Examination of the powder patterns of the alleged sodium hexatitanate revealed a decrease in "$d$" spacings compared with the potassium compound, which is in approximate agreement with that expected upon replacement of potassium atoms by the smaller sodium atoms in the same structure.

A comparison of interplanar spacings determined from powder patterns of the original $K_2Ti_6O_{13}$ and $Na_2Ti_6O_{13}$ obtained by replacement with those calculated from the lattice parameters of Berry, et al.,[1] is shown in Table III. It is to be noted that agreement is quite satisfactory.

Microscopic examination reveals identical fi-

brous character for both potassium and sodium hexatitanate.

This evidence, together with the observations described in the tracer replacement experiments, indicates that fibrous sodium hexatitanate has been prepared by the exchange of ions in a flux.

**Acknowledgments.**—The foregoing investigation forms part of a program of research on distribution of ions between melts and solid phases using radioactive tracers which is supported by contract AT(30-1)-1154 with the Atomic Energy Commission. The authors wish to thank Dr. Roland Ward for his continued interest and suggestions throughout the course of this investigation.

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# Components of Charge and Potential in the Inner Region of the Electrical Double Layer: Aqueous Potassium Chloride Solutions in Contact with Mercury at 25°

BY DAVID C. GRAHAME[1a] AND ROGER PARSONS

Following similar work with potassium iodide solutions,[1b] the differential capacity of the interface between mercury and aqueous potassium chloride solutions of seventeen different concentrations between 0.01 and 4 $M$ has been measured at 25°. The components of the charge in the solution have been computed and analyzed into contributions from the diffuse layer and from the inner layer. The potential drop across the inner region due to the ionic double layer has been computed from the experimental measurements. Using these results, the inner layer capacity has been analyzed into a capacity at constant amount of specific adsorption and one at constant charge on the mercury. The former is similar to that for the potassium iodide system and hence to the total inner layer capacity for potassium fluoride solutions. The latter is considerably larger than that for the potassium iodide system indicating that the inner Helmholtz layer is probably thicker for the chloride ion than for the iodide ion. Somewhat less laborious methods have been developed for calculating the relative thicknesses of inner and outer Helmholtz layers and the potential at an anion site in the inner Helmholtz plane, although it is clear that the value of these results is limited by the simplicity of the model assumed for the inner layer.

## Introduction

A recent analysis[2] of the structure of the inner region of the double layer at the mercury–aqueous solution interface has been applied to experimental results for the mercury-aqueous potassium iodide interface.[1b] The experimental results were in satisfactory agreement with the theory and in fact led to a somewhat simpler model of the inner layer than might have been expected a priori. Nevertheless certain anomalies were apparent and were expressed in terms of a non-uniform dielectric constant in the inner region. The measurements reported here were undertaken to extend and confirm this analysis.

## Experimental Details and Methods of Calculation

The experimental measurement of the capacity of the mercury electrode in contact with aqueous solutions of potassium chloride at 25° followed the methods described previously.[1b,3,4] Twice recrystallized reagent grade salt was dissolved in conductivity water to make solutions of seventeen concentrations.

The calculation of the surface excess of cations and anions in the double layer was carried out precisely as described for the potassium iodide system.[1b] Values of the potential of the electrocapillary maximum were taken from previous work.[5a,5b]

## Results

For direct comparison with the results for the potassium iodide system, the present results are plotted in two ways. In Fig. 1, $n_i$ is plotted against log $a_{\pm}$ for a given value of $q$. The corresponding plot for KI gave straight lines whenever $n^i$ was greater than about 6 $\mu$coul. cm.$^{-2}$. These results on the other hand show marked curvature at all values of $q$ irrespective of the value of $n_i$, though there is some suggestion that each curve approaches linearity at the higher concentrations. Further, it is worth noting that the slope of this approximately linear region is about twice that of the straight lines obtained for KI. If $n^i$, the surface concentration of specifically adsorbed ions, is plotted against $q$, the charge density on the mercury surface, for each solution, the plot is very similar to that for KI and, as previously noted, the slope of the approximately linear section is nearly the same for KI and for KCl. The main difference noticeable is that the curves for the more dilute solutions are more crowded together for KCl than they are for KI. In Fig. 2, the potential across the inner region, $\psi^u$, is plotted against $n^i$ for a given value of $q$. Like the data for KI, these suggest that the relation between $\psi^u$ and $n^i$ is approximately linear. However, for KCl quite large deviations from linearity are apparent with

(1) (a) Late professor at Amherst College. (b) D. C. Grahame, THIS JOURNAL, **80**, 4201 (1958).

(2) D. C. Grahame, Z. Elektrochem. **62**, 264 (1958).

(3) D. C. Grahame, THIS JOURNAL, **71**, 2975 (1949).

(4) D. C. Grahame, Z. Electrochem., **59**, 740 (1955).

(5) (a) D. C. Grahame, E. M. Coffin and J. I. Cummings, Techn. Rep. No. 2 to the Office of Naval Research March 9, 1950; (b) J. R.

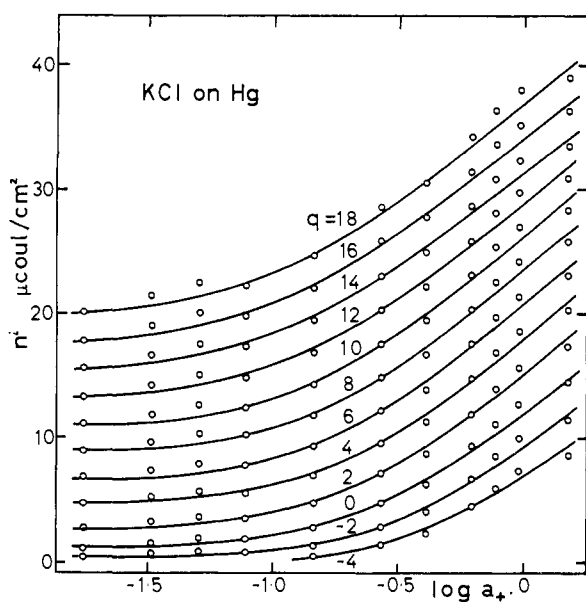Sams, Jr., C. W. Lees and D. C. Grahame, J. Phys. Chem., **63**, 2032 (1959).

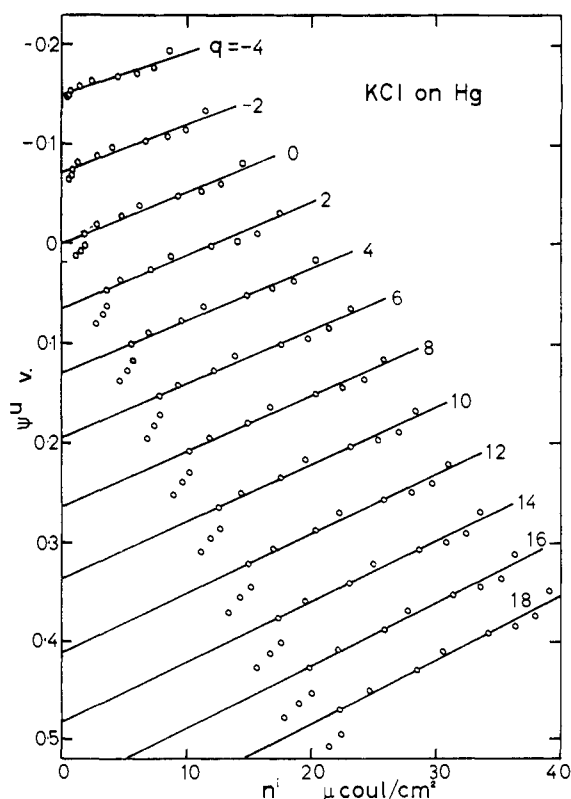Fig. 1.—Amount of specifically adsorbed anion $n^i$ as a function of log $a_\pm$.



Fig. 2.—Potential across the inner region of the double layer $\psi^u$ as a function of amount of specifically adsorbed anion $n^i$.



Fig. 3.—Integral capacity $K^{02}$ of the inner region of the double layer at constant $n^i$; comparison of an adsorbed and a non-adsorbed electrolyte.

because it is uncertain at present why the deviations should occur. Comparison of the results shown in Figs. 1 and 2 with the corresponding results for KI does suggest that the $n^i$ values obtained for the dilute KCl may be too high, but at present no convincing reason for this has been found.

If it is assumed that the straight lines drawn in Fig. 2 are correct, then these results may be analysed in a way similar to that used previously. It is clear from Fig. 2 that the potential $\psi^u$ across the inner region depends upon two quantities $q$ and $n_i$. Thus, it may formally be written as

$$\psi^u = \psi^v + \psi^{02} \qquad (1)$$

where $\psi^v$ depends only upon $n_i$ and $\psi^{02}$ only upon $q$. This dependence may be expressed in terms of integral capacities

$$\psi^v = n_i/K^n \qquad (2)$$
$$\psi^{02} = q/K^{02} \qquad (3)$$

It may be noted that the quantity $\lambda$ defined in the previous paper is the reciprocal of $K^n$ and that $K^{02}$ is the integral capacity related to the differential capacity $C^{02}$ of the previous paper by

$$K^{02} = \frac{1}{\psi^{02}} \int_0^{\psi^{02}} C^{02} \, d\psi^{02} \qquad (4)$$

Thus

$$\psi^u = n_i/K^n + q/K^{02} \qquad (5)$$

and it is evident that $K^n$ is obtained directly from the slope of the lines drawn in Fig. 2, whereas $K^{02}$ is simply related to the shift of the line in a direction parallel to the $\psi^u$ axis. Since $K^n$ is not constant, it is evident that $K^{02}$ must depend to some extent on the value of $n^i$ for which it is calculated. The values shown in Fig. 3 are those obtained from the intercept on the potential axis and therefore correspond to $n^i = 0$. This slight dependence of $K^{02}$ upon $n^i$ was also noted for the KI system; it is much less remarkable than the similarity between the values of $K^{02}$ and the integral capacity of the inner region for the KF system which was mentioned before and is shown in Fig. 3. Comparison of the integral rather than the differential capacity seems more satisfactory because it does not require such high accuracy in the data.

It may be noted at this point that the dependence of $K^n$ upon $q$ and hence of $K^{02}$ upon $n^i$ (cf. 6) means that equation 1 is only approximately valid. Nevertheless, it seems to be a sufficiently good

the results from the most dilute solutions. It would be possible to smooth these results on the assumption that the straight line is correct, as done previously with KI. However, deviation is larger for KCl than for KI and also apparent in several measurements. Consequently, the results presented have not been smoothed in this way
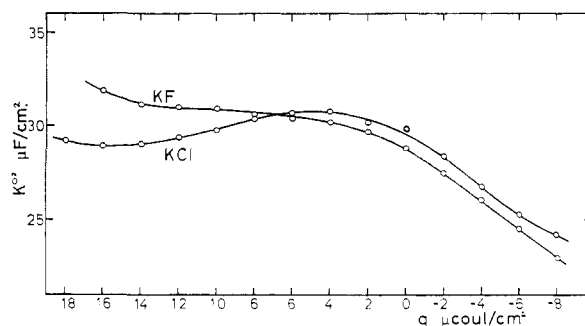
(6) R. Parsons, Trans. Faraday Soc., 55, 999 (1959).

Fig. 4.—Potential across the inner region of the double layer $\psi^u$ as a function of $\log (n^i/a_\pm) - \psi^\circ F/2.303\ RT$ for a mercury electrode in aqueous KI.
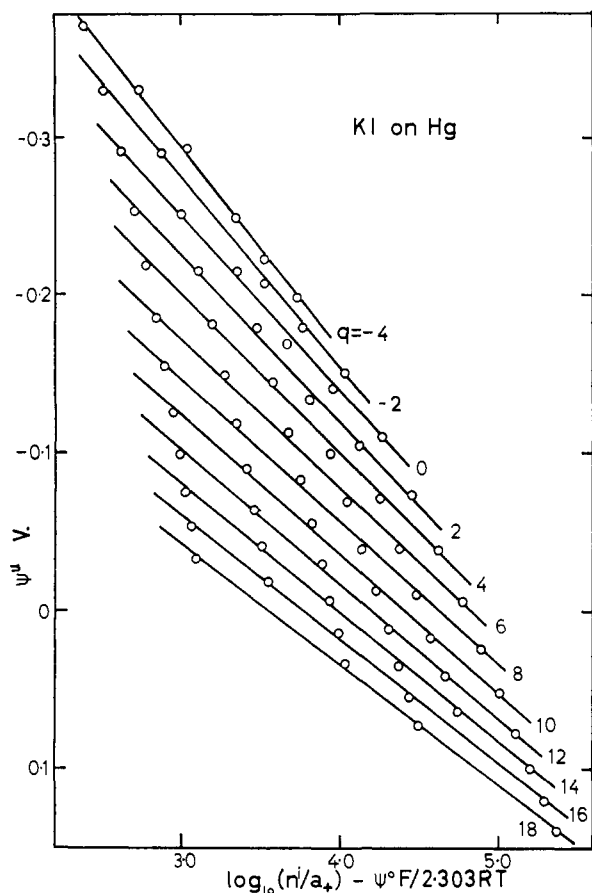


Fig. 5.—Potential across the inner region of the double layer $\psi^u$ as a function of $\log (n^i/a_\pm) - \psi^\circ F/2.303\ RT$ for a mercury electrode in aqueous KCl.

working approximation to be retained for the present. A possibility which should be considered is that equation 1 is strictly valid but that $K^n$ depends upon $n^i$ only and $K^{02}$ depends upon $q$ only. This would mean that the lines of Fig. 2 are not straight but are curves which could be superposed by shifting in a direction parallel to the potential axis. Inspection of Fig. 2 and the corresponding graph for KI suggests that the lines would not superpose in this way and an attempt to superpose the lines in the KCl diagram showed that the misfit is larger than seems consistent with the accuracy expected for the data.

In the previous paper[1b] the electrical potential $(\psi^i)$ at an anion site in the inner region was calculated by a method based upon the equation

$$n^i = Ka_\pm \exp (\phi F/RT) \exp (\psi^i F/RT) \quad (6a)$$

$$= K'a_\pm \exp (\psi^i F/RT) \quad (6b)$$

This is essentially an expression of the concentration of ions in the inner region in terms of a Boltzmann distribution law with an energy difference $(\phi + \psi^i)$ (expressed as a potential) between the bulk solution and the inner region. The division of this energy into two parts is to be thought of as an attempt to separate it into a chemical part $\phi$ and an electrical part $\psi^i$. The chemical part is analogous to Stern's specific adsorption potential and it is assumed that it may depend upon $q$ since
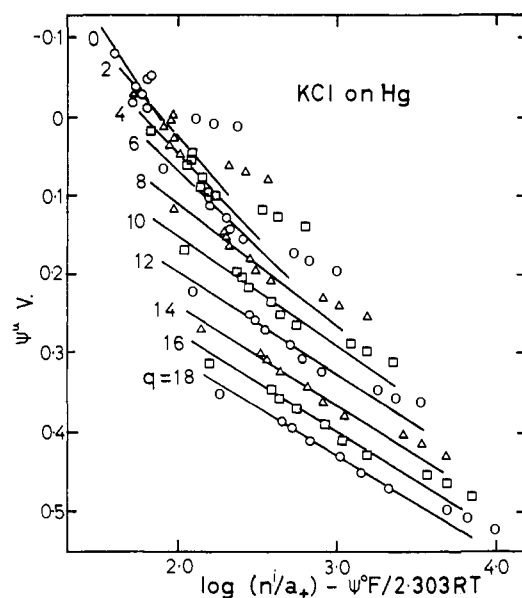
the charge on the electrode may affect the strength of the chemical bond between the metal and an adsorbed atom. $K$ is a constant for a given system but $K'$ is a function of $q$. A somewhat simpler method will be used to calculate $\psi^i$ from the experimental data using (6) than was used previously. Besides its simplicity, it has the advantage that some of the assumptions necessary for the earlier method need not be made (for example, it is not necessary to express $n^i$ in terms of $\psi^u$ and then to differentiate equation 6).

The potential difference, $\psi^i - \psi^0 = \psi^A$, between the inner and outer Helmholtz planes may be expressed as a fraction of the potential difference across the inner region

$$\psi^i - \psi^0 = \psi^u \gamma/(\beta + \gamma) \quad (7)$$

This is equation 12 of ref. 1b, which was derived assuming a linear potential drop across the inner region. Strictly, a linear drop of potential is implied only if $\beta$ and $\gamma$ are identified with the distances between metal surface and inner Helmholtz plane and between the latter and the outer Helmholtz plane, respectively. If equation 7 is substituted into equation 6b, the resulting equation can be rearranged to obtain

$$\ln (n^i/a_\pm) - \psi^0 F/RT = \log K' + (\psi^u F/RT)\gamma/(\beta + \gamma) \quad (8)$$

All the quantities on the left hand side are known and when plotted against $\psi^u$ at a constant value of $q$ will give a linear plot if $\gamma/(\beta + \gamma)$ is independent of $n^i$. In this way, both $\gamma/(\beta + \gamma)$ and $K'$ can be obtained. Fig. 4 shows a plot of this type using the KI results of ref. 2. Satisfactory straight lines are obtained and the resulting values of $\gamma/(\beta + \gamma)$ and $K'$ are in excellent agreement with those found previously, which indicates that the assumptions made earlier were valid. Fig. 5 shows the same type of plot for the KCl results. The points here do not lie so close to straight lines.
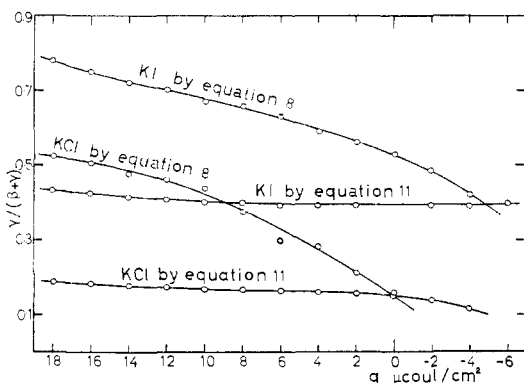
Fig. 6.—$\gamma/(\beta + \gamma)$ as a function of surface charge density $q$ as computed by equation 8 or by equation 11 for KI and KCl.



Fig. 7.—Specific adsorption potential log $K'$ as a function of surface charge density $q$ for KI and KCl.

In view of the discussion above concerning Figs. 1 and 2, the straight lines in Fig. 5 have been drawn, giving more weight to the points from higher concentrations than those from the lower concentrations. The results for $\gamma/(\beta + \gamma)$ and $K'$ obtained from these are compared with the values for KI in Figs. 6 and 7.

It is possible to calculate $\gamma/(\beta + \gamma)$ in another way depending rather more on the detailed model of the inner region. From the picture of the potential generated by a plane of adsorbed ions, discussed in ref. 2, it follows that this potential is (equation 4, ref. 1b)

$$\psi^{v} = - 4\pi n^{i}\gamma/DD_{0} \qquad (9)$$

Similarly the potential due to the charge on the electrode is (equation 18, ref. 1b)

$$\psi^{02} = - 4\pi q(\beta + \gamma)/DD_{0} \qquad (10)$$

If it is assumed that the value of $D$ is the same in these two equations, then it follows from them and from equations 2 and 3 that

$$\frac{\gamma}{\beta + \gamma} = \frac{\psi^{v}}{n^{i}} \frac{q}{\psi^{02}} = \frac{K^{02}}{K^{n}} \qquad (11)$$

Values of $\gamma/(\beta + \gamma)$ calculated from equation 11 are plotted in Fig. 6.

## Discussion

Although the two different methods of computing $\gamma/(\beta + \gamma)$ lead to different values, it is evident from Fig. 6 that according to either method, $\gamma/(\beta + \gamma)$ is smaller for KCl than for KI. This could be caused either by an increased value of $\beta + \gamma$, the thickness of the outer Helmholtz layer or a decrease in $\gamma$ when the iodide ion is replaced by the chloride ion. Since $K^{02}$ is very similar for both systems, it seems less likely that there is a change in $\beta + \gamma$. The alternative explanation that $\gamma$ is smaller for the chloride ion than for the iodide ion suggests that the center of charge of an adsorbed chloride ion is further from the mercury than is an adsorbed iodide ion. This interpretation is in agreement with the fact that $K^{n}$ (which is reciprocally proportional to $\gamma$ according to equation 9) is larger for KCl than for KI. The values of $K^{n}$ correspond to values of $\gamma$ of approximately 0.12 $D$ Å. for KI and 0.05 $D$ Å. for KCl. The corresponding value of $\beta + \gamma$ for both systems is
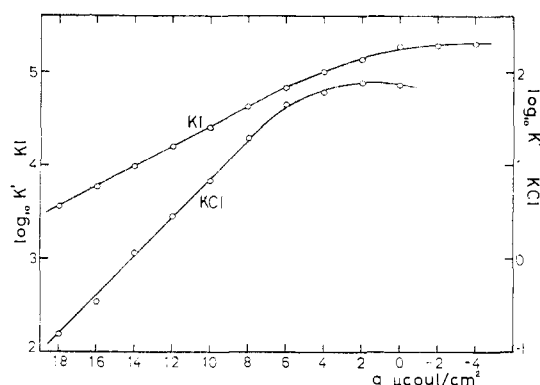
about 0.3 $D$ Å. (These are all rough figures to give an idea of the orders of magnitude involved.) Since the diameter of an iodide ion with a complete first shell of water molecules is about 10 Å., it seems that the largest possible value for $D$, the dielectric constant, is about 30. If this value is used throughout, then the center of charge of the iodide ion is about 5.4 Å. from the mercury, while that of the chloride ion is about 7.5 Å. These values are probably still too large, especially if a specifically adsorbed ion is visualized as forming a chemical bond with the mercury surface.

It is possible as suggested in ref. 1b that the decrease of $\gamma$ in the series iodide, bromide and chloride is a result of the decreasing tendency to bond formation with the mercury. This is confirmed by the relative values of $K'$ in equation 6b. It can be seen from Fig. 7 that $K'$ for chloride is much smaller than it is for iodide at any given charge on the mercury. Although it seems reasonable to use this as a measure of the relative strengths of the bonds of the adsorbed ion to the surface, it must be noted that for both ions $K'$ *decreases* as $q$ becomes more positive. With the simple interpretation of $K'$ this must mean that the strength of the chemical bond between mercury and halogen ions weakens as the metal becomes more positively charged, while the increase in adsorption is due to the increased electrostatic attraction. This is contrary to expectation and suggests that this method of dividing the adsorption energy into "chemical" and "electrical" parts is unsatisfactory.

Besides variation in the dielectric constant of the inner region, the anomalies discussed above may arise from an over-simplification of the model of the inner region. One possible source of anomalies is the treatment of the double layer as two independent parts: the inner region and the diffuse outer region. Simple equations for the potential across the inner regions are obtained by assuming that the potential drop within the region is linear. This model is only strictly correct when the field caused by the adsorbed ions does not penetrate into the metal or into the diffuse layer. The latter condition implies that the thickness of the diffuse layer is infinitesimal. This may be approximately true in very concentrated solutions but is not a particularly good approximation in solutions of about molar

concentration and below. In fact this model of the double layer involves a discontinuity in the field at the outer Helmholtz plane. This may be most clearly brought out by considering the situation when $\psi^u$ is zero, which has been taken here to indicate that the field in the inner region is zero. However, it is found that $\psi^0$ has a finite value under these conditions, e.g., in 1 $M$ solution it is about $-0.038$ v. and in 0.02 $M$ solution about $-0.040$ v. These values of $\psi^0$ correspond to field strengths at the outer Helmholtz plane of $1.4 \times 10^6$ and $2 \times 10^6$ volt cm.$^{-1}$, respectively.

Another way of looking at the discontinuity between the models of the inner and outer regions of the double layer arises from a consideration of the use of the method of images. The potential drop due to the adsorbed ions is calculated by assuming that the equal and opposite charge in the diffuse layer may be represented by the images of the adsorbed ions reflected in the outer Helmholtz plane. The method of images is of course a hypothetical device for the purposes of calculation which ensures that the reflecting plane is an equipotential. In the real situation this must mean that the charge density in the outer Helmholtz layer depends on the coördinates parallel to the electrode surface. In contrast the ionic distribution in the diffuse layer is treated as a one-dimensional problem, depending only on the coordinate perpendicular to the electrode surface.

It appears that further progress in the interpretation of experimental quantities such as those presented in this paper must depend on a more accurate solution of the problem of the potential distribution in the inner layer. This must be treated as a three-dimensional problem including the inner and diffuse layers simultaneously. In the meantime experimental studies related to the first approximation developed in refs. 1b and 2 have provided a considerable insight into the structure of the inner layer.

## Appendix

**On a Discrepancy Between Capacity and Electrocapillary Measurements.**—It is of interest to compare the results obtained from measurement of capacity with those obtained from measurement of interfacial tension. A simple way of making this comparison is to use the values of surface excess at the point of zero charge as determined from capacity measurements and to integrate these to obtain the charge of interfacial tension as a function of solution composition. This curve can be compared with that measured directly and the precision of both curves should be high. This comparison is shown in Fig. A-1 for aqueous KCl. Interfacial tension measurements for KCl are taken from Gouy[7] and from Devanathan and Peries.[8] Some results for NaCl[9] are also included since the difference from KCl is undoubtedly small. The integrated curve is adjusted so that it agrees with the direct measurements at 0.01 $M$. It is evident that the two curves diverge markedly in the more concentrated solutions. The discrepancy is 1.0 dyne cm.$^{-1}$ for the 1 $M$ solution and increases with concentration. It indicates that the surface excess of salt at the point of zero charge calculated
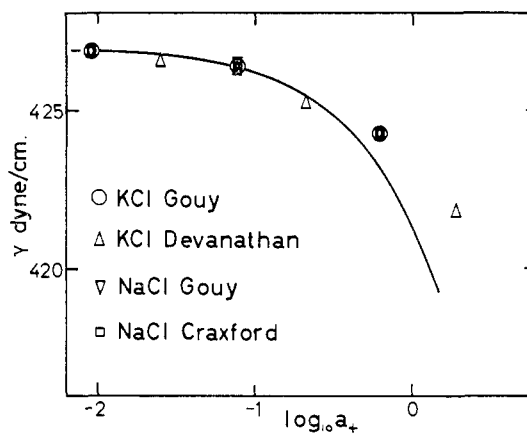


Fig. A-1.—Interfacial tension $\gamma$ as a function of log $a_\pm$ from direct measurement (points) and by integration (line).

from the electrocapillary measurements is considerably smaller than that obtained from the capacity measurements. It is the purpose of this appendix to suggest an explanation for this.

While the calculations from interfacial tension depend on the experimental measurements and thermodynamics only, those from the capacity measurements depend also on the theory of the diffuse layer. Thus one of the required integration constants is calculated by assuming that at a sufficiently large negative charge on the mercury surface there is no specific adsorption and the surface excesses are equal to those calculated by diffuse layer theory. This may be incorrect either if specific adsorption persists to the chosen negative charge or if diffuse layer theory is inaccurate. There is no evidence for the former for KCl solutions; in particular, if it occurred, the deviation between the integrated curve of Fig. A-1 and the interfacial tension would be even greater. Defects in the theory of the diffuse layer as such are unlikely to have a great effect on the calculation of a surface excess of a cation on a strongly negatively charged surface because, as pointed out elsewhere,[10] under these conditions the calculation is very insensitive to the detailed structure of the diffuse layer. A more important correction was suggested by Harrison and Randles.[11] In the calculation of surface excess using simple diffuse layer theory, the equation for the cation of a 1:1 electrolyte is (equation 67, ref. 12)

$$\eta_+{}^d = n_{ol}\,\epsilon \int_x^\infty (e^{-\Psi} - 1)\,dx \qquad (A\text{-}1)$$

where $\Psi = \epsilon\,\psi/kT$, $n_{oi}$ is the bulk concentration of ions of species $i$ whose charge is $\epsilon$ and $\psi$ is the potential at a distance $x$ from the electrode. The integration is carried out by substituting for $x$ in terms of $\psi$ and integrating from $\psi^0$ the potential of the outer Helmholtz layer to zero, the potential in the bulk of the solution at $x = \infty$. This in effect gives the surface excess with the Gibbs reference surface placed in the outer Helmholtz plane. In contrast, the calculation of surface excess from the interfacial tension is carried out by placing the Gibbs surface so that the surface excess of the solvent, water, is zero. This appears to be the basic reason for the discrepancy in Fig. A-1.

An approximate verification of this can be obtained by calculating the difference between the surface excesses obtained with the two different locations of the Gibbs surface. For each ion this will be given by an integral like (A-1) in which the exponential is zero (corresponding to complete exclusion of the ion from this region) and which is integrated between values of $x$ corresponding to the two positions of the Gibbs surface. If this distance is $x_g$, then the integral is simply evaluated as $n_{oi}\,\epsilon x_g$. Hence

$$\epsilon\Gamma_{i(w)} = \eta_i{}^d - n_{oi}\,\epsilon x_g \qquad (A\text{-}2)$$

where $\Gamma_{i(w)}$ is the surface excess of component $i$ when the

(7) G. Gouy, *Ann. chim. phys.*, **29**, 145 (1903).

(8) M. A. V. Devanathan and P. Peries, *Trans. Faraday Soc.*, **50**, 1236 (1954).

(9) S. R. Craxford, *ibid.*, **36**, 85 (1940).

(10) K. M. Joshi and R. Parsons, *Electrochimica Acta*, in press.

(11) J. A. Harrison and J. E. B. Randles, Informal meeting on Electrochemistry, Newcastle, April, 1959.

(12) D. C. Grahame, *Chem. Revs.*, **41**, 441 (1947).

Gibbs surface is placed so that the surface excess of water is zero. Equation A-2 can be substituted into the electrocapillary equation and integrated if $x_g$ is assumed to be constant; this is likely to be true except in very concentrated solutions. The result is

$$\gamma^0 - \gamma = \frac{kT}{\epsilon} \int_{a_\pm\ =\ 0}^{a_\pm} \eta_i{}^d \, d \ln a_\pm{}^2 + $$

$$2kTx_g \, n_{oi} \left\{ 1 + \int_0^{a_\pm} d \ln f_\pm \right\} \quad (A\text{-}3)$$

where $\gamma^0$ is the interfacial tension between mercury and pure water. The first term on the right-hand side of (A-3) is the curve plotted in Fig. A-1. Apart from the activity correction which is not important, the second term on the right-hand side of (A-3) is proportional to the bulk concentration. A plot of the difference of the integrated curve and the interfacial tension from Fig. A-1 against concentration is approximately linear and leads to a value of $x_g$ of about 2.5 Å. Since $x_g$ may be expected to be about equal to the thickness of the outer Helmholtz layer, this value seems reasonable.

It is now necessary to discuss which location for the Gibbs surface is appropriate for the calculation of the amount of specific adsorption which is the main object of the present paper. When the anion only of a binary electrolyte is specifically adsorbed, equation A-2 becomes

$$\epsilon\Gamma_+ \text{ (w)} = \eta_+{}^d - n_{oi} \, \epsilon x_g \quad (A\text{-}4)$$

$$\epsilon\Gamma_- \text{ (w)} = n^i + \eta^d - n_{oi} \, \epsilon x_g \quad (A\text{-}5)$$

if it is assumed that the outer Helmholtz plane is at the same position for each ion. The simple theory of the diffuse layer permits the calculation of $\eta_-{}^d$ from $\eta_+{}^d$, but if values of $\Gamma_+(w)$ and $\Gamma_-(w)$ are given, it is then only possible to calculate $n^i$, the amount of specific adsorption if a value of $x_g$ can be found. On the other hand if the Gibbs surface is fixed at the outer Helmholtz plane, the surface excess of cations and anions is $\eta_+{}^d$ and $n^i + \eta_-{}^d$, respectively, from which $n^i$ is readily obtained. Consequently, it appears preferable for this purpose to fix the Gibbs surface at the outer Helmholtz plane as has been done so far in all calculations based on capacity measurements.

Finally it may be noted that the use of two different locations of the Gibbs surface may account for the discrepancies between the results of Iofa and Frumkin[13] and those of ref. 5b.

(13) Z. A. Iofa and A. N. Frumkin, *Acta Physicochim. U.R.S.S.*, **10**, 473 (1939).

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION, UNIVERSITY OF CALIFORNIA, LIVERMORE, CALIFORNIA]

# An Electron Spin Resonance Study of Nitro Group–Alkali Metal Interactions in Aromatic Hydrocarbons[1]

BY RAYMOND L. WARD

RECEIVED OCTOBER 3, 1960

The reaction of potassium and sodium with nitrobenzene, o-dinitrobenzene, m-dinitrobenzene, p-dinitrobenzene, sym-trinitrobenzene, nitromesitylene, dinitromesitylene and trinitromesitylene in 1,2-dimethoxyethane (DME) has been carried out, and the resulting paramagnetic solutions studied using electron spin resonance techniques. The nitrogen hyperfine coupling constants have been determined for each molecule, while proton hyperfine coupling constants have been determined in a few cases. All polynitro compounds studied, except o-dinitrobenzene, possess only *one* nitrogen hyperfine interaction. This is in contrast to the results obtained in the electrolytic preparation of these free radicals by Maki and Geske who find two equal nitrogen coupling constants in each of the isomeric dinitrobenzenes. A comparison of the resulting hyperfine structure of the electrolytically and chemically produced free radicals is presented and a strong ion-pair theory proposed for the differences obtained.

In general, dilute solutions of free radicals exhibit a complex hyperfine structure, which is due to an isotropic hyperfine interaction[2] between the unpaired electron's magnetic moment and the various magnetic moments of nuclei present in the molecule. A detailed analysis of this complex hyperfine structure, usually by means of isotopic substitution, will yield coupling constants for the various magnetic nuclei, and these coupling constants then can be used as a sort of unpaired electron density map of the molecule. Anisotropic hyperfine interactions are, however, averaged to zero by molecular tumbling in solution,[3a] and therefore the splittings observed must arise from the s-character of the odd electron at the nucleus in question.

In the planar aromatic hydrocarbon free radicals the isotropic hyperfine interaction at the position of the protons, which lie in the plane of the molecule, is due to a σ–π configuration interaction.[3b–6] The magnitude of this hyperfine interaction, for

a given proton, is proportional to the unpaired electron density in the π-orbital of the contiguous carbon atom.[7] In polyatomic free radicals such as nitrobenzene negative ion, which contain a heteroatom, there are two mechanisms whereby an isotropic hyperfine interaction may arise at the nitrogen atom. A σ–π configuration interaction may take place similar to that for protons and/or the spacial overlap of the $P_z$ functions of the carbon and nitrogen atoms may produce appreciable odd electron density at the nitrogen. The former mechanism seems more plausible in a planar configuration with pure sp² hybridization, and the latter mechanism plausible in a non-planar configuration. In either case the hyperfine interaction observed is a measure of the s-character of the odd electron at the position of the nucleus in question.

Recent studies on the negative ions of nitrobenzene and the isomeric dinitrobenzenes have led to some very interesting results. The observed hyperfine spectrum for the potassium salt of m-dinitrobenzene dissolved in 1,2-dimethoxyethane (DME) exhibits a hyperfine interaction with all the protons in the molecule, but with only *one* of the two nitrogens.[8] This is in great contrast

(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) E. Fermi, *Z. Physik*, **60**, 320 (1930).

(3) (a) S. I. Weissman, *J. Chem. Phys.*, **22**, 1378 (1954); (b) **25**, 890 (1956).

(4) H. M. McConnell, *ibid.*, **24**, 764 (1956).

(5) H. S. Jarrett, *ibid.*, **25**, 1289 (1956).

(6) R. Bersohn, *ibid.*, **24**, 1066 (1956).

(7) H. M. McConnell and D. Chestnut, *ibid.*, **28**, 107 (1958).

(8) R. L. Ward, *ibid.*, **32**, 410 (1960).