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The Determination of Crown–Cation Complexation Behavior in Dioxane/Water Mixtures by Conductometric Studies

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ABSTRACT

Using conductance measurements, an attempt has been made to gain detailed information about the specific molecular interactions of crown compounds with metal ions in a 1,4-dioxane/water binary system. Analyses of the transport data of dioxane/water mixtures yielded the mobility of the crown compound action complexes and the ion-pair dissociation constant of the crown compound–electrolyte complex. Binary mixed aqueous solvents are frequently employed in broad areas of chemistry. Their applicability ranges from synthetic and mechanistic studies in organic chemistry to biophysical chemistry, with emphasis on molecular interactions in biologically significant structures. Stability constants of crown compound complexes are determined by various methods, such as potentiometry (with ion selective electrodes), polarography, voltammetry, spectrophotometry, nuclear magnetic resonance, calorimetry and solubility.

In this study the conductometry measurements have been carried out with high precision at optimal concentrations in dioxane/water systems. Structures of crown–cation complexes in dioxane/water mixtures are estimated from the conductance parameters (κ*,* Λ *and* α*) as well as the complex formation constant,* $K_e = (\Lambda_{MAm} - \Lambda) / (\Lambda - \Lambda_{MaLbAm})\ [L]$.

The conductance behavior of Na^+*,* K^+ *chlorides and* Na^+ *perchlorates with 18-crown-6, 15-crown-5, and 12-crown-4 have been studied in various dioxane/water systems (50%, 80%, and 85%) at 25°C. The all experimental studies have been made by the ratio 1:1 of the metal-ion and the crown ether,* K_e*. For the calculations, Excel. 5.0 was used as an application program. © 1998 John Wiley & Sons, Ltd.*

KEYWORDS: conductometry; complex formation; crown ether; metal ions; dioxane–water binary systems

INTRODUCTION

Binary dioxane aqueous solvents are frequently employed in broad areas of chemistry. However, the physical properties of these aqueous binaries are only partly understood and 1,4-dioxane/water mixture constitutes a notable example.

This system owes its popularity largely to the possibility of attaining a large range of dielectric constants ($2.2 < \varepsilon \leq 78$; 25°C) by varying the solvent composition. In the literature, however, there is a long-standing controversy regarding the effect of

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1,4-dioxane on the three-dimensional hydrogen bond network of water [1–3].

The ability of macrocyclic polyethers (crown ethers) to form stable complexes mainly with alkali and alkaline earth cations has spurred interest in these compounds [6–9]. Recently published studies include conductometric measurement of some electrolytes in non aqueous solvents (tetrahydrofuran [10], tetrahydropyran [10], acetonitrile [11, 12] and methanol [12] in the presence of crown ethers. Studies carried out in solutions of alkali metal salts and crown ethers in acetonitrile and methanol showed decreases in conductivities of the solutions.

In the present work the conductance behavior of Na^+ and K^+ chlorides and Na^+ perchlorates with 18-crown-6 (18C6), 15-crown-5 (15C5) and 12-crown-4 (12C4) were studied in various dioxane/water mixtures (50%, 80% and 85%) at 25°C.

The study indicates 1:1, 1:2, 2:1, 2:2, 2:3 and 3:2 complex formation between the alkali metal-ion and electrically neutral crown ether. However, we now report 1:1 complexes in such a system.

EXPERIMENTAL

18-Crown-6 (Aldrich), 15-crown-5 (Aldrich) and 12-crown-4 (Aldrich) were used without further purification. Alkali halides (NaCl and KCl, Merck) were recrystallized three times from a conductivity water–ethanol mixture and alkali perchlorate ($NaClO_4$, Merck) was recrystallized three times with conductivity water. The salts were then heated to below their decomposition temperature at reduced pressure. Water used was redistilled from alkaline permanganate.

All solutions were prepared in a dry box and transferred to the dry conductivity cell. All conductances were measured at 25 ± 0.05°C. The measuring equipment consisted of a glass vessel (type Ingold) with an external jacket connected to a thermostatted water-bath (25 ± 0.05°C) and a conductivity cell (Cole Parmer 19050-66) with a conductometer (Suntex SC-170 Model).

The cell constant was determined as $0.769\,\mathrm{cm}^{-1}$ at 25°C by measuring the conductivity of aqueous potassium chloride solutions of different concentrations [13]. The molar conductivity of the pure metal ion solution (Λ_{MA}) was obtained at the appropriate electrolyte concentration before any addition of ligand was made.

RESULTS AND DISCUSSION

Various methods to calculate stability constants from measurements of properties involving intrinsic factors, such as molar conductivity, etc. have been described in the literature [14, 15].

When a crown compound forms an *a*:*b* (M:L) complex with a cation, the equilibrium equation is written as

$$\begin{array}{ccc} a\mathrm{M}^{m+} + b\mathrm{L} & \rightleftharpoons & \mathrm{M}_a\mathrm{L}_b^{m+} \\ \alpha\mathrm{C_M} \quad \mathrm{C_L} - (1-\alpha)\mathrm{C_M} & & (1-\alpha)\mathrm{C_M} \end{array} \tag{1}$$

where M^{m+}, L and α are the cation, crown compound and fraction of free cations, respectively. Thus the equilibrium constants K_e of different ratios of complex formation were calculated using the following equations:

$$K_\mathrm{e} = \frac{[\mathrm{M}_a\mathrm{L}_b^{m+}]}{[\mathrm{M}^{m+}]^a[\mathrm{L}]^b} \tag{2}$$

$$C_\mathrm{M}/C_\mathrm{L} = 1 \tag{3}$$

$$C_\mathrm{M} = [\mathrm{M}_a^{m+}] + [\mathrm{M}_a\mathrm{L}_b^{m+}] \tag{4}$$

$$C_\mathrm{L} = [\mathrm{L_b}] + [\mathrm{M}_a\mathrm{L}_b^{m+}] \tag{5}$$

$$\alpha = [\mathrm{M}_a^{\mathrm{m}+}]/C_\mathrm{M} \tag{6}$$

$$P = \frac{[\mathrm{M}_a\mathrm{L}_b^{m+}]}{C_\mathrm{M}} = \frac{\mathrm{K_e}[\mathrm{L_b}]}{1 + K_\mathrm{e}[\mathrm{L}_b]} \tag{7}$$

The observed conductivity, κ, is given by

$$\kappa = \kappa_{\mathrm{M}a}^{m+} + \kappa_{\mathrm{M}a\mathrm{L}b}^{m+} \tag{8}$$

The molar conductivities are

$$\Lambda_{\mathrm{MA}m} = \frac{\kappa_{\mathrm{MA}a}^{m+}}{[\mathrm{M}_\mathrm{a}^{m+}]} \tag{9}$$

$$\Lambda_{\mathrm{M}a\mathrm{L}b}^{m+} = \frac{\kappa_{\mathrm{M}a\mathrm{L}b}^{m+}}{[\mathrm{M}_a\mathrm{L}_b^{m+}]} \tag{10}$$

$$\Lambda = \frac{\kappa}{C_\mathrm{M}} \tag{11}$$

$$\Lambda = \alpha\Lambda_{\mathrm{M}a}^{m+} + (1-\alpha)\Lambda_{\mathrm{M}a\mathrm{L}b}^{m+} \tag{12}$$

As a result of eq. (12), eq. (2) can be transformed into

$$K_\mathrm{e} = \frac{\Lambda_{\mathrm{M}a}^{m+} - \Lambda}{(\Lambda - \Lambda_{\mathrm{M}a\mathrm{L}b}^{m+})[L_b]} \tag{13}$$

where

$$[\mathrm{L}_b] = C_\mathrm{L} - C_M \cdot \mathrm{P}$$

and

$$[\mathrm{L}_b] = C_\mathrm{L} - C_\mathrm{M} \cdot (\Lambda_{\mathrm{M}a}^{m+} - \Lambda)/(\Lambda_{\mathrm{M}a}^{m+} - \Lambda_{\mathrm{M}a\mathrm{L}b}^{m+})$$

C_M, C_L are the total concentrations of alkali metal and crown ether, respectively; $[\mathrm{M}_a^{m+}]$, $[\mathrm{L}_b]$ and $[\mathrm{M}_a\mathrm{L}_b^{m+}]$ are the concentrations of uncomplexed cation, uncomplexed crown ether and complexed cation, respectively; P is the experimental mole fraction of the complexed cation or the ligand, for a 1:1 complex, and a and b are the complexing degrees of both sides in the case of several degrees of complexing (eqs 1–13) $\kappa_{\mathrm{M}a}^{m+}$, $\kappa_{\mathrm{M}a\mathrm{L}b}^{m+}$, are the observed conductivities of the electrolyte and the crown compound–electrolyte complex, respectively; $\Lambda_{\mathrm{M}a}^{m+}$ and $\Lambda_{\mathrm{M}a\mathrm{L}b}^{m+}$ are the designated molar conductivities of the electrolyte and the crown compound–electrolyte complex, respectively.

The Na^+ and K^+ ions association constants of 18C6, 15C5 and 12C4 in various dioxane/water mixtures at 25°C with conductometry were studied. This binary solvent mixture is among those that enhance macrocycle–cation interactions [10–20].

In the present work, considerable solvent effects

TABLE 1. The Association Constants (K_e) and Free Enthalpies (ΔG^θ) of NaCl, $NaClO_4$ and KCl with 18C6, 5C5 and 12C4 with (1 : 1) in Various Dioxane/Water Mixtures at 25°C

$NaClO_4$ 50% dioxane	$K_{e\ (1:1)}$	$-\Delta G^\theta_{1:1}$	*Corr. Coeff.*	*Error*
$Na(18C6)ClO_4$	1.039	23.00	0.99997	±0.566
$Na(15C5)ClO_4$	0.759	−163.01	0.99997	±0.000
$Na(12C4)ClO_4$	–	–	–	–
$NaClO_4$ 85% dioxane				
$Na(18C6)ClO_4$	6.312	1091.00	0.99940	±4.508
$Na(15C5)ClO_4$	3.709	776.00	0.99940	±2.085
$Na(12C4)ClO_4$	4.681	914.00	0.99940	±3.376
NaCl 50% dioxane				
Na(18C6)Cl	3.506	4494.00	0.99964	±1.425
Na(15C5)Cl	2.437	1164.00	0.99964	±0.935
Na(12C4)Cl	1.586	878.00	0.99964	±0.289
NaCl 80% dioxane				
Na(18C6)Cl	–	–	–	–
Na(15C5)Cl	–	–	–	–
Na(12C4)Cl	–	–	–	–
KCl 50% dioxane				
K(18C6)Cl	4.338	869.00	0.99993	±0.524
K(15C5)Cl	1.627	288.00	0.99993	±0.043
K(12C4)Cl	0.403	−539.00	0.99993	±0.134
KCl 80% dioxane				
K(18C6)Cl	–	–	–	–
K(15C5)Cl	–	–	–	–
K(12C4)Cl	9.897	1357.00	0.99756	±2.175

of water were displayed for 18C6, 15C5 and 12C4 owing to differences in K_e that depend on the solvent composition. The selectivity for a given salt is a factor not only of the crown ether, but of the solvent as well [21]. These various selectivities depend on the crown ether interactions with the cations governed by charge density.

The binding power of the ion–dipole interactions primarily depends on the oxygen number as well as molecular conformations of a macromolecule, even if the ligand–ion exchange rate and role of mother solvent mostly orients the ligand selectivity.

In our work, the binding power of sodium and potassium ions to 18C6, 15C5 and 12C4 for various ratios of dioxane/water solutions was studied with a conductometry cell at 25°C; Table 1. The use of eqs. (2) and (13) allowed us to obtain the equilibrium constants [21] and structures of crown compound–cation complexes in dioxane/water were estimated from eqs (1)–(13). above. In addition, the information on the interactions of crown–

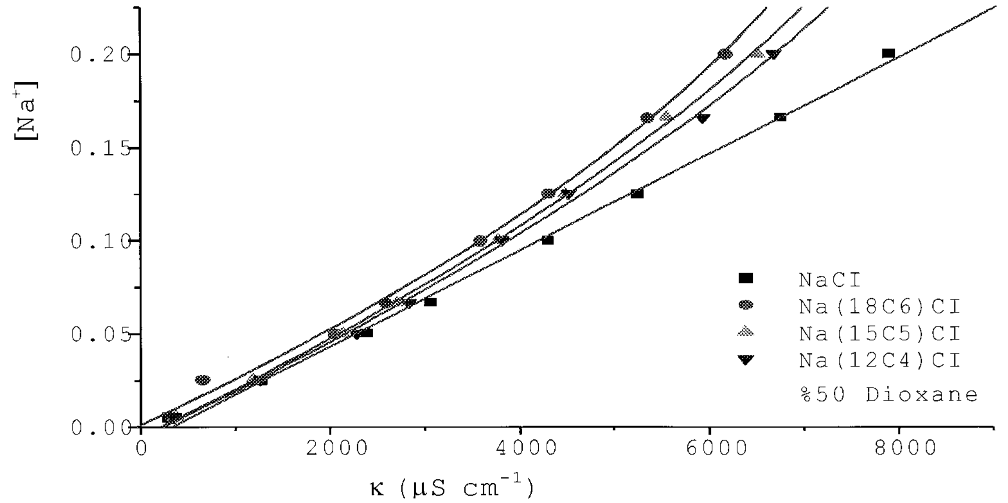

FIGURE 1. The graphics of $[Na^+]$ (mol/L) versus observed conductivity of NaCl with 18-crown-6, 15-crown-5 and 12-crown-4 in 50% dioxane/water mixtures at 25°C.

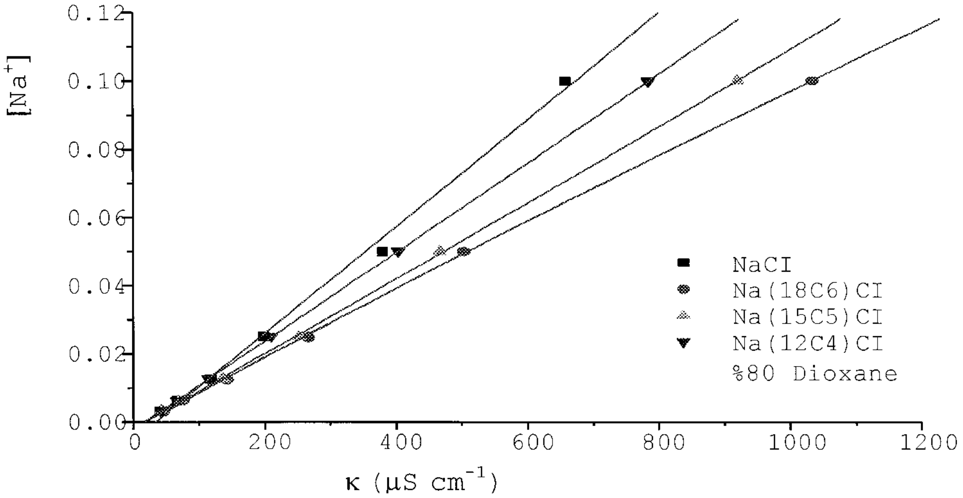

FIGURE 2. The graphics of [Na$^+$] (mol/L) versus observed conductivity of NaCl with 18-crown-6, 15-crown-5 and 12-crown-4 in 80% dioxane/water mixtures at 25°C.

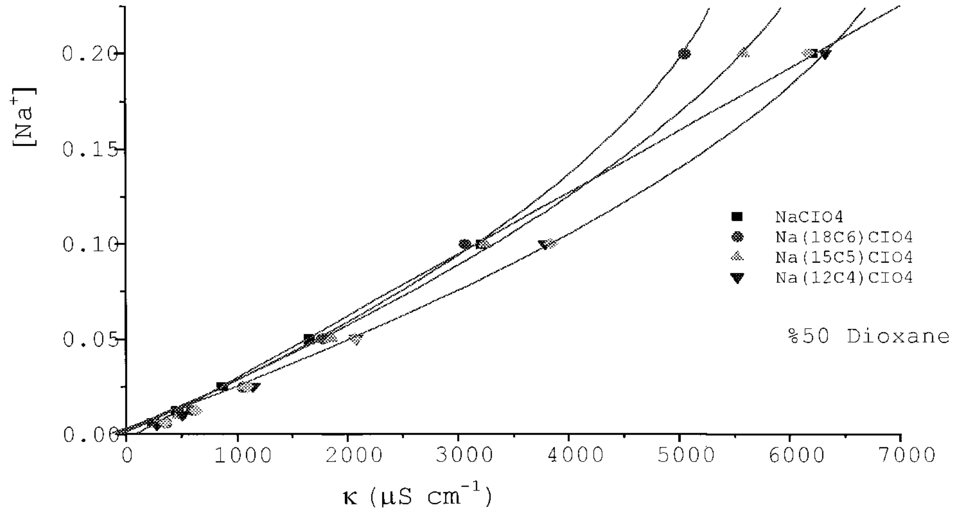

FIGURE 3. The graphics of [Na$^+$] (mol/L) versus observed conductivity of NaClO$_4$ with 18-crown-6, 15-crown-5 and 12-crown-4 in 50% dioxane/water mixtures at 25°C.

cation complexes with dioxane/water binary solvents and different anions (Cl$^-$ and ClO$_4$$^-$) was also obtained from these three conductance parameters. The data in Figs 1–6 show only 1:1 complexes and the equilibrium constants, K_e, Table 1. However, different ratios of complex formation (metal:crown, a:b) may be given. The higher stoichiometries of the ligand and the cation interactions involved larger free energies, ΔG^θ [20].

For the thermodynamic interpretations of the cation–macrocyclic ether interactions, a sodium complexed 18C6 structure tested by *ab initio* calculation showed that the conformational energy is even higher with two moles more of water in coordination shell [22]. Accordingly, in the dioxane/water–crown ether solutions, ions are most probably structured as axially complexed ion-pairs with a 1:1 ratio of unit two complex [23]. In 50% dioxane/water mixtures, it was observed that the κ versus [M_a^{m+}] plots of the 18C6, 15C5 and 12C4 with NaCl and KCl in Figs 1 and 5 show a decrease of κ with an increase in the crown ether concentration. This indicates that complexation occurs between the crown ethers and the alkali metal ions, and that the crown ether–alkali metal ion complexes are less mobile that the free alkali metal ions. It can be expected that stabilities of the 1:1 complexes of these three crown ethers with the same alkali metal ion in 50% dioxane/water mixtures decrease in the order 18C6 > 15C5 > 12C4. The complex formations of 18C6 with Na$^+$ and K$^+$ in 1:1 stoichiometry have already been reported [16–20, 23–25].

In 80% dioxane/water mixtures, for the κ versus [M_a^{m+}] plots in Figs 2 and 6, an increase of κ with crown ether concentration occur except for the 12C4-Na$^+$ and K$^+$ system. This indicates that 18C6 and 15C5 form complexes that are more mobile than the corresponding alkali metal ions [15]. From Figs 3 and 4, in the case of crown ethers in the

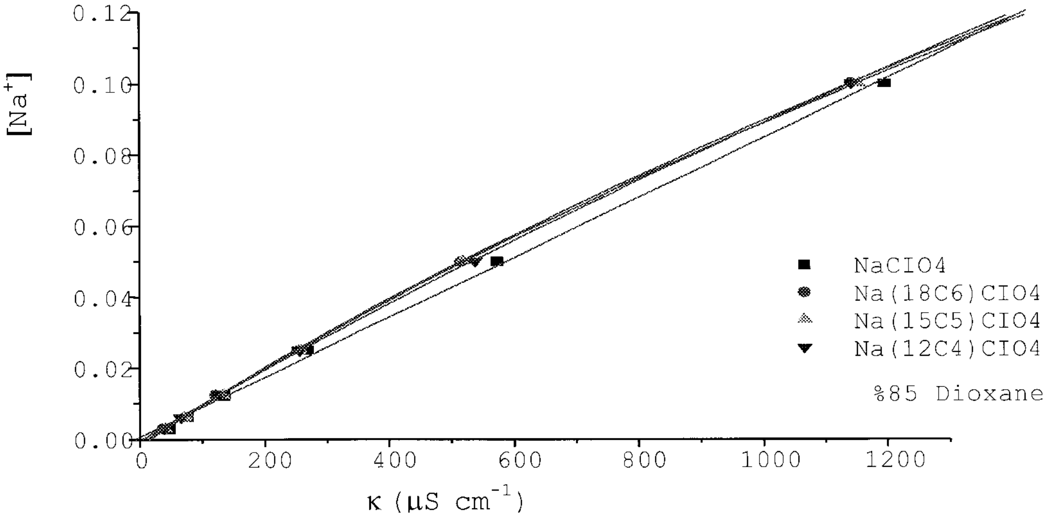

FIGURE 4. The graphics of [Na$^+$] (mol/L) versus observed conductivity of $NaClO_4$ with 18-crown-6, 15-crown-5 and 12-crown-4 in 85% dioxane/water mixtures at 25°C.

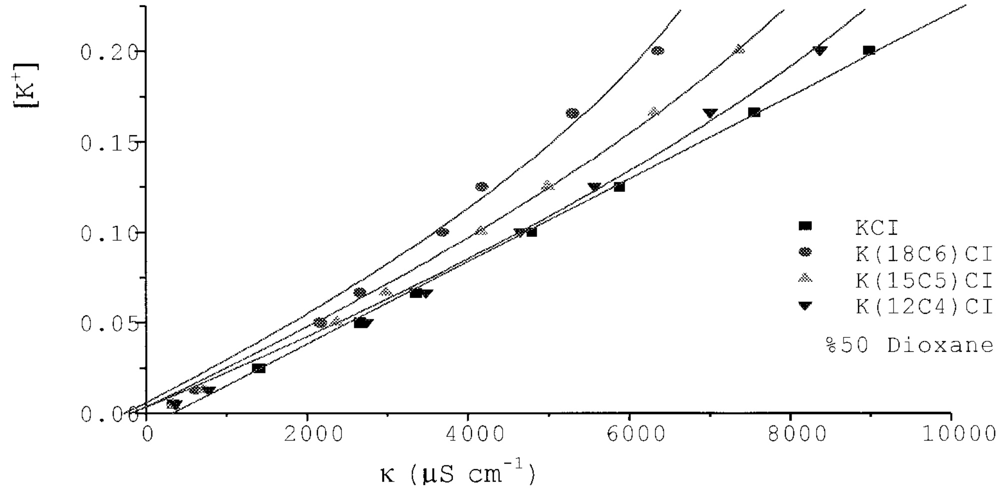

FIGURE 5. The graphics of [K$^+$] (mol/L) versus observed conductivity of KCl with 18-crown-6, 15-crown-5 and 12-crown-4 in 50% dioxane/water mixtures at 25°C.

$NaClO_4$ systems in 50% dioxane/water mixtures, Fig. 3, the slope of each curve increases at the higher ether concentrations indicating the complex formation with Na^+ ion. In the 85% dioxane/water mixtures Fig. 4, no such clear increase or decrease of κ occur, with an increase in the crown ether concentration. Two factors may be responsible for this negligible change in κ despite an increase in the crown ether concentration: (1) ions most probably form ion-pairs and scarcely any complexation occurs between the crown compounds and the cations; and (2) mobilities of a resulting crown compound–cation complex and the corresponding cation are equal at the same concentration because of the first factor [15].

Thermodynamic parameter values (ΔG^θ) of 1:1, 1:2, 2:1, 2:2, 2:3 and 3:2 complexation reactions between crown ethers and alkali metals in various dioxane/water could be determined by conductometric methods [20]. The K_e values determined by conductometry agrees with those by the other methods [14, 16–20].

Selectivity of 18C6, 15C5 and 12C4 for the alkali metal ions (Na^+ and K^+) depends on the relative sizes of the action and crown cavity so that the most stable complex found is the 18C6 complex in 50% dioxane/water mixtures since there is a relationship between stability of crown–alkali metal ion complex and dielectric constant of the solvent mixtures. From the κ versus [M_a^{m+}] plots in Figs 2 and 6, the slope sequences of crown complexes in 80% and 85% dioxane/water mixtures (12C4 < 15C5 < 18C6) are completely reversed (12C4 > 15C5 > 18C6). It was found that stabilities of complexes of the Na^+ ions with crown compound at 25°C are affected not only by the relative sizes of the cation and the crown ether cavity but also by different anions (Cl^- and ClO_4^-) and by the dielectric properties of dioxane/water mixtures [26].

In 85% and 80% dioxane/water mixtures, since

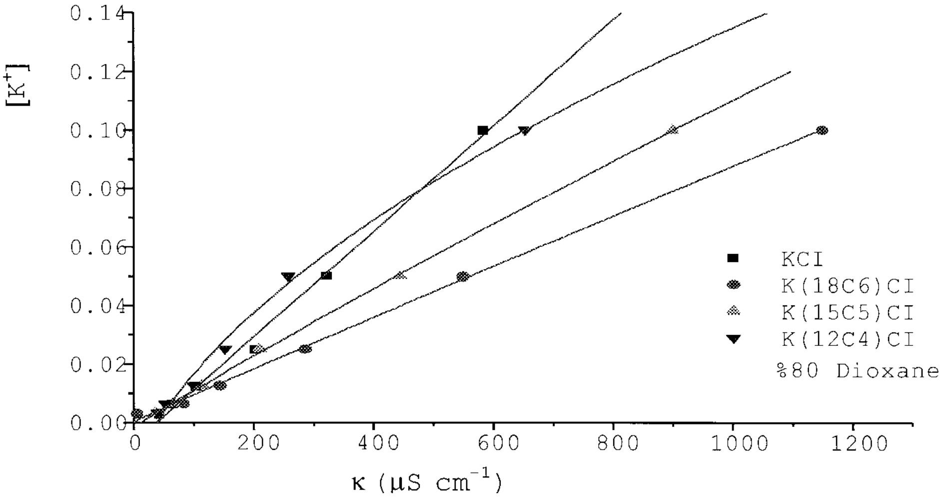

FIGURE 6. The graphics of [K^+] (mol/L) versus observed conductivity of KCl with 18-crown-6, 15-crown-5 and 12-crown-4 in 80% dioxane/water mixtures at 25°C.

Na^+ ion is smaller than the 18C6 cavity and it has a greatest charge density than K^+ ion, Na^+ ion held in the cavity may attract the donor oxygen atoms of the crown ether much more strongly than the K^+ ion [26].

It was observed that for the K^+ complexes with 18C6, 15C5 and 12C4 in both 50% and 80% dioxane/water mixtures, the K_e values were dependent on the chemical characteristics of all ligands and solvents, indicating that the electrostatic ion–dipole forces, which depend on the macroscopic dielectric constant of the solvent mixtures and on the dipole moment of the ligands, are the strongest factors in the complexation processes in such a system.

It is interesting that, in contrast to other crown ethers, 12C4 forms much the most stable complex with K^+ ion in 80% dioxane/water mixture, and Na^+ has a more suitable size for the cavity of 18C6 than for those of other crown compounds in 85% dioxane/water mixtures [16–20, 23–25]. However, the lower symmetry of 18C6 causes more unfavorable orientation of donor oxygen atoms with the less size-fitted K^+ cation in 80% dioxane/water mixture.

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