BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (5), 1246—1249 (1976)

# Formation Constants of Dibenzo-18-crown-6 Complexes with Alkali Metal Ions in DMSO, DMF, and PC at 25 °C

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(Received November 12, 1975)

The formation constants ($K_f$) for the 1: 1 complexes of dibenzo-18-crown-6 (DBC) with alkali metal ions in DMSO (dimethyl sulfoxide), DMF (*N,N*-dimethyl formamide), and PC (propylene carbonate) have been determined conductometrically. The formation constant sequences of the alkali metal ions with DBC in DMSO, DMF, and PC are $K^+>Rb^+>Cs^+\cong Na^+\gg Li^+$, $K^+>Rb^+>Cs^+>Na^+>Li^+$, and $K^+\gg Na^+>Rb^+>Cs^+>Li^+$ respectively. The $K_f$ value series about the same alkali metal ion among these nonaqueous solvents are given in the order of DMSO<DMF<PC. These results show that the selectivity of DBC toward the alkali metal ions is dependent on the ionic diameter and the ring-hole size of DBC, and that the donor number of the organic solvent as a component factor is important in determining the process of the formation of the DBC complexes constant.

In a number of recent papers Pedersen[1)] has described many macrocyclic polyethers synthesized by him; these compounds form complexes with various salts. The complexing of alkali cations by neutral molecules is an uncommon and only recently observed phenomenon. The formation of the complexes between cyclic polyethers and alkali metal salts has been determined by several methods, for example, by a calorimetric titration technique by Izatt *et al.*,[2)] by potential and conductance measurements by McLaughlin *et al.*,[3)] by spectroscopic methods by Wong *et al.*,[4)] by UV spectra and solvent extraction by Pedersen,[1b)] and by potentiometry with cation-selective electrodes by Frensdorff.[5)] They have reported the formation constants for complexing of these polyethers with several cations, and suggested that the specificity of the complexation is due to the surrounding solvent for the free cation and the required fit between the ionic radius and the hole size of the cyclic polyether ring. The present study was undertaken in order to quantify the strength of complexing in a solution as a function of the ionic radius, the hole size of the cyclic polyether ring, and the physical properties of the solvent. In this paper the formation constants for 1:1 complexes of dibenzo-18-crown-6 (DBC) with alkali metal ions ($Li^+$, $Na^+$, $K^+$, $Rb^+$, $Cs^+$) in DMSO (dimethyl sulfoxide), DMF (*N,N*-dimethyl formamide) and PC (propylene carbonate) have been determined conductometrically.

## Experimental

*Conductance Cell.* The conductance cell was similar to those reported previously.[6)]

*Apparatus and Procedure.* The measurements were carried out by means of a Yokogawa-Hewlette-Packard Universal Bridge. Cell solutions were thermostated to 25± 0.02 °C in a double water bath. The solution in the cell was stirred by means of a magnetic stirrer so that we might quickly obtain a temperature equilibrium. The cell temperature change was readily detected by the shift of resistance readings exceeding 0.01%. For the first run, DBC and alkali metal perchlorate were dissolved in the solvent in order to make the concentration of DBC equal that of alkali metal perchlorate. After a constant value of resistance had been attained, a 30-ml portion of the solution was siphoned out and equal volume of the solvent was added to the cell. This procedure was continued. The concentration range was from $7.6\times10^{-4}$ to $3.1\times10^{-3}$ M. For the second run, DBC of about $7.5\times10^{-3}$ M was added to the solvent in the cell and the resistance of the solution was measured. Then a step-by-step increase in the alkali metal perchlorate concentration was effected by a quick transfer from the weighing bottle to the conductance cell. The concentration range was from $1.0\times10^{-4}$ to $1.5\times10^{-2}$ M. The $\Lambda$ *vs.* $\sqrt{C}$ curve for this series is given by (3) in Figs. 1—5.

*Materials.* The method of the purification of solvents and electrolytes was as has previously been described.[7)] Dibenzo-18-crown-6 was obtained from the Aldrich Chemical Company, Inc. DBC was dissolved in chloroform and filtered.

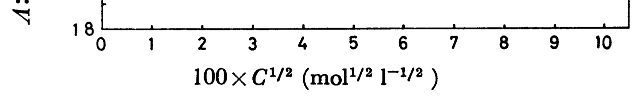

Fig. 1. $\Lambda$ *vs.* $\sqrt{C}$ curves for $LiClO_4$ and its complex with DBC in PC at 25 °C.

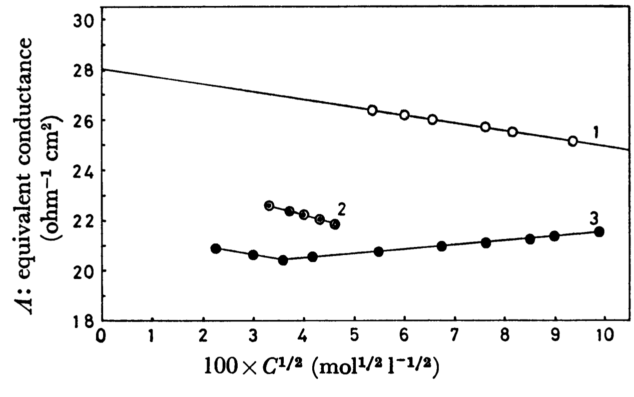

Fig. 2. $\Lambda$ *vs.* $\sqrt{C}$ curves for $NaClO_4$ and its complex with DBC in PC at 25 °C.

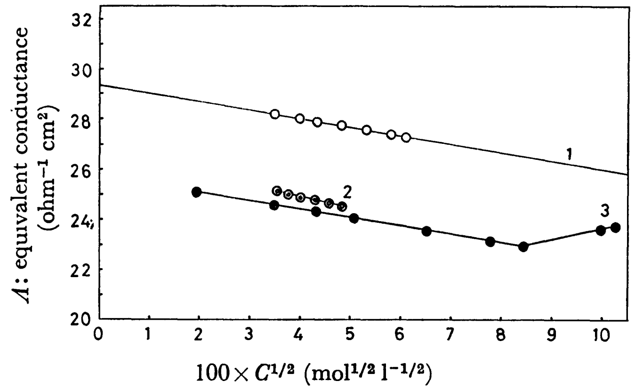

Fig. 3. $\Lambda$ *vs.* $\sqrt{C}$ curves for $KClO_4$ and its complex with DBC in PC at 25 °C.

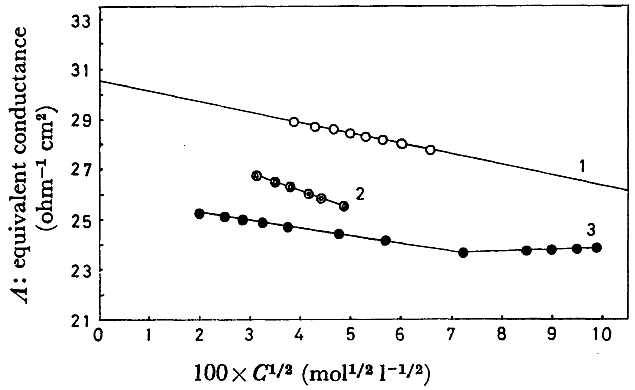

Fig. 4. $\Lambda$ *vs.* $\sqrt{C}$ curves for $RbClO_4$ and its complex with DBC in PC at 25 °C.

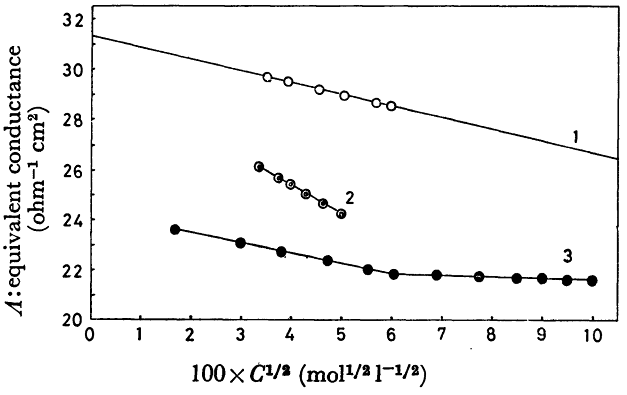

Fig. 5. $\Lambda$ *vs.* $\sqrt{C}$ curves for $CsClO_4$ and its complex with DBC in PC at 25 °C.

1: $\Lambda$ *vs.* $\sqrt{C}$ curve for alkali metal perchlorate in PC at 25 °C —phoreogram-1.

2: $\Lambda$ *vs.* $\sqrt{C}$ curve for the same concentration of alkali metal perchlorate as that of DBC in PC at 25 °C —phoreogram-2.

3: $\Lambda$ *vs.* $\sqrt{C}$ curve for the stepwise increase of the alkali metal perchlorate concentration against the constant DBC concentration in PC at 25 °C — phoreogram-3.

Then it was recrystallized from benzene five times and, before use, dried at 50 °C in a vacuum oven.

## Results

The $\Lambda$ *vs.* $\sqrt{C}$ curves for alkali metal perchlorates and their complexes with DBC in PC at 25 °C are given in Figs. 1—5. Figures 1,2,3,4, and 5 correspond to the cases of lithium, sodium, potassium, rubidium, and cesium perchlorate respectively. The experimental curves in DMSO and DMF are similar and hence have been omitted. The phoreogram-3 consists of either one linear line or two different ones. The former is found only in the case of $NaClO_4$ in DMSO, and the slope of the $\Lambda$ *vs.* $\sqrt{C}$ curve is negative. The latter has three types. In the case of the first type, the slope changes from positive to negative with an increase in the concentration, as can be seen in Fig. 1. This type can also be seen in the case of the $NaClO_4$ in DMF. In the case of the second type, the slope changes from negative to positive, as can be seen in Figs. 2—4. In the case of the last type, both slopes are negative, the absolute values of these two slopes are different from each other, and the absolute value of the slope changes from large to small with an increase in the concentration, as can be seen in Fig. 5. This type can also be seen in the cases of $LiClO_4$, $KClO_4$, $RbClO_4$, and $CsClO_4$ in DMSO and DMF. Accordingly, the phoreogram-3 obtained can be classified into the four types. In every case, however, the phoreogram-2 always lies between the phoreogram-1 and the phoreogram-3. That is, the phoreogram-1 is at the top, the phoreogram-2 is in the middle, and the phoreogram-3 is at the bottom. It may be noted from Figs. 1—5 that the distance from the phoreogram-2 to the phoreogram-1 differs from that from the phoreogram-2 to the phoreogram-3 in the concentration range of the phoreogram-2. These tendencies in DMSO and DMF are similar. It seems that the 1:1 complex of DBC with the alkali metal ion is larger than the alkali metal ion itself. Therefore, it can be supposed that the former is more mobile than the latter in these solutions. Judging from the above, it is assumed that, in the case of the phoreogram-3, most of the alkali metal ions form complexes with DBC and that these complexes are of the 1:1 type when the concentration of DBC exceeds that of alkali metal ions. As the phoreogram-2 lies between the phoreogram-1 and the phoreogram-3, it is considered that the uncomplexed cation and the complexed cation attain to a chemical equilibrium in the case of the phoreogram-2. The equilibrium equation is given by;

$$\underset{C(1-\alpha)}{M^+} + \underset{C(1-\alpha)}{DBC} \overset{K_f}{\rightleftharpoons} \underset{C\alpha}{M(DBC)^+} \quad (1)$$

where $C$ is the initial molar concentration of the alkali metal ion and DBC, while $\alpha$ is the fraction of the cation in the 1:1 complex. Accordingly, the complex formation constant, $K_f$, is given by;

$$K_f = \frac{[M(DBC)^+]}{[M^+][DBC]} = \frac{\alpha}{C(1-\alpha)^2} \quad (2)$$

where $[M^+]$, $[M(DBC)^+]$, and $[DBC]$ are the molarities of the uncomplexed cation, the complexed cation, and uncomplexed DBC respectively. The observed specific conductance, $\kappa_{ob}$, is given by;

$$\kappa_{ob} = \kappa_{M^+} + \kappa_{M(DBC)^+} + \kappa_{ClO_4^-} \quad (3)$$

where $\kappa_{M^+}$, $\kappa_{M(DBC)^+}$, and $\kappa_{ClO_4^-}$ are the specific conductances of the uncomplexed cation, the complexed cation, and the perchlorate ion respectively. The ionic equivalent conductances are given by;

$$\lambda_{M^+} = \frac{\kappa_{M^+}}{[M^+]} = \frac{\kappa_{M^+}}{C(1-\alpha)} \tag{4}$$

$$\lambda_{M(DBC)^+} = \frac{\kappa_{M(DBC)^+}}{[M(DBC)^+]} = \frac{\kappa_{M(DBC)^+}}{C\alpha} \tag{5}$$

$$\lambda_{ClO_4^-} = \frac{\kappa_{ClO_4^-}}{[ClO_4^-]} = \frac{\kappa_{ClO_4^-}}{C} \tag{6}$$

where $\lambda_{M^+}$, $\lambda_{M(DBC)^+}$, and $\lambda_{ClO_4^-}$ are the ionic equivalent conductances of the uncomplexed cation, the complexed cation, and the perchlorate ion respectively. As a consequence of Eqs. 4, 5, and 6, Eq. 3 would be transformed into;

$$\Lambda_{ob} = \frac{\kappa_{ob}}{C} = (1-\alpha)\Lambda_{MClO_4} + \alpha\Lambda_{M(DBC)ClO_4} \tag{7}$$

where $\Lambda_{ob}$ is the observed equivalent conductance and where $\Lambda_{MClO_4}$ and $\Lambda_{M(DBC)ClO_4}$ are the equivalent conductances of alkali metal perchlorate and alkali metal DBC perchlorate respectively. If the $\alpha$ value is obtained, the value of $K_f$ at each concentration can be calculated. The procedure for obtaining the $\alpha$ value is as follows. First, the $\alpha$ value is estimated arbitrarily. Using this $\alpha$ value, the concentrations of alkali metal perchlorate and alkali metal DBC perchlorate are found to be $C(1-\alpha)$M and $C\alpha$M respectively. As the values of $\Lambda_{MClO_4}$ and $\Lambda_{M(DBC)ClO_4}$ at these concentrations can be obtained from the phoreogram-1 and the phoreogram-3 respectively, the right side of Eq. 7 can be calculated. As the value of the left side of Eq. 7 is the observed one, these calculations are continued until the value of the right side of Eq. 7 becomes equal to that of the left side of Eq. 7. When the value of $\alpha$ is finally obtained, $K_f$ can be calculated from Eq. 2. As a result, the formation constants of the 1:1 complexes of DBC with alkali metal ions for each concentration are as shown in Table 1. It may be noted from Figs. 1—5 and Table 1 that the closer the phoreogram-2 approaches the phoreogram-3, and the more the phoreogram-2 departs from the phoreogram-1, the larger the value of the $K_f$ of each concentration becomes. These phenomena in DMSO and DMF are similar. The formation constant sequences of the alkali metal ions with DBC in PC at 25 °C are $K^+ \gg Na^+ > Rb^+ > Cs^+ > Li^+$. In the cases of DMSO and DMF, however, they are $K^+ > Rb^+ > Cs^+ \simeq Na^+ \gg Li^+$ and $K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$ respectively.

TABLE 1. FORMATION CONSTANTS FOR THE 1:1 COMPLEXES FOR ALKALS CATIONS WITH DBC

| $10^3C$ | DMSO | | $10^{-3}K_f$ | | |
|---|---|---|---|---|---|
| | $Li^+$ | $Na^+$ | $K^+$ | $Rb^+$ | $Cs^+$ |
| 1.44 | nil | 1.99 | 2.44 | 2.28 | 2.01 |
| 1.52 | nil | 2.03 | 2.47 | 2.32 | 2.03 |
| 1.60 | nil | 2.04 | 2.68 | 2.34 | 2.04 |
| 1.68 | nil | 2.05 | 2.74 | 2.39 | 2.07 |
| 1.76 | nil | 2.03 | 2.61 | 2.34 | 2.07 |

| $10^3C$ | DMF | | $10^{-3}K_f$ | | |
|---|---|---|---|---|---|
| | $Li^+$ | $Na^+$ | $K^+$ | $Rb^+$ | $Cs^+$ |
| 1.44 | 0.99 | 2.11 | 3.43 | 3.20 | 2.99 |
| 1.52 | 0.98 | 2.26 | 3.59 | 3.30 | 3.03 |
| 1.60 | 1.15 | 2.19 | 3.54 | 3.49 | 3.09 |
| 1.68 | 1.12 | 2.39 | 3.66 | 3.57 | 3.16 |
| 1.76 | 1.21 | 2.31 | 3.72 | 3.55 | 3.20 |

| $10^3C$ | PC | | $10^{-3}K_f$ | | |
|---|---|---|---|---|---|
| | $Li^+$ | $Na^+$ | $K^+$ | $Rb^+$ | $Cs^+$ |
| 1.44 | 1.86 | 7.60 | 131 | 5.86 | 3.43 |
| 1.52 | 1.68 | 7.20 | 125 | 5.55 | 3.49 |
| 1.60 | 1.81 | 7.50 | 119 | 5.74 | 3.32 |
| 1.68 | 1.96 | 7.14 | 113 | 5.96 | 3.66 |
| 1.76 | 2.00 | 7.50 | 110 | 5.22 | 3.77 |

## Discussion

The $K_f$ value series about the same alkali metal ion among these nonaqueous solvents are given in the order of DMSO<DMF<PC from Table 1. The formation constant sequences of the complex in PC differ from those in DMSO and DMF. Of all the alkali metal ions, the $K_f$ value of $K^+$ is the largest, and that of $Li^+$ is the smallest, in each solvent. These results show that the ability of the alkali metal ion to form complexes with DBC in these solvents is dependent on the ionic diameter, as can be seen in Table 2, and that the solvent used is important in determining the formation constant in these systems. This can be considered to reflect the competition between complex formation and solvation. This is supported by the $K_f$ values in Table 1, which show, that for alkali metal cations of approximately the same ionic diameters, *i.e.*, $K^+$ (2.66 Å), the $K_f$ value of $K^+$ is the largest. Pedersen[1] has observed that the complexing power can be expected to be weak when the hole of the polyether is too small or too large for the cation, because the salt-polyether complexes are formed by ion-dipole interaction between the cation and the negatively charged oxygen atoms symmetrically arranged in the polyether ring. In addition, the poor selectivity for $Li^+$ is probably due to its small size (ionic diameter, 1.20 Å) as compared to the size of the hole of DBC (hole size, 2.6—3.2 Å). The solvation is very important in determining cation selectivity, and in this respect it will be more difficult to strip the solvent molecules from $Li^+$ than from all the other alkali metal ions. Of course, this will depend very greatly on the nature of the solvent. The potential series on the

TABLE 2. IONIC DIAMETERS AND HOLE SIZE (Å)[a]

| Cation | Ionic diameter | Polyether | Hole size |
|---|---|---|---|
| $Li^+$ | 1.36 | All 18-crown-6 | 2.6—3.2 |
| $Na^+$ | 1.94 | | |
| $K^+$ | 2.66 | | |
| $Rb^+$ | 2.94 | | |
| $Cs^+$ | 3.34 | | |

a) H. K. Frensdorff, *J. Am. Chem. Soc.*, **93**, 600 (1971).

normalized potential scale were given in the order of DMSO$<$DMF$<$PC, indicating that the metal ion-solvent interaction increases with an increase in the electron-donor property of the solvent.[8] The $K_f$ value sequences were given in the order of DMSO ($\varepsilon=46.7$[9]) $<$DMF ($\varepsilon=36.7$[9]) $<$PC ($\varepsilon=64.4$[9]). Accordingly, it seems that the donor number of the solvent is a very influential factor in the alkali metal ion-DBC complexing. Pedersen[1b] has reported that the selectivity of polyethers with respect to the complexation of alkali metal ions increases as the dielectric constant of the organic solvent is lowered. However, it seems that the donor number is a main factor in determining the selectivity of DBC for the alkali metal ion in the organic solvent.

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