Kinetic and Thermodynamic Requirements to Extend Solvent Compatibility in Thermal-Assisted Extraction of Inert Platinum Group Metals

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Experimental Procedure.

All of the chemicals were of reagent grade and used without further purification. 2,6-pyridinedicarbonyl dichloride (1.96 g, Wako Chemical Ltd.) and triethylamine (2.68 mL = 1.95 g, Kanto Chemical Co., Inc.) were dissolved to THF (40 mL, Kanto Chemical Co., Inc.) in 100 mL round-bottom flask. The mixture was cooled on ice bath. After THF (5 ml) which containing di-n-butylamine (3.25 mL=2.49 g, Tokyo Chemical Industry Co., LTD.) was slowly added by a dropping funnel, additional THF (10 ml) was further loaded. The mixture was stirred for 1 h on the ice bath, and stirred at RT for overnight. White precipitate was removed. The filtrate was concentrated by rotary evaporator. The residue in the flask was dissolved in dichloromethane (30 mL, FUJIFILM Wako Pure Chemical Corporation), and mixed with 2 M HCl(aq) (6 mL). The organic layer was transferred to another flask, mixed with small portion of K_2CO_3 and $MgSO_4$, and rested for 15 min. Then solid materials were removed by filtration. Any volatile materials in the filtrate was removed by the rotary evaporator to give yellow oil of TBPDA (2.17 g, 58% yield). The obtained compound was characterized by ^{1}H and ^{13}C NMR spectroscopy (JEOL JNM ECX-400). ^{1}H NMR ($CDCl_3$, δ/ppm *vs.* TMS) 0.79 (t, 6H, $NCH_2CH_2CH_2CH_3$), 0.98 (t, 6H, $NCH_2CH_2CH_2CH_3$), 1.14 (sextet, 4H, $NCH_2CH_2CH_2CH_3$), 1.40 (sextet, 4H, $NCH_2CH_2CH_2CH_3$), 1.54 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.66 (m, 4H, $NCH_2CH_2CH_2CH_3$), 3.30 (dd, 4H, $NCH_2CH_2CH_2CH_3$), 3.49 (dd, 4H, $NCH_2CH_2CH_2CH_3$), 7.61 (d, 2H, 3,5-H), 7.86 (t?, 1H, 4-H). ^{13}C NMR ($CDCl_3$, δ/ppm *vs.* TMS) 13.83, 14.01, 19.88, 20.41, 29.70, 31.10, 45.73, 48.71, 123.90, 137.91, 153.64, 168.30.

The pre-equilibrated HNO_3(aq) which containing a metal ion (M) like 5 mM Ru(III) or 5 mM Rh(III) was loaded into a screw-capped vial with a pre-equibrated organic solvent (1-octanol or [choline][Tf_2N]) which containing 30 mM TBPDA. The volume ratio between aqueous and organic phases were always kept in 1:1. The mixture was stirred at 800 rpm and constant temperature in aluminum block bath on a hot stirrer. For analysis, small amount of mixture was cooled to RT then centrifuged. The M concentration in aqueous layer was determined by ICP-AES (Thermo Scientific iCAP7200 Duo). The extraction efficiency (*E*%) and the distribution ratio (*D*) were calculated as follows.

$$E\% = 100 \times ([M]_{ini} - [M]_{aq})/[M]_{ini} \quad (1)$$

$$D = ([M]_{ini} - [M]_{aq})/[M]_{aq} \quad (2)$$

where $[M]_{ini}$ and $[M]_{aq}$ denote the metal concentrations in the aqueous phase at the initial state and after the extraction, respectively.

Lithium salts of Tf_2N^-, TfO^-, BF_4^-, PF_6^-, and ClO_4^- (500 mM) were dissolved in the pre-equilibrated 0.5 M HNO_3(aq). The partition behavior of these anions was examined by contacting with the pre-equilibrated 1-octanol at 1:1 volume ratio. After 1 h mixing for equilibration, the organic layer (70 μL) was mixed with a DMSO-d_6 solution (630 μL) dissolving a standard material. Concentrations of Tf_2N^-, TfO^-, and BF_4^- in organic layer were determined by ^{19}F NMR peak integrals compared with that of tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as a reference. LiTf_2N was employed as a reference for PF_6^-. The log *P* of ClO_4^- was indirectly determined from distribution of Li^+ evaluated by ICP-AES.

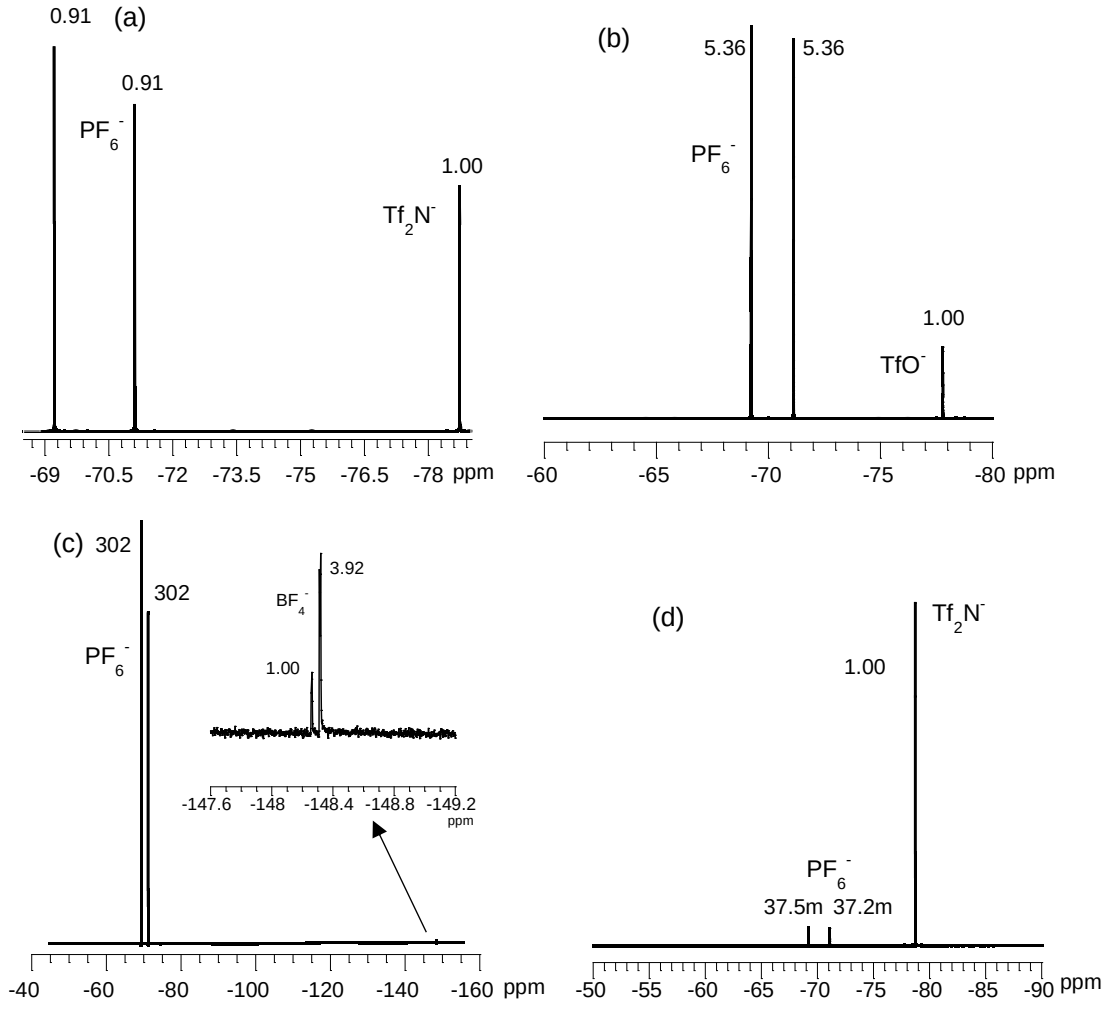

Figure S1. ^{19}F NMR spectra of Tf_2N^- (a) , TfO^- (b), BF_4^- (c) and PF_6^- (d) in DMSO-d_6. Concentration of each anion in the organic phase was determined after partitioning 1-octanol / 0.5 M HNO_3(aq). TBAPF$_6$ was employed as a standard for Tf_2N^- , TfO^-, and BF_4^-, while that for PF_6^- was LiTf$_2$N.

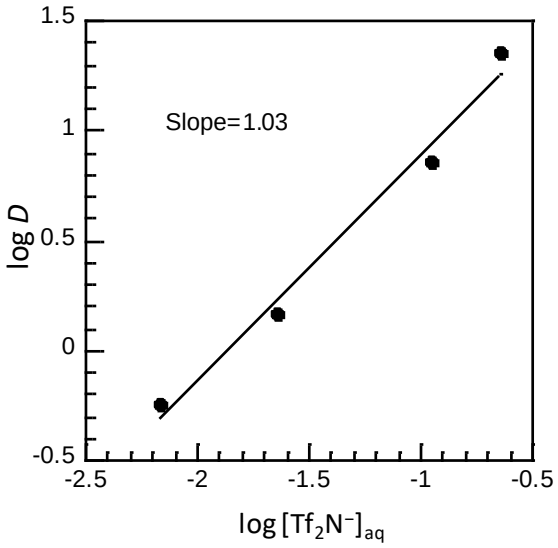

Figure S2. Effect of total concentration of Tf_2N^- ($[Tf_2N^-]_{aq}$) to Ru(III) (5 mM) extraction from 0.5 M HNO_3(aq) to 1-octanol containing 30 mM TBPDA at 356 K in terms of *D*.

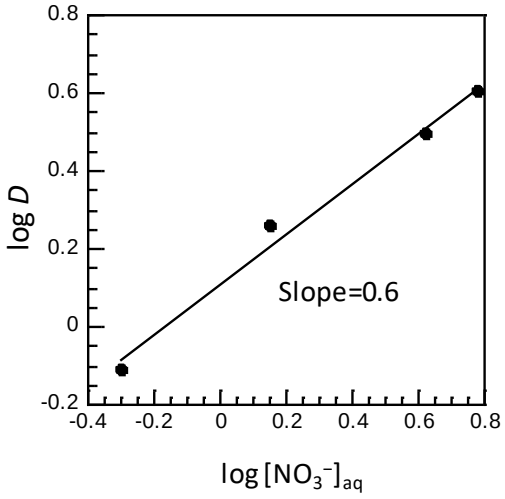

Figure S3. Effect of concentration of NO_3^- to Ru(III) (5 mM) extraction from (H,Na)NO_3(aq) containing 0.5 M H^+ to 1-octanol containing 60 mM TBPDA at 356 K in terms of *D*.

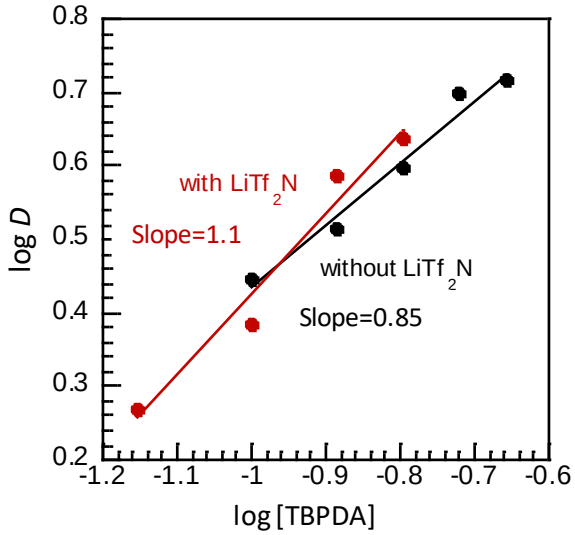

Figure S4. Effect of concentration of TBPDA to Ru(III) (5 mM) extraction from 0.5 M HNO_3(aq) containing 50 mM LTf_2N (red) and without LTf_2N (black) to 1-octanol at 356 K in terms of *D*.

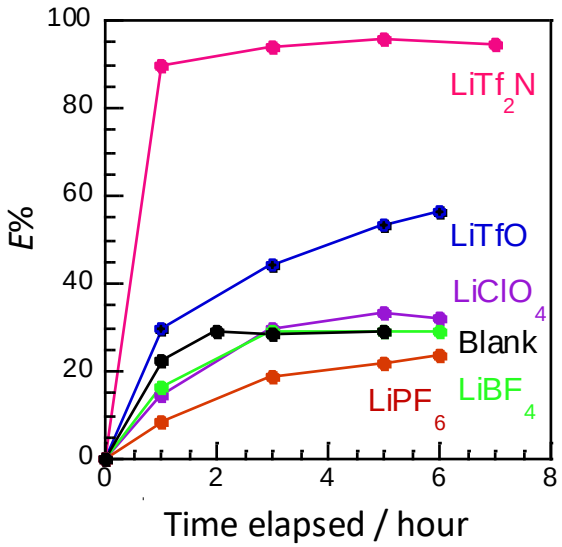

Figure S5. Extraction efficiency (*E%*) of Ru(III) as a function of elapsed time in 0.5 M HNO_3(aq)/1-octanol system. Condition: [Ru(III)] = 5 mM, [TBPDA] = 30 mM, [anion] = 500 mM, *T* = 356 K.

Table S1. Correlation between Partition Coefficient (log *P*) and Ru(III) (5 mM) Extraction Behavior in 0.5 M HNO_3(aq)/1-Octanol System

anion	log *P*	*E*%	log *D*
Tf_2N^-	0.09	94.8	1.36
TfO^-	-0.64	56.4	0.11
PF_6^-	-1.09	23.6	−0.51
ClO_4^-	-1.40	32.0	−0.33
BF_4^-	-1.91	29.3	−0.38

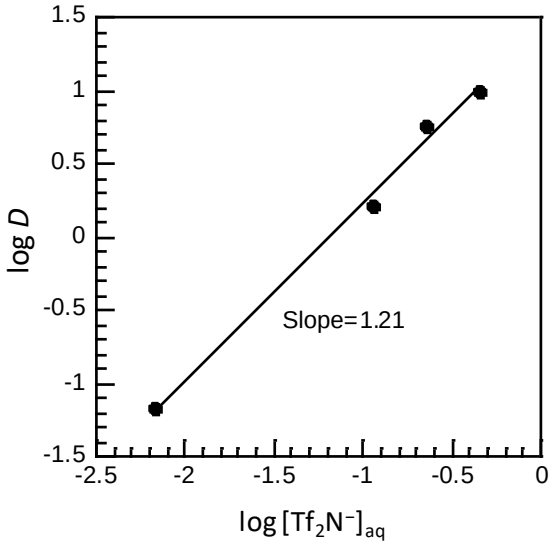

Figure S6. Effect of total concentration of Tf_2N^- ($[Tf_2N^-]_{tot}$) to Rh(III) (5 mM) extraction from 0.5 M HNO_3(aq) to 1-octanol containing 30 mM TBPDA at 356 K in terms of *D*.