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Conductometric Determination in Various Solvents of the Association Constant of Salts of Potassium Complexed with 4,4′(5′)-Di-*tert*-butyldibenzo-18-crown-6

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A conductance study has been made of several potassium salts complexed with the crown (L) mentioned in the title in dipolar aprotic solvents and alcohols. From this study association constants, $K_A(LKX)$, of complexed potassium salts and the mobility of LK^+, $\lambda_0(LK^+)$, have been derived. The Walden products $\lambda_0(LK^+)\eta$ are relatively close to being a constant (0.15_8) in the various solvents. The deviation from constancy is attributed to partial solvation of K^+ in LK^+ in the different solvents.

Introduction

After the introduction of crown ethers by Pedersen (*1*) in 1967 and his fundamental studies of characteristics of these ligands, many papers have been written on their properties (including their complexes with cations). Frensdorff (*2*) found many new properties of crown ethers and together with Pedersen (*3*) reviewed the chemistry and applications of crown ethers known in the early 1970s. Their reviews included stability (formation) constants, $K^f(LM^+)$, of some crown ethers with alkali ions in water and methanol (*3*). Since 1971 values of $K^f(LM^+)$ (alkali and alkaline-earth ions) in a host of solvents, particularly dipolar aprotic solvents, have been published (*4*).

Hardly any data are found in the literature on the values of K^f of complexed salts, $K^f(LMX) = [LMX]/[L][MX]$. One reason probably is that the calculation of this constant requires knowledge of the association constants $K_A(LKX) = [LKX]/[LK^+][X^-]y^{\pm 2}$ and of $K_A(KX)$. It is easily shown that values of $K^f(LMX)$ are found from the relation

$$K^f(LMX)/K^f(LM^+) = K_A(LMX)/K_A(MX) \qquad (1)$$

The present study is confined to complexes of potassium ($M^+ = K^+$). This ion has about the same size as the cavity of 18-crown-6 and its derivatives. As the solubility of dibenzo-18-crown-6 in several organic solvents is low, difficulty is encountered in the estimation of $K^f(LK^+)$ and $K_A(LKX)$ for application of eq 1. It was anticipated that a bulky substituent on dibenzo-18-crown-6 might enhance the solubility of L while preserving the rigidity of the ligand. Indeed, it was found that 4,4′(5′)-di-*tert*-butyldibenzo-18-crown-6, referred to as L, is a suitable ligand for our purposes.

Pederson (*1*), who first synthesized this ligand, found it to be slightly soluble in water, while being much more soluble in organic solvents. In the present work its solubility at 25 °C in water was found to be equal to $1.4_1 \times 10^{-6}$ M. Complexation of this ligand with Pb^{2+} and lanthanide ions in propylene carbonate has been a subject of a recent potentiometric study (*5*). In the present paper we have determined values of $K_A(LKX)$, the mobilities of LK^+, and $\lambda_0(LK^+)$ in the various solvents, as well as $\lambda_0(K^+)$ in isopropyl alcohol and *n*-butyl alcohol, using the conductance method. The following potassium salts have been used: chloride, bromide, nitrate, perchlorate, picrate, and tetraphenylborate. The following solvents were used: acetonitrile (AN), acetone (AC), propylene carbonate (PC), *N*,*N*-dimethylformamide (DMF), methyl alcohol (MeOH), isopropyl alcohol (*i*-PrOH), *n*-butyl alcohol (*n*-BuOH), and *tert*-butyl alcohol (*t*-BuOH).

Mean ionic activity coefficients, $y^{\pm}$, have been estimated by using the Debye-Hückel relation, $-\log y^{\pm} = A\mu^{1/2}/(1 + bB\mu^{1/2})$. Values of A and B have been tabulated by Covington and Dickinson (*6*) for the various solvents while b was taken as 3.0 Å for $LKClO_4$ and $LKBPh_4$ and 4.0 Å for LKCl, LKBr, and LKPi. These are the same as those of the uncomplexed salts. All experiments were at 25 ± 0.01 °C, excepting those in *tert*-butyl alcohol, which were done at 30 ± 0.01 °C (mp of *tert*-butyl alcohol is 25.8 °C).

In a subsequent paper values of $K^f(LK^+)$, $K^f(LKX)$, $K^{sp}(LKX)$ as well as values of the free energies of transfer of the various complexed species between AN or MeOH and the various solvents will be reported.

Experimental Section

Chemicals. Di-*tert*-butyldibenzo-18-crown-6 was synthesized according to Pedersen (*1*). The product was distilled under high vacuum and was then recrystallized 4 times from isopropyl alcohol. Purity of the product was confirmed from the NMR spectra, from its molecular weight (osmometrically), and by C, H analysis.

Solvents. Acetonitrile ("Merck pro analysi") was refluxed for 1 day over phosphorous pentoxide, distilled at atmospheric pressure, refluxed for 12 h over anhydrous potassium carbonate, and finally distilled over nitrogen in a 2.5-m column packed with glass rings. Only the middle two-third fraction was retained. Acetone ("Merck pro analysi") was dried over molecular sieves for 25 h and then distilled over nitrogen. Propylene carbonate ("Merck by synthesis") was distilled in vacuo. The central fraction was passed through a column filled with activated alumina and then distilled in vacuo (bp 97 °C). *N*,*N*-Dimethylformamide (UCB pour analyse) was purified as described elsewhere (*7*). Methyl alcohol, isopropyl alcohol, and *n*-butyl alcohol were distilled over sodium.

Specific conductivities of solutions of the crown in the absence of salt were in the range 0.8×10^{-6}–1.2×10^{-6} Ω^{-1} cm^{-1} in AN, $\sim 2 \times 10^{-7}$ in DMF, $< 5 \times 10^{-8}$ in PC and AC, 1×10^{-6}–1.5×10^{-6} in MeOH, 1×10^{-7}–3×10^{-7} in *i*-PrOH, 0.6×10^{-7}–2×10^{-7} in *n*-BuOH, and 4×10^{-9}–6×10^{-9} in *t*-BuOH. These were subtracted from the specific conductances of solutions of crown and salt.

Salts. Potassium chloride, bromide, and nitrate were "Merck pro analysi" and were dried at 100 °C in vacuo. Potassium picrate and dichloropicrate were prepared by neutralization of picric acid (Merck "pro analysi") or dichloropicric acid (a product used previously (*8*)) with potassium carbonate in aqueous solution. Potassium picrate was recrystallized 3 times from water and the dichloropicrate once from water and then from a 2:1

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Table I. Ionic Mobilities and Association Constants in Various Solvents of Salts Containing Potassium Ion Complexed with Di-*tert*-butyldibenzo-18-crown-6

solvent	salt	Λ_0(LKX)	λ_0(X^-)	λ_0(LK^+)η	K_A(LKX)	a(LKX)[k]
AN	LKCl	145.2 ± 0.2	98.4[a]	0.159	26 ± 1.3	5.1 ± 0.5
AN	LKBr	146	100.7[b]	0.154	11	
AN	$LKClO_4$	147.55 ± 0.2	103.7[b]	0.149	0.0	7.4 ± 0.5
AN	LKPi	125.36 ± 0.15	77.7[b]	0.162	16.3 ± 1.2	4.2 ± 0.3
AN	$LKNO_3$	153	106.4[c]	0.159	53	
AN	$LKBPh_4$	101.7 ± 0.1	58.3[b]	0.148	0.0	
AC	LKBr	170	115.9[h]	0.164	$4.1_5 \times 10^2$	
AC	$LKNO_3$	177	120.1[h]	0.173	7.0×10^2	
PC	LKCl	24.9	18.26[g]	0.168	0.0	
PC	$LKNO_3$	26.4_5	20.42[g]	0.152	0.0	
DMF	LKCl	74.0	55.1[d]	0.150	0.0	
DMF	$LKNO_3$	75.8	57.3[d]	0.147	0.0	
MeOH	LKCl	83.6 ± 0.2	52.35[c]	0.170	4.0 ± 2.2	6.4 ± 0.7
MeOH	$LKClO_4$	98.35 ± 0.09	70.8[c]	0.150	6.1 ± 1	
MeOH	LKPi	74.88 ± 0.01	47.05[c]	0.152	19.5 ± 0.2	3.8 ± 0.3
MeOH	$LKBPh_4$	64.44 ± 0.02	36.6[c]	0.152	23.8 ± 1.3	4.9 ± 0.3
i-PrOH	LKCl	18.78 ± 0.05	10.55[e]	0.171	262 ± 4	4.6 ± 0.1
i-PrOH	$LKClO_4$	20.06 ± 0.03	15.24[e]	(0.100)	(248 ± 1)	1.5 ± 0.1
i-PrOH	LKPi	20.11 ± 0.01	12.8[f]	0.152	998 ± 2	3.68 ± 0.02
i-PrOH	$LKBPh_4$	18.64 ± 0.02	9.55[e]	(0.189)	786 ± 4	2.84 ± 0.05
n-BuOH	LKCl	13.98 ± 0.04	7.76[i]	0.159	188 ± 5	4.3 ± 0.1
n-BuOH	$LKClO_4$	16.02 ± 0.02	11.22[i]	0.123	437 ± 4	3.06 ± 0.03
n-BuOH	LKPi	15.11 ± 0.02	9.18	0.152	624 ± 3	3.82 ± 0.02
n-BuOH	$LKBPh_4$	12.92 ± 0.01	7.69[i]	0.134	272 ± 1	3.03 ± 0.01
t-BuOH	LKCl	10.5			8.2×10^4 ($1.6_5 \times 10^5$)[j]	
t-BuOH	$LKClO_4$	15.5			7.3×10^4	
t-BuOH	LKPi	8.0			2.8×10^4 (2.4×10^4)[j]	
t-BuOH	$LKBPh_4$	10.5			$2.3_5 \times 10^4$	

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cyclohexane–ethyl alcohol mixture. Tetraethylammonium picrate (*7*) and dichloropicrate (*8*) were products used previously. All picrate salts were dried at 60 °C in vacuo. Potassium tetraphenylborate was prepared following the directions of Kunze and Fuoss (*9*). Absence of sodium was verified by flame emission spectrophotometry.

Conductivity Measurements. As the accuracy of the conductometric measurements was at best 0.1%, all solutions were prepared by volume rather than by weight. Viscosity corrections were not made. Solutions containing both *crown and salt* were prepared as follows: Aliquots of stock solutions of known concentration of potassium chloride, perchlorate, picrate, or tetraphenylborate in MeOH or MeOH–water mixtures were taken to dryness by gently heating in a nitrogen stream and then dried at 60 °C in vacuo. The anhydrous salts were dissolved in a known volume of 0.012 M crown in the solvent under study.

For precise (0.1%) measurements a homemade bridge was used (*10*) in conjunction with an oscillator and oscilloscope as null detector. Homemade cells were used, provided with four unplatinized Pt electrodes. Cell constants were 0.123_7 and 0.945_7, respectively. For less precise (1%) measurements a YS I Model 31 conductivity bridge with a cell having a constant of 0.24_7 was used. Cell constants were determined with standard aqueous potassium chloride solutions.

Results

Conductance Data of LKX. Precision conductance data (0.1%) in acetonitrile, propylene carbonate, *N,N*-dimethylformamide, methyl alcohol, isopropyl alcohol, and *n*-butyl alcohol solutions 0.012 M in di-*tert*-butyldibenzo-18-crown-6 and from 2×10^{-4} to 3×10^{-3} M in potassium chloride, bromide, nitrate, perchlorate, or tetraphenylborate, respectively, were treated according to the Fuoss–Hsia conductance equation for associated electrolytes (*11*, *12*)

$$\Lambda = \Lambda_0 - Sc^{1/2}\alpha^{1/2} + E\alpha c \ln(\alpha c) + J_1\alpha c - J_2(\alpha c)^{3/2} - K_A\Lambda\alpha c y^{\pm 2} \quad (2)$$

In eq 2 Λ_0, K_A, J_1, and J_2 are adjustable parameters, the latter two being functions of the "center-to-center contact distance" a(LKX). The degree of dissociation, α, used to compute K_A in eq 2 has been obtained from the relation $\alpha = \Lambda/(\Lambda_0 - S\cdot(c\Lambda/\Lambda_0)^{1/2})$. Under the experimental conditions potassium can be regarded to be present entirely as LK^+ and LKX, even in DMF, in which $K^f(LK^+) = [LK^+]/[L][K^+]$ is only $10^{3.3}$ (from a subsequent paper). With the exception of $LKClO_4$, $LKBPh_4$ in AN, $LKClO_4$ and $LKNO_3$ in PC and DMF (in which the salts are completely dissociated under the experimental conditions) values of Λ_0, K_A, J_1, and J_2 can be found such that, when introduced into eq 2, the latter yields a value of Λ in agreement with the experimental one. Ion triplets, which were reported previously (*13*) to be present in tetramethylammonium chloride solutions in isopropyl alcohol, *tert*-butyl alcohol, and *n*-hexyl alcohol, appear to be absent in solutions of LKX under our experimental conditions. Conductance data of solutions of unassociated electrolytes mentioned above were treated according to the graphical method of Shedlowsky (*14*).

Mobility of LK^+. Results from conductance data of LKX in the various solvents are summarized in Table I (*15*). The mobility of LK^+ at infinite dilution and the Walden product, $\lambda_0(LK^+)\eta$ in the fifth column (η being viscosity), were calculated from Λ_0(LKX) in the third column and the most reliable value of $\lambda_0(X^-)$ taken from the literature (fourth column). (Values of $\lambda_0(LK^+)$ in a given solvent can be considered reasonably independent of the counteranion. Exceptions are values of $\lambda_0(LK^+)$ in *i*-PrOH and *n*-BuOH derived from the perchlorate salt, which are considerably smaller than the average, while $\lambda_0(LK^+)$ in methyl alcohol from the chloride is larger.) These were excluded from the average. The average value of $\lambda_0(LK^+)$ is $45.5_5 \pm 1.4$ in AN, 55.5 ± 1.4 in AC, 6.33 ± 0.31 in PC, 18.7 ± 0.2 in DMF, 27.74 ± 0.13 in MeOH, 8.21 ± 0.59 in *i*-PrOH, and 5.80 ± 0.37 in *n*-BuOH.

The last two columns of Table I list the association constant, $K_A(LKX)$, and the so-called "center-to-center distance of closest approach" (in angstroms), $a(LKX)$, of LK^+ and LK^+ and X^- in the ion pair as calculated from the Fuoss-Hsia treatment.

***Mobility of K^+*.** The mobility of K^+ at infinite dilution has been reported to be 83.6 in AN (*16*), 11.17 in PC (*17*), 30.8 in DMF (*18*), and 52.45 in MeOH (*19*). As values of $\lambda_0(K^+)$ in *i*-PrOH and *n*-BuOH were not available, they were estimated in the present work from conductance data of tetraethylammonium and potassium dichloropicrates. Unlike potassium picrate, which has a low solubility, potassium dichloropicrate is soluble to at least 0.02 M in these alcohols. Since $\lambda_0(Pi^-)$ has not been reported in *n*-BuOH, the conductivity of solutions of tetraethylammonium picrate has been measured in this solvent. From a Fuoss and Kraus treatment of less precise conductance data (±1%) the following values of Λ_0 and K_A were obtained: Et_4NPiCl_2 ($PiCl_2^-$ = dichloropicrate), 27.0, $7.3_2 \times 10^2$ in *i*-PrOH and 18.7_1, $1.0_8 \times 10^3$ in *n*-BuOH; $KPiCl_2$, 22.5, $1.0_2 \times 10^3$ in *i*-PrOH and 17.9_8, $1.7_2 \times 10^3$ in *n*-BuOH; Et_4NPi, 19.5_8 and $8.3_1 \times 10^2$, respectively, in *n*-BuOH. From Λ_0 of Et_4NPiCl_2, $KPiCl_2$, and Et_4NPi and $\lambda_0(Et_4N^+) = 14.6_8$ in *i*-PrOH (*20*) and 10.40 in *n*-BuOH (*21*), $\lambda_0(K^+) = 10.1_8$ and 9.6_7 in *i*-PrOH and in *n*-BuOH, respectively, while $\lambda_0(Pi^-) = 9.1_8$ in *n*-BuOH.

Discussion

From the average values of $\lambda_0(LK^+)$ and $\lambda_0(K^+)$ presented in the Results section, the ratio $\lambda_0(LK^+)/\lambda_0(K^+)$ is found to be equal to 0.54_5 in AN, 0.56_5 in PC, 0.61 in DMF, 0.53 in MeOH, 0.81 in *i*-PrOH, and 0.60 in *n*-BuOH. The markedly decreased mobility of LK^+ as compared to that of K^+ must be ascribed to partial replacement of the solvation layer(s) around K^+ by the bulky ligand. This effect, which varies with the solvent, is promoted by screening of the charge on K^+ in LK^+ as a consequence of binding to the six oxygens of the crown. Takeda (*22*) arrived at the same conclusion for the 18-crown-6 K^+ complex salt in DMF. The reduction in ion mobility is less when potassium is complexed with the less bulky 18-crown-6 and dibenzo-18-crown-6 ligands than with di-*tert*-butyldibenzo-18-crown-6. The ratio $\lambda_0(\text{18-cr-6 } K^+)/\lambda_0(K^+) = 8.91/11.1_7 = 0.80$ in PC (*23*) and $24.6/30.8 = 0.80$ in DMF (*22*), while in PC $\lambda_0(\text{DB-18-cr-6 } K^+)/\lambda_0(K^+)$ derived from the perchlorate salt is $(25.80\ (24) - 18.44\ (17))/11.1_7 = 0.66$. In methyl alcohol this ratio is equal to $32.9/52.4_5 = 0.62_6$ (*25*).

The solvodynamic radius of LK^+ in the various solvents cannot be calculated by using the Stokes-Einstein equation, considering the nonspherical nature of the *tert*-butylbenzo crown ether (the same is true for dibenzo-18-crown-6). However, it may be noted that the average value of $\lambda_0(LK^+)\eta$ of $0.15_5 \pm 0.2$ (Table I) is comparable to that of *n*-heptylammonium ion in many solvents.

The relation between solvated and contact ion pairs on the one hand and the values of *a* will be discussed in a subsequent paper.

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Hydrogen Solubility in Organic Liquids

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The solubility of hydrogen was measured in α-methylstyrene, cumene, cyclohexene, cyclohexane, and cyclohexanone at temperatures between 30 and 100 °C and pressures between 100 and 1000 psig. Henry's constants calculated from the solubility data were correlated as a function of temperature.

The hydrogen solubility in organic liquids is needed in the analysis and design of multiphase reactors. Hydrogen solubility data at high temperature and pressure are rather limited (*1*). Most of the data were measured near room temperature and atmospheric pressure (*2*).

The purpose of this study is to determine the solubility of hydrogen in organic liquids by a simple and accurate method. The liquids α-methylstyrene, cumene, cyclohexene, cyclohexane, and cyclohexanone were studied. Solubility measurements in α-methylstyrene reported in the literature (*3*, *4*) indicate large discrepancies. Berty et al. (*5*) published a com-

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