ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

STUDIES OF THE ELECTRICAL DOUBLE LAYER AT THE WATER/O-DICHLOROBENZENE INTERFACE

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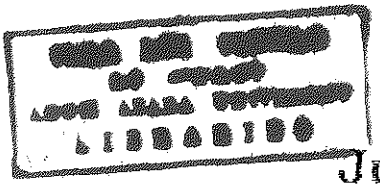

June 1993

STUDIES OF THE ELECTRICAL DOUBLE LAYER AT THE WATER/O-DICHLOROBENZENE INTERFACE

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Feyera Beyene

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ABSTRACT

Studies of the electrical double layer across the water/o-dichlorobenzene interface have been made using the impedance technique. The in-phase and quadrature components of the ac current have been converted to capacitance data by standard methods for various supporting electrolytes in the organic and aqueous phases and at different concentrations.

The potential of zero charge was determined by using the streaming jet electrode technique. The potentials of the capacitance minimums have been compared with the potentials of the streaming electrode. From these data, no specific ionic adsorption was observed for most of the electrolytes. However, the TDA^+ cation seems to show specific ionic adsorption. The experimental interfacial capacitances were also compared with the theoretical diffuse layer capacitances calculated from the Gouy-Chapman theory.

1. INTRODUCTION

Electrochemical studies at an interface which behaves, within a certain potential region, as an ideally polarizable interface, have recently attracted attention from both a theoretical and practical point of view. Studies of the electrical double layer at the interface between two immiscible electrolyte solution (ITIES) has so far been made only for a limited number of systems, namely the water/nitrobenzene and water/1,2-dichloroethane systems [1]. In addition to these studies solvents like chloroform [52,53], acetophenone [54], o-nitrophenylether [54], benzonitrile [52,55], dichloromethane [56] and nitroethane [58] have been used for the investigation of ion transfer across the water/organic solvent interface. Most of the understanding of the double layer at ITIES is confined to their properties at equilibrium, i.e. under circumstances where the average flow of ions into building up the layer is either zero or else so small as not to appreciably affect the nature of the layer. Ionic charge transfer processes across the ITIES can be studied by transient electrochemical methods. Investigation of the ITIES may help in the modelling of biochemical processes, in electroanalytical chemistry, and processes taking place during phase transfer catalysis.

o-dichlorobenzene (o-DCB) with $\varepsilon = 9.93$ [2], $\rho = 1.306$ g/cm^3, $\eta = 1.324$ cp, solubility in water 2.7×10^{-3} mole/L, solubility of water in o-DCB 2.2×10^{-1} mol/L [3]) is a promising organic solvent for studies of the liquid/liquid interface.

The aim of this work was to investigate the double layer at the [illegible] interface and to obtain [illegible]

structure, about which little is known, except for some preliminary work done in this department [3,4].

Impedance measurements by means of phase-selective detection were used for gathering the structure - sensitive capacitance data for the ideally polarizable interface between the aqueous and o-dichlorobenzene electrolyte solutions. The supporting electrolytes used were μ-nitrido-bis(triphenylphosphorus) 3,3-como-bis(undecahydro-1,2-dicarba-3-cobalt) dodecaborate (BTPPCC), tetradodecylammonium tetraphenylborate (TDATPB), tetraheptylammonium tetrakis(4-chlorophenyl)borate (THeATPBCl), tetrapentylammonium tetraphenylborate (TPeATPB) and tetradodecylammonium-3,3-como-bis(undecahydro-1,2-dicarba-3-cobalt) dodecaborate (TDADCC). All the salts were of polarographic purity.

The potentials of zero charge were also measured using the streaming mercury electrode technique.

Experimental capacitance data at various concentrations for the different supporting electrolytes were compared with the capacitance of the diffuse double layer calculated on basis of the Gouy-Chapman theory

2. LITERATURE REVIEW

The distribution of the ionic and dipolar components across the liquid/liquid interface due to an excess of electrical charge on one side of an interface, which has to be compensated by the excess opposite charge on the other side is usually referred to as the electrical double layer. The electrical properties of such an interface between two immiscible electrolyte solutions have been established through the works of Nernst and Riesenfeld [1] as early as 1902. The treatment of the electrical double layer formed between two immiscible electrolyte solutions is similar to that at the metal/electrolyte interface where the electrode side is described as being the site of a diffuse double layer - a region with an excess of charge balancing the charge on the electrode [2]. For such a model the theory of Gouy and Chapman [3,4] can be applied giving information on the capacitance of the double layer. Some time after the initial work of Gavach and Guastalla [5] on the measurement of the capacitance of the electrical double layer at the ITIES was initiated by Verwey and Niessen [6] who showed that the electrical potential difference across the water/organic solvent interface can be divided into a surface potential caused by the orientation of dipoles and a double layer potential related to ionic space charge.

The reason for the unusual role of the electrical capacitance and potential in the Gouy-Chapman model is that the ions are considered as point charges while real, physical ions have finite radii. Ions in water, however, the ions have finite sizes and the centers of the ions cannot

This fact was included in Stern's modification of the GC theory and an analogous treatment on liquid/liquid interface which appeared under the name of the modified Verway-Niessen (MVN) model [1,8] was used by Gavach et al. [7]. These investigators introduced the concept of an ion-free layer (compact layer) with oriented molecules of both solvents separating two space charge regions. Girault and Schiffrin [9], on the other hand, suggested a model where the interface can be regarded as a mixed solvent layer with not more than two or three molecular thickness. These authors proposed that a continuous change in composition from one phase to the other is a more realistic picture at the ITIES. Samec et al. [10,11] supported the probability of finding an ion in the inner layer region as nonzero, and attempted to develop this idea by considering the MVN model, in which ions were allowed to penetrate into the inner layer over some distance. Torrie and Valleau [12] have examined several features of ITIES. They considered (a) ion-ion correlations within the space charge region, (b) ion-ion correlations between the two space charge regions, (c) interpenetration of the two space charge regions, and (d) image forces. On the other hand, Joos and Van Bockstaele [13] have presented a model, which accounts for the specific ion adsorption at the ITIES.

The processes at the interface between two immiscible electrolytes have been studied exclusively with water/organic solvent systems. For such electrochemical processes, Koryta and Vanysek [14] have listed the following requirements for the choice of the non-aqueous solvent:

(i) The organic solvent must dissolve only a small amount of water, since otherwise the electrolytes cannot be confined to their respective phases and

no suitable potential range for polarization of the interface would be found.

(ii) The solvent should be sufficiently polar (with minimum relative permitivity of about 10).

(iii) Its density must differ considerably from water in order to form a physically stable interface.

Most of the experimental results on the electrical double layer at the ITIES were obtained for the ideally polarizable interface, the thermodynamic state of which is controlled by electrochemical polarization. Generally, this can be accomplished by means of a four-electrode cell [15-18] with two pairs of electrodes, one pair measuring the potential (reference) and the second pair supplying current (counter). In such kind of cells flatness of the interface and geometric configuration of the four electrodes are of critical importance for ensuring uniform polarisation [1,19,20]. Electrochemical cells with a planar or spherical liquid/liquid boundary have been in common use [21-25].

When an electrical current flows through the ITIES there is always a potential difference (ohmic potential drop) between the tip of the Luggin capillary and the point just outside the interfacial region on each side of the interface. As a result the actual potential difference at the ITIES differs from the measured value. Once measured, e.g., at the high-frequency limit of the interfacial impedance [26-27] or the potential step on the galvanostatic transient [28], the ohmic potential drop can be compensated by means of positive feedback [15] or algebraic subtraction [28,29] under potentiostatic or galvanostatic conditions, respectively. The application of a potentiostat based on a periodic current interruption to a four electrode system was recently used [30] for IR drop elimination.

Suitable experimental methods for the investigation of a double layer use impedance techniques [31] and interfacial tension techniques. The differential capacitance of the double layer at ITIES has to be evaluated through careful analysis of the direct experimental interfacial tension. Gavach et al. [32] used the drop-weight and Buck et al. [33] the maximum bubble pressure methods to measure the surface tension of the water/nitrobenzene interface in the presence of sodium bromide in water and tetralkylammonium tetraphenylborates in nitrobenzene. Comparison of the results with that calculated by the GC theory indicated that the potential difference is concentrated in the diffuse double layer. Electrocapillary curves for the ideally polarizable interface between a nitrobenzene solution of tetrabutylammonium tetraphenylborate and an aqueous solution of LiCl were measured by Kakiuchi and Senda [21,22] by the drop-weight/drop-time method. The zero-charge potential difference was practically independent of the concentration of both electrolytes. An independent measurment of the potential of zero-charge by the streaming-jet electrode technique [34] gave a value identical with the potential of the electrocapillary maximum.

On the other hand, Girault and Schiffrin [35] used the video image technique for studying immiscible systems containing water and n-heptane, nitrobenzene or 1,2-dichloroethane. The picture which emerges from these findings is in disagreement with the concept introduced by Gavach et al. [7] on the existence of compact layers at the interface between two immiscible electrolyte solutions. Girault and Schiffrin [35] have found that at least for alkali metal chlorides, a presence of charge free dielectric layer between water and polar organic solvent is unlikely. It must be concluded that the

properties of the interface are changing continuously across the boundary from one medium to the other. It is also proposed that for this reason no apparent potential drop across the "compact layer" exists. The interface is being viewed more as a smeared out plane due to the possibility of interfacial mixing and ion pairing.

A more recent report on the double layer has shown that impedance investigations [21,27,36] of the interface separating two immiscible electrolyte solutions is one of the most promising ways of obtaining information about the structure of the interface. The impedance of the ideally polarizable ITIES was measured by means of an alternating-current bridge [27] or by phase selective detection [26,27,37-39]. Results were usually presented in the form of the complex plane impedance. The high frequency semi-circle observed in some cases was shown[36,38] to be due to a capacitive coupling between the reference electrodes or was ascribed to the geometric bulk-phase capacitance [9,39]. An alternative new method for evaluation of the capacitance of ITIES and the overall ohmic potential drop is the fast performance galvanostatic pulse technique [28,40,41]. When a current step is applied, the charging current decreases with time, whereas the faradaic current increases. With proper numerical treatment the two components of the current are functions of the interfacial capacitance. Hence the magnitude of the evaluated capacitance should be equal in all respects to the value that can be obtained from impedance measurments.

A similar analysis of capacitance data for the water/1,2-dichloroethane system has not been possible yet, though there has been some evidence indicating that the inner-layer potential difference is small [36,42].

Samec et al. [43] applied the weak-coupling equations to the primitive model of an ITIES and compared the effect of image forces for the water/nitrobenzene and water/1,2-dichloroethane interfaces. They concluded that the image forces together with the within-layer ion correlations are more likely to be responsible for a virtual rise of the experimental capacitance of the water/1,2-dichloroethane interface over the GC value than the interfacial ion pairing [44]. Recently, through impedance measurements in low conductivity media, Chechirlian et al. [45] have shown that the conductivity of the media, the design of the reference electrode and the geometry of the cell all have a role in affecting impedance measurments at the high frequency limit.

By measuring surface tension [9,22,33] and impedance [27,36,42], capacitance data have so far been reported for the water/nitrobenzene and water/1,2-dichloroethane systems at various concentrations in the presence of different electrolytes.

3. THEORY

3.1. EQUILIBRIUM SITUATION

Consider a system containing an ion i of charge Z partitioned between two immiscible liquid phases (w) and (o)

$$i\,(w) \;\text{====}\; i\,(o) \tag{1}$$

At equilibrium, the electrochemical potential $\bar{\mu}_i$ of the ion in the two phases are equal.

$$\bar{\mu}_i\,(w) \;\text{====}\; \bar{\mu}_i\,(o) \tag{2}$$

or

$$\mu^0_i\,(w) + RT \ln a_i\,(w) + Z_i F\phi_i\,(w) \;\text{====}\; \mu^0_i\,(o) + RT \ln a_i\,(o) + Z_i F\phi_i\,(o) \tag{3}$$

Here, $\mu^0_i\,(w)$ and $\mu^0_i\,(o)$ are the standard chemical potentials, $a_i\,(w)$ and $a_i\,(o)$ are the activities and $\phi_i\,(w)$ and $\phi_i\,(o)$ are the inner potentials in phases (w) and (o) respectively. The Galvani potential difference $\Delta^{w}_{o}\phi_i$ between the two phases can be obtained from rearrangement of Eq. 3 cf. [46,47]

$$\Delta^{w}_{o}\phi_i = (\mu_i^{o,(o)} - \mu_i^{o,w})/Z_iF + (RT/Z_iF)\ln(a_i^{(o)}/a_i^{w}) \tag{4}$$

or

$$\Delta^{w}_{o}\phi_i = -\Delta G^{o}_{tr,i}{}^{w\to o}/Z_iF + (RT/Z_iF)\ln(a_i^{(o)}/a_i^{w}) = \Delta^{w}_{o}\phi^{o}_i + (RT/Z_iF)\ln(a_i^{(o)}/a_i^{w}) \tag{5}$$

where $\Delta G^{o}_{tr,i}{}^{w\to o}/Z_iF = (\mu_i^{o,(o)} - \mu_i^{o,w})/Z_iF = \Delta^{w}_{o}\phi^{o}_i$

$\Delta^{w}_{o}\phi^{o}_i$ is the standard Galvani potential difference, which is defined as the **equilibrium value of the Galvani potential difference $\Delta^{w}_{o}\phi_i$ at unit ratio of ion** activities. $\Delta G^{o}_{tr,i}{}^{w\to o}$ is the standard Gibbs energy of transfer of ion i from

solvent (w) to solvent (o).

Depending on the type of system the difference of the inner electrical potential $\Delta^{w}_{o}\phi_i$ between water (w) and an organic solvent (o) can be controlled by means of the equilibrium partition of a salt (nonpolarizable ITIES), or electrical charge supplied from the outside (ideally polarizable ITIES).

3.2. NON-POLARIZABLE INTERFACE

A non-polarizable interface is formed in the case of one electrolyte distributed between two immiscible solvents (w) and (o). In each phase, a single binary electrolyte RX can dissociate into a cation R^+ and an anion X^- according to

$$RX \quad === \quad R^+ + X^- \tag{6}$$

As a result of the partition equilibrium in the system that can be represented as [1]

$$\begin{matrix} R^+X^- & // & R^+X^- \\ (w) & & (o) \end{matrix} \tag{7}$$

where the perpendicular strokes represent the interface, an equilibrium potential difference (distribution potential) $\Delta^{w}_{o}\phi$ will be established [46].

$$\Delta^{w}_{o}\phi = (-{}^{w}_{o}\phi^{o}_{R} + \Delta^{w}_{o}\phi^{o}_{X})/2 + (RT/2F)(\gamma^+(o)\gamma^-(w)/\gamma^+(w)\gamma^-(o)) \tag{8}$$

where γ's are the activity coefficients of the species in the respective phases.

3.3. IDEALLY POLARIZABLE INTERFACE

As shown in detail in [47], the system with two different electrolytes B_1A_1 and B_2A_2 in the phases (w) and (o), respectively, can have the property of an ideally polarizable electrode. This can be represented as

$$\begin{matrix} B_1A_1 & // & B_2A_2 \\ (w) & & (o) \end{matrix} \qquad (9)$$

Besides, the equilibrium of the exchange reactions

$$\begin{aligned} A^-_1\,(w) + A^-_2\,(o) &=== A^-_1\,(o) + A^-_2\,(w) \\ B^+_1\,(w) + B^+_2\,(o) &=== B^+_1\,(o) + B^+_2\,(w) \end{aligned} \qquad (10)$$

are strongly shifted to the left-hand side. In other words, the standard potential of transfer of the cation of phase (w) B^+_1 and anion of phase (o) A^-_2 are very positive and the potential of transfer of the anion of phase (w) A^-_1 and cation of phase (o) B^+_2 are very negative [47-49]. The potential range, often termed as the potential window, at which no ion passes the interface has the properties of an ideally polarizable interface [49]. It is rather the double layer charging than the activities of ions that determines the potential of such interface.

Fig. 3.1 (after Koryta [48]) depicts a case of charging of an ideally polarizable interface. In the case of a metallic electrode in an electrolyte solution the charge supplied to or removed from the metallic side are electrons, while in the case of an ITIES only ion transport to and from the

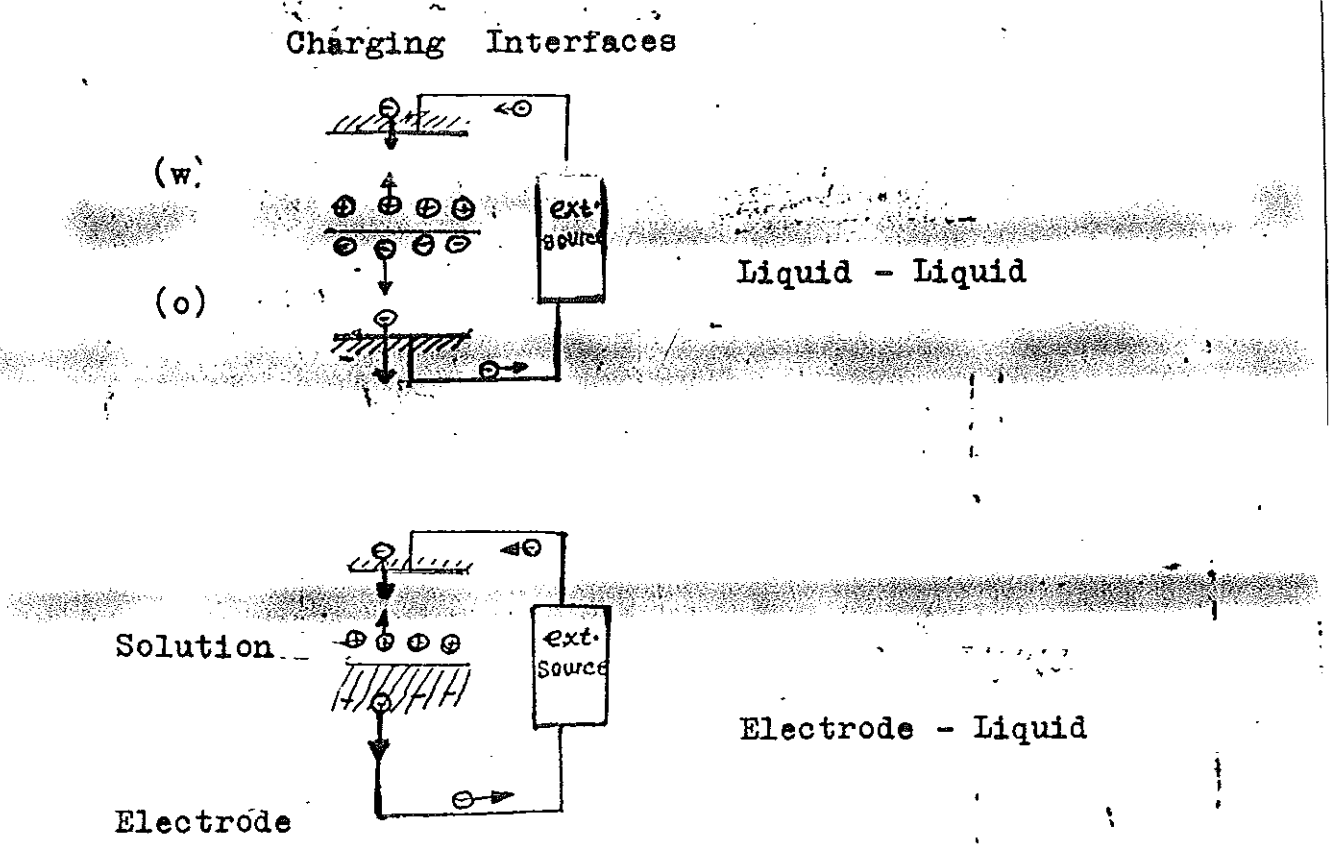


Fig. 3.1 : The [illegible] face between two immisible electrolyte solutions is compared with an ideally polarized metallic electrode - electrolyte solution interface, when both interfaces are charged from an external source.

interface takes place.

The ideally polarizable interface can be used for studies of a double layer or it can be used as a tool for the investigation of ions whose potential of transfer lie within the potential window.

3.4. EQUIVALENT CIRCUIT OF A CELL

An electrochemical system is merely an impedance to a perturbing electrical signal with a small amplitude [50]. The electrical behaviour of an interface can therefore be represented by an electrical equivalent circuit (Fig. 3.2), where R_s is the solution resistance between the tips of the Luggin capillaries, C is the capacitance of the interface, and Z_f is the faradaic impedance for the interfacial transfer of the electrolyte ions.

Since ion transfer is a rather fast process, the faradaic impedance Z_f becomes equal to the Warburg impedance Z_W. In particular, at low angular frequencies [28,42], the real Z′ and imaginary Z″ components are given by

$$Z' = |Z| \cos\delta = R_s + Z_c X[(X+1)^2+1]^{-1} \qquad (11)$$

$$Z'' = |Z| \sin\delta = Z_c X(X+1)[(X+1)^2+1]^{-1} \qquad (12)$$

where $X = (Z\omega / Z_c)2^{1/2}$ and $Z_c = 1/\omega C$, δ is the phase shift and ω is the angular frequency.

At higher frequencies, $Z' = R_s + Z_c X^{-1}$, and

$$Z'' = Z_c$$

Near the low-frequency limit, $Z' = R_s + Z_W 2^{1/2}$, and

$$Z'' = Z' - R_s$$

The interfacial capacity C can be evaluated from the capacitance Z_c of Eq. 12, at a chosen frequency ω and potential E. Only those data of C are included, which correspond to the linear part of $1/Z_c$ vs. ω [42].

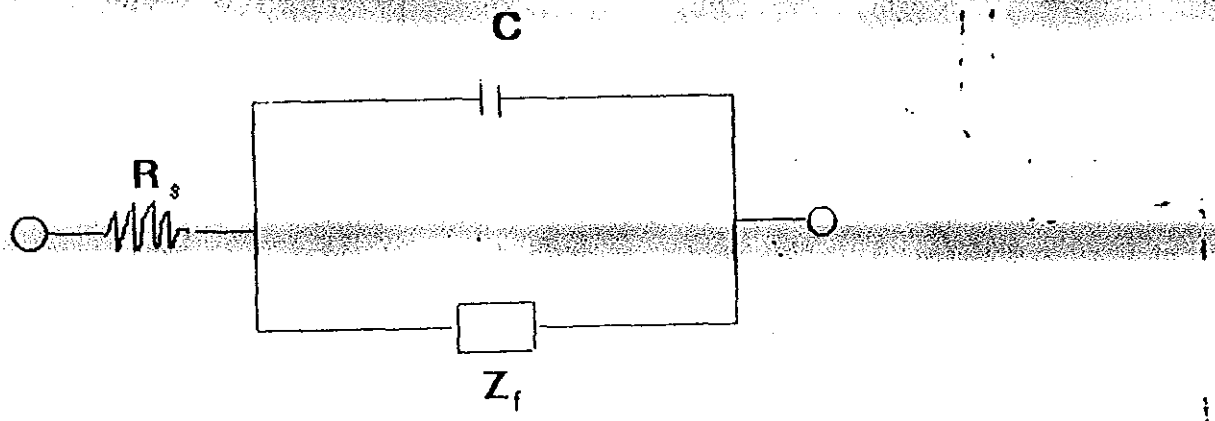


Fig. 3.2 Equivalent circuit for the interface between two immiscible electrolyte solutions. C is the capacity of the interface, Z_f is the faradaic impedance and R_s is the solution resistance between the tips of Luggin capillaries.

The impedance of the interface Z can be evaluated from [28]

$$Z = V_0 / [I(0^0)^2 + I(90^0)^2)]^{1/2} \qquad (13)$$

where V_0 is the ampiitude of the sinusoidal voltage and $I(0^0)$ or $I(90^0)$ are the in-phase or out of phase components of the sinusoidal current flowing through the interface.

The phase shift between the applied and measured signal, which is related to the real $Z' = |Z| \cos\delta$ and imaginary $Z'' = |Z| \sin\delta$ part, can be calculated from the relation

$$\tan^{-1}[I(90^0)/I(0^0)]$$

3.5. THE CAPACITANCE OF THE WATER/ORGANIC SOLVENT INTERFACE

Following the MVN model [1] the galvani potential difference between two phases (w) and (o) in contact splits into the inner and diffuse layer contributions:

$$\Delta^{\alpha}_{\beta}\phi = \phi(w) - \phi(o) = \Delta^{w}_{o}\phi_i + \phi_2(o) - \phi_2(w) \qquad (15)$$

where $\Delta^{w}_{o}\phi_i = \phi(X_2^{w}) - \phi(X_2^{o})$ is the inner layer and $\phi_2(o) = \phi(X_2^{o}) - \phi(o)$ or $\phi_2(w) = \phi(X_2^{w}) - \phi(w)$ are the potential difference across the space charge regions in the phases (o) and (w), respectively (Fig. 3.3). The electroneutrality condition requires that

$$q(w) = -q(o) \qquad (16)$$

where q(w) and q(o) are surface excess charge densities on the water and organic side of the interface respectively.

In the absence of specific ion adsorption, the double layer capacitance can be represented as a series combination of the inner-layer capacitance and the diffuse layer capacitance [41,42].

$$C^{-1} = C_i^{-1} + C_{2\text{-}w}^{-1} + C_{2\text{-}o}^{-1} \qquad (17)$$

where $C_i = dq(w)/d\Delta^{w}_{o}\phi_i$ is the capacity of the inner - layer and $C_{2\text{-}w} = -dq(w)/d\phi_2(w)$ or $C_{2\text{-}o} = -dq(o)/d\phi_2(o)$ are the capacitances of the diffuse layers in the phase (w) or (o) respectively.

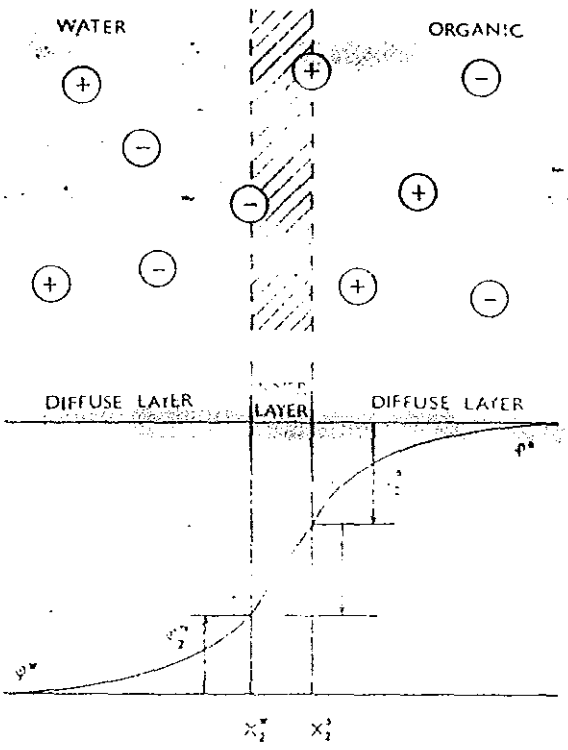


Fig. 3.3 : Modified Verwey-Niessen model of an ITIES and definition of potential differences involved. Full circles repersent the point-charge ions. and X_2^w or X_2^o are positions of ions in planes of closest approach(outer Helmolz planes)to the hypothetical plane of contact in the phase(w) or(o),respectively. Taken from ref.[1].

For a symmetrical electrolyte, the GC theory can be used to describe the excess surface charge density when a potential difference is applied across the interface.

Hence, $$q(w) = -2A^{w} \sinh (ZF\phi_2(w)/2RT) \quad (18)$$

$$q(o) = -2A^{o} \sinh (ZF\phi_2(o)/2RT)$$

and consequently,

$$C_{2\text{-}o} = (ZFA^{o}/RT) \cosh (ZF\phi_2(o)/2RT) \quad (19)$$

$$C_{2\text{-}w} = (ZFA^{w}/RT) \cosh (ZF\phi_2(w)/2RT)$$

where Z is the ionic charge number and

$$A^{w(o)} = (2RT\epsilon^{w(o)} C^{w(o)})^{1/2}$$

$\epsilon^{w(o)}$ is the dielectric constant and $C^{w(o)}$ is the bulk concentration of the respective phases. It is clear that the capacitance of the diffuse double-layer has a minimum at q(w) = -q(o), which is proportional to the square root of the electrolyte bulk concentration [10,42].

Assuming the inner potential drop is zero, the potential drop across the water diffuse layer is given by [7,37]

$$\phi_2(w)=(RT/F)\{[(\epsilon^{w}C^{w})^{1/2}+(\epsilon^{o}C^{w})^{1/2}\exp(F\phi_a/2RT)]/(\epsilon^{w}C^{w})^{1/2}+(\epsilon^{o}C^{w})^{1/2} \times \exp(-F\phi_a/2RT)\} \quad (20)$$

where ϵ and C stand for their usual meanings and ϕ_a is the applied potential drop across the interface.

The potential drop across the organic diffuse layer is similar to that of Eq. (20) or can be expressed as

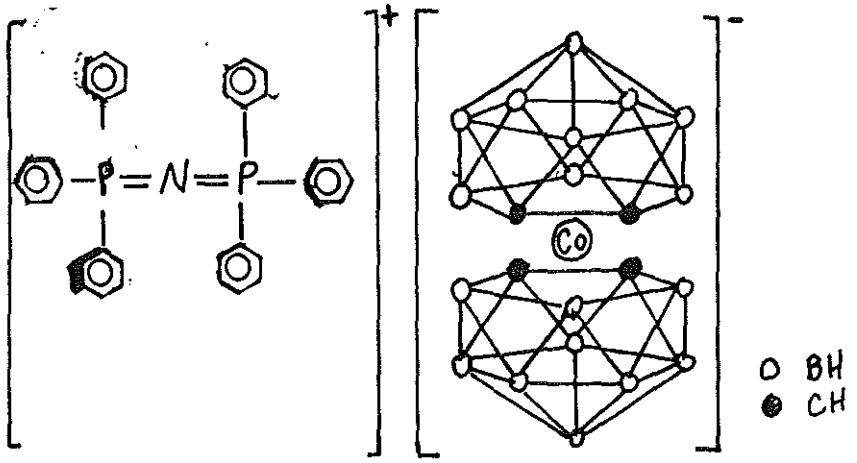
$$\phi_2(o) = \phi_a - \phi_2(w) \qquad (21)$$

4. EXPERIMENTAL

o-dichlorobenzene (Riedel-de-Haen) was distilled under reduced pressure and the middle half of the distillate was used. In all experiments doubly distilled water followed by deionization using ion exchange resins was used.

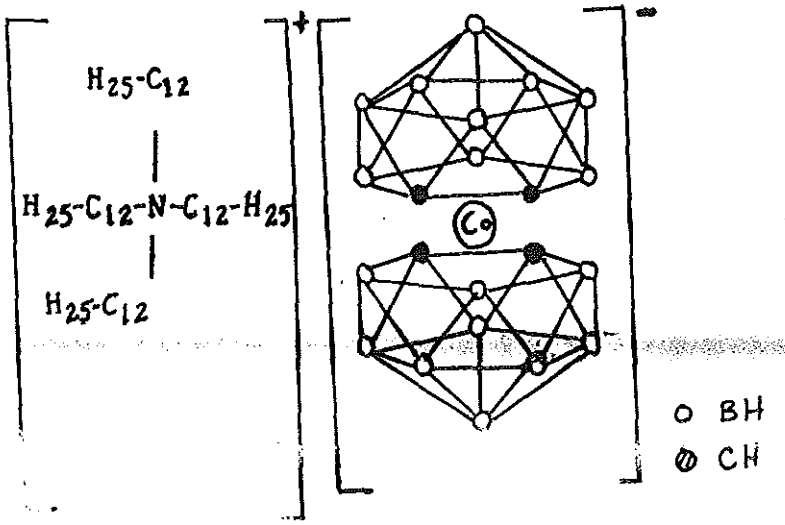
μ-nitrido-bis(triphenylphosphorus)3,3-como-bis(undecahydro-1,2-dicarba-3-cobalta-closododecabor)ate (PNPDCC) was prepared by mixing

PNPDCC



equimolar amounts of acetone (Riedel-de-Haen) solutions of PNPCl (Fluka) and CsDCC. CsDCC was the generous gift of Dr. K. Base, Institute of Inorganic Chemistry, Czechoslovak Academy of Science.

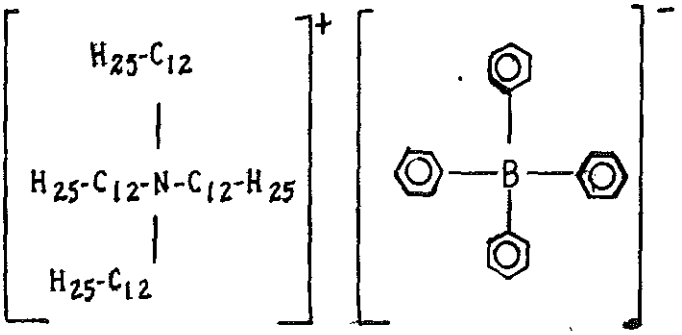
TDADCC



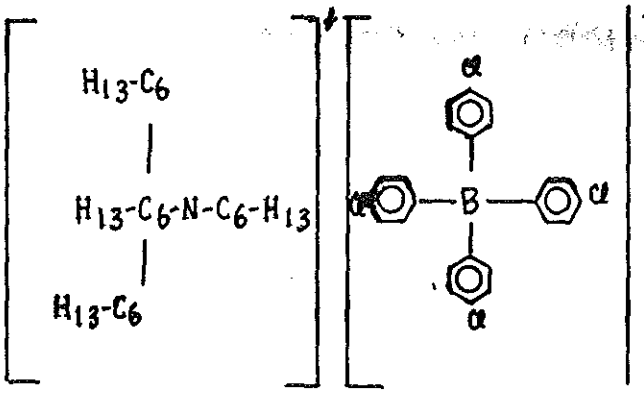
Tetradodecylammonium 3,3-como-bis(undecahydro-1,2-dicarba-3-cobalta-closododecabor)ate (TDADCC), was prepared by mixing equimolar amounts of TDABr (Fluka) with CsDCC both dissolved in aceton. The precipitate of CsBr was filtered off and the crude orange product was obtained after evaporating the solvent. It was recrystalized twice from methanol.

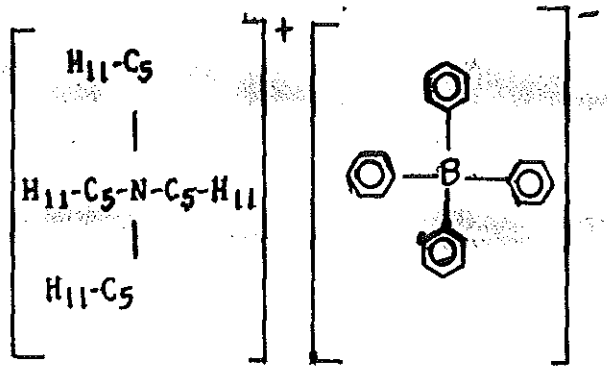
Tetradodecylammonium tetraphenylborate (TDATPB), tetrahexylammonium tetrakis(4-chlorphenyl)tetraphenylborate (THATCTPB), and tetrapentylammonium tetraphenylborate (TPeATPB) were prepared in methanol by mixing equimolar solutions of TDABr with NaTPB (Fluka), THACl (Fluka) with KTClTPB (Fluka) and TPeACl with NaTPB. The precipitates formed were washed several times with water and recrystallized from acetone.

TDATPB



THATClTPB



TPeATPB 

The above salts were used as supporting electrolytes in the organic phase. Whereas LiF (BDH), LiCl (Fluka), KCl (Analar), NaCl (Analar) and Li_2SO_4 (Merck) were used as supporting electrolytes in the aqueous phase.

Impedance measurments with different concentrations (5 mM, 10 mM, 15 mM, 20 mM, and 50 mM) of LiCl (Fluka 98 %) in the aqueous phase and PNPDCC in the organic phase were made in order to calculate the capacitance of the double layer.

In order to check the stability of the reference electrode in the experiments, perchlorate (ClO_4^-) anion was used as an internal reference ion. After the completion of each impedance measurment, a drop of 20 mM $LiClO_4$ was added to the aqueous side of the electrochemical cell and the ac voltammogram of its transfer from water to 0-DCB was determined.

4.1 ELECTROCHEMICAL CELL ARRANGEMENT

The electrochemical cell used for the measurments is shown in Fig. 4.1 The upper part of the cell (glass vessel) was filled with aqueous solutions of supporting electrolytes and the lower part (teflon body) was filled with the organic phase. The two solutions were brought into contact and an interface of geometric area 0.709 cm^2 was formed. A U-shaped glass capillary tube filled partly with the organic phase containing supporting electrolyte and partly with an aqueous solution of saturated KCl was inserted from the bottom into the teflon body close to the interface. This capillary served as the electrolyte compartment for the reference electrode in the organic phase.

The cell contained four electrodes. Two $Ag/AgCl/Cl^-$ electrodes (reference electrodes in both phases) were used to monitor the potential difference at the water/o-dichlorobenzene interface. For this purpose, they were positioned as closely as possible to each side of the interface. Such an arrangement helps to lower the ohmic resistance between the two reference electrodes. The remaining two platinum electrodes served as current supplying and withdrawing electrodes (counter electrodes). The cell was connected to the electronic set-up through the four-electrode potentiostat with IR drop compensation.

Fig. 4.2. shows the diagram of the cell employed for the measurment of the potential of zero charge. The aqueous solution served as a streaming-jet electrode so that the potential of the cell corresponded to the condition of zero charge.

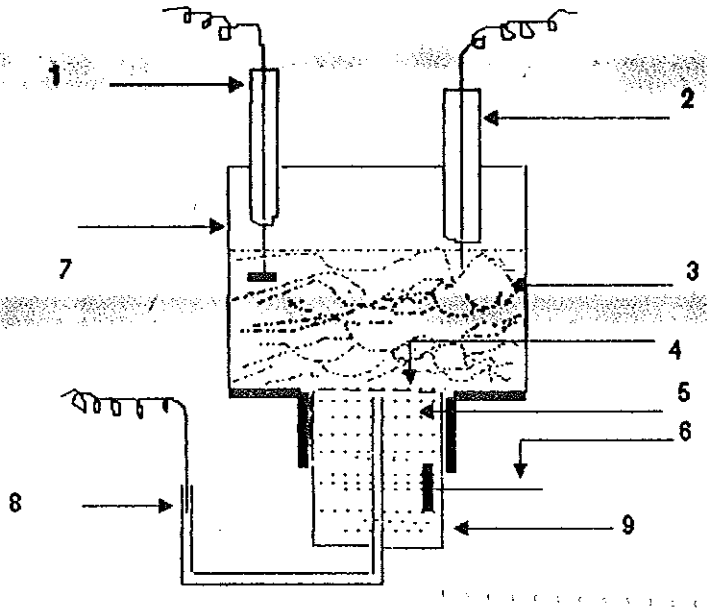


Fig. 4.1 The electrochemical cell employed in the study

1. Counter electrode (water phase)
2. Reference electrode (water phase)
3. Aqueous phase
4. The interface
5. Organic phase
6. Counter electrode (organic)
7. Glass vessel
8. Reference electrode (organic)
9. Teflon body

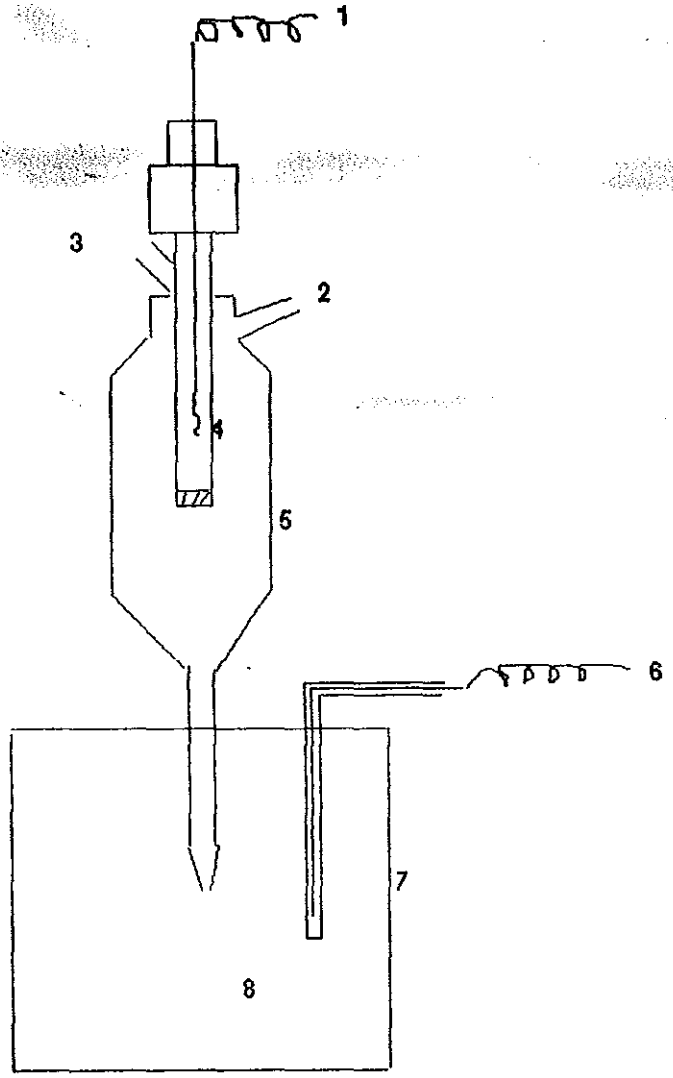


Fig. 4.2 Diagram of the cell used for the measurement of the point of zero charge.

1. Reference electrode (water)
2. Pressure inlet
3. Opening to equalize the pressure
4. Aqueous phase
5. Aqueous solution reserviour
6. Reference electrode (organic)
7. Streaming electrode reserviour
8. Organic phase

The temperature was kept constant at 24 ±2 ^{0}C. The reference electrode (Ag/AgCl/Cl^{-}) in the pressurized vessel had an opening to equalize the pressure.

4.2. ELECTRONIC SET-UP

The block diagram of the electronic set-up used for both dc and ac cyclic voltammetry measurments is shown in Fig. 4.3.

For dc voltammetric measurments, a small triangular voltage ramp of sweep rate 25 mV/s was generated using a PM 1502 Electroanalyzer (Mckee Pedersen Instruments). For ac cyclic voltammetric measurments, a 5 mV peak to peak) sinusoidal voltage signal from a frequency generator (Tektronix FG 501) was superimposed on the slow triangular voltage ramp of sweep rate 10 mV/s and fed to the potentiostat. The current output of the potentiostat was connected to a lock-in-analyzer (PAR Model 5204) which was used for the continuous measurements of the in-phase and quadrature components of the ac-current. The output of the lock-in-analyzer was in turn connected to an X-Y recorder. To regulate the proper compensation of the IR drop across the interface, the output of the potentiostat was also connected to an oscilloscope (Tektronix Model 501). IR compensation was set to the nearest point before oscillation.

The in-phase and quadrature components of the sinusoidal current flowing through the interface were measured at the out-put of the lock-in-analyzer at frequencies between 30 Hz and 100 Hz. They were transformed into the real Z' and the imaginary Z'' impedance components

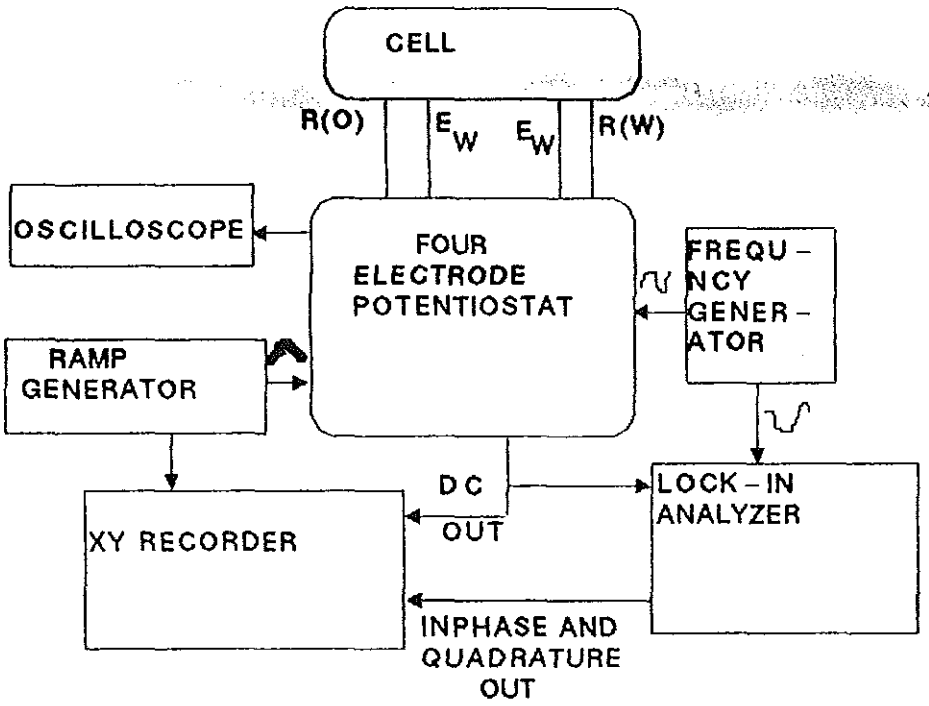


Fig. 4.3 Block diagram of the electronic setup. E(o) and E(w) are the counter electrodes in the organic phase and the aqueous phas respectively, and R(o) and R(w) are the reference electrodes.

5. RESULTS AND DISCUSSION

Fig. 5.1. shows an example of the electrical current flowing through the water/o-dichlorobenzene interface based on the convention that the positive current corresponds to the transfer of positive charge from the aqueous to the non-aqueous phase and transfer of negative charge from non-aqueous to the aqueous phase. In the presence of NaCl in the aqueous phase and PNPDCC in the organic phase the potential window in the negative potential range is limited by the transfer of Cl^- or PNP^+ and by the transfer of Na^+ in the positive potential range. In the voltammetric experiment the principal aim was to find the range within which the boundary behaves as an ideally polarizable interface, i.e., the condition in which ion transfer is negligible.

In the potential region between 0.15 V and 0.63 V the current is controlled mainly by charging the interface while at more positive or more negative potentials the transfer of the ions of the base electrolytes prevails. In order to minimize the faradaic contribution, all impedance measurements were carried out within the stated potential range.

On the other hand, Fig. 5.2. shows the ac voltammograms of the in-phase and quadrature components at a frequency of 35 Hz for the same system. The in-phase and quadrature components of the ac current were recorded as a function of potential at a given frequency between 35 and 100 Hz. They were transformed into complex impedance Z and phase angle δ using equation (13) and (14) respectively. The real Z' and the imaginary Z'' components of the complex impedance (Table I) can be easily obtained using equations (11) and

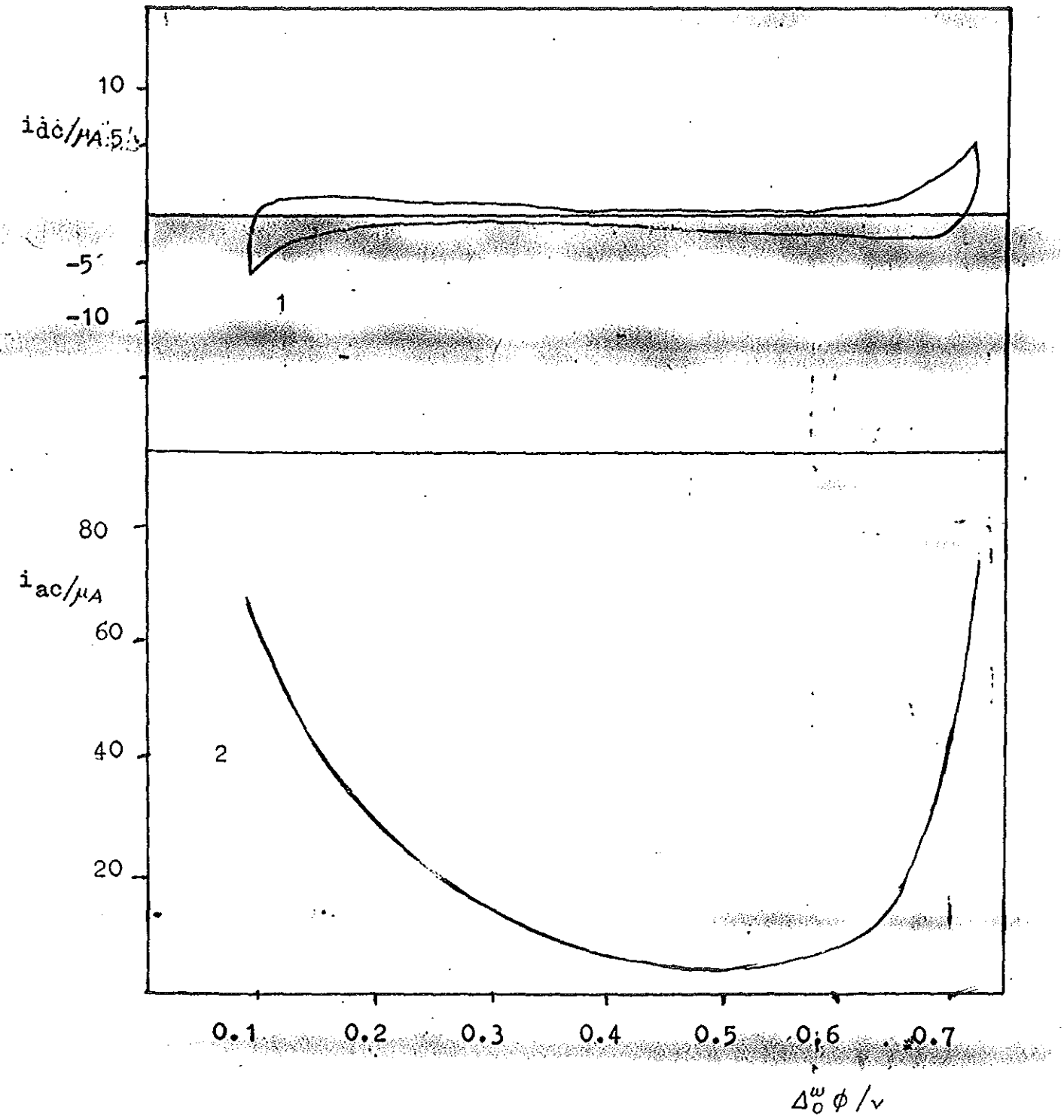


Fig. 5.1 : dc (1) and ac (2) cyclic Voltammogram for the interface between 10mm Nacl(w) and 10mm PNPDCC(0-DCB). Sweep rate 25mv/s(1) and 10mv/s(2) , f=35Hz(2)

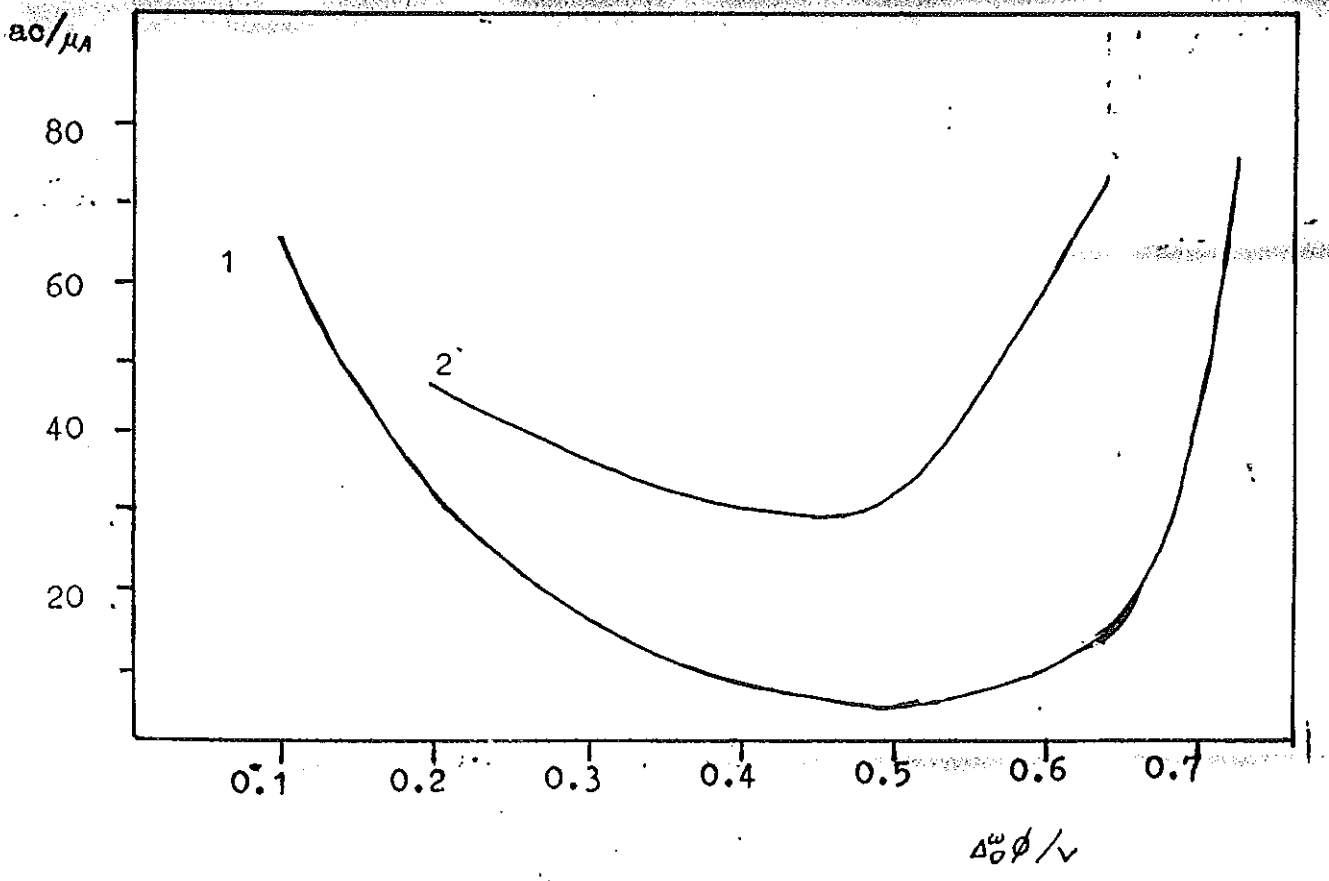


Fig. 5.2 : Inphase (1) and quadrature (2) components of ac impedence measurements for the interface between 10mM NaCl and 10mM PNPDCC(O-DCB).
Sweep rate 10mV/s ,f=35Hz

(12). Results were presented in the form of Z'' versus Z' whose typical shape is illustrated in figure 5.3. Such plots were resolved for the electrical equivalent circuit of Fig. 5.3. The plots indicate that the impedance tends to converge at a certain point on the Z' - axis, with an increase in frequency, which can be used to obtain the small uncompensated solution resistance. In other words, the result tends to a semi-circle for the parallel RC circuit as expected.

Figure 5.4 shows the plot of the imaginary impedance Z'' vs ω^{-1} from the slope of which the capacitance of the system: 10 mM LiCl in water and 10 mM PNPDCC in o-dichlorobenzene was obtained (Table I). A similar analysis of the capacitance data for various supporting electrolytes in the organic phase is summarized in Table II.

As can be seen from Table II, TDADCC and TDATPB show the same potential of capacitance minimums $\Delta^{w}_{o}\phi_{m}$ whereas the magnitudes of their potential of zero charge $\Delta^{w}_{o}\phi_{z}$ differ by 66 mV. The difference between $\Delta^{w}_{o}\phi_{m}$ and $\Delta^{w}_{o}\phi_{z}$ ($\Delta\Delta^{w}_{o}\phi$), for TDADCC is relatively large as compared to TDATPB. However both electrolytes show large values of $\Delta\Delta^{w}_{o}\phi$.

On the other hand TPEATPB and THATCITPB have identical $\Delta^{w}_{o}\phi_{m}$ and $\Delta^{w}_{o}\phi_{z}$ values respectively. This observation indicates that the capacitance minima of the above two electrolytes correspond to $\Delta^{w}_{o}\phi = 0$. The value of $\Delta\Delta^{w}_{o}\phi$ for PNPDCC (-41 mV) is in accordance to other results [4,58]. According to these workers, $\Delta\Delta^{w}_{o}\phi$ has a value of about -40 mV as observed for several immiscible systems such as the water/1,2-dichloroethane, water/nitrobenzene, water/nitroethane and water/organic mixtures [58]. In the present work the

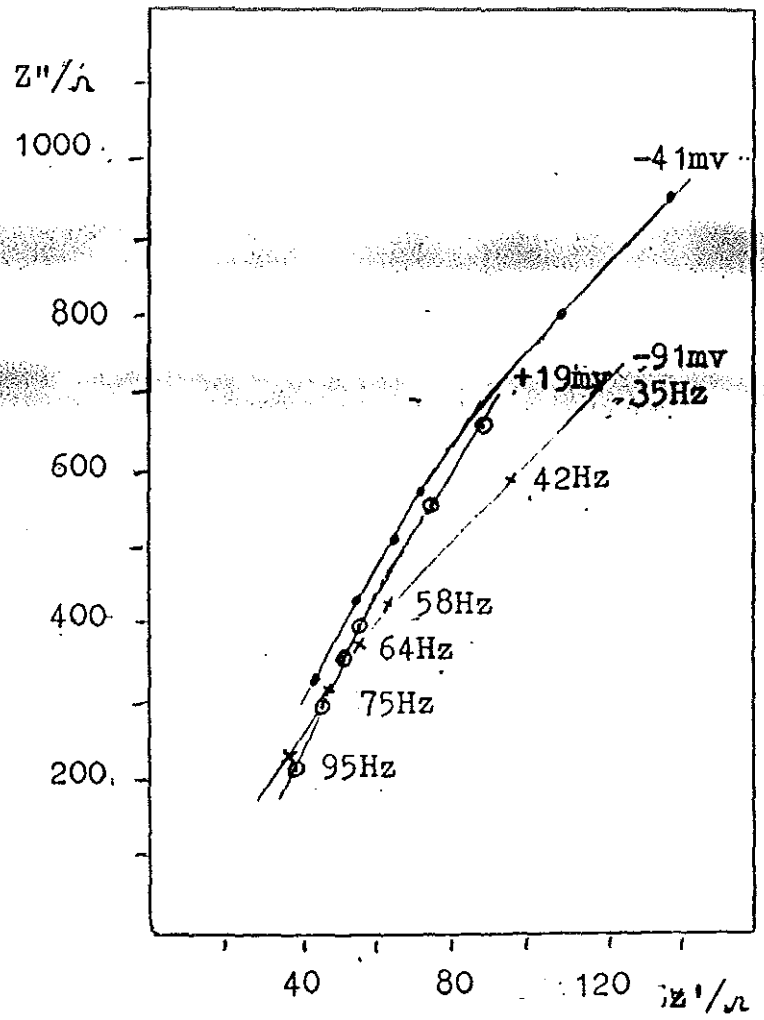


Fig. 5.3 : Impedence plot for the interface between 10mm LiCl(w) and 10mm PNPDCC(O-DCB) at various potentials. Numbers on the line indicate the frequency in Hz.

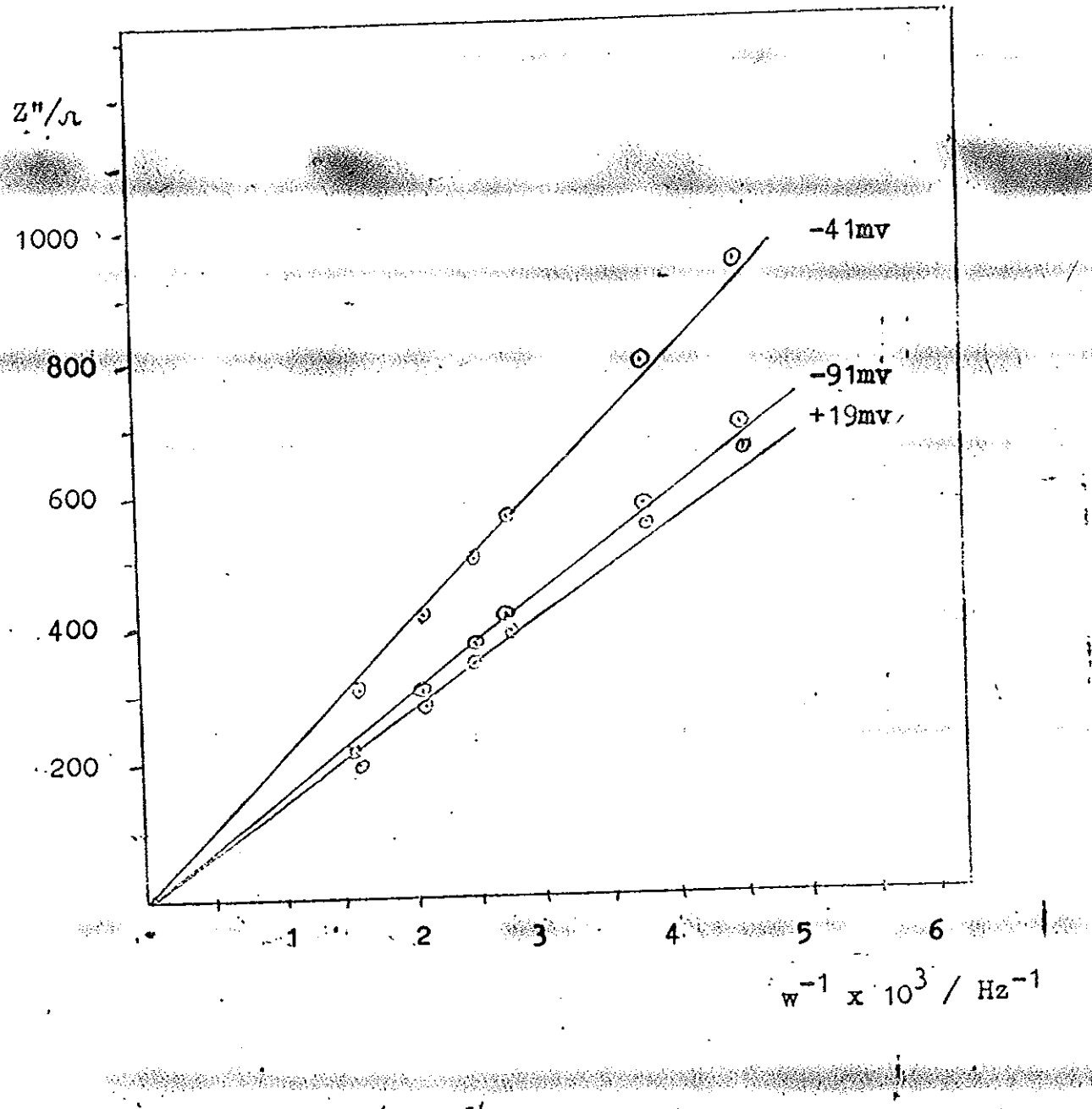


Fig. 5.4 : Plot of Z'' Vs W^{-1} for the system :10mm LiCl(U) and 10mm PNPDCC(O-DCB).

Table I. values of the real and imaginary components of the measured impedance at three potentials

Potential (mV)	Frequency (Hz)	Real Part (ohm)	Imaginary part (ohm)
-41	35	0.135657+03	0.964673+03
-41	42	0.108206+03	0.805252+03
-41	58	0.708212+02	0.576871+03
-41	64	0.637393+02	0.516805+03
-41	75	0.532322+02	0.430642+03
-41	95	0.427209+02	0.320042+03
	C = 0.476862-05F = 0.672584 - 05 F/cm^2		
-91	35	0.117460+03	0.712036+03
-91	42	0.945622+02	0.595050+03
-91	58	0.614215+02	0.425950+03
-91	64	0.557095+02	0.381468+03
-91	75	0.461406+02	0.313120+03
-91	55	0.373163+02	0.223898+03
	C = 0.648124-05F = 0.914139 - 05 F/cm^2		
-19	35	0.862876+02	0.667290+03
-19	42	0.731413+02	0.560750+03
-19	58	0.534957+02	0.402791+03
-19	64	0.496467+02	0.357456+03
-19	75	0.427679+02	0.296524+03
-19	95	0.376157+02	0.217061+03
	C = 0.688174-05 F = 0.970626 - 05 F/cm^2		

Table II. Values of the capacitance minimum and potential of zero charge for 10 mM aqueous solution of LiCl and 10 mM o-dichlorobenzene solutions of various supporting electrolytes.

Organic phase	$\Delta^{w}_{o}\phi_{m}$ / mV	$\Delta^{w}_{o}\phi_{s}$ / mV	$\Delta\Delta^{w}_{o}\phi$ / mV	C_{m} / Fm^{-2}
TDADCC	-8	+124	-132	0.05
PNPDCC	+38	+79	-41	0.07
TDATPB	-8	+58	-66	0.05
TPeATPB	+34	+34	0	0.07
THATClTPB	+6	+6	0	0.08

Table III. Values of the capacitance minimum and potential of zero charge for 10 mM PNPDCC (o-DCB) and 10 mM aqueous solution of various supporting electrolytes.

Aqueous phase	$\Delta^{w}_{o}\phi_{m}$ / mV	$\Delta^{w}_{o}\phi_{s}$ / mV	$\Delta\Delta^{w}_{o}\phi$ / mV	C_{m} / Fm^{-2}
LiF	+40	+80	-40	0.07
LiCl	+38	+79	-41	0.07
Li_2SO_4	+40	+70	-30	0.05
NaCl	+56	+90	-34	0.08
KCl	+46	[illegible]	-35	0,08

obtained $\Delta\Delta^{w}_{o}\phi$ values for TDADCC and TDATPB may indicate the presence of specific ionic adsorption. This conclusion can be supported from the view point of the long chains of the alkyl groups of the TDA^{+} cation.

Comparison of the capacitance minima of the electrolytes of Table II also shows that the TDA^{+} cation has the lowest value (0.05 Fm^{-2}).

Table III shows the $\Delta^{w}_{o}\phi_{m}$, $\Delta^{w}_{o}\phi_{s}$, $\Delta\Delta^{w}_{o}\phi$ and C_{m} values for 10 mM PNPDCC in o-dichlorobenzene and 10 mM aqueous solutions of various supporting electrolytes. In general the aqueous base electrolytes have comparable $\Delta^{w}_{o}\phi_{m}$ and $\Delta^{w}_{o}\phi_{s}$ values. The $\Delta^{w}_{o}\phi_{m}$ values for LiF, LiCl and Li_2SO_4 are close to each other, implying that the anions of these electrolytes have no effect in shifting the potential of the capacitance minimum. Similar behaviours are also observed for NaCl and KCl.

The $\Delta\Delta^{w}_{o}\phi$ values for the five aqueous electrolytes are very close to -40 mV and the differences between them are within the range of the experimental error. These results are in good agreement with the results obtained by other workers [4,58]. The corresponding differential capacitance vs the potential difference plots are shown in Fig. 5.5.

Fig. 5.6 shows the plot of interfacial capacitance as a function of potential for five different electrolyte concentrations. The potential of zero charge at minimum capacitance is independent of concentration as summarized in Table IV.

It is apparent from Table IV that both $\Delta^{w}_{o}\phi_{m}$ and $\Delta^{w}_{o}\phi_{s}$ for the different concentrations of LiCl in water and PNPDCC in o-dichlorobenzene have comparable magnitudes. Based on this fact, one can possibly conclude

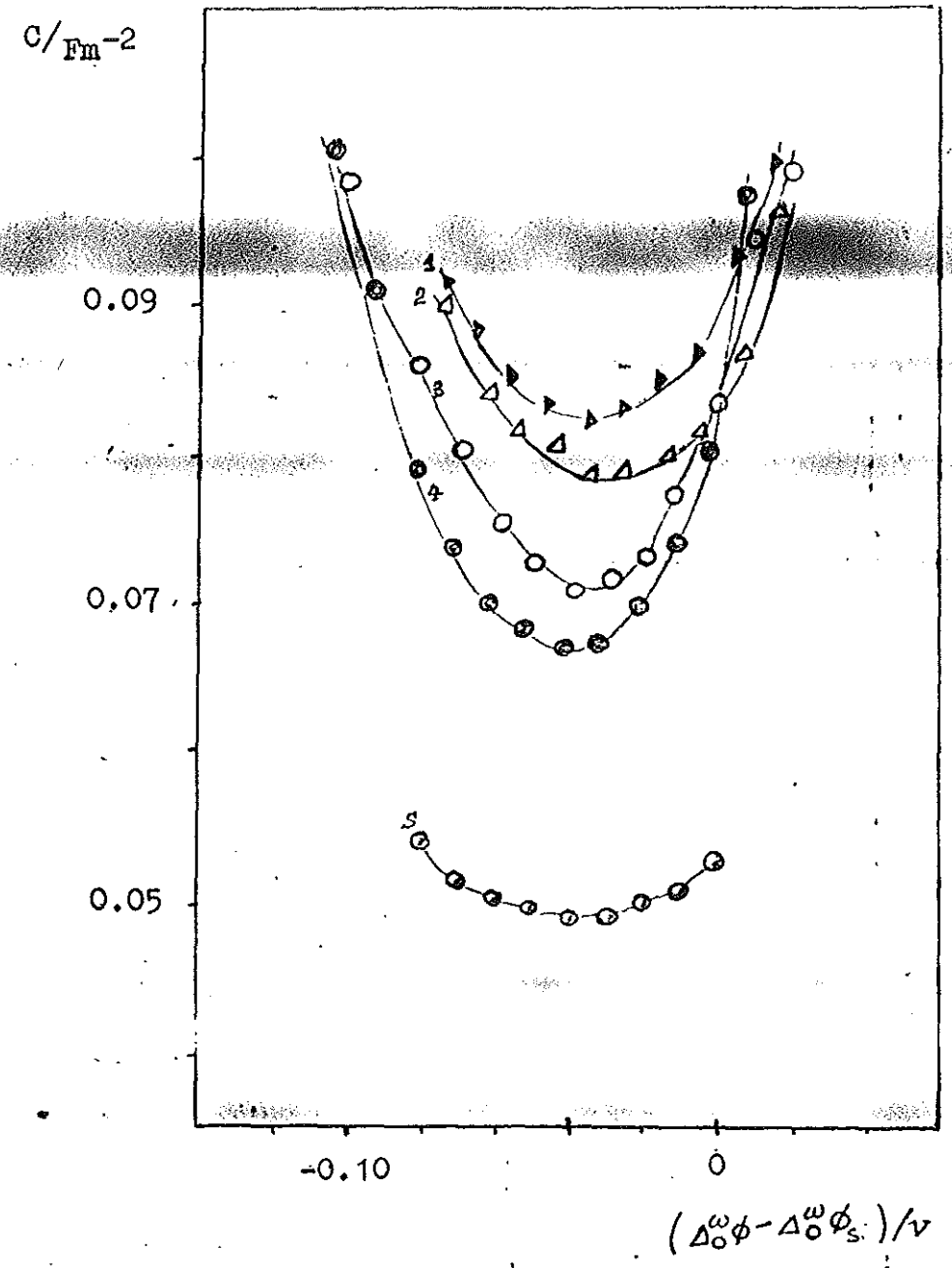


Fig. 5.5 : Differntial capacitance C of the double layer at the interface between 10mm Kcl(1), Nacl(2), LiF(3), Licl(4), 5mM Li_2SO_4 (5) in water and 10mm PNPDCC in O-dichlorobenzene.

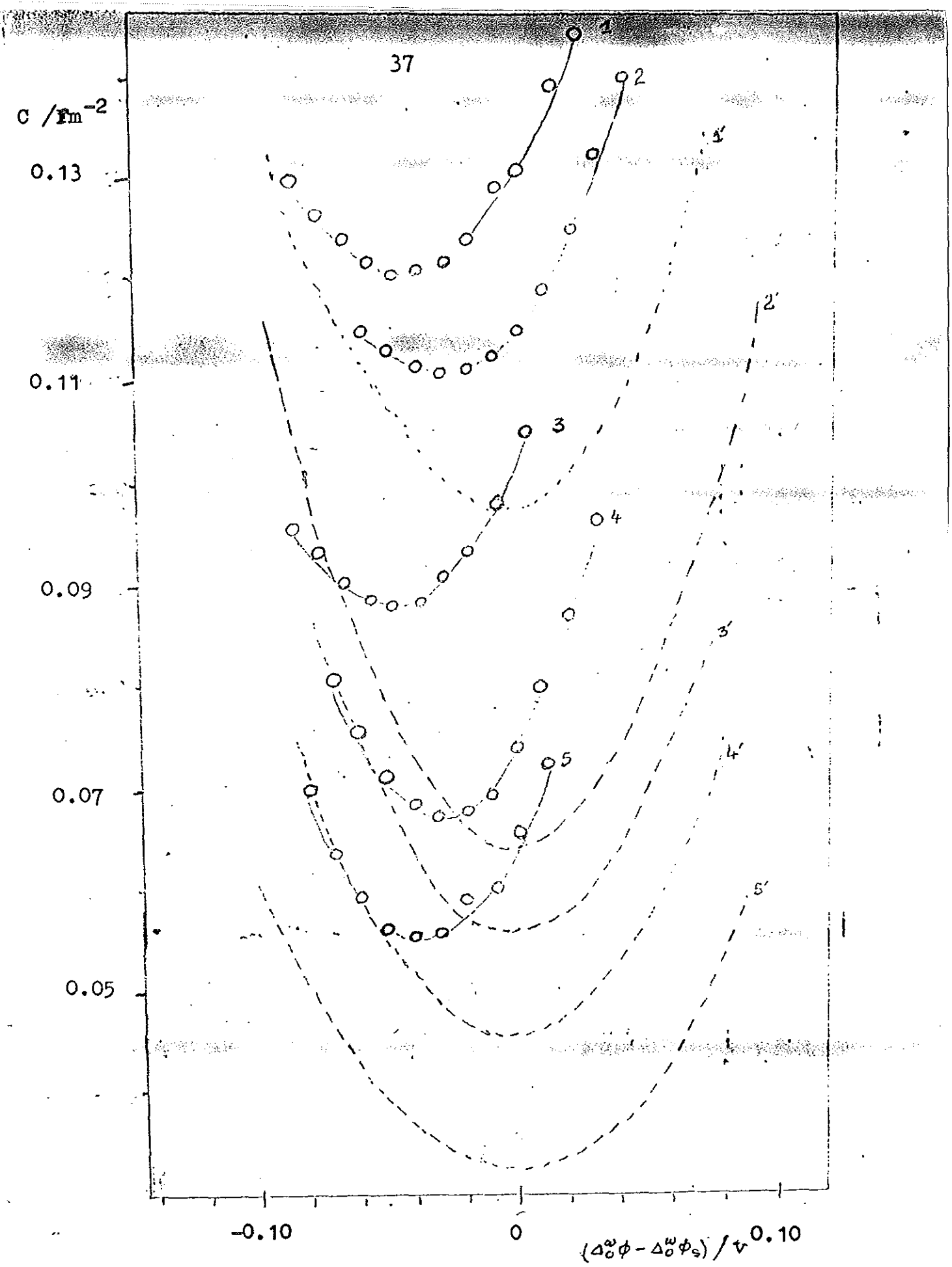


Fig. 5.6 : Diferntial capacitance C of the double layer at the water/o-DCB interface for various concentrations(in mol/m³) and temperatures(in °C): 50(1,1'); 20(2,2'); 10(3,3'); (4,4'); (5,5'). Dashed lines:Capacitance of the diffuse double layer calculated with the GC theory assuming the

Table IV. Potential difference at minimum capacitance of the water/o-DCB interface in the presence of PNPDCC in o-DCB and LiCl in water.

Concentration/mM	$\Delta^{w}_{o}\phi_{m}$ / mV	$\Delta^{w}_{o}\phi_{s}$ / mV	$\Delta\Delta^{w}_{o}\phi$ / mV	C_{m} / Fm^{-2}
50	+26	+70	-44	0.12
20	+36	+70	-34	0.11
15	+24	+69	-45	0.09
10	+38	+79	-41	0.07
5	+31	+65	-34	0.05

Table V. Capacitance minimum of theoretical and experimental values between LiCl (w) and PNPDCC (o-DCB).

Concentration/mM	50	20	15	10	5
Experimental Capacitance/Fm^{-2}	0.12	0.11	0.09	0.07	0.05
Theoretical Capacitance/Fm^{-2}	0.10	0.06	0.05	0.04	0.03

that these potentials are concentration independent. Furthermore the values of $\Delta\Delta^{W}_{0}\phi$ are very close to -40 mV showing that $\Delta\Delta^{W}_{0}\phi$ is invariant with concentration. Hence it is possible to conclude that the system LiCl (w) / PNPDCC (o-DCB) does not show any specific ionic adsorption.

The values of the experimental capacitance were compared with the capacitance values of the diffuse double layer which were calculated by means of the GC theory assuming that the inner layer potential difference is zero (see the dashed lines of Fig. 5.6. and the values in Table V). For all concentrations studied, the GC theory underestimates the capacitance of the space charge region through the direct relationship between electrolyte concentration and interfacial capacitance is observed.

Another sensitive method to verify the diffuse layer theory and detect specific ionic adsorption is illustrated in Fig. 5.7. This shows the experimental inverse capacitance C^{-1} at zero surface charge plotted against the inverse GC capacitance of the diffuse double layer C_d^{-1}. Based on Eq. 17 this correlation satisfies approximately a straight line of unit slope with reciprocal inner layer capacitance C_i^{-1} as the intercept. In spite of the large variation of diffuse layer capacitance with concentration, the inner layer capacitance is roughly constant at constant charge. The value of the inner layer capacitance as obtained by extrapolation (Fig. 5.7) is rather high, about ten times the GC capacitance of the diffuse double layer at low electrolyte concentrations. Hence, the major contribution to the double layer capacity is due to the inner layer component through out a considerable range of concentrations and also indicates the presence of [illegible] (Fig. 5.7).

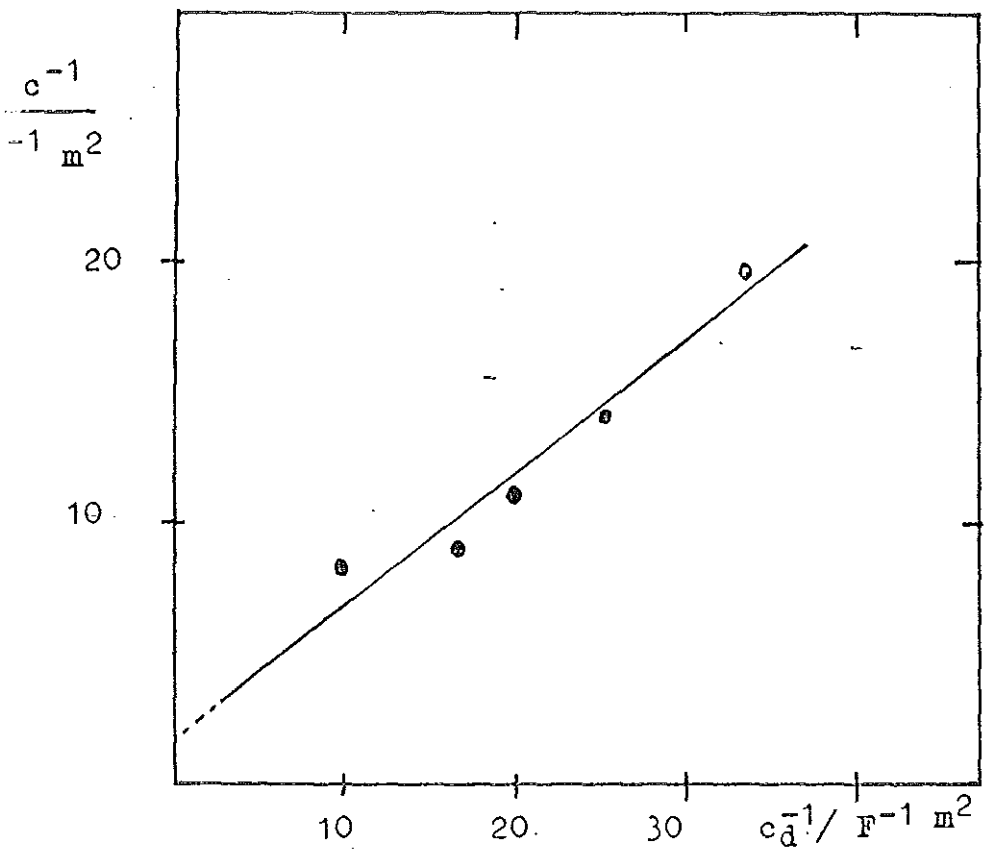


Fig. 5.8 Inverse capacitance C^{-1} at zero surface charge vs. the inverse capacitance of the diffuse double layer C_d^{-1} calculated with the GC theory for LiCl(w) and PHPOCC(O-OCB):

6. CONCLUSION

The electrical double layer at the water/o-dichlorobenzene interface has shown the absence of specific ionic adsorption for most of the electrolytes studied. On the other hand the TDA^+ cation appears to be specifically adsorbed.

Comparison of the experimental capacitance with the calculated capacitance using the Gouy-Chapman theory indicates that there is a good agreement from qualitative point of view except for the absence of a capacitance valley at low electrolyte concentration. However the quantitative agreement is not good. In general it has been found that the GC theory describes the space charge region in the aqueous phase rather well unless the electrolyte concentration is relatively very large.

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Declaration

I, the udersigned, declare that thic thesis is my work and all sources of materials used for the thesis have been fully acknowledged.

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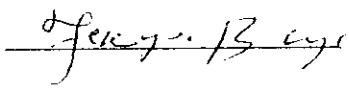
Signature 

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