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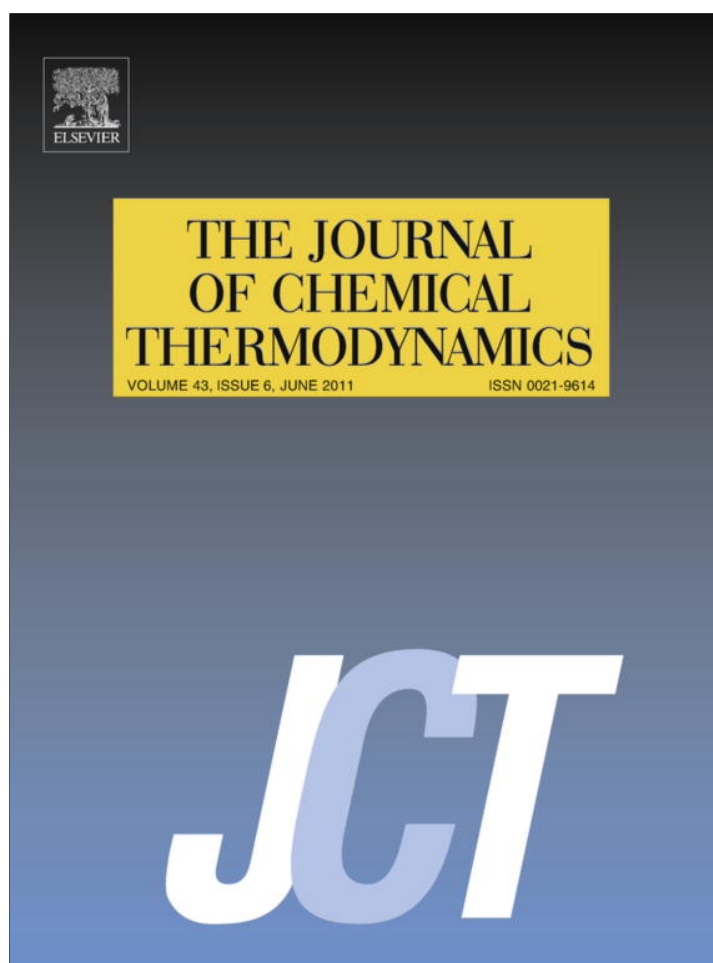
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## Standard Gibbs free energies for transfer of actinyl ions at the aqueous/organic solution interface

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### ABSTRACT

Standard Gibbs free energies for transfer ( $\Delta G_{tr}^\circ$ ) of actinyl ions ( $AnO_2^{z+}$ ;  $z = 2$  or  $1$ ;  $An$ : U, Np, or Pu) between an aqueous solution and an organic solution were determined based on distribution method combined with voltammetry for ion transfer at the interface of two immiscible electrolyte solutions. The organic solutions examined were nitrobenzene, 1,2-dichloroethane, benzonitrile, acetophenone, and 2-nitrophenyl octyl ether. Irrespective of the type of organic solutions,  $\Delta G_{tr}^\circ$  of  $UO_2^{2+}$ ,  $NpO_2^{2+}$ , and  $PuO_2^{2+}$  were nearly equal to each other and slightly larger than that of  $Mg^{2+}$ . The  $\Delta G_{tr}^\circ$  of  $NpO_2^+$  was extraordinary large compared with those of ordinary monovalent cations. The dependence of  $\Delta G_{tr}^\circ$  of  $AnO_2^{z+}$  on the type of organic solutions was similar to that of  $H^+$  or  $Mg^{2+}$ . The  $\Delta G_{tr}^\circ$  of  $An^{3+}$  and  $An^{4+}$  were also discussed briefly.

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### 1. Introduction

The standard Gibbs free energy for the transfer of an ion ( $\Delta G_{tr}^\circ$ ) between an aqueous solution (W) and an organic solution (O) is one of the important physicochemical parameters which determine principally the distribution ratio in solvent extraction [1–4]. The potential and selectivity of an ion at an ion-selective electrode [5,6] or the selectivity in the separation of ions by a liquid membrane [7,8] depend on  $\Delta G_{tr}^\circ$  of the object ions. The  $\Delta G_{tr}^\circ$  is also useful for the evaluation of the transfer of an ion through a biomembrane under the assumption that O is a simple model of a biomembrane [9,10], and may give useful suggestions in the evaluation of the condensation of the ions in living bodies. For actinyl ions ( $AnO_2^{z+}$ ;  $z = 2$  or  $1$ ;  $An = U, Np, \text{ or } Pu$ ), their  $\Delta G_{tr}^\circ$  are important to understand solution chemical properties of  $AnO_2^{z+}$ , and to improve the separation method of actinide in the reprocessing of the spent nuclear fuel or the disposal of nuclear waste. Here, the selectivity of an ion in ion-pair extraction [11] or chelate extraction [3] can be evaluated by using  $\Delta G_{tr}^\circ$  of the ion and those of diverse ions.

The methods applied to the determination of  $\Delta G_{tr}^\circ$  so far have been ion-pair extraction [4,11–14], potentiometric measurement of potential difference at the W/O interface [15], voltammetry for ion transfer at the interface of two immiscible electrolyte solutions (VITIES) [16,17], solubility measurement of salts in W and O [18–20], etc. By using these methods,  $\Delta G_{tr}^\circ$  have been determined for ions which are not very hydrophilic such as alkali metal, alkaline earth metal, transition metal, organic, or organometallic complex ions. On the other hand,  $\Delta G_{tr}^\circ$  of highly hydrophilic metal ions ( $M^{z+}$ ) such as lanthanide or actinide ions have scarcely been determined [21,22], because these ions are easily hydrolyzed in W and hence the coexistence of high concentration of  $H^+$  is required in the investigation of  $\Delta G_{tr}^\circ$  of aqua complexes of the ions. Here, since  $H^+$  transfers from W to O more easily than the highly hydrophilic  $M^{z+}$ , the coexistence of  $H^+$  disturbs the determination of  $\Delta G_{tr}^\circ$  by potentiometry at the W/O interface and VITIES. Determination of  $\Delta G_{tr}^\circ$  by solubility measurement is also difficult because of low solubility of the highly hydrophilic  $M^{z+}$  in O.

Ion-pair extraction is expected to be available for the determination of  $\Delta G_{tr}^\circ$  of highly hydrophilic  $M^{z+}$  in the presence of high concentration of  $H^+$ , taking into account works by Hung [23] on the theory of distribution potentials of ions at the W/O interface in the presence of various kinds of ions and by Rais and coworkers [4,12] on the determination of  $\Delta G_{tr}^\circ$  of alkali and alkaline earth me-

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tal ions based on the ion exchange at the W/O interface. However, the applicability of ion-pair extraction to the determination of  $\Delta G_{tr}^\circ$  of a very hydrophilic  $M^{z+}$  in the presence of high concentration of  $H^+$  in W has not been demonstrated experimentally yet except for the previous work of the present authors [24].

In the previous work [24], a method for the determination of  $\Delta G_{tr}^\circ$  of a hydrophilic ion was proposed based on ion-pair extraction of the ion from an acidic W to O, and the usefulness of the method was demonstrated experimentally by comparing  $\Delta G_{tr}^\circ$  of  $Mg^{2+}$  from W to nitrobenzene (NB) or 1,2-dichloroethane (DCE) determined by the proposed method with that obtained by VITIES. Here, VITIES is considered to be the most reliable method for the determination of  $\Delta G_{tr}^\circ$  as far as the system does not contain large amounts of ions that transfer more easily than an object ion, since the influence of coexisting ions on the transfer of the object ion can be evaluated from the current–potential curve recorded by VITIES [5,16,17]. The proposed method was applied to the determination of  $\Delta G_{tr}^\circ$  of  $AnO_2^{z+}$  from W to NB.

In the present work, the ion-pair extraction method is applied to the determination of  $\Delta G_{tr}^\circ$  of  $UO_2^{2+}$ ,  $NpO_2^{2+}$ ,  $PuO_2^{2+}$ , and  $NpO_2^{2+}$  between W containing high concentration of  $H^+$  and O. The O examined were NB, DCE, benzonitrile (BN), acetophenone (AP), and 2-nitrophenyl octyl ether (NPOE). In this connection, NB, DCE and NPOE have been used for ion-pair extraction (NB), the measurement by VITIES (NB and DCE), or the preparation of ion-selective electrodes (NPOE).

## 2. Theoretical consideration

The determination of  $\Delta G_{tr}^\circ$  of  $AnO_2^{z+}$  ( $\Delta G_{tr,AnO_2^{z+}}^\circ$ ) in the present work was carried out by comparing the distribution ratio ( $D$ ) of  $AnO_2^{z+}$  with that of the reference ion of which  $\Delta G_{tr}^\circ$  had been determined separately based on electrochemical method. Here,  $H^+$  was adopted as the reference ion in the present work, since  $H^+$  is not extremely hydrophilic and hence the  $\Delta G_{tr}^\circ$  of  $H^+$  ( $\Delta G_{tr,H^+}^\circ$ ) can be determined by VITIES. Another reason is that  $H^+$  is usually coexisted with the hydrophilic  $AnO_2^{z+}$  in order to avoid the hydrolysis of  $AnO_2^{z+}$ .

In the previous work [24], the distribution equilibrium of ions in a W/O system was discussed by adopting W containing  $M^{z+}$ ,  $H^+$  and a hydrophilic monovalent counter anion ( $X^-$ ) and O containing  $M^{z+}$ ,  $H^+$  and a hydrophobic monovalent counter anion ( $Y^-$ ) in order to evaluate the  $\Delta G_{tr}^\circ$  of  $M^{z+}$  from W to O ( $\Delta G_{tr,M^{z+}}^\circ$ ). Equation (1) was derived as the relation among  $D$  of species relative to  $M^{z+}$  and  $H^+$  ( $D_{M^{z+}}$  and  $D_{H^+}$ , respectively),  $\Delta G_{tr,M^{z+}}^\circ$ ,  $\Delta G_{tr,H^+}^\circ$  and formation constants of ion pairs of  $M^{z+}Y_n^-$  and  $H^+Y_n^-$  in O ( $K_{ip,M^{z+}Y_n^-}$  and  $K_{ip,H^+Y_n^-}$ , respectively) expressed as equations (2) and (3)

$$\ln \left( \frac{D_{M^{z+}}^{1/z}}{D_{H^+}} \right) = \frac{(\Delta G_{tr,H^+}^\circ - \Delta G_{tr,M^{z+}}^\circ / z)}{RT} + \ln \left\{ \frac{\gamma_{H^+,O}^{1/z} \gamma_{M^{z+},W}^{1/z} \left[ 1 + \sum K_{ip,M^{z+}Y_n^-} (\gamma_{M^{z+},O}^{1/z} \gamma_{Y_n^-,O}^{1/z} / \gamma_{M^{z+}Y_n^-,O}^{1/z}) C_{Y_n^-,O}^{1/z} \right]^{1/z}}{\gamma_{H^+,W}^{1/z} \gamma_{M^{z+},O}^{1/z} (1 + K_{ip,H^+Y_n^-} \gamma_{H^+,O} \gamma_{Y_n^-,O} C_{Y_n^-,O})} \right\} \quad (1)$$



In equation (1),  $R$  and  $T$  denote the gas constant and the absolute temperature, respectively. The  $\gamma_{i,\alpha}$  denotes the activity coefficient of species  $i$  in phase  $\alpha$ , and  $C_{Y^-,O}$  the concentration of  $Y^-$  in O. The derivation of equation (1) was carried out under the assumptions as follows. (i) Volumes of W and O are the same. (ii)

$X^-$  and  $Y^-$  are ions that hardly distribute from W to O and from O to W, respectively. (iii) Ion pairs are formed only in O of which relative dielectric constant ( $\epsilon$ ) is much lower than that of W.

When the ion-pair formations in O are negligibly small (i.e.  $K_{ip}$  or  $C_{Y^-,O}$  is small), and all  $\gamma$  are assumed to be equal to unity, equation (1) can be simplified as

$$\ln \left( D_{M^{z+}}^{1/z} / D_{H^+} \right) = (\Delta G_{tr,H^+}^\circ - \Delta G_{tr,M^{z+}}^\circ / z) / RT. \quad (4)$$

Rewriting equations (1) and (4), equations (5), and (6), respectively, are obtained

$$\Delta G_{tr,M^{z+}}^\circ = z \left( \Delta G_{tr,H^+}^\circ + RT \ln D_{H^+} \right) - RT \times \ln D_{M^{z+}} + RT \ln \left\{ \frac{\gamma_{H^+,O}^{1/z} \gamma_{M^{z+},W}^{1/z} \left[ 1 + \sum K_{ip,M^{z+}Y_n^-} (\gamma_{M^{z+},O}^{1/z} \gamma_{Y_n^-,O}^{1/z} / \gamma_{M^{z+}Y_n^-,O}^{1/z}) C_{Y_n^-,O}^{1/z} \right]^{1/z}}{\gamma_{H^+,W}^{1/z} \gamma_{M^{z+},O}^{1/z} (1 + K_{ip,H^+Y_n^-} \gamma_{H^+,O} \gamma_{Y_n^-,O} C_{Y_n^-,O})} \right\}, \quad (5)$$

$$\Delta G_{tr,M^{z+}}^\circ = z \left( \Delta G_{tr,H^+}^\circ + RT \ln D_{H^+} \right) - RT \ln D_{M^{z+}}. \quad (6)$$

These equations indicate that  $\Delta G_{tr,M^{z+}}^\circ$  can be evaluated when  $D_{M^{z+}}$ ,  $D_{H^+}$ ,  $\Delta G_{tr,H^+}^\circ$ ,  $K_{ip,M^{z+}Y_n^-}$ , and  $K_{ip,H^+Y_n^-}$  are determined by appropriate methods.

## 3. Experimental

### 3.1. Chemicals

Solutions of U and Np ions were prepared by dissolving a uranium metal (JAERI-U4, of natural isotopic abundance) and  $^{237}\text{Np(IV)}$  dioxide (CEA, Fontenay-aux-Roses) in concentrated nitric acid solution. The solution of Pu ion was prepared by dissolving a plutonium metal (NBS-949c of isotopic abundance of  $^{239}\text{Pu}$ , 97.40%;  $^{240}\text{Pu}$ , 2.56%;  $^{241}\text{Pu}$ , 0.031%) in hydrochloric acid. The solutions of Np and Pu thus obtained were flowed through an anion exchange resin column in order to remove  $^{233}\text{Pa}$  and  $^{241}\text{Am}$  [25,26], respectively. The stock solutions of  $AnO_2^{z+}$  were obtained as follows. An aliquot of the actinide solution was heated to almost dryness. Then, the residue was dissolved in 5 M (=mol · dm<sup>-3</sup>)  $\text{HClO}_4$  and heated to dryness at the temperature of the fuming of  $\text{HClO}_4$ . The  $\text{HClO}_4$  fuming procedure was repeated three times, by which the oxidation state of U, Np, or Pu was adjusted to hexavalent (i.e.  $AnO_2^{2+}$ ). Finally, the  $AnO_2^{2+}$  was dissolved in 1 M  $\text{HClO}_4$ . The solutions of actinide ions of other oxidation states were prepared by reducing  $AnO_2^{2+}$  by controlled potential electrolysis at a platinum mesh electrode [27,28]. In the preparation of  $\text{Pu}^{4+}$ ,  $\text{PuO}_2^{2+}$  was reduced to  $\text{Pu}^{3+}$ , and then oxidized to  $\text{Pu}^{4+}$ . Oxidation states of the actinide ions were confirmed spectrophotometrically [29] by using an ultraviolet–visible spectrophotometer (UV-3100, Shimadzu Co.).

Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ( $\text{TFPB}^-$ ) was employed in the present work as  $Y^-$  in O. A  $\text{Na}^+$  salt of  $\text{TFPB}^-$  ( $\text{Na}^+\text{TFPB}^-$ ) was synthesized based on Grignard reaction [30] followed by recrystallization from DCE. The organic solution of  $\text{H}^+\text{TFPB}^-$  was prepared by shaking an O containing  $5 \cdot 10^{-2}$  M  $\text{Na}^+\text{TFPB}^-$  with the same volume of an aqueous solution of 1 M  $\text{H}_2\text{SO}_4$ , and exchanging  $\text{Na}^+$  in O with  $\text{H}^+$ . This procedure was repeated five times. The concentration of  $\text{Na}^+$  in the resulted O was confirmed to be less than 0.5% by using a flame spectrophotometer (Hitachi 180-70). A sulfate salt of tetraphenylarsonium ion ( $\text{TPhAs}_2^+\text{SO}_4^{2-}$ ) was synthesized by titrating  $\text{TPhAs}^+\text{Cl}^-$  with  $\text{Ag}_2\text{SO}_4$  in an aqueous solution [31]. A  $\text{Mg}^{2+}$  salt of tetraphenylborate ( $\text{Mg}^{2+}\text{TPhB}_2^-$ ) was synthesized by the procedure proposed by Ueno *et al.* [32].

The O containing  $AnO_2^{z+}\text{TFPB}_2^-$  was prepared by shaking O containing  $5 \cdot 10^{-2}$  M  $\text{Na}^+\text{TFPB}^-$  with the same volume of W

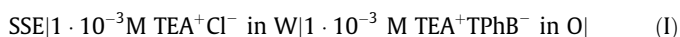
containing 1 M  $\text{AnO}_2^{z+}$  ( $\text{ClO}_4^-$ ), and exchanging  $\text{Na}^+$  in O for  $\text{AnO}_2^{z+}$ . Here, the pH of W was about 4 (not buffered). This procedure was repeated five times. It was confirmed by measuring the radioactivity with the aid of a liquid scintillation counter (S-1287C, OHYO KOKEN KOGYO Co.) that more than 98% of  $\text{Na}^+$  in O was exchanged for  $\text{AnO}_2^{z+}$ .

A  $\text{TFPB}^-$  salt of bis(triphenylphosphoranylidene)ammonium ion ( $\text{BTPPA}^+\text{TFPB}^-$ ) was used as the supporting electrolyte in O in the measurement of voltammogram for the transfer of  $\text{H}^+$ ,  $\text{TPhAs}^+$ , or  $\text{TPhB}^-$ . The salt was obtained as a precipitate by mixing a methanol solution of  $\text{BTPPA}^+\text{Cl}^-$  (Aldrich) with a methanol solution of  $\text{Na}^+\text{TFPB}^-$ , and purified by recrystallization from ethanol. A  $\text{TFPB}^-$  salt of tetrabutylammonium ion ( $\text{TBA}^+\text{TFPB}^-$ ) used in the determination of the molar conductivity of  $\text{TFPB}^-$  in O was obtained following to the procedure for the preparation of  $\text{BTPPA}^+\text{TFPB}^-$ , but using  $\text{TBA}^+\text{Cl}^-$  (Aldrich) instead of  $\text{BTPPA}^+\text{Cl}^-$ . A  $\text{TPhB}^-$  salt of tetraethylammonium ion ( $\text{TEA}^+\text{TPhB}^-$ ) used in the preparation of the reference electrode in O was obtained following to the procedure for the preparation of  $\text{BTPPA}^+\text{TFPB}^-$ , but using  $\text{TEA}^+\text{Cl}^-$  (Aldrich) and  $\text{Na}^+\text{TPhB}^-$  (Aldrich) instead of  $\text{BTPPA}^+\text{Cl}^-$  and  $\text{Na}^+\text{TFPB}^-$ , respectively. The purities of  $\text{BTPPA}^+\text{TFPB}^-$ ,  $\text{TBA}^+\text{TFPB}^-$ , and  $\text{TEA}^+\text{TPhB}^-$  were confirmed by elemental analysis,  $^{13}\text{C}$  and  $^1\text{H}$  NMR to be more than 98%.

All other reagents used were of reagent grade.

### 3.2. Measurement of voltammograms at the micro-W/O interface

The voltammograms for transfer of various ions at the W/O interface were measured by using a cell with a micro-W/O interface [33]. The cell was composed of W and O separated by a polyester film of 16  $\mu\text{m}$  thick with a micro-hole of 30  $\mu\text{m}$  in diameter where the micro-W/O interface was formed. The voltammogram was recorded by scanning the potential difference applied at the interface ( $E$ ) and measuring the current due to the ion transfer [33–35]. The  $E$  was measured as the potential of a silver–silver chloride reference electrode (SSE) with 1 M LiCl in W versus a TEA $^+$  selective electrode (TEAE) [36] which worked as a reference electrode in O. The configuration of TEAE was:



A potentiostat–galvanostat, a function generator, and an X–Y recorder used in the measurement of voltammograms were Model HA-502, Model HB-104 (Hokuto Denko Co.), and Type 3086 (Yokogawa Electric Works Ltd.), respectively. Voltammetric measurements were performed at  $25 \pm 0.5^\circ\text{C}$ .

### 3.3. Measurement of conductivity of O

The ion-pair formation constants of  $\text{H}^+$  and  $\text{AnO}_2^{z+}$  with  $\text{TFPB}^-$  in O ( $K_{\text{ip,H}^+\text{TFPB}^-}$  and  $K_{\text{ip,AnO}_2^{z+}\text{TFPB}^-}$ , respectively) were evaluated based on conductivities of O measured with a conductometer (ES-51, Horiba Ltd.) and a conductivity cell of immersion type (3552-10D, Horiba Ltd.) in which two platinum electrodes coated with platinum black were used. The cell constant of the conductivity cell was  $95.3 \text{ m}^{-1}$ . The viscosities ( $\eta$ ) of organic solvents were measured by using a viscometer (VISCOMATE VM-1G, CBC Materials Co., Ltd.) in order to evaluate the molar conductivities of ions based on the Walden product [37]. The measurements of conductivity and  $\eta$  were carried out at  $25 \pm 0.5^\circ\text{C}$ .

### 3.4. Determination of distribution constants

In order to determine  $D_{\text{M}^{z+}}$  for  $\text{AnO}_2^{z+}$  ( $D_{\text{AnO}_2^{z+}}$ ) and  $D_{\text{H}^+}$ , a distribution system consisted of 10 ml of W containing  $\text{HClO}_4$  in the presence of  $\text{AnO}_2^{z+}$  and 10 ml of O containing  $\text{H}^+\text{TFPB}^-$  was equi-

brated by shaking the system for 1 h, and two phases were separated with the aid of centrifugation. This procedure was carried out at  $25 \pm 0.5^\circ\text{C}$ . Then, the concentration of  $\text{H}^+$  in W was measured by pH meter (D-51, HORIBA Ltd.). Hydrogen ion and  $\text{AnO}_2^{z+}$  in O were back-extracted to W by shaking the O with W containing 0.2 M  $\text{TEA}^+\text{Br}^-$ . Then, the concentration of  $\text{H}^+$  was determined by measuring pH of W. The concentration of  $\text{UO}_2^{2+}$  was determined spectrophotometrically based on the complex formation with Arsenazo-III [38], and those of Np and Pu were determined by measuring the radioactivity with a liquid scintillation counter. The oxidation states of actinide species were confirmed spectrophotometrically [28].

## 4. Results and discussion

The  $\Delta G_{\text{tr,AnO}_2^{z+}}^\circ$  can be estimated based on equations (1) and (5) by regarding  $\text{AnO}_2^{z+}$  and  $\text{TFPB}^-$  as  $\text{M}^{z+}$  and  $\text{Y}^-$ , respectively, and using  $\Delta G_{\text{tr,H}^+}^\circ$  determined by VITIES,  $D_{\text{AnO}_2^{z+}}$  and  $D_{\text{H}^+}$  determined by distribution method and  $K_{\text{ip,H}^+\text{TFPB}^-}$  and  $K_{\text{ip,AnO}_2^{z+}\text{TFPB}^-}$  in O determined by conductometry.

### 4.1. Evaluation of $\gamma$ of $\text{H}^+$ , $\text{AnO}_2^{z+}$ and $\text{TFPB}^-$

Since  $\gamma$  of  $\text{H}^+$ ,  $\text{AnO}_2^{z+}$  and  $\text{TFPB}^-$  were necessary for the determination of  $\Delta G_{\text{tr,AnO}_2^{z+}}^\circ$  [see equation (1) or equation (5)], they were estimated based on the extended Debye–Hückel theory. The ion size parameters ( $a_0$ ) of  $\text{H}^+$  and  $\text{ClO}_4^-$  used in the calculation were those reported in the literature [39] (0.9 and 0.35 nm, respectively). The  $a_0$  of  $\text{TFPB}^-$  and  $\text{UO}_2^{2+}$  were assumed to be identical to their diameters ((0.85 and 0.9) nm, respectively) estimated from their Stokes radii ( $r_s$ ) following the approach of Sadek and Fuoss [40]. The  $a_0$  of the ion pair of  $\text{UO}_2^{2+}$  with  $\text{TFPB}^-$ , i.e.  $\text{UO}_2^{2+}\text{TFPB}^-$ , was assumed to be the sum of  $a_0$  of  $\text{UO}_2^{2+}$  and  $\text{TFPB}^-$  (about 1.75 nm). The  $a_0$  of  $\text{NpO}_2^{2+}$ ,  $\text{PuO}_2^{2+}$ , and  $\text{NpO}_2^+$  were assumed to be identical to that of  $\text{UO}_2^{2+}$ , since thermochemical radii of these ions had been estimated to be nearly equal each other by Marcus and Loewenschuss [41,42]:  $\text{UO}_2^{2+}$ , 0.28;  $\text{NpO}_2^{2+}$ , 0.28;  $\text{PuO}_2^{2+}$ , 0.29;  $\text{NpO}_2^+$ , 0.29 nm. The  $a_0$  of  $\text{An}^{3+}$  and  $\text{An}^{4+}$  were considered to be identical to those of trivalent lanthanide ions (0.9 nm) and  $\text{Th}^{4+}$  (1.1 nm), respectively, reported in the literature [39]. The concentration of  $\text{TFPB}^-$  used for the calculation of  $\gamma$  was corrected for the formation of  $\text{H}^+\text{TFPB}^-$  in O using  $K_{\text{ip,H}^+\text{TFPB}^-}$ .

### 4.2. Determination of $\Delta G_{\text{tr,H}^+}^\circ$ by VITIES at the W/O interface

#### 4.2.1. Determination of the potential of TEAE with various O

In the evaluation of  $\Delta G_{\text{tr,H}^+}^\circ$  by VITIES, it is necessary to know the potential of TEAE (reference electrode in O) referred to a standard potential called as tetraphenyl electrode potential (TPhE) which corresponds to  $\Delta G_{\text{tr}} = 0$ . The TPhE was determined based on the Parker's extrathermodynamic assumption [43] that  $\Delta G_{\text{tr}}^\circ$  of  $\text{TPhAs}^+$  and  $\text{TPhB}^-$  ( $\Delta G_{\text{tr,TPhAs}^+}^\circ$  and  $\Delta G_{\text{tr,TPhB}^-}^\circ$ , respectively) are equal irrespective of the pair of solvents examined

$$\Delta G_{\text{tr,TPhAs}^+}^\circ = \Delta G_{\text{tr,TPhB}^-}^\circ \quad (7)$$

This equation is equivalent to equation (8) taking into account equation (9)

$$E_{\text{TPhAs}^+}^\circ = -E_{\text{TPhB}^-}^\circ, \quad (8)$$

where  $E_{\text{tr}}^\circ$  means the standard Galvanic potential difference for the transfer of  $i^2$  between W and O, and is defined as the potential of W referred to that of O

$$\Delta G_{\text{tr}}^\circ = zFE^\circ \quad (9)$$

where  $F$  is the Faraday constant. It is obvious from equation (8) that the mean of  $E_{\text{TPhAs}^+}^\circ$  and  $E_{\text{TPhB}^-}^\circ$  is the TPhE.

The TPhE was determined by VITIES at the micro-W/O interface in the present work according to the procedure described previously [24] as follows. The voltammograms for transfer of  $\text{TPhAs}^+$  and  $\text{TPhB}^-$  at the interface between W containing  $1 \cdot 10^{-3} \text{ M TPhAs}^+\text{Cl}^-$  and  $5 \cdot 10^{-4} \text{ M Mg}^{2+}\text{TPhB}_2^-$ , respectively, and O containing  $1 \cdot 10^{-3} \text{ M TPhAs}^+\text{TPhB}^-$  were measured at the micro-interface by using SSE and TEAE as reference electrodes in W and O, respectively. Then, the  $E$  (versus TEAE) where the current was zero ( $E_{i=0}$ ) in the voltammogram was determined. The  $E_{i=0}$  for  $\text{TPhAs}^+$  ( $E_{i=0,\text{TPhAs}^+}$ ) and that for  $\text{TPhB}^-$  ( $E_{i=0,\text{TPhB}^-}$ ) are expressed as equations (10) and (11) [24], respectively

$$E_{i=0,\text{TPhAs}^+} = E_{\text{TPhAs}^+}^\circ + \frac{RT}{F} \ln \left( \frac{a_{\text{TPhAs}^+,\text{O}}}{a_{\text{TPhAs}^+,\text{W}}} \right) - \frac{RT}{F} \ln \left( 1 + K_{\text{ip,TPhAs}^+\text{TPhB}^-} a_{\text{TPhB}^-,\text{O}} \right) \quad (10)$$

$$E_{i=0,\text{TPhB}^-} = E_{\text{TPhB}^-}^\circ - \frac{RT}{F} \ln \left( \frac{a_{\text{TPhB}^-,\text{O}}}{a_{\text{TPhB}^-,\text{W}}} \right) + \frac{RT}{F} \ln \left( 1 + K_{\text{ip,TPhAs}^+\text{TPhB}^-} a_{\text{TPhAs}^+,\text{O}} \right), \quad (11)$$

where  $a_{i^2,\alpha}$  is the activity of  $i^2$  in phase  $\alpha$ . Since  $a_{\text{TPhAs}^+,\text{O}}$  and  $a_{\text{TPhB}^-,\text{O}}$  are equal, the midpoint of  $E_{i=0,\text{TPhAs}^+}$  and  $E_{i=0,\text{TPhB}^-}$  corresponds to TPhE.



The potentials of TEAE with NB, DCE, BN, AP, or NPOE versus TPhE were determined to be those listed in table 1.

#### 4.2.2. Determination of $\Delta G_{\text{tr},\text{H}^+}^\circ$

The  $\Delta G_{\text{tr},\text{H}^+}^\circ$  was determined following to the procedure described previously [24] based on  $E^\circ$  versus TPhE for the transfer of  $\text{H}^+$  as follows. The voltammogram for the transfer of  $\text{H}^+$  was measured at the micro-interface between W containing  $5 \cdot 10^{-4}$  M  $\text{H}_2\text{SO}_4$  and O containing  $1 \cdot 10^{-3}$  M  $\text{H}^+\text{TFPB}^-$ . The  $E_{\text{H}^+}^\circ$  was determined based on equation (12) by using  $E_{\text{I}=0}$  (versus TPhE) in the voltammogram for the transfer of  $\text{H}^+$  ( $E_{\text{I}=0,\text{H}^+}$ ) and  $K_{\text{ip},\text{H}^+\text{TFPB}^-}$  determined by the conductivity measurement (see Section 4.2.3)

$$E_{\text{I}=0,\text{H}^+} = E_{\text{H}^+}^\circ + \frac{RT}{F} \ln \left( \frac{a_{\text{H}^+,\text{O}}}{a_{\text{H}^+,\text{W}}} \right) - \frac{RT}{F} \ln (1 + K_{\text{ip},\text{H}^+\text{TFPB}^-} a_{\text{TPhB}^-\text{O}}) \quad (12)$$

Then,  $E_{\text{H}^+}^\circ$  was converted to  $\Delta G_{\text{tr},\text{H}^+}^\circ$  based on equation (9). The measurements of voltammetry were carried out for four times with each O. The averages and the standard deviations of  $\Delta G_{\text{tr},\text{H}^+}^\circ$  were listed in table 1. The  $\Delta G_{\text{tr},\text{H}^+}^\circ$  at W/DCE or W/NB interface agreed well with the literature value. However,  $\Delta G_{\text{tr},\text{H}^+}^\circ$  at W/NPOE interface was smaller than that reported by Ulmeanu *et al.* [44] which was estimated by cyclic voltammetry at supported liquid membrane with higher concentration of  $\text{H}^+$  than the present study, although the reason has not been clarified.

#### 4.2.3. Determination of $K_{\text{ip},\text{H}^+\text{TFPB}^-}$

In order to determine  $K_{\text{ip},\text{H}^+\text{TFPB}^-}$  in O, the molar conductivity ( $\Lambda$ ) of  $\text{H}^+\text{TFPB}^-$  in O was measured by changing the concentration of  $\text{H}^+\text{TFPB}^-$  in O. The result is summarized in figure 1. When O was NB or NPOE,  $\Lambda$  decreased slightly and almost linearly with the increase of  $c_{\text{H}^+\text{TFPB}^-}^{1/2}$ , indicating that  $K_{\text{ip},\text{H}^+\text{TFPB}^-}$  in NB or NPOE is negligible. On the other hand, when O was DCE, BN, or AP, the decrease of  $\Lambda$  with the increase of  $c_{\text{H}^+\text{TFPB}^-}^{1/2}$  was not linear and larger than that in NB or NPOE, indicating that  $K_{\text{ip},\text{H}^+\text{TFPB}^-}$  in DCE, BN, or AP is not negligible [45]. The extrapolation of the line to  $c_{\text{H}^+\text{TFPB}^-}^{1/2} = 0$  gives the limiting molar conductance ( $\Lambda_0$ ) for  $\text{H}^+\text{TFPB}^-$ .

The relation between  $\Lambda$  and the concentration ( $c$ ) of an electrolyte that contains the ion of interest can be described by equation (13) proposed by Shedlovsky [46], when  $K_{\text{ip}}$  is large enough

$$\frac{T_s}{\Lambda} = \frac{1}{\Lambda_0} + \frac{K_{\text{ip}} c \gamma^2 \Lambda}{\Lambda_0^2 T_s} \quad (13)$$

where  $T_s$  is a reciprocal of the Shedlovsky extrapolation function [46] given as,

$$1/T_s = \left( Z/2 + \sqrt{1 + (Z/2)^2} \right)^2 \quad (14)$$

with

$$Z = [8.2 \cdot 10^5 \Lambda_0 / (\epsilon T)^{3/2} + 82 / \eta (\epsilon T)^{1/2}] (c \Lambda)^{1/2} / \Lambda_0^{3/2}. \quad (15)$$

The values of  $T_s/\Lambda$  were plotted as the function of  $c \gamma^2 \Lambda/T_s$  for  $\text{H}^+\text{TFPB}^-$  in NB, DCE, BN, or AP. The plots were linear as expected from equation (13). The intercepts ( $1/\Lambda_0$ ) were 0.034, 0.015, 0.026, 0.041, and 0.23, and the slopes ( $K_{\text{ip}}/\Lambda_0^2$ ) were about 0, 0.11, 0.037, 0.16, and about 0 when O were NB, DCE, BN, AP, and NPOE, respectively. The  $\Lambda_0$  and  $K_{\text{ip},\text{H}^+\text{TFPB}^-}$  were determined by using the intercept and the slope, respectively, to be those listed in table 2.

#### 4.3. Determination of $D_{\text{AnO}_2^{2+}}$ , $D_{\text{H}^+}$ , and $K_{\text{ip},\text{AnO}_2^{2+}\text{TFPB}^-}$

For the determination of  $\Delta G_{\text{tr},\text{AnO}_2^{2+}}^\circ$  based on equation (1),  $D_{\text{AnO}_2^{2+}}$ ,  $D_{\text{H}^+}$ , and  $K_{\text{ip},\text{AnO}_2^{2+}\text{TFPB}^-}$  are necessary.

##### 4.3.1. Determination of $D_{\text{AnO}_2^{2+}}$ and $D_{\text{H}^+}$ between W and O

A 10 ml volume of W containing  $2 \cdot 10^{-3}$  M  $\text{AnO}_2^{2+}$  and  $1 \cdot 10^{-2}$  M  $\text{HClO}_4$  was shaken for 1 h with the same volume of O containing ( $2 \cdot 10^{-3}$  to  $5 \cdot 10^{-2}$ ) M  $\text{H}^+\text{TFPB}^-$ . Here,  $\text{HClO}_4$  was chosen as the acid coexisting in W because the complex formation of a cation with  $\text{ClO}_4^-$  is negligible and the exchange of  $\text{ClO}_4^-$  in W with  $\text{TFPB}^-$  in O is not serious [24]. After phase separation, the concentrations of  $\text{H}^+$  and  $\text{AnO}_2^{2+}$  in W and O were determined by the methods described in Section 3.4. By using the concentrations determined,  $D_{\text{AnO}_2^{2+}}$  and  $D_{\text{H}^+}$  were obtained.

TABLE 1

Potentials of tetraethylammonium ion selective electrode (TEAE) versus tetraphenyl electrode potential (TPhE) and the standard Gibbs free energy for transfer of  $\text{H}^+$  between aqueous and organic phases ( $\Delta G_{\text{tr},\text{H}^+}^\circ$ ) determined by voltammetry for ion transfer at two immiscible electrolyte solutions.

Solvent	Potential of TEAE/(V versus TPhE)	$\Delta G_{\text{tr},\text{H}^+}^\circ / (\text{kJ} \cdot \text{mol}^{-1})$	
		Present study	Literature value
Nitrobenzene (NB)	−0.058	$32.4 \pm 0.6$	33 [24]
1,2-Dichloroethane (DCE)	0.019	$54.4 \pm 0.4$	56.4 [42]
Benzonitrile (BN)	−0.014	$17.2 \pm 0.7$	
Acetophenone (AP)	0.044	$15.7 \pm 0.9$	
2-Nitrophenyl octyl ether (NPOE)	−0.003	$33.4 \pm 0.4$	44.2 [42]

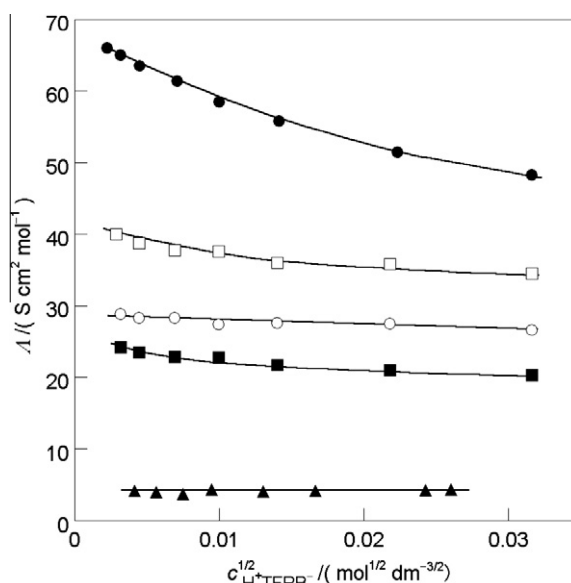


FIGURE 1. Relations between the molar conductance ( $\Lambda$ ) and the concentration of  $\text{H}^+\text{TFPB}^-$  ( $c_{\text{H}^+\text{TFPB}^-}$ ) in various organic solvents: ○, nitrobenzene; ●, 1,2-dichloroethane; □, benzonitrile; ■, acetophenone; ▲, 2-nitrophenyl octyl ether.

Figure 2 illustrates the relation between  $\ln(D_{\text{AnO}_2^{2+}}^{1/2}/D_{\text{H}^+})$  and  $\ln c_{\text{H}^+\text{TFPB}^-}$ . The  $\ln(D_{\text{AnO}_2^{2+}}^{1/2}/D_{\text{H}^+})$  is not a constant and depends on  $\ln c_{\text{H}^+\text{TFPB}^-}$ , suggesting  $K_{\text{ip},\text{AnO}_2^{2+}\text{TFPB}^-}$  is not negligible in O.

#### 4.3.2. Determination of $K_{\text{ip},\text{AnO}_2^{2+}\text{TFPB}^-}$

The  $K_{\text{ip},\text{AnO}_2^{2+}\text{TFPB}^-}$  was determined by adopting  $\text{UO}_2^{2+}$  as  $\text{AnO}_2^{2+}$  based on conductivity measurement of O which contained ( $1 \cdot 10^{-6}$  to  $6 \cdot 10^{-4}$ ) M  $\text{UO}_2^{2+}\text{TFPB}_2^-$ . Figure 3 shows so-called Onsager plot [47,48] which is the relation between  $\Lambda$  and the square root of the concentration of  $\text{UO}_2^{2+}\text{TFPB}_2^-$  in O ( $c_{\text{UO}_2^{2+}\text{TFPB}_2^-}^{1/2}$ ). The present investigation on  $K_{\text{ip},\text{AnO}_2^{2+}\text{TFPB}^-}$  was carried out by assuming that the formation of 1:1 type ion pair between  $\text{UO}_2^{2+}$  and  $\text{TFPB}^-$ , i.e.  $\text{UO}_2^{2+}\text{TFPB}^-$ , but neglecting the formation of ion pairs of higher orders such as 1:2 type. Equation (16) proposed by Fuoss and Edelson [49] and modified by Doe *et al.* [50] for  $K_{\text{ip}}$  of an ion pair composed of one divalent cation and one monovalent anion was applied to the determination of  $K_{\text{ip},\text{AnO}_2^{2+}\text{TFPB}^-}$  based on  $\Lambda$  and  $c_{\text{UO}_2^{2+}\text{TFPB}_2^-}$

$$\Lambda\Phi = \Lambda_0 - \frac{K_{\text{ip},\text{AnO}_2^{2+}\text{TFPB}^-}}{\Lambda_0} X \quad (16)$$

with

$$X = c_{\text{TFPB}^-} \gamma_{\text{AnO}_2^{2+}} \Lambda\Phi(\Lambda\Phi - \Lambda_0/2), \quad (17)$$

$$\Phi = \left[ \left( 1 - \frac{\delta c_{\text{TFPB}^-}^{1/2}}{1 + B a_0 I^{1/2}} \right)^{-1} + (\Lambda_0 - \lambda_0)/2\Lambda \right] [1 + (\Lambda_0 - \lambda_0)/2\Lambda]^{-1}, \quad (18)$$

where  $\delta$  is a parameter obtained by dividing the slope of the Onsager plot by  $\Lambda_0$ ,  $I$ ,  $a_0$ , and  $B$  are the ionic strength, the ion size parameter, and the constant, respectively, in the extended Debye–Hückel theory. The  $\lambda_0$  is the limiting conductivity of a monovalent counter anion.

When  $\Lambda\Phi$  for O into which  $\text{UO}_2^{2+}\text{TFPB}_2^-$  had been added was plotted as the function of  $X$  according to equation (16), a linear relation was found irrespective of the type of O. The linear relation supports that 1:1 ion pair, i.e.  $\text{UO}_2^{2+}\text{TFPB}^-$ , is mainly

TABLE 2

Limiting molar conductivities ( $\Lambda_0$  or  $\lambda_0$ ) of  $\text{H}^+\text{TFPB}^-$ ,  $\frac{1}{2}\text{UO}_2^{2+}\text{TFPB}_2^-$  or  $\text{TFPB}^-$ , formation constants ( $K_{\text{ip}}$ ) of ion pairs of  $\text{H}^+$  or  $\text{UO}_2^{2+}$  with  $\text{TFPB}^-$  in various organic solvents, and viscosities of solvents ( $\eta$ ).

Solvent	$\Lambda_0$ of $\text{H}^+\text{TFPB}^-$ / ( $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ )	$\Lambda_0$ of $\frac{1}{2}\text{UO}_2^{2+}\text{TFPB}_2^-$ / ( $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ )	$\lambda_0$ of $\text{TFPB}^-$ / ( $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ )	$\log [K_{\text{ip}, \text{H}^+\text{TFPB}^-} / (\text{mol}^{-1} \cdot \text{dm}^3)]$	$\log [K_{\text{ip}, \text{AnO}_2^{2+}\text{TFPB}^-} / (\text{mol}^{-1} \cdot \text{dm}^3)]$	$\eta^a$ / ( $\text{mPa} \cdot \text{s}$ )
NB	28	30	11	<1	1.73	1.8
DCE	66	85	25	2.70	4.08	0.77
BN	39	40	16	1.76	2.53	1.2
AP	24	25	11	1.96	3.24	1.7
NPOE	4.3	3.6	1.8	<1	2.21	11

<sup>a</sup> Values of organic solution saturated with water.

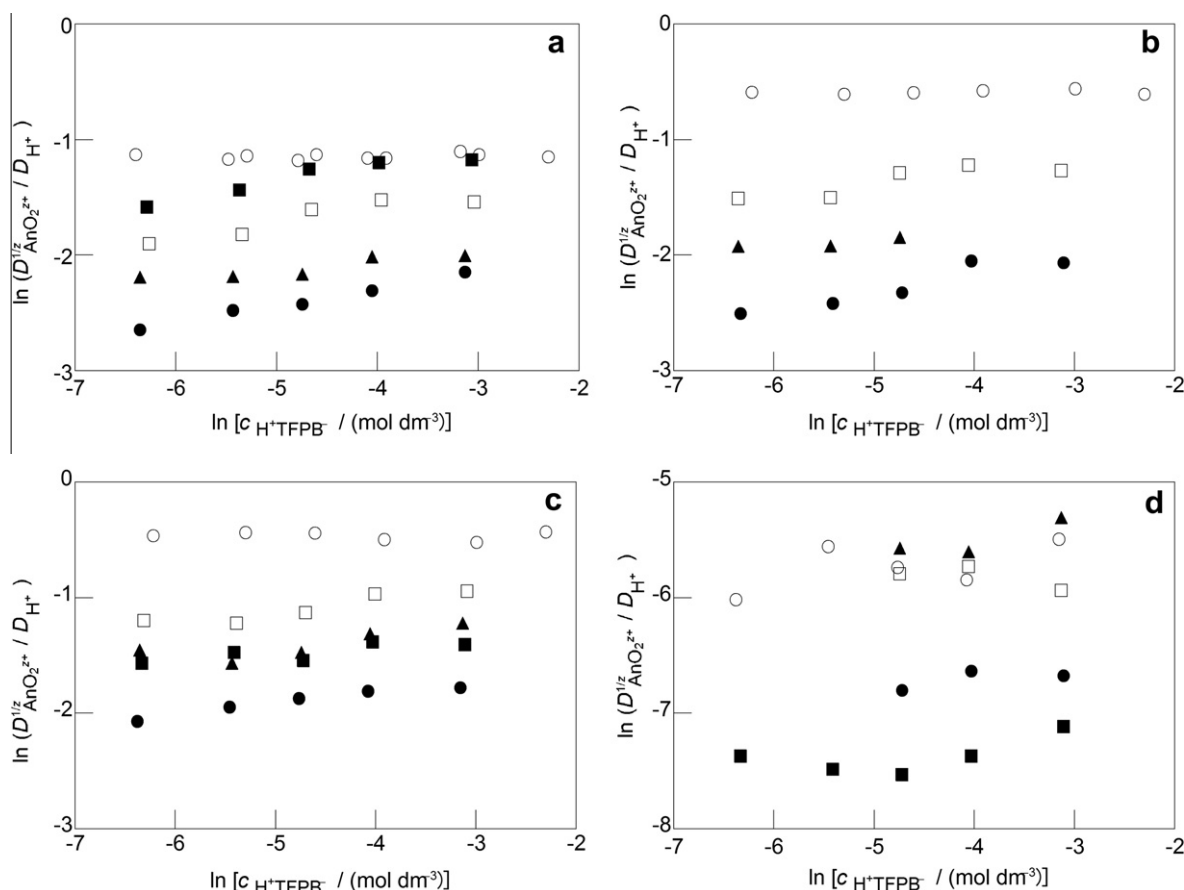


FIGURE 2. Relations between  $\ln(D_{\text{AnO}_2^{2+}}^{1/2}/D_{\text{H}^+})$  of (a)  $\text{UO}_2^{2+}$ , (b)  $\text{NpO}_2^{2+}$ , (c)  $\text{PuO}_2^{2+}$ , or (d)  $\text{NpO}_2^+$  and the concentration of  $\text{H}^+\text{TFPB}^-$  ( $c_{\text{H}^+\text{TFPB}^-}$ ):  $\circ$ , nitrobenzene;  $\bullet$ , 1,2-dichloroethane;  $\square$ , benzonitrile;  $\blacksquare$ , acetophenone;  $\blacktriangle$ , 2-nitrophenyl octyl ether.

formed in O. The intercepts ( $\Lambda_0$ ) were 30, 85, 40, 25, and 3.6, and the slopes ( $K_{\text{ip}, \text{AnO}_2^{2+}\text{TFPB}^-}/\Lambda_0$ ) were  $-1.8$ ,  $-140$ ,  $-8.6$ ,  $-70$ , and  $-46$ , when O used were NB, DCE, BN, AP, and NPOE, respectively. The  $\Lambda_0$  and  $K_{\text{ip}, \text{UO}_2^{2+}\text{TFPB}^-}$  in O were determined from the intercepts and the slopes to be those listed in table 2. In this connection,  $\lambda_0$  of  $\text{TFPB}^-$  in O used in the plot of  $\Lambda\Phi$ -X relation was estimated based on the Walden rule as follows:

$$\lambda_0\eta = \text{const.} \quad (19)$$

At first,  $\Lambda$  of  $\text{TBA}^+\text{TFPB}^-$  were measured in acetonitrile and methanol containing ( $1 \cdot 10^{-4}$  to  $1 \cdot 10^{-2}$ ) M  $\text{TBA}^+\text{TFPB}^-$ , and  $\Lambda_0$  of  $\text{TBA}^+\text{TFPB}^-$  in acetonitrile and methanol were determined to be (118 and  $74.1$ )  $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ , respectively. Here,  $\Lambda$  of  $\text{TBA}^+\text{TFPB}^-$  decreased linearly with the increase of the square root of the concentration of  $\text{TBA}^+\text{TFPB}^-$ , suggesting that  $\text{TBA}^+\text{TFPB}^-$  dissociates completely in these solvents [45] when the concentration is less than  $10^{-2}$  M. Then,  $\lambda_0\eta$  for  $\text{TFPB}^-$  was estimated to be  $19.3 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1} \cdot \text{mPa} \cdot \text{s}$  by using the average of  $\Lambda_0\eta$  for  $\text{TBA}^+\text{TFPB}^-$  determined in both solvents ( $40.6 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1} \cdot \text{mPa} \cdot \text{s}$ ) and  $\lambda_0\eta$  reported for  $\text{TBA}^+$  ( $21.3 \pm 0.2 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1} \cdot \text{mPa} \cdot \text{s}$ ) [51]. Finally,  $\lambda_0$  of  $\text{TFPB}^-$  in O saturated with water were calculated to be those listed in table 2 by using  $\eta$  of O measured.

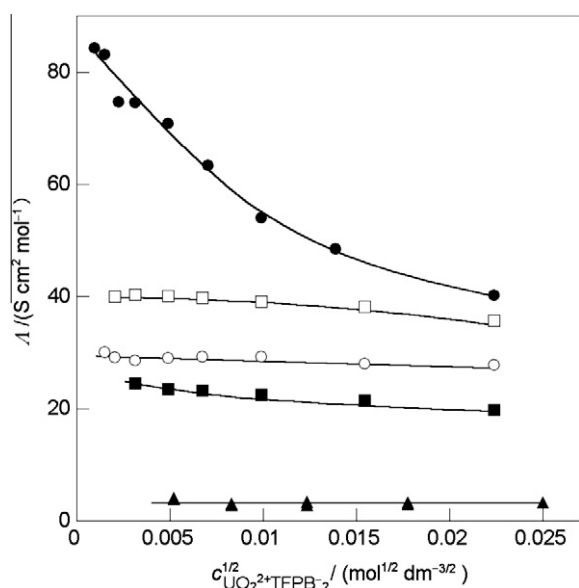
The  $K_{\text{ip}}$  of  $\text{NpO}_2^{2+}$  and  $\text{PuO}_2^{2+}$  were not determined in the present study. They were assumed to be identical to  $K_{\text{ip}, \text{UO}_2^{2+}\text{TFPB}^-}$  because electric charges of these ions are the same as that of  $\text{UO}_2^{2+}$  and the ionic sizes as well as the ionic structures of  $\text{UO}_2^{2+}$ ,  $\text{NpO}_2^{2+}$ , and  $\text{PuO}_2^{2+}$  resemble closely each other as described by Marcus and Loewenschuss [41,42].

The  $K_{\text{ip}}$  of  $\text{NpO}_2^+$  with  $\text{TFPB}^-$  in O ( $K_{\text{ip}, \text{NpO}_2^+\text{TFPB}^-}$ ) could not be determined by conductivity measurement since  $\text{NpO}_2^+$  is much more hydrophilic than  $\text{H}^+$  as described later, and hence the preparation of  $\text{NpO}_2^+\text{TFPB}^-$  by the substitution of  $\text{NpO}_2^+$  in W for  $\text{H}^+$  of  $\text{H}^+\text{TFPB}^-$  in O was difficult.

The  $K_{\text{ip}}$  of  $\text{AnO}_2^{2+}$  with  $\text{ClO}_4^-$  in W were also investigated by conductivity measurement, and were found to be negligibly small, that is less than 10.

#### 4.4. $\Delta G_{\text{tr}, \text{AnO}_2^{2+}}^\circ$ determined with various O

The  $\Delta G_{\text{tr}, \text{AnO}_2^{2+}}^\circ$  for  $\text{UO}_2^{2+}$ ,  $\text{NpO}_2^{2+}$ ,  $\text{PuO}_2^{2+}$ , or  $\text{NpO}_2^+$  from W to O was calculated based on equation (5) by substituting  $D_{\text{AnO}_2^{2+}}$ ,  $D_{\text{H}^+}$ ,  $\Delta G_{\text{tr}, \text{H}^+}^\circ$ ,  $K_{\text{ip}, \text{AnO}_2^{2+}\text{TFPB}^-}$ , and  $K_{\text{ip}, \text{H}^+\text{TFPB}^-}$  determined experimentally,  $c_{\text{H}^+\text{TFPB}^-}$  examined and  $\gamma$  evaluated by using the extended Debye-Hückel equation. Table 3 summarizes the average values of  $\Delta G_{\text{tr}, \text{AnO}_2^{2+}}^\circ$  obtained with various  $c_{\text{H}^+\text{TFPB}^-}$ . Here,  $\Delta G_{\text{tr}, \text{AnO}_2^{2+}}^\circ$  for the transfer of

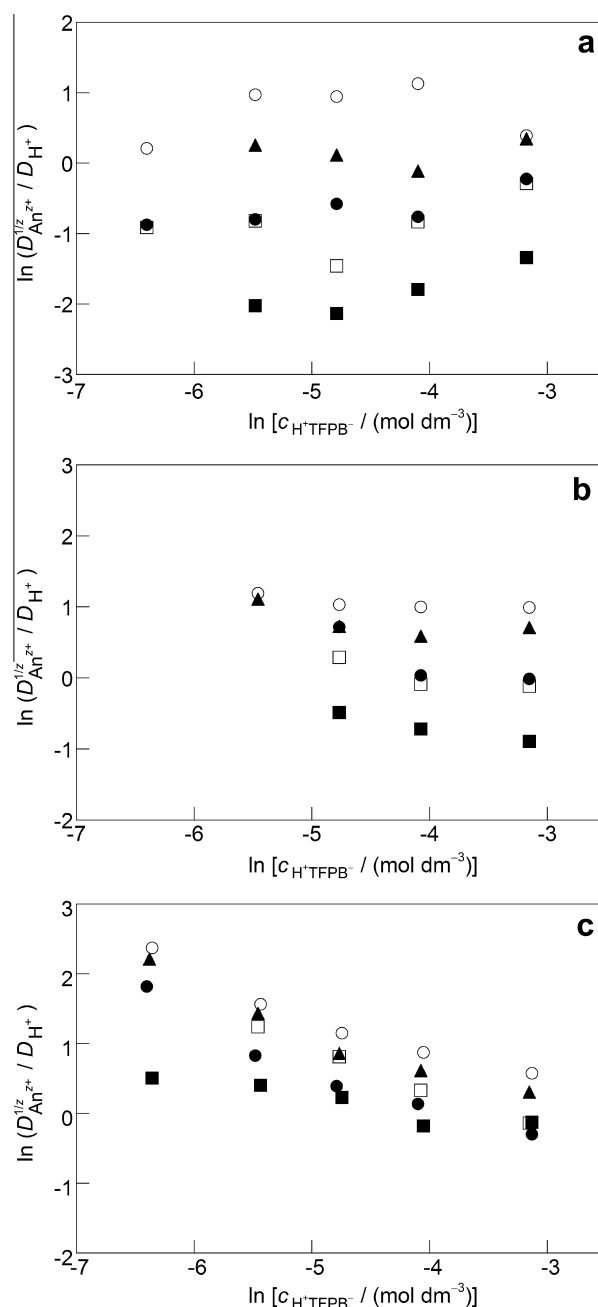


**FIGURE 3.** Relations between the molar conductance ( $\Lambda$ ) of  $\frac{1}{2}\text{UO}_2^{2+}\text{TFPB}_2^-$  and the concentration of  $\text{UO}_2^{2+}\text{TFPB}_2^-$  ( $c_{\text{UO}_2^{2+}\text{TFPB}_2^-}$ ) in various organic solvent:  $\circ$ , nitrobenzene;  $\bullet$ , 1,2-dichloroethane;  $\square$ , benzonitrile;  $\blacksquare$ , acetophenone;  $\blacktriangle$ , 2-nitrophenyl octyl ether.

$\text{UO}_2^{2+}$  from W to NB determined in the present work ( $71.5 \pm 1.3 \text{ kJ} \cdot \text{mol}^{-1}$ ) agreed well with that reported previously ( $72$  or  $71.7 \text{ kJ} \cdot \text{mol}^{-1}$ ) [24,52]. The  $\Delta G_{\text{tr}}^\circ, \text{AnO}_2^{2+}$  for  $\text{NpO}_2^{2+}$  could not be determined when O was AP since  $\text{NpO}_2^{2+}$  was reduced by AP. When O was NPOE containing  $\text{H}^+\text{TFPB}^-$  of concentration higher than  $0.01 \text{ M}$ , a part of  $\text{NpO}_2^{2+}$  was reduced. Therefore,  $\Delta G_{\text{tr}}^\circ, \text{AnO}_2^{2+}$  for  $\text{NpO}_2^{2+}$  was determined by using  $D_{\text{AnO}_2^{2+}}$  obtained with  $\text{H}^+\text{TFPB}^-$  of concentration less than  $0.01 \text{ M}$ . Since  $K_{\text{ip}, \text{NpO}_2^{2+}\text{TFPB}^-}$  could not be determined by conductivity measurement as described in Section 4.3.2, the calculation of  $\Delta G_{\text{tr}}^\circ, \text{AnO}_2^{2+}$  for  $\text{NpO}_2^{2+}$  was carried out under the assumption that  $K_{\text{ip}, \text{NpO}_2^{2+}\text{TFPB}^-}$  was identical to  $K_{\text{ip}, \text{NpO}_2^{2+}\text{TFPB}^-}$  because both  $\text{NpO}_2^{2+}$  and  $\text{H}^+$  are monovalent cation. In this regard, the error in the determination of  $\Delta G_{\text{tr}}^\circ, \text{AnO}_2^{2+}$  of  $\text{NpO}_2^{2+}$  is  $1 \text{ kJ} \cdot \text{mol}^{-1}$  at the most even if the  $K_{\text{ip}, \text{NpO}_2^{2+}\text{TFPB}^-}$  value is over- or under-estimated one order of magnitude.

#### 4.5. Estimation of $\Delta G_{\text{tr}}^\circ$ of $\text{An}^{3+}$ and $\text{An}^{4+}$

Distribution behaviors of trivalent and tetravalent actinide ions,  $\text{An}^{z+}$  ( $z = 3$  or  $4$ ), were also investigated. Figure 4 shows the relations between  $\ln(D_{\text{An}^{z+}}^{1/2}/D_{\text{H}^+})$  and  $\ln c_{\text{H}^+\text{TFPB}^-}$  observed for  $\text{Pu}^{3+}$ ,  $\text{Np}^{4+}$ , and  $\text{Pu}^{4+}$ . The distribution of  $\text{U}^{3+}$ ,  $\text{U}^{4+}$ , or  $\text{Np}^{3+}$  could not be examined since these ions were oxidized during the experiment. The charge of  $\text{An}^{z+}$  is large and hence its ion-pair formation is considered to be serious. The formation of higher order ion pairs might also occur in addition to 1:1 ion pair. Therefore, the determination of  $K_{\text{ip}}$  was difficult for  $\text{An}^{z+}$ , and hence it was not easy to estimate  $\Delta G_{\text{tr}}^\circ$  of  $\text{An}^{z+}$  ( $\Delta G_{\text{tr}}^\circ, \text{An}^{z+}$ ) precisely. In the present work, however,  $\Delta G_{\text{tr}}^\circ, \text{An}^{z+}$  of  $\text{Pu}^{3+}$ ,  $\text{Np}^{4+}$ , and  $\text{Pu}^{4+}$  were estimated as reference values by using the mean values of  $\log D_{\text{An}^{z+}}$  and neglecting the contribution of  $K_{\text{ip}}$ . In the estimation, the correction for  $\gamma$  was made based on the extended Debye–Hückel equation. The estimated values are listed in table 3. In this regard, when the  $\Delta G_{\text{tr}}^\circ$  were estimated under the assumption that  $K_{\text{ip}}$  values for 1:1 ion pair of  $\text{An}^{4+}$  or  $\text{An}^{3+}$  with  $\text{TFPB}^-$  ( $K_{\text{ip}, \text{An}^{4+}\text{TFPB}^-}$ ) or ( $K_{\text{ip}, \text{An}^{3+}\text{TFPB}^-}$ ) were  $3 \cdot 10^4$  or  $1 \cdot 10^4$  in NB ( $\epsilon = 34.8$ ),



**FIGURE 4.** Relations between  $\ln(D_{\text{An}^{z+}}^{1/2}/D_{\text{H}^+})$  of (a)  $\text{Pu}^{3+}$ , (b)  $\text{Np}^{4+}$ , or (c)  $\text{Pu}^{4+}$  and the concentration of  $\text{H}^+\text{TFPB}^-$  ( $c_{\text{H}^+\text{TFPB}^-}$ ):  $\circ$ , nitrobenzene;  $\bullet$ , 1,2-dichloroethane;  $\square$ , benzonitrile;  $\blacksquare$ , acetophenone;  $\blacktriangle$ , 2-nitrophenyl octyl ether.

$3 \cdot 10^9$  or  $1 \cdot 10^7$  in DCE ( $\epsilon = 10.4$ ),  $2 \cdot 10^5$  or  $3 \cdot 10^4$  in BN ( $\epsilon = 25.2$ ),  $4 \cdot 10^6$  or  $2 \cdot 10^5$  in AP ( $\epsilon = 17.4$ ) and  $2 \cdot 10^5$  or  $3 \cdot 10^4$  in NPOE ( $\epsilon = 24.2$ ),  $\Delta G_{\text{tr}}^\circ$  values were

**TABLE 3**

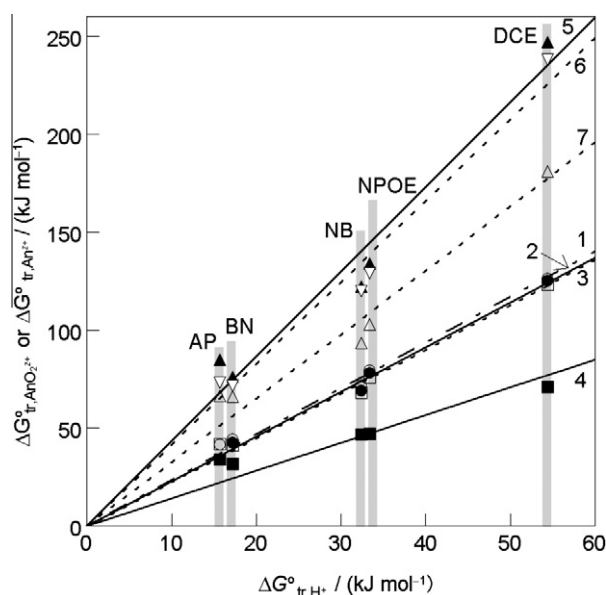
$\Delta G_{\text{tr}}^\circ$  for actinide ions from aqueous to various organic phases.

Solvent	$\Delta G_{\text{tr}}^\circ / (\text{kJ} \cdot \text{mol}^{-1})$						
	$\text{UO}_2^{2+}$	$\text{NpO}_2^{2+}$	$\text{PuO}_2^{2+}$	$\text{NpO}_2^{2+}$	$\text{Pu}^{3+}$ <sup>a</sup>	$\text{Np}^{4+}$ <sup>a</sup>	$\text{Pu}^{4+}$ <sup>a</sup>
NB	$71.5 \pm 1.3$ ( $72^b$ )	$69^b$	$68^b$	$46.6 \pm 0.8$	$93.4 \pm 3.6$	$122 \pm 4$	$120 \pm 8$
DCE	$126 \pm 1$	$125 \pm 1$	$123 \pm 1$	$70.8 \pm 0.5$	$181 \pm 5$	$247 \pm 10$	$238 \pm 21$
BN	$44.2 \pm 1.5$	$42.5 \pm 1.5$	$41.2 \pm 1.5$	$31.6 \pm 0.8$	$66.0 \pm 6.2$	$76.1 \pm 5.2$	$71.5 \pm 9.8$
AP	$41.3 \pm 1.8$		$41.9 \pm 1.9$	$33.9 \pm 1.0$	$66.4 \pm 3.0$	$85.0 \pm 6.7$	$73.1 \pm 9.0$
NPOE	$79.4 \pm 1.0$	$77.7 \pm 0.9$	$75.9 \pm 1.0$	$47.0 \pm 0.6$	$103 \pm 2$	$134 \pm 6$	$129 \pm 12$

<sup>a</sup> Not corrected for  $K_{\text{ip}}$  between  $\text{An}^{z+}$  and  $\text{TFPB}^-$ .

<sup>b</sup> Previous work [24].





**FIGURE 5.** Relations between  $\Delta G_{\text{tr}}^{\circ}$  of actinide ion ( $\Delta G_{\text{tr},\text{AnO}_2^{z+}}^{\circ}$  or  $\Delta G_{\text{tr},\text{An}^{z+}}^{\circ}$ ) and that of  $\text{H}^+$  ( $\Delta G_{\text{tr},\text{H}^+}^{\circ}$ ):  $\circ$  and line 1,  $\text{UO}_2^{2+}$ ;  $\bullet$  and line 2,  $\text{NpO}_2^{2+}$ ;  $\square$  and line 3,  $\text{PuO}_2^{2+}$ ;  $\blacksquare$  and line 4,  $\text{NpO}_2^{3+}$ ;  $\blacktriangle$  and line 5,  $\text{Np}^{4+}$ ;  $\nabla$  and line 6,  $\text{Pu}^{4+}$ ;  $\triangle$  and line 7,  $\text{Pu}^{3+}$ .

about  $5 \text{ kJ} \cdot \text{mol}^{-1}$  larger than the values listed in table 3. Here, the values of  $K_{\text{ip},\text{An}^{4+},\text{TFPB}^-}$  or  $K_{\text{ip},\text{An}^{3+},\text{TFPB}^-}$  assumed above might be much larger than the actual values since Stokes radius of  $\text{An}^{4+}$  or  $\text{An}^{3+}$  ((1.1 or 0.9) nm) which determines the distance ( $d$ ) between  $\text{An}^{4+}$  or  $\text{An}^{3+}$  and  $\text{TFPB}^-$  is similar to that of  $\text{UO}_2^{2+}$  (0.9 nm) which determines  $d$  between  $\text{UO}_2^{2+}$  and  $\text{TFPB}^-$ , and hence  $K_{\text{ip},\text{An}^{4+},\text{TFPB}^-}$  or  $K_{\text{ip},\text{An}^{3+},\text{TFPB}^-}$  is considered to be not larger than twice of  $K_{\text{ip},\text{UO}_2^{2+},\text{TFPB}^-}$  (see, table 2), taking into account that  $K_{\text{ip}}$  is determined by the Coulomb's force between the cation and the anion which is proportional to the product of charges of the cation and the anion and to the reciprocal of  $d^2$ .

#### 4.6. Relation between $\Delta G_{\text{tr}}^{\circ}$ for $\text{AnO}_2^{z+}$ or $\text{An}^{z+}$

Although  $\Delta G_{\text{tr}}^{\circ}$ ,  $\text{AnO}_2^{z+}$  or  $\Delta G_{\text{tr},\text{An}^{z+}}^{\circ}$  determined above were plotted against various physicochemical parameters [53] of O such as  $\epsilon$ , solubility parameter, heat of vaporization, heat capacity, donor or acceptor numbers as proposed by Gutmann,  $E_{\text{T}}$  value by Dimroth *et al.* and  $\pi^*$  value by Kamlet and Taft, any clear systematic relations were not found, which indicates that it is difficult to interpret the  $\Delta G_{\text{tr}}^{\circ}$  by using one solvent parameter. On the other hand, when  $\Delta G_{\text{tr},\text{AnO}_2^{z+}}^{\circ}$  or  $\Delta G_{\text{tr},\text{An}^{z+}}^{\circ}$  observed with one O were plotted against  $\Delta G_{\text{tr},\text{H}^+}^{\circ}$  observed with the same O as shown in figure 5,  $\Delta G_{\text{tr},\text{AnO}_2^{z+}}^{\circ}$  or  $\Delta G_{\text{tr},\text{An}^{z+}}^{\circ}$  was found to be almost proportional to  $\Delta G_{\text{tr},\text{H}^+}^{\circ}$  regardless of the kind of  $\text{AnO}_2^{z+}$  or  $\text{An}^{z+}$ , suggesting that solvations of  $\text{AnO}_2^{z+}$  or  $\text{An}^{z+}$  in W and various O that control  $\Delta G_{\text{tr}}^{\circ}$  are not special, but similar to those of  $\text{H}^+$ .

## 5. Conclusions

The values of  $\Delta G_{\text{tr}}^{\circ}$ ,  $\text{AnO}_2^{z+}$  were determined, and those of  $\Delta G_{\text{tr},\text{An}^{z+}}^{\circ}$  were estimated by using various O in the present work. The values indicate that  $\Delta G_{\text{tr},\text{AnO}_2^{z+}}^{\circ}$  of  $\text{UO}_2^{2+}$ ,  $\text{NpO}_2^{2+}$ , and  $\text{PuO}_2^{2+}$  are similar to each other irrespective of the type of O, and are somewhat larger than  $\Delta G_{\text{tr}}^{\circ}$  of  $\text{Mg}^{2+}$  which is a fairly hydrophilic divalent ion. Here,  $\Delta G_{\text{tr}}^{\circ}$  of  $\text{Mg}^{2+}$  from W to NB [24,54] or DCE [24] was reported to be 64 to 69.6 or 114  $\text{kJ} \cdot \text{mol}^{-1}$ , respectively. The values of  $\Delta G_{\text{tr},\text{AnO}_2^{z+}}^{\circ}$  for  $\text{NpO}_2^{2+}$  are much larger than those for  $\text{AnO}_2^{2+}$  divided by  $z$  ( $=2$ ) or  $\Delta G_{\text{tr},\text{H}^+}^{\circ}$  (table 1), and hence  $\Delta G_{\text{tr},\text{AnO}_2^{z+}}^{\circ}$  for  $\text{NpO}_2^{2+}$  with any O investigated are considered to be particularly large.

The  $\Delta G_{\text{tr}}^{\circ}$  values of  $\text{AnO}_2^{z+}$  determined in the present study were those between W and O of relatively large dielectric constants. These O have seldom been used for the solvent extraction of  $\text{AnO}_2^{z+}$ . However, the  $\Delta G_{\text{tr}}^{\circ}$  of  $\text{AnO}_2^{z+}$  determined might be useful to explore a guideline for selection of solvent for the extraction or to design an extraction reagent selective for  $\text{AnO}_2^{z+}$  because

the ability of the extraction system depends not only on the stability constant of the ion with the extraction reagent in O but also on the  $\Delta G_{\text{tr}}^{\circ}$  of the ion in the absence of the extraction reagent. In this regard, in order to extend the procedure of determination of  $\Delta G_{\text{tr}}^{\circ}$  described in the present paper to O of low dielectric constant which has been used for the practical extraction of  $\text{AnO}_2^{z+}$ , more sensitive methods to determine the concentration and the conductivity of  $\text{AnO}_2^{z+}$  are necessary because of small solubility and dissociation constant of  $\text{AnO}_2^{z+}$  in the O of low dielectric constant.

Finally, although  $\text{AnO}_2^{z+}$  or  $\text{An}^{z+}$  are considered to be hydrated partly even after transfer to O, the chemical states of  $\text{AnO}_2^{z+}$  or  $\text{An}^{z+}$  in O were not discussed in the present paper, and remained as the subject of the further investigation.

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