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Kinetic Solvent Effects on $K^+/K(Hg)$Electrodes in Some Dipolar Aprotic Solvent Systems by Cyclic Voltammetry

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The rate constants (${}_sk_R$) of $K^++e\ (Hg) \rightleftharpoons K(Hg)$ in the dipolar aprotic solvents like propylene carbonate (PC), *N*, *N*-dimethylformamide (DMF), acetonitrile (AN), and their several binary mixtures have been determined at 25 °C on a hanging mercury drop electrode (HMDE) by cyclic voltammetric measurements. The observed nature of the cyclic voltammograms indicates that the reaction is quasi-reversible in the range of the sweep rates 1.0—0.01 V s^{-1}. An insight to the composition profiles of the free energies of activation ($\Delta G^{\neq}$) relative to that in the chosen reference solvent (r) in the respective solvent (s) systems: $-\delta\Delta G^{\neq}(=RT \ln {}_sk_R/{}_rk_R)$ reveals that not only the solvation of K^+ but also that the transition state (TS) are responsible in dictating the rate constants. Also the solvation of TS is being guided by the dispersion interactions as well as the availability of the fraction of the free surfaces $(1-\theta_s)$ for varying adsorption of the solvent molecules on the electrodes, all relative to that of the respective reference solvents.

The galvanic reactions involving alkali metal ions and alkali metal amalgams $M^+/M(Hg)$ have lately drawn particular attention because of their wide utility in high energy nonaqueous batteries.[1-5] These reactions are also important from the point of academic interest[1,6] because of their simplicity of involving one electron transfer devoid of complication of extra phase generation and coupled reactions. The main object of using these $M^+/M(Hg)$ galvanic elements as the chief anode materials is to increase the emf of the cell. But performance of a galvanic cell[7] depends not only on the intensive factors like the standard electrode potentials but also on the capacitive factors like the exchange current densities (i_o) or the rate constants (k_R) which again depend upon various factors at the electrode–electrolyte junctions. Thus the measurements of i_o or k_R of the concerned reactions under different conditions, have lately become[8,9] one of the most important objectives for the development of nonaqueous batteries. Moreover, i_o or k_R is greatly influenced not only by the nature of the electrode substrates[8a] or composition of the electrolyte[8b] but also by the nature of the sovlents i.e. the medium effects of the reactants and products in different solvent systems.

Unfortunately however, only a few works[6,10,11] have been reported so far on the medium effects of the $M^+/M(Hg)$ redox couple in pure solvents and practically no work has been done in the mixed solvents which often play a better role[6,11,13] over the pure solvents. Notably again, the highly encouraging results of our earlier study[5] on the charging-discharging properties of cell (A)

$$K(Hg)/KI, \text{solv.}/I_2(Pt) \qquad (A)$$

in propylene carbonate (PC), *N*,*N*-dimethylformamide (DMF), acetonitrile (AN), and their binary mixtures, also point out the importance and usefulness of such studies. The outcome of these studies showed that the discharging efficiency of cell (A) passes through a maxima in (PC+DMF) and (DMF+AN) solvent systems. In search of the reasons behind it, it was considered highly useful to measure the rate constants of the reaction

$$K^+\,(\text{solv}) + e(Hg) \rightleftharpoons K\,(Hg) + \text{solv}. \qquad (B)$$

in the pure dipolar aprotic solvent like PC, DMF, and AN and their binary mixtures.

It is now increasingly recognized that the determination of exchange current (i_o) or rate constant (k_R) can be achieved by many techniques[14,15] viz d.cx. polarography with or without rotating disk (RD) and rotating ring disk (RRD) electrodes, AC impedance, faradaic rectification, chronopotentiometry with or without current reversals etc. But most of such techniques are cumbersome, tedius, and time consuming, while the method of widely applicable cyclic voltammetry[16,17] is rather simple, easy to follow, and free of extra hazards. Therefore, we used cyclic voltammetric method in this study, following Parker,[18] although the measurements are somewhat approximate in nature.

Experimental

AN, DMF, and PC were purified by the methods previously described.[19-21] The working electrolyte $KClO_4$ (Fluka, AG) and the supporting electrolyte tetrabutyl ammonium (TBA) perchlorate [Bu_4NClO_4] (Fluka, AG/Fischer Scientific Co., PG) are dried under a vacuum desiccator. Since there are strong evidences[6,11] that the rates of alkali metal cation reductions depend on the size of the cation of the supporting electrolyte, a single suitable supporting electrolyte, i.e. Bu_4NClO_4 has been chosen for the present study. The supporting electrolyte being common to all the solvent systems, the relative kinetic scheme of $K^++e(Hg)=K(Hg)$ reaction in cell (B) will not be much altered.

The basic experimentation involved a three electrode cell assembly in a glass vessel which provides an inlet and an outlet of an inert gas like N_2 through the system. The method for finding out the rate constant (k_R) through cyclic voltammetry[16] in essence involved the measurement of the cathodic and anodic peak potentials $[(E_p)_f$ and $(E_p)_b]$ and peak currents $(I_p)_f$ as a funtion of the voltage scan rate (v). An approprate scan rate had been chosen so that $\Delta E_p=[(E_p)_f-(E_p)_b]$ falls almost in the range of 60—120 mV where the error limit is only 5% for the deviation of the transfer coefficient α from 0.5.[16,18] Cyclic voltammetric measurements were performed at a hanging mercury drop electrode (HMDE) employing the appropriate appliances of PAR Electrochemistry system ECS 370.8, i.e. potentiostat (model 173) together with a universal programmer (model 175) and a Houston Omnigraphic (series 2000) X-Y-t recorder. Voltage sweep rates in the range 1.0—0.010 V s^{-1}, had been used. The lower range of the scan rates was however limited by incapability of the capillary used to hold the amalgam drop, as the surface tension decreases with the increase of impressed high negative potential for the reduction reaction. The Ag/Ag^+ (solvent) reference electrode was kept separated from the test solutions by a porosity 4-sintered Gooch cap but placed as close as possible to the working HMDE electrode (WE) using a Luggin capillary to ensure minimum IR-drop when the current was passed. The test solutions were pretreated with pure and dry N_2 for about 10—15 minutes.

Results

A few typical voltammograms (CVG's) of different solvents containing 0.0005 M $KClO_4$ and 0.1 M Bu_4NClO_4 (1 M=1 mol dm^{-3}) at 0.5 V s^{-1} in (PC+DMF) system have been presented in Fig. 1. At a concentration higher than 0.001 M of $KClO_4$, IR-drop is large so as to increase the cathodic and anodic peak potentials $[(E_p)_f$ and $(E_p)_d]$ and hence the ΔE_p values with the increase of the said concentration. At concentrations of 0.1 M of Bu_4NClO_4 and above, the IR-drop is negligibly small in the concentration range 0.005—0.0005 M of $KClO_4$, as it is evident from the constancy of the peak potentials and ΔE_p values with the concentration in the said range. Further lower values of concentration of $KClO_4$ are difficult to work with, since the current at these concentrations are comparable with the charging current of the system.[16]

A typical CVG in 75 wt% PC+25 wt% AN (wt= weight) solvent has been shown in Fig. 2 in order to indicate the variation of ΔE_p with concentration. For each solvent such variations of ΔE_p's with concentration have been measured. But only those values which remain invariant with concentration are taken into consideration as IR-free correct $(E_p)_f$ and $(E_p)_b$ values and the corresponding ΔE_p values are noted in Table 2. From the observed variation of ΔE_p and $(I_p)_f$ with the scan rate, it is evident[14,15] that the reaction is quasi-reversible in nature in the range of scan rates studied here. The k_R values were therefore evaluated by use of Nicholson's equation[16] correlating the rate constant k_R with the scan rate v.

$$\psi = \gamma^{\alpha} k_R / \left(\frac{n\pi F v}{RT} D_o\right)^{1/2} \qquad (1)$$

where ψ=Nicholson's function[16] and D_o=diffusion coefficient of K^+, $\gamma=(D_o/D_R)^{1/2}=1$ by convention, and other terms have usual significance.[16b] ψ values at different ΔE_p separations, corresponding to different respective scan rates for a given electrolyte solution, are obtained from Nicholson's plot of ψ versus $\Delta E_p \times n$.[16b]

The diffusion coefficient of K^+ ion $[D_o(K^+)]$ in each solvent has been evaluated by masuring the peak current at 0.010 V s^{-1} where ΔE_p value lies very near to 60 mV. The essential equation used is

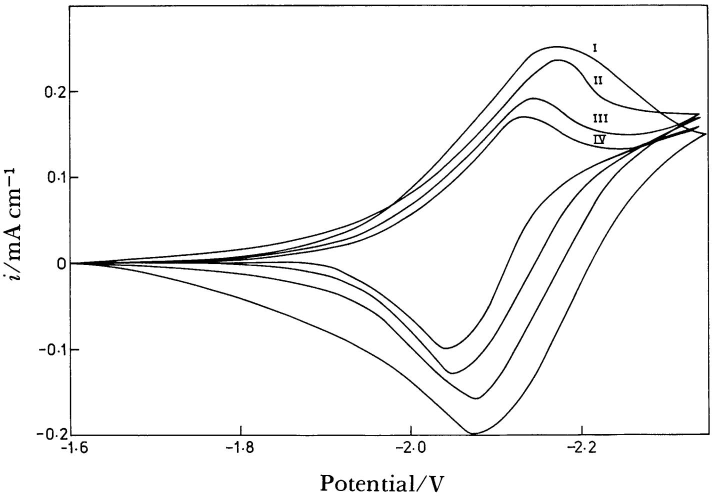

Fig. 1. Typical cyclic voltammogram at 0.5 V s^{-1} of 0.0005(M) $KClO_4$+0.1(M) Bu_4NClO_4 solution in DMF(I), 75%DMF+25%PC(II), 50%DMF+50%PC(III), 25%DMF+75%PC(IV) solvents at 25 °C.

$$i_{p(\mathrm{rev})} = 2.72 \times 10^5\, n^{3/2}\, C_o D_o^{1/2}\, v^{1/2}. \qquad (2)$$

The average surface area of each hanging Hg-drop was obtained with assumption of perfect spherical shape, by weighing approximately 25 such drops in a previously weighed dry glass pot.

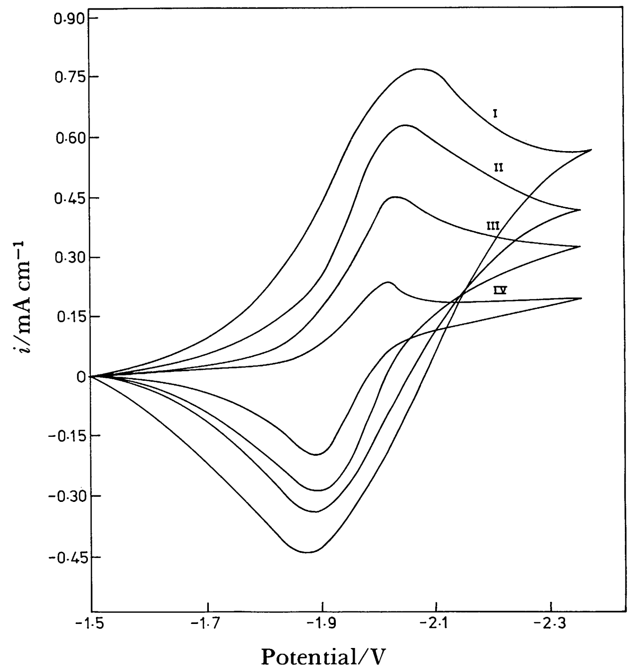

Fig. 2. Typical variation of peak potential (E_p) and ΔE_p vs. concentration of K^+ ion at the scan rate of 0.5 V s^{-1}. The curve shown is for [(75%PC+25%AN solvent+x(M)$KClO_4$+0.1(M) Bu_4NClO_4] electrolyte. x=0.0020(M)K^+ for I, x=0.0015(M)K^+ for II, x=0.001(M)K^+ for III, x=0.0005(M)K^+ for IV.

The authenticity of those D_o values presented in Table 1 is however checked by comparing them with those computed from Stokes–Einstein's (SE) relation[7b)]

$$D_o(\mathrm{i}) = (RT/F^2)\lambda_o(\mathrm{i}) \qquad (3)$$

where λ_o(i) is the limiting equivalent conductance of an ion i. The required $\lambda_o(K^+)$ values in the solvents have been recently evaluated in this laboratory (loc lit) by partitioning the measured values of λ_o (KI) using Krumgalz's assumption[22)] that

$$\lambda_o\,(\mathrm{TBA}^+)\,\eta_o = 0.213 \qquad (4)$$

is valid irrespective of solvents. Here λ_o (TBA$^+$) is limiting equivalent conductance of (TBA$^+$) and η_o is the viscosity coefficient of the solvent in poise. The diffusion coefficient D_o(i) thus obtained however corresponds to that at infinitely dilute solution, $D_{o(c=0)}$. So the appropriate D_o values at the experimental ionic strength (C) of 0.1 M, $D_{o(c=0.1)}$, were evaluated using Nernst–Hartley[7b)] relation (5)

$$D_{o(c=0.1)} = D_{o(c=0)}\,[1 + \mathrm{d}\ln f/\mathrm{d}\ln c] \qquad (5)$$

and the limiting form of Debye–Hückel (DH) equation for the activity coefficient f:

$$\log f \approx -\,AC^{1/2} \qquad (6)$$

which leads to the relation

$$D_{o(c=0)} = D_{o(c=0.1)}\,(1 - 1/2\,AC^{1/2}) \qquad (7)$$

Here DH constant,

$$A = 1.8246 \times 10^6\,(\varepsilon_s T)^{-3/2} \qquad (8)$$

and ε_s is the dielectric constant of the solvent.

Thus the diffusion coefficient values at infinitely dilute solution $D_{o(c=0)}$ were calculated from the conductivity data and those at 0.1 M ionic strength by use of relation (7). All these values together with those obtained from CV measurements are presented in

Table 1. Values of $(i_p)_{\mathrm{rev}}$ in mA cm^{-2} at 0.010 V s^{-1} Scan Rate, $D(K^+)$ as Computed from $(i_p)_{\mathrm{rev}}$ Using Eq. 2, Limiting Equivalent Conductance of K^+ Ion [$\lambda_o(K^+)$], Debye-Hückel Parameter A, and Other Diffusion Coefficients [$D_{c=0}(K^+)$ and $D_{c=0.1}(K^+)$ as Computed from S.E. Relation (3), at Various Solvent Compositions at 25 °C

Solvent	$(i_p)_{\mathrm{rev}}$/ mA cm^{-2}	$D(K^+)$/cm^2 s^{-1} (CV data)×10^5	$\lambda_o(K^+)$/ohm^{-1} cm^2 equiv^{-1}	$D(K^+)$/cm^2 s^{-1} $C\to 0\times 10^5$	A/mol$^{-1/2}$ l$^{1/2}$	$D_{c=0.1}(K^+)$/ cm^2 s^{-1}×10^5
PC	0.0197	0.21	10.43	0.28	0.6858	0.25
75%PC+25%DMF	0.0247	0.33	12.81	0.34	0.7439	0.30
50%PC+50%DMF	0.0313	0.53	20.25	0.54	0.8882	0.46
25%PC+75%DMF	0.0339	0.62	25.87	0.69	1.1510	0.56
DMF	0.0385	0.80	32.97	0.88	1.5935	0.66
75%PC+25%AN	0.0330	0.59	23.72	0.63	0.8435	0.55
50%PC+50%AN	0.0447	1.08	43.15	1.15	1.0146	0.96
25%PC+75%AN	0.0547	1.62	60.42	1.61	1.2353	1.29
AN	—	—	85.44	2.27	1.6442	1.68
75%DMF+25%AN	0.0441	1.05	43.10	1.15	1.6059	0.86
50%DMF+50%AN	0.0502	1.36	50.28	1.34	1.6185	1.00
25%DMF+75%AN	0.0554	1.66	62.59	1.67	1.6313	1.24

Table 2. Variations of Forward and Backward Peak Potentials [$(E_p)_f$ and $(E_p)_b$] and Peak Potential Difference $\Delta E_p[=(E_p)_f-(E_p)_b]$ in Volts, Forward Peak Current $(i_p)_f$ in $\mu A\ cm^{-2}$, Nichalson's Function ψ and Rate Constant k_R in $cm\ s^{-1}$, with Solvent Compositions at 25 °C

Scan rate/ $V\ s^{-1}$	Parameters	PC	75%PC+ 25%DMF	50%PC+ 50%DMF	25%PC+ 75%DMF	DMF	75%PC+ 25%AN	50%PC+ 50%AN	25%PC+ 75%AN	75%AN+ 25%DMF	50%AN+ 50%DMF	25%AN+ 75%DMF
0.5	$(E_p)_f$	2.120	2.125	2.140	2.170	2.175	2.111	2.125	2.155	2.125	2.155	2.165
	$(I_p)_f$	110.2	141.1	175.0	190.3	215.2	189.1	249.1	303.7	245.2	279.1	302.2
	$(E_p)_b$	2.025	2.039	2.047	2.080	2.070	2.019	2.035	2.075	2.011	2.076	2.073
	ΔE_p	0.095	0.086	0.093	0.090	0.105	0.092	0.090	0.079	0.114	0.081	0.092
	ψ	0.68	0.92	0.61	0.79	0.50	0.74	0.79	1.28	0.40	1.17	0.74
	$k_R \times 10^3$	7.64	12.96	10.89	15.26	10.97	13.94	20.14	39.96	12.64	33.46	18.60
0.2	$(E_p)_f$	2.112	2.110	2.130	2.162	2.165	2.002	2.110	2.050	2.110	2.148	2.140
	$(I_p)_f$	84.12	106.2	136.1	147.2	168.1	143.6	195.7	240.6	193.1	220.1	240.6
	$(E_p)_f$	2.029	2.033	2.046	2.082	2.074	1.920	2.029	1.978	2.013	2.076	2.060
	ΔE_p	0.083	0.077	0.084	0.080	0.091	0.082	0.081	0.072	0.097	0.072	0.080
	ψ	1.06	1.42	0.98	1.24	0.78	1.10	1.17	2.02	0.64	2.02	1.24
	$k_R \times 10^3$	7.54	12.65	11.07	15.15	10.82	13.11	18.86	39.88	12.80	36.54	19.71
0.1	$(E_p)_f$	2.110	2.092	2.125	2.155	2.158	1.993	2.105	2.045	2.095	2.140	2.132
	$(I_p)_f$	61.32	77.18	98.01	98.89	120.6	103.4	140.1	172.1	138.1	157.4	171.8
	$(E_p)_b$	2.033	2.020	2.048	2.082	2.076	1.918	2.031	1.976	2.008	2.071	2.057
	ΔE_p	0.077	0.072	0.077	0.073	0.082	0.075	0.074	0.069	0.087	0.069	0.075
	ψ	1.43	2.02	1.43	1.86	1.10	1.62	1.70	2.68	0.89	2.70	1.62
	$k_R \times 10^3$	7.19	12.73	11.42	16.06	10.79	13.65	19.38	37.42	12.57	34.54	18.21
0.05	$(E_p)_f$	2.104	2.080	2.120	2.150	2.150	1.991	2.090	2.035	2.080	2.132	2.122
	$(I_p)_f$	43.31	54.56	69.32	75.01	85.28	73.16	99.23	121.72	97.83	111.50	121.72
	$(E_p)_f$	2.034	2.012	2.047	2.080	2.074	1.91	2.020	1.969	2.000	2.065	2.052
	ΔE_p	0.070	0.068	0.073	0.070	0.076	0.070	0.070	0.066	0.080	0.067	0.070
	ψ	2.40	3.00	1.87	2.40	1.52	2.4	2.40	4.00	1.24	3.8	2.40
	$k_R \times 10^3$	8.53	13.37	10.56	14.66	10.54	14.29	19.35	39.49	12.39	34.37	19.07
0.02	$(E_p)_f$	2.095	2.075	2.116	2.146	2.144	1.986	2.087	2.182	2.074	2.127	2.115
	$(I_p)_f$	27.51	34.52	43.85	47.44	53.00	46.32	62.80	76.91	61.90	70.51	76.00
	$(E_p)_b$	2.027	2.010	2.048	2.078	2.074	1.919	2.020	2.119	2.002	2.063	2.048
	ΔE_p	0.068	0.065	0.068	0.068	0.070	0.067	0.067	0.063	0.072	0.064	0.067
	ψ	3.02	4.66	3.06	3.80	2.40	3.80	3.80	6.8	2.02	6.00	3.80
	$k_R \times 10^3$	6.79	13.13	10.93	15.45	10.53	14.32	19.37	42.45	12.77	34.32	19.10
Average	$k_R \times 10^3$	7.54	12.97	10.97	15.32	10.73	13.86	19.42	39.84	12.64	34.65	18.94

Table 3. Values of Rate Constants (k_R) and $-\delta(\Delta G^{\neq})$ for the Cathodic Reaction: K^+ (solv.)$^+$+e^-(Hg) ⟶ K(Hg) and Transfer Free Energies of K^+ and TS at Different Solvent Compositions at 25 °C

Mole fraction cosolvent	$10^3\,k_R$/cm s^{-1}	$-\delta(\Delta G^{\neq})=RT\ln {}_sk_R/{}_rk_R$/kJ	$\Delta G_t^\circ(K^+)$/kJ mol^{-1}	ΔG_t°(TS)/kJ mol^{-1}
		PC ⟶ (PC+AN)		
0.00	7.54	0.00	0.0	0.0
0.45	13.86	1.51	1.5	0.0
0.71	19.42	2.35	2.5	0.2
0.88	39.84	4.13	3.8	−0.3
		PC ⟶ (PC+DMF)		
0.32	12.97	1.34	−4.4	−5.7
0.58	10.97	0.93	−7.4	−8.3
0.80	15.32	1.76	−8.6	−10.4
1.00	10.73	0.87	−9.7	−10.6
		DMF ⟶ (DMF+AN)		
0.00	10.73	0.00	0.0	0.0
0.30	18.94	1.41	1.3	−0.1
0.44	34.65	2.91	4.1	1.2
0.79	12.64	0.41	7.4	7.0
1.00	—	—	14.8	—

Table 1 for comparison. From this table it is evident that all the diffusion coefficient values agree fairly well with each other at least for the present purpose of determining k_R.

The k_R values for all the solvents at different scan rates ranging between 0.50—0.02 V s^{-1} and obtained by use of Eq. 1 and the other relevant data viz. $(E_p)_f$, $(I_p)_f$, $(E_p)_b$, ΔE_p, and ψ values are presented in Table 2.

The k_R values for the solvents, as determined by taking the averages of all the measured k_R values at different scan rates [vide Table 2] are displayed in Table 3. Moreover, in order to facilitate the explanation of the observed solvent effect on k_R the values of free energy of activation (${}_s\Delta G^{\neq}$) in the solvent (s) relative to that in the chosen reference solvent (r) i.e. $\delta(\Delta G^{\neq})$ [$={}_s\Delta G^{\neq}-{}_r\Delta G^{\neq}=-2.303\,RT\log {}_sk_R/{}_rk_R$], transfer free energies of K^+, $\Delta G_t^\circ(K^+)$ and that of the transition state TS, ΔG_t°(TS), are also presented in Table 3.

Discussion

Branski and Fawcett[6,8] in similar studies on rate constants k_R in some dipolar aprotic solvents observed that a direct correlation exists between $-RT\ln k_R$ and the free energies of solvation of alkali metal cations. Seemingly, the observed nonlinear variation of relative rate constants $RT\ln({}_sk_R/{}_rk_R)$ versus $\Delta G_t^\circ(K^+)$ (viz. Table 3) indicate that other factors are playing a vital role in dictating the values of k_R in these solvent systems. So, for a proper insight to the relative effects of these factors on the reaction rates, the well-known Eyring equation

$$k_R = (kT/h)\exp(-\Delta G^{\neq}/RT) \qquad (9)$$

where $\Delta G^{\neq}$ is the free energy of activation of the process:

$$K^+\,(\text{solv.}) + e^-(\text{Hg}) \longrightarrow \text{TS} \longrightarrow \text{K(Hg)} + \text{solv.} \qquad (A)$$

was used to correlate the solvent effect on the relative rate constants $-\delta(\Delta G^{\neq})[=RT\ln{}_sk_R/{}_rk_R]$ with the transfer free energies (ΔG_t°) of K^+ and the transition state (TS). Thus,

$$\begin{aligned}2.303\,RT\log({}_sk_R/{}_rk_R) &= -\,\delta(\Delta G^{\neq})\\ &= \Delta G_t^\circ(K^+) - \Delta G_t^\circ(\text{TS}). \qquad (10)\end{aligned}$$

From this it appears that it is not only the relative solvation of K^+ but also that of TS is likely to be responsible for the observed kinetic solvent effect of the cathodic reaction. Again, ΔG_t°(TS) seemingly depends on two factors: (i) stabilization of TS by solvation through its exposed part towards the bulk of the solution and (ii) stabilization of TS on the electrode surface as guided by $(1-\theta_s)$ where θ_s stands for the coverage by solvent molecules.

Thus, effectively three factors are responsible for influencing the relative reaction rate constants $-\delta(\Delta G^{\neq})$. Firstly, the relative solvation of K^+ as reflected from $\Delta G_t^\circ(K^+)$ values; secondly, the stabilization of TS by solvent molecules and thirdly, by the availability of free sites on Hg-electrode surface on which the adsorption of the TS takes place. In fact, the greater the value of $\Delta G_t^\circ(K^+)$ i.e. the relatively less solvated is K^+, the greater will be the rate. From the values of $\Delta G_t^\circ(K^+)$ in these solvent systems [vide Table 3], as taken from an earlier work,[23] it appears that the change of rate of the reaction due to this factor only will be in the order: AN>PC>DMF.

Again, if the formation of the intermetalic adions $[K(Hg)]^{\alpha+}$ (α=0.5 say) be taken as the TS, the solution side of the adions will be stabilized mainly through ion-dipole[24] and dispersion[19] interactions. If such interactions increase, so will be the rate of the reaction.

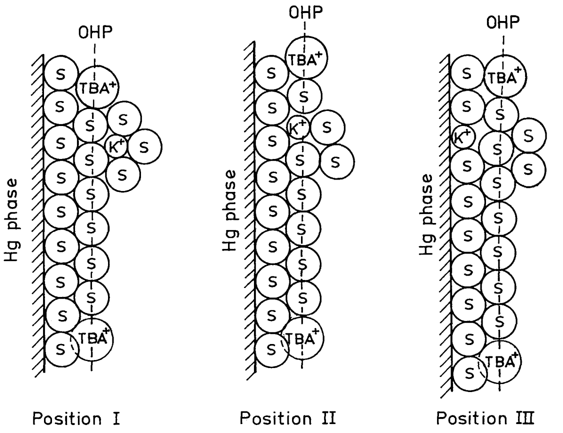

Fig. 3. Model for the passage of K+ ion through the compact region of the double layer. The solvent (S), supporting electrolyte (TBA+ or Bu_4N^+) and K+ ions are represented as hard spheres. Positions I, II, and III correspond to passage of the reactant from a fully solvated ion at its distance of closest approach (I) to a contact adsorbed atom or ion at the metal phase in which it is adsorbed. Electron tunneling from the metal surface to the ion take place at any positions of the three steps.

The effect of this factor on the reaction rate will be in the following order: PC>DMF>AN, since polarizability and dipole moment of the three solvent molecules AN, DMF, and PC are (4.41, 7.88, 8.56/Å^3) and (3.92, 3.86, 4.98 D) respectively. If donor property[25)] of the solvent also plays a significant role, the effective order of solvation would be DMF≫PC>AN as the donor numbers[26)] are 26.6, 15.1, and 14.1 kcal mol^{-1} respectively (1 cal=4.184 J). However, the donor numbers being enthalpy data rather than free energy, they can hardly be taken as true measures of the solvating tendency of the solvents. The latter in fact is partly guided by polarizability and dipole moment besides the electronic and structural configuration of the solvent molecules.

From the work of Branski et al.,[8)] it is expected that whatever be the mechanism, the electrode surface is largely covered, even at the high negative potentials, partly by the solvent molecules and partly by supporting electrolyte cations TBA+. And the essential path towards alkali metal ion (K+) reduction is likely to involve the steps nearly similar to that shown in positions I—III in Fig. 3. Evidently, availability of the free surface relative to that of the reference solvent would be partly responsible for dictating the relative rates in the solvents.

At a given negative potential the degree of adsorption of solvent molecules (θ_s) on the Hg surface is likely to be dictated by the relative magnitudes of the surface potential and the dipole moment of the solvent molecules rather than its acceptor property.[26)] From a study of Na+ reduction in some nonaqueous solvents, Jorne and Pai[10)] have determined the surface potentials in PC, DMF, and AN solvents as 0.179, 0.147, and 0.132 V. As is well-known, the sign of the surface potential is determined by the orientation of the solvent dipole towards vacuum. Also, as a general rule, it can be assumed that if the surface potential is positive or negative, the same respective end of the solvent dipoles will point towards the electrode. Thus the positive surface potential values for the three solvents indicate that all the three solvents, PC, AN, and DMF will point towards the negatively charged electrode through their positive ends. Furthermore, the works of Payne[26)] on capacitance measurements, Brasseur and Hurwitz[27)] on conformational studies, and Yeager[28)] on spectroscopic measurements also indicate the same order of surface potentials for the three solvents concerned. Evidently, from a close perusal of the dipole moment and surface potential values of the three solvents the expected order of θ_s is PC>DMF>AN.

Since the solvation of TS and hence the reaction rates are likely to be partly determined by the extent of free surface i.e. by $(1-\theta_s)$, their relative order in absence of other factors, would be as follows: AN>DMF>PC. Thus, the magnitude of k_R depending on several factors including the relative solvation of K+ and the relative coverage θ_s of the electrodes by the solvent molecules, which act oppositely to one another, an extremum is expected among these binary solvent mixtures. This has been actually observed in the composition containing 25 wt% PC+75 wt% DMF in (PC+DMF) solvent system.

In (PC+DMF) system, as one adds on DMF to PC, both the K+ ion and the TS get solvated more and more due to greater cavity effect and also charge-transfer type interactions[23)] for K+ ion and increased availability of the free space $(1-\theta_s)$ for the TS. But since the transition state remains much more stabilized than K+ ion in the whole composition range (Table 3), these result in the observed increase of the reaction rate. However, at the compositions containing 75—100 wt% DMF, where an almost complete replacement of adsorbed PC molecules by DMF molecules on the Hg-surface is expected, the stabilization of the TS, unlike that of K+ ion, reaches a saturation point, because the free energy change due to solvent desorption factor remains invariant at this stage. This results in the observed maxima of the relative rate (Table 3) at 75 wt% DMF composition of (PC+DMF) solvent system.

In (PC+AN) system, on addition of AN to PC, K+ ion is increasingly desolvated due to the well-known cationophobic[19b)] characteristics of AN, as also reflected from the observed increasingly positive magnitudes of $\Delta G_t^\circ(K^+)$ from PC to AN (Table 3). Notably, however, as reflected in Fig. 3, the stabilization of TS remains unaltered possibly because of two equally strong opposing effectes: (1) the increased desolvation of TS due to smaller dispersion interaction of AN than PC and (2) increased solvation of TS due to larger $(1-\theta_s)$ factor on the Hg-surface in the AN-rich compositions of the solvent system. The observed increase in the rate constants is therefore dictated by the increased destabilization of K^+ with the increased AN composition.

In (AN+DMF) system, the observed maxima in the 50 wt% DMF+50 wt% AN mixture is seemingly guided by the increased desolvation K^+ in AN-rich composition due to lack of charge transfer and less dispersion type of interactions as compared to the less desolvation of the TS (Table 3). The combined effect of two opposing factors, desolvation of TS by AN and increased $(1-\theta_s)$ factor in the AN-rich compositions of the system leads $\Delta G_t^\circ(\mathrm{TS})$ to pass through a minimum in the lower AN-composition of the system. The overall effect is however a maximum in the relative rate at 25 wt% DMF+75 wt% AN composition of the system.

Significantly enough, the observed percent discharge efficiency values of cell A[5] lie almost in the same sequential order as the above-noted k_R values do. The maxima in the discharge efficiency were at 75 wt% DMF+25 wt% PC and at 75 wt% DMF+25 wt% AN, just as the relative rate constant composition profiles exhibit similar maxima in the said compositions in the respective solvent systems. Thus the k_R values observed herein show a complete accord with the discharge efficiency resulted in our previous studies.[5]

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