Lithium and Potassium Ions Transfer Processes across the ITIES in The Presence of Crown Ethers

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Abstract

The electrolytic cell with the electrolyte dropping electrode comprised Ag/AgCl as working electrode, Ag/AgCl reference electrode and platinum wire counter electrode. This cell evaluated by the determination of the thermodynamics data for lithium and potassium ions transfer across a liquid-liquid interface in the presence of the crown ethers. In the present system we intend to demonstrate the use of a simple three-electrode assembly with electrolyte dropping electrode for the study of the interfacial ion transfer.

In particular, we focused on the transfer of lithium and potassium ions from water to 1, 2- dichloroethane (1, 2-DCE) facilitated by complex formation with benzo-15-crown -5 (B15C5), 18-crown -6 (18C6), dibenzo-18 – crown-6 ($B_2$18C6) and dicyclohexyl-18- crown -6 (Cy_2 18C6).

Extensive   thermodynamics   data,   suggest   that   the   standard Gibbs energies of transfer of lithium and potassium ions from water to 1,2-DCE and stability constant of crown ether complexes depends on the relative cation and ligand cavity size, the number and special arrangements of the ligand binding sites and the substitution on the macrocyclic ring.

Ag /   Ag / AgCl

.   AgCl

-

-2 1

-18-   6 -   -18   5-   -15 -

.6 -   -18-   6-

-2 1

(ITIES)

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Introduction

Polarographic with the electrolyte dropping electrode **(**EDE**)** was pioneered by Koryta et, al. [1, 2]. A general deal of deserved interest has centered on the nature of ionophore facilitated transfer of ions, such as Li^+, K^+ and other alkali-metal cations across the aqueous-immiscible organic liquid interface. A reaction attracting attention from groups as diverse as neuro- physiologists and electro analytical chemists.

The results of electrochemical investigations made on the transfer of ionizable drugs at the interface between two immiscible electrolyte solutions (ITIES) in the last decade have been presented [3].

. **T**he transfer of alkali metal cation facilitated from water to nitrobenzene (NB) and 1, 2- dichloroethane (1, 2-DCE) has been evaluated from linear potential sweep voltammetry measurements at the interface between two immiscible electrolyte solutions (ITIES). The procedure involved an implicit use the tetraphenyl arsonium tetraphenyl borate [4]. **T**he transfer of Li^+ and K^+ facilitated by valinomycin [5,6], nonactin [7], and crown ethers[5,7] has been extensively studied by Koryta and his group.

Studied the voltammetric and AC-impedance behavior of the protonated ion of several local anesthetics of the o-nitrophenyl octyl ether/water interface. It was observed that the pharmacological activity of local anesthetic increases with a decrease in their ion-transfer standard potential, which is consistent with the data obtained at the nitrobenzene/water interface[8,9] .

. **S**amec and Papoff [10] demonstrated that the (current scan) polarographic

waves observed represented the transfer of alkali metal cations from water to NB or 1,2-DCE facilitated by complex formation with $B_2 18C6$, $B_2 24C8$ or $B_2 30C10$ were used to clarify the mechanism of the ion transfer and to evaluate the stability constant of crown ether complex .

Recently, Sildenafil (Viagra) was examined for its ionization and lipophilicity by electrochemistry at ITIES and two-phase titration in the 1,2-dichloroethane water system[11].

Experimental Section

1-Aqueose phase:

0.5M MgSO4. H2O was used as a supporting electrolyte with Lithium chloride and Potassium chloride in the electrolytic cell which were prepared by dissolving an appropriate amount of the salt in 100ml of deionized water.

2-Organic phase:

Samples were prepared individually by dissolving appropriate amounts of crown ethers in 100ml in 1,2-DCE .Each 25ml of sample was mixed with a fixed amount of 0.4188gm of tetraphenylarsonium chloride and analyzed using dropping water electrode.

1,2- dichloroethane(1,2-DCE) (Aldrich Chemical Company Inc.) was used without further purification . LiCl and KCl Salts from BDH. benzo-15-crown -5(B15C5), 18-crown -6 (18C6) , dibenzo-18 – crown-6 ($B_2 18C6$) and dicyclohexyl-18- crown -6 ($Cy_2 18C6$) [Fluka AG]. The supporting electrolyte of the aqueous phase was 0.5 M magnesium sulfate mono hydrate and that of the organic phase was 0.01M. Tetraphenyl arsonium chloride hydrate (C6H5)4 $AsCl._X H_2 O$ (Aldrich Chemical Co.Ltd.),water was doubly distilled deionized.
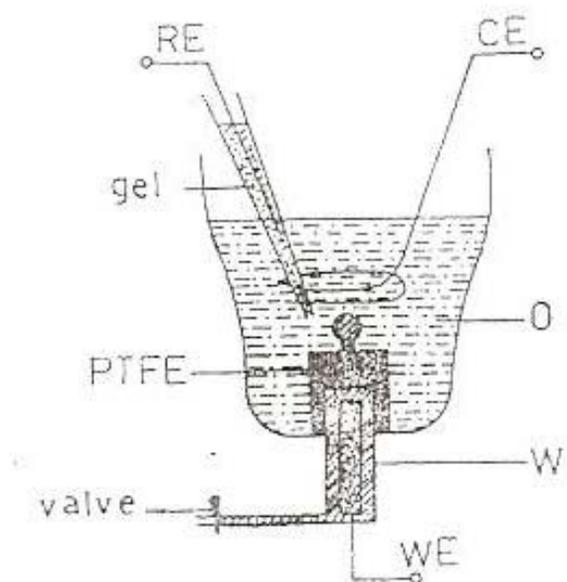
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Figure (1). Three- electrodes polarographic cell with the electrolyte dropping electrode: (WE) Ag/ AgCl working electrode, (RE) Ag/ AgCl reference electrode, (CE) platinum wire counter electrode.

Electrolytic cell. Figure(1) shows the scheme of the electrolytic cell .The aqueous phase (density 1.051 g cm^{-3}) was dropping upward into 1,2-DCE(density1.251 g cm $^{-3}$) from a PTFE capillary with the flow rate v   ≈ 0.0679 g S $^{-1}$ and the drop time td = 0.6 -1.2 S. The column height of the aqueous electrolyte solution (57 cm to the orifice of the capillary) and the volumes of the organic and the aqueous electrolyte solutions in the cell were held constant.

The reference Ag/AgCl electrode for the organic solvent phase (RE) was dipped into the 0.01M TPhAsCl aqueous agar-agar gepulvent solution in a Pasteur pipette, the tip of which was about 0.2 cm far from the drop .The counter electrode (CE) was a platinum wire wound round the drop as shown in figure (1).

A falt water/1,2–dichloroethane solvent interface, was formed in a three-electrode glass cell [10,12].

Ag	AgCl	xM (LiCl or KCl) +0.5M MgSO$_4$.H$_2$O (w)	0.01M TPhAsCl +0.01M ML (0)	0.01M TPhAsCl (w$^-$)	AgCl	Ag$^-$
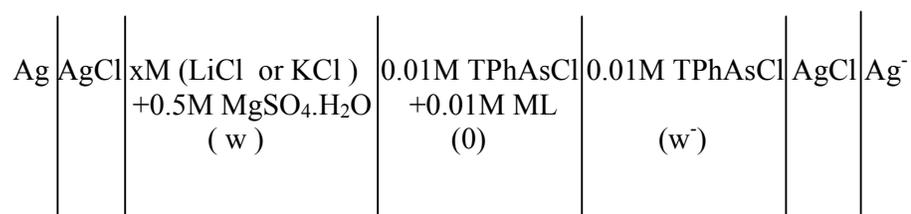
Where X =0.01 or 0.1   and   L =B15C5, 18C6 ,B$_2$ 18C6 and Cy$_2$ 18C6, was controlled by means of a conventional three – electrode potentiostat .

Results and Discussion

Figures (2,3) illustrate the polarographic behavior of various ion transfer systems (Base electrolytes, Ions in the presence of crown ether). The electrical current at the positive potential limit is connected with the transfer of either the cation (Li^+ or K^+) to the 1,2 – DCE or the anion Cl^- to water .Owing to the ion association in 1,2- DCE, the current I of the cation transfer to the organic solvent phase is to be expressed as the sum of two contributions. The first contribution is due to the simple ion transfer, e. g.

$$B^+ (w) \leftrightarrow B^+ (o) \ \ldots\ldots\ldots (1)$$
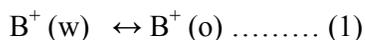
and the second one is due to the formation of the ion pair with the counter ion in the organic solvent phase, e. g.

$$B^+ (w) + A^- (o) \leftrightarrow B^+A^- (0)\ldots..(2)$$
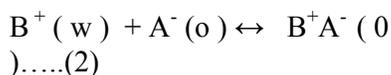
In the case that the bulk concentration of the counter ion is much higher than that of the transferred ion, the reversible half – wave potential ($E_{1/2}$)^{rev} ,which can be derived from the polarogram of a diffusion–controlled charge transfer [13] (e.g. Fig.(2)), Should correspond to the half-wave Galvanic potential difference

$$\Delta_o^w \cent^{rev} = \Delta_o^w \cent^{rev} (RT/F) \ln (\gamma^o/ \gamma^w) + (RT/2F)_{1/2} \ln(D^w / D^o)\ \_-$$
$$(RT/F) \ln[1\ K^o_a\ \alpha\ C^o(\gamma^o)^2\ (D^o_a / D^o)^2\ ] \ \ldots\ldots (3)$$

where $\Delta_o^w \cent^o$ is the standard Galvanic potential difference of the simple ion transfer, $D^{w,o}$ is the diffusion coefficient of the ion ,D^o_a or K^o_a is the diffusion coefficient or the association constant of the ion pair B^+A^-, respectively ,C^o is the bulk concentration of the organic base electrolyte and α is the degree of its dissociation in the organic solvent phase . The parameters γ^o and α can be evaluated by solving the system of equation [4] :
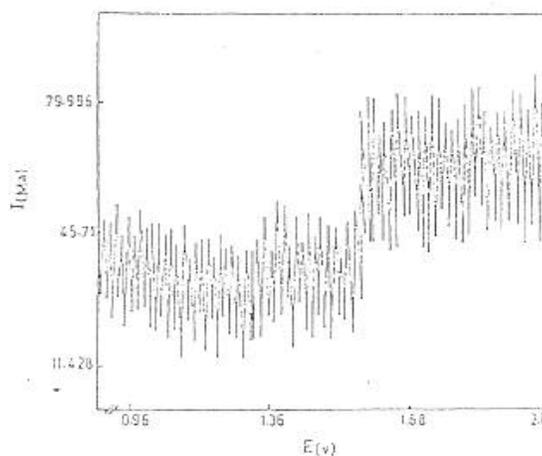
$$\overline{-} \log \gamma^o = A\sqrt{C^o\ \alpha}\ / (1+ Ba\ \sqrt{C^o\ \alpha})\ldots..(4)$$

$$K^o_{ab} = (1- \alpha\ ) / (\gamma^o)^2\ C^o\ \alpha^2\ \ldots.(5)$$

Where A, B and an are the parameters of the Debye – Hückel theory and K^o_{ab} is the association constant of the base electrolyte in the 1,2 DCE solvent phase .
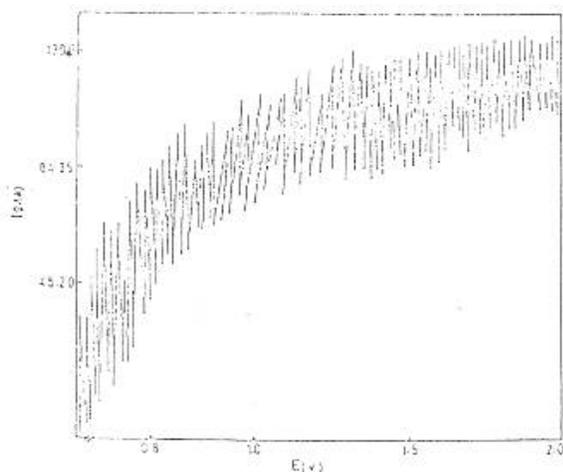
Figure (2). .Potential – scan polarogram: 0.01M LiCl + 0.5M MgSo$_4$ in Water and 0.01M TphAsCl + 0.01M 18 C 6 in 1,2-DCE. I= 6 * 10^{-1} Amm^{-1} ,td =1.2S and Scan rate= 3..33 mVS^{-1}

Figure (3). .Potential – scan polarogram: 0.01M LiCl + 0.5M MgSo$_4$ in Water and 0.01M TphAsCl + 0.01M B$_2$18C6 in 1,2-DCE. I= 10 * 10^{-1} Amm^{-1} ,td =0.8S and Scan rate= 8.88 mVS^{-1}

Figure (2,3) show the effect of the (Li^+ or K^+) on the polarogram of the water / 1,2 –DCE interface . The change in the positive polarization limit indicates that this limit is determined by the Gibbs- energy of transfer of the alkali metal cations. Equation [3] was applied to the Li^+ or K^+ ions transfer. In the case of the Potential differences, which were then converted into the half-wave potential differences $\Delta_o \cent_{1/2}$. The corresponding standard potential differences $\Delta_o \cent$ were obtained using eq. [3] and are summarized in table I.In either case , the onset of the faradic current is governed by the standard Gibbs energy of transfer $\Delta^w_o \cent$ of this ion from water to the organic solvent [2]. This quantity determines the standard potential difference of the ion transfer reaction.

$$\Delta_o^w \cent = \Delta G_{tr}^{o,w \to o} / z F \quad \ldots\ldots (6)$$

Where z is the ionic charge. In such case, the equation for the revisable anodic polarographic wave should apply [14].

$$E = E^{rev}_{1/2} + (RT / F) \ln I (I_d − I)^{-1} \ldots\ldots(7)$$

Where $E^{rev}_{1/2}$ the reversible half –wave potential, I is the electrical current, and I_d is the limiting electrical current . In fact, the plot of log I ($I_d − I)^{-1}$) vs. E is a straight line with the slope of 62 ± 2mV, giving values $E^{rev}_{1/2}$ are shown in figures (4) and (5).

A comparison eq.(3) with data for other organic solvents has indicated that Gibbs energies of transfer of alkali- metal cations correlate with the Gutmann donor numbers [11] , i.e. the highest transfer energies are found for the transfer to solvents having the lowest donating strength ; cf. Table II . Large and positive values of ion transfer energies seem to be responsible for the high stability of complexes ions in these solvents.
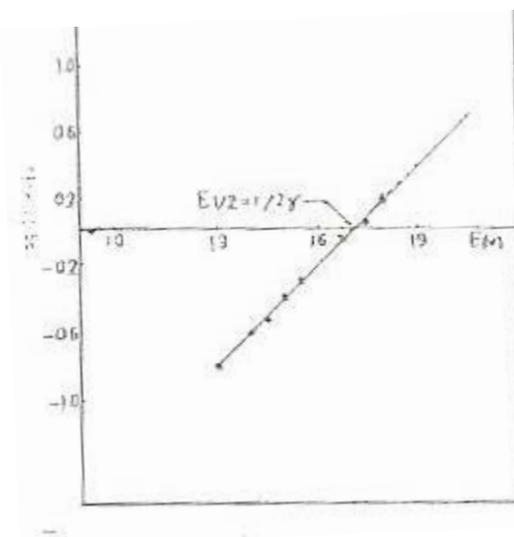
Fig. (4). Plot of the log (I/I$_d$-I) and applied potential for wave of Lithium cation in presence of 0.01 M of 18C6.
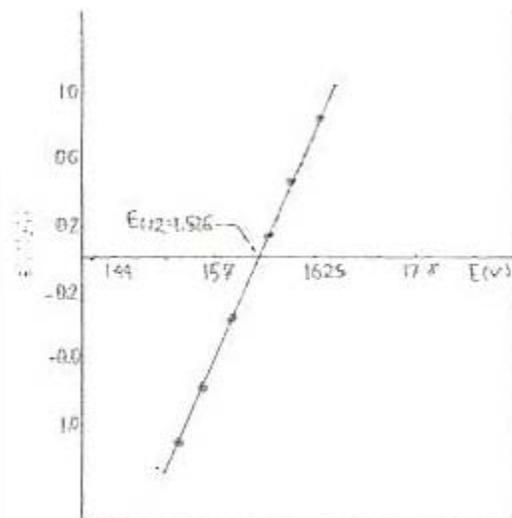
Fig. (5). Plot of the log (I/I$_d$-I) and applied potential for wave of Potassium cation in presence of 0.01 M of B$_2$18C6.

Consequently, the standard Gibbs energies of transfer of these cations from water to 1,2-DCE is negative, as one would expect for bulky hydrophobic ions. On the other hand, it is clear from table (I). A comparison with data for other organic solvents has indicated that Gibbs energies of transfer of alkali-metal cations correlate with the Guttmann donor number[15] ,i.e. the highest transfer energies are found for the transfer to solvents having the lowest donating strength (Table II). Large and positive values of ion transfer energies seem to

be responsible for the high stability of complexes ions in these solvents. A comparison of the cavity size of B$_2$18 C6 and the diameters of unsolvated ions shows that the optimal spatial fit is reached for the potassium cation [16, 17] , Actually. In 1,2-DCE the selectivity sequence is quite different, Li$^+$ > K$^+$ and it seems to follow mainly the change in the cation salvation. The cavity size effect no longer dominates. A similar behavior was found for the other three crown ethers studied.

Table I. polarographic data for the facilitated ion transfer from water to 1,2-DCE.

ion	B15C5		18C6		B$_2$18C6		Cy$_2$18C6	
	Li$^+$	K$^+$	Li$^+$	K$^+$	Li$^+$	K$^+$	Li$^+$	K$^+$
E rev $_{1/2}$	1.462	1.440	1.720	1.420	1.540	1.578	1.326	1.234
Δ G ^{o,w} $\rightarrow$ ^{o}KJ mol$^-$$_1$ tr	38.23	36.19	63.21	34.21	45.84	49.32	25.19	16.22

Table II. Relative stabilities of $B_2 18$ C6 complexes
of K+ ion in various solvents.

* solvent	** DN,Kcal mol $^{-1}$	*** $\Delta G^{o,w} \rightarrow {}^{o}KJ\,mol^{-1}$ tr	*** Log K
DMSO	29.8	-13.0	3.43
DMF	26.6	-10.3	3.55
MeOH	19.0	9.6	5.00
H_2O	18.0	0.0	1.60
PC	15.1	5.3	5.08
MeCN	14.1	8.1	4.80
NB	4.4	23	7.20
1,2-DCE	0.0	49.32	9.90

* Abbreviations : DMSO, dimethyl sulfoxide; DMF, N,N-dimethyl formamide; MeOH, methanol; PC,1,2-propylene carbonate; MeCN, actonitrile; NB, nitro benzene; 1,2-DCE, 1,2- dichloro ethane.
** The Guttmann donor numbers from ref. (15).
*** From ref. (10) and table I.

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