

Short communication

Contribution to the Thermodynamics of Sc^{3+} , Y^{3+} , La^{3+} and Trivalent Lanthanide Cations in the Two-Phase Water-Nitrobenzene Extraction System

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Abstract

From the exchange extraction constants corresponding to the general equilibrium $\text{M}^{3+}(\text{aq}) + 3\text{H}^+(\text{nb}) \rightleftharpoons \text{M}^{3+}(\text{nb}) + 3\text{H}^+(\text{aq})$ occurring in the two-phase water–nitrobenzene system ($\text{M}^{3+} = \text{Sc}^{3+}, \text{Y}^{3+}, \text{La}^{3+}, \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}, \text{Dy}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}, \text{Tm}^{3+}, \text{Yb}^{3+}, \text{Lu}^{3+}$; aq = aqueous phase, nb = nitrobenzene phase), the individual extraction constants of 16 trivalent metal cations were calculated. It was found that these individual extraction constants in the mentioned two-phase system increase in the following cation order: $\text{Sc}^{3+} < \text{Yb}^{3+} < \text{Ho}^{3+} < \text{Er}^{3+} < \text{Tm}^{3+}, \text{Lu}^{3+} < \text{Y}^{3+}, \text{Dy}^{3+} < \text{Tb}^{3+} < \text{Gd}^{3+} < \text{Eu}^{3+} < \text{Sm}^{3+} < \text{Nd}^{3+} < \text{Pr}^{3+} < \text{La}^{3+}, \text{Ce}^{3+}$.

Keywords: Thermodynamics, individual extraction constants, water–nitrobenzene system, trivalent cations

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.^{1–23} Nitrobenzene is also suitable for accurate conductometric measurements.²⁴ A considerable attention has been paid to the study of charge transfer across the water/nitrobenzene interface.^{25–27}

The dicarbollylcobaltate anion and some of its halogen derivatives are very useful reagents for the extraction of various metal cations (especially Cs^+), and also – in the presence of polyoxyethylene compounds (e. g., crown ethers, PEG 400, Slovafof 909) – for the extraction of Sr^{2+} and Ba^{2+} from aqueous solutions into an organic polar phase, both under laboratory conditions for purely theoretical or analytical purposes,¹ and on the technological scale for the separation of some high-activity isotopes in the reprocessing of spent nuclear fuel and acidic radioactive waste.^{28–30}

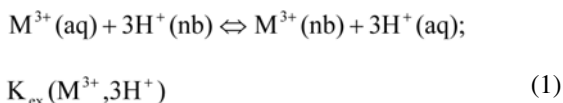
In order to estimate the individual extraction constants of some univalent ions in the water-nitrobenzene

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.³² 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 were evaluated in the water-nitrobenzene system.^{31,36,37} Recently, analogous thermodynamic data concerning some divalent metal cations and univalent organic cations have been reported.^{38,39} On the other hand, in the current communication, the individual extraction constants for a series of 16 trivalent metal cations in the considered two-phase system are presented.

2. Results and Discussion

Regarding the results of previous papers,^{1,31,36–40} the two-phase water–M(NO₃)₃ (M³⁺ = Sc³⁺, Y³⁺, La³⁺, Ce³⁺, Pr³⁺, Nd³⁺, Sm³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺, Tm³⁺, Yb³⁺, Lu³⁺)–nitrobenzene–hydrogen dicarbollycobaltate^{1–}–system can be described by the following general equilibrium



with the corresponding exchange extraction constant $K_{\text{ex}}(\text{M}^{3+}, 3\text{H}^+)$; aq and nb denote the presence of the species in the aqueous and nitrobenzene phases, respectively.

The changes of the standard Gibbs energies corresponding to the transfer of the mentioned trivalent metal cations M³⁺ and H⁺ from the aqueous into the nitrobenzene phase



are given by definitions

$$\Delta G_{\text{tr},\text{M}^{3+}}^{0,\text{aq}\rightarrow\text{nb}} = \mu_{\text{M}^{3+}}^{0,\text{nb}} - \mu_{\text{M}^{3+}}^{0,\text{aq}}, \quad (4)$$

$$\Delta G_{\text{tr},\text{H}^+}^{0,\text{aq}\rightarrow\text{nb}} = \mu_{\text{H}^+}^{0,\text{nb}} - \mu_{\text{H}^+}^{0,\text{aq}}. \quad (5)$$

Here $\mu^0 - s$ are the standard chemical potentials of the ions M³⁺ and H⁺ in the two phases concerned.

The individual extraction constants $K_{\text{M}^{3+}}^i$ and $K_{\text{H}^+}^i$ for the considered cations M³⁺ and H⁺, respectively, in the water–nitrobenzene extraction system are defined by^{1,31,36–39}

$$\Delta G_{\text{tr},\text{M}^{3+}}^{0,\text{aq}\rightarrow\text{nb}} = -RT \ln K_{\text{M}^{3+}}^i, \quad (6)$$

$$\Delta G_{\text{tr},\text{H}^+}^{0,\text{aq}\rightarrow\text{nb}} = -RT \ln K_{\text{H}^+}^i. \quad (7)$$

Combination of the relation

$$\begin{aligned} -RT \ln K_{\text{ex}}(\text{M}^{3+}, 3\text{H}^+) &= \\ &= \mu_{\text{M}^{3+}}^{0,\text{nb}} + 3\mu_{\text{H}^+}^{0,\text{aq}} - \mu_{\text{M}^{3+}}^{0,\text{aq}} - 3\mu_{\text{H}^+}^{0,\text{nb}} \end{aligned} \quad (8)$$

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

$$\log K_{\text{ex}}(\text{M}^{3+}, 3\text{H}^+) = \log K_{\text{M}^{3+}}^i - 3\log K_{\text{H}^+}^i. \quad (9)$$

Furthermore, the standard Galvani potential difference of the trivalent metal cation M³⁺ between the nitrobenzene and aqueous phases (see, e. g., References 41

and 42), denoted by the symbol $\Delta_{\text{aq}}^{\text{nb}}\phi_{\text{M}^{3+}}$, is defined by the following relation

$$\Delta_{\text{aq}}^{\text{nb}}\phi_{\text{M}^{3+}}^0 = -\Delta G_{\text{tr},\text{M}^{3+}}^{0,\text{aq}\rightarrow\text{nb}}/3F. \quad (10)$$

Using the constants $\log K_{\text{ex}}(\text{M}^{3+}, 3\text{H}^+)^{40}$ given in Table 1, the value $\log K_{\text{H}^+}^i = -5.7$,³¹ and applying Eq. (9), we obtain the logarithms of the individual extraction constants of the trivalent metal cations M³⁺ (M³⁺ = Sc³⁺, Y³⁺, La³⁺, Ce³⁺, Pr³⁺, Nd³⁺, Sm³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺, Tm³⁺, Yb³⁺, Lu³⁺), $\log K_{\text{M}^{3+}}^i$, in the two-phase water–nitrobenzene system. These thermodynamic data are also summarized in Table 1. Besides this, by means of Eqs (6) and (10), one gets the thermodynamic data $\Delta G_{\text{tr},\text{M}^{3+}}^{0,\text{aq}\rightarrow\text{nb}}$ and $\Delta_{\text{aq}}^{\text{nb}}\phi_{\text{M}^{3+}}$, respectively, reviewed in Table 1 as well.

Table 1. Thermodynamic data for some trivalent metal cations M³⁺ in the two-phase water–nitrobenzene extraction system at 25 °C (for the meaning of the constants see text).

M ³⁺	log K _{ex} (M ³⁺ , 3H ⁺) ^a	log K _{M³⁺} ⁱ ^b	ΔG _{tr,M³⁺} ^{0, aq→nb} (kJ mol ⁻¹) ^c	Δ _{aq} ^{nb} φ _{M³⁺} ⁰ (V) ^d
Sc ³⁺	0.76	-16.34	93.29	-0.322 3
Y ³⁺	1.13	-15.97	91.17	-0.315 0
La ³⁺	1.42	-15.68	89.52	-0.309 3
Ce ³⁺	1.42	-15.68	89.52	-0.309 3
Pr ³⁺	1.40	-15.70	89.63	-0.309 7
Nd ³⁺	1.38	-15.72	89.75	-0.310 1
Sm ³⁺	1.27	-15.83	90.37	-0.312 2
Eu ³⁺	1.22	-15.88	90.66	-0.313 2
Gd ³⁺	1.21	-15.89	90.72	-0.313 4
Tb ³⁺	1.15	-15.95	91.06	-0.314 6
Dy ³⁺	1.13	-15.97	91.17	-0.315 0
Ho ³⁺	1.09	-16.01	91.40	-0.315 8
Er ³⁺	1.10	-16.00	91.35	-0.315 6
Tm ³⁺	1.12	-15.98	91.23	-0.315 2
Yb ³⁺	1.07	-16.03	91.52	-0.316 2
Lu ³⁺	1.12	-15.98	91.23	-0.315 2

^a Ref. 40; ^b Calculated from Eq. (9); ^c Calculated from Eq. (6);

^d Calculated from Eq. (10).

Finally, from the data given in Table 1 it follows that the individual extraction constants $K_{\text{M}^{3+}}^i$ in the water–nitrobenzene system increase in the series of Sc³⁺ < Yb³⁺ < Ho³⁺ < Er³⁺ < Tm³⁺, Lu³⁺ < Y³⁺, Dy³⁺ < Tb³⁺ < Gd³⁺ < Eu³⁺ < Sm³⁺ < Nd³⁺ < Pr³⁺ < La³⁺, Ce³⁺. At this point it should be noted that the mentioned constants express, in principle, the affinity of the considered cations M³⁺ for the nitrobenzene phase. It means that the $K_{\text{M}^{3+}}^i$ constants are a quantitative measure of the hydrophobicity, as well as the extractability of the ions M³⁺ from the aqueous into the nitrobenzene phase.

In conclusion, it is necessary to emphasize that the thermodynamic constants $\log K_{\text{M}^{3+}}^i$, $\Delta G_{\text{tr},\text{M}^{3+}}^{0,\text{aq}\rightarrow\text{nb}}$ and $\Delta_{\text{aq}}^{\text{nb}}\phi_{\text{M}^{3+}}$, listed in Table 1 can be employed, e. g., for the

studies of chemical equilibria in the two-phase water-nitrobenzene extraction system, analogously as in some previous papers.^{43–48}

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Povzetek

V dvofaznem sistemu voda-nitrobenzen (nb) smo za različne ione raziskovali ravnotežja porazdelitve, ki jih lahko ponazorimo z enačbo $M^{3+}(\text{aq}) + 3H^+(\text{nb}) \rightleftharpoons M^{3+}(\text{nb}) + 3H^+(\text{aq})$, $M^{3+} = \text{Sc}^{3+}, \text{Y}^{3+}, \text{La}^{3+}, \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}, \text{Dy}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}, \text{Tm}^{3+}, \text{Yb}^{3+}, \text{Lu}^{3+}$. Iz ravnotežnih konstant porazdelitve (konstant ekstrakcije) smo določili konstante ekstrakcije za posamezne ione ter ugotovili, da v proučevanem dvofaznem sistemu le te sledijo v zaporedju $\text{Sc}^{3+} < \text{Yb}^{3+} < \text{Ho}^{3+} < \text{Er}^{3+} < \text{Tm}^{3+}, \text{Lu}^{3+} < \text{Y}^{3+}, \text{Dy}^{3+} < \text{Tb}^{3+} < \text{Gd}^{3+} < \text{Eu}^{3+} < \text{Sm}^{3+} < \text{Nd}^{3+} < \text{Pr}^{3+} < \text{La}^{3+}, \text{Ce}^{3+}$.