*Inorganica Chimica Acta, 114* (1986) 145–149

# Thermodynamic Studies of the Complexation of Dibenzo-27-crown-9 and Dibenzo-24-crown-8 with Cesium Ion in mixed Nonaqueous Solvents

GHOLAMHOSSEIN ROUNAGHI and ALEXANDER I. POPOV*

*Department of Chemistry, Michigan State University, East Lansing, Mich. 48824, U.S.A.*

Received August 30, 1985

## Abstract

Thermodynamic parameters for the complexation of the cesium ion by macrocyclic polyethers, dibenzo-27-crown-9, (DB27C9), and dibenzo-24-crown-8, (DB24C8), were determined in dimethylformamide–acetonitrile binary solvent systems by cesium-133 NMR technique. Enthalpies and entropies of the complex formation were obtained from the temperature dependence of the complexity constant. In all cases the complexes are enthalpy stabilized but entropy destabilized and both parameters are quite sensitive to the solvent composition.

## Introduction

While the thermodynamics of macrocyclic polyether complex formation have been studied by several investigators [1–7], most of the studies have been carried out in water, water–methanol mixtures, or in pure nonaqueous solvents. The only available information on complexation reactions in mixed solvents appear to be for 18-crown-6 complexes with the $Na^+$ and $K^+$ cations in methanol–water mixtures [4, 8]. It was of interest to us, therefore, to extend such studies to mixed aprotic nonaqueous solvents in order to see how the thermodynamics of complexation are affected by the solvent composition, especially in view of the fact that macrocyclic ligands have been shown to be appreciably solvated by a number of common nonaqueous solvents [9, 10] and that this solvent–ligand interaction can influence significantly the complexation reaction. It should also be noted that solvating abilities of solvents in mixtures can be very different from those of the neat media [11].

In the present work we report a variable temperature cesium-133 NMR study of the cesium ion complexation by large macrocyclic crown ethers, dibenzo-27-crown-9 and dibenzo-24-crown-8 in dimethylformamide–acetonitrile binary mixtures of various compositions. Formation constants were calculated from the variation of the $^{133}Cs$ chemical shift as a function of [ligand]:[$Cs^+$] mole ratio and the enthalpy and entropy of the reactions were obtained from the temperature dependence of the formation constant.

## Experimental

### *Reagents*

Complexing agents, dibenzo-27-crown-9 and dibenzo-24-crown-8, were obtained from Parish Chemical Company. They were purified by recrystallization from normal heptane (Mallinckrodt) and then dried under vacuum over granulated barium oxide for three days. Cesium thiocyanate (Rocky Mountain Research, Inc.) was recrystallized from reagent grade methanol and dried under vacuum at 50 °C for several days. The solvents were purified and dried by the previously described methods [12]. The water content of purified solvents was checked by Karl Fischer titration and was always less than 100 ppm.

### *Instrumental Measurements*

Cesium-133 NMR measurements were performed on a highly modified Varian Associate DA-60 spectrometer in the Fourier Transform mode, operating at 7.87 MHz. An external proton field lock was employed to maintain the field stability. Non-spinning 10 mm o.d. NMR tubes (Wilmad) were used. The temperature was monitored using a thermocouple housed in a 10 mm NMR tube and inserted in the solvent. During measurements the temperature was constant to within ±1 °C. Because the resonance frequency of the reference varies with the temperature, an insulated reference tube [13] was used. In order to reach the equilibrium temperature, each sample tube was left in the probe for at least 15 min before measurements. Chemical shifts obtained in these studies were referenced to an aqueous 0.5 M solution of cesium bromide. However, all of the chemical shifts are ultimately referenced to infinitely dilute aqueous solution of $Cs^+$ ion and they are corrected for differences in the bulk dia-

---

*Author to whom correspondence should be addressed.

0020-1693/86/$3.50

magnetic susceptibility of the solvent or solvent mixture.

The formation constants were calculated by fitting the observed $^{133}$Cs chemical shifts at various (L)/Cs$^+$ mole ratios to a previously derived equation [14] which expresses the observed shifts as a function of the total cation and ligand concentrations, the chemical shift of the free and of the complexed cation and the formation constant. A non-linear least squares program KINFIT was used [15]. The details are given in a previous publication [14].

## Results and Discussion

The interaction between large macrocyclic crown ethers, dibenzo-27-crown-9 and dibenzo-24-crown-8 with the cesium ion were studied in dimethylformamide–acetonitrile binary mixtures at various temperatures. At each temperature, the chemical shifts of the cesium-133 were monitored as a function of DB27C9/Cs$^+$ or DB24C8/Cs$^+$ mole ratios. In all cases, the exchange of the Cs$^+$ ion between the free and the complexed sites was fast and only one, population averaged, NMR signal was observed irrespective of the ligand/Cs$^+$ mole ratio.

Examples of the plots of the cesium-133 chemical shifts as a function of DB27C9/Cs$^+$ mole ratio are shown in Figs. 1 and 2. As the temperature decreases the plots show more pronounced curvature which is an indication of the increasing stability of the complex at lower temperatures.

The formation constants of the above mentioned complexes for the various compositions of DMF/MeCN system at different temperatures are listed in Table I. A monotonic increase in the stability constants of these complexes is observed as the temperature decreases. Plots of ln $K_f$ *versus* $1/T$ are shown in Fig. 3, and the calculated thermodynamic parameters, together with the calculated uncertainties, are given in Table II. These data show that in the case of the DB24C8·Cs$^+$ complex, a decrease in the concentration of dimethylformamide results in an increase in the stability of the complex due to two factors, more negative $\Delta H_c$ values and less negative $\Delta S_c$ values, *i.e.* as the concentration of acetonitrile is increased, the complex is increasingly enthalpy-stabilized and less entropy-destabilized. In a strongly solvating solvent, such as dimethylformamide, the solvation of the metal ion (and possibly of the ligand) should be stronger than in a solvent of lower solvating ability such as acetonitrile (as given by the Gutmann donor numbers [16], 14.1 and 26.6 for MeCN and DMF respectively). Therefore, less energy should be necessary for the desolvation step of the cation (and probably of the ligand) in the case of acetonitrile than for dimethylformamide. It would be expected, therefore, that the $\Delta H_c^\circ$ values for complexation reaction will be more negative as the acetonitrile composition of DMF/MeCN mixture increases, and the $\Delta S_c^\circ$ values will increase due to the additional solvent molecules which may be released in the complexation.

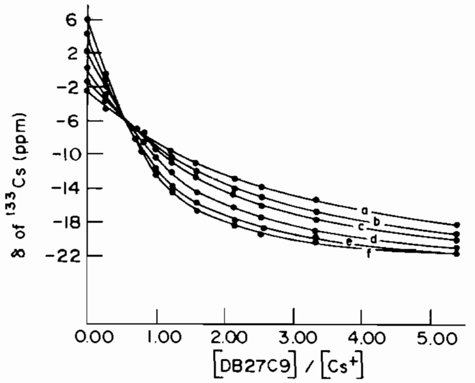

Fig. 1. Cesium-133 chemical shifts as a function of the (DB27C9)/(Cs$^+$) mole ratio in neat DMF at different temperature in 10 °C intervals from (a) at 40 °C to (f) at −10 °C.

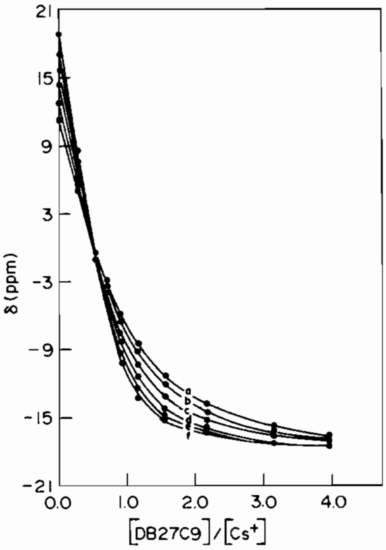

Fig. 2. Cesium-133 chemical shifts as a function of the (DB27C9)/(Cs$^+$) mole ratio in a 22.7–77.3 mol% DMF–MeCN mixture at different temperatures in 10 °C intervals from (a) 50 °C to (f) 0 °C.

As it is seen from Table II, while the thermodynamic parameters of DB24C8·Cs$^+$ are influenced by the solvent and vary regularly with the solvent composition, this order is not followed by the DB-27C9·Cs$^+$ complex, where, although the stability of the complex increases with increasing concentration of acetonitrile, the changes in the values of $\Delta H_c$ and $\Delta S_c$ are not monotonic. It should be noted that the calculated standard deviations for this case are quite large. At this point the data do not

TABLE I. Formation Constants of DB27C9 and DB24C8 Complexes with the $Cs^+$ Ion[a] in MeCN/DMF Binary Mixtures of Different Temperatures

| DB27C9 | | | DB24C8 | | |
|---|---|---|---|---|---|
| Medium | Temperature (°C) | log $K_f$ | Medium | Temperature (°C) | log $K_f$ |
| Pure DMF | 40 | 2.05 ± 0.01 | Pure DMF | 50 | 1.89 ± 0.01 |
| | 30 | 2.20 ± 0.01 | | 40 | 2.02 ± 0.01 |
| | 20 | 2.33 ± 0.01 | | 30 | 2.15 ± 0.03 |
| | 10 | 2.58 ± 0.01 | | 20 | 2.32 ± 0.01 |
| | 0 | 2.78 ± 0.01 | | 10 | 2.46 ± 0.03 |
| | −10 | 2.89 ± 0.01 | | 0 | 2.65 ± 0.02 |
| 86.04% DMF +13.96% MeCN[b] | 40 | 2.17 ± 0.05 | 61.50% DMF +38.50% MeCN | 40 | 2.29 ± 0.03 |
| | 30 | 2.28 ± 0.01 | | 30 | 2.44 ± 0.03 |
| | 20 | 2.50 ± 0.01 | | 20 | 2.54 ± 0.02 |
| | 10 | 2.64 ± 0.02 | | 10 | 2.78 ± 0.02 |
| | 0 | 2.79 ± 0.01 | | 0 | 2.98 ± 0.02 |
| | −10 | 2.96 ± 0.01 | | −10 | 3.11 ± 0.02 |
| 61.5% DMF +38.50% MeCN | 30 | 2.55 ± 0.01 | 22.69% DMF +77.31% MeCN | 50 | 2.68 ± 0.02 |
| | 20 | 2.69 ± 0.01 | | 40 | 2.85 ± 0.02 |
| | 10 | 2.89 ± 0.01 | | 30 | 3.03 ± 0.01 |
| | 0 | 3.03 ± 0.02 | | 20 | 3.18 ± 0.01 |
| | −10 | 3.20 ± 0.01 | | 10 | 3.35 ± 0.02 |
| | −20 | 3.50 ± 0.04 | | 0 | 3.59 ± 0.05 |
| 22.69% DMF +77.31% MeCN | 50 | 2.84 ± 0.02 | Pure MeCN | 75 | 3.19 ± 0.03 |
| | 40 | 3.01 ± 0.02 | | 60 | 3.45 ± 0.04 |
| | 30 | 3.20 ± 0.02 | | 50 | 3.57 ± 0.05 |
| | 20 | 3.34 ± 0.03 | | 40 | 3.77 ± 0.03 |
| | 10 | 3.45 ± 0.02 | | 30 | 3.94 ± 0.07 |
| | 0 | 3.51 ± 0.03 | | 5 | 4.50 ± 0.05 |
| Pure MeCN | 77 | 3.09 ± 0.02 | | | |
| | 63 | 3.30 ± 0.02 | | | |
| | 45 | 3.63 ± 0.01 | | | |
| | 30 | 3.89 ± 0.01 | | | |
| | 17 | 4.17 ± 0.04 | | | |
| | 9 | 4.24 ± 0.04 | | | |

[a] Concentration of CsSCN = 0.005 M. [b] Compositions of the binary systems are expressed as mol% of each solvent.

allow us to speculate about the reasons for the variations of enthalpy and entropy with solvent composition.

Experimental values of $\Delta H_c^\circ$ and $\Delta S_c^\circ$ for DB27-C9·$Cs^+$ and DB24C8·$Cs^+$ complexes show that in all cases these complexes are enthalpy stabilized but entropy destabilized. It seems reasonable to assume that the decrease in entropy upon complexation is related to a change in the conformational entropy of the ligand. It is known that large macrocyclic ligands such as dibenzo-27-crown-9 and dibenzo-24-crown-8 are rather flexible in the uncomplexed states, therefore, the negative entropy changes may be partially attributed to the increased ligand rigidity upon coordination. A change in the ligand conformation upon complexation was postulated as early as 1972 by Chock [17] and has been amply demonstrated by recent kinetic studies of Eyring and Petrucci and their co-workers [18]. It should be noted, however, that the conformational change of the ligand is not the only factor governing the change in the entropy of complexation. For example, complexation reaction involves a change in the solvation of the cation and of the ligand [9]. The relative enthalpy and entropy changes can be better understood if ligand solvation is taken into consideration.

It is interesting to compare our results with those obtained by Izatt *et al.* for the 18C6·$Na^+$ complex in water–methanol mixtures [8] (Table II). The stability of the complex increases with increasing concentration of methanol, which agrees with

TABLE II. Thermodynamic Parameters for DB27C9·$Cs^+$ and DB24C8·$Cs^+$ Complexes in DMF and MeCN and Their Binary Mixtures

| Medium | log $K_f$ (30 °C) | $\Delta G_c^\circ$ (30 °C) (kcal mol$^{-1}$) | $\Delta H_c^\circ$ (kcal mol$^{-1}$) | $\Delta S_c^\circ$ (e.u.) |
|---|---|---|---|---|
| DB27C9·$Cs^+$ | | | | |
| pure DMF | 2.20 ± 0.01 | -3.05 ± 0.01 | -7.20 ± 0.37 | -13.71 ± 1.19 |
| 86.04% DMF + 13.95% MeCN[a] | 2.28 ± 0.01 | -3.16 ± 0.01 | -6.08 ± 0.25 | -9.48 ± 0.87 |
| 61.50% DMF + 38.50% MeCN | 2.55 ± 0.01 | -3.54 ± 0.01 | -6.51 ± 0.29 | -9.88 ± 1.05 |
| 22.69% DMF + 77.31% MeCN | 3.20 ± 0.02 | -4.44 ± 0.03 | -6.30 ± 0.43 | -6.32 ± 1.41 |
| pure MeCN | 3.89 ± 0.03 | -5.39 ± 0.04 | -7.93 ± 0.42 | -7.95 ± 1.40 |
| DB24C8·$Cs^+$ | | | | |
| pure DMF | 2.15 ± 0.03 | -2.98 ± 0.04 | -6.12 ± 0.12 | -10.29 ± 0.42 |
| 61.50% DMF + 38.50% MeCN | 2.44 ± 0.03 | -3.38 ± 0.04 | -6.40 ± 0.31 | -9.98 ± 1.09 |
| 22.69% DMF + 77.31% MeCN | 3.03 ± 0.01 | -4.20 ± 0.01 | -7.19 ± 0.21 | -9.94 ± 0.72 |
| pure MeCN | 3.94 ± 0.07 | -5.47 ± 0.10 | -8.12 ± 0.16 | -8.66 ± 0.48 |
| 18C6·$Na^+$ [b] | | | | |
| 0[c] | 0.4[d] | | | |
| 20 | 0.72 ± 0.03 | | -1.77 ± 0.02 | -2.6 |
| 40 | 1.17 ± 0.12 | | -2.63 ± 0.11 | -3.5 |
| 60 | 1.64 ± 0.04 | | -3.78 ± 0.08 | -5.2 |
| 70 | 1.96 ± 0.10 | | -3.82 ± 0.07 | -3.7 |
| 80 | 2.26 ± 0.02 | | -8.32 ± 0.03 | -17.6 |

[a] Composition of binary mixtures are expressed as mol% of each solvent. [b] Data from ref. 8. [c] Weight % MeOH. [d] At 25 °C

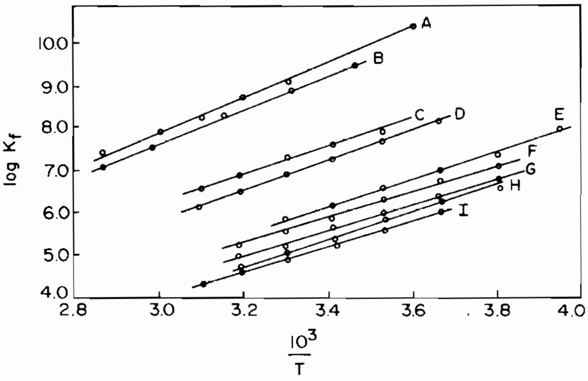

Fig. 3. The variation of log $K$ with inverse absolute temperature. Plots A, D, F and I are for the DB24C8-$Cs^+$ system in neat MeCN, 77.3–22.7, 38.5–61.5 mol% MeCN–DMF and neat DMF respectively. Plots B, C, E, G and H are for the DB27C9-$Cs^+$ system in neat MeCN, 77.3–22.7, 38.5–61.5, 14.0–86.0 mol% MeCN–DMF and neat DMF respectively.

the relative donor numbers of the two solvents (25.7 for MeOH [19] and 33 for water [20] as obtained from the sodium-23 chemical shifts). The complex is enthalpy-stabilized but entropy-destabilized; both values generally become more negative in methanol-rich mixtures. In our case an increase in the concentration of the less solvating solvent (MeCN) results in more negative enthalpies but slightly less negative entropies. However, since there are many unknown factors which contribute to changes in complexation entropies, one should not expect strict parallelism in behavior between mixtures of associated hydrogen-bonding solvents and mixtures of aprotic solvents.

## Acknowledgement

The authors gratefully acknowledge the support of this study by an National Science Foundation Grant CHE-8515974.

## References

1 R. M. Izatt and D. P. Nelson, *Science, 164,* 443 (1969).
2 R. M. Izatt, D. J. Eatough and J. C. Christensen, *Struct. Bonding (Berlin), 16,* 161 (1973).
3 H. K. Frensdorff, *J. Am. Chem. Soc., 33,* 600 (1971).
4 J. D. Lamb, R. M. Izatt, J. J. Christensen and D. J. Eatough, in G. A. Melson (ed.), 'Coordination Chemistry of Macrocyclic Compounds', Plenum, New York, 1979 p. 145–217.
5 E. Mei, A. I. Popov and J. L. Dye, *J. Am. Chem. Soc., 99,* 6532 (1977).
6 M. Shamsipur, Gh. Rounaghi and A. I. Popov, *J. Solution Chem., 9,* 701 (1980).
7 R. M. Izatt, J. H. Rytting, D. P. Nelson, B. L. Haymore and J. J. Christensen, *J. Am. Chem. Soc., 93,* 1619 (1971).
8 R. M. Izatt, R. G. Terry, D. P. Nelson, Y. Chan, D. J.

Eatough, J. S. Bradshaw, L. D. Hansen and J. J. Christensen, *J. Am. Chem. Soc.*, *98*, 7626 (1976).

9 P. A. Mosier-Boss and A. I. Popov, *J. Am. Chem. Soc.*, *107*, 4822 (1985).

10 A. Knochel, *Paper presented at the 10th International Symposium on Macrocyclic Chemistry,* Provo, Utah, 5–7 August, 1985.

11 J. B. Kinsinger, M. M. Tannahill, M. S. Greenberg and A. I. Popov, *J. Phys. Chem.*, *77*, 2444 (1973).

12 R. M. Farmer, Y. Sasaki and A. I. Popov, *Aust. J. Chem.*, *36*, 1785 (1983).

13 E. Mei, J. L. Dye and A. I. Popov, *J. Am. Chem.Soc.*, *99*, 5308 (1977).

14 E. T. Roach, P. R. Handy and A. I. Popov, *Inorg. Nucl. Chem. Lett.*, *9*, 359 (1973).

15 J. L. Dye and V. A. Nicely, *J. Chem. Educ.*, *48*, 443 (1971).

16 V. Gutmann and E. Wychera, *Inorg. Nucl. Chem. Lett.*, *2*, 257 (1966).

17 P. B. Chock, *Proc. Nat. Acad. Sci. U.S.A.*, *69*, 1939 (1972).

18 H. Richman, Y. Harada, E. M. Eyring and S. Petrucci, *J. Phys. Chem.*, *89*, 2393 (1975) and refs. therein.

19 M. S. Greenberg, R. L. Bodner and A. I. Popov, *J. Phys. Chem.*, *77*, 2449 (1973).

20 R. H. Erlich, E. Roach and A. I. Popov, *J. Am. Chem. Soc.*, *92*, 4989 (1970).