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DYNAMICS OF A CONFORMATIONAL CHANGE IN AQUEOUS 18-CROWN-6 BY AN ULTRASONIC ABSORPTION METHOD

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by

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Introduction

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Introduction

Macrocyclic polyethers exist in solution in at least two, and more probably, three conformations. These three conformations are [1]: "(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." This description was given for dibenzo-30-crown-10 and has recently been borne out by an H^1 and C^{13} nmr study of 18-crown-6, benzo-18-crown-6, dibenzo-18-crown -6, and dibenzo-30-crown-10 in their complexed and uncomplexed states in various solvents [2]. The nmr data indicate that in the absence of complexing cations these macrocycles undergo a rapid syn- to anti gauche rotamer conversion with an interconversion rate faster than 10^3 sec.$^{-1}$ In addition, a rapid rotamer interconversion of the ether linkages in the complexed crown ethers is observed with a slowing of the rate in $CDCl_3$. Benzo substituents in the ring do not affect these structural observations.

Chock [1] wrote the following mechanistic scheme for crown ether complexation

$$(1)\quad CR_1 \underset{\leftarrow}{\overset{k_{12}}{\rightleftarrows}} CR_2$$

$$(2)\quad CR_2 + M^{n+} \underset{\leftarrow}{\overset{k_{23}}{\rightleftarrows}} \text{Complex}$$

where CR_1 is the unreactive crown ether species, M^{n+} denotes a metal ion, etc. He further observed that the complexation of dibenzo-30-crown-10, in methanol, was preceded by a fast conformational rearrangement of the ligand ($\tau<1$ μsec). Conformational rearrangements of aqueous 18-crown-6 and 15-crown-5 have since been observed with relaxation times of 1.6 and 6.9 ns, respectively [3,4]. In these recent studies the above reaction scheme, eqs. (1) and (2), was used to analyze successfully the measured relaxation times.

Equilibrium constants for the rapid conformational rearrangement of the uncomplexed crown ethers, eq. (1), have not been published. The transient relaxation methods have proven useful in establishing the thermodynamics for such transitions [5] with quite reasonable accuracy. It should be noted that the thermodynamic parameters are obtained from amplitude data and not relaxation times. Unfortunately, the conformational rearrangements of some, if not all, of the crown ethers are too rapid to be investigated by readily available transient methods. Use of

ultrasonic absorption [6] (a stationary relaxation method) in determining thermodynamic properties has been challenged [7] because of certain necessary assumptions. However, ultrasonic methods have appeared lately [8,9] that seem to yield reliable thermodynamic data. The method of Farber and Petrucci [9] is the simplest, stringent method and has been utilized in this study to obtain the thermodynamic parameters for the conformational equilibrium, eq. (1), of aqueous 18-crown-6.

A knowledge of the conformational equilibrium constant is quite important since in the above reaction scheme, eqs. (1) and (2), the experimentally determined rate constant, k'_{23}, is related to the specific rate, k_{23}, of the second discrete reaction step by the relation [3]:

$$(3)\quad k'_{23} = \frac{k_{23}}{1 + K_{21}}$$

where K_{21} is the conformational equilibrium constant for reaction (1). If K_{21} is relatively large then k_{23} must be significantly larger than k'_{23}. Also it has been suggested [10] that the barrier to dissociation of the Na^+ - dibenzo-18-crown-6 complex is just the energy required to effect a conformational rearrangement of the crown ether complex. Thus a comparison of the activation energy barrier for the conformational equilibrium with that observed for the dissociation of the aqueous K^+ - 18-crown-6 complex might lend some credence to this hypothesis.

In the present work we have applied measured relaxation times, amplitudes and sound velocities, at several temperatures, obtained from ultrasonic absorption measurements of the uncomplexed aqueous 18-crown-6, to the determination of the equilibrium constant and the thermodynamic and activation parameters for a conformational change of this cyclic polyether. New data on the temperature dependence of the complexation-decomplexation rates of aqueous potassium ions with 18-crown-6 have been included to provide activation parameters susceptible to comparison with those of the ligand conformational change.

Experimental

The 18-crown-6 was purchased (Parish Chemical Corp., Provo, UT) as an acetonitrile complex. The acetonitrile was removed under vacuum desiccation (1.3 Pa) for three days. The sharp melting point of the pure polyether was 38-39° (lit. [11] 39-40°). All solutions were prepared with triply distilled, deionized water. The potassium chloride was reagent grade.

Ultrasonic absorption measurements were made using a laser acousto-optic technique [12] between 15 and 255 MHz at the odd harmonics of a 5 MHz quartz crystal. Velocity measurements, made by an interferometric technique after a minor modification of the same ultrasonic apparatus, had an accuracy of 0.1 meter sec^{-1}. Density measurements were made using a 10 ml Kimax-Brand pycnometer, calibrated with pure water at 25.0 ± 0.1°. Sample temperatures were maintained constant to at least ± 0.3° with a Lauda K-2/RD circulating bath.

Results

The absorption coefficient α measured at each frequency f was cast in the form, α/f^2. Relaxation parameters were then obtained from the equation

$$(4)\quad \alpha/f^2 = \sum_i A_i \left[1 + (f/f_{r,i})^2\right]^{-1} + B$$

In all cases B was not known and was treated as an added parameter when solving eq. (4). Only one relaxation was observed so i=1. Concentrations of aqueous 18-crown-6 investigated were 1.00, 0.750, and 0.500 M at temperatures of 16.3° ± 0.3°, 25.0 ± 0.1° (see ref. 3 for data), 30.8° ± 0.3°, and 35.4° ± 0.1°. Table I lists experimental α/f^2 values at various frequencies and temperatures for the investigated concentrations. Table II presents measured velocities, densities, relaxation frequencies, amplitudes, and background B for each concentration at the indicated temperatures.

Table III contains the experimental α/f^2 values and the corresponding frequencies for each concentration of aqueous potassium-18-crown-6 and Table IV gives the resultant absorption amplitudes and relaxation frequencies. For the aqueous potassium-18-crown-

6 system the background absorption, B, was determined from α/f^2 for water at each of the various temperatures (see reference [3] for 25.0° data).

The method of obtaining the thermodynamic and activation parameters for the conformational change is that used by Farber and Petrucci [9] which in turn is partially based on a method devised by Lamb [13]. Only an outline of the thermodynamic and activation parameter analysis will be presented here:

(i) Plot $\ln (\frac{\tau^{-1}}{T})$ vs $(\frac{1}{T})$ from which the slope, m, and intercept, b, are respectively

$$m = \frac{-\Delta H_{21}^{\neq}}{R} - (\frac{K_{12}}{1+K_{12}}) \frac{\Delta H^{o}}{R}$$

$$b = \ln (\frac{k}{h}) + \frac{\Delta S_{21}^{\neq}}{R}$$

where k is the Boltzmann constant, h Planck's constant, and R the gas constant.

(ii) Evaluate $\frac{K_{12}}{1+K_{12}} \frac{\Delta H^{o}}{R}$ from the slope of a plot of $\ln (\frac{(\alpha\lambda)^{ch}_{max} T}{\rho u^2})$ vs $(\frac{1}{T})$

where ρ is the density of the solution, u is the velocity of sound and $(\alpha\lambda)^{ch}_{max}$ is the ultrasonic absorption per wave length at the relaxation frequency, due to the chemical transformation. In this case the slope and intercept are given by

$$m = \left(\frac{K_{12}}{1+K_{12}}\right) \frac{\Delta H^{o}}{R}$$

and

$$b = \ln \left(\frac{\pi \Delta V^2}{2R} [CR_2] \right)$$

(iii) Using the slope in step (ii) evaluate $\Delta H_{21}^{\neq}$ and $\Delta S_{21}^{\neq}$ via the slope and intercept in step (i). ΔV may be evaluated from the intercept in step (ii).

(iv) Evaluate the first-order rate constant k_{21} from the relation

$$k_{21} = (\frac{kT}{h}) \exp [\frac{-\Delta H_{21}^{\neq}}{RT}] \exp [\frac{\Delta S_{21}^{\neq}}{R}]$$

(v) Since τ^{-1} is known from ultrasonic measurements, K_{12} is obtained from the relation

$$K_{12} = \frac{\tau^{-1}}{k_{21}} - 1$$

(vi) If $K_{21} << 1$ then a plot of $\ln (\frac{\tau^{-1}}{T})$ vs $(\frac{1}{T})$ has a slope

and an intercept

$$b = \ln\left(\frac{k}{h}\right) + \frac{\Delta S_{12}^{\neq}}{R}$$

since

$$\tau^{-1} = k_{12}\,(1 + K_{21}) \simeq k_{12}$$

Figures 1 and 2 are plots of $\ln(\tau^{-1}/T)$ vs $\left(\frac{1}{T}\right)$ and $\ln\left(\frac{(\alpha\lambda)^{ch}_{max}\,T}{\rho u^2}\right)$ vs $\left(\frac{1}{T}\right)$ while Table V is a listing of the resultant values.

The reaction mechanism previously discussed, eqs. (1) and (2), was used to analyze the relaxation times for the potassium-18-crown-6 complexation study. Figure 3 is a least squares plot of τ_2^{-1} versus a concentration term at three temperatures from which the complexation and decomplexation specific rates were obtained. Table VI contains the resultant complexation and decomplexation rates together with the activation parameters. Note that since $K_{21} = 1.6 \times 10^{-2}$ the observed complexation rate is equal to the discrete step specific rate. Thus a plot of k_{23} vs $1/\tau$ will not be influenced by the temperature dependence of K_{21}.

Discussion

Table V has several interesting features. The first and most important is that K_{21} has a value of $2\ (\pm 2) \times 10^{-2}$, much less than unity. Thus previously reported [3,14] observed complexation rate constants k'_{23} $\left(= \frac{k_{23}}{1 + K_{21}}\right)$ equal, within experimental error, the specific rate constant for aqueous 18-crown-6 complexation. In addition, since $[CR_1] \simeq 10^{-2}\,[CR_2]$, the relaxation time for the complexation step of aqueous 18-crown-6 may be written in the particularly simple form

$$(5)\quad \tau_2^{-1} = k_{23}\left([CR_2] + [M^{n+}]\right) + k_{32}$$

This is the appropriate equation if reactions 1 and 2 occur independent of one another as for example would be true if the first equilibrium, eq. (1), is shifted predominantly to the complexing form so that a pertubation of the second reaction, eq. (2), cannot appreciably affect the first reaction, eq. (1). Alternatively, this

same conclusion may be arrived at by considering the roots of the secular determinant for the two reactions [eqs. (1) and (2)].

$$(6)\quad \frac{1}{\tau_{I,II}} = \lambda_{I,II} = \frac{1}{2}\left[a_{11} + a_{22} \pm \sqrt{(a_{11} - a_{22})^2 + 4a_{12}a_{21}}\right]$$

where

$$a_{11} = \tau_I^{-1} = k_{12} + k_{21}$$

$$a_{22} = \tau_{II}^{-1} = k_{23}\left([CR_2] + [M^{n+}]\right) + k_{32}$$

$$a_{12} = -k_{21}$$

$$a_{21} = -k_{23}[M^{n+}].$$

As is clear from Table VII (where values of a_{11}, a_{12}, a_{21} and a_{22} are listed)

$$(a_{11} - a_{22})^2 >> 4\, a_{12}\, a_{21}$$

so that eq. (6) becomes

$$(7)\quad \tau_I^{-1} = a_{11} = k_{12} + k_{21}$$

$$(8)\quad \tau_{II}^{-1} = a_{22} = k_{23}\left([M^{n+}] + [CR_2]\right) + k_{32}$$

The following relationship exists between the overall thermodynamic equilibrium constant K_T and the two equilibrium constants already considered:

$$(9)\quad K_T = \frac{K_{23}}{1 + K_{21}}$$

Since $K_{21} = 1.6 \times 10^{-2}$, eq. (9) simplifies to

$$(10)\quad K_T = K_{23}$$

From the observation that reactions (1) and (2) are uncoupled, the normal reactions and amplitude factors Γ_i may be determined. These are [4]

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

$$(11)\quad \left(\frac{a_{12}}{a_{22}-a_{11}}\right)\ CR_1 + M^{n+} \underset{\leftarrow}{\overset{k_{23}}{\rightleftharpoons}} \text{Complex} + \left[\frac{a_{12}}{a_{22}-a_{11}} - 1\right]\ CR_2$$

$$(12)\quad \Gamma_1 = \left[\frac{1}{[CR_1]} + \frac{1}{[CR_2]}\right]^{-1}$$

$$(13)\quad \Gamma_2 = \left[\frac{\left(\frac{a_{12}}{a_{22}-a_{11}}\right)^2}{[CR_1]} + \frac{1}{[M^{n+}]} + \frac{1}{[\text{Complex}]} + \frac{\left(\frac{a_{12}}{a_{22}-a_{11}} - 1\right)^2}{[CR_2]}\right]^{-1}$$

Table VII lists values of Γ_2 based on earlier data [3] and the above equations. With the relation [15]

$$(14)\quad (\alpha/f^2)^{ch}_{max} = \frac{2\pi^2\rho u}{RT}\ (\Delta V)_i^2\ \Gamma_i\ \tau_i$$

wherein the subscript i = 2 for the case of interest to us here the Γ_2 values in Table VII may be used to determine the $(\Delta V)^2$ and thus the magnitude $|\Delta V|$ for each cation studied in ref. [3] and [14]. Values of ρ and u are taken to be those of water since the solutions are relatively dilute.

Finally the magnitude of $|\Delta V|$ for the conformational step is evaluated from the intercept of $\ln\left(\frac{(\alpha\lambda)^{ch}_{max}\ T}{2}\right)$ vs $\left(\frac{1}{T}\right)$ as discussed in step (ii) of "Results". Table VIII lists the $|\Delta V|$ for each cation and the conformational change.

It is interesting to compare $|\Delta V|$ values in Table VIII for the various cations since this represents an overall volume change for the complexation reaction step. Fig. 4 is a plot of $|\Delta V|$ versus reciprocal ionic radius for the cations studied. The pattern in $|\Delta V|$ vs $\frac{1}{r}$ closely parallels that for the stability constants vs $\frac{1}{r}$. Fig. 5 is a linear least squares line for log K_T versus $|\Delta V|$. Except for the sodium ion (and lithium ion, which is not plotted because only a limiting value of K_T has been reported) the fit is excellent: The greater the volume change for formation of complex ion, the greater the stability of the complex A speculative explanation for the failure of sodium and lithium ions to fit this correlation for 18-crown-6 is that the ring size is too large to compete successfully with solvent for

first coordination sphere sites on these smaller metal ions.

Turning now to the activation parameters, the enthalpy of activation and therefore activation energy for $CR_2 \rightarrow CR_1$ (Table V) closely resembles that for CR_2K^+ dissociation (Table VI). This similarity suggests that the hypothesis that the barrier to decomplexation is simply the energy required to effect a conformational rearrangement of the ligand [10] may have some merit. It is at least qualitatively consistent with the conclusion of an nmr study [2] that a rapid ($\tau < 10^{-3}$ sec) rotamer interconversion of ether linkages in free crown ethers persists in the metal ion complexes though on a somewhat longer time scale.

If the rate determining step in the decomplexation of metal ion by crown ether is a conformational change of the ligand, the activation energy for the decomplexation reaction should be the same for all cations dissociating from a particular crown ether. Using simple absolute rate theory, it is possible to deduce from recent nmr kinetic data [10,16] that in methanol the activation enthalpy and entropy of decomplexation are 12.0 kcal/(mol) and 4.83 e.u. for K^+ - dibenzo-18-crown-6 (DBC-6) and 11.1 kcal/(mol) and -2.3 e.u. for Na^+ - DBC6. The decomplexation rate for Na^+ - DBC6 in methanol, is 1.4×10^4 sec^{-1} and for K^+ - DBC6 it is 1.1×10^5 sec^{-1} (extrapolated to room temperature). While the similarity of these $\Delta H^{\neq}$ values is interesting, a more persuasive argument would have to be based on kinetic data for a single crown ether reacting with more than two metal ions and in several different solvents over a substantial temperature range.

Finally, if the rate of decomplexation of cations by crown ether does indeed determine the size of stability constants [3,4,14] yet the activation enthalpies for decomplexation are very similar if not actually identical, it is clear that variations in stability constants are determined by $\Delta S^{\neq}$ for decomplexation.

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Table I

Experimental Ultrasonic Absorption Data as (α/f^2) and Frequencies for Aqueous 18-Crown-6 at 16.28°

[18-Crown-6] = 1.00 M		[18-Crown-6] = 0.750 M	
$10^{17}\{\alpha/f^2\}$ exptl., Np cm^{-1} sec^2	f, MHz	$10^{17}\{\alpha/f^2\}$ exptl., Np cm^{-1} sec^2	f, MHz
108.0	15.19	76.14	15.10
87.05	25.20	63.41	25.23
79.04	35.30	60.02	35.32
73.15	45.50	54.81	45.51
68.49	55.57	51.72	55.53
64.58	65.67	48.15	65.63
61.01	75.76	47.23	75.74
58.97	85.88	45.84	85.84
56.74	95.92	44.31	95.94
54.57	106.0	40.07	106.1
49.82	116.1	38.40	116.2

Table I (Continued)

[18-Crown-6] = 0.500 M

$10^{17}\{\alpha/f^2\}$ exptl., Np cm^{-1} sec^2	f, MHz
60.05	15.18
53.12	25.28
46.52	35.28
43.94	45.46
42.97	55.57
41.33	65.68
39.96	75.78
38.20	85.89
38.12	95.99
37.11	106.1
36.53	116.2

Table I (Continued)

Experimental Ultrasonic Absorption Data as (α/f^2) and Frequencies for Aqueous 18-Crown-6 at [illegible]°

[18-Crown-6] = 1.00 M		[18-Crown-6] = 0.750 M	
$10^{17}\{\alpha/f^2\}$ exptl., Np cm^{-1} sec^2	f, MHz	$10^{17}\{\alpha/f^2\}$ exptl., Np cm^{-1} sec^2	f, MHz
45.51	15.12	37.69	15.12
44.97	25.21	38.11	25.20
42.72	35.30	37.57	35.28
42.62	45.44	36.32	45.44
41.25	55.51	34.99	55.51
41.16	65.60	34.04	65.60
38.85	75.69	33.55	75.69
38.36	85.78	33.01	85.79
36.79	95.86	31.40	95.88
35.57	106.0	30.47	105.9
35.17	116.0	30.22	116.0
34.52	126.1	29.37	126.1
33.29	136.3	29.06	136.2
32.14	146.3	28.18	146.3
31.94	156.4	27.60	156.4
30.16	166.5	26.82	166.5
29.75	176.7	26.37	176.6
30.12	186.7	27.73	186.7
30.17	196.8	26.42	196.8
28.58	206.8	25.78	206.9
		25.82	217.0
		25.11	227.0
		24.66	237.1
		23.40	247.2
		23.29	257.3

Table I (Continued)

[18-Crown-6] = 0.500 M		[18-Crown-6] = 0.500 M	
$10^{17}\{\alpha/f^2\}$ exptl., Np cm^{-1} sec^2	f,MHz	$10^{17}\{\alpha/f^2\}$ exptl., Np cm^{-1} sec^2	f,MHz
29.24	15.10	19.00	247.2
30.30	25.21	18.49	257.4
29.60	35.30	18.68	267.5
28.90	45.45	18.00	277.6
28.34	55.51	18.14	287.7
27.49	65.60		
26.17	75.69		
26.67	85.79		
25.89	95.86		
25.07	105.9		
24.44	116.0		
24.21	126.1		
22.95	136.2		
23.59	146.3		
23.15	156.4		
22.39	166.5		
22.42	176.6		
21.93	186.7		
21.86	196.8		
21.10	206.9		
21.68	217.0		
20.67	227.1		
20.87	237.2		

Table I (Continued)

Experimental Ultrasonic Absorption Data as (α/f^2) and Frequencies for Aqueous 18-Crown-6 at 35.4°

[18-Crown-6] = 1.00 M		[18-Crown-6] = 0.750 M	
$10^{17}\{\alpha/f^2\}$ exptl., Np cm^{-1} sec^2	f,MHz	$10^{17}\{\alpha/f^2\}$ exptl., Np cm^{-1} sec^2	f,MHz
46.75	15.10	33.26	15.11
44.06	25.22	33.59	25.20
43.32	35.30	33.48	35.28
42.45	45.44	32.83	45.46
41.44	55.50	32.05	55.51
40.81	65.59	31.46	65.61
39.72	75.68	31.09	75.70
39.19	85.79	29.78	85.80
37.23	95.88	28.99	95.88
36.52	106.0	28.96	106.0
35.03	116.1	27.81	116.1
34.25	126.2	26.85	126.2
33.59	136.3	26.56	136.2
32.48	146.4	25.44	145.3
32.49	156.5	25.67	156.4
31.49	166.6	25.41	166.5
31.00	176.7	23.44	176.6
30.63	186.7	24.18	186.7
29.81	196.8	23.80	196.7
29.77	207.1	22.58	206.8
		22.65	216.9

Table I (Continued)

[18-Crown-6] = 0.500 M

$10^{17} \alpha/f^2$ exptl., Kp cm^{-1} sec^2	f, MHz
25.15	25.19
25.93	35.27
24.94	45.45
24.65	55.51
24.15	65.59
23.93	75.69
23.36	85.73
22.98	95.85
22.29	105.9
22.27	116.0
20.93	126.1
20.97	136.2
21.06	146.3
21.50	156.4
20.15	166.5

Table II

Ultrasonic Parameters for the Conformational Equilibrium of Aqueous 18-Crown-6

$CR_1 \rightleftarrows CR_2$

Conc., M	Temp, °C	f_r, MHz	A, 10^{-17} Np $cm^{-1}sec^2$	B, 10^{-17} Np $cm^{-1}sec^2$	u, 10^5 cm sec^{-1}	Density gcm^{-3}
1.0	16.3° ± 0.3°	62.92 ± 6.0	53.44	41.63	169540 ± 30	1.057[a]
0.75	16.3° ± 0.3°	62.92 ± 6.0	36.07	31.00	164640 ± 30	1.051[a]
0.50	16.3° ± 0.3°	62.92 ± 6.0	18.26	32.31	158060 ± 30	1.029[a]
1.0	25.0° ± 0.1°	100.7 ± 3.3	33.23	25.00	168440 ± 10	1.053 ± 0.002
0.75	25.0° ± 0.1°	100.7 ± 3.3	15.21	25.13	164250 ± 10	1.048 ± 0.002
0.50	25.0° ± 0.1°	100.7 ± 3.3	13.54	21.59	159240 ± 10	1.025 ± 0.002
1.0	30.8° ± 0.3°	129.9 ± 6.0	23.7	21.7	167790 ± 10	1.050 ± 0.002
0.75	30.8° ± 0.3°	129.9 ± 6.0	16.44	21.5	164410 ± 10	1.046 ± 0.002
0.50	30.8° ± 0.3°	129.9 ± 6.0	11.89	21.0	160100 ± 10	1.023 ± 0.002
1.0	35.4° ± 0.1°	153.9 ± 7.0	21.45	19.00	167610 ± 30	1.048 ± 0.002
0.75	35.4° ± 0.1°	153.9 ± 7.0	17.33	16.28	164420 ± 30	1.043 ± 0.002
0.50	35.4° ± 0.1°	153.9 ± 7.0	9.28	16.38	160280 ± 30	1.021 ± 0.002

[a]Estimated value

Table III

Experimental Ultrasonic Absorption Data, (α/f^2), and Frequencies for Aqueous Potassium Chloride and 18-Crown-6 at 35.7°

$[K^+]_o^a$ = 0.403 F, $[18\text{-Crown-6}]_o^a$ = 0.0971 M		$[K^+]_o^a$ = 0.305 F, $[18\text{-Crown-6}]_o^a$ = 0.0958 M	
$10^{17}\{\alpha/f^2\}$ exptl., Np cm^{-1} sec^2	f, MHz	$10^{17}\{\alpha/f^2\}$ exptl., Np cm^{-1} sec^2	f, MHz
58.11	15.08	82.45	15.10
50.36	25.13	63.23	25.15
40.09	35.19	44.95	35.17
33.80	45.30	35.60	45.31
30.45	55.36	30.28	55.35
26.84	65.41	27.05	65.41
25.14	75.48	24.93	75.47
23.12	85.54	23.40	85.52
22.09	95.61	21.79	95.60
20.64	105.6	20.84	105.7
20.14	115.7	20.11	115.7
18.90	125.8	18.54	125.8
18.36	135.8	17.84	135.8
18.04	145.9	18.18	145.9
18.45	155.9	17.49	156.0
		17.52	166.0
		17.87	176.1
		17.08	186.1
		17.39	196.2

[a]Subscript zero denotes initial concentration in this and subsequent tables.

Table III (Continued)

$[K^+]_o^a = 0.0928$ F, $[18\text{-Crown-6}]_o^a = 0.207$ M		$[K^+]_o^a = 0.0439$ F, $[18\text{-Crown-6}]_o^a = 0.107$ M	
$10^{17}\{\alpha/f^2\}$ exptl., Np $cm^{-1}sec^2$	f,MHz	$10^{17}\{\alpha/f^2\}$ exptl., Np $cm^{-1}sec^2$	f,MHz
135.1	15.10	88.83	15.08
69.08	25.15	50.43	25.14
44.69	35.18	34.85	35.19
34.44	45.29	27.95	45.28
29.71	55.35	24.70	55.34
26.46	65.41	22.75	65.40
23.85	75.48	21.40	75.47
23.18	85.52	19.73	85.53
21.17	95.58	19.79	95.57
19.93	105.6	19.04	105.6
19.15	115.7	18.88	115.7
18.90	125.8	18.15	125.8
18.21	135.8	18.17	135.8
18.18	145.9	17.59	145.9
17.55	155.9	17.31	155.9
17.19	166.0	17.46	166.0
17.42	176.1	17.17	176.1
		17.25	186.1
		16.63	196.2

Table III (Continued)

Experimental Ultrasonic Absorption Data as (α/f^2) and Frequencies for Aqueous Potassium Chloride and 18-Crown-6 at 40.3°

$[K^+]_o$ = 0.403 F, $[18\text{-Crown-6}]_o$ = 0.0971 M		$[K^+]_o$ = 0.305 F, $[18\text{-Crown-6}]_o$ = 0.0958 M	
$10^{17}\{\alpha/f^2\}$ exptl., Np $cm^{-1}sec^2$	f, MHz	$10^{17}\{\alpha/f^2\}$ exptl., Np $cm^{-1}sec^2$	f, MHz
75.54	15.07	93.74	15.06
54.52	25.12	69.04	25.10
42.52	35.18	49.90	35.15
36.00	45.29	38.96	45.25
31.20	55.33	32.01	55.30
27.47	65.39	28.45	65.36
24.93	75.45	24.33	75.42
23.04	85.50	22.80	85.47
20.69	95.55	21.63	95.52
19.95	105.6	20.45	105.6
19.20	115.7	19.49	115.6
18.25	125.7	18.21	125.7
17.55	135.8	17.90	135.7
17.17	145.9	17.02	145.8
16.62	155.9	16.75	155.8
16.35	166.0	16.33	165.9
16.08	176.0	15.50	176.0
15.66	196.2		

Table III (Continued)

$[K^+]_o$ = 0.0929 F, [18-Crown-6]$_o$ = 0.207 M		$[K^+]_o$ = 0.0439 F, [18-Crown-6]$_o$ = 0.107 M	
$10^{17}\{\alpha/f^2\}$ exptl., Np cm^{-1}sec^2	f, MHz	$10^{17}\{\alpha/f^2\}$ exptl., Np cm^{-1}sec^2	f, MHz
162.8	15.06	118.2	15.09
77.33	25.11	56.82	25.15
49.40	35.16	38.92	35.17
36.56	45.21	29.30	45.28
29.62	55.26	25.84	55.34
26.29	65.32	22.49	65.40
23.63	75.39	21.81	75.46
21.04	85.44	20.47	85.51
20.74	95.49	19.31	95.57
18.99	105.5	18.65	105.6
18.20	115.6	18.16	115.7
17.57	125.6	17.79	125.7
17.00	135.7	17.09	135.8
16.56	155.8	16.61	145.9
16.58	165.9	16.50	155.9
15.90	175.9	15.98	166.0
15.13	186.0	16.78	176.0
		15.40	186.1

Table III (Continued)

Experimental Ultrasonic Absorption Data (α/f^2) and Frequencies for Aqueous Potassium Chloride and 18-Crown-6 at 45.8°

$[K^+]_o$ = 0.403 F, $[18\text{-Crown-6}]_o$ = 0.0971 M		$[K^+]_o$ = 0.305 F, $[18\text{-Crown-6}]_o$ = 0.0958 M	
$10^{17}\{\alpha/f^2\}$ exptl., Np cm^{-1} sec^2	f, MHz	$10^{17}\{\alpha/f^2\}$ exptl., Np cm^{-1} sec^2	f, MHz
68.13	15.09	94.16	15.07
56.73	25.15	70.88	25.12
44.88	35.18	51.18	35.17
36.10	45.25	40.36	45.28
29.97	55.31	34.42	55.32
27.26	65.37	28.75	65.38
25.21	75.43	25.14	75.43
23.04	85.49	22.81	85.49
20.91	95.55	21.17	95.55
19.60	105.6	19.59	105.6
18.16	115.7	18.76	115.7
17.33	125.7	17.27	125.7
16.76	135.8	16.71	135.8
16.03	145.8	16.34	145.8
15.69	155.9	16.03	155.9
15.52	166.0	15.86	166.0
		15.27	176.0
		15.69	186.1
		14.81	196.1

Table III (Continued)

$[K^+]_o$ = 0.0928 F, [18-Crown-6]$_o$ = 0.207 M		$[K^+]_o$ = 0.0439 F, [18-Crown-6]$_o$ = 0.107 M	
$10^{17}\{\alpha/f^2\}$ exptl., Np cm^{-1}sec^2	f,MHz	$10^{17}\{\alpha/f^2\}$ exptl., Np cm^{-1}sec^2	f,MHz
169.4	15.08	113.1	15.10
85.12	25.13	60.28	25.14
52.54	35.19	40.32	35.19
38.95	45.24	31.31	45.26
31.80	55.29	25.66	55.32
26.68	65.35	22.25	65.38
23.64	75.42	20.47	75.44
21.33	85.47	19.10	85.50
20.52	95.52	18.21	95.56
18.55	105.6	16.90	105.6
18.42	115.6	16.43	115.7
17.45	125.7	15.76	125.7
17.00	135.7	15.48	135.8
15.89	145.8	14.86	145.8
15.65	155.9	14.42	155.9
15.40	166.0	14.10	165.9
14.48	176.0	14.02	176.0
15.31	186.1	14.02	186.1
14.37	196.2	13.79	196.1

Table IV

Relaxation Parameters from Computer Analysis for Aqueous Potassium Chloride and 18-Crown-6 at 35.7, 40.3 and 45.8°[a]

$[K^+]_o$, F	$[18\text{-Crown-6}]_o$, M	f_r[b], MHz	10^{17} A[c,d] Np $cm^{-1}sec^2$	10^{17} R.M.S.[e]
0.403	0.0971	28.50, 27.80, 34.97	65.45, 77.31, 65.80	0.46, 0.19, 0.14
0.305	0.0958	23.00, 23.72, 27.08	84.22, 112.0, 106.6	0.61, 0.13, 0.09
0.0928	0.207	12.10, 12.00, 11.89	30.63, 36.18, 407.7	0.29, 0.42, 0.19
0.0439	0.107	7.11, 7.00, 11.36	42.03, 66.51, 278.7	0.33, 0.27, 0.15

[a] All symbols as defined in text.

[b] Relaxation frequencies, f_r, appear in ascending temperature for each concentration.

[c] Amplitudes, A, appear in ascending temperature for each concentration.

[d] Background, B, at 35.7° is 16.28; at 40.3° is 14.80 and at 45.8° is 12.67.

[e] Root mean square deviation, in ascending temperature for each concentration.

Table V

Equilibrium and Thermodynamic Parameters for the Aqueous 18-Crown-6 Conformational Rearrangement

$$CR_1 \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} CR_2$$

at 25°

[a] τ_1^{-1}	=	$6.3 \pm 0.2 \times 10^{8}$ sec^{-1}
[b] K_{21}	=	$2 \pm 2 \times 10^{-2}$
[c] $\Delta H^{\neq}_{21}$	=	10.2 ± 1.0 kcal/mol
[c] $\Delta S^{\neq}_{21}$	=	7.7 ± 0.2 cal/mol deg
[c] $\Delta H^{\neq}_{12}$	=	7.4 ± 1.0 kcal/mol
[c] $\Delta S^{\neq}_{12}$	=	7.7 ± 0.2 cal/mol deg
[d] $\Delta H°$	=	-2.6 ± 1.0 kcal/mol
[e] $\Delta S°$	=	0 ± 0.2 cal/mol deg
[f] k_{12}	=	$6.2 \pm 0.2 \times 10^{8}$ sec^{-1}
[f] k_{21}	=	$1.0 \pm 0.3 \times 10^{7}$ sec^{-1}

[a] See ref. [3] for the determination of this relaxation time.

[b] Equilibrium constant determined from kinetic data. See text for evaluation.

[c] See text for evaluation of these activation parameters.

[d] $\Delta H° = \Delta H^{\neq}_{12} - \Delta H^{\neq}_{21}$

[e] $\Delta S° = \Delta S^{\neq}_{12} - \Delta S^{\neq}_{21}$

[f] See text for method of determining these rate constants.

Table VI

Rate constants and activation parameters obtained for K^+ complexation by aqueous 18-crown-6, at several temperatures [K^+ + 18-crown-6 $\underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}}$ Complex$^+$].

Temperature °C	k_{23} $m^{-1}sec^{-1}$	k_{32} sec^{-1}	$\Delta H^{\neq}_{23}$ kcal/mole	$\Delta H^{\neq}_{32}$ kcal/mole	$\Delta S^{\neq}_{23}$ eu	$\Delta S^{\neq}_{32}$ eu	$\Delta H°$ kcal/mole	$\Delta S°$ eu
25.0	4.3×10^8	3.7×10^6	4.0	10.2	-8.0	3.1	-6.2	-11.1
35.7	5.9×10^8	7.9×10^6						
40.3	5.8×10^8	9.1×10^6						
45.8	6.3×10^8	1.2×10^7						

Table VII[a]

Data for tabulation of the amplitude factor, Γ_2, for the complexation of a cation by 18-crown-6, at 25°

Cation	$[M^{n+}]_o$	$[CR_T]_o$	a_{11}	a_{12}	a_{21}	a_{22}	Γ_2 ml/mole
K^+	0.40	0.10	6.33×10^8	-1.0×10^7	-1.4×10^8	1.4×10^8	2.5×10^{-6}
K^+	0.30	0.10	6.33×10^8	-1.0×10^7	-9.2×10^7	9.7×10^7	3.4×10^{-6}
Cs^+	0.35	0.10	6.33×11^8	-1.0×10^7	-1.4×10^6	9.2×10^7	1.3×10^{-6}
Cs^+	0.10	0.10	6.33×11^8	-1.0×10^7	-3×10^6	1.0×10^8	1.1×10^{-5}
Cs^+	0.25	0.10	6.33×10^8	-1.0×10^7	-8.4×10^6	1.5×10^8	2.1×10^{-5}
Ag^+	0.40	0.10	6.33×10^8	-1.0×10^7	-3.5×10^8	3.9×10^8	1.4×10^{-5}
Ag^+	0.25	0.10	6.33×10^8	-1.0×10^7	-1.9×10^8	2.4×10^8	1.2×10^{-5}
Ag^+	0.13	0.10	6.33×10^8	-1.0×10^7	-7.2×10^7	1.4×10^8	1.6×10^{-5}
Tl^+	0.35	0.10	6.33×10^8	-1.0×10^7	-2.2×10^8	2.3×10^8	1.9×10^{-6}
Tl^+	0.24	0.10	6.33×10^8	-1.0×10^7	-1.3×10^8	1.4×10^8	3.2×10^{-6}
Tl^+	0.12	0.05	6.33×10^8	-1.0×10^7	-6.8×10^7	7.6×10^7	2.7×10^{-6}
NH_4^+	0.09	0.10	6.33×10^8	-1.0×10^7	-2.9×10^7	1.1×10^8	1.6×10^{-5}
NH_4^+	0.36	0.10	6.33×10^8	-1.0×10^7	-1.6×10^8	-2.2×10^8	1.5×10^{-5}
NH_4^+	0.30	0.10	6.33×10^8	-1.0×10^7	-1.3×10^8	1.9×10^8	1.7×10^{-5}
NH_4	0.18	0.10	6.33×10^8	-1.0×10^7	-6.8×10^7	1.3×10^8	1.9×10^{-5}
Na^+	0.20	0.10	6.33×10^8	-1.0×10^7	-3.4×10^7	7.8×10^7	1.4×10^{-5}
Na^+	0.30	0.10	6.33×10^8	-1.0×10^7	-5.3×10^7	1.1×10^8	2.1×10^{-5}
Na^+	0.40	0.10	6.33×10^8	-1.0×10^7	-9.3×10^7	1.1×10^8	1.9×10^{-5}
Rb^+	0.40	0.10	6.33×10^8	-1.0×10^7	-1.2×10^8	1.4×10^8	7.0×10^{-6}

Table VII (Continued)

Cation	$[M^{n+}]_o$	$[CR_T]_o$	a_{11}	a_{12}	a_{21}	a_{22}	Γ_2 ml/mole
Rb^+	0.2	0.05	6.33×11^8	-1.0×10^7	-6.3×10^7	7.8×10^7	5.7×10^{-6}
Rb^+	0.20	0.10	6.33×11^8	-1.0×10^7	-5.2×10^7	7.3×10^7	1.8×10^{-5}
Li^+	0.40	0.20	6.33×11^8	-1.0×10^7	-2.7×10^6	9.8×10^7	3.7×10^{-5}
Li^+	0.40	0.10	6.33×11^8	-1.0×10^7	-2.9×10^7	9.5×10^7	1.8×10^{-5}

[a] See text for a discussion of a_{11}, a_{12} etc. Data needed to determine a_{11}, a_{12}, etc. taken from ref. [3] and [14].

Table VIII

Volume change for various cations complexed by aqueous 18-crown-6, at 25°

Cation	$\lvert\Delta V\rvert$ ml/mole
K^+	15.2 ± 0.1
Cs^+	8.7 ± 0.5
Rb^+	10.2 ± 1.0
$T\ell^+$	16.1 ± 1.0
Na^+	13.6 ± 1.0
Ag^+	10.6 ± 1.0
NH_4^+	8.0 ± 0.3
Li^+	3.0 ± 1.0
[a] 18-crown-6	10.3 ± 1.2

[a] Volume change for the conformational rearrangement of the crown ether.

Figure Captions:

Figure 1. Plot of log (τ_1^{-1}/T) versus T^{-1} for aqueous 18-crown-6 that is the basis of a determination of a conformational equilibrium constant. The experimental points have been fitted to a least squares straight line.

Figure 2. Plot of log $T(\alpha\lambda)^{ch}_{max}/\rho u^2$ versus T^{-1} also necessary in the determination of a conformational equilibrium constant for aqueous 18-crown-6. The straight line is a least squares fit of the experimental points.

Figure 3. Plots at three different temperatures of the experimental reciprocal relaxation time, τ_2^{-1} versus a concentration term. The slope of the least squares straight line through the origin of coordinates yields an observed specific rate of complexation, k'_{23}, of aqueous potassium ion by 18-crown-6.

Figure 4. A plot of ΔV and log K_T vs. 1/r for cation complexation by aqueous 18-crown-6 at 25°.

Figure 5. Plot of log K_T versus $|\Delta V|$ for several monovalent cations complexed by aqueous 18-crown-6 at 25°. Probable error in values of $|\Delta V|$ is indicated by horizontal bars through the experimental points. A least squares fit of all points except that for Na^+ is given by the diagonal straight line.

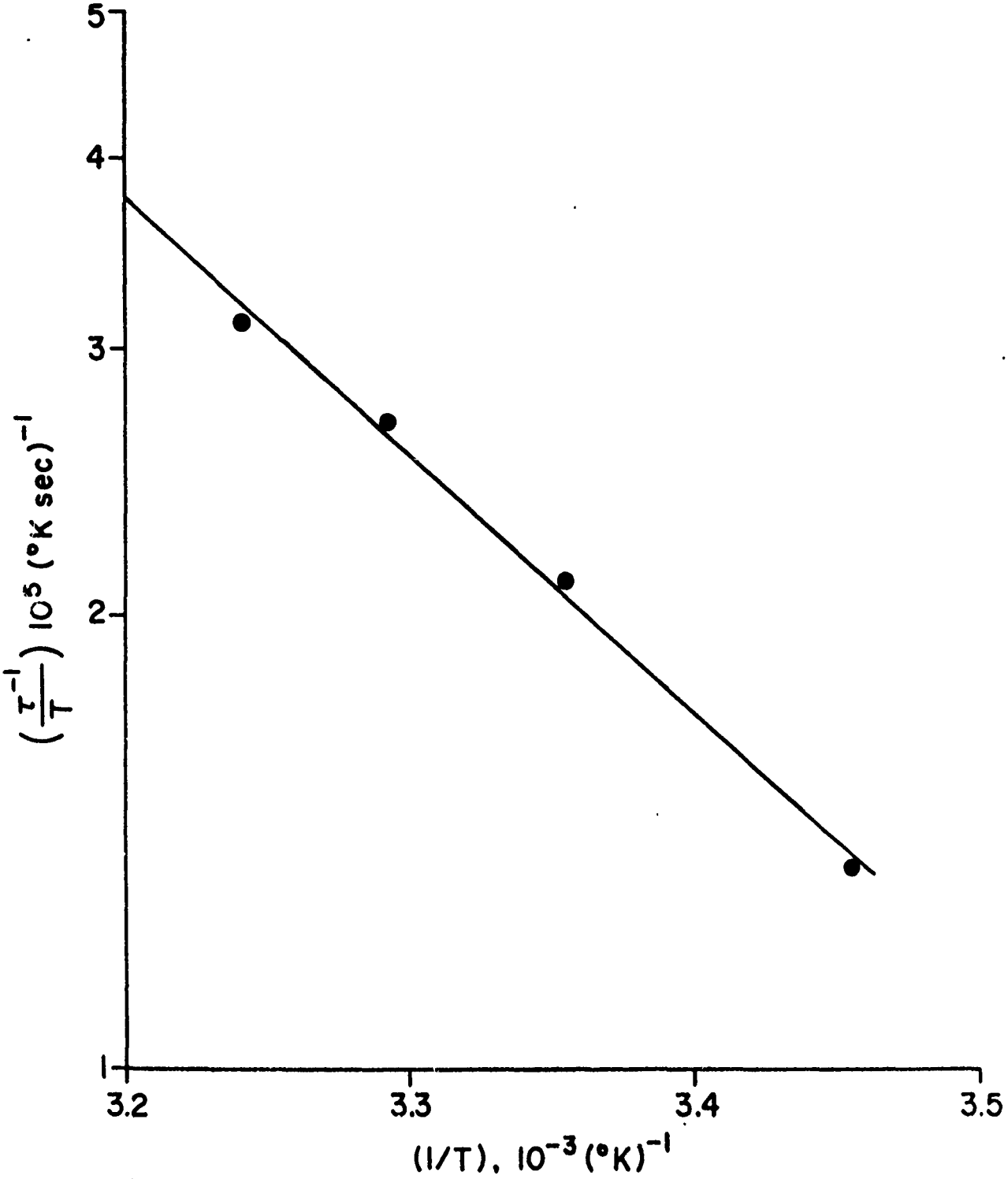


Figure 1.

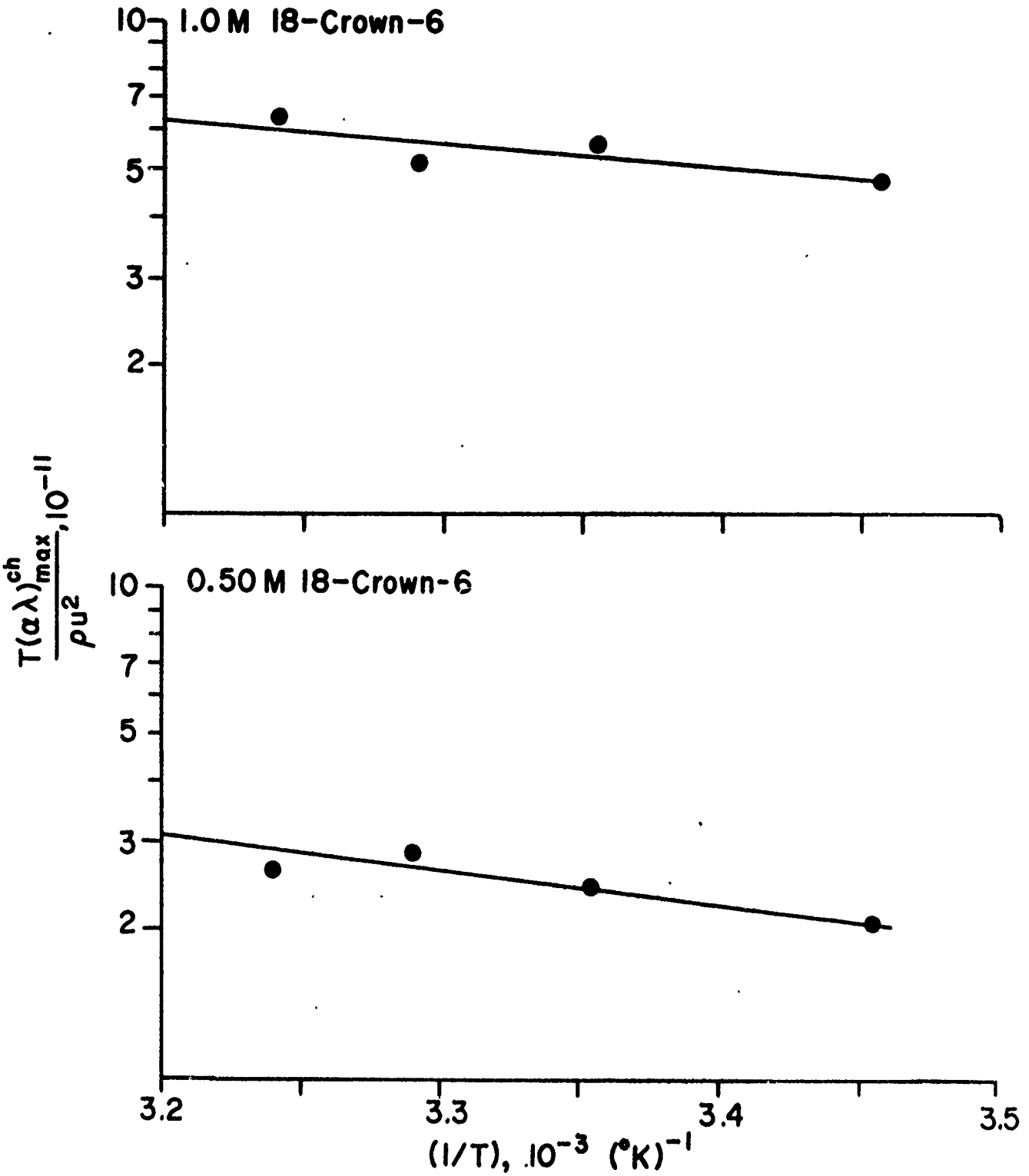
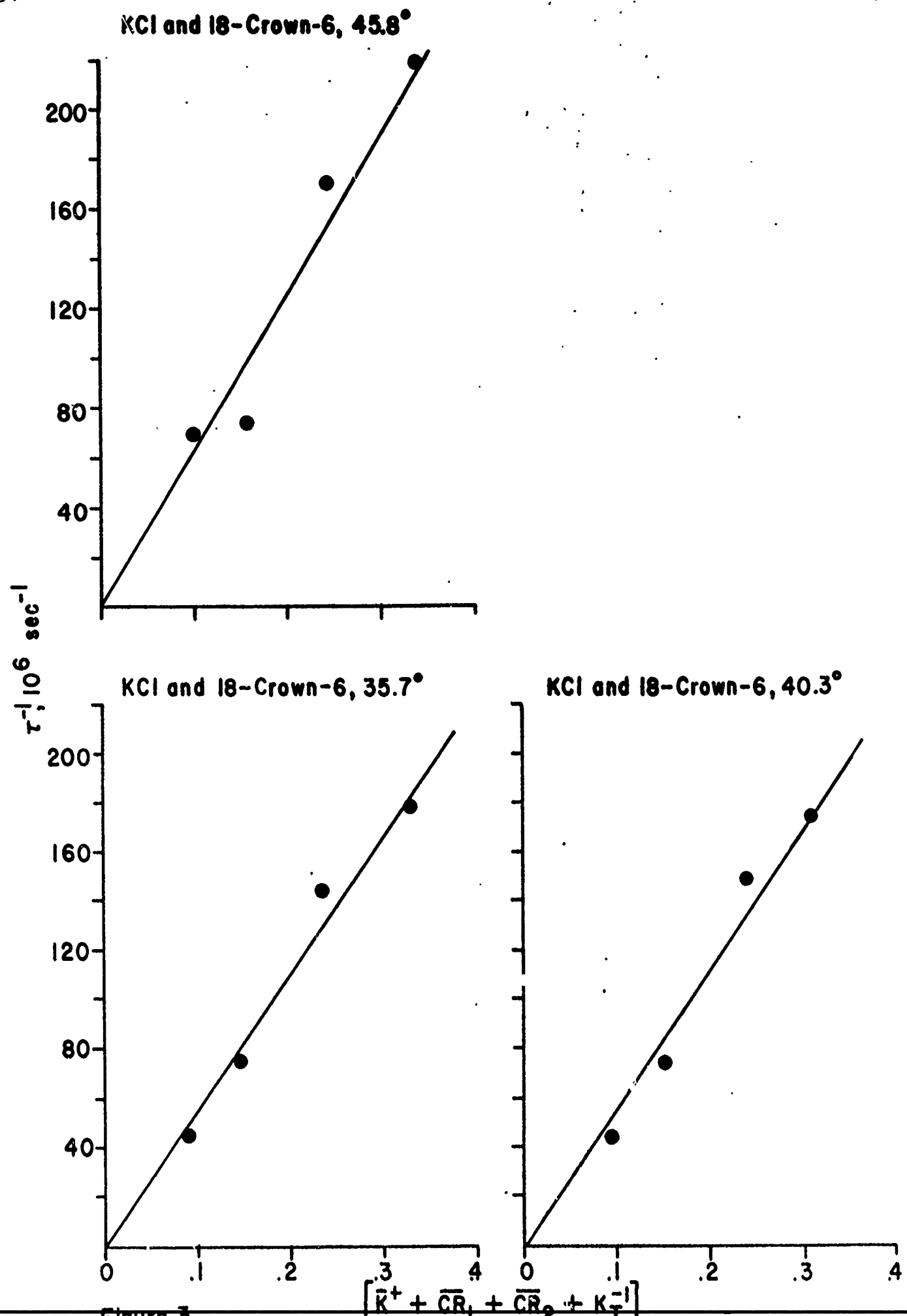

1.0 M 18-Crown-6
0.50 M 18-Crown-6
10
7
5
3
2
$\frac{T(\alpha\lambda)^{ch}_{max}}{\rho u^2}, 10^{-11}$
3.2
3.3
3.4
3.5
$(1/T), .10^{-3}\ (°K)^{-1}$

Figure 2.


KCl and 18-Crown-6, 45.8°
KCl and 18-Crown-6, 35.7°
KCl and 18-Crown-6, 40.3°
200
160
120
80
40
τ^{-1}; 10^6 sec^{-1}
0
.1
.2
.3
.4
$[\bar{K}^+ + \overline{CR}_1 + \overline{CR}_2 + K_T^{-1}]$

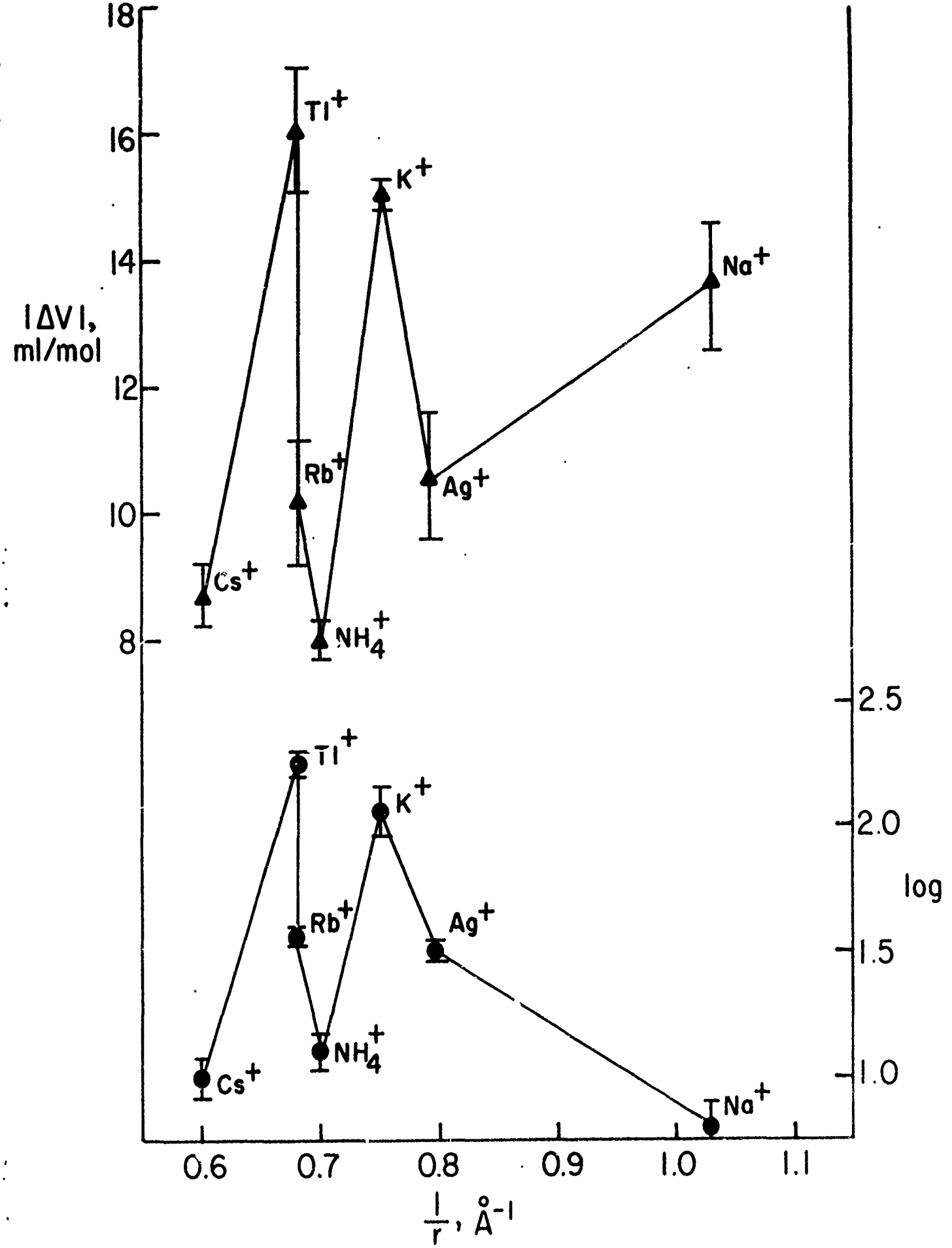

18
16
14
12
10
8
|ΔV|, ml/mol
Tl+
K+
Na+
Rb+
Ag+
Cs+
NH4+
2.5
2.0
1.5
1.0
log
0.6
0.7
0.8
0.9
1.0
1.1
1/r, Å-1

Figure 4

10

Figure 5