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Pressure Effects on the Complexation of *t*-Butylammonium Perchlorate by Crown Ether

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Synopsis. The effects of hydrostatic pressure on the complexation of *t*-butylammonium perchlorate by crown ether in methanol were studied by means of a high-pressure high-resolution NMR method at 33.5 °C. The complexation was shown to be promoted upon pressurization.

Among the crown ethers with an aryl-sub-unit, xylyl crown ethers have been studied in great detail.[1)] Recently, a ^{1}H NMR method has been developed to determine the association constants of complexes of these crown ethers and alkylammonium salts. Among them, the association constants of the so-called "1,3-xylyl-18-crown-5" (2,5,8,11,14-pentaoxa[15]metacyclophane) (**1**) and *t*-butylammonium perchlorate (**2**) were shown to be capable of being calculated directly from the chemical-shift difference of the *t*-butyl protons of the salt in complex **3** and in the free form **2**.[2)]

$$\underset{\mathbf{1}}{\text{1,3-xylyl-18-crown-5}} + \underset{\mathbf{2}}{(\mathrm{CH_3})_3\mathrm{CNH_3ClO_4}} \overset{K_\mathrm{m}}{\rightleftharpoons} \underset{\mathbf{3}}{\text{1,3-xylyl-18-crown-5}\cdot(\mathrm{CH_3})_3\mathrm{CNH_3ClO_4}} \qquad (1)$$

Because of a rapid exchange (on the NMR time scale) the observed chemical shift of the *t*-butyl protons (δ_obsd) is the weighted average of the chemical shift of *t*-butyl protons in free *t*-BuNH$_3$ClO$_4$ (δ_f) and that in complex **3** (δ_c):

$$\delta_\mathrm{obsd} = (1/F_0)\left\{(F_0 - X_\mathrm{c})\,\delta_\mathrm{f} + X_\mathrm{c}\delta_\mathrm{c}\right\}, \qquad (2)$$

where

$$\begin{aligned} X_\mathrm{c} &= \text{the equilibrium concentration of } \mathbf{3} \\ &= (1/2K_\mathrm{m})\Big[1 + K_\mathrm{m}(F_0 + E_0) \\ &\quad - \left\{1 + 2K_\mathrm{m}(F_0 + E_0) + K_\mathrm{m}{}^2(F_0 - E_0)^2\right\}^{1/2}\Big], \end{aligned}$$

$$E_0 = \text{the initial concentration of } \mathbf{1},$$

and

$$F_0 = \text{the initial concentration of } \mathbf{2}.$$

This study was aimed at investigating the effect of the hydrostatic pressure on the complexation equilibrium (1) by means of high-pressure high-resolution NMR spectroscopy.

Experimental

1,3-Xylyl-18-crown-5 and *t*-butylammonium perchlorate were prepared according to the procedures of Reinhaudt et al.[3)] and Kyba et al.,[4)] respectively. High-pressure NMR measurements[5)] were conducted on a 100-MHz continuous-wave spectrometer at a sample temperature of 33.5 °C. The temperature was calibrated by measuring the methanol chemical shift[6)] under the same conditions as those for the high-pressure experiment. A high-pressure glass cell (o.d./i.d. = 3.5 mm/1 mm) having a fine capillary tail (o.d. = 0.3—0.5 mm, ca. 300 mm length) was used by connecting the tail to a high-pressure system. The field control was effected by means of an internal lock to the methanol methyl protons. The chemical shifts from internal TMS were calibrated using a frequency counter, and were reproducible within ±0.2 Hz.

For a series of samples, the salt concentration (F_0) was held constant at 0.129 mol kg^{-1}, while the crown ether concentration (E_0) was varied from 0.0 to 4.3 mol kg^{-1}.[7)] On each of these solutions, the chemical shift of the *t*-butyl protons (δ_obsd) was measured at different pressures up to 150 MPa. The δ_f at each pressure was obtained by measuring the chemical shift for the solution with $E_0 = 0$. The association constant (K_m) was calculated by minimizing the function

$$F(X_\mathrm{c}, \delta_\mathrm{c}) = \sum_i \left[\delta_{\mathrm{obsd},i} - \left\{(F_0 - X_\mathrm{c})\,\delta_\mathrm{f} + X_{\mathrm{c},i}\delta_\mathrm{c}\right\}F_0{}^{-1}\right]^2 \qquad (3)$$

for X_c and δ_c using an iterative method.

Results and Discussion

The *t*-butyl protons of free *t*-BuNH$_3$ClO$_4$ have a chemical shift (δ_f) of 136.1 Hz, ($\nu_0 = 100$ MHz) in CH$_3$OH at 33.5 °C and at ordinary pressure. On the other hand, the chemical shift in complex **3** (δ_c) is shown to be at a considerably high field (ca. 50 Hz, calculated value, as is explained later). This upfield shift has been attributed to the fact that in the complex the *t*-butyl protons are located in a shielding zone of the aromatic ring of the crown ether, as shown in a schematic representation (Fig. 1).[9)]

The observed chemical shifts (in Hz) of the *t*-butyl protons (δ_obsd) at different crown ether : salt ratios of

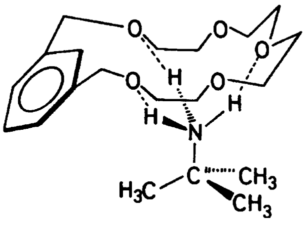

Fig. 1. Schematic representation of the structure of complex **3**.

Table 1. Association Constants of Complex **3** at Different Pressures

P/MPa	K_m/kg mol^{-1}	δ_f/Hz	δ_c/Hz
0.1	3.51	136.1	86.3
50	3.85	135.1	85.2
100	4.04	134.2	83.3
150	4.54	133.7	82.8

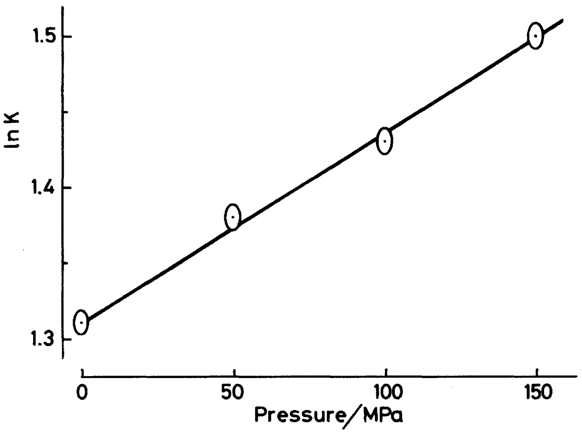

Fig. 2. Pressure effect on the association constant.

0.00, 1.04, 3.03, and 4.23 were, for example, 136.1, 123.3, 109.7, and 104.6 at 0.1 MPa, respectively, and 133.7, 118.7, 104.0, and 98.8 at 150 MPa, respectively. At higher pressures, as well as upon the addition of more crown ether, a larger high-field shift was observed, that can be attributed in both cases to increased association.

The calculated association constant (K_m) and calculated chemical shift of the *t*-butyl protons in the complex (δ_c) are presented in the Table 1. Upon pressurization, a slightly larger high field shift of δ_c, as compared with that of δ_f, was noted. This may be attributed to a slightly closer proximity of the *t*-butyl group to the benzene ring at high pressure.

In Fig. 2, the pressure dependence of $\ln K_m$ is depicted by open circles. Approximating a linear relation between $\ln K_m$ and P, the volume change upon complexation (ΔV) is calculated to be -4.2 cm^3 mol^{-1}. This indicates that the complexation of *t*-butylammonium perchlorate with the crown ether accompanies a decrease in the volume.

It should be pointed out that the presently observed result is opposed to that obtained for the complexation of crown ether with K^+ in an aqueous solution, where $\Delta V = +12$ cm^3 mol^{-1} was observed. This large positive ΔV has been explained in terms of a diminution of hydration (and hence a decrease in the electrostriction) to the K^+ ion upon complexation.$^{10)}$

At present, we cannot give an unequivocal interpretation for our finding. However, a partial explanation may be sought in the fact that the electrostriction to the free *t*-butylammonium perchlorate is weak in methanol solvent, so that the positive contribution to the ΔV is very small, being overcome by a volume decrease due to an hydrogen bonding formation between ammonium hydrogens and crown ether oxygens (and an occupation of the crown ether cavity with the ammonium group) upon complexation.$^{11)}$

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9) This interpretation is supported by X-ray analysis of *p*-bromo-1,3-xylyl-18-crown-5·*t*-BuNH$_3$PF$_6$.$^{1)}$

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11) In general, a volume decrease of 3—4 cm^3 mol^{-1} is caused per one O···H hydrogen bonding.$^{12,13)}$

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