STUDIES OF ION TRANSFER ACROSS IMMISCIBLE ELECTROLYTE SOLUTIONS

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Studies of Ion Transfer Across Immiscible Electrolyte Solutions

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DEDICATION

To Ato Taye Berhane, Menbere Taye
and
to my Parents.

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Abstract

The transfer of ions across the water/acetophenone interface has been investigated by ac cyclic voltammetry. The reversibility of the ion transfer at low sweep rates, as well as precise half-wave potential values have been determined from the observed ac cyclic voltammograms. The reversibility of the ion transfer across the water/acetophenone interface at low sweep rates has also been further established by using the dc cyclic voltammetric technique. Values of standard Gibbs energies of transfer from water to acetophenone for several ions have been evaluated. These have been compared with theoretically calculated values for this system.

Such studies of ion transfer have been extended for the water/nitrobenzene and water/chlorobenzene-nitrobenzene mixture systems using dc cyclic voltammetry. The values of the standard Gibbs energies of transfer for many ions obtained in these systems have been compared with theoretically estimated values. The present experimental results for the water/nitrobenzene system are in very good agreement with those calculated from partition (extraction) experiments by other workers. Attempts have also been made to correlate standard Gibbs energies of transfer with the dielectric constants of the organic mixtures.

1. Introduction

Electrolysis at the interface of two immiscible electrolyte solutions (ITIES) was recently developed as a new electroanalytical method [1,2,3]. In contrast to the study of the metal/electrolyte solution interface, investigation of the polarization of two immiscible electrolyte solutions has been comparatively small in scope. However, studies of such systems may be used to enlarge the field of analytical voltammetric methods, and at the same time may serve as a very simple membrane model. Therefore electrolysis at ITIES can provide useful information for understanding the processes occuring at biological membranes, as well as, for assessing the selectivity of liquid-membrane ion selective electrodes. It may also help to elucidate the processes of phase transfer catalysis and for obtaining ideas about charge transfer process.

Nernst and Riesenfeld as quoted in Ref. [2] were the first to investigate the electrolysis at ITIES with the same electrolyte dissolved in both phases. They theoretically predicted and experimentally proved the effect of accumulation and depletion of the transported salt at ITIES depending on the direction of the current and on the values of transport numbers. Their study was based on chronopotentiometric method.

For several decades investigations of ITIES were restricted to the study of equilibrium potential differences between aqueous and organic phases in contact in the presence of various electrolytes. Bauer and Kronman [4] made e.m.f. measurments across ITIES by adding a picrate or strychnine salt in the aqueous phase. The results obtained characterized the potential differences as ionic adsorption potentials. Other potential difference measurements were made at the junction of the intact surfaces of plants and aqueous salt solutions [5], and the observed results made clear some bioelectric phenomena. Similar e.m.f. study by the same worker [6] at ITIES showed the dependence of the e.m.f. on the partition coefficients of salts dissolved between water and the organic liquid. Beutner and others [7,8,9] carried out further e.m.f. measurments across ITIES. A thermodynamic treatment of these results was made by Bonhoeffer et al. [10], who made experiments at the interface of quinoline/water and determined the "oil membrane potential" for various concentrations of quinoline-HCl and LiCl. From these results an analogy was drawn between this system and an ion-exchange medium. Similar systems were also studied by Karpfen and Randles [11], and by Boguslavsky et al [12,13].

A change in the interfacial tension of ITIES in the system of cetyltrimethylammonium bromide in water and nitrobenzene was observed by Guastalla [14,15,16,17] during the flow of current across the interface. He called this effect electroadsorption and assumed that it is caused by the electric field arising at the electrode during current flow. Watanabe et al [18,19] obtained electrocapillary curves for oil-water systems containing surface active agents by applying "electrostatic voltage" and observed the change in the interfacial tension with the anions and cations present in the systems. Dupeyrat and Michel [20,21] did experiments concerning the mechanism of electroadsorption at the water-nitrobenzene interface, using octadecyltrimethylammonium bromide, and picrate. They drew a conculsion that the variations in the interfacial tension as a function of applied potential could not be explained only by electrocapillary adsorption. Blank [22] studied the effects due to the flow of current across a water/nitrobenzene interface in the presence of a cationic surface active agent and analyzed the interfacial tension data, using the Nernst-Riesenfeld approach. He showed that the effect of electroadsorption was exclusively due to the accumulation or depletion of surface active electrolytes at the interface, which depended on the concentration of ions in both phases, the current and the transport numbers. A similar approach was used by Joos et al [23,24]. They studied the system water/nitrobenzene in which cetyltrimethylammonium bromide was dissolved as a surface active electrolyte. They explained the change of the interfacial tension during the flow of current due to a difference in transport numbers of the cation in both phases and gave a mathematical analysis. d'Epenoux et al [25,26] also did similar investigations, and accounted for the variation of the interfacial tension under galvanostatic conditions as related to the change of the ionic concentration in the interfacial layer due to the ion transfer between the two immiscible solutions.

The electrical phenomena of the current-potential relationship at ITIES was investigated in much detail by Gavach and co-workers. These authors studied the polarizability of ITIES during current flow in the presence of KCl in water and tetramethylammonium picrate in nitrobenzene [27] using the technique of chronopotentiometry. The over potential of ITIES was studied [28,29,30,31,32], by decomposing it into the ion transfer overvoltage and the diffusion overvoltage. Using the same method they determined kinetic parameters for the transfer of tetralkylammonium ions from water to nitrobenzene [33]. They calculated the kinetic parameters of transfer for bromide ion across the water/ nitrobenzene interface from experimentally obtained curves [34]. They extended the classical treatment of the double layer and measured the interfacial tension for the water/nitrobenzene tetralkylammonium bromide systems [35]. They also investigated the structure of the double layer of similar systems. To prove reversibility of the transfer process, chronopotentiometry with current reversal has also been employed by Homolka et al [36]. The chronopotentiograms obtained by Gavach and co-workers [29,30] completely resemble those recorded with a mercury electrode in aqueous solutions.

An electrolyte dropping electrode (EDE) [37] was designed and used for polarographic investigation of processes at ITIES. Current-potential curves (polarograms) were obtained for NaBr and tetrabutylammonium-tetraphenylborate base electrolytes in the aqueous and in the nitrobenzene phase respectively using tetraethylammonium cation as the ion to be investigated. Distinct polarographic waves, however, could not be found. The same method was extended [38] and various base electrolyte systems were studied for better S-chaped polarographic curves. However, the limiting currents were found to be higher than those predicted by the Ilkovic equation. Other workers [39] showed the feasibility of polarography using the EDE for quantitative analysis by eliminating the ohmic potential drop which was the cause for the distortion of the polarograms.

Suppression of polarographic maxima by the addition of a surface active substance was also reported [40]. Vanysek [41] used the method for investigation of transfer of anions across the water/nitrobenzene interface using crystal violet as the base electrolyte in the non-aqueous phase.

ITIES has also been investigated using cyclic voltammetry. Samec et al [42] demonstrated that the method of cyclic voltammetry with four-electrode system would give a clear picture of the charge transfer processes across ITIES by using 0.01M LiCl in water and 0.05M tetrabutylammoniumtetraphenylborate in nitrobenzene. The polarization curves indicated the transfer of tetrabutylammonium cation from the nitrobenzene to the aqueous phase and the reverse curves showed the transfer to the non-aqueous phase. In another communication [43], the method was employed for the investigation of Cs^+ and tetralkylammonium ions transfer across the water/nitrobenzene interface by using a positive feedback for the elimination of the ohmic potential drop with four electrode system. The standard inner potential differences and kinetic parameters were deduced for the studied ions. For an electron transfer reaction across ITIES using the stationary Nernst-diffusion layer treatment, the relationship between the current and the inner potential difference across water/nitrobenzene interface has been derived and analyzed [44]. Using this formulation electron transfer between hexacyanoferrate(III) in water and ferrocene in nitrobenzene was investigated [45] by cylic voltammetry with four-electrode system. Qualitative interpretations had been given based on the theory of the stationary current-potential curve worked out in [44]. However, quantitative analysis of the results were not possible. The method was found to be also suitable for facilitated cation transfer in the presence of macrocyclic complex formers (ionophores) in the organic phase [36], for ion transfer across the water/1,2-dichloroethane interface [46.47], and for studying the transfer of strong hydrophilic anions, by employing crystal violet tetraphenylborate which would widen the useful range toward the negative potential [48]. The technique of ac-cyclic voltammetry has been applied to the study of ion transfer across the water-nitrobenzene interface [49]. The difference between the ion transport across an interface separating electrolyte solutions in immiscible liquids and processes occuring at the metal/electrolyte solution interface have been analyzed recently by Melroy et al [50].

As can be seen from the above, in all the various electrical techniques employed for the investigation of ion transfer processes across ITIES, the most often used solvent is nitrobenzene. Only 1,2-dichloroethane and few other solvents like 1-phenyl-1-propanone (propiophenone), 4-isopropyl-1-methyl-2-nitrobenzene (2-nitro-p-cyanene), and 4-methyl-2-pentanone (methylisobutylketone) [2,46,47] have been tried with success. This is due to the restrictions imposed on the organic solvent for such system. The requirements for the choice of the nonaqueous solvent are:

1. The solvent must dissolve only a small amount of water, since otherwise the base electrolytes cannot be confined to their respective phases and no suitable potential range for polarization of the interface would be found.
2. The solvent should be sufficiently polar (with minimum relative permittivity about 10) to safeguard sufficient conductivity of the nonaqueous phase.
3. It should differ considerably from water in its density so that a stable interface could be found. As a result, the standard Gibbs energies of transfer for various ions from water to nitrobenzene and from water to 1,2-dichloroethane only have been reported so far using the electrochemical techniques.

Abraham et al [51,52] have determined the standard Gibbs energies of transfer (ΔG_t^o) for single ions from water to dry 1,2-dichloroethane and to 1,1-dichlorethane from solubility and calorimetric measurments. Partition data for quaternary ammonium salts in 1,2-dichloroethane plus water system have been extrapolated by Czapkiewicz and Czapkiewecz-Tutaj [53] to zero concentrations to yield the limiting partition coefficients of electrolytes from partition experiments. Values of standard Gibbs energies of transfer for cations and anions obtained from these experiments (ΔG_p^o) were compared with the solubility data of Abraham et al [51,52]. These two results revealed reasonable conformity in the observed trends and some of the values were identical even though those derived from partition data were for the transfer of ions in a mutually saturated two-phase system. This was not the case for values reached through the measurement of the solubility of the salts in pure water and pure organic solvent. Recently Abraham and Liszi [54] calculated standard Gibbs energies of solvation of ions in an organic solvent using their new electrostatic method, and these were combined with the standard Gibbs energies of hydration to yield the standard Gibbs energies of transfer of the ions from water to the organic solvent. It was shown that for the solvent systems water/1,2-dichloroethane, dichloromethane, chloroform, O-dichlorobenzene, chlorobenzene, and nitrobenzene there was good agreement between the calculated ΔG_t^o values and the observed standard Gibbs energies of transfer for partition of ions, ΔG_p^o. However, for organic phase in which water was quite soluble, for example 1-octanol, 1-pentanol, ethylacetate, and methylisobutylketone, the calculated ΔG_t^o values were always more positive than the observed partition values ΔG_p^o. This effect was explained as due to hydration of the ions in the wet organic phase. It has been concluded that ΔG_t^o which refers to the transfer of ions between two pure solvents concerned cannot be identical to ΔG_p^o which refers to the partition of ions between water saturated with the organic phase and the organic phase saturated with water, in which there is the possibility that the ions are extracted into the organic phase as hydrated entities. The theoretical calculations therefore might provide useful information as to the state of the dissociated ions in the wet organic solvent.

2. Theory

The electrochemical behavior of the interface of two immiscible electrolyte solutions (ITIES) depends largely on the ionic composition of the two immiscible electrolyte solutions. When one of the solvent is water and the other is an organic liquid and when the aqueous phase contains a strongly hydrophilic electrolyte (e.g Li_2SO_4) and the organic phase a strongly hydrophobic electrolyte like tetrabutylammonium tetraphenylborate, then the properties of the ITIES become completely analogous to those of a polarizable electrode. On the other hand if there is sufficiently large concentration of ions with high exchange rates present in both phases, the ITIES behaves like a non-polarized electrode.

In a system consisting of water (phase α) in contact with an immiscible organic solvent (phase β), and containing an ion i of charge Z, which is transferred from one phase to another, the condition for equilibrium can be stated as follows. The electrochemical potential of the ion in phase α must be the same as that in phase β. That is

$$\tilde{\mu}_i^{\alpha} = \tilde{\mu}_i^{\beta} \qquad (1)$$

on

$$\mu_i^{o,\alpha} + RT \ln a_i^{\alpha} + ZF\, \psi_i^{\alpha} = \mu_i^{o,\beta} + RT \ln a_i^{\beta} + ZF\, \psi_i^{\beta} \qquad (2)$$

where $\mu_i^{o,\alpha}$ and $\mu_i^{o,\beta}$ - are standard chemical potentials of the ion i in phase α and β.

a_i^{α} and a_i^{β} are the activities of the ion i in phase α and β

ψ_i^{α} and ψ_i^{β} are the inner potentials of i in the respective phases.

From equation (2) the inner potential difference between α and β is described by the following equation as

$$\Delta_{\beta}^{\alpha}\psi_i = \psi_i^{\alpha} - \psi_i^{\beta} = \frac{\mu_i^{o,\beta} - \mu_i^{o,\alpha}}{ZF} + \frac{RT}{ZF} \ln \frac{a_i^{\beta}}{a_i^{\alpha}} \qquad (3)$$

where $\Delta_{\beta}^{\alpha}\psi_i$ is the inner potential difference between phase α and phase β.

Equation (3) can be written in the form

$$\Delta_{\beta}^{\alpha}\psi_i = \Delta_{\beta}^{\alpha}\psi_i^{o} + \frac{RT}{ZF} \ln \left(\frac{a_i^{\beta}}{a_i^{\alpha}}\right) \qquad (4)$$

where

$$\Delta_{\beta}^{\alpha}\psi_i^{o} = (\mu_i^{o,\beta} - \mu_i^{o,\alpha}) / ZF \qquad (5)$$

$$= \frac{\Delta G_{t,i}^{o,\alpha \rightarrow \beta}}{ZF}$$

and $\Delta G_{t,i}^{o,\alpha \rightarrow \beta}$ is the standard Gibbs energy of transfer of the ion i from phase α to phase β. $\Delta_{\beta}^{\alpha}\psi_{i}^{o}$ is the standard inner potential difference between these phases.

The determination of standard Gibbs energies of transfer of ions is possible from equation (5), provided that the standard inner potential difference can be obtained experimentally (from voltammetric or chronopotentiometric measurements). The transfer of ions across ITIES studied by cyclic voltammetry follows formally the same laws as those governing the electron transfer at the metal/electrolyte solution interface. At low sweep rates the ions transfer is diffusion controlled, hence the current response of the system to a triangular potential signal can be treated like a reversible electron transfer reaction [55,56]. Thus the current potential relationship is given by the equation

$$i = Z^{3/2} F A C_i^b D_i^{1/2} V^{1/2} \pi^{1/2} \chi(at) \qquad (6)$$

where A = area of the interface (cm^2)

C_i^b = bulk concentration (mole dm^{-3})

V = sweep rate (volt sec^{-1})

$\chi(at)$= current function (Its values are tabulated by Nicholson and Shain [56]).

The cyclic dc voltammetric peak potential ($\Delta_{\beta}^{\alpha}\psi_{p,i}$) for ion transfer at 298^{o}k is related to the polarographic half-wave potential ($\Delta^{\alpha}_{\beta}\psi_{1/2,i}$) by the relationship

$$\Delta^{\alpha}_{\beta}\psi_{p(i)} = \Delta^{\alpha}_{\beta}\psi_{1/2,i} \pm \frac{0.0285}{/Z/} \qquad (7)$$

(+) stands for the positive electrical current peak potential and (-) stands for the negative electrical current peak potential. $\Delta^{\alpha}_{\beta}\psi_{1/2,i}$ is in turn related to the standard inner potential difference by the equation

$$\Delta^{\alpha}_{\beta}\psi_{1/2,i} = \Delta^{\alpha}_{\beta}\psi^{o}_{i} + \frac{RT}{ZF} \ln \left[\frac{D^{\alpha}_{i}}{D^{\beta}_{i}}\right]^{1/2} \left[\frac{\gamma^{\beta}_{i}}{\gamma^{\alpha}_{i}}\right] \qquad (8)$$

D^{α}_{i}, D^{β}_{i} are diffusion coefficients and γ^{α}_{i}; γ^{β}_{i} are the activity coefficients of the ion i in the two phases α and β. The activity coefficients of the ion i in the two solvents can be calculated by the extended Debye-Huckel Law. For fairly dilute solutions, the term $(\gamma^{\beta}_{i}/\gamma^{\alpha}_{i})$ may be taken as unity. The error arising from this assumption is very small and approximated to be about 0.6 KJ mol^{-1} [47]. The diffusion coefficient of the ion i in a given solvent may be obtained using the relationship

$$D_{i} = \frac{TR\lambda^{o}_{i}}{/Z_{i}/F^{2}} = U_{i}RT \qquad (9)$$

Where, λ_i^o = single ion equivalent conductivity and
U_i = ion mobility.

It is possible to derive a scale of single ion conductivities in a given organic solvent like nitrobenzene based indirectly on tetraisoamylammonium tetraisoamylborate as a reference electrolyte, and assuming Walden's product will hold for the reference electrolyte in the solvent. Using this reference electrolyte Coetzee and Cunningham [57] had evaluated single ion conductivities for acetonitrile, nitromethane and indirectly for nitrobenzene. From eq. (8) $\Delta^{\alpha}_{\beta}\Psi^{o}_{i}$ can be obtained and from eq. (5) $\Delta G^{o,\alpha \rightarrow \beta}_{t;i}$ can be calculated.

Alternatively one can obtain $\Delta^{\alpha}_{\beta}\Psi_{1/2}$, from ac cyclic experiments using the theory of ac cyclic voltammetry [58,59]. Based on this theory, for completely reversible ion transfer process the forward and reverse dc scans should yield overlaping peaks in the plot of i (ωt) vs $\Delta^{\alpha}_{\beta}\Psi_{dc}$, passing through a maximum at $\Delta^{\alpha}_{\beta}\Psi_{1/2}$. In addition to the overlap of forward and reverse peaks, the half-peak widith is 90 mv regardless of the sweep rate, if the system behaves reversibly. But, if the ion transfer process itself is rate determining, the peaks observed in the forward and reverse scans will not overlap as in the reversible case.

The standard Gibbs energy transfer of an ion i in pure solvents α and β is given as the difference of standard Gibbs energies of solvation of i in both solvents. The standard Gibbs energy of transfer of an electrolyte can be obtained from solubility or partition experiments. Since the two phases are in contact equilibrium and are mutually saturated in partition experiments, $\Delta G^{o}_{t,i}$ values obtained by this method would not be exactly the same as those calculated from solubility experiments in which the solvents are dry and free from each other [53,54].

However, $\Delta G^{o}_{t,i}$ of individual ions are not accessible to a direct measurment (from solubility or partition data), and to make possible their quantitative determination possible, an extra thermodynamic assumption must be made. Very often the "tetraphenylarsoniumtetraphenylborate (TPAsTPB) assumption" which states that the standard Gibbs energies of transfer of tetraphenylarsonium cation and tetraphenylborate anion are equal for any pair of solvents [60]. Both these ions are quite voluminous so that the charge of the central atoms acts only electrostatically on the solvent dipoles. The interaction of the benzene rings with the solvent is the same for both ionic species. Thus, the same standard Gibbs energy of transfer from an arbitrary solvent α to another solvent β can be attributed to both ions [61].

$$\Delta G^{o,\alpha \dashrightarrow \beta}_{t,TPAs^+} = \Delta G^{o,\alpha \dashrightarrow \beta}_{t,TPB^-} = 1/2\ \Delta G^{o,\alpha \dashrightarrow \beta}_{t,TPAsTPB} \qquad (10)$$

On the basis of this assumption a scale for standard Gibbs energies of transfer of ions from one solvent to the other one can be obtained. For example, when this quantity is to be determined for the iodide ion from partition experiment, it is sufficient to determine $\Delta G^{o,\alpha \dashrightarrow \beta}_{t}$ for TPAsTPB and for TPAsI between the two solvents. The result for the iodide ion is given by the relationship

$$\Delta G^{o,\alpha \dashrightarrow \beta}_{t,I^-} = \Delta G^{o,\alpha \dashrightarrow \beta}_{t,TPAsI} - 1/2\ \Delta G^{o,\alpha \dashrightarrow \beta}_{t,TPAsTPB} \qquad (11)$$

In voltammetric experiments, the TPAsTPB assumption can be employed in order to get absolute values for the standard potential difference for ion transfer processes. If TPAsTPB is used as the base electrolyte in the organic phase and Li_2SO_4 or LiF in the aqueous phase, the voltammogram will be limited at negative potentials by the transfer of $TPAs^+$ from the organic phase to water and back to the organic phase, at positive potentials by the transfer of TPB^- from the organic phase to water and back to the organic phase. From the initial part of the potential current curve related to the transfer of these two ions $\Delta^{\alpha}_{\beta}E_{1/2}(TPAs^+)$ and $\Delta^{\alpha}_{\beta}E_{1/2}(TPB^-)$ can be obtained. Then the zero point of the potential scale is fixed by

$$\left(\frac{\Delta_{\beta}^{\alpha}E_{1/2}TPAs^{+} + \Delta_{\beta}^{\alpha}E_{1/2}TPB^{-}}{2}\right) = \Delta_{\beta}^{\alpha}E = \Delta_{\beta}^{\alpha}\Psi = 0 \qquad (12)$$

Thus the assumption helps for the transformation of the actual potential scale into the $\Delta_{\beta}^{\alpha}\Psi_i$ scale.

Theoretically $\Delta G_{t,i}^{o,\alpha \rightarrow \beta}$ can be estimated from the standard Gibbs energies of solvation of the ion i in the two solvents (organic and aqueous) [54] using the equation

$$\Delta G_{t,i}^{o,\alpha \rightarrow \beta} = \Delta G_{s,i}^{o} - \Delta G_{h,i}^{o} \qquad (13)$$

$\Delta G_{h,i}^{o}$ is the standard Gibbs energy of hydration of an ion. $\Delta G_{s,i}^{o}$ is the standard Gibbs energy of solvation of the ion i in the organic solvent and is split into an electrostatic term and a neutral term.

$$\Delta G_{s}^{o} = \Delta G_{el}^{o} + \Delta G_{n}^{o} \qquad (14)$$

The electrostatic term, ΔG_{el}^{o} is approximated from a modified form of the simple Born equation, and is expressed for nonhydrated and fully hydrated ions in the organic phase.

ΔG_{el}^{o} for ions nonhydrated in the organic phase, refers to an ion of radius a and dielectric constant $\epsilon_i = 1$ which is surrounded by a solvent layer of thickness (b - a) and dielectric constant ϵ_1, immeresed in the bulk solvent of dielectric constant ϵ_o.

ΔG^o_{el} is given as

$$\Delta G^o_{el} = 166\ [(\frac{1}{\epsilon_1} - 1)(\frac{1}{a} - \frac{1}{b}) + (\frac{1}{\epsilon_o} - 1)\ \frac{1}{b}]\quad (15)$$

In which ϵ_1 = dielectric constant of a local solvent layer surrounding the ion, and has been fixed to have a value of 2.

ϵ_o = the known bulk dielectic constant of the organic solvent.

a = ionic radius of the ion

b = the thickness of the local layer (solvent molecule radius) plus the ionic radius of the ion (ΔG^o_{el} is given in kcal mol^{-1}).

ΔG^o_{el} for ions fully hydrated in the organic phase can be calculated using a model in which a fully hydrated ion in a wet organic solvent is surrounded by a layer of water molecules. As usual, the first electrostatic layer is taken as having ϵ_1 = 2 and as having as thickness the radius of the solvent (i.e., water) molecule, (b - a) = 1.553Å. The second electrostatic layer will also be water, since the total water layer will be of thickness equivalent to the diameter of a water molecule, 3.106Å, and will again have a thickness 1.553Å, denoted as (c - b). Using the Onsager equation [74] the dielectric constant in the second electrostatic layer can be estimated, and is found to be $\epsilon_m = 29$; outside the second electrostatic layer is the bulk solvent with $\epsilon = \epsilon_o$. Thus ΔG^o_{el} for fully hydrated ions in the organic phase is given by equation (16).

$$\Delta G^o_{el} = 166\ [(\frac{1}{\epsilon_1} - 1)\ (\frac{1}{a} - \frac{1}{b}) + (\frac{1}{\epsilon_m} - 1)\ (\frac{1}{b} - \frac{1}{c}) + (\frac{1}{\epsilon_o} - 1)\ \frac{1}{c}] \qquad (16)$$

The neutral term ΔG^o_n, is regarded as the standard Gibbs energy of solvation of a nonpolar solute of the same size as the ions in question. For ions of radii less than or equal to 3Å, the neutral contribution is given by equation (17).

$$\Delta G^o_n = ma + c \qquad (17)$$

m and c are constants the values of which are known for several solvents [62]. They can be estimated experimentally at standard states for a given solvent as the slope and intercept from the plot of standard Gibbs energies of solvation of nonpolar solutes vs the radii of the solutes. For $a > 3$Å, ΔG^o_n can be obtained using the data collected by Abraham [63].

Calculation of ΔG^o_{el} and ΔG^o_n enables values of ΔG^o_s to be obtained. Application of equation (13) then enables $\Delta G^{o,\alpha \rightarrow \beta}_{t,i}$ to be found for ions whose standard Gibbs energies of hydration are known.

3. Experimental

3.1. Chemicals and Preparation of Reagents

Acetophenone (Analar, BDH), Nitrobenzene (Analar, BDH), Chlorobenzene (Hopkin and Williams), Li_2SO_4 (BDH), $KClO_4$ (BDH), $KClO_3$ (BDH), KIO_4 (BDH), KNO_3 (BDH), KI (BDH), NH_4SCN (BDH), Tetrabutylammonium Chloride, TBACl (Fluka), Tetraethylammonium bromide, TEABr (BDH), Tetramethylammonium bromide, TMABr (BDH), Sodiumtetraphenylborate, NaTPB (MERCK), Tetraphenylarsonium Chloride, TPAsCl (Fluka), Crystalviolet chloride (BDH), were used as such without further purification.

Crystalviolet tetraphenylborate (CVTPB) was prepared by mixing equimolar amounts of crystalviolet chloride and the sodium salt of tetraphenylborate, both dissolved in methanol. After evaporating the solvent, the CVTPB was extracted with benzene and precipitated from the benzene solution by addition of n-hexane. The melting point of the violet powder obtained was found to be 114 - 115°C. Tetraphenylarsonium tetraphenylborate (TPAsTPB) was prepared by mixing an aqueous solution of tetraphenylarsonium chloride with an aqueous solution of sodium tetraphenylborate. The white precipitate, tetraphenylarsonium tetraphenylborate was recrystallized twice from acetone (Analar).

0.01M CVTPB and 0.01M TPAsTPB solutions were used independently as the base electrolytes in the organic solvents, whereas 0.01M Li_2SO_4 was used as the base electrolyte in the aqueous solution. CVTPB was employed in the organic phase as the base electrolyte in order to extend the potential range towards the more negative potentials [48], whereas TPAsTPB was used mainly to fix the zero of potential. Following the usual sign convention, the transfer of cations from the organic phase to water is indicated by a negative current, and for the transfer of anions from the organic phase to water is shown by a positive current. The current reported in the graphs are total currents, not normalized to unit area.

Stock solutions were prepared at a concentration of 0.01M for all the studied electrolytes, and were diluted with redistilled water as necessary, immediately prior to use. In all experiments, the organic and the aqueous phase were equilibrated with each other before use. The measurments were made at a laboratory temperature of 22 ± 1°C.

3.2. Cell Arrangement

The electrochemical cell which was employed for the studies was similar to that used by Samec et al [43],

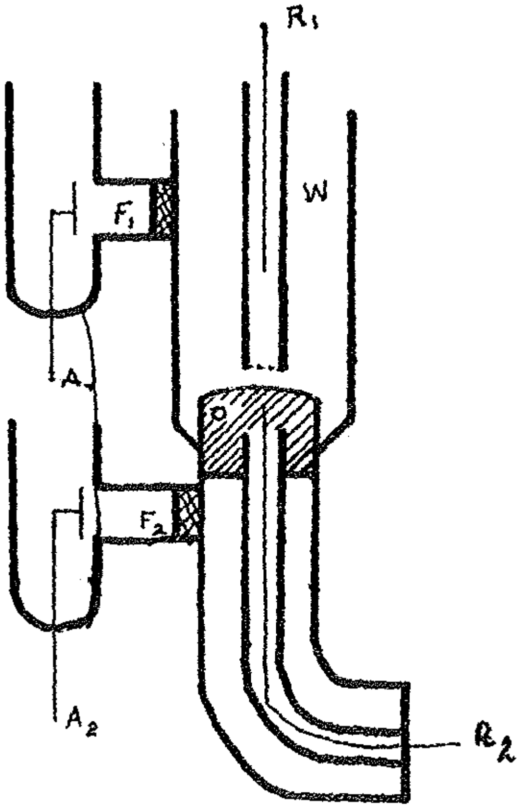

Fig. 1. Electrochemical cell for voltammetric investigatio
at ITIES. R_1 and R_2 are reference electrodes in t
aqueous and organic phase respectively. A_1 and A
auxilary electrodes separated by glass frits F_1 an

and is shown in Figure 1. For both ac cyclic and dc cyclic voltammetric investigations, the electrochemical cell contained four-electrodes. Two electrodes, R_1 and R_2, serving as the reference electrodes in the aqueous and organic phase respectively, were inserted as closely as possible to each side of the interface in order to eliminate the IR drop in the system. R_1 was Ag/AgCl/ saturated, KCl aqueous, separated from the test solution by a glass tube having a glass frit at the tip and containing 0.01M Li_2SO_4 in gelatin. R_2 was Ag wire dipped in the organic phase. The platinum auxilary electrodes, A_1 and A_2, for the aqueous and organic phase, respectively, were immersed in 0.01M Li_2SO_4. A_2 was separated from the organic phase using 0.01M Li_2SO_4 in gelatin contained within a tube having a frit at the tip. The cross section area of the interface was 0.33 cm^2. Schematic representation of the interface is given as follows.

ORGANIC PHASE	AQUEOUS PHASE
R^+R^-, $10^{-2}M$	A^+B^-, $C \leq 10^{-3}M$
	Li_2SO_4, $10^{-2}M$

ITIES

where A^+B^-, is any test electrolyte and R^+R^- is the organic base electrolyte (CVTPB or TPAsTPB).

3.3. Electronic Set-up

The block diagram of the electronic set-up used for the ac cyclic voltammetric experiments is shown in Fig. 2. In these experiments a four-electrode potentiostat (constructed and made available by courtesy of the Department of Chemistry, of the University of Southampton) with automatic IR compensation was employed. The superimposed sinusoidal potential was of magnitude ΔE = 5mv peak to peak and was fed from a frequency generator (Tektronix FG 501). The current output of the potentiostat was connected to the input of a lock-in-analyzer (PAR Model 5204) which was used for the continuous measurment of the inphase component of the ac-current. The voltammograms were observed using a storage oscilloscope (Tektronix Model 5441) and an X-Y recorder (Philips PM 8041).

For the dc cyclic voltammetric experiments, the same potentiostat was used. The triangular voltage ramp was generated using the MP - 1502 Electroanalyzer (McKee Pedersen Instruments). The current output of the potentiostat was connected directly to the storage oscilloscope and X-Y recorder.

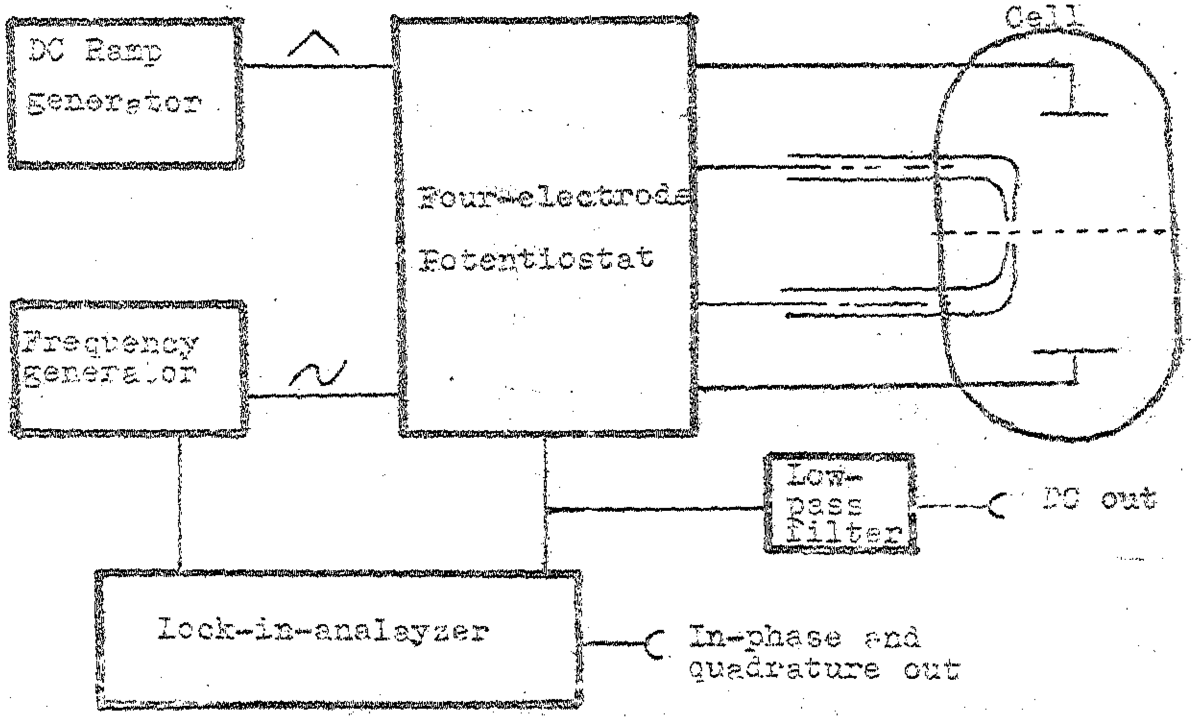

Fig. 2. Block diagram of the electronic set-up.

Results and Discussion

4.1. Determination of the Standard Gibbs Energies of Transfer of Ions in the Water/Acetophenone System

In these studies ion transfer processes for the water/acetophenone system for various ions of concentration 5 x 10^{-4}M in the aqueous phase have been investigated at low sweep rates using ac cyclic voltammetry. In order to transfer the ΔE_{dc} potential scale to $\Delta^{w}_{ac}\Psi$ scale the tetraphenylarsoniumtetraphenylborate assumption has been employed and the zero point of the potential axis ($\Delta^{w}_{ac}\Psi = 0$) was fixed as described in the theoretical part.

Figure 3 compares the cyclic dc voltammogram for the transfer of ClO_4^- ion across the water/acetophenone interface with the cyclic ac voltammogram recorded as the in phase component of the ac current at a frequency of 55HZ and a sweep rate of 20 mv S^{-1}. The peak potentials obtained by dc cyclic voltammetry are ± 28 mv separated from the ac current peak potential of the in phase component. This shows the reversibility of the ClO_4^- transfer across the interface of the system. The in-phase component of the ac current peak potential lies exactly on the position of the half-wave potential ($\Delta^{w}_{ac}\Psi_{1/2}$) of the dc voltammogram and this indicates the usefulness of the ac cyclic method to yield good results

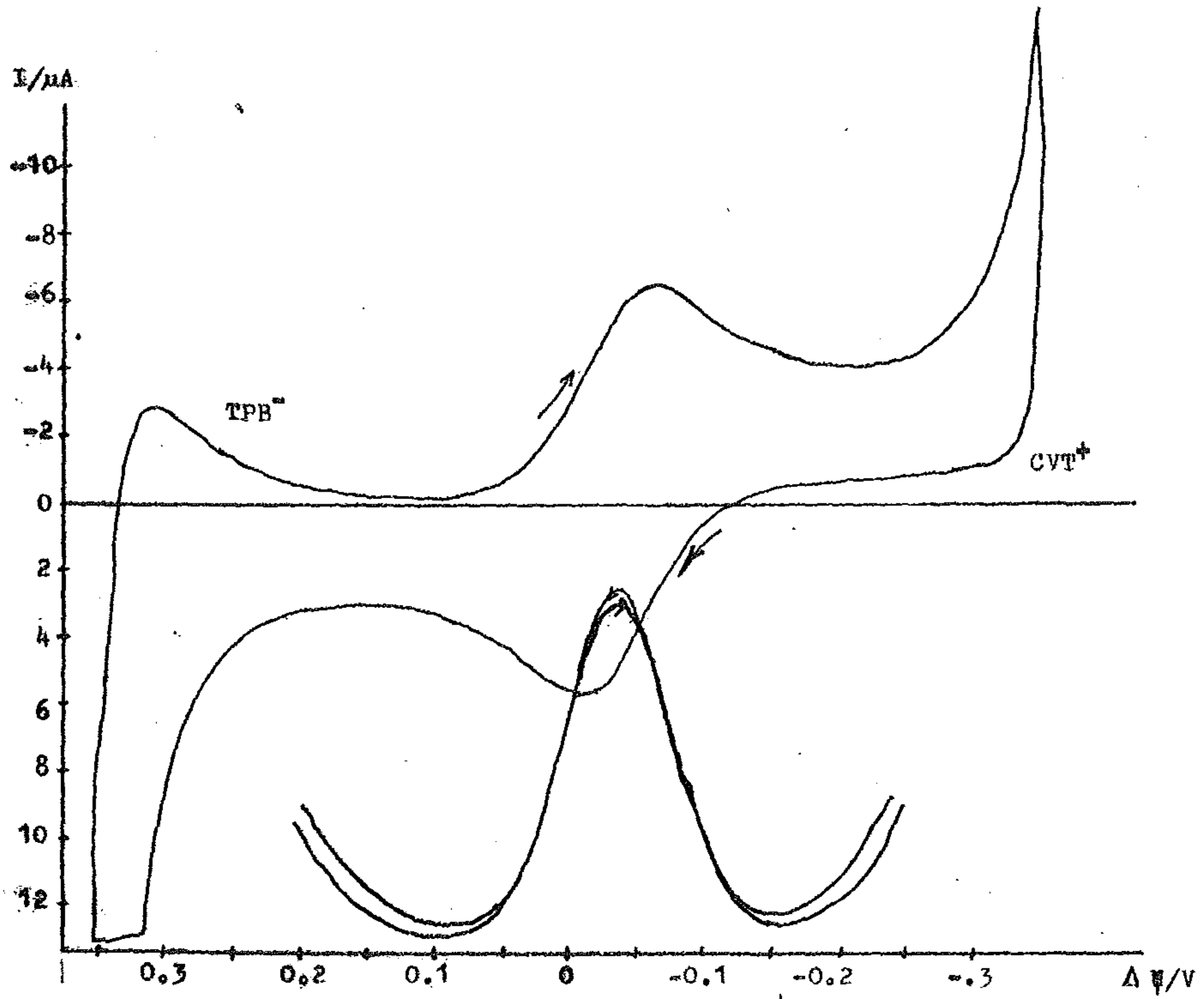

Fig. 3. Ac and dc cyclic voltammograms of 5×10^{-4}M ClO_4^-(aq.) from water to acetophenone and back, at sweep rate of 0.008 VS^{-} and at frequency of 55 HZ. Base electrolyte 0.01M Li_2SO_4 in water and 0.01M CVTPB in acetophenone.

for the precise determination of $\Delta\Psi_{1/2}$, which is identical with the in-phase component of the ac current peak potential. The observed ac current peak of the in-phase component has a half width potential of 90 mv, which again proves the reversible nature of the transfer process [58,59]. Figure 4 shows the ac cyclic voltammograms recorded as the in-phase component of the ac current at a frequency of 55HZ and at different sweep rates for the transfer of $TPAs^+$ and ClO_4^- across the interface. In the figure the various ac current peaks at different sweep rates appear at the same potentials for the individual ions. The observed ac current peaks do not exhibit complete overlap of the forward and reversed scans as predicted for the reversible behaviour of the ion transfer at low sweep rates; however, there is no difference in the peak potential in these scans. Similarly, ac voltammograms have been obtained for the transfer of $TPAs^+$ and IO_4^- at different sweep rates. The $\Delta_{ac}^{W}\Psi_{1/2}$ values of these ions are observable from the ac peaks. After obtaining $\Delta_{ac}^{W}\Psi_{1/2}$ values of ClO_4^- and IO_4^-, these ions have been used as internal standards for the determination of $\Delta_{ac}^{W}\Psi_{1/2}$ values of TBA^+, I^-, SCN^-, ClO_3^- and NO_3^-.

Figure 5(a) and 5(b) show the ac cyclic voltammograms of ClO_4^- and I^-, IO_4^- and I^- respectively. In

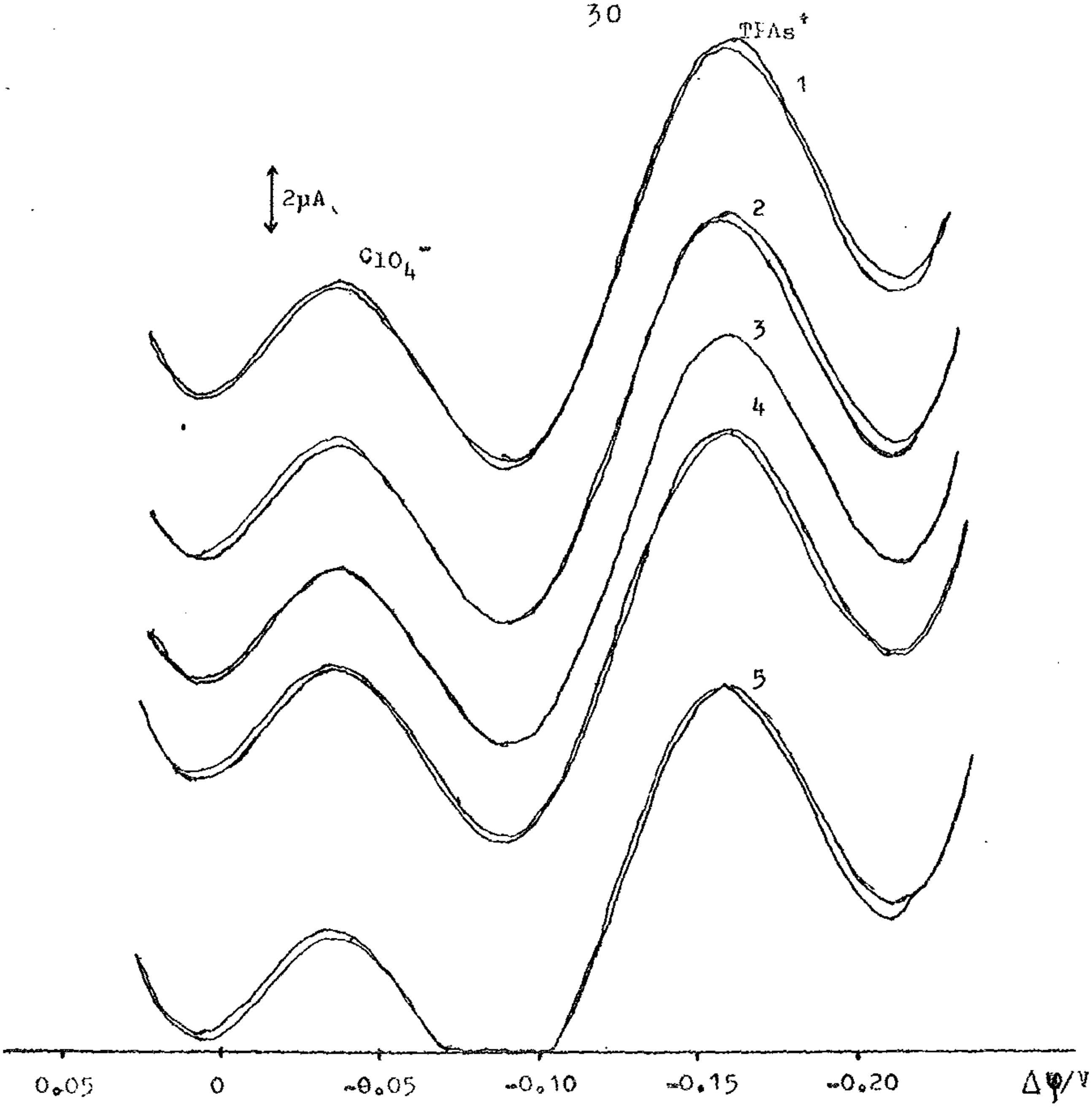

Fig. 4. Ac cyclic voltammograms of the tansfer of 5×10^{-4}M ClO_4^-(aq.) and 0.01M TPAs$^+$(**act.**) from water to acetophenone and back to water at varying sweep rates: (1) 0.004VS$^-$; (2) 0.008VS$^-$; (3) 0.016VS$^-$; (4) 0.032VS$^-$; (5) 0.040VS$^-$. Base electolytes 0.01M $LiSO_4$ in water and 0.01M CVTPB in acetophenone, and frequency 55 HZ.

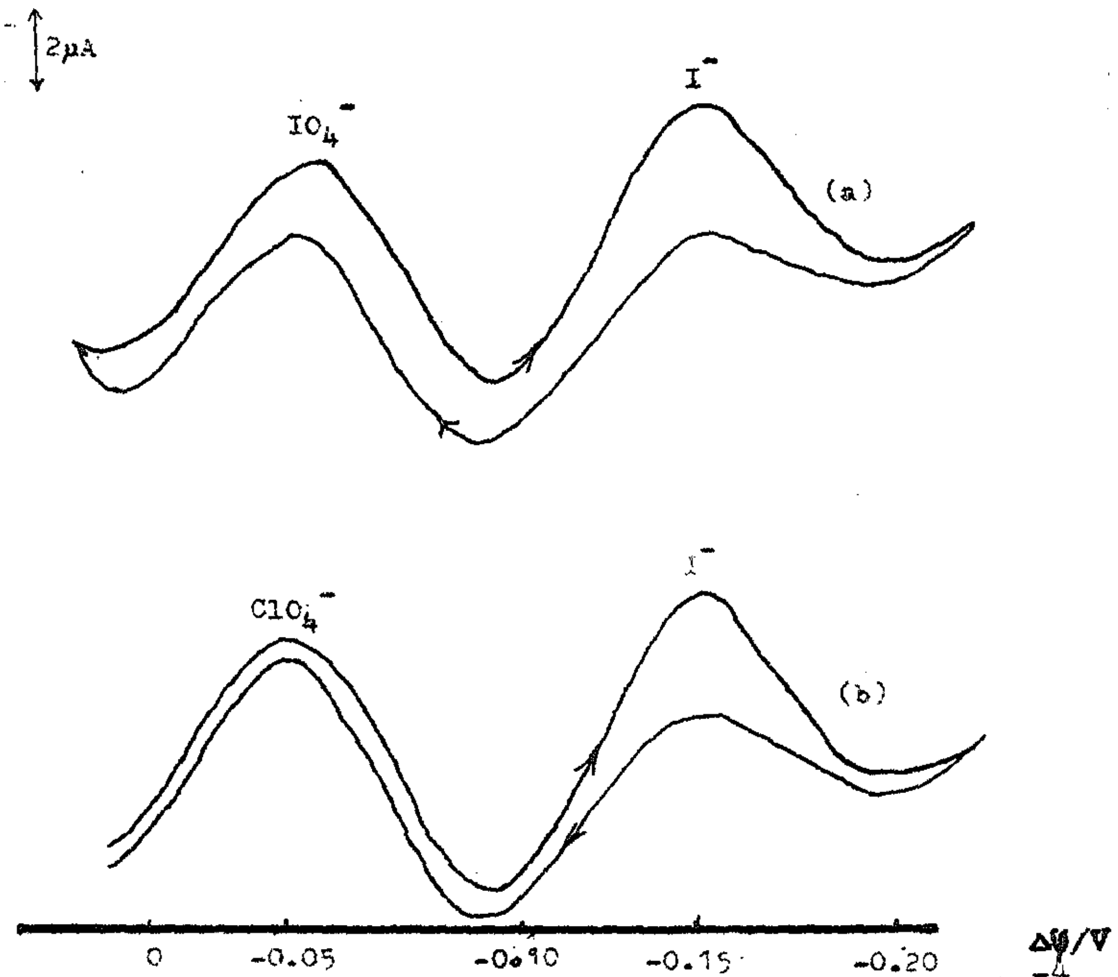

Fig. 5. Ac cyclic voltammograms for the transfer of 5×10^{-4} M concentration of ions from water to acetophenone and back to water at 0.008VS^{-1} sweep rate and 55HZ frequency. Base electrolytes: 0.01M Li_2SO_4 in water, 0.01M CUTPB in acetophenone.

both figures $\Delta^{w}_{ac}\Psi_{1/2}$ value of I^- is found to be the same. Measurements of $\Delta^{w}_{ac}\Psi_{1/2}$ values from the ac cyclic peaks lead, via equation (8) and (5), to $\Delta G^{o,w \longrightarrow ac}_{t,i}$ values, using unit activity coefficients. Ion association is not expected to be a significant factor for solutions less that 10^{-3}M concentration. Since the diffusion coefficients of the ions in acetophenone are not available they have been estimated from the ratio of the viscosity coefficient of acetophenone to that of water (1.816) and from the diffusion coefficients of the ions in water. The diffusion coefficients, ionic radii and hydration energies are given in Table 1.

Table 2 lists the half-wave potentials $(\Delta^{w}_{ac}\Psi_{1/2})$, standard inner potential differences $(\Delta^{w}_{ac}\Psi^{o}_{i})$, observed and calculated standard Gibbs energies of transfer from water to acetophenone for cations and anions. Standard Gibbs energies of transfer for non-hydrated and fully hydrated ions have been calculated from eqn. (14) and (13) using m and c values of acetone and r value of methylisobutyl ketone assuming the radius of this organic solvent molecule equals that of acetophenone. Theoretical $\Delta G^{o,w \longrightarrow ac}_{t}$ values for $TPAs^+$ and TPB^- are not tabulated in the table due to lack of data of the neutral terms (ΔG^{o}_{n}) which are required in the calculations. Details of the calculations for the rest of the ions are given in Table 3.

Table 1. Diffusion coefficients of ions in water (D_w) and in acetophenone (D_{ac}), ionic radii (a) and hydration energies (ΔG_h^o) of ions used in the calculations

Ion	a (Å)	ΔG_h^o Kcal mol^{-1}	$D_w \times 10^{-6}$ $cm^2\ sec^{-1}$	$D_{ac} \times 10^{-6}$ $cm^2\ sec^{-1}$
	a		b	c
TMA^+	2.58	-48.00	11.9	6.55
TEA^+	3.10	-41.00	8.7	4.79
TBA^+	3.83	-32.30	5.2	2.86
$TPAs^+$	3.97^e		5.58	3.07
I^-	2.20	-52.63	20.5	5.65
SCN^-	1.95^d	-60.91	17.5	4.82
IO_4^-	2.54^f	-45.55	14.5	3.99
ClO_4^-	2.45	-47.00	17.9	4.93
ClO_3^-	2.00^d	-59.62	17.2	4.74
NO_3^-	1.95	-60.50	19.0	5.23
TPB^-	3.86^e		5.58	3.07

[a] From reference [54] unless shown otherwise.

[b] Calculated from conductivity data reference [64].

[c] Calculated from viscosity data. [d] Reference [65].

[e] Calculated from molar volumes using the Stearn-Eyring formula reference [67]. [f] Reference [75]

Table 2. Standard Gibbs energies of transfer from water to acetophenone $\Delta G^{o,w \rightarrow ac}_{t,i}$; half-wave potential $\Delta^{w}_{ac}\Psi_{1/2,i}$ and of standard inner potential differences $\Delta^{w}_{ac}\Psi^{o}_{i}$ between these phases for various ions.

Ion	$\Delta^{w}_{ac}\Psi_{1/2(i)}$ (V)	$\Delta^{w}_{ac}\Psi^{o}_{i}$ (V)	$\Delta G^{w \rightarrow ac}_{t,i}$ KJ mol^{-1}	$\Delta G^{o,w \rightarrow ac}_{t,i}$ Kcal mol^{-1}		
		a		a	b	c
TBA$^+$	-0.155	-0.162	-15.63	-3.74	-2.98	-5.98
TPAs$^+$	-0.160	-0.168	-16.21	-3.83		
I$^-$	-0.144	-0.128	12.35	2.95	4.68	-0.98
SCN$^-$	-0.131	-0.114	11.00	2.63	8.09	1.73
IO_4^-	-0.032	-0.015	1.45	0.35	2.58	-2.29
ClO_4^-	-0.036	-0.019	1.83	0.44	2.86	-2.20
ClO_3^-	-0.217	-0.200	19.30	4.61	7.88	1.66
NO_3^-	-0.227	-0.211	20.36	4.87	7.68	1.32
TPB$^-$	0.160	0.168	-16.21	-3.87		

[a] Calculated using experimental data. [b] Calculated for nonhydrated ions in the acetophenone phase. [c] Calculated for fully hydrated ions in the acetophenone phase.

Table 3. Calculation of partition values in the water/acetophenone system in Kcal mol^{-1}

Ion	ΔG^o_{el}	ΔG^o_n	ΔG^o_s	ΔG^o_t	$\Delta G^{o\,c}_t$	ΔG^o_{el}	ΔG^o_n	ΔG^o_s	ΔG^o_t	$\Delta G^{o\,c}_t$
			a					b		
TBA^+	-32.48	-3.92	-36.39	-4.09	-2.98	-35.48	-3.92	-39.39	-7.09	-5.98
I^-	-51.94	2.88	-49.06	3.57	4.68	-57.60	2.88	-54.72	-2.09	-0.98
SCN^-	-57.50	3.57	-57.93	6.98	8.09	-63.87	3.57	-60.29	0.62	1.73
ClO_4^-	-47.43	2.18	-45.25	1.75	2.86	-52.49	2.18	-50.31	-3.31	-2.2
IO_4^-	-46.01	1.93	-44.08	1.47	2.58	-50.88	1.93	-48.95	-3.40	-2.29
NO_3^-	-57.50	3.57	-53.93	6.57	7.68	-63.87	3.57	-60.29	0.21	1.32
ClO_3^-	-56.29	3.43	-52.86	6.77	7.88	-62.50	3.43	-59.07	0.55	1.66

[a] Calculated for nonhydrated ions in the organic phase.

[b] Calculated for fully hydrated ions in the organic phase.

ΔG^o_n Calculated using data for acetone (m = -2.7822 and c = 8.9993) [62]. ΔG^o_e Calculated for nonhydrated ions in the organic phase using the radius of methylisobutylketone (r = 2.968Å). ΔG^o_t obtained from the ΔG^o_s value and the ΔG^o_h value in table 1 mole fraction scale. [c] After addition of 1.11 Kcal mole^{-1} to the previous column to correct to the molar scale.

Table 4. Standard Gibbs energies of transfer from water to nonaqueous solvents in Kcal mol^{-1} at 25°C in molar scale.

Ion	Acetophenone	1,2-Dichloroethane	Acetone	Methanol	Acetonitrile	N,N-Dimethylformamide
	a	b	c	d		
TBA^+	-3.74	-4.20		-5.2	-7.9	-6.8
$TPAs^+$	-3.87	-7.80		-5.6	-7.8	-9.1
I^-	2.95	6.02	3.13	1.6	4.5	4.5
SCN^-	2.63			1.4		3.9
IO_4^-	0.35					
ClO_4^-	0.44	4.05	-0.17	1.4		0.1
ClO_3^-	4.61					
NO_3^-	4.87					
TPB^-	-3.87	-7.80		-5.6	-7.9	-9.1
Dielectric constant	17.37	10.23	20.7	32.6	36	36.7

[a] Observed from our voltammetric experiments. [b] Reference [51].

[c] Reference [62]. [d] Reference [66].

The observed $\Delta G_t^{o,w \rightarrow ac}$ value for SCN^- is close to the calculated value using the model for fully hydrated ion in the organic phase and this seems as though there is full hydration of this ion in the wet organic phase, while the observed $\Delta G^{o,w \rightarrow ac}$ values for ClO_4^-, ClO_3^-, NO_3^-, IO_4^- and I^- show partial hydration, and for TBA^+ little or no hydration in the wet acetophenone phase. Since $\Delta G_t^{o,w \rightarrow ac}$ values of ions have not been so far reported for this system it has not been possible to make comparison with the present results. However, in order to reveal consistency of the observed trend of these values with already existing values of other systems, ΔG_t^o values of ions for different systems are listed in table 4. As can be seen from this table the general orders are in good agreement though direct comparsion of the values for each ion in the various systems is not simple due to variety of differences in properties of the organic solvents.

The experimental $\Delta G_t^{o,w \rightarrow ac}$ values are found in the ranges of the theoretically calculated values, (values obtained using the models of nonhydrated and fully hydrated ions in the organic phase) and this agreement between the observed and calculated values shows the reliability of the obtained results as well as the experimental method. In these studies the useful potential range for water/acetophenone system has been found to be much more narrow than for the water/nitrobenzene or water/1,2-dichloroethane system and we suspect that this may be caused by the higher mutual solubility of the two solvents.

4.2. Studies of the Dependence of Peak Current on Concentration and Square Root of Sweep Rate in the Water/Acetophenone System

To check further the reversibility of ion transfer process at low sweep rates in the water/acetophenone system and to estimate the diffusion coefficients of ions in water, the transfer of I^- and SCN^- ions from water to acetophenone and back to water has been studied using dc cyclic voltammetric technique.

Fig. 6 shows the dc cyclic voltammogram of the transfer of 7.5×10^{-4}M I^- ion from water to acetophenone and back at varying sweep rates. It is seen that the peak potentials for both forward and reverse scan are independent of the sweep rates, and that the peaks are separated from each other by about 0.055 V. This value nearly coincides with the theoretical value of a diffusion controlled reversible charge transfer reaction [56]. The same behaviour was observed for the transfer of SCN^- ion from water to acetophenone. Therefore it can be said that, the transfer of these two ions from water to acetophenone and back is a diffusion controlled reversible process at sweep rates up to 0.20 VS^{-1}. These observations are, in general, supported by Koryta et al [36] who have pointed out that charge transfer across the interface of two immiscible electrolyte solution is usually rapid.

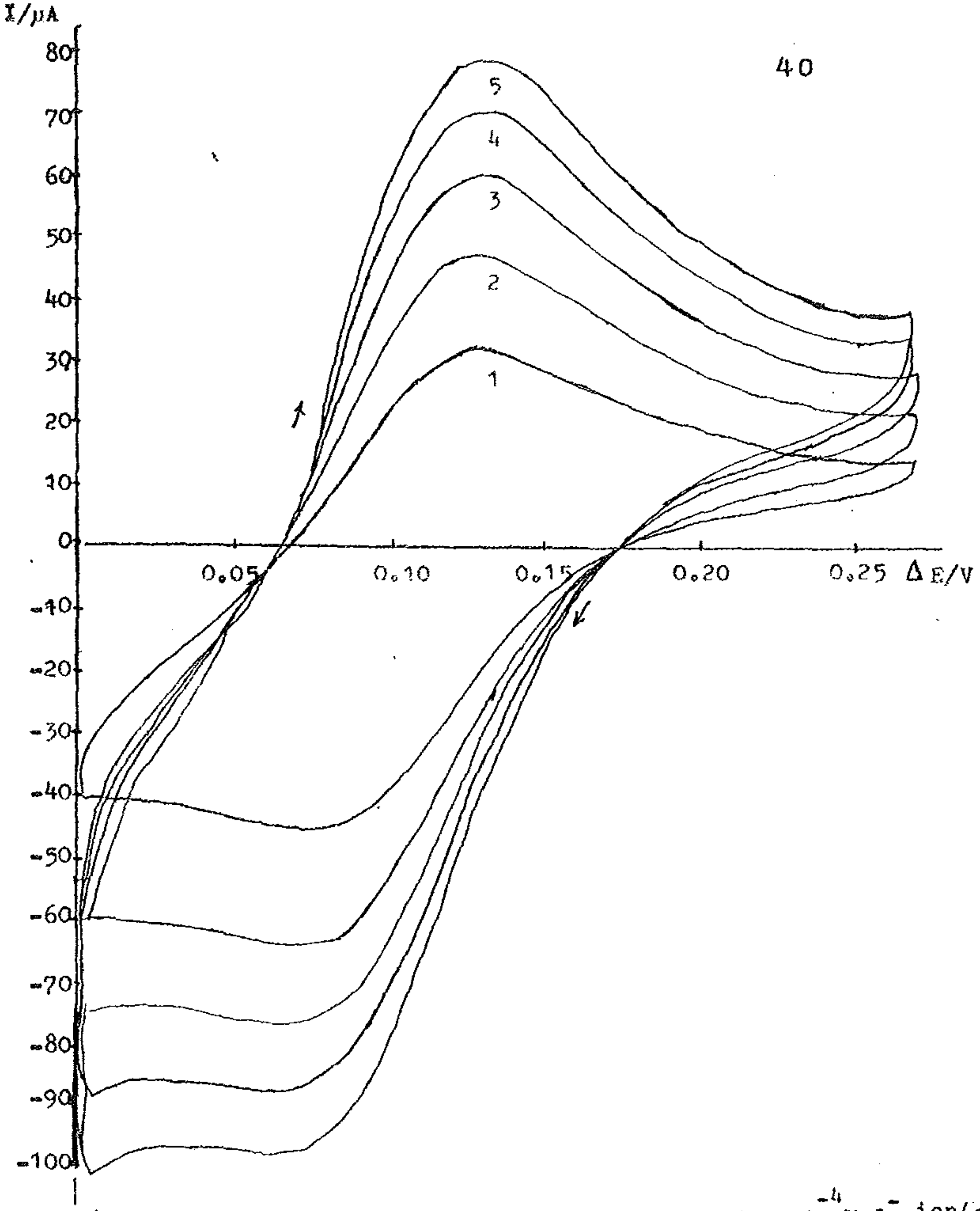

Fig. 6. Dc cyclic voltammograms of the tansfer of 7.5×10^{-4} M I^- ion(aq.) from nitorobenzen and back at varying sweep rates; (1) 0.02VS$^-$ (2) 0.04VS$^-$, (3) 0.06VS$^-$; (4) 0.08VS$^-$; (5) 0.10VS$^-$; Base electrolytes: 0.01M $LiSO_4^-$ in water and 0.01M CVTPB in acetopenone.

Table 5. Values of sweep rate V, square root of the sweep rate $V^{1/2}$, negative peak current I_p, corresponding to the transfer of I^- ion from water to acetophenone for dirrerent concentrations of I^- ion in water.

V Vs^{-1}	$V^{1/2}$ $V^{1/2}s^{-1/2}$	$I_p/\mu A$ $10^{-4}M\ I^-$	$I_p/\mu A$ $2.5x10^{-4}M\ I^-$	$I_p/\mu A$ $5x10^{-4}M\ I^-$	$I_p/\mu A$ $7.5x10^{-4}M\ I^-$
0.02	0.141	7.2	17	30	47
0.04	0.200	10.6	23	43	66
0.06	0.245	12.2	28	51	78
0.08	0.283	13.0	32	59	89
0.10	0.316	15.0	35	65	98
0.12	0.346	16.0	38	71	--
0.16	0.400	19.0	44	82	-
0.18	0.424	20.0	47	88	-
0.20	0.447	21.0	49	93	-

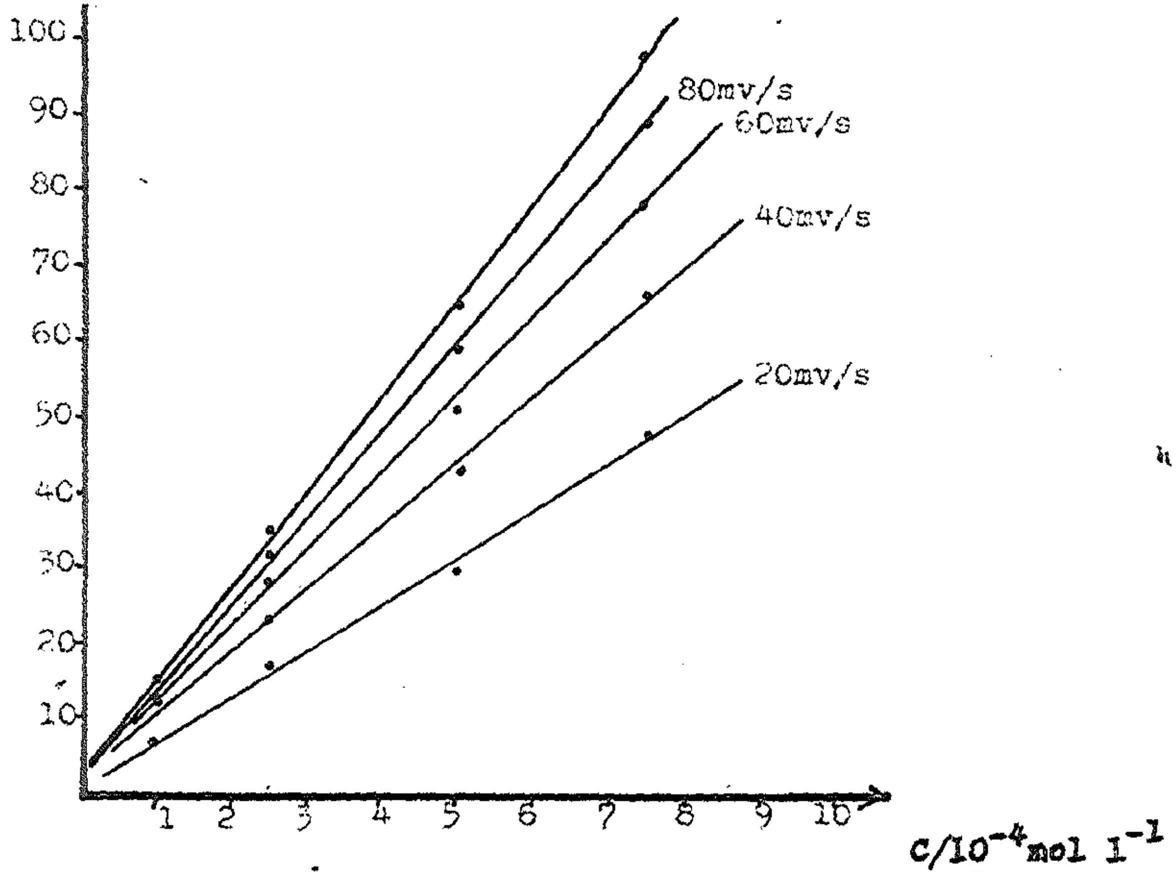

Fig. 7. Concentration dependence of peak current of I^- ion in water for the water/acetophenone system at different sweep rates. Base electrolytes: 0.01M Li_2SO_4 (aqueous), 0.01M CVTPB (acetophenone).

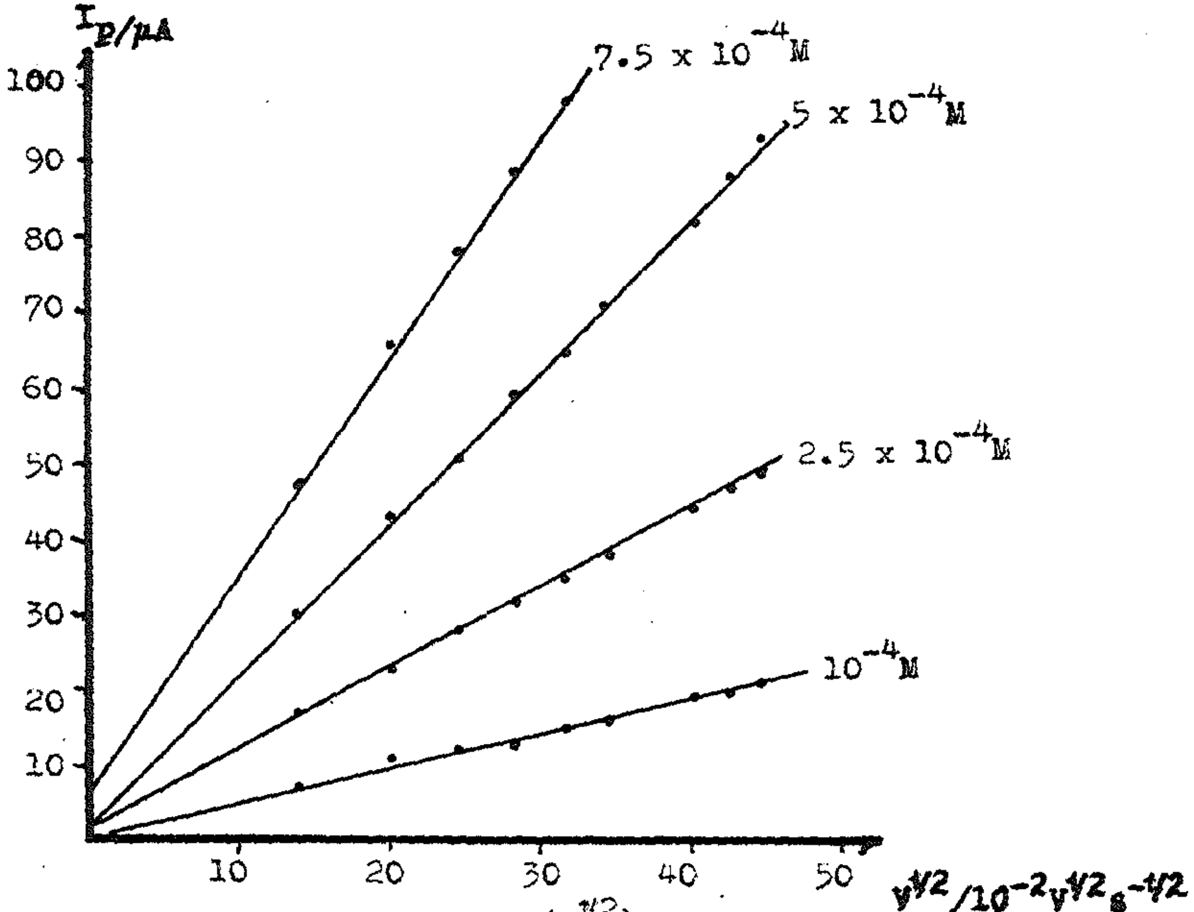

Fig. 8. Square root of sweep rate ($V^{1/2}$) dependence of peak current of I^- ion in water for the water/acetophenone system for different concentrations of I^- ion. Base electrolyte : 0.01M Li_2SO_4 (aqueous), 0.01M CVTPB (acetophenone).

Table 5 lists values of sweep rate V, square root of the sweep rate $V^{1/2}$, peak current I_p, corresponding to the transfer of I^- ion from water to acetophenone for different concentrations of the ion in water.

Fig. 7 depicts the dependence of the peak current on the concentration of I^- ion at various sweep rates, and Fig. 8 illustrates the dependence of the peak current on the square root of the sweep rate for different concentrations. As can be seen from the figures, the peak current is directly proportional to the concentration as well as to the square root of the sweep rate. From the slopes of the plots the diffusion coefficient of I^- ion in water has been evaluated based on eq. (6). The calculations yielded the average value D_{I^-} (W) = $2.18 \times 10^{-5} cm^2 s^{-1}$ at four different concentrations of I^-, and an average value D_{I^-} (W) = $2.17 \times 10^{-5} cm^2 s^{-1}$ from the plot of I_p vs $V^{1/2}$. These two values are in very good agreement with the value estimated from conductivity data at infinite dilution $D^o_{I^-}$ (W) = $2.05 \times 10^{-5} cm^2 s^{-1}$ [64]. In an analogous manner the diffusion coefficient of SCN^- ion in water was found to be D_{SCN^-} (W) = $1.66 \times 10^{-5} cm^2 s^{-1}$ from I_p vs C_o, and D_{SCN^-} (W) = $1.91 \times 10^{-5} cm^2 s^{-1}$ from the plot of I_p vs $V^{1/2}$. Again these values are comparable to the values obtained from conductivity data at infinite dilution in which $D^o_{SCN^-}$ (W) = $1.75 \times 10^{-5} cm^2 s^{-1}$ [68].

4.3. Determination of Standard Gibbs Energies of Transfer of Ions in the Water/Nitrobenzene and Water/Chlorobenzene-Nitrobenzene Mixture Systems

In these investigations dc cyclic voltammetry experiments were carried out for the transfer of various cations and anions in the water/organic solvent systems. The organic solvents were nitrobenzene, and nitrobenzene - chlorobenzene mixtures of different ratios by volume. Nitrobenzene is a more polar organic solvents ($\epsilon_0 = 35.75$ at 25°C) than chlorobenzene ($\epsilon_0 = 5.70$ at 25°C), thus by changing the composition of these solvents in their mixtures, it has been possible to vary the dielectric constant. As stated in the theory part "the TPAsTPB assumption" was employed to fix the $\Delta\psi = 0$ position using 0.01 M concentration of this salt as the base electrolyte in the organic phase. Whenever there was the need to extend the applicable potential range to more negative potentials, this base electrolyte was substituted by 0.01 M CVTPB.

Fig. 9 compares the voltammogram obtained by using TPAsTPB as the base electrolyte in nitrobenzene and 0.01 M Li_2SO_4 in water with the voltammogram where CVTPB has been used. The applicable potential range for the latter is extended to about 0.10 V towards more negative potentials. Thus the introduction of CVTPB as the base electrolyte for the organic phase has allowed the investigations of the transfer of anions such as NO_3^-, I^-, and SCN^-. In the potential region from -0.235 V to 0.0235 V

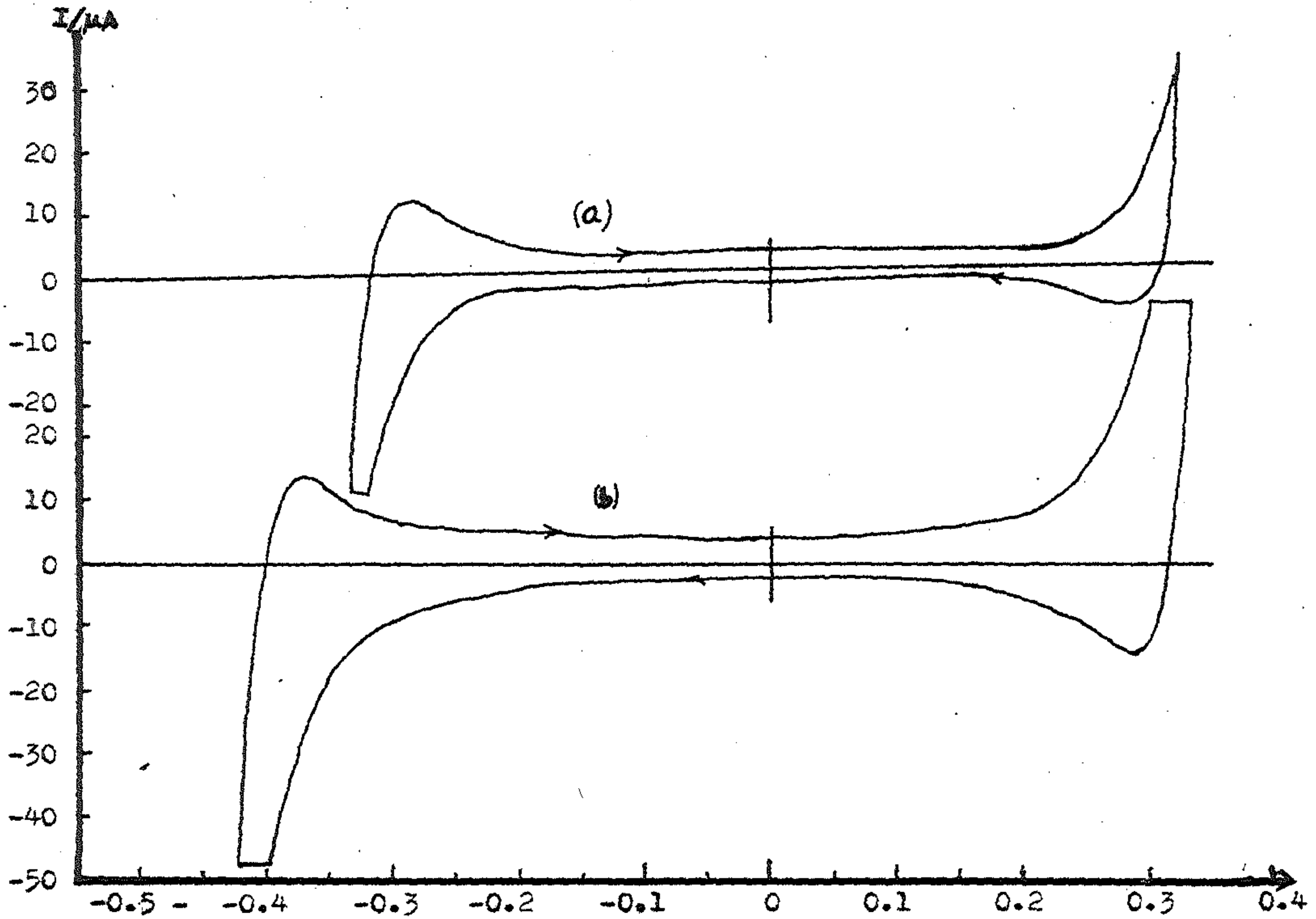

Fig. 9. Cyclic voltammograms of the base electrolytes: 0.01M Li_2SO_4 in water and 0.01M TPAsTPB in nitrobenzene (a);,and 0.01M CVTPB in nitrobenzene (b); at sweep rate of 0.008 VS^{-}.

and from -033 V to 0.230 V the current is controlled mainly by the charging of the interface, while at more positive or more negative potentials the control is by the transfer of the ions of the base electrolytes from the aqueous phase to the nitrobenzene, or vice versa.

Fig. 10 shows the dc cyclic voltammogram of 5×10^{-4}M ClO_4^- ion in the aqueous phase for the water/nitrobenzene system with the voltammogram of ClO_4^- ion of the same concentration in the aqueous phase for the system water/chlorobenzene nitrobenzene mixture, where the ratio of chlorobenzene to nitrobenzene was two to one by volume. First, for both systems, at the indicated sweep rate, the peak on reverse scan is shifted with respect to the peak on forward scan by 0.058 V towards more negative potentials. This shift coincides with the theoretical value of about 0.060 V for diffusion controlled charge transfer process [56]. Second, it follows from Fig. 10 that the half-peak potential difference $\Delta E_{p/2}$ precedes the peak potential difference ΔE_p by 0.055 V. This value is in good agreement with the theoretical value of 0.0565 V [56]. Similar behaviour was observed for sweep rates up to $0.20 vs^{-1}$ for all studied ions in different systems containing water/chlorobenzene - nitrobenzene mixtures. The above observations reveal the reversibility of the ion transfer process at lower sweep rates, and it can be concluded that the transfer process was controlled

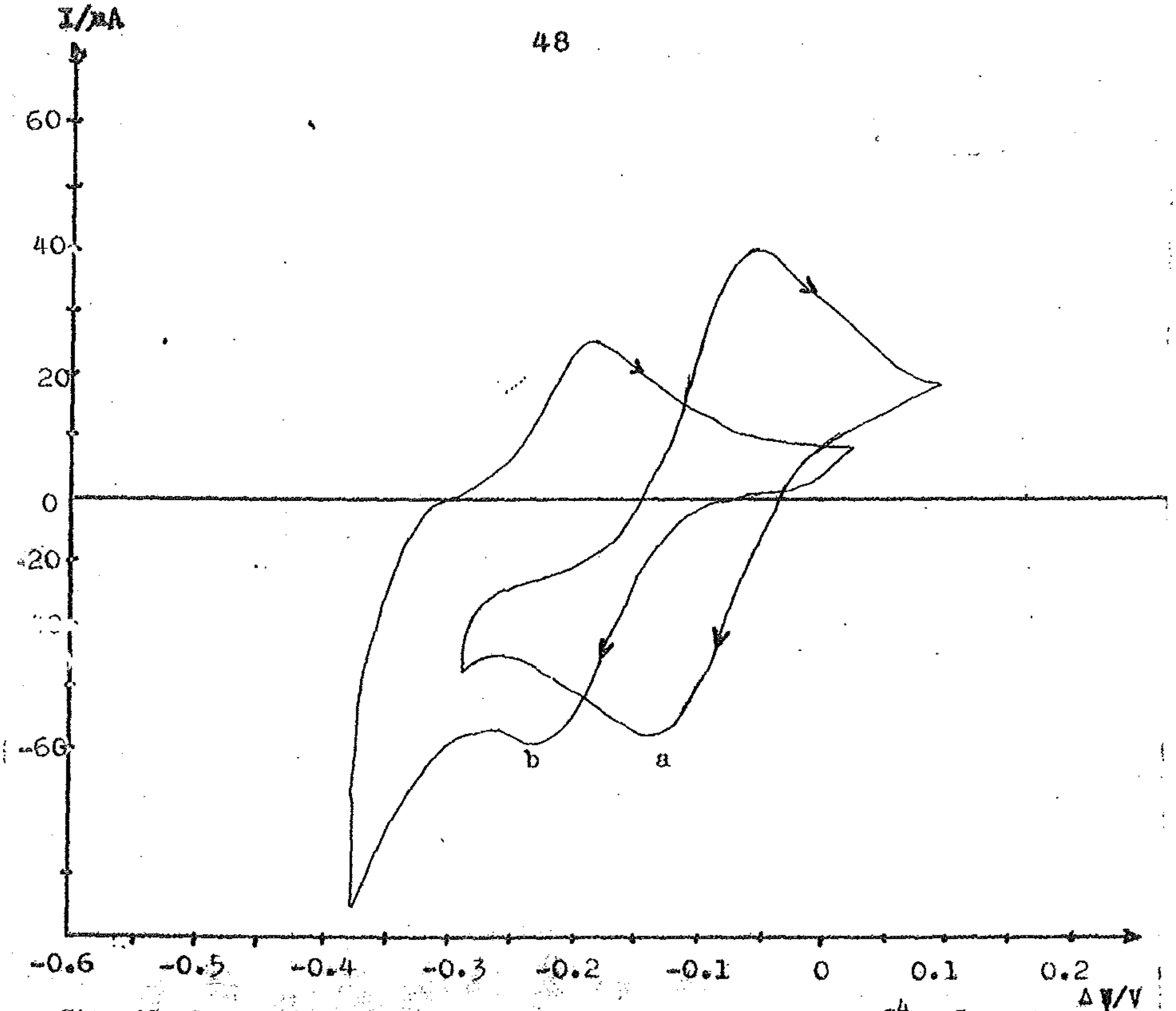

Fig. 10. Dc cyclic voltammograms for the transfer of 5×10^{-4} ClO_4^- ion(aq), from water to nitrobenzen and back(a) , and from water to chlorobenzene-nitrobenzene mixture (2:1 ratio by volume) and back(b), at sweep rate of 0.008 VS^{-1}.

by diffusion. In the concentration range from 10^{-3} to 10^{-4}M, the peak potential was independent of concentration.

Measurements of peak potentials from the voltammograms and application of equation (7) yielded the polarographic-half wave potentials ($\Delta_o^w\psi_{1/2}$). By using eq. (8) the standard inner potential differences ($\Delta_o^w\psi_i^o$) were obtained for the ions studied in the different systems containing water/chlorobenzene-nitrobenzene mixtures. From the values of $\Delta_o^w\psi_i^o$ and from equation (5) the standard Gibbs energies of transfer of ions were calculated.

In equation (8) the diffusion coefficients of ions in water and in the organic solvent are necessary. Since the diffusion coefficients of ions in the organic mixtures are not available, these were estimated from single ion conductivites in the organic mixtures by following the work of Coetzee and Cunningham [57], and using equation (9) as described in the theory part. The values of diffusion coefficients are listed in Table 6.

In these studies experiments for the water/nitrobenzene system were first performed, because for this system there are other experimental values of $\Delta G_{t,i}^{o,w \rightarrow NB}$ from partition (extraction) experiments by Rais [69] and other workers [70,71], and from solubility experiments by Abraham [72]. It seemed reasonable to compare the present result with their

Table 6. Diffusion coefficients of ions in water (D_W), nitrobenzene (D_{NB}) and in chlorobenzene - nitrobenzene mixtures ($D_{CB:NB}$) in $10^{-6} cm^2 s^{-1}$.

Ion	D_W	D_{NB}	$D_{CB:NB}$ (2:1)	$D_{CB:NB}$ (1:1)	$D_{CB:NB}$ (1:2)	$D_{CB:NB}$ (1:3)	$D_{CB:NB}$ (1:4)	$D_{CB:NB}$ (1:5)
	a	b			c			
TMA^+	11.9	4.5	8.4	7.3	6.3	5.7	5.4	5.2
TEA^+	8.70	4.3	7.7	6.9	6.0	5.5	5.1	4.9
TBA^+	5.20	3.1	5.7	4.9	4.3	3.9	3.7	3.5
$TPAs^+$	5.58	2.9	5.3	4.6	4.0	3.6	3.4	3.3
ClO_4^-	17.90	4.7	8.8	7.6	6.5	5.9	5.6	5.4
SCN^-	17.50	5.6	1.1	9.0	7.8	7.1	6.7	6.4
I^-	20.50	5.7	1.1	9.1	7.8	7.1	6.7	6.4
NO_3^-	19.00	6.0	1.1	9.8	8.4	7.6	7.2	6.9
TPB^-	5.58	2.9	5.3	4.6	4.0	3.6	3.4	3.3

[a] Calculated from conductivity data reference [64,68].

[b] From reference [57]. [c] Calculated from conductivity data coupled to viscosity measurments done in our laboratory and based on the method indicated in reference [57].

Table 7. Solvent properties used in the calculations for chlorobenzene (CB), nitrobenzene (NB), and their mixtures at different ratios by volume at 25°C.

Solvent	Dilectric constant of the bulk (ϵ_o)	Viscosity η (m poise)	Solvent molecule radius (Å)	Constants m	Constants c
	a	b	c	d	
CB	5.70	7.01	2.769	-3.3070	9.
NB	35.75	16.40	2.773	-3.2165	10.18
CB:NB 2:1	13.50	8.80	2.769	-3.3070	9.96
CB:NB 1:1	18.00	10.16	2.771	-3.2616	10.07
CB:NB 1:2	23.50	11.74	2.772	-3.2165	10.1
CB:NB 1:3	26.50	13.00	2.772	-3.2165	10.18
CB:NB 1:4	28.08	13.74	2.773	-3.2165	10.18
CB:NB 1:5	29.00	14.34	2.773	-3.2165	10.18

[a] From reference [73]. [b] Observed from our experiments.
[c] From reference [54]. [d] From reference [62]

The dielectric constants of nitrobenzene, chlorobenzene, and mixtures of these two solvents have been published by Daniel Decroocq [73]. Since ϵ_o does not change linearly with the mixtures compositions, there is small uncertainty in some of the values.

data, so as to confirm the validity of the present mode of calculation.

Table 8 lists values of peak potentials ($\Delta_{NB}^{W}\psi_{p}$), half-wave potentials ($\Delta_{NB}^{W}\psi_{1/2}$), standard inner potential differences ($\Delta_{NB}^{W}\psi_{i}^{o}$), observed and calculated standard Gibbs energies of transfer for the water/nitrobenzene system ($\Delta G_t^{o,W \rightarrow NB}$) as obtained by the methods outlined in the theory part. The theoretical ΔG_t^{o} values using the model for fully hydrated ion and nonhydrated ion in the organic phase were evaluated using the necessary data for the calculations from Table 1 and Table 7.

It is observed from Table 8 that the $\Delta G_t^{o,W \rightarrow NB}$ values from the present work and those from the partition experiments reveal reasonable conformity in the observed trends. Some of the values are even close to each other, and the differences are within experimental errors. Again there is a fair agreement between calculated $\Delta G^{o,W \rightarrow NB}$ and experimental $\Delta G_t^{o,W \rightarrow NB}$. The observed $\Delta G_t^{o,W \rightarrow NB}$ values of TMA^{+}, TEA^{+}, and SCN^{-} ions show that these ions are partially hydrated in nitrobenzene, and this observation for the first two ions is supported by Gerin and Fresco [70]. The values of TBA^{+}, ClO_4^{-}, and I^{-} ions indicate the presence of these ions in the organic phase as nonhydrated ions.

Table 8. Standard Gibbs energies of transfer from water to nitrobenzene $\Delta G^{o,w \rightarrow NB}_{t,i}$ peak potentials $\Delta^{w}_{NB}\phi_{p,i}$, half-wave potentials $\Delta^{w}_{NB}\phi_{1/2,i}$ and of standard inner potential differences $\Delta^{w}_{NB}\phi^{o}_{i}$ between these phases for various ions.

	$\Delta^{w}_{NB}\phi_{p,i}$ (V)	$\Delta^{w}_{NE}\phi_{1/2,i}$ (V)	$\Delta^{w}_{NB}\phi^{o}_{i}$ (V)	$\Delta G^{o,w \rightarrow NB}$ KJmol^{-1}	$\Delta G^{o,w \rightarrow NB}_{t,i}$ Kcal mol^{-1}				
			a		a	b	c	d	e
TMA$^+$	0.110	0.082	0.070	6.76	1.61	0.82	3.30	4.10	-0.14
TEA$^+$	-0.015	-0.043	-0.051	-4.92	-1.18	-1.36	1.40	1.62	-1.81
TBA$^+$	-0.215	-0.243	-0.250	-24.13	-5.77	-5.74		-4.40	-7.08
TPAs$^+$	-0.30	-0.328	-0.332	-32.04	-7.66	-8.58			
ClO_4^-	-0.125	-0.097	-0.080	7.72	1.85	1.91 1.40[f]		1.45	-3.03
IO_4^-	-0.105	-0.077	-0.062	5.98	1.43			1.18	-3.15
SCN^-	-0.205	-0.177	-0.162	15.63	3.74	3.70[g]		6.70	1.02
I^-	-0.225	-0.197	-0.181	17.47	4.17	4.49 3.90[f]	2.80	3.28	-1.75
NO_3^-	-0.270	-0.242	-0.227	21.91	5.24	4.7[h]		6.28	0.61
TPB^-	0.300	0.328	0.332	-32.04	-7.66	-8.58			

[a] The present experimental results. [b] Observed from partition experiments ref. [69] unless indicated otherwise. [c] Observed from solubility experiments [72]. [d] Calculated for nonhydrated ions in the organic phase. [e] Calculated for fully hydrated ions in the organic phase. [f] Observed from partition experiments ref. [70]. [g] From ref. [2]. [h] From [illegible] [71].

Similarly $\Delta G_t^{o,w \dashrightarrow o}$ values were determined by this method for the systems containing water/chlorobenzene/nitrobenzene mixtures. The observed and calculated $\Delta G_t^{o,w \dashrightarrow o}$ values for these systems are listed in Tables 9-14, and all the $\Delta G_t^{o,w \dashrightarrow o}$ values are summarized in Table 15. These values have been found to be reproducible under the experimental conditions, and they fairly agree with the theoretical values.

It can be seen from the voltammogram of Fig. 10, that the peak potential due to the transfer of ClO_4^- ion from the aqueous phase to the organic mixture is shifted by about 0.10 V towards more negative potentials relative to the peak potential associated with the transfer of the ion from water to nitrobenzene. As a result, the standard Gibbs energy of transfer of ClO_4^- ion from water to the 2:1 mixture is more positive by 2.49 Kcal mol^{-1} than $\Delta G_t^{o,w \dashrightarrow NB}$ value of ClO_4^- ion from water to nitrobenzene.

Fig. 11 depicts the correlation between the standard Gibbs energies of transfer with the organic bulk dielectric constant (ϵ_o), where $\Delta G^{o,w \dashrightarrow o}$ is plotted <u>vs</u> the reciprocal of the dielectric constant ($\frac{1}{\epsilon_o}$) for some selected ions. As shown in the figure there is no linear relationship between the two; however, there is a certain regular trend which indicates that as

Table 9. Standard Gibbs energies of transfer from water to chlorobenzene-nitrobenzene mixture (2:1 ratio by volume) $\Delta G^{o,w \rightarrow o}_{t,i}$, peak potentials $\Delta^{w}_{o}\phi_{p,i}$, half-wave potentials $\Delta^{w}_{o}\phi_{1/2,i}$, and of standard inner potential differences $\Delta^{w}_{o}\phi^{o}_{i}$ between these phases for various ions.

Ion	$\Delta^{w}_{o}\phi_{pi}$ (V)	$\Delta^{w}_{o}\phi_{1/2,i}$ (V)	$\Delta^{w}_{o}\phi^{o}_{i}$ (V)	$\Delta G^{o,w \rightarrow o}_{t,i}$ KJ mol^{-1}	$\Delta G^{o,w \rightarrow}_{t,i}$ Kcal mol^{-1}		
	a				a	b	c
TMA^+	0.175	0.147	0.138	13.32	3.18	4.91	0.59
TEA^+	0.035	0.007	0.005	0.48	0.12	2.10	-1.41
TBA^+	-0.150	-0.178	-0.177	-17.08	-4.08	-4.46	-7.11
$TPAs^+$	-0.275	-0.303	-0.306	-29.53	-7.06		
ClO_4^-	-0.225	-0.197	-0.188	18.14	4.34	2.47	-2.11
IO_4^-	-0.175	-0.147	-0.140	13.51	3.23	2.15	-2.25
SCN^-	-0.260	-0.232	-0.225	21.71	5.19	7.91	2.13
I^-	-0.300	-0.272	-0.264	25.48	6.09	4.39	-0.73
NO_3^-	-0.345	-0.317	-0.309	29.82	7.13	7.50	1.72
TPB^-	0.275	0.303	0.306	-29.63	-7.08		

[a] The present experimental data. [b] Calculated for nonhydrated ions in the organic phase. [c] Calculated for fully hydrated ions in the organic phase.

Table 10. Standard Gibbs energies of transfer from water to chlorobenzene-nitrobenzene mixture (1:1 ratio by volume) $\Delta G^{o,w \to o}_{t,i}$, peak potentials $\Delta_o^w \Psi_{p,i}$, half-wave potentials $\Delta_o^w \Psi_{1/2,i}$, and of standard inner potential differences $\Delta_o^w \Psi_i$ between these phases for various ions.

Ion	$\Delta_o^w \Psi_{pi}$ (V)	$\Delta_o^w \Psi_{1/2,i}$ (V)	$\Delta_o^w \Psi_i^o$ (V)	$\Delta G^{o,w \to o}_{t,i}$ KJ mol^{-1}	$\Delta G^{o,w \to o}_{t,i}$ Kcal mol^{-1}		
	a				a	b	c
TMA^+	0.145	0.117	0.111	10.71	2.56	4.73	0.44
TEA^+	0.030	0.002	-0.001	- 0.10	-0.02	1.99	-1.49
TBA^+	-0.155	-0.183	-0.184	-17.76	-4.24	-4.34	-7.16
$TPAs^+$	-0.280	-0.308	-0.311	-30.01	-7.17		
ClO_4^-	-0.170	-0.142	-0.131	12.64	3.02	2.10	-2.44
IO_4^-	-0.165	-0.137	-0.128	12.35	2.95	1.80	-2.57
SCN^-	-0.230	-0.202	-0.193	18.62	4.45	7.46	1.72
I^-	-0.300	-0.272	-0.262	25.28	6.04	4.00	-1.10
NO_3^-	-0.340	-0.312	-0.304	29.34	7.01	7.05	1.38
TPB^-	0.280	0.308	0.311	-30.01	-7.17		

[a] The present experimental data. [b] Calculated for nonhydrated ions in the organic phase. [c] Calculated for fully hydrated ions in the organic phase.

Table 11. Standard Gibbs energies of transfer from water to chlorobenzene-nitrobenzene mixture (1:2 ratio by volume) $\Delta G^{o,w \rightarrow o}_{t,i}$, peak potentials $\Delta^w_o\phi_{p,i}$, half-wave potentials $\Delta^w_o\phi_{1/2,i}$, and of standard inner potential differences $\Delta^w_o\phi^o_i$ between these phases for various ions.

Ion	$\Delta^w_o\phi_{pi}$ (V)	$\Delta^w_o\phi_{1/2,i}$ (V)	$\Delta^w_o\phi^o_i$ (V)	$\Delta G^{o,w \rightarrow o}_{t,i}$ KJ mol^{-1}	$\Delta G^{o,w \rightarrow o}_{t,i}$ Kcal mol^{-1}		
	a				a	b	c
TMA^+	0.140	0.112	0.104	10.04	2.40	4.56	2.05
TEA^+	0.025	-0.003	-0.008	-0.77	-0.18	2.03	-1.42
TBA^+	-0.175	-0.203	-0.205	-19.78	-4.73	-4.07	-6.73
$TPAs^+$	-0.285	-0.313	-0.317	-30.60	-7.31		
ClO_4^-	-0.145	-0.117	-0.104	10.04	2.40	1.91	-2.60
IO_4^-	-0.140	-0.112	-0.102	9.84	2.35	1.62	-2.72
SCN^-	-0.220	-0.192	-0.182	17.56	4.20	7.38	1.50
I^-	-0.230	-0.202	-0.190	18.34	4.38	3.77	-1.29
NO_3^-	-0.320	-0.292	-0.282	27.21	6.50	6.80	1.09
TPB^-	0.285	0.313	0.317	-30.60	-7.31		

[a] The present experimental data. [b] Calculated for nonhydrated ions in the organic phase. [c] Calculated for fully hydrated ions in the organic phase.

Table 12. Standard Gibbs energies of transfer from water to chlorobenzene-nitrobenzene mixture (1:3 ratio by volume) $\Delta G^{o,w \to}_{t,i}$, peak potentials $\Delta^{w}_{o}\phi_{pi}$, half-wave potentials $\Delta^{w}_{o}\phi_{1/2,i}$ and of standard inner potential differences $\Delta^{w}_{o}\phi^{o}_{i}$ between these phases for various ions.

Ion	$\Delta^{w}_{o}\phi_{pi}$ (V)	$\Delta^{w}_{o}\phi_{1/2,i}$ (V)	$\Delta^{w}_{o}\phi^{o}_{i}$ (V)	$\Delta G^{o,w \to o}_{t,i}$ KJ mol^{-1}	$\Delta G^{o,w \to o}_{t,i}$ Kcal mol^{-1}		
	a				a	b	c
TMA^+	0.110	0.082	0.073	7.04	1.68	4.41	1.91
TEA^+	0.015	-0.013	-0.019	-1.83	-0.44	1.90	-1.55
TBA^+	-0.180	-0.208	-0.212	-20.46	-4.89	-4.19	-6.85
$TPAs^+$	-0.295	-0.323	-0.329	-31.75	-7.59		
ClO_4^-	-0.135	-0.107	-0.093	8.97	2.14	1.76	-2.75
IO_4^-	-0.130	-0.102	-0.090	6.69	2.06	1.48	-2.86
SCN^-	-0.125	-0.187	-0.175	16.89	4.04	7.21	1.34
I^-	-0.225	-0.197	-0.183	17.66	4.22	3.61	-1.44
NO_3^-	-0.310	-0.282	-0.270	26.06	6.23	6.63	0.93
TPB^-	0.295	0.323	0.329	-31.75	-7.59		

[a] The present experimental data. [b] Calculated for nonhydrated ions in the organic phase. [c] Calculated for fully hydrated ions in the organic phase

Table 13. Standard Gibbs energies of transfer from water to chlorobenzene-nitrobenzene mixture (1:4 ratio by volume) $\Delta G_{t,i}^{o,w \rightarrow o}$, peak potentials $\Delta_o^w \phi_{p,i}$, half-wave potentials $\Delta_o^w \phi_{1/2,i}$, and of standard inner potential differences $\Delta_o^w \phi_i^o$ between these phases for various ions.

Ions	$\Delta_o^w \phi_{pi}$ (V)	$\Delta_o^w \phi_{1/2,i}$ (V)	$\Delta_o^w \phi_i^o$ (V)	$\Delta G^{o,w \rightarrow o}$ KJ mol^{-1}	$\Delta G_{t,i}^{o,w \rightarrow o}$ Kcal mol^{-1}		
	a				a	b	c
TMA^+	0.110	0.082	0.072	6.95	1.66	4.34	0.06
TEA^+	0.005	-0.023	-0.030	-2.90	-0.69	1.84	-1.61
TBA^+	-0.195	-0.223	-0.227	-21.91	-5.24	-4.25	-6.90
$TPAs^+$	-0.295	-0.323	-0.329	-31.75	-7.59		
ClO_4^-	-0.135	-0.107	-0.092	8.88	2.12	1.69	-2.81
IO_4^-	-0.130	-0.102	-0.090	8.69	2.06	1.41	-2.92
SCN^-	-0.215	-0.187	-0.175	16.89	4.04	6.97	1.25
I^-	-0.225	-0.197	-0.183	17.66	4.22	3.54	-1.58
NO_3^-	-0.270	-0.242	-0.230	22.20	5.30	6.55	0.86
TPB^-	0.295	0.323	0.333	-31.75	-7.59		

[a] The present experimental data. [b] Calculated for nonhydrated ions in the organic phase. [c] Calculated for fully hydrated ions in the organic phase.

Table 14. Standard Gibbs energies of transfer from water to chlorobenzene-nitrobenzene mixture (1:5 ratio by volume) $\Delta G^{o,w \rightarrow o}_{t,i}$, peak potentials $\Delta^{w}_{o}\psi_{pi}$, half-wave potentials $\Delta^{w}_{o}\psi_{1/2,i}$, and of standard inner potential differences $\Delta^{w}_{o}\psi^{o}_{i}$ between these phases for various ions.

Ion	$\Delta^{w}_{o}\psi_{pi}$ (V)	$\Delta^{w}_{o}\psi_{1/2,i}$ (V)	$\Delta^{w}_{o}\psi^{o}_{i}$ (V)	$\Delta G^{o,w \rightarrow o}_{t,i}$ KJ mol^{-1}	$\Delta G^{o,w \rightarrow o}_{t,i}$ Kcal mol^{-1}		
		a			a	b	c
TMA^+	0.100	0.072	0.061	5.89	1.41	4.31	0.05
TEA^+	0.005	-0.023	-0.030	-2.90	-0.69	1.80	-1.64
TBA^+	-0.215	-0.243	-0.248	-23.93	-5.72	-4.28	-6.92
$TPAs^+$	-0.295	-0.323	-0.330	-31.85	-7.61		
ClO_4^-	-0.125	-0.097	-0.082	7.91	1.89	1.66	-2.84
IO_4^-	-0.130	-0.107	-0.094	9.07	2.17	1.38	-2.95
SCN^-	-0.200	-0.172	0.159	15.34	3.67	6.93	1.23
I^-	-0.225	-0.197	-0.182	17.56	4.20	3.50	-1.54
NO_3^-	-0.270	-0.242	-0.229	22.10	5.28	6.51	0.82
TPB^-	0.295	0.323	0.330	-31.85	-7.61		

[a] The present experimental data. [b] Calculated for nonhydrated ions in the organic phase. [c] Calculated for fully hydrated ions in the organic phase.

Table 15. Standard Gibbs energies of transfer from water to chlorobenzene (CB)-nitrobenzene (NB) mixtures $\Delta G^{o,w \dashrightarrow o}_{t,i}$ in Kcal mol^{-1} and bulk dielectric constants of the mixtures (ratio by volume).

Ion	CB:NB 2:1	CB:NB 1:1	CB:NB 11:2	CB:NB 1:3	CB:NB 1:4	CB:NB 1:5	NB
TMA^+	3.18	2.56	2.40	1.68	1.66	1.41	1.61
TEA^+	0.12	-0.02	-0.18	-0.44	-0.69	-0.69	-1.18
TBA^+	-4.08	-4.24	-4.73	-4.89	-5.24	-5.72	-5.77
$TPAs^+$	-7.06	-7.17	-7.31	-7.59	-7.59	-7.61	-7.66
ClO_4^-	4.34	3.02	2.40	2.14	2.12	1.89	1.85
IO_4^-	3.23	2.95	2.35	2.06	2.06	2.17	1.43
SCN^-	5.19	4.45	4.20	4.04	4.04	3.67	3.74
I^-	6.09	6.04	4.38	4.22	4.22	4.20	4.17
NO_3^-	7.13	7.01	6.50	6.23	5.30	5.28	5.24
TPB^-	-7.06	-7.17	-7.31	-7.59	-7.59	-7.61	-7.66
ϵ_o	13.50	18.00	23.50	26.50	28.10	29.00	35.7
X_{NB}	0.332	0.498	0.666	0.749	0.800	0.833	1

Where ϵ_o = bulk dielectric constant at 25°C

X_{NB} = mole fraction of nitrobenzene

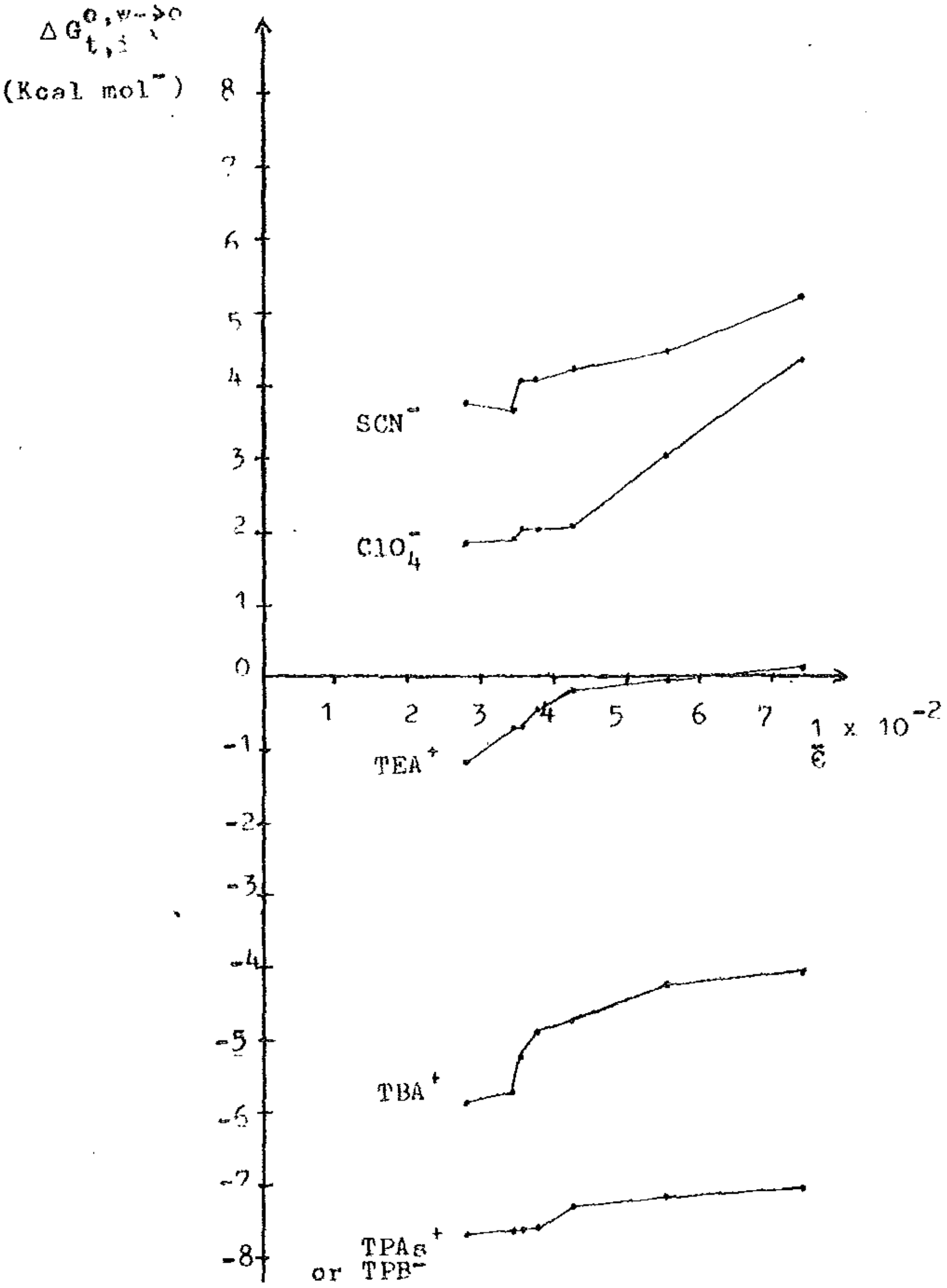

Fig. 11. Correlation of $\Delta G^{o,w\to o}_{t,i}$ with $\frac{1}{\varepsilon}$

the organic solvent polarity decreases, the standard Gibbs energy of transfer becomes more positive and vice versa. This experimental observation can be rationalized according to [66] on the basis of electrostatic models for the solvation of ions, which states that the Gibbs energy of solvation increases (becomes more positive) with decreasing dielectric constant of the organic media and hence the Gibbs energy of transfer becomes more positive. The deviation from linearity can be attributed to the fact that the standard Gibbs energy of transfer consists of additive contributions from the nonelectrostatic interactions of the ions with the organic solvents, and these effects would not allow one to obtain linear correlation.

In general "the TPAsTPB assumption", and the employment of TPAsTPB as base electrolyte in the organic phase make voltammetric determination of standard Gibbs energies of transfer independent of the application of an internal standard. Thus voltammetric method with this base electrolyte, and with its assumption is direct, accurate, and satisfactory method for the measurment of standard Gibbs energies of transfer. In addition to that, the modified form of the Born equation of Abraham and Liszi [54] explains satisfactorly the solvation of ions and predicts well ΔG_t^o values which can be justified by experimental results.

5. Conclusion

DC and AC Cyclic voltammetry have been used for the determination of standard Gibbs energies of transfer of anions and cations across immiscible electrolyte solutions. These techniques have been found to yield results in agreement with those obtained employing other methods. Studies of ion transfer across such solutions had so far been made for the water/nitrobenzene and water/1,2-dichloroethane systems, and the present work has extended these studies to other immiscible electrolyte solutions, namely water/acetophenone and water/nitrobenzene-chlorobenzene. The choice of these systems was based on relatively high electrical conductivity of electrolytes in the organic solvent, relatively high dielectric constant of the organic solvent, low miscibility with water, and the posibility of systematically increasing the dielectric constant of the organic solvent using different ratios of structurally similar (but, polarity-wise, different) organic solvents.

From the studies made on these systems, it has been possible to observe regular trends in the values of the standard Gibbs energies of transfer of anions and cations across immiscible electrolyte solutions as a function of the dielectric constant of the organic solvent.

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DECLARATION

I, the undersigned, declare that this thesis is my work and that all sources of material used for the thesis have been duly acknowledged.

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