

Short communication

Individual Extraction Constants of Some Univalent Anions in the Two-Phase Water–Phenyltrifluoromethyl Sulfone System

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Abstract

From extraction experiments and γ -activity measurements, the extraction constants corresponding to the general equilibrium $\text{Cs}^+(\text{aq}) + \text{A}^-(\text{aq}) \rightleftharpoons \text{Cs}^+(\text{org}) + \text{A}^-(\text{org})$ taking place in the two-phase water–phenyltrifluoromethyl sulfone (FS 13) system ($\text{A}^- = \text{I}^-, \text{ClO}_4^-, \text{MnO}_4^-, \text{Br}_3^-, \text{I}_3^-$, picrate, tetraphenylborate (BPh_4^-); $\text{aq} = \text{aqueous phase}$, $\text{org} = \text{FS 13 phase}$) were evaluated. Furthermore, the individual extraction constants of these 7 anions in the mentioned two-phase system were calculated; they were found to increase in the series of $\text{I}^- < \text{ClO}_4^- < \text{Br}_3^- < \text{MnO}_4^-$, picrate $< \text{I}_3^- < \text{BPh}_4^-$.

Keywords: Univalent anions, water–phenyltrifluoromethyl sulfone system, individual extraction constants

1. Introduction

Nitrobenzene, a dipolar aprotic solvent, has frequently been used in liquid-liquid extraction, especially in the separation of cesium, strontium, barium, europium and americium from aqueous solutions.^{1–24} Nitrobenzene is also suitable for accurate conductometric measurements.²⁵ A considerable attention has been paid to the study of charge transfer across the water/nitrobenzene interface.^{26–28} Moreover, a process involving chlorinated cobalt dicarbollide, polyethylene glycol (PEG 400) and diphenyl-*N,N*-dibutylcarbamoymethyl phosphine oxide (DPDBCMPPO), also called UNEX, has been reported for the simultaneous recovery of cesium, strontium, lanthanides and actinides from highly acidic media into phenyltrifluoromethyl sulfone (abbrev. FS 13).^{29,30} At this point it should be noted that the mentioned FS 13 diluent was developed for the UNEX process as an alternative organic diluent to the highly polar nitrobenzene. Besides this, FS 13 has the advantage of low viscosity and very good solubility of the UNEX extractants and metal solvates.³⁰ On the other hand, nitrobenzene derivatives have been suc-

cessfully utilized as diluents for cobalt dicarbollide processes in Russia, however, they are deemed unsuitable for use in the United States due to the perceived hazards associated with nitrobenzene.

In order to estimate the individual extraction constants of some univalent ions in the water–nitrobenzene system,³¹ a nonthermodynamic assumption of equal extractabilities of the tetraphenylarsonium cation, Ph_4As^+ , and the tetraphenylborate anion, BPh_4^- , of the “reference” electrolyte³² from the aqueous into nitrobenzene phase, expressed by the identity $\log K_{\text{Ph}_4\text{As}^+}^i = \log K_{\text{BPh}_4^-}^i = 6.3$,³¹ was adopted. Both these ions are sufficiently and practically equally bulky and their phenyl group “covers” are identical. Thus, it is quite justifiable to assume that their specific interactions with the molecule of the solvent are very limited and virtually equal. The above-mentioned “ $\text{Ph}_4\text{AsBPh}_4$ assumption” was further employed for a number of the two-phase water–polar organic solvent systems.^{33–35}

The individual extraction constants of many univalent ions have been evaluated in the water–nitrobenzene system.^{31,36–38} Recently, analogous thermodynamic data

concerning some divalent and trivalent metal cations, as well as some univalent organic cations, have been reported for this two-phase system.^{39–41} On the other hand, in the current communication, the individual extraction constants for a series of 7 univalent anions in the two-phase water–FS 13 system are presented.

2. Experimental

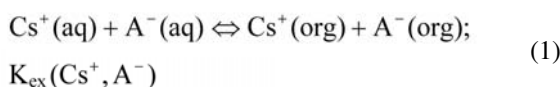
Phenyltrifluoromethyl sulfone (FS 13) was supplied by Khlopin Radium Institute, St. Petersburg, Russia. Cesium iodide (CsI), cesium perchlorate (CsClO₄), cesium permanganate (CsMnO₄), cesium tribromide (CsBr₃), cesium triiodide (CsI₃) and cesium tetraphenylborate (CsBPh₄) were purchased from Aldrich and were employed as received. The radionuclide ¹³⁷Cs⁺ (Techsnaveksport, Russia) was of standard radiochemical purity. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. A solution of cesium picrate in water was prepared by dissolving stoichiometric amount of picric acid in an aqueous solution of CsOH.

The extraction experiments were carried out in 10 mL glass test-tubes with polyethylene stoppers: 2 mL of FS 13 and microamounts ¹³⁷Cs⁺ were added to 2 mL of an aqueous solution of Cs⁺, A⁻ (A⁻ = I⁻, ClO₄⁻, MnO₄⁻, Br₃⁻, I₃⁻, picrate, BPh₄⁻) of the concentration in the range from 1 × 10⁻⁴ to 1 × 10⁻³ mol/L. The test-tubes filled with the solutions were shaken for 2 h at 25 ± 1 °C, using a laboratory shaker. Then the phases were separated by centrifugation. Afterwards, 1 mL samples were taken from each phase and their γ-activities were measured using a well-type NaI(Tl) scintillation detector connected to a γ-analyzer NK 350 (Gamma, Budapest, Hungary).

The equilibrium distribution ratios of cesium, D_{Cs}, were determined as the ratios of the measured radioactivities of ¹³⁷Cs⁺ in the FS 13 and aqueous samples.

3. Results and Discussion

With respect to the results of previous papers,^{1,31,36,37} the two-phase water–Cs⁺A⁻ (A⁻ = I⁻, ClO₄⁻, MnO₄⁻, Br₃⁻, I₃⁻, picrate, BPh₄⁻)–FS 13 extraction system (see Experimental) can be described by the following general equilibrium



with the corresponding extraction constant K_{ex}(Cs⁺, A⁻); aq and org denote the presence of the species in the aqueous and FS 13 phases, respectively.

The changes of the standard Gibbs energies corresponding to the transfer of the ions Cs⁺ and A⁻ (A⁻ = I⁻, ClO₄⁻, MnO₄⁻, Br₃⁻, I₃⁻, picrate, BPh₄⁻) from the aqueous in-

to FS 13 phase



are given by definitions

$$\Delta G_{\text{tr,Cs}^+}^{0,\text{aq} \rightarrow \text{org}} = \mu_{\text{Cs}^+}^{0,\text{org}} - \mu_{\text{Cs}^+}^{0,\text{aq}} \quad (4)$$

$$\Delta G_{\text{tr,A}^-}^{0,\text{aq} \rightarrow \text{org}} = \mu_{\text{A}^-}^{0,\text{org}} - \mu_{\text{A}^-}^{0,\text{aq}} \quad (5)$$

Here μ⁰ – s are the standard chemical potentials of the ions Cs⁺ and A⁻ in the two phases concerned.

The individual extraction constants K_{Cs⁺}ⁱ and K_{A⁻}ⁱ (A⁻ = I⁻, ClO₄⁻, MnO₄⁻, Br₃⁻, I₃⁻, picrate, BPh₄⁻) for the considered univalent ions in the water–FS 13 extraction system are defined by

$$\Delta G_{\text{tr,Cs}^+}^{0,\text{aq} \rightarrow \text{org}} = -RT \ln K_{\text{Cs}^+}^i \quad (6)$$

$$\Delta G_{\text{tr,A}^-}^{0,\text{aq} \rightarrow \text{org}} = -RT \ln K_{\text{A}^-}^i \quad (7)$$

Combination of the relation

$$-RT \ln K_{\text{ex}}(\text{Cs}^+, \text{A}^-) = \mu_{\text{Cs}^+}^{0,\text{org}} + \mu_{\text{A}^-}^{0,\text{org}} - \mu_{\text{Cs}^+}^{0,\text{aq}} - \mu_{\text{A}^-}^{0,\text{aq}} \quad (8)$$

corresponding to Equilibrium (1) with Eqs (4) – (7) yields

$$\log K_{\text{ex}}(\text{Cs}^+, \text{A}^-) = \log K_{\text{Cs}^+}^i + \log K_{\text{A}^-}^i \quad (9)$$

The standard Galvani potential difference of the considered anion A⁻ between the FS 13 and aqueous phases (see, e. g., Refs 42 and 43), denoted by the symbol Δ_{aq}^{org} φ_{A⁻}⁰, is defined by the following relation

$$\Delta_{\text{aq}}^{\text{org}} \phi_{\text{A}^-}^0 = \Delta G_{\text{tr,A}^-}^{0,\text{aq} \rightarrow \text{org}} / F \quad (10)$$

Taking into account the conditions of electroneutrality in the organic and aqueous phases of the system under study (see Experimental)

$$[\text{Cs}^+]_{\text{org}} = [\text{A}^-]_{\text{org}} \quad (11)$$

$$[\text{Cs}^+]_{\text{aq}} = [\text{A}^-]_{\text{aq}} \quad (12)$$

and the measured equilibrium distribution ratio of cesium

$$D_{\text{Cs}} = [\text{Cs}^+]_{\text{org}} / [\text{Cs}^+]_{\text{aq}} \quad (13)$$

then combination of relations (11) – (13) with the expression for K_{ex}(Cs⁺, A⁻) (see Equilibrium (1)) in the form

$$K_{\text{ex}}(\text{Cs}^+, \text{A}^-) = \frac{[\text{Cs}^+]_{\text{org}} [\text{A}^-]_{\text{org}}}{[\text{Cs}^+]_{\text{aq}} [\text{A}^-]_{\text{aq}}} \quad (14)$$

gives the final expression for the extraction constant $K_{\text{ex}}(\text{Cs}^+, \text{A}^-)$:

$$K_{\text{ex}}(\text{Cs}^+, \text{A}^-) = D_{\text{Cs}}^2 \quad (15)$$

In this study, from the extraction experiments and γ -activity measurements (see Experimental) by means of Eq. (15), the logarithms of the constants $K_{\text{ex}}(\text{Cs}^+, \text{A}^-)$ were determined, as listed in Table 1.

Table 1. Thermodynamic data for some univalent organic anions in the two-phase water–FS 13 extraction system at 25 °C (for the meaning of the constants see text).

A^-	$\log K_{\text{ex}}(\text{Cs}^+, \text{A}^-)^a$	$\log K_{\text{A}^-}^i{}^b$	$\Delta G_{\text{tr,A}^-}^{0,\text{aq}\rightarrow\text{org}}$ (kJ/mol) ^c	$\Delta_{\text{aq}}^{\text{org}} \varphi_{\text{A}^-}^0$ (V) ^d
I^-	-7.8	-3.5	20.0	0.207
ClO_4^-	-6.0	-1.7	9.7	0.101
MnO_4^-	-4.2	0.1	-0.6	-0.006
Br_3^-	-5.9	-1.6	9.1	0.095
I_3^-	-1.8	2.5	-14.3	-0.148
picrate	-4.2	0.1	-0.6	-0.006
BPh_4^-	0.9	5.2	-29.7	-0.308

^a Calculated from Eq. (15); ^b Calculated from Eq. (9); ^c Calculated from Eq. (7); ^d Calculated from Eq. (10).

Using the constants $\log K_{\text{ex}}(\text{Cs}^+, \text{A}^-)$ given in Table 1, the value $\log K_{\text{Cs}^+}^i = -4.3$,⁴⁴ and applying Eq. (9), we obtain the logarithms of the individual extraction constants of the univalent anions A^- ($\text{A}^- = \text{I}^-$, ClO_4^- , MnO_4^- , Br_3^- , I_3^- , picrate, BPh_4^-), $\log K_{\text{A}^-}^i$, in the two-phase water–FS 13 system. These data are summarized in Table 1. Besides this, by means of Eqs (7) and (10), one gets the thermodynamic data $\Delta G_{\text{tr,A}^-}^{0,\text{aq}\rightarrow\text{org}}$ and $\Delta_{\text{aq}}^{\text{org}} \varphi_{\text{A}^-}^0$, respectively, reviewed in Table 1 as well.

Finally, from the data given in Tables 1 and 2 it follows that the individual extraction constants $\log K_{\text{A}^-}^i$ in the water–FS 13 system increase in the sequence of $\text{I}^- < \text{ClO}_4^- < \text{Br}_3^- < \text{MnO}_4^-$, picrate $< \text{I}_3^- < \text{BPh}_4^-$, whereas $\log K_{\text{A}^-}^i$ in the water-nitrobenzene system increase in the following anion order: $\text{I}^- < \text{ClO}_4^- < \text{picrate} < \text{I}_3^- < \text{BPh}_4^-$. In this context it should be noted that the $\log K_{\text{A}^-}^i$ constants express, in principle, the affinity of the considered anions A^- for the organic phase, i. e., the $\log K_{\text{A}^-}^i$ constants are a quantitative measure of the hydrophobicity, as well as the extractability

Table 2. Individual extraction constants ($\log K_{\text{A}^-}^i$) of I^- , ClO_4^- , picrate, I_3^- and BPh_4^- in the two-phase water–nitrobenzene system at 25 °C (according to Ref. 31).

A^-	$\log K_{\text{A}^-}^i{}^a$
I^-	-3.3
ClO_4^-	-1.4
picrate	0.8
I_3^-	4.1
BPh_4^-	6.3

^a Ref. 31.

of the A^- ions from the aqueous into organic phase. This means – with regard to the experimental data presented in Tables 1 and 2 – that the extractability of the anions I^- , ClO_4^- , picrate, I_3^- and BPh_4^- from the aqueous phase is somewhat higher into the nitrobenzene phase than into the FS 13 one.

In conclusion, it is necessary to emphasize that the thermodynamic constants $\log K_{\text{A}^-}^i$, $\Delta G_{\text{tr,A}^-}^{0,\text{aq}\rightarrow\text{org}}$ and $\Delta_{\text{aq}}^{\text{org}} \varphi_{\text{A}^-}^0$ listed in Table 1 can be employed, e. g., for the studies of

chemical equilibria in the two-phase water–FS 13 system, analogously as in some previous papers.^{45–50}

4. Acknowledgement

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Povzetek

Z uporabo ekstrakcijskih eksperimentov in meritev γ -aktivnosti smo v dvofaznem sistemu voda-feniltrifluorometilsulfon (FS 13) določili konstante ekstrakcije za ravnotežja, ki jih splošno lahko zapišemo kot $\text{Cs}^+(\text{aq}) + \text{A}^-(\text{aq}) \rightleftharpoons \text{Cs}^+(\text{org}) + \text{A}^-(\text{org})$; $\text{A}^- = \text{I}^-, \text{ClO}_4^-, \text{MnO}_4^-, \text{Br}_3^-, \text{I}_3^-$, pikrat, tetrafenilborat (BPh_4^-); $\text{aq} = \text{vodna faza}$, $\text{org} = \text{faza FS 13}$. Izračunali smo tudi konstante ekstrakcije za posamezne anione in ugotovili, da naraščajo v smeri: $\text{I}^- < \text{ClO}_4^- < \text{Br}_3^- < \text{MnO}_4^-$, pikrat $< \text{I}_3^- < \text{BPh}_4^-$.