

THE INFLUENCE OF CATIONS ON THE INTERFACE BETWEEN THE MERCURY ELECTRODE AND NON-AQUEOUS CH₃CN

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ABSTRACT

The double layer capacity of the Hg/non-aqueous CH₃CN (supporting electrolyte) system has been investigated for different alkali metal, NH₄⁺ and tetraalkylammonium perchlorates in the potential range from +0.5 to -2.9 V. Alkali metal ions and small tetraalkylammonium ions reveal Gouy-Chapman behaviour to a good approximation. The influence of different ion size on the double layer capacity and the potential of zero charge is discussed. With increasing length of the alkyl chain in the tetraalkylammonium ions, adsorption effects influence the double layer capacity.

INTRODUCTION

Acetonitrile is a very important solvent frequently used in electrochemical experiments. A systematic investigation of the double layer properties of non-aqueous acetonitrile electrolytes is not available. From the aspects of solubility and usable potential range, tetraalkylammonium cations dominate practical electroorganic chemistry. Therefore, we investigated the double layer capacities of these cations and compared their double layer properties with those of NH₄⁺ and alkali metal ions.

EXPERIMENTAL

Materials

Ultra pure substances are necessary in the field of double layer investigations, therefore the purification of the substances used in our experiments is described in some detail.

Commercial grade acetonitrile (AN) (Merck 99%) was rectified using a 1.5 m column filled with glass helices (reflux ratio 120). The fraction with a boiling point of 81.8°C/760 Torr was used for further purification; it showed $E = 0.1$ at 226 nm and $E = 0.5$ at 218 nm ($d = 1$) in its absorption spectrum. The acetonitrile was saturated with Ar (Messer-Griesheim 99.998%) and treated with NaH or LiAlH₄; all the following procedures were carried out in an argon atmosphere. In a second

distillation a small pre-run ($\sim 5\%$) was rejected, and the main fraction passed through a column filled with activated charcoal and alumina (Woelm acid, neutral, basic). Again a small pre-run ($\sim 5\%$) was rejected. The resulting AN showed a small shoulder in the absorption spectrum at 200 nm ($E = 0.3$, $d = 1$). In a third rectification with a reflux ratio of at least 120, several pre-runs were rejected until the extinction in the absorption spectrum was smaller than 0.05 ($\lambda = 200$ nm, $d = 1$ cm). The quality of this AN could not be improved by further purification steps. No impurities were detected by gas chromatography or by electrochemical methods.

The purified AN was stored for months without loss of quality in pre-dried glass vessels in an argon atmosphere using Teflon stops provided with O-rings.

Supporting electrolytes: Tetramethylammonium perchlorate (TMA) was prepared by neutralization of tetramethylammonium hydroxide (Fluka) with perchloric acid (Fluka, puriss). The precipitate was recrystallized twice from a mixture of methanol + triply distilled water (10:1). To eliminate traces of surfactants, TMA was precipitated from solutions in absolute methanol by dry, peroxide-free diethyl ether. After drying in vacuo at $100^\circ\text{C}/0.1$ Pascal, TMA with an $fp > 300^\circ\text{C}$ was obtained.

Tetraethylammonium- (TEA), tetra-*n*-propyl-ammonium- (TPA) and tetra-*n*-butyl-ammonium (TBA) perchlorates (Fluka purum) were dissolved in acetone and treated with charcoal and silica (Woelm). The further purification steps were identical to those described for TMA. The glassware used in the purification procedure has to be completely free of grease. The melting points of the salts obtained in this way were identical to literature data.

Alkali-metal perchlorates (Fluka puriss, Merck p.a.) were recrystallized twice from triply distilled water and (except LiClO_4) from absolute ethanol. The salts were dehydrated at 200°C in vacuo (0.1 Pascal) and stored in an argon atmosphere.

Ammonium perchlorate (AP) was prepared according to ref. 1, recrystallized three times from triply distilled water and dried at 130°C in vacuo.

Mercury (Merck puriss) was treated with KMnO_4 solution and dilute nitric acid and distilled twice in vacuo.

Cobalticinium perchlorate was prepared and purified according to ref. 2.

Measurement of capacities

All the experiments were performed at $20 \pm 1^\circ\text{C}$ in a DURAN[®] glass cell under argon atmosphere (Messer Griesheim 99.998% treated with Oxisorb[®]). To avoid contamination of the solutions with grease, only Teflon tightened connections were used. The DME was a tapered capillary from PAR with a flow rate of 1.146 mg/s at a mercury height of 56 cm. The natural drop time in AN solutions was 7–9 s depending on the potential and electrolyte. The capillary was not siliconized; no penetration of solvent was observed. During the measurement, the drop times were controlled with a drop timer (PAR). Drop times of 1–5 s were used; no dependence of the double layer capacity on the drop time was observed. The counter-electrode was a platinum wire (2 cm²). To avoid contamination by H_2O , Ag^+ , Cl^- , the

following reference electrode system was used: $\text{Ag}/\text{AgCl}/0.1 \text{ M } \text{M}^+ \text{ClO}_4^-$, AN, (M^+ is the cation of the solution under investigation). For separation of reference and cell electrolyte, a pin of clay (Haldenwanger TZ) was used. Compared with the reversible redox couple cobaltocene/cobalticinium [3], the potential of the reference system (-963 mV) is constant for months. Due to the high input resistance of the potentiostat the reference electrode was not polarized. The small liquid junction potential between the reference electrode and the cell electrolyte was measured [4] and considered in the potentials given in this paper.

The dropping electrode was polarized with a voltage of the function generator RG with respect to the reference electrode and a superimposed sine wave ac voltage of 10 mV (peak to peak) under potentiostatic control (Fig. 1). The ac frequency was $60\text{--}10000 \text{ Hz}$ depending on the cell resistance. By the lock-in technique, the in-phase and out-of-phase components of the cell current could be measured separately.

In the absence of faradaic currents, which has been proved carefully, the cell impedance is represented by the uncompensated resistance and the double layer capacity in series [5,6]; no frequency dispersion occurred in the frequency range under consideration. The double layer capacity was evaluated according to procedures given elsewhere [5–7].

The potential of zero charge (pzc) was determined in every experiment using a streaming electrode [8,9]. The performance of the circuit was checked by using a dummy cell and by reproducing the capacity data of aqueous NaF solutions given by Grahame [10].

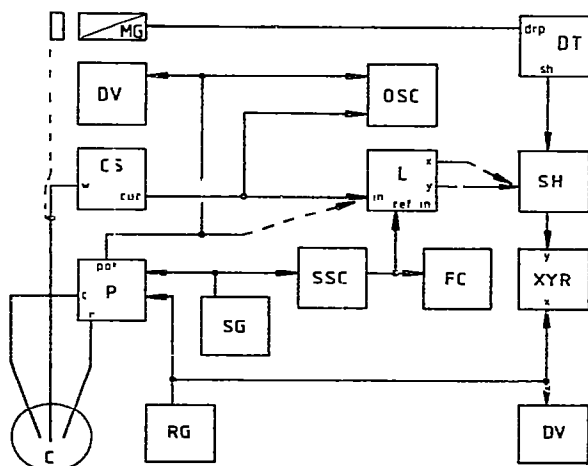


Fig. 1. Experimental device for capacity measurements (C) Electrochemical cell; (P) potentiostat [68], (CS) current sink, (MG) magnetic drop remover; (RG) ramp generator (Werkling), (SG) sine wave generator (HP), (SSC) small sine to large square converter, (L) lock-in amplifier (PAR), (DV) digital voltmeter, (OSC) oscilloscope, (XYR) X-Y recorder (Rohde u Schwarz), (SH) sample and hold unit, (DT) drop timer; (FC) frequency counter.

RESULTS

The capacity-voltage curves of the mercury/AN (electrolyte) system were measured for tetraalkylammonium ions ($R = \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_3\text{H}_7, n\text{-C}_4\text{H}_9, n\text{-C}_7\text{H}_{15}$),

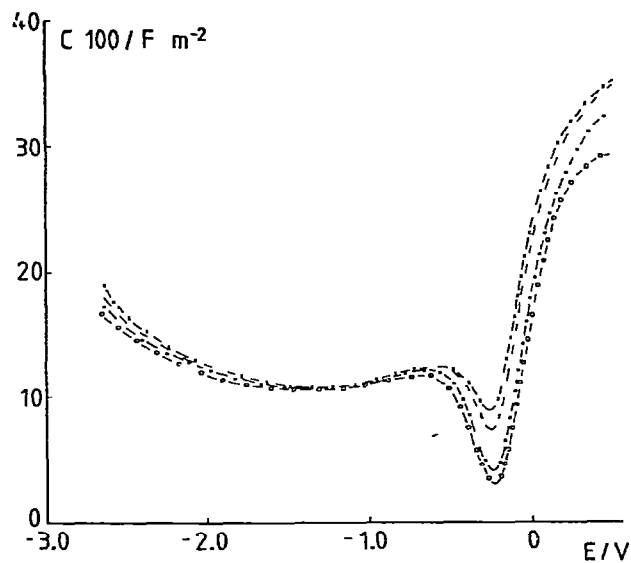


Fig 2 Capacity-voltage curves of tetramethylammonium perchlorate (TMA) $c/M = (-\times-)$ 1×10^{-2} ; $(---)$ 5×10^{-3} , $(-\bullet-)$ 1×10^{-3} , $(-\circ-)$ 5×10^{-4} .

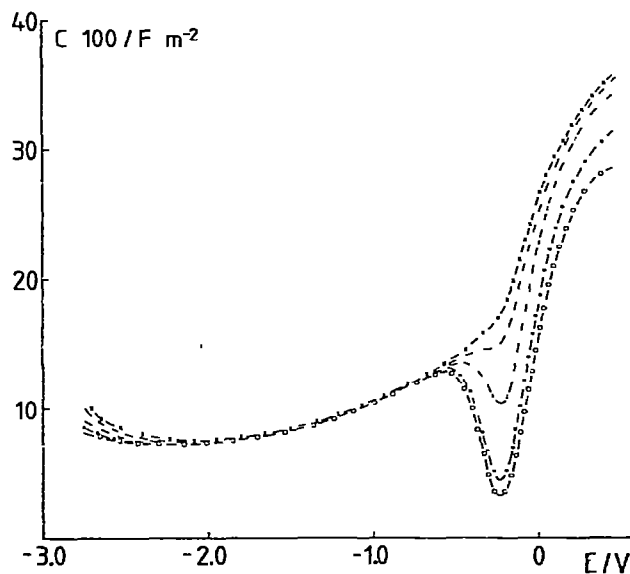


Fig 3. Capacity-voltage curves of tetraethylammonium perchlorate (TEA) $c/M = (-\times-)$ 1×10^{-1} ; $(---)$ 5×10^{-2} , $(-\bullet-)$ 1×10^{-2} , $(-\bullet-)$ 1×10^{-3} , $(-\circ-)$ 5×10^{-4} .

NH_4^+ and alkali metal ions (Li^+ , Na^+ , K^+ , Cs^+) in the range 0.5 V to the appearance voltage of faradaic processes. The range of concentration investigated was usually 5×10^{-4} to 0.1 M, respectively, the limit of solubility. Figures 2–7 show

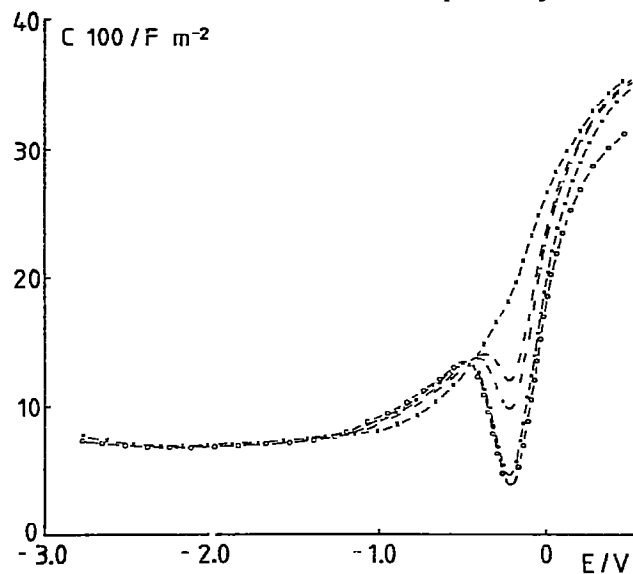


Fig. 4. Capacity–voltage curves of tetra-*n*-propylammonium perchlorate (TPA). $c/M = (-\times-)$ 1×10^{-1} , $(--)$ 1×10^{-2} , (\dots) 5×10^{-3} ; $(-\circ-)$ 7×10^{-4} ; $(-\bullet-)$ 5×10^{-4} .

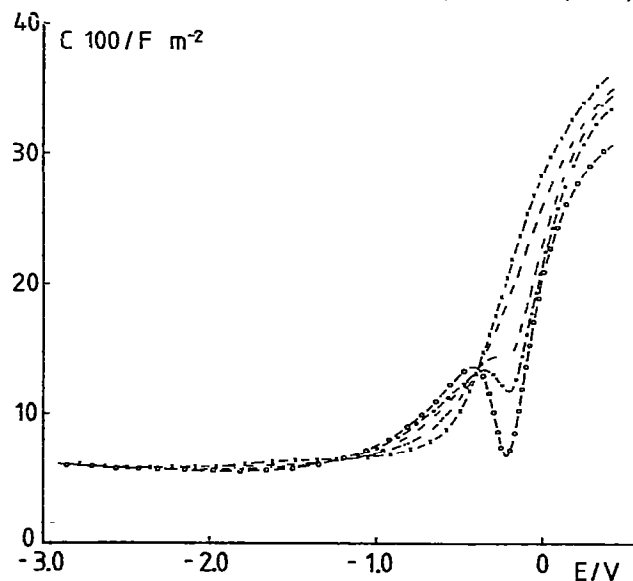


Fig. 5. Capacity–voltage curves of tetra-*n*-butylammonium perchlorate (TBA). $c/M = (-\times-)$ 1×10^{-1} ; $(--)$ 5×10^{-2} ; (\dots) 1×10^{-2} ; $(-\bullet-)$ 5×10^{-3} ; $(-\circ-)$ 1×10^{-3} .

the capacity-voltage curves of tetraalkylammonium ions and NH_4^+ at different concentrations. The capacity-charge curves of tetraalkylammonium ions and NH_4^+ at $10^{-2} M$ are shown in Fig. 8. For comparison, the capacity-potential curves of

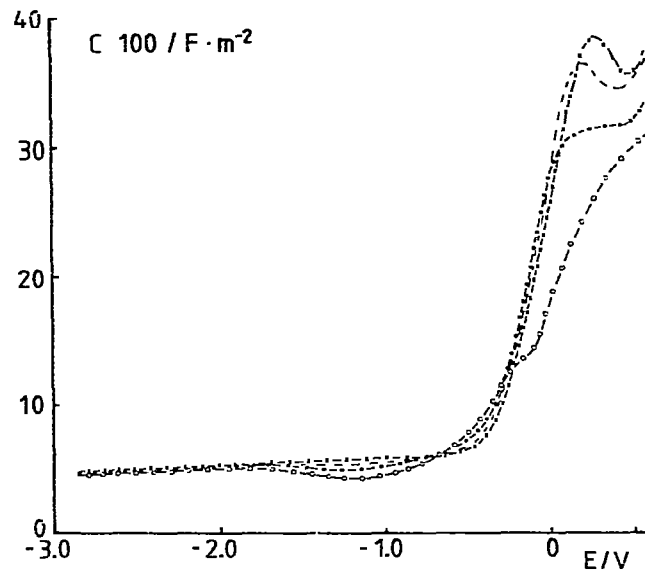


Fig. 6 Capacity-voltage curves of tetra-*n*-heptylammonium perchlorate (THA) $c/M = (-\times-)$ 1.0×10^{-1} ; $(-- --)$ 5×10^{-2} ; $(-\bullet-)$ 1×10^{-2} $(-\circ-)$ 1×10^{-3} .

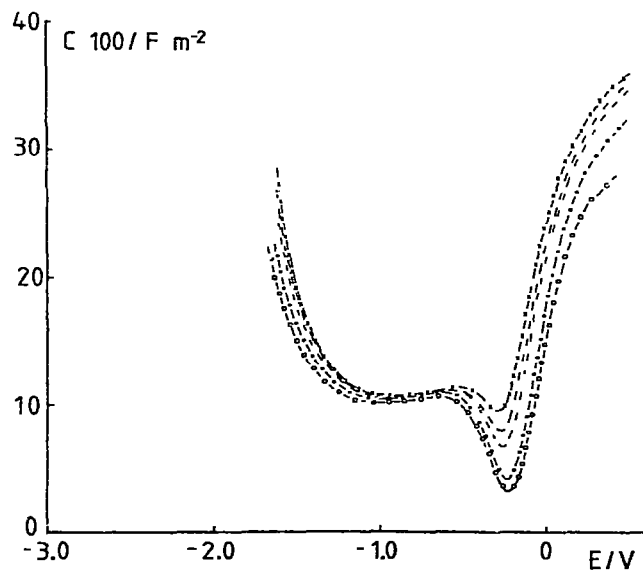


Fig. 7. Capacity-voltage curves of ammonium perchlorate. $c/M = (-\times-)$ 1.97×10^{-2} ; $(-- --)$ 9.86×10^{-3} ; $(-\bullet-)$ 5×10^{-3} ; $(-\circ-)$ 1.11×10^{-3} ; $(-\circ-)$ 5.67×10^{-4} .

alkali metal ions are represented in Fig. 9. The capacity-charge curves were calculated by computer integration of the capacity-voltage curves. The potentials of zero charge (pzc) and the potentials of the minima of capacity are given in Table 1.

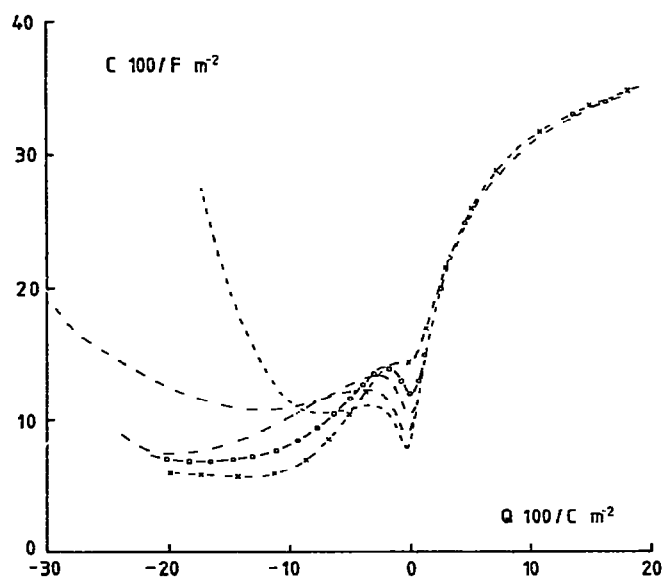


Fig. 8 Capacity-charge curves at $c = 10^{-2} M$. (---) NH_4^+ ; (-●-) TMA, (····) TEA, (-○-) TPA, (-●-×-) TBA

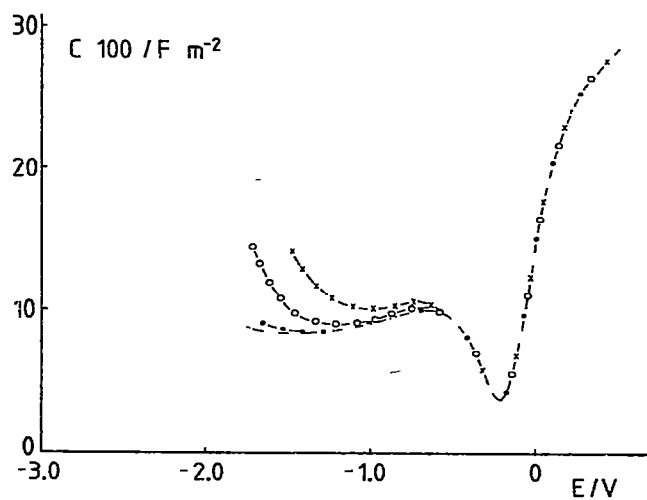


Fig. 9. Capacity-potential curves of alkali metal perchlorates at $c = 10^{-3} M$. (····) Li^+ , (-●-) Na^+ ; (-○-) K^+ ; (-×-) Cs^+

TABLE I

 E_{min} and pzc at different concentrations of the supporting electrolyte

Supporting electrolyte	c/M	$-E_{\text{min}}/V$	$-E_{\text{pzc}}/V$
LiClO ₄	5×10^{-4}	0.235	0.233
	1×10^{-3}	0.248	0.239
	1×10^{-2}	0.280	0.245
	5×10^{-2}	0.317	0.244
	1×10^{-1}	—	0.243
NaClO ₄	5×10^{-4}	0.222	0.221
	1×10^{-3}	0.232	0.227
	5×10^{-3}	0.257	0.235
	1×10^{-2}	0.274	0.238
	5×10^{-2}	0.318	0.242
KClO ₄	5×10^{-4}	0.221	0.222
	1×10^{-3}	0.230	0.224
	5×10^{-3}	0.237	0.227
	1×10^{-2}	0.243	0.230
CsClO ₄	5×10^{-4}	0.222	0.220
	1×10^{-3}	0.232	0.219
	5×10^{-3}	0.238	0.219
AP	5×10^{-4}	0.224	0.218
	1×10^{-3}	0.237	0.225
	5×10^{-3}	0.257	0.233
	1×10^{-2}	0.270	0.239
TMA	5×10^{-4}	0.221	0.221
	1×10^{-3}	0.238	0.225
	5×10^{-3}	0.251	0.234
	1×10^{-2}	0.263	0.238
	3×10^{-2}	0.286	0.241
TEA	5×10^{-4}	0.233	0.232
	1×10^{-3}	0.233	0.233
	1×10^{-2}	0.238	0.233
	5×10^{-2}	0.273	0.232
TPA	5.55×10^{-4}	0.248	0.246
	7.05×10^{-4}	0.228	0.244
	5.01×10^{-3}	0.224	0.238
	1×10^{-2}	0.226	0.233
TBA	1×10^{-3}	0.224	0.233
	5×10^{-3}	0.214	0.221
	1×10^{-2}	0.212	0.217
THA	1×10^{-3}	—	0.184
	1×10^{-2}	—	0.145
	5×10^{-2}	—	0.129
	1×10^{-1}	—	0.124

DISCUSSION

The models of the double layer used for the explanation of the double layer capacity have been subject to a historical evolution [11,12]. Simple models essentially use two parameters, the radii of the ions for the distance of the planes of charge and a dielectric constant for the region between them. The influence of the electrode potential is expressed by two terms contributing to the total capacity: the diffuse layer capacity and the inner layer capacity. In recent years more sophisticated models have been published, which consider additionally solvent orientation [13–15], jellium contribution [16,17] and the effect of different ion sizes [18,19]. Unfortunately, the observation of capacity data predicted by double layer models in practice is frequently obscured by adsorption effects. Capacity–voltage curves of Li^+ , Na^+ and Cs^+ in acetonitrile have been reported [20–24]. The capacity values observed at negative potentials are systematically lower by a factor of about 2 compared with those in aqueous systems; the significant “hump” [25] observed in aqueous systems, which frequently is explained by rearrangement processes of water molecules in the double layer, does not appear in acetonitrile systems.

In ethylene carbonate [26], propylene carbonate [27], dimethyl sulfoxide [28], nitromethane [29], formamide and substituted amides [30], sulfolane [31], methanol [32], acetone [33] and lactones [34], double layer capacities of the same order as that in acetonitrile are observed. No correlation exists between the bulk dielectric constant of the solvents and the double layer capacity. The outstanding position of water is probably due to the structure of liquid water.

The ion size and the solvation of the electrode govern the distance of closest approach of the ions to the electrode. The ion size may be expressed either by Stokes radii for solvated ions or by crystal radii for unsolvated ions. From conductance measurements of Li^+ , Na^+ and K^+ in acetonitrile a radius of approximately 0.3 nm is obtained for these ions and of 0.24 nm for Cs^+ [35,36]. By comparison with crystal radii [37] one concludes that Li^+ , Na^+ and K^+ are solvated in acetonitrile and Cs^+ is not solvated in acetonitrile. The experimental double layer capacities of the solvated alkali perchlorates in acetonitrile do not show a significant difference in the potential range between +0.5 and -1 V. This is in agreement with a model where the nearest approach of the ions to the electrode results either from the radii of the solvated ions or from the sum of the Stokes radii plus the radii of the solvent molecules at the electrode surface. In contrast to aqueous solutions, the dielectric constant in the inner layer obviously remains unchanged over a wide range of negative potentials. This means dielectric saturation effects, which have been discussed for aqueous solutions on Hg [10] and single-crystal surfaces of Ag [38], are much less pronounced in AN solutions. The capacity values of Cs^+ solutions are slightly increased in comparison with those of the other alkali metal ions; this can be explained by the smaller radius of this ion. With K^+ and Cs^+ a remarkable increase of the double layer capacity is observed below $E = -1$ V. In aqueous solutions, this effect has been interpreted by the closer approach of the cations to the electrode surface caused by partial desolvation in the electric field [39,40]. This interpretation

may be adopted for the behaviour of K^+ ions in acetonitrile. On the other hand, it cannot be excluded that polarization effects by the strong electric field influence the capacity.

The double layer of the Hg/acetonitrile (supporting electrolyte) system can be described approximately by the Gouy–Chapman theory [22–24]. A more detailed consideration reveals that the potentials of zero charge as well as the minima E_{\min} , originating from the influence of the diffuse layer, depend on the ion concentrations (Table 1). The pzc and the minima E_{\min} are shifted to more negative potentials with increasing electrolyte concentration; E_{\min} shows a more pronounced shift than the pzc.

This behaviour could be explained by contact adsorption of perchlorate ions. However, recent theoretical investigations [18,19] show that this result may follow from the different approach of cations and anions to the electrode surface [41]. In acetonitrile the unsolvated perchlorate ions [35,36] are smaller than the solvated alkali metal ions Li^+ , Na^+ and K^+ ; ClO_4^- ions have the same Stokes radius as Cs^+ . In agreement with the theoretical prediction [19] we observe a shift of the capacity minimum E_{\min} and the pzc towards negative potential, except for Cs^+ where no shift has been observed. This result confirms Vaileau's arguments; however, it should not be overestimated because weak adsorption of Cs^+ besides ClO_4^- would create the same effect. NH_4^+ is a link between the atomic alkali ions and the molecular tetraalkylammonium ions. The crystal radius of NH_4^+ equals that of K^+ ; the Stokes radius of NH_4^+ in acetonitrile is not available from literature data; it has been given for a variety of other organic solvents [35], but no systematic correlation between the solvent properties and Stokes radii of NH_4^+ exists. The capacity–voltage curve of the Hg/AN(NH_4^+) system is very similar to those of the alkali metal ions, but there is a striking steep ascent at high negative potentials, which hardly can be explained exclusively by desolvation. The influence of strong electric fields on the molecular geometry and the charge distribution in NH_4^+ is at present under investigation from a theoretical point of view [42].

The properties of the double layer of the Hg/water (tetraalkylammonium) system are partly known [43–45] because the solubility of the tetraalkylammonium salts limits the choice of concentration range and anions. Therefore, only data on bromides, iodides and sulfates in a small concentration range exist. The capacity–voltage curves are dominated by specific adsorption.

The enrichment of organic molecules in the Hg/aqueous electrolyte interface is a well-known feature [46] and is probably connected with the structure of liquid water. The structure of liquid water and aqueous electrolytes is still an open question [47,48]. The different approaches to this problem involve the common assumption that structured time-averaged regions exist, which originate from intermolecular hydrogen bonding. Concerning the adsorption of organic substances from aqueous solutions at the electrode, it cannot be decided whether the decrease in the Gibbs energy of the system results preferably from the reorganization of the water molecules in the bulk or from the interaction of the adsorbed species with the electrode surface.

In contrast to water, the structure of liquid acetonitrile seems to be simple.

Correlation clusters, in which pairs of antiparallel orientated acetonitrile participate, have been confirmed by X-ray diffraction [19], neutron scattering [50] and theoretical calculations [51]. From literature data [52,53] concerning the energetics of the bulk equilibrium of association ($\Delta H = -4.3$ kJ/mol, $\Delta S = -25.1$ J K⁻¹ mol⁻¹, $\Delta G = +3.2$ kJ/mol), one may conclude that in the bulk and in the double layer region monomers dominate. It cannot be excluded that the electrode is solvated by weakly bound acetonitrile; this point will be discussed below. De Battisti and Trasatti [54] measured $\Delta G = -9.1$ kJ/mol for the equilibrium of adsorption of acetonitrile from aqueous solutions. It should be mentioned that this value includes the acetonitrile-water interaction and is not representative for the bond energy of acetonitrile at mercury.

In acetonitrile, adsorption of tetraalkylammonium ions at the electrode is less pronounced. The shape of the capacity-voltage curves of tetraalkylammonium ions varies systematically with the length of the alkyl chain (Figs. 2-7). The behaviour of TMA is similar to that of the alkali metal ions; THA in acetonitrile apparently reveals adsorption behaviour. In contrast to the alkali metal ions, the double layer capacity of tetraalkylammonium ions depends on the radii of the cations. Spectroscopic investigations [36], conductance measurements [55,56] and data of the apparent molal volumes and molal heat capacities [57] show that the tetraalkylammonium ions are not solvated in acetonitrile and that association and ion-pair formation are negligible in the range of concentration relevant for our measurements. In the potential range of about -1 to -1.5 V, a linear relationship between C and $1/R$ holds to a good approximation. The dielectric constant of the inner layer can be calculated to be ~ 3 . This result favours a parallel plate condenser model of the inner layer consisting of tetraalkylammonium ions and acetonitrile.

At more negative potentials, the situation obviously becomes more complicated because the decay and re-ascent of the capacity-voltage curves for different ions does not vary systematically with their size. Nevertheless, this result indicates that unsolvated cations which participate in the double layer structure may be in touch with the mercury surface.

In contrast to alkali metal ions, tetraalkylammonium ions can exist in different conformations. The energy difference between different conformers is small ($\Delta E \sim kT$). At high negative potentials conformers may be preferred which allow a minimum distance between the centre of the positive charge and the negative electrode. The electric field may induce changes of the conformation, which bring the centre of the positive charge closer to the surface. This effect has to be considered especially in ions with long alkyl chains (TBA, THA) since it increases the capacity. On the other hand, the large cations displace per unit charge a larger number of acetonitrile molecules from the surface region than smaller molecules and the accumulation of alkyl groups decreases the dielectric constant in the double layer; as this effect correlates roughly with R^2 to R^3 , the increase in capacity originating from changes in the conformations will be overcompensated. The experimental graduation of capacities at high negative potentials can thus be explained qualitatively.

In addition, it can be estimated from charge-potential curves that TPA and TBA because of their large volume may contribute to a decrease of charge density of the diffuse layer. This effect, which is not considered in the simple Gouy-Chapman theory [58], may contribute to a decrease in the capacity at moderate and high negative potentials [59,60].

Differences in the shapes of the capacity-voltage curves of alkali metal ions and tetraalkylammonium ions are observed, especially near the potential of zero charge. In contrast to the behaviour of alkali metal ions, the influence of the diffuse layer decreases with increasing radius of the tetraalkylammonium ions. This is displayed clearly in the Parsons-Zobel plots [25,61] (Fig. 10). Using the bulk dielectric constant of acetonitrile (36.5) [62], one expects a linear relationship between C^{-1} and $c^{-1/2}$ with a reciprocal slope of $1.59 \text{ F}^{1/2} \text{ m}^{-2} \text{ mol}^{-1/2}$. This value results from TMA, if the small association of these ions [63] is considered according to the procedure given by Damaskin and co-workers [64]. Significant deviations, which means higher slopes, are found for larger tetraalkylammonium ions; TBA shows non-linear behaviour. This effect is, in the literature [61] usually attributed to adsorption. The shift of the pzc towards positive potentials with increasing con-

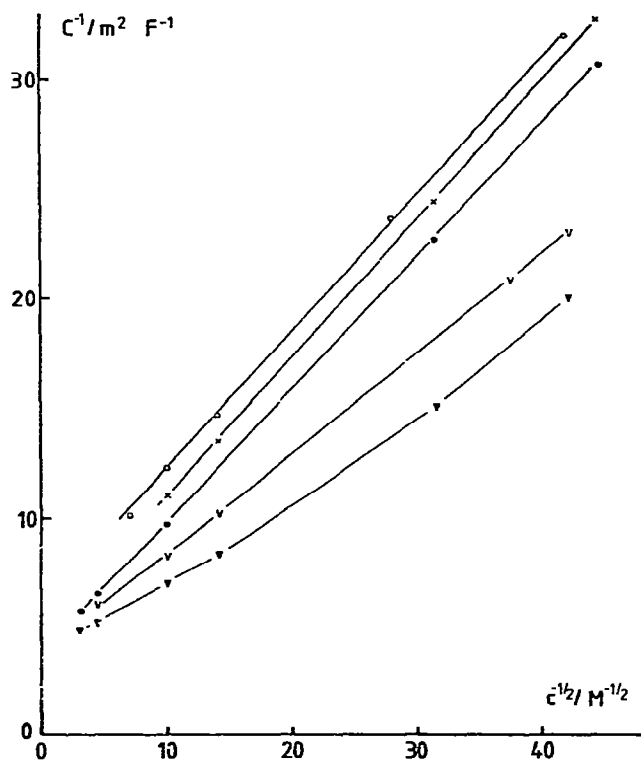


Fig. 10 Parsons-Zobel plots of ammonium perchlorate and different tetraalkylammonium perchlorates. (○) NH_4^+ , (×) TMA; (●) TEA, (∇) TPA, (▼) TEA

centration of the cation confirms the existence of adsorption. With increasing length of the alkyl chain, the influence of adsorption becomes more obvious. It dominates in the capacity-voltage curves of THA (Fig. 6); even at low concentrations of this electrolyte no minimum corresponding to the contribution of diffuse layer capacity is observed. In addition, the shape of the capacity-voltage curve reveals a maximum at positive potentials and a broad maximum with low values of capacity at negative potentials. These maxima can be attributed to pseudo-capacities originating from desorption and rearrangement processes.

The relation between chain length of the alkyl group and strength of adsorption has been confirmed in the system Hg/AN (electrolyte) (alkane C₆-C₁₂) [65].

CONCLUSION

From the results reported in this paper we conclude that acetonitrile is weakly bound to the electrode surface. The increase of adsorption with increasing chain length of the alkyl groups offers the possibility of adsorbing, at the electrode, neutral alkanes and supporting electrolytes of the tetraalkylammonium type with different charges at different potentials. This may open up a deeper insight for the explanation of the influence of different supporting electrolytes and solvents on the rate of heterogeneous electron transfer reported recently [66,67].

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