Solubilization of Potassium Ethylenediaminetetra-acetatocobaltate(III) by Crown Ethers in Aceto-nitrile

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Received October 11, 1984

Various inorganic salts have been found to be solubilized by macrocyclic polyether, a so-called crown ether, in organic solvents since Pedersen reported that for example $KMnO_4$ is solubilized by dicyclohexyl 18-crown-6 in benzene [1]. These findings led to development of new organic syntheses [2, 3]. It is, however, somewhat surprising to note that only a few systematic studies have been reported on the solubilizing ability of crown ethers in organic solvents. This might be because salts such as $KMnO_4$ and $K_2Cr_2O_7$ are sometimes quite reactive, even in solvents containing crown ether only, and salts such as potassium halides are colorless and thereby the solubility could not be precisely and readily determined.

On the other hand, it was found that potassium ethylenediaminetetraacetatocobaltate(III) dihydrate, K[Co(edta)]·$2H_2O$, is solubilized by crown ethers in a variety of organic solvents such as acetone, acetonitrile, ethanol and methanol. This salt, which is one of the most familiar cobalt(III) complex salts, is quite stable in a variety of solvents and has an intense d–d absorption band (ϵ = 324 at 536 nm in water) in the visible region. The solubility is thus readily determined by the spectrophotometric method. Therefore this complex salt could be used as a standard compound for estimating the solubilizing ability of crown ether in organic solvents*.

From this point of view, the solubility of this complex salt was measured in acetonitrile solutions of crown ethers: 18-crown-6 (18C6), 15-crown-5 (15C5), 12-crown-4 (12C4), dicyclohexyl 18-crown-6 (DC18C6), and dibenzo 18-crown-6 (DB18C6). This result was tentatively compared with that for $K_2Cr_2O_7$, which is obtained against decomposition**.

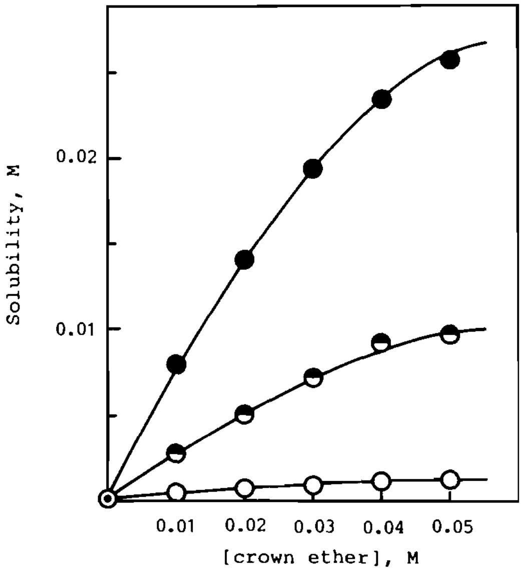

Fig. 1. Solubilities of K[Co(edta)]·$2H_2O$ in acetonitrile (⊙) and in acetonitrile solutions of 18-crown-6 (●), 15-crown-5 (◓), and 12-crown-4 (○).

The complex was prepared by the usual method [4]. Solubilities were determined by measuring the absorption at 536 nm. Solution equilibration was attained in a glass vessel kept at 25.0 °C. The acetonitrile solution to which the solid cobalt complex had been added, containing crown ether ranging in concentration from 0.01 to 0.05 M, was stirred magnetically for 1 to 2 days. An aliquot of the solution was pipetted out through a glass filter and completely dried at 40 °C with an evaporator. This was diluted appropriately in a volumetric flask with water for measuring the absorption.

Figure 1 shows the solubilities of K[Co(edta)]·$2H_2O$ in acetonitrile solutions containing crown ethers: 18C6, 15C5 and 12C4. This complex is sparingly soluble in pure acetonitrile (S = 0.00020 M), but is strikingly solubilized by these crown ethers, especially by 18C6. The solubility is enhanced by a factor of about 100 upon addition of 0.05 M 18C6. The order of increasing solubility ($S_{18C6} > S_{15C5} > S_{12C4}$) seems to be closely correlated to that of increasing stability constant between crown ether and potassium ion. Reported values of stability constants in methanol are as follows [5]: log

*Some other potassium salts of cobalt(III) complexes are tried to be solubilized in acetonitrile, but this is not successful for K[Co(ox)$_2$en], K[Cooxedda], and K[Co(ida)$_2$]: ox = oxalato, en = ethylenediamine, edda = ethylenediamine-diacetato, and ida = iminodiacetato.

**$K_2Cr_2O_7$ is decomposed in acetonitrile solution and a dark green precipitate appears in several hours. The measurement is completed within 3 h and the absorption is measured in acetonitrile solution and not in aqueous solution.

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TABLE I. Solubilities of $K_2Cr_2O_7$ in Acetonitrile Solutions of 0.05 M Crown Ethers: 12-crown-4, 15-crown-5, 18-crown-6, dicyclohexyl 18-crown-6, and of 0.03 M dibenzo-18-crown-6.

crown ether	0	12C4	15C5	18C6	DC18C6	DB18C6
solubility	0.005 M	0.009 M	0.017 M	0.025 M	0.026 M	0.016 M

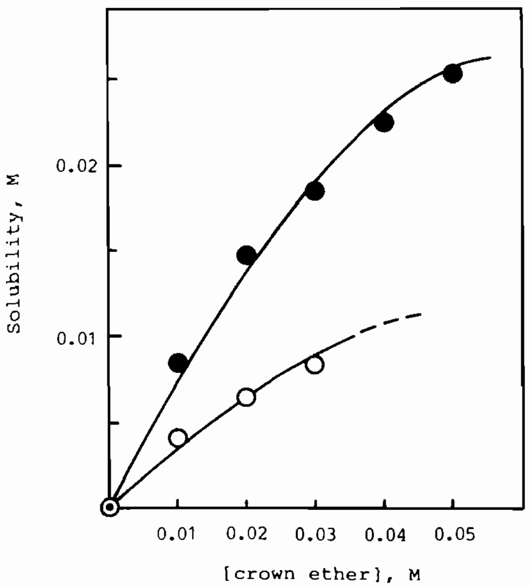

Fig. 2. Solubilities of K[Co(edta)]•$2H_2O$ in acetonitrile (○) and in acetonitrile solutions of dicyclohexyl 18-crown-6 (●) and dibenzo 18-crown-6 (○).

K_{18C6} = 6.08, log K_{15C5} = 3.43, and log K_{12C4} = 1.74. Namely, $K_{18C6} > K_{15C5} > K_{12C4}$. These are the values in methanol but it was reported that the values in acetonitrile are quite similar to those in methanol [6].

In this context, DC18C6 could be an excellent solubilizing agent since this crown has a great value of stability constant (log K = 6.01 or 5.38 in methanol [7], log K = 5.63 in acetonitrile [6]) which is similar in order to that of 18C6. In fact, Fig. 2 indicates that DC18C6 enhances the solubility of the complex in the same magnitude as 18C6 does. This means that the solubilizing abilities of these crown ethers are controlled by the magnitude of the association with potassium ion. In contrast, the case of BC18C6 is not so simple. The stability constant of BC18C6 with potassium ion (log K = 5.00 in methanol [7], log K = 4.83 in acetonitrile [6]) is much greater than that of 15C5 and is similar to the stability constant of 18C6. However, DB18C6 increases the solubility in a similar manner as 15C5 does (Fig. 2)†. Other factors could play a role in the solubilizing ability in this case.

These results lead to the conclusion that the solubility enhancement is dependent primarily on the magnitude of the association constant of crown ether with potassium ion, and secondly on the other factor which may be concerned with the magnitude of the interaction (solvation) of K^+–crown with acetonitrile.

The behavior is similar to that observed for the solubilization of $K_2Cr_2O_7$ in acetonitrile. Table I shows that 18C6 and DC18C6 solubilize this salt in acetonitrile to the greatest extent, and the solubility increases in the same order (DC18C6 ≈ 18C6 > 15C5 > 12C4) as that for K[Co(edta)]•$2H_2O$. Thus, this complex salt could be utilized as a standard for estimating the solubilizing ability of crown ether in place of potassium salts such as $K_2Cr_2O_7$ and $KMnO_4$, which are not stable in many solvents.

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†DB18C6 can be dissolved in acetonitrile in concentration up to 0.03 M.