Ultrasonic Absorption Kinetic Studies of the Complexation of Aqueous Potassium and Cesium Ions by 18-Crown-6

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Abstract: Reaction rate constants for a rapid conformational rearrangement of aqueous 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) and its slower complexation of potassium and cesium ions at 25 °C in aqueous solutions have been determined from ultrasonic absorption data covering the 9–340 MHz frequency range. A concentration-independent absorption with a maximum at ~100 MHz occurs in aqueous solutions of 18-crown-6 with no alkali metal cations present. This relaxation was attributed to a conformational rearrangement of the crown ether. Complexation of aqueous alkali metal ions by the polyether was then investigated kinetically at various polyether and metal ion concentrations with concentration-dependent relaxations occurring between ~10 and ~30 MHz. These data, together with the conformational rearrangement data, were analyzed in terms of a two-step mechanism (eq 1 and 4). The complexation rate constant k_{23} is the same for K^+ and Cs^+ and the relative stabilities of the complexes are determined by differences in the dissociation rate constants, k_{32}. Estimates of rate constants associated with a conformational equilibrium are made on mechanistic grounds, since the conformational equilibrium constant is unknown. Comparisons are made with results from prior studies of crown ether–metal ion systems.

The macrocyclic polyethers[2] exhibit a pronounced selectivity for the complexation of certain cations.[3] They have consequently found wide application in chemistry.[4-8]

Much work has already been done in elucidating the mechanism by which selective binding of cations to the polyethers occurs.[9-15] However, the complete kinetic mechanism has been difficult to establish because of a suspected, but not easily measurable, ultrarapid conformational rearrangement of the polyether prior to cation complexation.[9,12]

Since the macrocyclic polyethers do not absorb visible light and only the benzo compounds absorb ultraviolet light, with one exception[9] these systems have not been studied kinetically by the temperature jump or electric field jump relaxation methods. Most of the kinetic studies have been carried out instead by NMR techniques.[10-12,15] Aqueous 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) is particularly suitable for kinetic study by ultrasonic absorption techniques because of its high water solubility. Thus substantial ultrasonic absorptions occur in a solvent whose background ultrasonic properties are well known.

Infrared[16] and x-ray crystallographic studies[17] indicate that the macrocyclic polyethers exhibit different conformations in the complexed and uncomplexed states. These earlier results and his temperature jump relaxation method data led Chock[9] to postulate at least three configurations of dibenzo-30-crown-10: "(i) an unreactive species; (ii) an open configuration, which is the predominant species in the absence of cations; and (iii) a closed configuration, which is stabilized by a monovalent cation". Temperature-dependent spectra ($\lambda \simeq 280$ nm) indicated a conformation change, but the corresponding concentration-independent relaxation was too fast to measure ($\tau < 1\ \mu s$).

Large ring systems such as dibenzo-30-crown-10 can completely replace the first coordination sphere solvent molecules of a cation.[17] Thus dibenzo-30-crown-10 is wrapped round the potassium ion rather like the seam on a tennis ball. On the other hand, small rings such as 18-crown-6 or 15-crown-5 have their ether oxygens arranged in a plane about the cation with the axial positions available for interaction with solvent molecules or anions.

An ultrasonic absorption kinetic study of the complexation of aqueous potassium ion by 18-crown-6 was undertaken because both the postulated rapid relaxation time of the conformational change of the ligand and the slower complexation relaxation time should be accessible to this experimental technique. A similar kinetic study of cesium ion complexation by 18-crown-6 is also reported here (the results of which permit the assignment of an upper limit on the equilibrium constant for a conformational change of 18-crown-6).

Experimental Section

The ultrasonic absorption kinetic measurements were made at a temperature of 25.0 ± 0.1 °C using a laser acousto optical technique developed in this laboratory.[18] A key component is a 2-W CW argon ion laser (Spectra-Physics) used to produce a λ 514.5 nm sampling beam. Measurement of very low-amplitude absorptions and high-frequency absorptions (approaching 340 MHz) was facilitated by interfacing to a Digital Equipment Corporation PDP 11/10 computer. The acoustic beam was modulated by a lock-in procedure and adjustments in the ultrasonic transducer position, mirror positions, and reorientations of the sample cell plane to the Bragg angle were all computer controlled. In addition to a 5-MHz fundamental frequency X-cut quartz crystal for the 15–340 MHz ultrasonic frequency range, a 1-MHz crystal was employed in the low-frequency range (9–25 MHz).

Solutions were prepared with deionized, triply distilled water. The 18-crown-6 purchased from Parish Chemical Company was in the form of an acetonitrile complex. The pure polyether was obtained from this complex by pumping off the acetonitrile in a vacuum desiccator maintained at 1.3 Pa for three days. The uncomplexed product melted between 38 and 39 °C. Stock solutions of polyether prepared by weight were used to prepare all sample solutions by volume. These latter solutions were filtered through a 40F fritted glass disk. Potassium chloride was Mallinckrodt analytical reagent grade. Cesium chloride was Matheson, Coleman, and Bell 99% purity.

Results

No thermodynamic equilibrium constant K_{12} (= $[CR_2]/[CR_1]$) has been reported for a conformational change

$$CR_1 \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} CR_2 \qquad (1)$$

of pure aqueous 18-crown-6, where CR_1 and CR_2 denote, respectively, two different conformations of the monomeric macrocyclic polyether. However, Frensdorff[19] and Izatt[20] have reported molar equilibrium constants

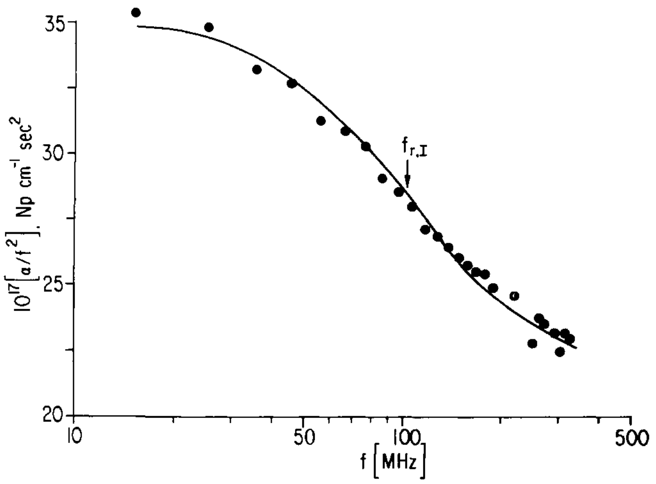

Figure 1. Plot of the ultrasonic absorption coefficient (α) divided by the square of the ultrasonic frequency (f) vs. frequency for an aqueous 0.50 M solution of 18-crown-6 with no salt added. Circles are experimental points.

Table II. Relaxation Parameters from Computer Analysis for Aqueous 18-Crown-6 at 25 °C[a]

[18-Crown-6], M	$f_{r,I}$, MHz	$10^{17} A$, Np cm^{-1} s^2	$10^{17} B$, Np cm^{-1} s^2	10^{18} rms[b]
1.0	97.72	33.23	25.00	1.3
0.75	101.97	15.21	25.13	1.8
0.50	99.78	13.54	21.59	0.7
0.375	103.25	12.12	20.25	0.9
$f_{r,I}$ average = 100.68 ± 3.25				

[a] All symbols as defined in text. [b] Root mean square deviation.

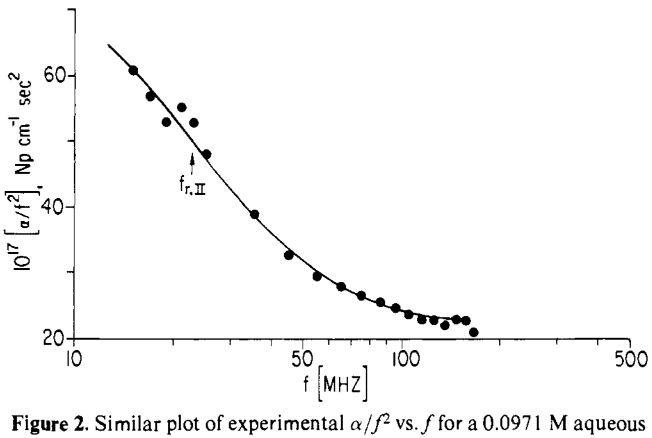

Figure 2. Similar plot of experimental α/f^2 vs. f for a 0.0971 M aqueous 18-crown-6 solution that is also 0.403 M in KCl.

Table IV. Relaxation Parameters from Computer Analysis for Aqueous Potassium Chloride and 18-Crown-6 at 25 °C[a]

$[K^+]_o$, M	[18-Crown-6]$_o$, M	$f_{r,II}$ MHz	$10^{17} A$, Np cm^{-1} s^2	10^{18} rms
0.403	0.0971	22.70	56.91	3.5
0.305	0.0958	15.35	114.1	1.6
0.0928	0.207	8.47	351.6	2.0
0.0439	0.107	5.33	379.8	5.5

[a] All symbols as defined in text.

$$K_T = [MCR_2^+]/[M^+][CR_1 + CR_2] \qquad (2)$$

where M^+ denotes a metal cation and MCR_2^+ the potassium ion complexed by 18-crown-6. Values found by these workers at 25 °C are log $K_T = 2.06 \pm 0.04$ and 2.03 ± 0.01, respectively. As will be shown, a knowledge of K_T is essential in assessing the significance of our ultrasonic absorption data. Since the crown ether is a nonelectrolyte, this equilibrium constant is not ionic strength dependent.

Figure 1 is a plot of the absorption coefficient α, in units of Np cm^{-1}, divided by the square of the ultrasonic frequency f vs. the frequency for a 0.5 M aqueous 18-crown-6 solution. The standard equation[21] for α/f^2 in terms of relaxational and nonrelaxational contributions to the ultrasonic absorption is

$$\alpha/f^2 = \sum_i A_i[1 + (f/f_{r,i})^2]^{-1} + B \qquad (3)$$

Here A_i is the relaxation amplitude of the ith process, f is the experimental frequency, $f_{r,i}$ is the relaxation frequency of the ith process, and B is the solvent absorption. As one can demonstrate by plotting the experimental data in Table I, the frequency of maximum absorption, 101 MHz for the solutions of 18-crown-6, is independent of concentration to within an experimental error of ±3 MHz (see Table II). As would be expected from solutions of increased viscosity, the background absorption (B) at high frequencies was above that of pure water alone, ranging from an increase of 4×10^{-17} Np cm^{-1} s^2 over water for the most concentrated solution (1 M) to no increase at 0.5 M.

Figure 2 shows a similar α/f^2 vs. f plot of ultrasonic absorption data (see Tables III and IV) for a 0.1 M aqueous 18-crown-6 solution that is also 0.4 M in KCl. The fact that no step is detected at 101 MHz is consistent with the fact that little free 18-crown-6 is present and the absorption of sound by free crown has a negligibly small amplitude compared to that by the potassium ion–crown complex. Since relatively high concentrations of electrolytes were employed (up to 0.4 M KCl), variable backgrounds were fitted to the data, and a $B = 21.7 \times 10^{-17}$ Np cm^{-1} s^2, essentially that of pure water,[22] always gave the best fit of the data.

Similar ultrasonic absorption data for aqueous solutions of cesium chloride and 18-crown-6 are presented in Tables V and VI.

Discussion

A mechanistic scheme

$$CR_1 \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} CR_2 \qquad (1)$$

$$M^+ + CR_2 \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} MCR_2^+ \qquad (4)$$

suggested by Chock[9] for the case of metal ion complexation by dibenzo-30-crown-10 in methanol can also be fitted to our 18-crown-6 experimental data. If the conformational change, eq 1, is very rapid compared to the complexation step, eq 4, the two relaxation times of this coupled system are given by

$$\tau_I^{-1} = 2\pi f_{I,r} = k_{12} + k_{21} \qquad (5)$$

$$\tau_{II}^{-1} = 2\pi f_{II,r} = k_{23}\left(([M^+]/(1 + K_{21})) + [CR_2]\right) + k_{32} \qquad (6)$$

wherein

$$K_{21} = [CR_1]/[CR_2] = k_{21}/k_{12} \qquad (7)$$

From the experimental concentrations and Frensdorff's value of $K_T = 10^{2.06}$ noted above, the equilibrium concentrations, $[K^+]$, $[KCR_2^+]$, and $[CR_1 + CR_2]$, can be calculated.

Equations 2, 5, and 6 could be solved analytically for the four rate constants if a value for K_{21} were known. No value has been reported. An attempt to calculate the rate constants by cyclic

Table VI. Relaxation Parameters from Computational Analysis for Aqueous Cesium Chloride and 18-Crown-6 at 25 °C[a]

$[Cs^+]_o$, M	$[18\text{-crown-6}]_o$, M	$f_{r,II}$ MHz	10^{17} A, Np cm^{-1} s^2	10^{18} rms
0.050[b]	0.100	12.51	132.56	3.1
0.100	0.100	16.07	131.92	2.2
0.2503	0.100	21.73	128.9	2.2
0.350	0.100	31.21	71.3	1.8
0.500	0.100	35.53	64.4	2.2

[a] All symbols as defined in text. [b] In the case of this first line of data where the most free crown was present a variable background was used with a best fit obtained with $B = 23.26 \times 10^{-17}$ Np cm^{-1} s^2.

Table VII. Equilibrium and Rate Constants Derived from Ultrasonic Absorption Data in Aqueous Solutions at 25 °C[a]

	K^+ plus 18-crown-6	Cs^+ plus 18-crown-6
K_{21}[c]	22.3	22.3
K_{23}[c]	2.7×10^3	1.8×10^2
k_{23}, M^{-1} s^{-1} [c]	1.0×10^{10}	7.8×10^9
k_{32}, s^{-1}	3.7×10^6	4.4×10^7
k_{12}, s^{-1} [b,c]	2.7×10^7	2.7×10^7
k_{21}, s^{-1} [b,c]	6.0×10^8	6.0×10^8

[a] All symbols as defined in text. [b] Calculated from the simultaneous equations $2\pi f_{r,I} = k_{12} + k_{21}$ and $K_{21} = k_{21}/k_{12}$, where $f_{r,I} = 101$ MHz (from Table II). [c] Upper limits, calculated assuming that the rate of complexation is truly diffusion controlled.

iteration on the eq 2, 5, and 6 is not successful, since the system is undetermined. However, with appropriate substitutions, eq 6 can be rewritten as

$$\tau_{II}^{-1} = (k_{23}/(1 + K_{21}))([M^+] + [CR_1 + CR_2]) + k_{32} \quad (8)$$

Given that $K_T = K_{23}/(1 + K_{21})$, eq 8 can be further simplified to

$$\tau_{II}^{-1} = k_{23}' ([M^+] + [CR_1 + CR_2] + K_T^{-1}) \quad (9)$$

where $k_{23}' = k_{23}/(1 + K_{21})$. Equation 9 gives a good fit to our experimental ultrasonic data for K^+ complexation (Figure 3), with a slope $k_{23}' = 4.3 \times 10^8$ M^{-1} s^{-1} and k_{32} equal to k_{23}'/K_T, has a value of 3.7×10^6 s^{-1}. The values for Cs^+ complexation are 4.3×10^8 M^{-1} s^{-1}, and 4.4×10^7 s^{-1}, respectively. For cesium complexation the more recent and precise value of log $K_T = 0.99 \pm 0.07$ from Izatt's laboratory[20] was used rather than Frensdorff's[19] value of 0.8. The relative stabilities of the metal-polyether complexes are obviously determined by the rates of dissociation only.

If the assumed mechanism is correct, then K_{21} is cation independent, in which case k_{23}' values are proportional to the k_{23} values for the respective cations.

It should be pointed out here that the observed rate constant k_{23}' is a lower limit for k_{23}. Since K_{21} must be greater than or equal to zero, then k_{23} is greater than or (when $K_{21} = 0$) equal to k_{23}'.

Since the k_{23}' values are equal for K^+ and Cs^+, the k_{23} values must also be equal. This equality for K^+ and Cs^+ complexation is quite different from observations[23] for K^+ and Cs^+ complexations with $EDTA^{4-}$ and NTA^{3-}. For example, with $EDTA^{4-}$ the values are 7.9×10^7 and 2.0×10^8 M^{-1} s^{-1}, respectively. For these polydentate ionic ligands the complexation mechanism is believed[23] to involve substitution of primary coordinated water on the cation. The present work and that of Chock[9] suggests that for polyether complexation a different process is rate determining.

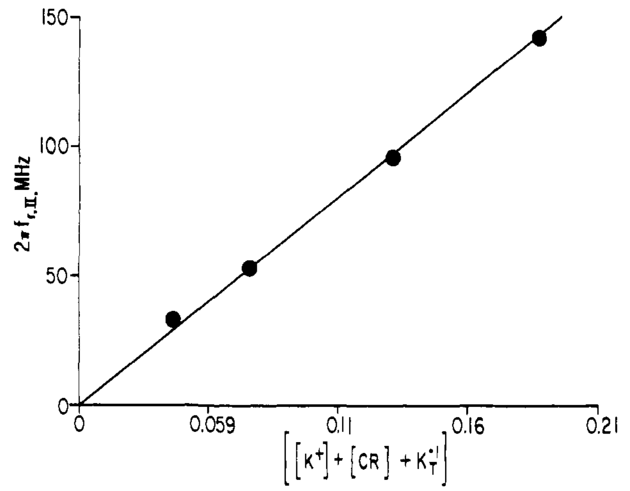

Figure 3. Plot of the reciprocal relaxation time $\tau_{II}^{-1} = 2\pi f_{r,II}$ vs. ($[K^+]$ + $[CR_1]$ + $[CR_2]$ + K_T^{-1}) for several aqueous solutions containing both KCl and 18-crown-6. The straight line is a linear least-squares fit of the experimental points. The diameter of the experimental points corresponds to the precision of the data.

Although it is not possible to derive a value for K_{21}, an upper limit can be assigned to it based upon mechanistic arguments. The von Smoluchowsky theoretical equation[24] for the maximum value of the rate constant of a diffusion-controlled reaction between an ion and a neutral molecule is

$$k_{23} = 4\pi N_A r_D (D_A + D_B) \quad (10)$$

N_A denotes Avogadro's number, r_D the distance of closest approach at which spontaneous reaction occurs, and D_A and D_B are the respective diffusion coefficients of the reacting species in the given solvent. No value of the diffusion coefficient for aqueous 18-crown-6 is available, but the literature indicates a reasonable value for similarly constituted neutral molecules is about one-third that for K^+. Thus taking $D_A = 2 \times 10^{-5}$ cm^2 s^{-1} for K^+ in water, $D_B \simeq 0.66 \times 10^{-5}$ cm^2 s^{-1} for 18-crown-6 in water, and assuming $r_D \simeq 5 \times 10^{-8}$ cm, an upper diffusion-controlled limit of $k_{23} = 1 \times 10^{10}$ M^{-1} s^{-1} is calculated. D_A for Cs^+ is 2.1×10^{-5} cm^2 s^{-1}, so the calculated k_{23} is essentially identical. If a diffusion-controlled mechanism is introduced to account for the constancy in k_{23}, then an upper limit to K_{21} is 22.3, such that the noncomplexing conformer, CR_1, is predominant in aqueous 18-crown-6 solutions. Using this upper limiting value for K_{21} of 22.3, the resultant maximum rate constants are: $k_{12} = 2.7 \times 10^7$; $k_{21} = 6.0 \times 10^8$; and $k_{23} = 1.0 \times 10^{10}$ M^{-1} s^{-1} for K^+.

The k_{23}' values reported[9] for K^+ and Cs^+ complexation with dibenzo-30-crown-10 in methanol (25 °C) are $(6 \pm 2) \times 10^8$ and $(8 \pm 1) \times 10^8$ M^{-1} s^{-1}, respectively. In order to make a comparison of K^+ complexation in methanol and water, a knowledge of how the diffusion coefficient varies is necessary. The diffusion coefficients for potassium ion are readily derivable[26] from limiting ionic conductances, which are $\lambda°$ 73.50 and 50.2 cm^2 ohm^{-1} $equiv^{-1}$ reported[25] for K^+ in water and methanol, respectively. The diffusion coefficient D is directly proportional to the limiting equivalent conductance $\lambda°$. Thus the expected rate of a diffusion-controlled reaction involving K^+ ion should be approximately 1.5 (= 73.5/50.2) times as rapid in water as in methanol if, as seems likely, the unreported diffusion coefficients of the crown ethers are smaller and experience the same decrease in a transfer from water to methanol. The k_{23}' for K^+ complexation with aqueous 18-crown-6 is smaller than that for K^+ complexation by methanolic dibenzo-30-crown-10. This is in the opposite direction of that to be expected if K$^+$ complexation with aqueous 18-crown-6 were a diffusion-controlled process. This comparison, however, neglects any possible variance in the equilibrium constants of the two crown ethers in the different solvents.

Our sum $k_{12} + k_{21} \simeq 6.3 \times 10^8\ \mathrm{s}^{-1}$ is of the same order as the corresponding sum, $2.5 \times 10^8\ \mathrm{s}^{-1}$, measured by Rhodes and Schimmel for a syn–anti rotation about the glycosidic bond of adenosine.[27,28] If temperature dependence kinetic data can be obtained over a sufficiently extended range for the macrocyclic polyether systems, it will be interesting to see whether there is a strong temperature dependence deduced for K_{21} analogous to that found by Hemmes et al.[29] for the syn–anti rotation of adenosine.

A recent low-temperature ^{39}K NMR kinetic study[10] of complexation of potassium ions by dibenzo-18-crown-6 in methanol agrees less satisfactorily with our results and those of Chock.[9] A $k_{32} = 610\ \mathrm{s}^{-1}$ at −34 °C extrapolated, using an activation energy of 12.6 kcal/mol, to 25 °C yields a $k_{32} = 1.1 \times 10^5\ \mathrm{s}^{-1}$. From Frensdorff's stability constant[19] $K_T = 10^{5.00}$, one may then calculate a $k_{23}' = 1.1 \times 10^{10}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ that is higher than our value for 18-crown-6 in water or Chock's value for dibenzo-30-crown-10 in methanol, though it equals the limiting value predicted by the von Smoluchowsky equation. In fairness it should be pointed out that in this ^{39}K complexation study the authors did not attempt this extrapolation.

As has been pointed out in several places[9,30] the near diffusion-controlled rate constants observed in the present work for the complexation of K$^+$ or Cs$^+$ by 18-crown-6 in water are consistent with a stepwise "redressing" mechanism for metal ion desolvation requiring flexibility in the polydentate ligand rather than with a complete stripping of solvent molecules from the metal cation prior to complexation. A process of the latter type would have a high activation energy inconsistent with the measured nearly diffusion-controlled kinetics.

It should be noted that if the complexation step were truly diffusion controlled it would be difficult to justify the equality of the complexation rates for K$^+$ and Cs$^+$. The similarity in the complexation rates suggest that there is a rate-determining step, such as a conformational rearrangement following first-bond formation.[31] Although a fast conformational rearrangement of 18-crown-6 ($\tau_I^{-1} = 6.3 \times 10^8\ \mathrm{s}^{-1}$) has been observed, this does not preclude the possibility of a slower conformational change upon complexation, since in this latter case the ligand is forced into a restricted rotation so as to effect second-bond formation. This is, however, a premature speculation and such a discussion must be deferred until the complexation kinetics of other cations with 18-crown-6 and a value of K_{21} have been reported.

As stated earlier, the relative stabilities of the metal–polyether complexes are determined by the rates of dissociation predominantly. This observation is in accord with other kinetic studies of the macrocyclic polyethers[12] and the macrocyclic polythioethers.[32]

The important contribution made by the present study is the identification and kinetic characterization of a fast conformational change in this comparatively simple crown ether, since such a conformational change must be present for the Eigen–Winkler stepwise desolvation mechanism to apply.

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Supplementary Material Available: Tables I, III, and V, containing experimental absorption data (6 pages). Ordering information is given on any current masthead page.

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