Solvent Extraction of Sodium Picrate with 15-Crown-5 into Carbon Tetrachloride. The Determination of the Dimer-formation Constant of a Crown Ether-Univalent Metal Salt 1 : 1 : 1 Complex

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Abstract. The theory is derived to determine the dimer-formation constant, K_2, of a crown ether-metal salt 1 : 1 : 1 complex in organic solvents of low dielectric constant by solvent extraction. The theoretical predictions are verified experimentally by extraction of sodium picrate (NaA) with 15-crown-5 (15C5) into carbon tetrachloride. All the experiments were conducted at 25°C. The log K_2 value of the Na(15C5)A complex in carbon tetrachloride has been determined to be 4.05 ± 0.11. Moreover, the partition constant of the complex is calculated.

Key words: Solvent extraction, determination of dimer-formation constant, 15-crown-5, sodium picrate, carbon tetrachloride.

1. Introduction

It is well-known that 15-crown-5 (15C5) forms a 1 : 1 : 1 complex with sodium picrate (NaA) in organic solvents of low dielectric constant [1]. But no study has been reported on the dimer formation of Na(15C5)A in the solvents.

This paper presents the theory to determine the dimer-formation constant, K_2, of a crown ether-metal salt 1 : 1 : 1 complex in organic solvents of low dielectric constant by solvent extraction. The theoretical predictions are verified experimentally by extraction of NaA with 15C5 into carbon tetrachloride. The log K_2 value of Na(15C5)A in carbon tetrachloride has been determined to be 4.05 ± 0.11 at 25°C.

2. Experimental

2.1. MATERIALS

15-Crown-5 (Nisso Co., Ltd.) was purified by distillation under vacuum (bp 167–168°C, 19 mmHg (1 mmHg ≈ 133.322 Pa)). Picric acid and sodium hydroxide

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were of analytical grade. Analytical grade carbon tetrachloride, which was purified by distillation, was washed four times with deionized water prior to use.

2.2. EXTRACTION OF SODIUM PICRATE WITH 15C5

A 10–13 mL portion of an organic solution of 15C5 ($2.0 \times 10^{-5} - 1.3 \times 10^{-2}$ M; 1 M = 1 mol dm^{-3}) and an equal volume of an aqueous solution of NaOH (($2.0 - 4.2) \times 10^{-2}$ M) and picric acid (($3.2 - 4.7) \times 10^{-3}$ M) in a stoppered glass tube were shaken in a thermostated water bath at $25 \pm 0.2°$C for 3 h and centrifuged. Extractions were conducted at pH 10.9–11.8. The picrate in the organic phase was back extracted into 0.01 M NaOH aqueous solution. The picrate concentration was determined spectrophotometrically at 356 nm ($\varepsilon = 1.44 \times 10^4$ cm^{-1} M^{-1}).

3. Theory, Results, and Discussion

In an equilibrium between an aqueous phase of sodium picrate (NaA) and an organic phase of 15C5 (L), the equilibrium constants are defined as

$$K_{ex} = [NaLA]_o/[Na^+][L]_o[A^-], \tag{1}$$

$$K_{D,L} = [L]_o/[L] \quad (K_{D,L} = 6.2 \times 10^{-2} \text{ at } 25°C \text{ [2]}), \tag{2}$$

$$K_{ML} = [NaL^+]/[Na^+][L] \quad (K_{ML} = 5.0 \text{ at } 25°C \text{ [3]}), \tag{3}$$

$$K_{MLA} = [NaLA]/[NaL^+][A^-], \tag{4}$$

$$K_{D,MLA} = [NaLA]_o/[NaLA], \tag{5}$$

$$K_{MA} = [NaA]/[Na^+][A^-] \quad (K_{MA} = 24 \text{ at } 25°C \text{ [4]}), \tag{6}$$

$$K_2 = [(NaLA)_2]_o/[NaLA]_o^2, \tag{7}$$

where the subscript 'o' and the lack of subscript denote the organic and the aqueous phase, respectively. From the low dielectric constant (ε_r) of carbon tetrachloride, it has been assumed that the dissociation of NaLA into NaL$^+$ and A^- in the organic phase is negligible.

Under very basic conditions (pH > 11), mass balances are as follows;

$$[Na]_t = [Na^+] + [NaL^+] + [NaA] + [NaLA] + [NaLA]_o + 2[(NaLA)_2]_o, \tag{8}$$

$$[L]_t = [L] + [L]_o + [NaL^+] + [NaLA] + [NaLA]_o + 2[(NaLA)_2]_o, \tag{9}$$

$$[HA]_t = [A^-] + [NaA] + [NaLA] + [NaLA]_o + 2[(NaLA)_2]_o, \tag{10}$$

the subscript 't' designating the total concentration. Equations (11), (12) and (13) are derived from Equations (8), (9), and (10);

$$a([L]_o[A^-])^2[Na^+]^2 + \{1 + K_{MA}[A^-] + (b + c[A^-])[L]_o\}[Na^+]$$

$$-[Na]_t = 0, \tag{11}$$

$$a([Na^+][A^-])^2[L]_o^2 + \{d + (b + c[A^-])[Na^+]\}[L]_o$$

$$-[L]_t = 0, \tag{12}$$

$$a([Na^+][L]_o)^2[A^-]^2 + \{1 + (K_{MA} + c[L]_o)[Na^+]\}[A^-]$$

$$-[HA]_t = 0, \tag{13}$$

where $a = 2K_2K_{ex}^2$, $b = K_{D,L}^{-1}K_{ML}$, $c = K_{D,L}^{-1}K_{ML}K_{MLA} + K_{ex}$, and $d = 1 + K_{D,L}^{-1}$.

The distribution ratio (D) of sodium is represented by

$$D_M = \{[NaLA]_o + 2[(NaLA)_2]_o\}$$

$$/([Na^+] + [NaA] + [NaL^+] + [NaLA]). \tag{14}$$

When $[Na^+] \gg [NaA] + [NaL^+] + [NaLA]$ and $[NaLA]_o \gg 2[(NaLA)_2]_o$, Equation (14) is transformed into

$$D_M = K_{ex}[L]_o[A^-]. \tag{15}$$

As a first approximation, the $[L]_o$ and $[A^-]$ values of Equation (15) are calculated from Equations (16) and (17), respectively:

$$[L]_o = ([L]_t - [NaLA]_o)/(d + b[Na^+]), \tag{16}$$

$$[A^-] = [HA]_t - [NaLA]_o, \tag{17}$$

where $[Na^+]$ (first approximate value) = $[Na]_t - [NaLA]_o$. Plots of $\log(D_M/[A^-])$ vs. $\log[L]_o$ always give a straight line with a slope of 1 (Figure 1). This indicates that the 15C5 forms a 1 : 1 complex with the Na^+ ion under these experimental conditions [5] and that the above assumptions are valid. The actual $[Na^+]$, $[L]_o$, and $[A^-]$ values are calculated from Equations (18), (19), and (20), respectively, by a successive approximation method;

$$[Na^+] = ([Na]_t - [NaLA]_o)/\{1 + b[L]_o + (K_{MA} + e[L]_o)[A^-]\}, \tag{18}$$

$$[L]_o = ([L]_t - [NaLA]_o)/\{d + (b + e[A^-])[Na^+]\}, \tag{19}$$

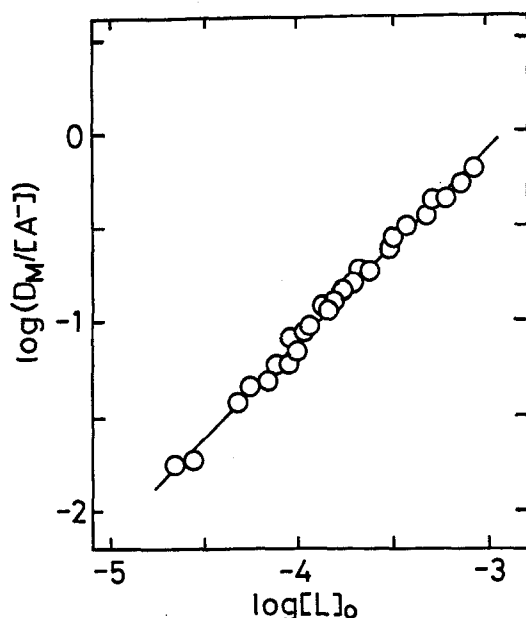$$[A^-] = ([HA]_t - [NaLA]_o)/\{1 + (K_{MA} + e[L]_o)[Na^+]\}, \tag{20}$$

Fig. 1.   log $(D_M/[A^-])$ vs. log $[L]_o$ plots for the 15C5/sodium picrate/CCl$_4$ system.

where $e = K_{D,L}^{-1} K_{ML} K_{MLA}$ and $K_{MLA} = 1.2_3 \times 10^4$ [2]. The actual log K_{ex} value is determined to be 4.05 ± 0.11. From the equation $K_{ex} = K_{D,L}^{-1} K_{ML} K_{MLA} K_{D,MLA}$, the log $K_{D,MLA}$ value is calculated to be -1.94.

When [Na$^+$] $\gg$ [NaA] + [NaL$^+$] + [NaLA] and $2[(NaLA)_2]_o \gg [NaLA]_o$, Equation (14) is transformed into

$$D_M = 2K_2 K_{ex}^2 [Na^+] [L]_o^2 [A^-]^2 . \tag{21}$$

As a first approximation, the [Na$^+$], $[A^-]$, and $[L]_o$ values of Equation (21) are calculated from Equations (22), (23), and (24), respectively;

$$[Na^+] = [Na]_t - 2[(NaLA)_2]_o , \tag{22}$$

$$e[Na^+] (1 + K_{MA}[Na^+]) [A^-]^2$$

$$+\{(d + b[Na^+]) (1 + K_{MA}[Na^+]) + e[Na^+] ([L]_t - [HA]_t)\} [A^-]$$

$$-\{[HA]_t - 2[(NaLA)_2]_o\} (d + b[Na^+]) = 0 \tag{23}$$

$$[L]_o = \{[L]_t - 2[(NaLA)_2]_o\}/\{d + (b + e[A^-]) [Na^+]\} \tag{24}$$

Plots of log $(D_M/[Na^+] [A^-]^2)$ vs. log $[L]_o$ always show a straight line with a slope of 2 (Figure 2). This indicates that the dimer $(NaLA)_2$ is formed
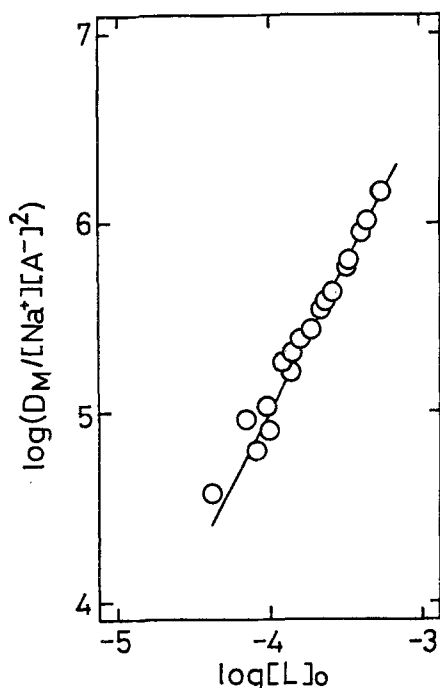
Fig. 2.   log $(D_M/[Na^+][A^-]^2)$ vs. log $[L]_o$ plots for the 15C5/sodium picrate/CCl$_4$ system.

in the carbon tetrachloride under these experimental conditions [6] and that the above assumptions are valid. The first approximate K_2 value is calculated from Equation (1), (25), and (7),

$$[Na]_{o,t} = [NaLA]_o + 2[(NaLA)_2]_o , \tag{25}$$

where $[Na]_{o,t}$ refers to the total concentration of sodium in the organic phase. The actual log K_2 value is calculated to be 4.05 ± 0.11 from Equations (1), (7), (11), (12), (13), and (25) by a successive approximation method.

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5. $[L]_t$ $3.8 \times 10^{-4} - 4.0 \times 10^{-3}$ M; $[Na]_t$ 4.0×10^{-2} M; $[HA]_t$ $(4.0 - 4.6) \times 10^{-3}$ M.
6. $[L]_t$ $4.1 \times 10^{-3} - 1.4 \times 10^{-2}$ M; $[Na]_t$ 4.0×10^{-2} M; $[HA]_t$ $(4.0 - 4.6) \times 10^{-3}$ M.