Spectrophotometric Method for the Determination
of Tetrabutylammonium ion[*]

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Abstract

The extraction-spectrophotometric determination of a trace amount of tetrabutylammonium ion (tba^+) with bis (maleonitriledithiolato) nickelate (II), $Ni(mnt)_2^{2-}$ is described. $Ni(mnt)_2^{2-}$ formed ion-pair with tba^+ and this was quantitatively extracted into chloroform ($Kex = [tba_2^+, Ni(mnt)_2^{2-}]_{(0)}/$ $[Ni(mnt)_2^{2-}][tba^+]^2 = 10^{13.89}$). The molar absorptivity of the ion-pair in chloroform was found to be 2.76×10^4 at 318 nm. Beer's law was confirmed in the range of $0 \sim 0.6\ \mu mol\ tba^+/10\ cm^3\ CHCl_3$. Moderate amounts of most of the anions did not interfere with the determination. This method was also successfully applied to estimation of the ion-pair extraction constant.

Introduction

Several authors[1] have reported on the spectrophotometric determinations of cationic detergents. All of their investigations involve the addition of coloured organic anion to samples. The anion forms a solvent-soluble compound with the cation. The compound is solvent extracted, and the amount of cationic in the sample is determined by the spectrophotometric method.

During the course of ion-pair extraction studies on anionic metal chelates species, it was found that maleonitriledithiolato (mnt, L^{2-}) chelates of some transition metal ions form very stable ion-pairs with tetrahexylammonium ion (Q^+) and can be quantitatively extracted into chloroform. The values of the extraction constants (Kex) were $10^{22} \sim 10^{23}$ for nickel (II), zinc (II), cadmium (II), mercury (II) and palladium (II)[2];

$$ML_2^{2-} + 2Q^+ \underset{}{\overset{Kex}{\rightleftharpoons}} Q_2[ML_2]_{(0)} \qquad (1)$$
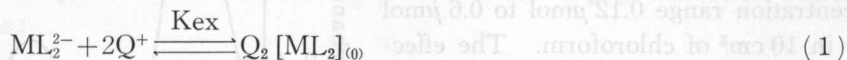
where the suffix (0) indicates the species in chloroform. Among these, nickel chelates (NiL_2^{2-}) is especially stable[***] and inert[3]. It has a well defined absorption band at 318 nm with molar absorptivity (ε) of 2.76×10^4. These data suggest that it should be worthwhile to study an application of the complex to the extraction-spectrophotometric determination of trace amounts of onium cations, especially, that of the tetrabutylammonium ion, which forms relatively unstable ion-pairs with the usual counter anions. Determination of the tba^+ ion is espe-

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cially important in connection with recent studies of the reversed phase ion-pair partition chromatography of anionic species in aqueous solutions[4].

In this paper, a highly selective and sensitive method for determining the tba⁺ ion is described and also its application to equilibrium studies.

Experimental

Bis (maleonitriledithiolato) nickelate (II) solution ($[NiL_2^{2-}] = 7.5 \times 10^{-4}$ mol dm⁻³) was prepared by mixing 2 cm³ of aqueous nickel (II) chloride solution ($[Ni^{2+}] = 3.75 \times 10^{-2}$ mol dm⁻³) and 0.0279 g of Na₂L, synthesized by Davison and Holm's method[5], and by diluting to 100 cm³ with distilled water. The solution was stable for about one week. Tetrabutylammonium ion solution ($[tba^+] = 1.2 \times 10^{-3}$ mol dm⁻³) was prepared by dissolving 0.0387 g of its bromide salt (Tokyo kasei Co. Ltd., Japan) in water and diluting to 100 cm³.

Recommended procedure: Take an aliquot, containing $0.12 \sim 0.6$ mol of tba⁺, to a 100 cm³ separatory funnel, add 5 cm³ of the NiL_2^{2-} solution, 2.5 cm³ of 0.1 mol dm⁻³ acetate buffer solution (pH 5.0), and dilute to 25 cm³ with water. Extract with 10.0 cm³ of chloroform by shaking for 5 minutes. After phase separation, measure the absorbance at 318 nm against a reagent blank.

Results and Discussion

Absorption spectra and the extraction behavior of NiL_2^{2-}: The ion-pair $(tba)_2[NiL_2]$ was quantitatively extracted into chloroform in the pH range of 4.5 to 12 by shaking for 4 minutes. The extracted ion-pair has absorption maxima at 271 nm ($\varepsilon = 4.33 \times 10^4$) and 318 nm ($\varepsilon = 2.76 \times 10^4$), and its absorbance was stable for at least 6 hours at room temperature.

Calibration curve: A straight line calibration curve was obtained over the concentration range 0.12 μmol to 0.6 μmol tba⁺ in 10 cm³ of chloroform. The effective molar absorptivity (ε') obtained from the calibration curve was 1.42×10^4 at 318 nm. The coefficient of variation was 0.66%, from 12 repeated observations with a sample solution containing 1.92×10^{-5} mol dm⁻³ of tba⁺ ion. For determination of the more dilute tba⁺ solution, larger volume ratios of aqueous phase/ organic phase, for example, 100 cm³/10 cm³ and 500 cm³/10 cm³ were successfully applied with ε' values of 1.46×10^4 and 1.80×10^4 cm² mol⁻¹, respectively. The appar-
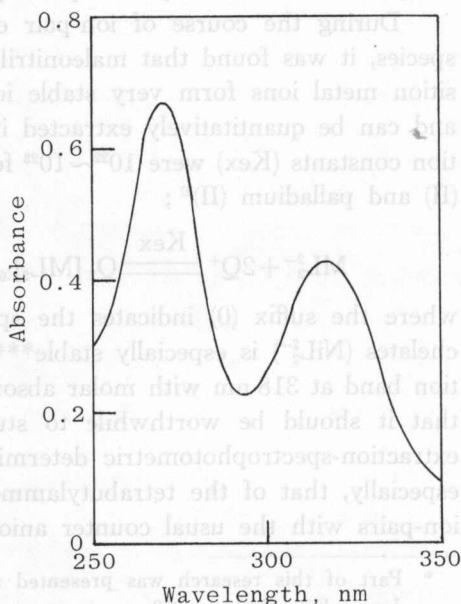
Fig. 1. Absorption spectra of (tba)₂ [NiL₂] complex in CHCl₃.
$[(tba)_2(NiL_2)] = 1.5 \times 10^{-5}$ mol dm⁻³.

ent increase in the ε' value is due to the dissolution of chloroform into the aqueous phase.

Extraction behavior of other onium cations: Onium cations (Q') of a larger size than tba$^+$ ions form more stable ion-pairs with NiL_2^{2-} complexes. However, their extraction behavior was quite unusual. For example, tetradecyldimethyl-benzylammonium chloride, cetyltrimethylammonium bromide and cetylpyridinium bromide did not give linear calibration curves. Furthermore, from the solutions containing excess amounts of cations against NiL_2^{2-}, for example, $[NiL_2^{2-}]_{Total}=1.2\times10^{-5}$ mol dm^{-3} and $[Q^+]_{Total}=6.0\times10^{-4}$ mol dm^{-3}, almost no ion-pairs were extracted into chloroform. Another finding was that by addition of sodium perchlorate or sodium iodine, in amounts of $[ClO_4^-]_{Total}$ or $[I^-]_{Total}=2\times10^{-2}$ mol dm^{-3}, to the solutions described just above, ion-pairs of $Q_2'[NiL_2]$ could be quantitatively extracted. Thus, in the precence of such cations described above, the sum of $[Q'^+]$ and $[tba^+]$ can be determined by addition of perchlorate or iodine. The role of these anions can be considered to be their ability to control the activity of Q'^+ ions in the aqueous phase by forming ion-pairs of moderate stability. That is, the pair of $(Q' ClO_4)_{(0)}/ClO_4^-$ or $(Q' I)_{(0)}/I^-$ can act as a suitable buffer for Q'^+ ions in each system.

These data strongly suggest that NiL_2^{2-} has an unusually large affinity towards the onium cations, so that it forms not only the neutral ion-pair $Q_2'[NiL_2]$ but also the cationic ion-pair $(Q_2'[NiL_2]Q_n')^{n+}$. It is extremely difficult to extract the latter into chloroform. The extraction behavior of tba$^+$ ions was quite normal under all conditions studied.

Effect of anions: Moderate amounts of most of the anions did not interfere with the determination. That is, the tolerance limits of anions were 10^{-1} mol dm^{-3} for Cl$^-$, Br$^-$, I$^-$, NO$_3^-$, HPO$_4^{2-}$ and SO$_4^{2-}$, 4×10^{-2} mol dm^{-3} for SCN$^-$, 2×10^{-2} mol dm^{-3} for ClO$_4^-$ and 10^{-2} mol dm^{-3} for C$_2$O$_4^{2-}$ and edta, respectively, for a determination of 1.92×10^{-5} mol dm^{-3} of tba$^+$.

Application: The proposed method was successfully applied to the estimation of ion-pair extraction constants (Kex). The ion-pair extraction reaction is given as;

$$n\ tba^+ + X^{n-} \underset{}{\overset{Kex}{\rightleftharpoons}} (tba)_n X_{(0)} \tag{2}$$
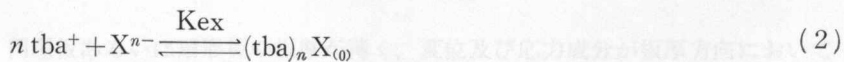
where

$$Kex = \frac{[(tba)_n X]_{(0)}}{[tba^+]^n [X^{n-}]} \tag{3}$$

and X^{n-} indicates simple anions or anionic metal chelates. The values of Kex of tba$^+$ ion-pairs with Br$^-$, I$^-$ and ClO$_4^-$ were determined by measuring the equilibrium concentration of tba$^+$ in aqueous solutions by the recommended procedure. The constant of the $(tba)_2[NiL_2]$ ion-pair was estimated from the two phase ion exchange reaction (eq. (4)) by measuring the concentration of $(tba)_2[NiL_2]_{(0)}$, spectrophotometrically.

$$(tba)_2\,[NiL_2]_{(0)} + 2\,ClO_4^- \overset{K}{\rightleftharpoons} 2\,(tba)\,[ClO_4]_{(0)} + NiL_2^{2-} \qquad (4)$$
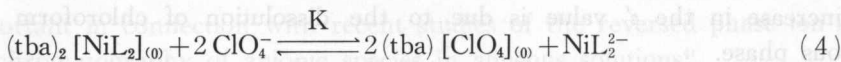
where

$$K = \left\{Kex\left((tba)\,(ClO_4)\right)\right\}^2 / Kex\left((tba)_2\,(NiL_2)\right)$$

The values of Kex obtained are summarized in Table I. They are in fair agreement with those reported by Gustavii[6]. That of the NiL_2^{2-} ion is very large compared with the other common anions, even if the difference in the charge number is taken into consideration. Based on these data, the selectivity of the proposed method against the common anions can be easily understood.

Table I. Extraction constants of tba$^+$ ion-pairs in CHCl$_3$

Anion	log Kex	I (Na$_2$SO$_4$)
Br$^-$	1.28	0.3
I$^-$	2.96	0.3
ClO$_4^-$	3.51	0.3
NiL$_2^{2-}$	13.89	0.5

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