previously been cooled was added, and the combination was mixed completely. The solution was transferred into a separatory funnel and 25 m*l* of a 0.1M TTA solution of isobutanol were added. The separatory funnel was mechanically shaken for 5 min, and the aqueous phase discarded. Then, Am(V) was back-extracted into the aqueous phase of a suitable composition, leaving Am(III) and Am(VI) in the organic phase. This solution was used as an aqueous phase for the following solvent extraction experiments.

Procedure for the Extraction. The solvent extraction was carried out by bringing in contact 10-m*l* portions of an organic phase and of an aqueous phase for 3 min at room temperature. After shaking, a suitable aliquot of each phase was placed in a polyethylene test tube and its γ-activity was counted with an accuracy of ±2%. The rest of the aqueous phase was used for the measurement of the pH.

The distribution ratio (D) and the percentage extracted (E%) were calculated by means of the usual relationship:

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[12] E. K. Hyde, "Radiochemical Separations of the Actinide Elements," in "The Actinide Elements," National Nuclear Energy Series, Division IV, Vol. 14A, ed. by G. T. Seaborg and J. J. Katz, McGraw-Hill Book Co., Inc., New York (1954), Chap. 15.

[13] F. L. Moore, *Anal. Chem.*, **35**, 715 (1963).

[14] J. R. Stokely, Jr., and F. L. Moore, *ibid.*, **39**, 994 (1967).

[15] S. C. Foti and E. C. Freiling, *Talanta*, **11**, 385 (1964).

$$D = \frac{\gamma\text{-activity per m}l\text{ of the organic phase}}{\gamma\text{-activity per m}l\text{ of the aqueous phase}}$$

$$E\% = \frac{100 \cdot D}{D + V_{aq}/V_{org}}$$

where V_{aq} and V_{org} are the volumes of the aqueous and organic phases respectively.

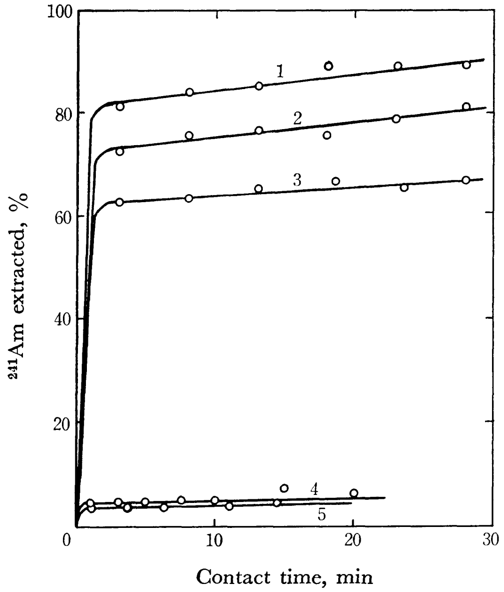

Fig. 1. The effect of the contact time on the TTA extraction of Am(V).
0.1M TTA-isobutanol: 1. pH=5.5, 2. pH=5.3, 3. pH=5.1
0.5M TTA-xylene: 4. pH=5.1, 5. pH=3.9

Results and Discussion

The Effect of the Contact Time on the TTA Extraction of Am(V). The effects of the contact time on the extraction of Am(V) with TTA solutions were investigated. A freshly-prepared Am(V) solution in 0.1M acetic acid-ammonium acetate was mixed with either 0.5M TTA in xylene or 0.1M TTA in isobutanol. The percentage of americium extracted is shown in Fig. 1 as a function of the contact time. As is clearly shown in Fig. 1, the percentage of americium extracted instantly reaches a nearly constant value and gradually increases afterward. This tendency holds irrespective of the kind of diluent and the pH value of the aqueous phase.

The gradual increase in the percentage of americium extracted may be attributable to the reduction of Am(V) to Am(III) in both phases during extraction, because Am(III) is much more extractable than Am(V). Am(V) is probably reduced either by the organic substances or by the radiolysis products produced in the solution by the absorption of alpha rays of ^{241}Am. In the TTA-xylene system the latter mechanism is more probable than the former, since the rate of the reduction of Am(V) is estimated from Fig. 1 to be several per cents/hr, a value which nearly agrees with the rate of self-reduction reported by Hall and Markin.[2] However, a portion of Am(V) is probably reduced isobutanol because the percentage of americium extracted in the isobutanol system increases at a rate which can not be explained simply by the self-reduction reaction of Am(V). In order to minimize the contribution of Am(III) to the distribution ratio of Am(V), it is desirable to select as short a contact time as possible. In view of both this and the rate of extraction, it has been decided to bring the two phases into contact for 3 min.

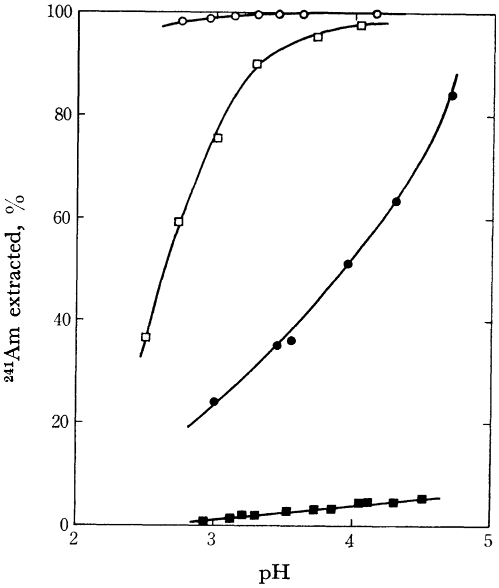

Fig. 2. The effect of pH on the extraction of Am(V) and Am(III) with TTA.
0.1M TTA-isobutanol: ○ Am(III), ● Am(V)
0.5M TTA-xylene: □ Am(III), ■ Am(V)

The Effect of the pH on the TTA Extraction of Am(V). Fig. 2 shows the effect of the pH of the aqueous phase on the extraction of Am(V) and Am(III). Am(III) is quantitatively extracted by the 0.1M TTA solution of isobutanol from 1M acetate buffer solutions when the pH of the solution is higher than 3. On the other hand, only 25% of Am(V) is extracted at pH 3, 40% at pH 4, and nearly 100% at pH 5. These results suggest the possibility of the preparation of Am(V) solutions; that is, when the aqueous solution which contains Am(III) and Am(V) is in contact with a 0.1M TTA solution of isobutanol, Am(III) and Am(V) will be extracted into the organic phase. When the organic phase is mixed with a new aqueous phase with a proper pH value, Am(V) will be selectively stripped into the aqueous phase, while all the Am(III) will remain in the organic phase. It is this fact that is used in the present study for the preparation of aqueous solutions of Am(V).

The dependence of the percentage of Am(V) and of Am(III) extracted on the pH in a 1.0M acetate buffer-0.5M TTA solution of the xylene system is shown in Fig. 2. Am(III) is also quantitatively extracted at pH above 4, while Am(V) is only partially extracted (10% at most). Besides xylene, chloroform, carbon tetrachloride, benzene and cyclohexane all failed to extract Am(V). Cyclohexanone and hexone extracted the Am(V) complex, but less readily than isobutanol did.

The influence and the role of the solvent in the extraction of chelate compounds have been discussed from various points of view, such as the polarity of the solvent, the solubility of the chelate compounds in the organic solvent, and the coordination of the solvent with or the addition of the solvent to the central atoms in chelate compounds, but no final conclusions have yet been reached. Alimarin and Zolotov, however, discussed the solvent effect from the point of view of the coordination number of the central atom in chelates;[16] their conclusion seems to be capable of explaining the results obtained in the present work. The molecules of a polar solvent displace the water molecules which occupy the free coordination positions of the central atom, making the chelate more organophilic; thus such polar solvents as isobutanol, cyclohexanone, and hexone extract the Am(V)-TTA chelate better than non-active solvents do.

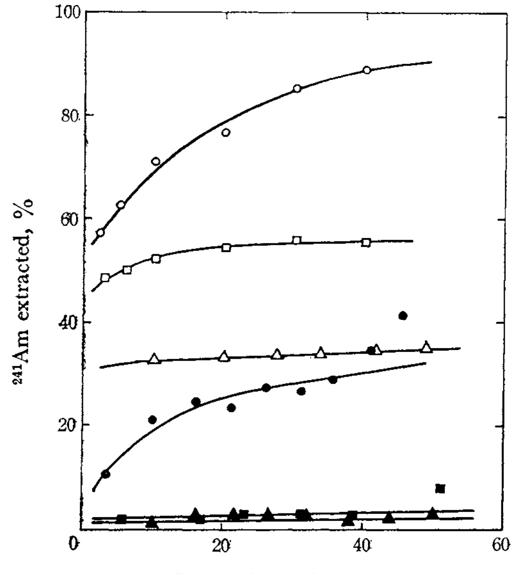

Fig. 3. Effect of time of standing in the TTA extraction of Am(V).
○ 0.1M TTA-isobutanol/0.1M sulfate (pH=4.4)
□ 0.1M TTA-isobutanol/0.1M acetate (pH=5.0)
△ 0.1M TTA-isobutanol/0.1M perchlorate (pH=4.5)
● 0.5M TTA-xylene/1.0M sulfate (pH=4.1)
■ 0.5M TTA-xylene/1.0M acetate (pH=3.4)
▲ 0.5M TTA-xylene/1.0M perchlorate (pH=4.5)

The Stability of the Valency State of Am(V) in Various Aqueous Solutions. The perchlorate, acetate, and sulfate solutions of Am(V) were stored at 0°C. Suitable aliquots of the solutions were subjected to TTA extraction after a definite time of standing. The variation in the percentage of americium is shown in Fig. 3 as a function of the time. In the cases of the acetate and perchlorate solutions, the variation in the percentage of americium extracted is about 3%/hr, which may be due to the reduction of Am(V) to Am(III), as has been discussed before. Thus, Am(V) is not very stable in either perchlorate or acetate solutions, but the contribution of Am(III) to the distribution ratio is negligible within about 10 min after the preparation of the Am(V) solutions. As Am(III) is gradually generated during storage, it is necessary before use to remove Am(III) by extraction with a 0.5M TTA solution of xylene at a pH value above 4. On the other hand, the tendency of the percentage of americium extracted in the sulfate system to increase with the standing time is faster than in the perchlorate and the acetate systems; that is, Am(V) seems to be less stable in sulfate solutions. The cause of the instability of Am(V) in sulfate media is not clear, but Coleman's observation[7] seems to suggest one reason; he

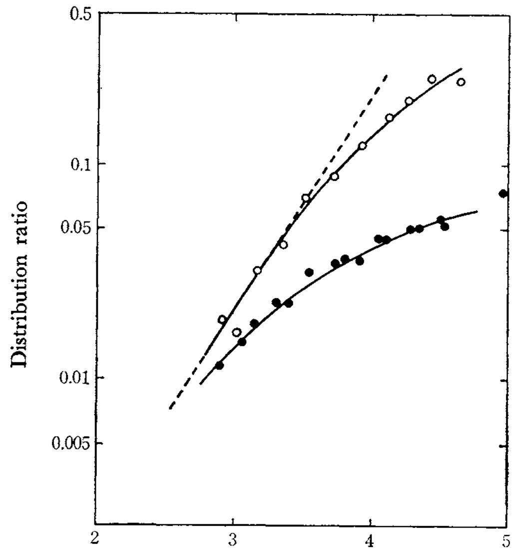

Fig. 4. The pH dependence of the distribution ratio of Am(V) in the TTA-xylene extraction.
○ 0.1M acetate solution
● 1.0M acetate solution

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16) I. P. Alimarin and Yu. A. Zolotov, *ibid.*, **9**, 891 (1962).

studied the rate of the disproportionation of Am(V) in various acid media and found that the rate constant in a sulfuric acid medium was many times greater than that in other acids, such as nitric and hydrochloric acids. In any case, the dependence of the rate of the decrease of Am(V) on the nature of the coexisting anion deserves further study. Attempts to prevent Am(V) from reduction using such holding oxidants as $(NH_4)_2S_2O_8$–Ag^+ and ozone failed; what is worse, a part of the TTA was decomposed by such strong oxidizing reagents.

The Determination of the Stability Constant of the Acetate Complex of Am(V). The pH dependence of the distribution ratio of Am(V) between a 0.5M TTA solution of xylene and a 1.0 or 0.1M acetate solution is shown in Fig. 4. The distribution ratios in the 0.1M acetate system are larger than those in the 1.0M acetate system at the same pH value; this observation suggests the formation of acetate complexes of Am(V). The curves in the figure in both systems approach a straight line with a slope of about one with the decrease in the pH. Irving and Edgington extracted Np(V) in a 0.05M HNO_3 solution with 0.05M TTA in cyclohexane, and demonstrated the first-order dependency of the distribution ratio on pH.[17]

As the chemical properties of Am(V) are expected to be similar to those of Np(V), the deviation of the distribution ratio from the straight line (the dotted line in Fig. 4) can be understood in terms of the formation of the acetate complexes of Am(V). It is apparent from the following equation that the acetate ion concentration, $[Ac^-]$, increases with an increase in the pH at a constant total acetic acid concentration, $[HAc]_t$:

$$\log \frac{[HAc]_t - [Ac^-]}{[Ac^-]} = pK_a - pH$$

where pK_a is the acid constant of acetic acid. The dependency of the distribution ratio on the TTA concentration in xylene is found to be second-order as is shown in Fig. 5; the same tendency holds in the case of Np(V).[17] Considering these results, it may be assumed, by analogy with Np(V), that Am(V) would be found in the form of AmO_2^+ in an aqueous solution containing no complex-forming reagent. This assumption is also warranted by the results of infrared spectroscopy by Jones and Penneman.[18] In the presence of acetate ions, AmO_2^+ forms acetate complexes. The species extracted in the organic phase are the neutral chelate compounds of AmO_2^+ and TTA. Therefore, the equilibria concerned in the extraction and in the acetate complex formation of Am(V) can be written as:

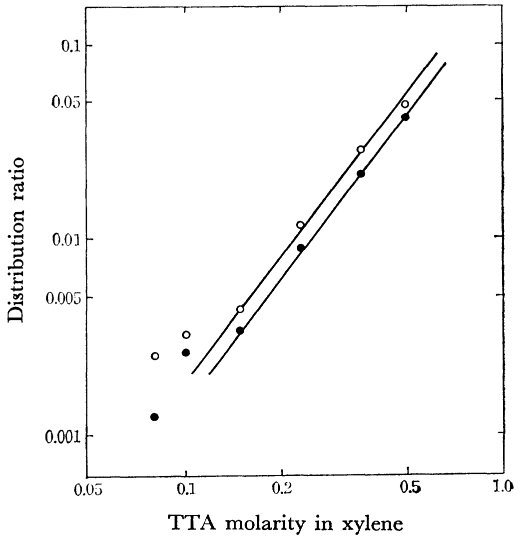

Fig. 5. Relationship between the distribution ratio and the concentration of TTA in xylene in the extraction of Am(V) from 0.1M acetate solution.
○ pH=4.6 ● pH=3.6

$$AmO_2^+ + 2HA_{org} \rightleftharpoons AmO_2HA_{2,org} + H^+ \quad (1)$$

$$AmO_2^+ + Ac^- \rightleftharpoons AmO_2Ac \quad (2)$$

$$AmO_2Ac + Ac^- \rightleftharpoons AmO_2Ac_2^- \quad (3)$$

where HA and Ac^- indicate the TTA molecule and the acetate ion respectively. The subscript "org" indicates the organic phase, while the unsubscripted species refer to the aqueous phase. The formation of a complex higher than $AmO_2Ac_2^-$ may be neglect-

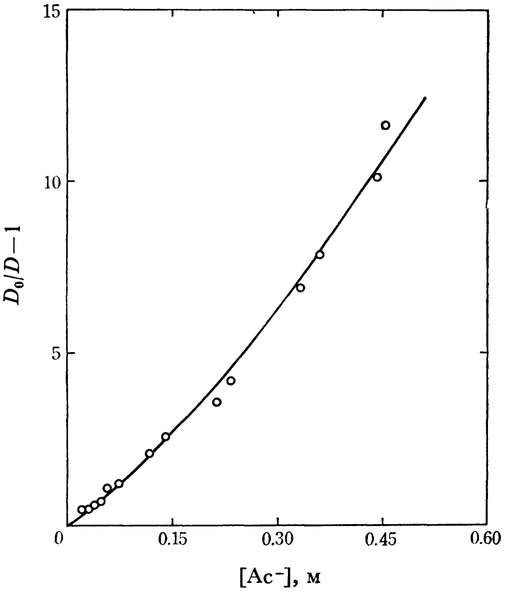

Fig. 6. Relationship between $(D_0/D-1)$ and acetate ion concentration.

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[17] H. Irving and D. N. Edgington, *J. Inorg. Nucl. Chem.*, **20**, 314 (1961).

[18] L. H. Jones and R. A. Penneman, *J. Chem. Phys.*, **21**, 542 (1953).

ed in the range of acetate-ion concentrations investigated. The distribution ratio of Am(V), D, can then be defined as:

$$D = \frac{[\mathrm{Am(V)}]_{\mathrm{org}}}{[\mathrm{Am(V)}]_{\mathrm{aq}}} = \frac{[\mathrm{AmO_2HA_2}]_{\mathrm{org}}}{[\mathrm{AmO_2}^+] + [\mathrm{AmO_2Ac}] + [\mathrm{AmO_2Ac_2}^-]} \qquad (4)$$

If one uses K_0 for the equilibrium constant of Reaction (1) and β_1 and β_2 for the stability constants of $\mathrm{AmO_2Ac}$ and $\mathrm{AmO_2Ac_2}^-$ respectively, Eq. (4) is reduced to:

$$D = \frac{K_0[\mathrm{HA}]^2_{\mathrm{org}}}{[\mathrm{H}^+](1+\beta_1[\mathrm{Ac}^-]+\beta_2[\mathrm{Ac}^-]^2)} \qquad (4')$$

where $[\mathrm{HA}]_{\mathrm{org}}$ is the concentration of TTA in the organic phase and while $[\mathrm{H}^+]$ and $[\mathrm{Ac}^-]$ are the concentrations of hydrogen ions and acetate ions respectively in the aqueous phase. One can then rewrite Eq. (4′) as:

$$D = D_0(1+\beta_1[\mathrm{Ac}^-]+\beta_2[\mathrm{Ac}^-]^2)^{-1} \qquad (5)$$

where D_0 is the distribution ratio when the acetate ion is absent and is defined as the inclination of the dotted line in Fig. 4. Using the experimental values of D and the corresponding values of D_0 read from the dotted line, the magnitudes of $(D_0/D-1)$ are calculated. The relation between $(D_0/D-1)$ and $[\mathrm{Ac}^-]$ is shown in Fig. 6. Using the method of least squares, the best-fit values for β_1 and β_2 were founds to be $(25.0\pm3.1)(\mathrm{mol}/l)^{-1}$ and $(12.8\pm1.2)(\mathrm{mol}/l)^{-2}$ respectively.

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