THE COMPLEXATION OF 18-CROWN-6 WITH NaCl IN DIOXANE–WATER AND DETERMINATION OF EQUILIBRIUM CONSTANTS WITH ION SELECTIVE ELECTRODES *

ÜMIT ÇAKIR and ÇAKIL ERK **

Chemistry Department, Faculty of Science, University of Dicle, Diyarbakır, 28101 (Turkey)

(Received 19 June 1990)

ABSTRACT

The complexation of 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) with Na^+ ions in dioxane–water was investigated with a sodium ion selective electrode and a glass electrode, and values of K_e (equilibrium constant) were determined according to the analytical expression $1/K_e \, [L_0]^{n+m-1} = (1 - nP')^n \, (1 - mP')^m/P'$. The $[L_0]$ is the concentration of a ligand L which is kept identical with the cation concentration, and $P' = 1/[1 + P(1 - m)]$, where P is the mole fraction of the complexed species.

INTRODUCTION

Macrocyclic ethers have aroused much interest because of the high stability of the complexes formed with alkali and alkaline earth cations [1–8]. Complex formation behaviour of such molecules has been studied by several methods, including UV spectroscopy [5], calorimetric measurements [6a,6b], ion selective potentiometry [1a,1b,4,6c,6d,10] and alkali metal NMR [7]. Recent studies with ^{13}C dipole–dipole relaxation time measurements as an NMR method evidenced the usual results on the complexing nature of such compounds [8,9].

Because of the high cation selectivity and the complete encapsulation of cations, the cryptates and crown ethers are believed to be reponsible for alkali ion transport across a membrane in various solvents [2–4].

In the present work, we studied the sodium ion complexation of 18-crown-6 in dioxane–water mixtures with a common potentiometric method. However, to ensure the compatibility of the results, we also tested a

---

* Submitted in partial fulfillment of requirements for the Degree of M.Sc. in Chemistry, Dicle University.
** Author to whom correspondence should be addressed. Present address: Chemistry Department, Technical University of Istanbul, Maslak, 80626, Istanbul, Turkey

formalism which we used recently to determine the equilibrium constants K_e precisely with a linear expression [9].

The earlier results obtained with methanol and water as the solvent components have revealed the complexing role but not the particular ion binding mechanism of the oligocyclic ethers. [1,6d,10]. We actually not only worked with dioxane–water mixtures, in which the hydration role of water on both the cation and the ligand is partly eliminated by dioxane, but also examined the role of ion pairing in such media.

EXPERIMENTAL

The 18-crown-6, a commercial product from Aldrich, was purified by distillation at low pressure provided by a Leybold–Heraus pump, model PD-400. Dioxane (Merck) was dried over sodium metal, then mixed with water doubly distilled over $KMnO_4$.
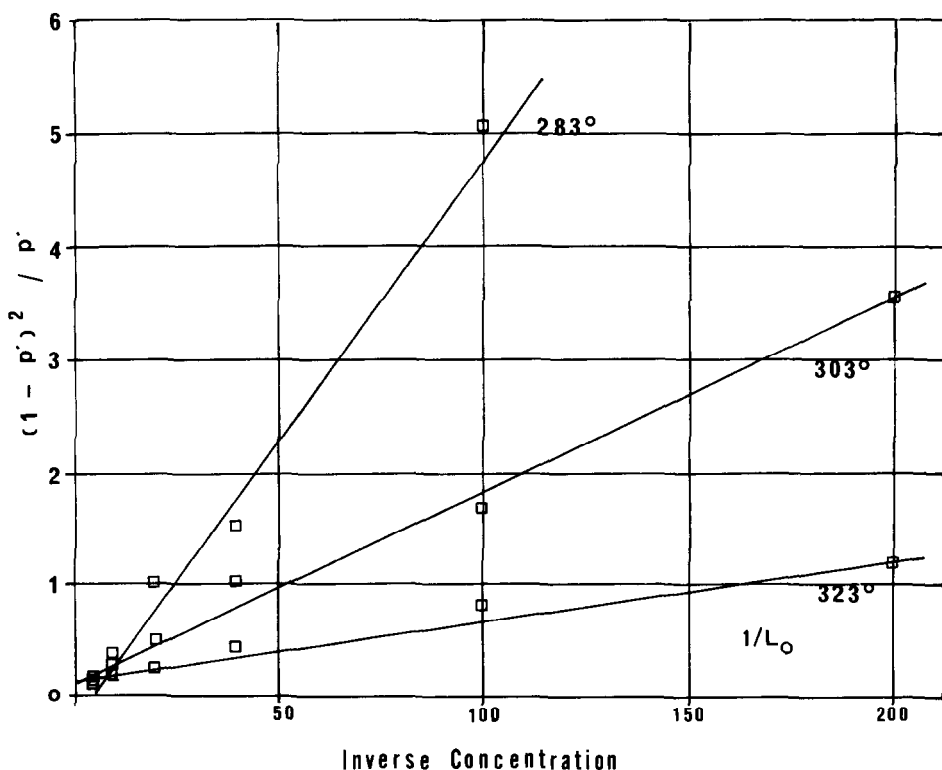

Fig. 1. Plot of $(1 - P')^2/P'$ versus $1/[L_0]$ for complexation of 18-crown-6 with sodium chloride at various temperatures in 1:1 water–dioxane mixtures obtained with a sodium selective solid state electrode from, eqn. (5).
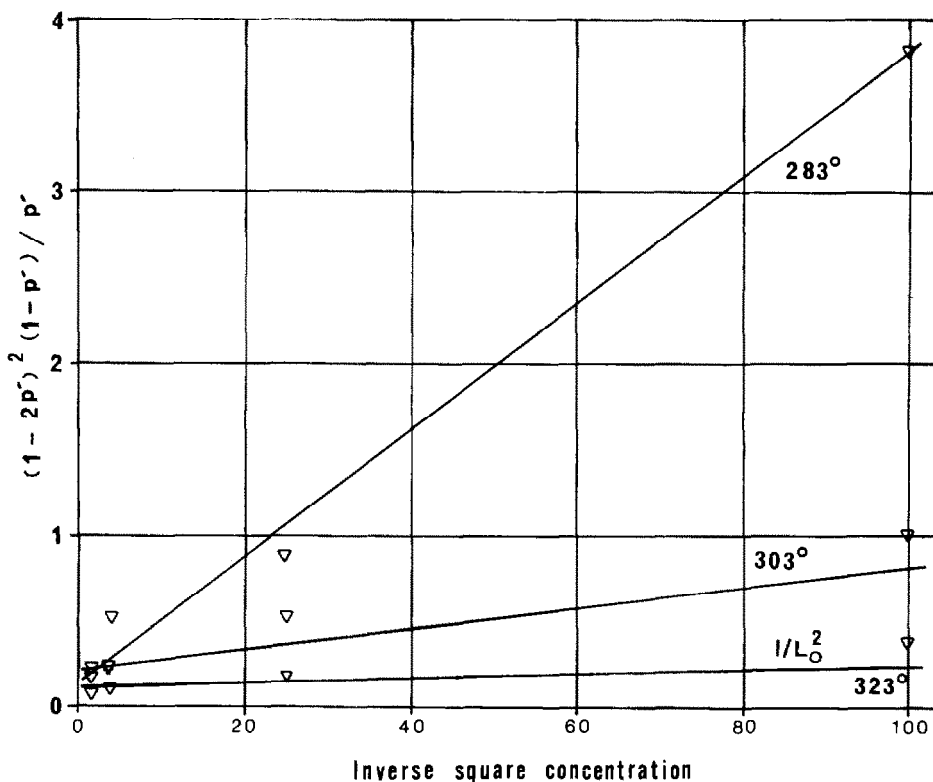
Fig. 2. Plot of $(1-P')(1-2P')^2/P'$ versus $1/[L_0]^2$ for complexation of 18-crown-6 with sodium chloride in $1:1$ water-dioxine mixtures at various temperatures obtained with a sodium selective solid state electrode; from eqn. (6).
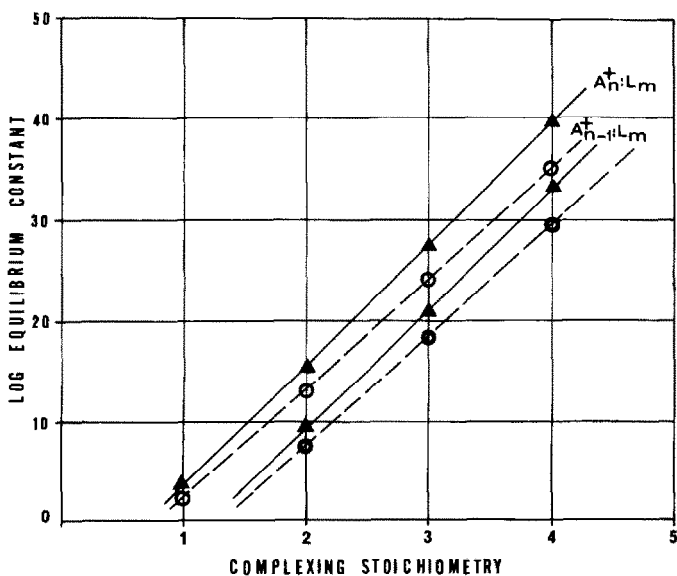

Fig. 3. Dependence of log equilibrium constants on the several complexing stoichiometries for $1:1$ dioxane-water mixture at $10\,^{\circ}C$. The solid line is obtained with the glass electrode and the dashed line with the sodium ion electrode.

The potentiometric measurements were carried out with an Orion ionmeter, model 701, equipped with a digital printer, Orion model 751. The electrode pairs were (a) sodium selective solid state type, Orion 94-11-00, with single junction reference electrode, Orion 90-01-00, and (b) glass electrode, Orion 97-11-00, with double junction reference electrode, Orion 90-02-00. The solutions were prepared at various concentrations, at constant 1 : 1 ratio of sodium to crown ether, in dioxane–water; see Figs. 1 and 2. The temperature of the thermostated cells containing the solutions of the complexes was set with a Beckman type thermometer with 0.01° C precision. The ionmeter readings were taken at 5 min intervals and averaged after 10–20 measurements.

The calculation of equilibrium constants was carried out with a PC computer on which the least squares fits and curve plotting were tested. Accordingly, the simulations and calculations and the corresponding plotting were carried out using the same tool with a BASIC compiler; the calculations were based on eqns. (5)–(7) (see Figs. 1–3).

RESULTS AND DISCUSSION

A knowledge of the direction and magnitude of the solvent effects is important for theoretical interpretations of ion selectivity and practical applications to synthesis and separations. In the presented work, a considerable solvent effect of water was displayed for 18-crown-6 owing to differences in K_e that depend on the solvent composition.

As was discussed by Cram, the binding power between the solvent and the host and that between the solvent and the guest is of similar type, in general, to those between the guest and the host. Accordingly, solvation free energy is composed of an enthalpy term favouring solvent binding and an entropy term opposed to solvent binding [3].

The equilibrium constants K_e of different ratios of complex formation could be expressed briefly as follows

$$n A^+ + mL \overset{K_e}{\rightleftarrows} A_n^+ L_m \tag{1}$$

$$K_e = [A_n^+ L_m] / [A^+]^n [L]^m \tag{2}$$

If $[A_0^+] = [L_0]$, then $P = [A_n^+ L_m] / \{[L_0] - (m-1)[A_n^+ L_m]\}$, since $[L_0] = [L] + m[A_n^+ L_m]$.

$$K_e = [A_n^+ L_m] / \{[A_0^+] - n[A_n^+ L_m]\}^n \{[L_0] - m[A_n^+ L_m]\}^m \tag{3}$$

If $P' = P / [1 + P(m-1)]$ is used for a simple expression of the com-

plexed ligand mole fraction, then K_e is given below

$$K_e = P'[L_0]/\{[L_0] - nP'[L_0]\}^n\{[L_0] - mP'[L_0]\}^m \tag{4}$$

$$1/K_e[L_0] = (1 - P')(1 - P')/P' \tag{5}$$

$$1/K_e[L_0]^2 = (1 - 2P')^2(1 - P')/P' \tag{6}$$

$$1/K_e[L_0]^{n+m-1} = (1 - nP')^n(1 - mP')^m/P' \tag{7}$$

where $[A_0^+]$ and $[L_0]$ are the identical initial cation and ligand concentrations, respectively; P is the experimental mole fraction of the complexed ligand or the cation, and n and m are the complexing degrees of both sides in the case of several degrees of complexing [eqns. (1)–(7)].

In our work we measured the power of sodium ion binding of 18-crown-6 for various ratios of water–dioxane solutions with a sodium cation selective electrode and a glass electrode at different temperatures; see Table 1. The use of eqns. (6) and (7) allowed us to obtain the equilibrium constants [9]. The P' value of a complexed ion or ligand mole fraction obtained by the analytical measurement was used to plot eqns. (5)–(7), and the slope gave the inverse of the equilibrium constant of the ion–dipole interaction. We observed primarily that an increasing amount of dioxane caused a higher power of ion binding, since the role of hydrogen bonding of water is diminished. Accordingly, a sodium complexed 18-crown-6 structure tested by ab initio calculation showed that the conformational energy is even higher with two moles more of water in a coordination shell [11]. Accordingly, in the dioxane–water–crown ether solutions, ions are most probably structured as axially complexed ion pairs [12] with a 1:1 ratio of unit-to-complex, since we also simulated the experimental mole fractions, P, for higher degrees of complexation stoichiometry from 1:2 to 3:3 and mostly linear relationships were verified; see Figs. 1–3.

TABLE 1

Equilibrium constants for 1:1, 1:2 and 2:2 $n:m$ ratio complexing of sodium chloride with 18-crown-6 in dioxane–water

Electrode	°C	Dioxan/water	log K_e	−ΔG	log K_e	−ΔG	log K_e	−ΔG
Na	10	50/50	2.25	1.266	7.62	4.287	13.05	7.338
	30	50/50	4.06	2.444	9.72	5.853	15.57	9.378
	50	50/50	5.23	3.336	11.20	7.191	17.66	11.336
	30	65/35	5.54	3.333	11.09	6.673	17.57	10.572
	30	75/25	5.67	3.417	11.72	7.061	18.52	11.152
Glass	10	50/50	3.95	2.224	9.59	5.392	15.39	8.654
	30	65/35	4.78	2.878	10.62	6.391	16.79	10.109
	30	75/25	4.98	3.003	10.86	6.539	17.15	10.328

TABLE 2

Equilibrium constants of NaCl complexing with 18-crown-6 in 1:1 (v/v) dioxane– water at 30°C measured with a sodium ion selective electrode. Equilibrium constants: $\log K_e(1:1) = 4.06$, $\log K_e(1:2) = 9.72$

$1/[L_0]$	P [a]	$(1-P')^2/P'$ [b]	Error [c]	$1/[L_0]^2$	$(1-P')(1-2P')^2/P'$	Error [d]
5	0.662	0.173	−0.008	25	0.062	−0.154
10	0.610	0.249	−0.018	100	0.096	−0.126
20	0.505	0.486	0.047	400	0.215	−0.025
40	0.379	1.020	0.064	2500	0.537	0.171
100	0.295	1.686	−0.131	10000	1.006	0.191
200	0.185	3.587	−0.046	40000	2.554	−0.058

[a] Experimental mole fraction of complexed ligand.
[b] Experimental data for 1:1 ratio, no least squares fitting.
[c] Experimental error for 1:1 ratio with least squares fitting (correlation coeff. 0.998).
[d] Experimental error for 1:2 ratio with least squares fitting (correlation coeff. 0.987).

However, our results for $\log K_e$ varied between 2.25 and 5.67 depending on the water–dioxane ratio for 1:1 complexation ratios.

The complex formation of 18-crown-6 with Na^+ in 1:1 and 1:2 stoichiometry has already been reported [1b,3,13]. However, we found that the second K_e is even larger then the first, which is strong evidence favouring the existence of axial charge separated (or ion paired) complex. We actually have further significant results to be reported [14].

The experimental values of complexed ligand mole fraction, P', were used for 1:1, 1:2 and 2:2 complexation stoichiometries and equilibrium constants K_e were obtained; see Table 2. However, over a large concentration range, any type of axial ion pairing structure and the degree of average aggregation should be affected by the mother solvent. In fact, this clearly explains the superior binding power of planar ionophores, such as spherands, as has been reported by Cram et al. [3]. It is interesting to mention that the reported $\log K_e$ value was 4.34 for 99% methanol medium [10]. This is in fact smaller than the value we found owing to the role of dioxane mixed with the water.

However, the formalism which we proposed for analytical work easily reveals the complexation mechanism for any type of ligand, as well as macrocylic host–guest interactions [3,9].

REFERENCES

1 (a) H.K. Frensdorff, J. Am. Chem. Soc., 93 (1971) 600. (b) I.M. Kolthoff and M.K. Chantooni, Anal. Chem., 52 (1980) 1039.
2 C.J. Pedersen, J. Am. Chem. Soc., 89 (1967) 7017.
3 D.J. Cram, Angew. Chem. Int. Ed. Engl., 25 (1986) 1039.
4 J.M. Lehn, Angew. Chem. Int. Ed. Engl., 27 (1988) 90.

5 T.E. Hogen Esch and J. Smid, J. Am. Chem. Soc., 91 (1969) 4580.

6 (a) J.J. Christensen, D. Sen, J.S. Bradshaw, S.A. Nielsen and R.M. Izatt, Chem. Rev., 85 (1985) 27. (b) J.D. Lamb, R.M. Izatt, C.S. Swain and J.J. Christensen, J. Am. Chem. Soc., 102 (1980) 475. (c) G. Michaux and J. Reisse, J. Am. Chem. Soc., 104 (1982) 6895. (d) G.W. Gokel and D.M. Dishong, J. Org. Chem., 47 (1982) 147.

7 B.D. Strasser, K. Hellenga and A.I. Popov, J. Am. Chem. Soc., 107 (1985) 789.

8 (a) Ç. Erk, Fresenius' Z. Anal. Chem., 316 (1983) 477. (b) Ç. Erk, Spectrosc. Lett. 18 (1985) 723. (c) E. Ozkan and Ç. Erk, Spectrosc. Lett., 19 (1986) 693. (d) K. Yurdakoç and Ç. Erk, Sepctrosc. Lett., 20 (1987) 983.

9 (a) Ç. Erk, J. Mol. Liquids, 37 (1988) 107. (b) Ç. Erk, Thermochim. Acta, 131 (1988) 125. (c) Ç. Erk, J. Mol. Liquids, 40 (1989) 143. (d) Ç. Erk, J. Mol. Liquids, (1990) in press.

10 (a) A.A. Kristin, and G.W. Gokel, J. Org. Chem., 51 (1986) 5015. (b) A.A. Kristin, L. Echegoyen and G.W. Gokel, J. Am. Chem. Soc., 109 (1987) 3713.

11 P. Kollman, Chem. Phys. Lett., 55 (1978) 555.

12 M. Szwarc, Pure Appl. Chem., 51 (1979) 49.

13 N.S. Poonia and A.V. Bajaj, Chem. Rev., 79 (1979) 389.

14 (a) Ç. Erk, Abstracts, IUPAC, 9th Physical Organic Chemistry Meeting, Regensburg, 1988. (b) Ç. Erk, Thermochim. Acta, (1990) in press.