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Determination of the Stability Constants of Crown Ether Complexes with Protonated Amines by Solvent Extraction

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Synopsis. Stability constants of crown ether complexes with protonated primary amines were determined by the solvent extraction method. Stability constants between protonated amines(AH^+) and 18-crown-6(L), log K_{AHL}, were found to be 0.4, 0.15, 0.1, −0.05, and −0.1 for protonated methylamine, ethylamine, propylamine, butylamine, and *iso*-propylamine at 25.0 °C, respectively.

Accurate determination of stability constants of small values are more difficult than those of higher values.[1] Here, we propose a method for the determination of stability constants. The method has been successfully applied to determing especially small values of stability constants between 18-crown-6 and protonated primary amine. Crown ether in an organic phase is extracted by complexation with primary amine hydrochloride (or sodium chloride etc.) in the aqueous phase, which can not be extracted into the organic phase. So, stability constants of crown ether with protonated primary amines can be determined by the analysis of the extraction equilibria.

In this paper, we describe the method for the determination of stability constant by back extraction, and discuss the results with data obtained in other literature.[3—5]

Theory

The following equations may be written for the extraction system composed of crown ether, water, organic solvent, and salts, such as potassium chloride, sodium chloride and ammonium chloride, which can not be extracted into the organic phase at the limited pH range.

$$L \rightleftharpoons L_o \qquad K_{d,L} = [L]_o/[L] \tag{1}$$

$$M^+ + L \rightleftharpoons ML^+ \quad K_{ML^+} = [ML^+]/([M^+][L]) \tag{2}$$

$$C_{M^+} = [M^+] + [ML^+] \tag{3}$$

$$C_L = [L] + (V_o/V)[L]_o + [ML^+] \tag{4}$$

where subscript "o" denotes the organic phase, $K_{d,L}$, K_{ML^+}, C_{M^+}, C_L, V_o, and V show the distribution coefficient of the crown ether, stability constant of crown ether complex (ML^+) in the aqueous phase, total concentration of M^+ and L, volume of organic and aqueous phase, respectively. In the case of protonated amines, the symbol AH^+ is used instead of M^+. Eq. 5 can be obtained when C_{M^+} is much larger than C_L.

$$\log C_L = \log [L]_o + \log (V_o/V + K_{d,L}^{-1}(1+K_{ML^+}C_{M^+})) \tag{5}$$

Log C_L against log $[L]_o$ plot should show a straight line of slope 1. Therefore, K_{ML^+} can be calculated from the value at the intercept of the log C_L axis. Thus, the stability constants can be determined under constant ionic strength by the method.

Experimental

A typical procedure was as follows. 25 ml of aqueous solution containing 0.5 mol dm^{-3} primary amine hydrochloride and 18-crown-6(5×10^{-5}—2×10^{-3} mol dm^{-3}) was mixed with 10 ml of 1,2-dichloroethane and shaken for 1 day in a thermostated bath at 25.0 °C. The concentration of alkali metal chloride or ammonium chloride were the same as in the above case except for the potassium ion, which was 0.1 mol dm^{-3}. The concentration of the 18-crown-6 in the organic phase was measured spectrophotometrically after extraction with potassium picrate.[2] The adjustment of the pH was made with dilute hydrochloric acid and lithium hydroxide solution. No other reagents and buffers were used during the experimental runs.

Results and Discussion

In order to check the validity of the Eq. 5, 18-crown-6, water, 1,2-dichloroethane and metal salt (KCl, NaCl, or NH_4Cl) system was chosen. It was found that cations (K^+, Na^+, NH_4^+) and anion(Cl^-) are not extracted into the 1,2-dichloroethane phase at least over the pH range of 3.5—6.0.

Distribution coefficient of 18-crown-6($K_{d,L}$) was determined to be 1.12 at 25.0 °C.

Plots of C_L against log $[L]_o$ are shown in Fig. 1. Linear relationships were obtained as expected from Eq. 5. The calculated values of log K_{ML^+} are found to be 2.08, 0.63, and 0.97 for potassium, sodium, and ammonium complexes with 18-crown-6 under the ionic strength 0.5 (0.1 in the case of KCl). These values agreed very closely with those in the literature,[3,4] in which 2.03, 0.8, and 1.23 were reported for the values of the respective complexes.

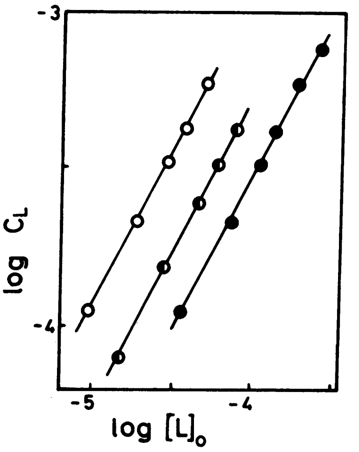

Fig. 1. log C_L *vs.* log $[L]_o$ plots in the presence of 0.1 mol dm^{-3} KCl(○), 0.5 mol dm^{-3} NH_4Cl(◐), and NaCl(●).

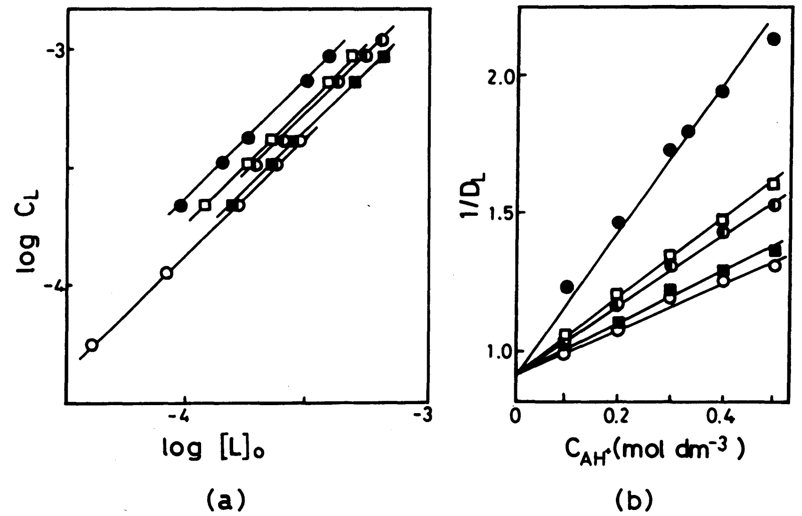

Fig. 2. log C_L *vs.* log $[L]_o$ and $1/D_L$ *vs.* C_{AH^+} plots for protonated primary amines.
(a) $C_{AH^+}=0.5$ mol dm^{-3}, (b) $C_L=2.4\times10^{-4}$ mol dm^{-3}.
●: methylamine, □: ethylamine, ◐: propylamine, ■: buthylamine, ○: isopropylamine

Methods for the determination of accurate stability constants having small values are very limited and such small values of stability constants sometimes contain errors.

Our method proposed here would, especially, be valid for the determination of stability constants of small values, because the concentration of crown ether in the organic phase can be determined accurately. The accuracy increases when the crown ether distributes more equally between both phases. The determination of stability constants of 18-crown-6 complexes with several protonated amines were then attempted. The experimental conditions are the same as those described before. Plots of log C_L against log $[L]_o$ are shown in Fig. 2a for protonated primary amines. Each plot has a straight line with a slope of 1. The result shows that the extraction system can be expressed by Eqs. 1—4.'

The log K_{AHL} values obtained are 0.4, 0.15, 0.1, −0.05, and −0.1 for protonated methylamine, ethylamine, propylamine, butylamine, and isopropylamine at a constant ionic strength (0.5).

The values obtained by Larson *et al.*[5] for protonated amine–18-crown-6 are obviously higher than the data obtained by us. Their values obtained by the glass electrode measurement may contain some errors. They determined the stability constants by the measurement of the pH difference before and after adding 18-crown-6 to the system containing an amine and the corresponding amine hydrochloride. For example, the pH difference for the trimethylamine system is only 0.074 pH units according to our calculation by using the stability constant 5.5 (log $K_{AHL}=0.74$) given by them. They reported that the uncertainties are equivalent to an error in pH of about ±0.02 pH units. This means that the stability constants especially for weak complexes such as 18-crown-6-protonated trimethylamine, contains about ±30% errors.

Another approach for the determination of stability constants is as follows. Equation 6 can be obtained by using Eqs. 1—4 and distribution ratio of crown ether, ($D_L=[L]_o/([L]+[AHL^+])$).

$$\frac{1}{D_L}=\frac{1}{K_{d,L}}+\frac{K_{AHL}C_{AH^+}}{K_{d,L}} \tag{6}$$

Plot of $1/D_L$ against C_{AH^+} should show a straight line and the intercept at $C_{AH^+}=0$ should show the value of $K_{d,L}^{-1}(=0.89)$. Hence, K_{AHL} can be also calculated from the slope analysis. The plot of $1/D_L$ *vs.* C_{AH^+} for protonated primary amines at fixed C_L (2.4×10^{-4} mol dm^{-3}) is shown in Fig. 2b. The extrapolation to $C_{AH^+}=0$ shows $1/K_{d,L}$, then the extraction mechanism could be expressed by Eqs. 1—4. Log K_{AHL} values obtained from this method agreed well with those obtained (deviations are within ±0.03) by the method under constant ionic strength.

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