BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (11), 3078 (1977)

Formation Constants of Dibenzo-18-crown-6 Complexes with Alkali Metal Ions in Dimethyl Sulfoxide, *N,N'*-Dimethyl Formamide, and Propylene Carbonate at 25 °C

Niro MATSUURA, Kisaburo UMEMOTO, Yasuyuki TAKEDA, and Atsuko SASAKI

Department of Pure and Applied Sciences, College of General Education, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153

(Received May 19, 1977)

In a previous paper[1] we reported formation constants for 1 : 1 complexes of dibenzo-18-crown-6 (DBC) with Li^+, Na^+, K^+, Rb^+, and Cs^+ measured in DMSO (dimethyl sulfoxide), DMF (*N,N'*-dimethyl formamide), and PC (propylene carbonate). The fraction (α) of the cation in the 1 : 1 complex $M(DBC)^+$ is given by

$$\alpha=\frac{\Lambda^1-\Lambda^2}{\Lambda^1-\Lambda^3},$$

where Λ^1, Λ^2, and Λ^3 denote the corresponding phoreograms (1, 2, and 3, Figs. 1—5).[1]

Since α is equal to 0 for complete dissociation, the phoreograms 1 and 2 should coincide at zero concentration. Actually in PC as well as in DMF the curves apparently converge. However, no such trend is found between the phoreograms 1 and 3. A well defined Λ_0^3 value will be obtained at extreme dilution, if extrapolation is made. However, a straightforward extrapolation is not good for a complexed salt in the presence of excess DBC, and we must be satisfied with the values of K_f (formation constant of a 1 : 1 complex) obtained in a concentration range in which an accurate conductance measurement can be carried out.

According to the definition of K_f (Eq. 2 of the previous paper)[1], the value of K_f is approximately equal to α/C when α is much smaller than unity, where α is the fraction of the cation in the 1 : 1 complex and C is the initial molar concentration of the alkali metal ion and DBC.

This condition, however, is not easily satisfied because α has a value of the order of 0.1 or greater as is shown in phoreogram 3.

The value of K_f for $Na(DBC)^+$ at 1.44×10^{-3} M of $NaClO_4$[1] is about three times larger than that given by Shchori *et al.* at 1.0×10^{-3} M of NaSCN.[2] At this stage no prediction can be made for the discrepancy between them, since it is likely that Na^+ and ClO^-_4 dissociate completely in DMF, whereas Na^+ and SCN^- associate slightly in DMF. Moreover the K_f values in Table 1[1] are practically constant within these concentration ranges.

References

1) N. Matsuura, K. Umemoto, Y. Takeda, and A. Sasaki, *Bull. Chem. Soc. Jpn.*, **49**, 1246 (1976).

2) E. Shchori, J. Jagur-Grodzinski, Z. Luz, and M. Shporer, *J. Am. Chem. Soc.*, **93**, 7133 (1971).