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The Adsorption of Bromide Ion at Mercury from Propylene Carbonate Solutions of
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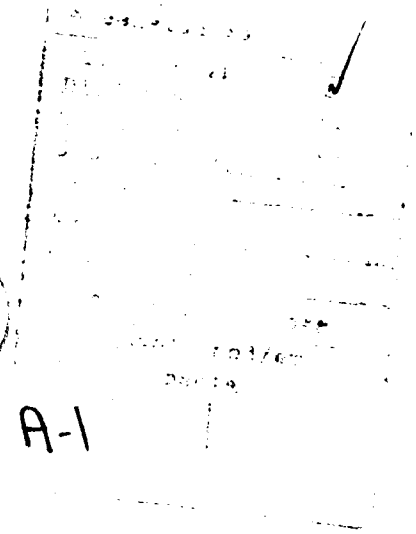
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**The Adsorption of Bromide Ion on Mercury from Propylene Carbonate Solutions
of Constant Ionic Strength**

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Abstract

The adsorption of Br^- anion has been studied from propylene carbonate solutions of low ionic strength (0.16 M) at mercury. A maximum on the capacity curve is observed at low Br^- ion concentration, a result which is unusual for strongly adsorbed ions. A new method of analyzing the interfacial thermodynamic data, which makes use of data obtained in the absence of Br^- ion is presented. Adsorption is shown to be very strong and can be represented by a virial adsorption isotherm over the range that data are available. The adsorption parameters can be rationalized on the basis of the electrostatic model for adsorption with the proviso that the system is complex because of varying inner layer parameters for a given electrode charge density. When the present data are compared with those obtained in other solvents, it is shown that the standard Gibbs energy of adsorption changes with solvent acidity and basicity due to corresponding changes in anion solvation in the bulk, and the Gibbs energy of solvent adsorption on mercury, respectively. The adsorption parameters at the point of zero charge are examined with respect to non-primitive statistical mechanical models for ionic adsorption, discussed recently in the literature.

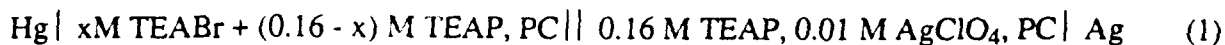
Introduction

The adsorption of halide ions and other monovalent anions has been studied at polarizable electrodes both as a function of the nature of the metal electrode and the solvent for the electrolyte [1]. In the case of Br^- ion adsorption at Hg, studies have been carried out in water [2-4] and N-methylformamide solutions [5,6] of both varying and constant ionic strength, and from dimethylformamide [7], dimethylsulfoxide [8], and acetonitrile solutions [9] of constant ionic strength. Although the adsorption of this ion can be classified as strong, because it leads to a change in the charge in the diffuse layer, significant variation in the extent of adsorption with solvent nature is seen for constant concentration in the bulk and electrical state of the interface.

Propylene carbonate (PC) is a solvent of considerable interest in electrochemistry because of its high dielectric constant (66.1 at 25 °C) and relatively inert chemical properties. It has been studied extensively as a solvent for high energy density batteries. Our interest was to investigate the adsorption of a strongly adsorbing ion like bromide from this medium, and to compare the adsorption parameters with those reported for other solvents. Although variation in the extent of ionic adsorption from a given solvent with the nature of the metal has been considered in the literature [1,10], much less attention has been paid to the role of the solvent in determining ionic adsorption at a given metal. In addition, the role of both the solvent and adsorbed ions in determining the dielectric properties of the interface have been discussed on the basis of non-primitive models for the double layer [11-13]. In the present paper, the adsorption parameters obtained in the present study are compared with those obtained for bromide adsorption in other solvents and discussed with respect to current theoretical developments.

Experimental

Differential capacity against potential data were obtained for the mercury/solution interface using the cell



where the concentration of tetraethylammonium bromide (TEABr) had the following values: 0, 0.0016, 0.004, 0.01, 0.025, 0.063, and 0.16. The ionic strength was maintained constant at 0.16 M using tetraethylammonium perchlorate (TEAP). The reference electrode was based on the Ag/Ag⁺ system. In order to reduce the liquid junction potential between the main solution and that in the reference compartment, 0.16 M TEAP was added to the latter. Effects due to variation in the activity coefficients of the ions in solution with solution composition were neglected. The potential of zero charge (p.z.c.) was determined against the same reference electrode using a streaming mercury electrode. All measurements were made on the bridge described previously [14] at a frequency of 500 Hz. The temperature of the cell was maintained at 25 ± 0.1 °C.

TEABr (Fisher Sci.) was purified by precipitation from chloroform using ether, whereas the TEAP (Fisher Sci.) was recrystallized from water. The PC was treated with molecular sieves and then fractionally distilled under a reduced pressure of nitrogen, the middle fraction being retained.

Method of Data Analysis

The capacity curves were integrated twice with respect to potential, once to obtain the charge density σ , and a second time to obtain the relative surface tension $\Delta\gamma$. The integration constant for the first integration was the experimentally determined p.z.c. for the system with no Br^- . In all other cases, it was the value of the charge ($-18 \mu\text{C cm}^{-2}$) at the most negative potential (-2.755 V) where adsorption of Br^- could be assumed absent. The value of $\Delta\gamma$ was arbitrarily set equal to zero at this potential and values at more positive potentials for equal increments in σ determined by back integration. Using these results, values of Parsons' function, $\xi = \Delta\gamma + \sigma E$, were evaluated as a function of charge density and Br^- ion concentration.

The method of estimating the adsorbed charge density σ_a used here differed somewhat from previously described techniques [15]. According to the Gibbs adsorption isotherm, σ_a is given by

$$\sigma_a = \frac{F}{RT} \left(\frac{\partial \xi}{\partial \ln x} \right)_{\sigma} \quad (2)$$

The numerical differentiation required to obtain σ_a is normally carried out by fitting ξ to a polynomial in $\ln x$, usually of third order, by least squares and calculating the first derivative from the coefficients. In this procedure, one cannot use the value of ξ in the solution without Br^- because $\ln x = -\infty$ and thus, one neglects an important reference point in each data set at constant charge density. This defect can be overcome by differentiating with respect to an alternate function of x whose value changes in a similar way to that of $\ln x$, but which does not go to $-\infty$ at $x = 0$. One such function is $x^{0.1}$. The first derivative is proportional to $x^{-0.9}$, that is, very close to that for $\ln x$ and it has a finite value at $x = 0$. Thus, values of σ_a were estimated using the relationship

$$\sigma_a = 0.1 x^{0.1} \frac{F}{RT} \left(\frac{\partial \xi}{\partial x^{0.1}} \right)_{\sigma} \quad (3)$$

with ξ being fitted to a quadratic equation in $x^{0.1}$. This provided much improved estimates of σ_a at low bulk Br^- concentrations and is clearly a better procedure when the number of concentrations at which values of ξ are available is small. Although a detailed analysis of this procedure using the

methods described previously [15] was not carried out, values of σ_a estimated at higher Br^- concentrations were essentially the same whether they were estimated on the basis of a polynomial in $\ln x$ or one in $x^{0.1}$.

Results

Differential capacity against electrode potential curves for the various Br^- ion concentrations are shown in Fig. 1. As expected, at the most negative potentials where the adsorption of Br^- ion is negligible, the curves are coincident. No dependence of the capacity on frequency was found in the range 200 to 1000 Hz. At potentials more positive than the p.z.c., a sharp capacity maximum attributed to Br^- adsorption was found at the two lowest concentrations. The maximum reaches $80 \mu\text{F cm}^{-2}$ at 1.6 mM Br^- and rises sharply with increase in concentration of the adsorbing anion. Because of the large rate of increase in capacity in the region of the peak, the error involved in the measured capacity is high. No attempt was made to make measurements at specific capacities greater than $120 \mu\text{F cm}^{-2}$. The fact that a maximum on the capacity curve was observed in these experiments at low Br^- ion concentration is attributed to the low ionic strength used. As the ionic strength decreases, the repulsive effect of the diffuse layer reduces the surface excess of adsorbed anion for constant bulk concentration and electrical state of the interface. To the best of our knowledge, such a maximum due to a strongly adsorbed anion has not been observed previously. On the other hand, capacity maxima due to ion adsorption are well known in the case of moderately adsorbed ions such as nitrate [16].

The values of adsorbed charge density were estimated by the numerical procedure described above. Comparison of the point of zero charge estimated in the back integration procedure with those obtained experimentally revealed that the two quantities agree to within 1 mV. Although errors in the potential are expected to be small, errors in the values of $\Delta\gamma$ and ξ can be large because of the steep rate of change of the experimental capacity with potential. For this reason, analysis of the data was limited to the potential region close to the p.z.c. Values of σ_a are plotted against σ for varying Br^- concentration in the bulk in Fig. 2. These plots demonstrate that Br^- adsorption is strong, and increases rapidly as the electrode is made more positive. When one compares the present results with those obtained in water [2], it is clear that adsorption from PC is significantly stronger for a given ionic strength. Comparison of the extent of adsorption with solvent nature is discussed in detail below.

The effect of specifically adsorbed bromide ions on the potential distribution in the inner layer was assessed on the basis of plots of the potential drop across the inner layer, ϕ^{md} against the specifically adsorbed charge density σ_a . According to the usual model of the inner part of the double layer [17] the relationship between these quantities is

$$\phi^{md} = \phi^m - \phi^d = \frac{\sigma}{K_{md}} + \frac{\sigma_a}{K_{ad}} \quad (4)$$

where K_{md} is the integral capacity of the inner layer, and K_{ad} , that of the region between the adsorption plane and the outer Helmholtz plane (o.H.p.). The potential of the metal phase on the rational scale, ϕ^m , was estimated by subtracting the potential of zero charge (p.z.c.) in the system with no bromide, E_0 , from the measured electrode potential E . The potential drop across the diffuse layer, ϕ^d , was estimated using the Gouy-Chapman theory. The resulting plots for the present system are shown in Fig. 3. The plots are approximately linear at negative charge densities where adsorption is small, but become curved as the extent of adsorption increases. Values of the integral capacities K_{md} and K_{ad} were determined from the intercept and the slope of the plots in the limit that σ_a goes to zero, respectively. The integral capacity K_{ad} decreases as the electrode charge density becomes more positive whereas K_{md} increases (Fig. 4). The latter result is what one would expect on the basis of the differential capacity observed in the solution with no Br^- ion (Fig. 1). These data give a value of $\lambda = K_{md}/K_{ad}$ equal to 0.64 at the p.z.c., a result which is typical for halide ion adsorption [18]. The curvature of the plots presented in Fig. 3 was also seen in the study of Br^- adsorption from aqueous solutions [4, 19], and indicates that the dielectric properties of the inner layer depend on the degree of coverage by the anion [19].

It was found that the data could be described by a virial isotherm which has often been used for halide ion adsorption from both aqueous and non-aqueous solutions [1]. Accordingly, one may write that

$$\ln (|\sigma_a| / c_a) = \Phi + \alpha \sigma_a + \beta \sigma \quad (5)$$

where c_a is the concentration of the adsorbing anion in the bulk of the solution, Φ is related to the standard free energy of adsorption at the p.z.c., α is the interaction coefficient and β , the

coefficient describing the variation in standard free energy of adsorption with charge density. As discussed below, this isotherm should be written with a term in $f\phi^d$ to account for the effect of the diffuse layer [18, 20, 21]. Then, the virial isotherm can be derived from an electrostatic model of the interface for the case that coverage of the electrode is small [20, 21]. However, the present form was used so that the derived isotherm parameters may be more directly compared with those reported for Br^- adsorption from other solvents [2-9]. Plots of $\ln (|\sigma_a| / c_a)$ against σ_a are shown in Fig. 5. It is clear that reasonable straight lines may be drawn for data considered at constant charge density, confirming that the virial isotherm also gives a good description of Br^- adsorption from PC. The standard Gibbs energy of adsorption determined from the intercepts of these plots is linear in the electrode charge density giving values of Φ equal to 9.80 and $\beta = -0.436 \text{ cm}^2 \mu\text{C}^{-1}$. The quality of the linear relationship was excellent, the value of the correlation coefficient r being 0.997. The standard states which determine the magnitude of Φ were $1 \mu\text{C cm}^{-2}$ for σ_a , and 1 mol l^{-1} for c_a . The slopes of the isotherm plots decrease as the electrode charge density becomes more positive indicating a corresponding decrease in the interaction parameter α . The value at the p.z.c. is $0.373 \text{ cm}^2 \mu\text{C}^{-1}$ or $5.98 \text{ nm}^2 \text{ molec}^{-1}$, a result which falls in the range observed for halide ion adsorption from a variety of solvents [1-9, 18].

Discussion

According to the electrostatic model for ionic adsorption [20, 21], the adsorption isotherm for the case that coverage of the electrode by the adsorbing anion is small may be written

$$\ln (|\sigma_a|/c_a) - f\phi^d = \Phi' + \alpha'\sigma_a + \beta'\sigma \quad (6)$$

This differs from the virial isotherm which has often been used to describe halide ion adsorption [1] by the term in $f\phi^d$ which gives the electrostatic work that the anion does in crossing the diffuse layer. By introducing the diffuse layer term, one changes the isotherm parameters from Φ , α and β to Φ' , α' and β' . It is of interest to examine the relationship between these parameters for the present case. On the basis of the Gouy-Chapman theory, $f\phi^d$ is given by

$$f\phi^d = 2 \sinh^{-1} \left(\frac{\sigma + \sigma_a}{2A} \right) \quad (7)$$

where A is the Gouy-Chapman constant which equals 2.086 in PC at an ionic strength of 0.15 M and temperature of 25 °C. Since the sum $|\sigma + \sigma_a|$ is never less than $4 \mu\text{C cm}^{-2}$, the above expression may be replaced by its limiting form for large values of the argument of the $\sinh^{-1}$ function. Then, eq. (7) becomes

$$f\phi^d = 2 \ln A - 2 \ln (|\sigma + \sigma_a|) \quad (8)$$

It follows that eq. (5) may be written

$$\ln (|\sigma_a|/c_a) - f\phi^d = \Phi - 2 \ln A + \alpha\sigma_a + \beta\sigma + 2 \ln (|\sigma + \sigma_a|) \quad (9)$$

Differentiating eqs. (6) and (9) with respect to σ_a at constant σ , one obtains the following expression for α' :

$$\alpha' = \alpha - \frac{2}{|\sigma + \sigma_a|} \quad (10)$$

This result demonstrates that the relationship between the two isotherms is complex, and that one cannot expect experimental data to follow both isotherms over a wide range of values of σ_a .

However, if one accepts that data plotted according to both equations give approximately linear plots over a limited range of σ_a , then it follows from eq. (10) that α' should be less than α . Such a result was obtained by Levi and Bagotskaya on the basis of data for the adsorption of Br^- and I^- ions from acetonitrile solutions of constant ionic strength [9]. In the present case, it would not be

possible to choose between these isotherms because of the limited range of the experimental results. However, on the basis of the usual model of the double layer, eq. (6) is clearly the better isotherm to describe ionic adsorption. As pointed out above the parameters obtained on the basis of eq. (5) are presented here so that they may be compared with those presented earlier in the literature for adsorption from other solvents.

A summary of parameters for Br^- ion adsorption obtained in six solvents using data analyzed on the basis of eq. (5) is given in Table 1. The parameter of greatest interest is Φ which is directly related to the standard Gibbs energy of adsorption at the p.z.c., ΔG_{ad}^0 :

$$\Phi = -\Delta G_{\text{ad}}^0 / RT \quad (11)$$

If one accepts that adsorption involves replacement of solvent molecules at the interface in the reaction



where S represents the solvent, and the subscripts 'ad' and 's' refer to the adsorbed and bulk solution states, respectively, then one may write for ΔG_{ad}^0 [1, 10],

$$\Delta G_{\text{ad}}^0 = G_{\text{ad}}^0(\text{Br}^-) + G_{\text{s}}^0(\text{s}) - G_{\text{ad}}^0(\text{s}) - G_{\text{s}}^0(\text{Br}^-) \quad (13)$$

where $G_j^0(i)$ represents the standard Gibbs energy of species i in location j . When the solvent is changed, the only quantity which remains unchanged to a good approximation is the Gibbs energy of the Br^- ion in the adsorbed state since this quantity reflects mainly interaction between the ion and the metal electrode, in this case, mercury. As discussed earlier [1, 10], ΔG_{ad}^0 reflects changes in the degree of solvation of the Br^- ion in the bulk of the solution through variation in $G_{\text{s}}^0(\text{Br}^-)$. This can be seen qualitatively from the data presented in Table 1. Since Br^- ion is most strongly solvated in water, Φ is smallest and adsorption weakest from this solvent. On the other hand, adsorption is strongest from aprotic solvents such as acetonitrile in which anions are weakly solvated. A good measure of the ability of a given solvent to solvate anions is the solvent acidity parameter E_{T} defined by Dimroth and Reichardt [22, 23]. It was shown previously that E_{T}

correlates very well with the free energy of solvation of simple inorganic anions in non-aqueous media [24], and thus should reflect the changes in $G_s^0(\text{Br}^-)$ with solvent. If the latter term changes the most with solvent, ΔG_{ad}^0 should be a linear function of E_T . A plot of Φ against E_T is shown in Fig. 6. A good linear correlation is found according to the equation

$$\Phi = 20.4 - 0.246 E_T \quad (14)$$

with a correlation coefficient, r equal to 0.889. It is clear from Fig. 6 that the relationship between Φ and E_T accounts mainly for the variation in Φ between the aprotic solvents as a group and the protic solvents NMF and water. Since E_T varies very little for the aprotic solvents, it is clear that the observed variation in Φ cannot be attributed to variation in $G_s^0(\text{Br}^-)$ alone.

The remaining component of ΔG_{ad}^0 which is solvent dependent is the free energy change accompanying adsorption of the solvent itself, $G_{\text{ad}}^0(\text{s}) - G_s^0(\text{s})$. At the point of zero charge, this quantity reflects the ability of an individual solvent molecule to act as a Lewis base to the mercury atoms at the interface. Among the four aprotic solvents considered here, acetonitrile is the weakest Lewis base and dimethylsulfoxide, the strongest. It follows that Br^- ion, a stronger Lewis base than any of the solvent molecules considered is most easily able to replace acetonitrile at the surface, so that adsorption is strongest from this solvent. The donor number, DN, proposed by Gutmann [23, 25] is the most commonly used measure of Lewis basicity. It follows that the variation in the parameter Φ with solvent should be described by an equation of the form

$$\Phi = \Phi_0 + a E_T + b \text{ DN} \quad (15)$$

where a is a coefficient related to the degree of anion solvation in the bulk and b , a coefficient related to the extent with which mercury atoms interact with solvent molecules as Lewis bases. A least squares fit of eq. (15) to the present data gives the result

$$\Phi = 24.9 - 0.27 E_T - 0.14 \text{ DN} \quad (16)$$

with a correlation coefficient of $r = 0.994$. This correlation involved only five solvents and did not include NMF because a reliable value of the DN is not available for this solvent [26].

Furthermore, the DN for water was set equal to 18.0, a value which reflects the properties of an

individual molecule [26]. Obviously, this simple model provides an excellent description of the variation in the free energy of adsorption with solvent nature, explaining 99% of the observed variation in Φ . On the basis of partial regression coefficients [24], one finds that 68.5% of the explained variation is due to variation in Br^- ion solvation in the bulk, and 31.5%, to variation in interaction of solvent molecules with mercury atoms at the interface. The decrease in Φ with E_T indicates that the extent of adsorption decreases as anion solvation in the bulk increases; the decrease with DN demonstrates that as the solvent interacts more strongly with mercury, anionic adsorption is weaker. Although eq. (15) has been applied successfully before in studies of ion solvation in bulk electrolyte solutions [24, 27], the present application is the first in which it has been applied to a thermodynamic property which relates to the interaction of a polarizable interface with solvent molecules. It is true that this relationship is phenomenological in nature, but it provides clear chemical insight into the solvent's role in determining the extent of anionic adsorption.

Considerable variation in the isotherm parameters α and β with solvent nature is also seen. The corresponding quantities α' and β' can be related to the integral capacities which were obtained from the plots shown in Fig. 3. According to the electrostatic model of adsorption [20, 21], these quantities are given by the equations,

$$\alpha' = \frac{f}{K_{ad}} \left(1 - g \frac{K_{md}}{K_{ma}} \right) \quad (17)$$

and

$$\beta' = f / K_{ad} \quad (18)$$

where K_{ma} is the integral capacity of the region between the metal and the adsorption plane and g , a dimensionless parameter close to unity [28]. On the basis of the plots shown in Fig. 3, the integral capacity K_{ad} varies with adsorbed charge density, the values reported in Fig. 4 being obtained in the limit that σ_α approaches zero. It follows that the isotherm parameters α' and β' , or α and β reported in Table 1 are average values valid only in the range of values of σ_a and σ where data were obtained. It is clear that comparison of these values with those obtained in other solvents is not possible. This is chiefly because the necessary data are often not available in the

literature, but also because the question of validity of the isotherm outside of the reported range is usually not addressed.

Recent discussion in the literature [13, 29, 30] has emphasized the importance of the surface dipole moment in assessing interaction of the adsorbed ion with the metal and surrounding solvent at the adsorption site. This quantity is estimated from the coefficient $(\partial\phi^{md}/\partial\Gamma_a)_{\sigma_d}$ where $\Gamma_a = -\sigma_a/F$ is the surface excess of adsorbed anions and σ_d , the charge density in the diffuse layer. Assuming that ϕ^{md} can be expressed as a function of the electrode charge density σ and the adsorbed charge density σ_a , then it is easily shown [29] that

$$\left(\frac{\partial\phi^{md}}{\partial\sigma_a}\right)_{\sigma_d} = \left(\frac{\partial\phi^{md}}{\partial\sigma}\right)_{\sigma_a} \left(\frac{\partial\sigma}{\partial\sigma_a}\right)_{\sigma_d} + \left(\frac{\partial\phi^{md}}{\partial\sigma_a}\right)_{\sigma} \sigma \quad (19)$$

On the basis of eq. (14), and recalling that

$$\sigma = -(\sigma_a + \sigma_d) \quad (20)$$

it follows that

$$\left(\frac{\partial\phi^{md}}{\partial\Gamma_a}\right)_{\sigma_d} = F \left(\frac{1}{K_{ad}} - \frac{1}{K_{md}} \right) \quad (21)$$

In deriving this relationship, it has been assumed that K_{md} and K_{ad} are independent of both σ_m and σ_a . This is obviously not true for the present system (see Fig. 3 and 4), or indeed for most systems studied at mercury. However, eq. (21) provides a good approximation to the required coefficient if it is estimated in the limit that both σ and σ_a approach zero. Finally, the surface dipole moment, p_s is given by [13, 29, 30]

$$p_s = \frac{\epsilon_0}{N_0} \left(\frac{\partial\phi^{md}}{\partial\Gamma_a}\right)_{\sigma_d} \quad (22)$$

where ϵ_0 is the permittivity of free space, and N_0 , Avogadro's number. For the present system, at $\sigma = 0$ and in the limit that σ_a goes to zero, K_{md} is $22.2 \mu F \text{ cm}^{-2}$ and K_{ad} , $34.65 \mu F \text{ cm}^{-2}$. The

resulting value of the coefficient $(\partial\phi^{md} / \partial\Gamma_a)_{\sigma_d}$ is $1.562 \times 10^5 \text{ Vm}^2 \text{ mol}^{-1}$. The corresponding value of the surface dipole moment is $2.30 \times 10^{-30} \text{ Cm}$, that is, 0.69 Debye. This compares with a value of 0.95 Debye estimated by Schmickler [30] using data for the adsorption of Br^- ion on Hg from aqueous solution, and with a value of 0.35 Debye estimated by Bange et al. [29] for the adsorption of Br^- ion on the 110 plane of single crystal silver under conditions of low coverage. Certainly, the result is in keeping with those discussed earlier [30] in that the surface dipole moment is much less than that for an isolated Br^- with a radius of 0.195 nm adsorbed on a perfect conductor which corresponds to 9.36 Debye. The present result confirms that the adsorbed ion is strongly shielded by an image charge due to the electron cloud in the metal, and to some extent by the solvent. The differences observed between adsorption from water and propylene carbonate may reflect the fact that propylene carbonate is more effective than water in shielding the adsorbed bromide ion, presumably because it has a much larger dipole moment and is more polarizable.

Schmickler and Guidelli [13] extended the non-primitive model for the double layer derived by Carnie and Chan [11, 12] to consider the effect of the nature of the metal on interfacial capacity [13]. This model only applies for low charge densities where the response of the system may be assumed to be linear, and also assumes no charge exchange between the adsorbed ions and the metal electrode. Under these circumstances the equation giving the potential drop ϕ^{md} is

$$\phi^{md} = \left[\frac{r_i}{\epsilon\epsilon_0} + \frac{r_s(\epsilon-1)}{\lambda\epsilon\epsilon_0} + \frac{1}{C_m} \right] \sigma + \left[\frac{r_s(\epsilon-1)}{\lambda\epsilon\epsilon_0(1+\lambda r_i/r_s)} \right] \sigma_a \quad (23)$$

where r_i is the radius of the adsorbing ion, r_s , the radius of the solvent molecule represented as a sphere, ϵ , the bulk dielectric constant of the solvent, C_m , the contribution of the metal to the interfacial capacity, and λ , a dimensionless parameter defined by the equation

$$\lambda^2 (1+\lambda)^4 = 16 \epsilon \quad (24)$$

It has been emphasized in discussion of this result [13, 30] that the coefficients in the square brackets in eq. (23) should not be identified with the integral capacities defined in eq. (4). This follows from the fact that these equations are based on quite different models of the double layer.

More specifically, the non-primitive model which leads to eq. (23) does not recognize the existence of an inner part of the double layer as a distinct region in the interphase [13].

On the basis of the molar volume of propylene carbonate ($85.2 \text{ cm}^3 \text{ mol}^{-1}$), the estimate of the solvent radius is 0.323 nm . Using eq. (24), the value of λ appropriate for propylene carbonate is 2.56 . Using these parameters, the coefficient multiplying σ_a in eq. (23) is estimated to be $5.51 \text{ m}^2 \text{ F}^{-1}$. The corresponding estimate of K_{ad} is $18.1 \text{ } \mu\text{F cm}^{-2}$, a result which is less than that observed experimentally ($34.65 \text{ } \mu\text{F cm}^{-2}$) by approximately a factor of two. The failure of the model to agree better with the experiment is not surprising since the model treats the solution components as hard spheres with embedded charges for the ions and point dipoles for the solvent molecules. Thus, the detailed chemical features of the system are ignored. These features may include specific interaction of the negative end of the solvent dipole with the atoms of the metal electrode, and partial charge transfer between the adsorbed ion and the electrode. However, considering the fact that the model is relatively simple, the fact that the estimate of K_{ad} is as close as it is to the experimental result is encouraging.

It is also interesting to estimate the value of C_m on the basis of the present data, and to compare it with previous estimates [30]. If one requires that the ratio $\lambda = K_{md}/K_{ad}$ for the coefficients estimated on the basis of eq. (23) ~~are~~^{be} equal to the experimental value (0.64), then the coefficient multiplying σ in this equation is equal to $8.64 \text{ m}^2 \text{ F}^{-1}$. The corresponding estimate of C_m is $-17.4 \text{ } \mu\text{F cm}^{-2}$. The negative sign for this contribution signifies that the electron density from the metal has penetrated the region of the double layer just outside of the metal lattice as described in the jellium model for the metal/electrolyte solution interface [31, 32]. The corresponding penetration distance discussed in previous analyses [13, 30] is 0.05 nm . This result agrees very well with the estimate made for mercury in aqueous solution (0.03 nm) [30].

In summary, the present study has resulted in two important conclusions relevant to the adsorption of anions from non-aqueous media. The first is that the change in the Gibbs energy of adsorption with solvent nature can be described on the basis of a simple phenomenological model in which the extent of adsorption decreases with increase in both the solvent's ability to act as a

Lewis base and as a Lewis acid. The second is that the simple non-primitive statistical mechanical model for ionic adsorption applied to the non-aqueous system studied here gives results which compare well with those reported for adsorption from aqueous systems [30]. The significance of this model for halide ion adsorption from other non-aqueous media will be examined in more detail in a future paper.

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References

1. M.D. Levi, A.V. Shlepakov, B.B. Damaskin and I.A. Bagotskaya, *J. Electroanal. Chem.*, 138, 1 (1982).
2. J. Lawrence, R. Parsons, and R. Payne, *J. Electroanal. Chem.*, 16, 193 (1968) .
3. A.R. Sears and P.A. Lyons, *J. Electroanal. Chem.*, 42, 69 (1973).
4. G.J. Hills and R.M. Reeves, *J. Electroanal. Chem.*, 42, 355 (1973) .
5. R.V. Ivanova, L.N. Kuznetsova, and B.B. Damaskin, *Elektrokhimiya*, 14, 1397 (1978) .
6. L.N. Kuznetsova, B.B. Damaskin, and R.V. Ivanova, *Elektrokhimiya*, 14, 1743 (1978).
7. I.M. Ganzhina, B.B. Damaskin, and R.V. Ivanova, *Elektrokhimiya*, 6, 712, 1540 (1970).
8. T.A. Severova, R.V. Ivanova, and B.B. Damaskin, *Elektrokhimiya*, 2, 873 (1973).
9. M.D. Levi and I.A. Bagotskaya, *Elektrokhimiya*, 18, 1102 (1982).
10. S. Trasatti, *J. Electroanal. Chem.*, 65, 815 (1975).
11. S. Carnie and D.Y.C. Chan, *Adv. Colloid Interface Sci.*, 16, 81 (1982).
12. S. Carnie and D.Y.C. Chan, *J. Chem. Soc. Faraday Trans II*, 78, 695 (1982).
13. W. Schmickler and R. Guidelli, *J. Electroanal. Chem.*, 235, 387 (1987).
14. Z. Borkowska and W.R. Fawcett, *Can. J. Chem.* 59, 710 (1981) .
15. W.R. Fawcett and J.E. Kent, *Can. J. Chem.*, 48, 47 (1970) .
16. W.R. Fawcett and J.B. Sellan, *Can. J. Chem.*, 55, 3871(1977).
17. D.C. Grahame and R. Parsons, *J. Am. Chem. Soc.*, 83, 1291 (1961).
18. W.R. Fawcett and M.D. Mackey, *J. Chem. Soc. Far. Trans I*, 69, 1153 (1973).
19. B.B. Damaskin and R.V. Ivanova, *Elektrokhimiya*, 18, 1483 (1982).
20. S. Levine, *J. Colloid Interface Sci.*, 37, 619 (1971).
21. W.R. Fawcett, *J. Electroanal. Chem.*, 84, 303 (1977).
22. K. Dimroth, C. Reichardt, T. Siepmann and F. Bohlmann, *Liebigs Ann. Chem.*, 661, 1 (1963).
23. Y. Marcus, *Ion Solvation*, Wiley-Interscience, New York (1985) Chap. 6.
24. T.M. Krygowski and W.R. Fawcett, *J. Am. Chem. Soc.*, 97, 2143 (1975).

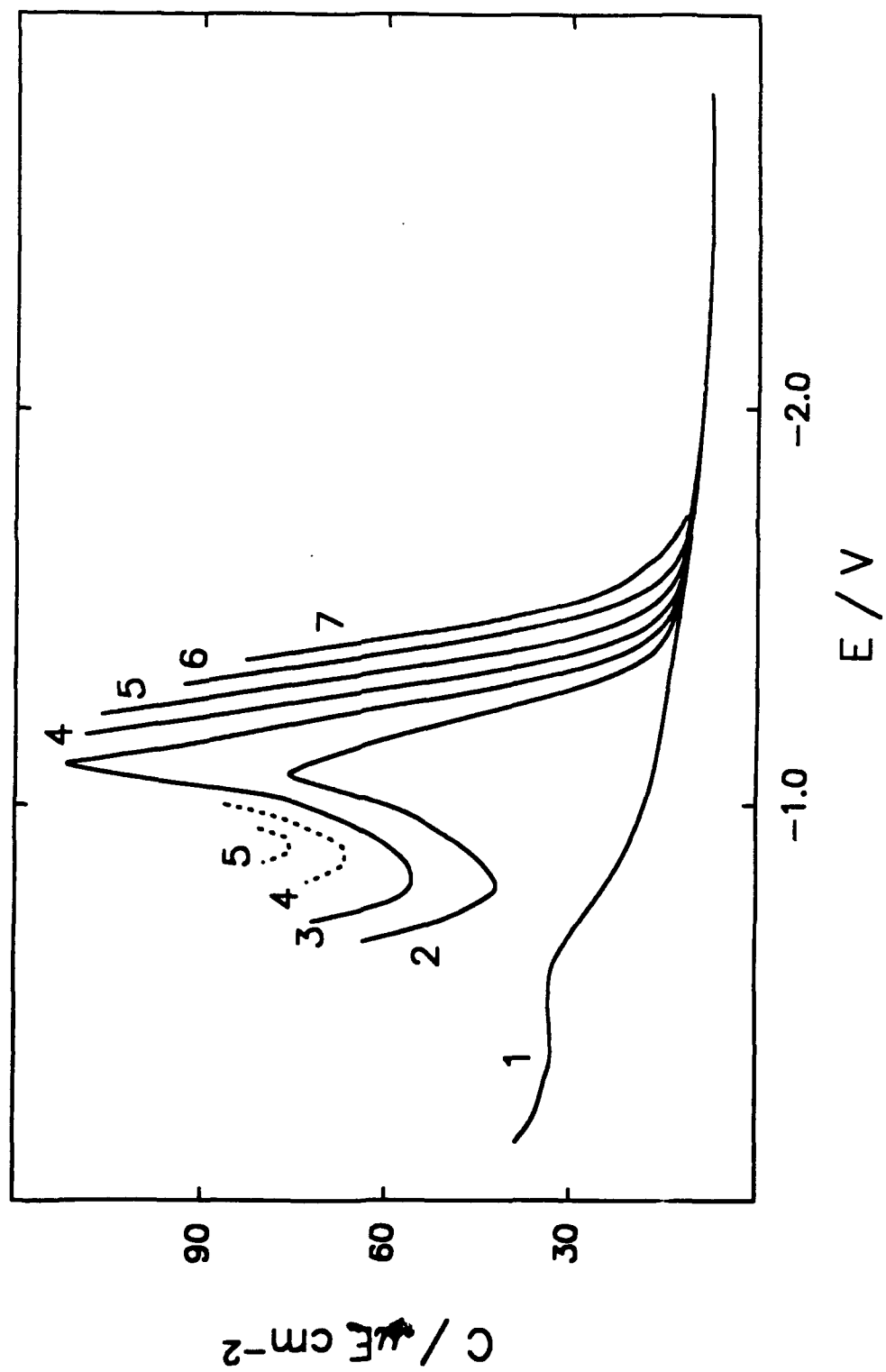
25. V. Gutmann, *Coord. Chem. Rev.*, 18, 225 (1976).
26. Y. Marcus, *J. Solution Chem.*, 13, 599 (1984).
27. W.R. Fawcett and T.M. Krygowski, *Can. J. Chem.*, 54, 3283 (1976).
28. K. Robinson and S. Levine, *J. Electroanal. Chem.*, 47, 395 (1973).
29. K. Bange, B. Strachler, J.K. Sass and R. Parsons, *J. Electroanal. Chem.*, 229, 87 (1987).
30. W. Schmickler, *J. Electroanal. Chem.*, 249, 25 (1988).
31. W. Schmickler and D. Henderson, *J. Chem. Phys.*, 80, 3381 (1984).
32. J.P. Badiali, *Electrochim. Acta*, 31, 149 (1986).

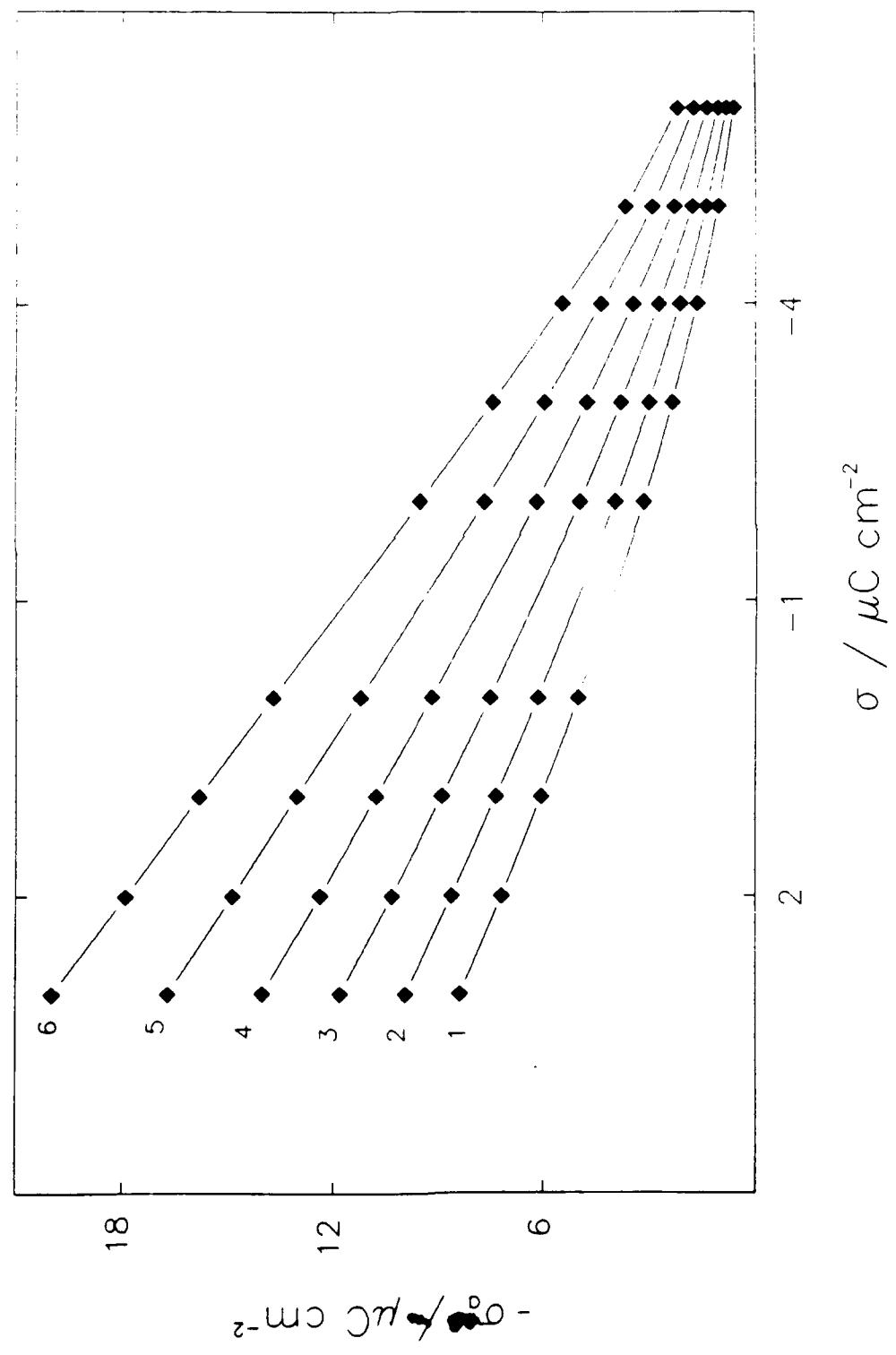
Table 1. Isotherm Parameters for Br⁻ Ion Adsorption from Various Solvents at Mercury

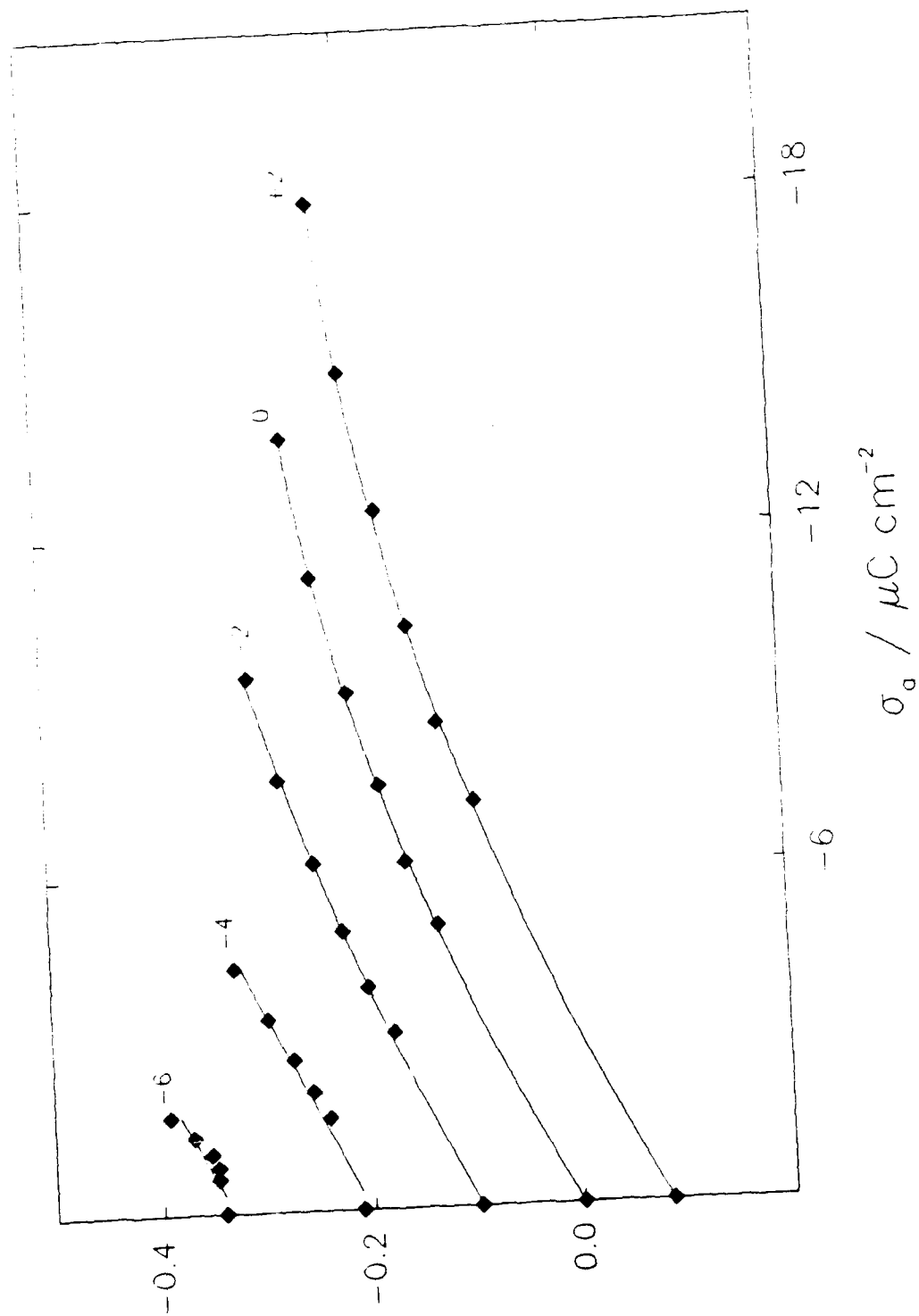
Solvent	Φ	α nm ² molec ⁻¹	β cm ² μ C ⁻¹
1. water (w) [4]	4.8	4.4	0.97
2. N-methylformamide (NMF) [6]	6.8	8.0	0.94
3. dimethylformamide (DMF) [8]	8.7	11.4	1.56
4. dimethylsulfoxide (DMSO) [8]	8.3	15.4	0.60
5. acetonitrile (AN) [9]	10.4	24.0	-
6. propylene carbonate (PC)	9.8	6.0	0.44

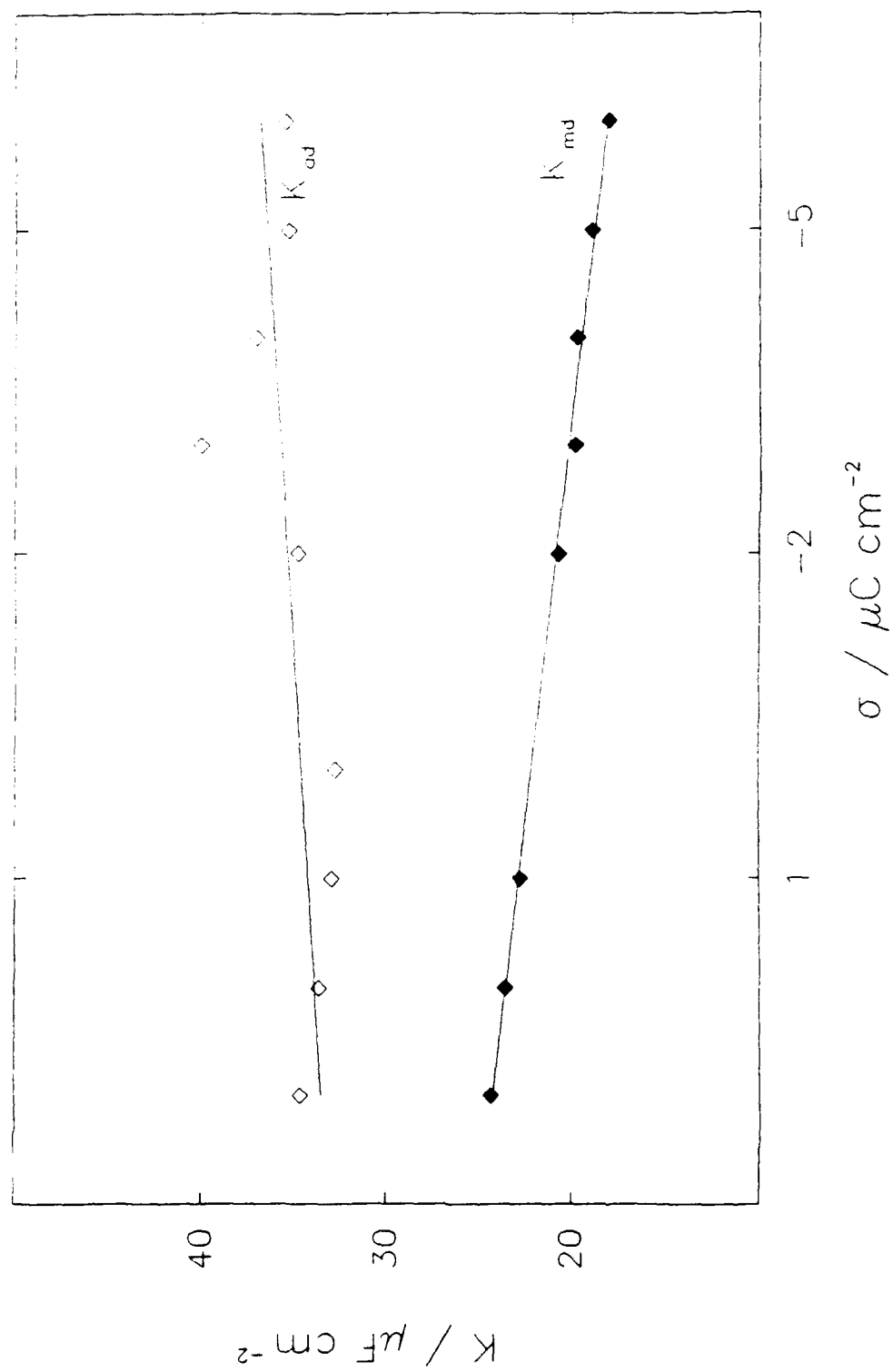
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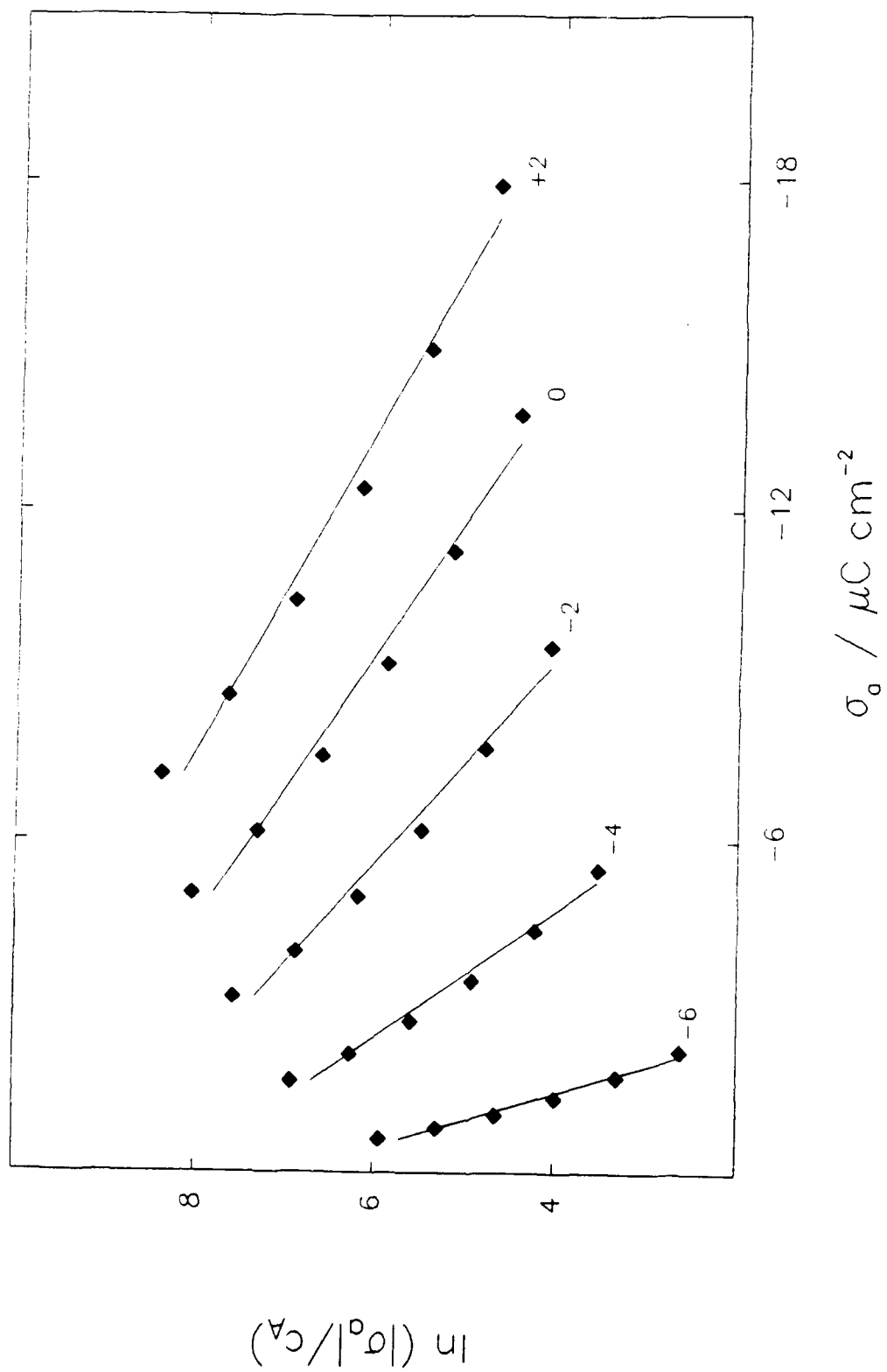
- Figure 1.** Plot of the differential capacity of the Hg / propylene carbonate interface against electrode potential for solutions containing x M TEA Br + $(0.16 - x)$ M TEAP where x has the values: (1) 0, (2) 0.0016, (3) 0.004, (4) 0.01, (5) 0.025, (6) 0.063 and (7) 0.16.
- Figure 2.** Plot of the specifically adsorbed charge of Br^- anion against electrode charge density σ at an ionic strength of 0.16 M for various Br^- ion concentrations: (1) 0.0016, (2) 0.004, (3) 0.01, (4) 0.025, (5) 0.063 and (6) 0.16.
- Figure 3.** Plots of the potential drop across the inner layer, $\phi^m - \phi^d$ against the adsorbed charge density due to Br^- anion, σ_a for constant electrode charge density. The integers at the end of each curve give the value of the charge density in $\mu\text{C cm}^{-2}$.
- Figure 4.** Plots of the integral capacity of the inner layer K_{md} , and of the outer region of the inner layer, K_{ad} against electrode charge density σ .
- Figure 5.** Plot of the adsorption data for Br^- ion at Hg according to the virial isotherm.
- Figure 6.** Plot of the isotherm parameter Φ determined in six different solvents against the Dimroth-Reichardt parameter, E_T . The abbreviations for the solvents are listed in Table I.

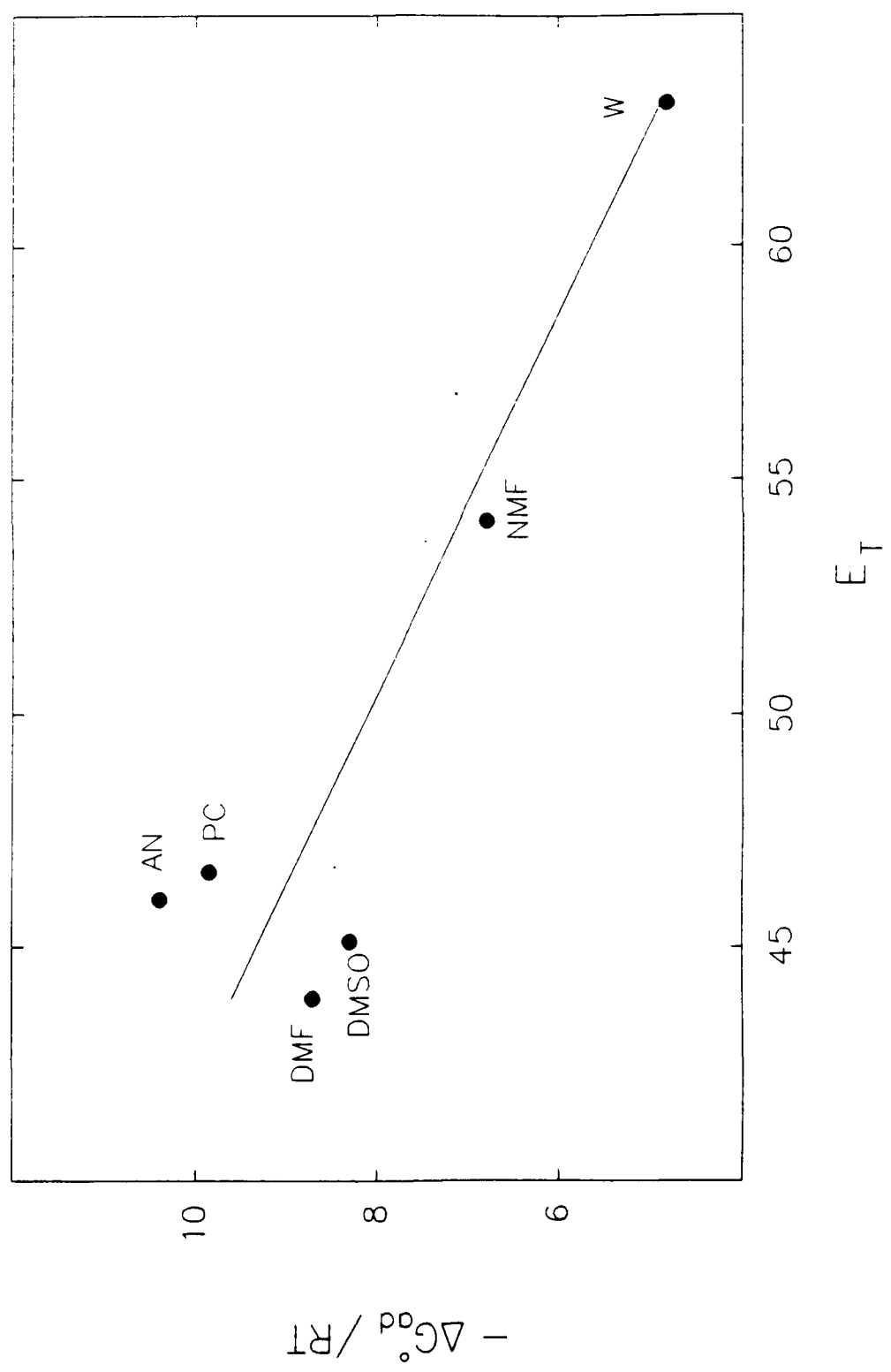












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