

rate constants and those of C & S by increasing the pressure in the azo-*n*-propane system.

The problem was approached in another way. The work of C & S was repeated in part, with the hope of lowering the pressure of the azomethane-*n*-butyraldehyde system to that comparable to the azo-*n*-propane studies. It was hoped that a direct analysis of the product *n*-hexane might be made so that the identical rate constant function IV might be evaluated without any assumptions concerning rates of combination reactions of radicals; this proved to be impossible since the large excess of azomethane came off the chromatography column at the same time as the *n*-hexane, so the same rate function calculated by C & S had to be employed again. At the same pressures of *n*-butyraldehyde and azomethane as that used by C & S, excellent agreement with their values for k_1 and E_1 were obtained. When the pressure was halved, however, the calculated rate constants k_1 increased somewhat, although the activation energy remained the same. Runs with a further decrease in pressure did not yield sufficient radical combination products to provide a reasonable accuracy. The apparent increase in k_1 with decrease in pressure was most surprising; it may be the result of non-homogeneous light absorption in the azomethane mixtures at the higher pressures used by C & S. Although the results lack the quantitative character desirable, the qualitative observations of this work show that the difference in pressure between the C & S and the present work is a factor in the difference between rate constants derived in the two studies.

The present work suggests the "high" value for the activation energy of the *n*-propyl radical decomposition in reaction 1. $E_1 \cong 35$ kcal./mole is consistent with the thermochemical estimates of $\Delta H_1 \cong 23$ –26 kcal./mole and $E_{-1} \cong 8.6$ kcal./mole reported by Brinton for methyl addition to ethylene.^{25,26} The entropy change, $\Delta S_1 \cong 14.2$

(25) J. A. Kerr and A. F. Trotman-Dickenson, *The Reactions of*

e.u., calculated²⁷ from the present data and those of Brinton, may be compared with that obtained from thermal entropy data and theoretical data: Bryant's²⁸ data give $\Delta S_1 \cong 12.1$ e.u. The difference between the two ΔS_1 estimates corresponds to a factor of 2.9 in the ratio of A_1/A_{-1} or an error of ± 1 kcal./mole in the difference $E_1 - E_{-1}$. In view of the uncertainties involved in the calculations and the present rate data and those of Brinton, the agreement is considered to be satisfactory and lends support to the "high" pre-exponential factor (about 10^{15} sec.⁻¹) for reaction 1. High A -factors have been reported also for the radical decomposition reactions of the *sec*-butyl²⁹ and the *t*-butyl free radicals.²² It is difficult to rationalize the "high" A -factors in terms of the Slater theory of unimolecular reactions; the Slater theory in its approximate form²⁴ restricts the limiting rate of unimolecular decomposition to the highest frequency normal vibration within the molecule. The model based on the theories of Hinshelwood, Kassel, Rice, Ramsperger and Marcus,³⁰ which allows free energy exchange between the different energy modes, can account satisfactorily for these "high" A -factors.

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Alkyl Radicals, "Progress in Reaction Kinetics," edited by G. Porter. Pergamon Press, London, in press.

(26) R. K. Brinton, *J. Chem. Phys.*, **29**, 781 (1958).

(27) The ΔS_1 was estimated from the pre-exponential factors for the forward and the reverse of reaction 1 using the relation $\Delta S_1 = R \ln (A_1/A_{-1})$. In the calculation we have assumed $k_2 = k_{11}$, and we have used the results of the highest pressure experiments derived in this work, conditions which match most closely those of Brinton.²⁸ The standard state is taken as 1 mole/cc.

(28) W. M. D. Bryant, *J. Polymer Sci.*, **6**, 359 (1951).

(29) J. G. Calvert, *Chem. Revs.*, **59**, 569 (1959).

(30) (a) R. A. Marcus and O. K. Rice, *J. Phys. Chem.*, **55**, 894 (1951); (b) R. A. Marcus, *J. Chem. Phys.*, **20**, 352, 255, 359 (1952).

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY, BATON ROUGE, LOUISIANA]

Local Field Effect and Failure of the Double Layer Correction in Electrode Kinetics

BY KAMEO ASADA,^{1a} PAUL DELAHAY AND A. K. SUNDARAM^{1b}

RECEIVED FEBRUARY 21, 1961

Failure of the theory of the diffuse double layer is to be expected for mixtures of electrolytes with different ionic valences because of local variations of potential in the plane of closest approach. Experimental evidence for this *local field effect* is given for the discharge of Ga^{+3} on mercury in perchlorate medium containing uni- or divalent positive ions (Na^+ , Mg^{+2}) whereas no local field effect was detected for Ga^{+3} discharge in presence of Al^{+3} . Classical theory accounts for the variations of overvoltage—at constant current density—with the concentration of indifferent electrolyte for Al^{+3} but fails for Mg^{+2} and, especially, for Na^+ . Alternate explanations are also considered. The corrected Tafel plot of $\ln I + (zF/RT)\Delta\phi$ against $E - \Delta\phi$ (z ionic valence of species being discharged; $\Delta\phi$ difference of potential across the diffuse double layer; I , E , F , R and T as usual) is suggested for the double layer correction in the absence of specific adsorption.

Introduction

It was pointed out recently by Parsons^{2a} that the classical theory of the diffuse double layer does not

account for variations of potential in planes parallel to the electrode because the Poisson equation is solved for one dimension. The difference between

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(2) (a) R. Parsons, "Advances in Electrochemistry and Electrochemical Engineering," Vol. I, P. Delahay, Editor, Interscience Publishers, Inc., New York, N. Y., 1961, Ch. 1, pp. 1–64. (b) A. N. Frumkin, N. Nikolajeva and R. Ivanov, *Can. J. Chem.*, **37**, 253 (1959).

the average potential in the plane of closest approach and the local potential was also pointed out by Frumkin.^{2b} We shall call this cause of departure of theory the *local field effect*. This effect could be detected, in principle, by comparison of experimental and calculated differential capacities of the double layer for mixtures of electrolytes (*cf.* Parsons^{2a}). Conclusions from such a comparison, however, might well be uncertain because of masking of the local field effect by an averaging out of potential in the plane of closest approach. Moreover, agreement between calculated and experimental capacities, though quite satisfactory, is far from perfect even in the most favorable case of sodium fluoride (Grahame³).

The local field effect should also cause a failure of proper correlation between the double layer structure and electrode kinetics when the difference of potential across the diffuse double layer ($\Delta\phi$) is calculated from the classical theory of the diffuse double layer. Two corrections for the double layer structure must be made for ionic reactants in the absence of specific adsorption of reactants and indifferent electrolyte according to Frumkin's model⁴ (1933): (a) correction of the ionic reactants concentrations in the plane of closest approach and (b) correction of the electrode potential for $\Delta\phi$. The change in overvoltage—at a given current density—resulting from a variation of $\Delta\phi$ upon addition of an indifferent electrolyte can be calculated with good approximation from the theory of the diffuse double layer. Agreement between theory and experiment is good for a variety of electrode reactions.⁵ An experimental study of the local field effect is given here for the discharge of a trivalent ion (Ga^{+3}) on mercury in perchlorate medium in presence of uni-, di- or trivalent ions (Na^+ , Mg^{+2} and Al^{+3}).

Experimental

Solutions.—A mother solution of $\text{Ga}(\text{ClO}_4)_3$ was prepared by attack at room temperature (to avoid reduction of ClO_4^- to Cl^-) of 10 g. of 99.9% Ga (Mackay, New York) in 1 *M* HClO_4 . Attack was activated by contact of a Pt wire with Ga. (H_2 overvoltage is lower on Pt than on Ga.) The attack was stopped after 1–2 days after dissolution of a few hundred mg. of Ga. The solution was chloride-free (Ag^+ test). $\text{Al}(\text{ClO}_4)_3$ was prepared in the same manner with aluminum foil and a globule of Hg instead of a Pt wire. About 1.5 g. was dissolved in a few hours, some Al remaining to avoid Hg attack. $\text{Mg}(\text{ClO}_4)_2$ was prepared by neutralization of HClO_4 with MgO , and NaClO_4 was obtained by neutralization with NaOH with methyl red as external indicator (to avoid contamination). All solutions were prepared with bidistilled (over KMnO_4) water. Ga and Al were determined by gravimetry as oxide. The total cation concentration was obtained by alkalimetry after conversion with a cation exchange resin (Amberlite IR-120). The free acid was obtained by difference. Acid was titrated directly in the sodium and magnesium solutions, and the rest of the procedure was the same as for Ga and Al.

(3) See, *e.g.*, D. C. Grahame, *Chem. Revs.*, **41**, 441 (1947).

(4) (a) For a review see ref. 2a. (b) See also Ch. 2 by A. N. Frumkin in ref. 2a. (c) For a brief review, see M. Breiter, M. Kleinerman and P. Delahay, *J. Am. Chem. Soc.*, **80**, 5111 (1958). (d) Also P. Delahay and Kleinerman, *ibid.*, **82**, 4509 (1960).

(5) This is somewhat surprising especially for rather high electrolyte concentrations ($C > 0.1$ *M*) in view of the simplified model of the theory of the diffuse double layer. *Cf.* discussion of L. Gierst's paper by P. Delahay in "Transactions of the Symposium on Electrode Processes, Philadelphia, 1959," E. Yeager editor, John Wiley and Sons, Inc., New York, N. Y., in course of publication.

Adsorbable impurities were removed by treatment with purified activated charcoal according to Barker.^{4d,6} Loss of Ga^{+3} by adsorption was not detected by polarography.

Cell.—An all-glass cell was used with four compartments I, II, III and IV separated by fritted glass disks (II–III, III–IV) and 1 mm.-bore capillary (I–II). I, II and III contained the working solution and IV a 1 *M* NaCl -calomel electrode which served as anode during electrolysis. The electrodes were: H_2 -electrode (I), D.M.E. or capillary of Lippmann electrometer (II), Pt cylinder for bridge measurements (II) and a high-resistance (no KCl leak) S.C.E. (III). The solution in II was deaerated with N_2 and a N_2 blanket was maintained during measurements. Gas purification: "Deoxo" (Fisher) catalyst cartridge for H_2 ; activated charcoal, pyrogallol in alkaline solution and the working solution for N_2 . The temperature was $25 \pm 0.1^\circ$.

Current-Potential Curves.—A Sargent polarograph model XXI in which the original recorder had been replaced by a 1.2 sec. full scale deflection recorder was used. The potential against the H_2 -electrode, current and drop time were measured at frequent intervals along the i - E curves (the polarograph potentiometer being stopped!). No correction was made for the variation of a_{H^+} with salt concentration since this correction did not exceed a few millivolts. The potential of the H_2 -electrode against S.C.E., -0.350 v., was in good agreement with the calculated value and did not vary by more than 2–3 mv. for the different solutions. Potentials are certainly correct to ± 1 mv. for a given solution. Uncertainty on the current, as measured at the end of drop life, was 0.01 microamp. or 0.3 microamp. cm^{-2} . The uncertainty for $E < -0.8$ v. (*vs.* H_2 electrode) was somewhat greater because the correction for H_2 -evolution was appreciable. Currents were corrected (a) for the residual current which was measured independently and (b) for mass transfer polarization. The correction factor $[1 - (i/i_d)]$ (i current, i_d diffusion current) was close to unity because conditions were such that $i < 0.1i_d$ in all cases and $< 0.05i_d$ for the ΔE versus $\Delta(\Delta\phi)$ plots. The correction for ohmic drop was entirely negligible.

Surface Tension Measurements.—An all-glass Lippmann electrometer according to Koenig⁷ was used. The variations in head of mercury were measured within 0.1 mm. with a cathetometer (Gaertner). The procedure—somewhat different from the conventional method—was as follows: the potentials E_1 and E_2 on each branch of the electrocapillary curve were determined at which Hg began flowing for a given head of mercury. Determinations were repeated once. The point of zero charge (E_z) was determined from the intersection of a plot of $(E_1 + E_2)/2$ against E_1 with the line representing E_1 against E_1 . The value of $E_z = -0.512$ v. (*vs.* N.C.E.) for 0.1 *M* KCl agreed quite well with $E_z = -0.506$ v. (*vs.* N.C.E.), as measured by Grahame.^{8b}

Differential Capacities of the Double Layer.—Measurements were made according to Grahame^{8a} at 1000 cycles per sec. A Hewlett-Packard wave analyzer, model 302A, served as oscillator and detector (frequency range 20 c.p.s. to 50 Kc.). The output was displayed on a DuMont cathode-ray oscilloscope, model 304A, after amplification with a Tektronix plug-in-unit model G (with Tektronix power supply, model 127). The bridge was balanced at the end of drop life. The wave analyzer has two advantages: no interference by hum and more precise balance than with an untuned amplifier because of elimination of harmonics (resulting from the variations of the capacity being measured with potential^{8a}). The particular wave analyzer in this work has a very sharp characteristic but response of the detector is somewhat sluggish (approximately 0.1 sec. delay). Readings were obtained within ± 0.003 microfarad., *i.e.*, ± 0.1 microfarad. cm^{-2} for the D.M.E. that was used, and the maximum error for repeated measurements was at the worst 2–3%. Differential capacities were measured with Ga^{+3} in solution since the contribution of this ion to the double layer structure, though small, is not entirely negligible. The capacitive component of the faradaic impedance for Ga^{+3} reduction was quite negligible.

Calculation of $\Delta\phi$.—The charge q on the electrode was calculated as a function of E by integration of the differential capacity from the point of zero charge (E_z) to E and q was plotted against E . The charge q was also com-

(6) G. C. Barker, in ref. 5.

(7) F. O. Koenig, *Z. physik. Chem.*, **A154**, 454 (1931).

(8) (a) D. C. Grahame, *J. Am. Chem. Soc.*, **68**, 301 (1946); **71**, 2975 (1949); (b) **71**, 2978 (1949).

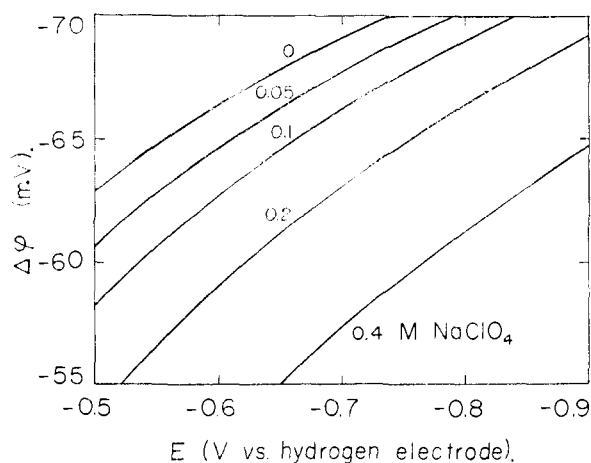


Fig. 1.—Plot of difference of potential across the diffuse double layer against potential for 1 mM Ga^{+3} , 20 mM HClO_4 and a varying concentration of NaClO_4 at 25° . Potential is referred to a hydrogen electrode operating at atmospheric pressure in the solution being tested. Points are calculated at 50 mv. intervals.

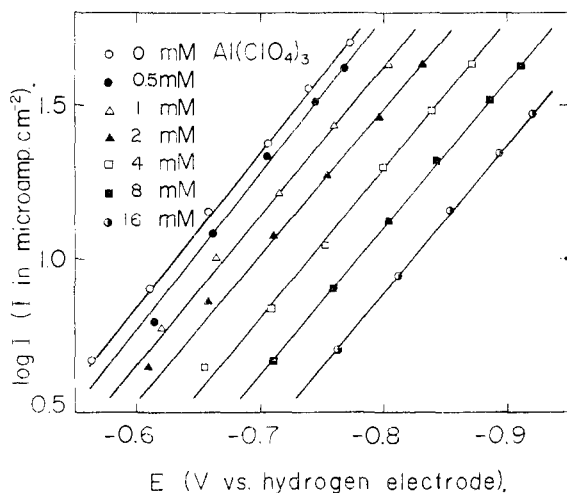


Fig. 2.—Tafel plots for the reduction of 1 mM Ga^{+3} in 20 mM HClO_4 on mercury at 25° for a varying concentration of $\text{Al}(\text{ClO}_4)_3$; same scale of potentials as in Fig. 1.

puted as a function of $\Delta\phi$ from the theory of the diffuse double layer,⁹ and q was plotted against $\Delta\phi$. The plot of $\Delta\phi$ against E (Fig. 1) was prepared from the q vs. E and q vs. $\Delta\phi$ plots.

Values of E_z against the hydrogen electrode for 1 mM Ga^{+3} , 20 mM HClO_4 with added perchlorate: -0.103 , -0.114 , -0.122 , -0.131 , -0.145 v. for 0, 0.05, 0.1, 0.2, 0.4 M NaClO_4 , respectively; -0.110 , -0.115 , -0.121 , -0.121 , -0.129 v. for 0.005, 0.01, 0.02, 0.04, 0.08 M $\text{Mg}(\text{ClO}_4)_2$, respectively; -0.104 , -0.108 , -0.108 , -0.108 , -0.109 , -0.113 v. for 0.0005, 0.001, 0.002, 0.004, 0.008, 0.016 M $\text{Al}(\text{ClO}_4)_3$. Note the significant specific adsorption of ClO_4^- , especially for the more concentrated solutions of NaClO_4 .

Concentration terms for the following ions were included in the calculation of q as a function of $\Delta\phi$: ClO_4^- , H^+ , Ga^{+3} and the added cation, *i.e.*, Na^+ , Mg^{+2} or Al^{+3} . Only the species Ga^{+3} and Al^{+3} were considered since the concentration of GaOH^{+2} did not exceed 6% and that of AlOH^{+2} was much lower.¹⁰ No correction was made for mass trans-

fer polarization of Ga^{+3} since this correction did not exceed a few per cent. The error of $\Delta\phi$ which was made by neglect of the above corrections on Ga^{+3} concentration was smaller than 1 mv. even for the most dilute solution.

Description and Discussion of Results

Results for Al^{+3} .—Discharge of Ga^{+3} on mercury is highly irreversible in perchlorate medium and good Tafel plots were obtained for different Al^{+3} concentrations (Fig. 2). It was also verified that Ga^{+3} discharge in this particular case is essentially of first order with respect to Ga^{+3} if due allowance is made for the change of $\Delta\phi$ with Ga^{+3} concentration. The corresponding current density (I)—potential relationship for a first-order process involving a single rate-determining step for which the backward reaction can be neglected is

$$I = I^0 \exp \left[\frac{(\alpha n - z)F}{RT} \Delta\phi \right] \exp \left[-\frac{\alpha n F}{RT} (E - E_e) \right] \quad (1)$$

where I^0 is the exchange current density; $E - E_e$ the overvoltage, E_e being the equilibrium potential; α the transfer coefficient; n the number of electrons in the rate-determining step; z the ionic valence of the species being discharged; and R , T and F have their usual significance. Equation 1 includes correction for $\Delta\phi$ and applies in the absence of specific adsorption.

Since $\Delta\phi$ varies with E , a plot of $\ln I$ against E is not necessarily linear and the usual Tafel plots only give an *apparent* value of αn . However, it follows from eq. 1, as written in the form

$$\ln I + \frac{zF}{RT} \Delta\phi = \ln I^0 + \frac{\alpha n F}{RT} E_e - \frac{\alpha n F}{RT} (E - \Delta\phi) \quad (2)$$

that a plot of $\ln I + (zF/RT)\Delta\phi$ against $E - \Delta\phi$ for a single electrolyte concentration is a straight line provided the double layer correction applies. The slope of this line gives αn directly. If αn is independent of the foreign electrolyte concentration, a single straight line is obtained regardless of the electrolyte concentration. Such *corrected Tafel plots* have not been used in general thus far despite their simplicity. (Some modified Tafel plots, however, are found in some of Frumkin's works.) Quite obviously, they are significant only when the double layer correction applies.

Figure 3 in which $z = 3$ for Ga^{+3} (*cf.* ref. 10) shows that the double layer correction essentially holds for Al^{+3} and that αn is independent of Al^{+3} concentration. One calculates from Fig. 3 $\alpha n = 0.23 \pm 0.01$, in comparison with the *apparent* value of $\alpha n \approx 0.3$ computed directly from the Tafel plot of Fig. 2. Results are also presented as a plot of the shift of potential against $\Delta\phi$ for a current density of 10 microamp. cm^{-2} (Fig. 4).

The above interpretation would be invalidated by specific adsorption of ClO_4^- , H^+ , Ga^{+3} and Al^{+3} , and this matter will now be taken up. There is some specific adsorption of ClO_4^- near the point of zero charge (see values of E_z in the Experimental Section on calculation of $\Delta\phi$), but specific adsorption certainly should be negligible for $-0.5 \leq E \leq -0.9$ v. (*vs.* hydrogen electrode) *i.e.*, at potentials approxi-

for $\text{Al}^{+3} + \text{OH}^- = \text{AlOH}^{+2}$; *ibid.*, p. 20; see also the related paper by C. Brosset, G. Biedermann and L. G. Sillén, *Acta Chem. Scand.*, **8**, 1917 (1954).

(9) See, *e. g.*, ref. 3, eq. 40.

(10) One has $\log K = 11.1$ for $\text{Ga}^{+3} + \text{OH}^- = \text{GaOH}^{+2}$; *cf.* J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability Constants, Part II," The Chemical Society, London, 1958, p. 21. $\log K \approx 9.5$

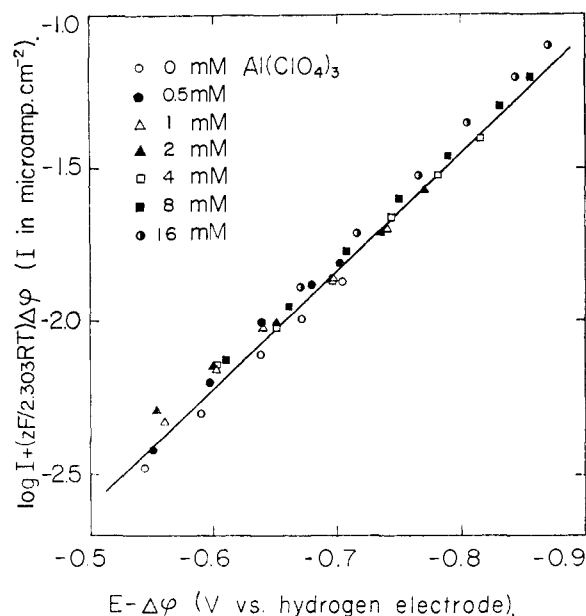


Fig. 3.—Corrected Tafel plot for the data of Fig. 2 and $z = 3$. Values of E are referred to the hydrogen electrode as in Fig. 1.

mately -0.4 to -0.8 v. more negative than the point of zero charge. Specific adsorption of H^+ for the present conditions is ruled out in view of previous work on the double layer correction for H^+ discharge on mercury at markedly more negative potentials than those considered here.¹¹ Specific adsorption of Ga^{+3} and Al^{+3} could not be detected: the electrocapillary curves for $0.1 M HClO_4$ plus $0.01 M Ga(ClO_4)_3$ or $0.01 M Al(ClO_4)_3$ were the same as for $0.1 M HClO_4$ within experimental errors.

Misinterpretation would also result from an appreciable shift of the point of zero charge as caused by gallium deposition. However, the solubility of gallium in mercury is too high¹² to allow formation of an insoluble gallium film at the surface of mercury; and further, the shift of the point of zero charge for very dilute amalgams is quite small even for metals with markedly different work functions.¹³

Results for Na^+ and Mg^{+2} .—Good Tafel plots were obtained for Ga^{+3} in presence of Na^+ or Mg^{+2} but the double layer correction failed. Corrected Tafel plots for different salt concentrations did not yield a single straight line (Fig. 5, compare with Fig. 3), and the plot of the shift of potential for a current density of 10 microamp. cm^{-2} against $\Delta\phi$ did not have the theoretical slope¹⁴ (Fig. 4). Further, disagreement was more pronounced for Na^+ than Mg^{+2} .

(11) For a review cf., e.g., ref. 4b. It is true that a very dilute gallium amalgam is involved here, but it is unlikely that this would result in a marked difference with mercury with respect to H^+ adsorption.

(12) O. Stelling, *Z. Elektrochem.*, **41**, 712 (1935). This author used a 0.25% Ga amalgam.

(13) Cf. A. N. Frumkin and A. W. Gorodetskaya, *Z. physik. Chem.*, **136A**, 451 (1928), for thallium amalgams. See also ref. 4d.

(14) The corrected value of αn is not known of course for Na^+ and Mg^{+2} since the $\Delta\phi$ correction failed. αn probably was not very different from the value $\alpha n = 0.23$ in the absence of Na^+ or Mg^{+2}

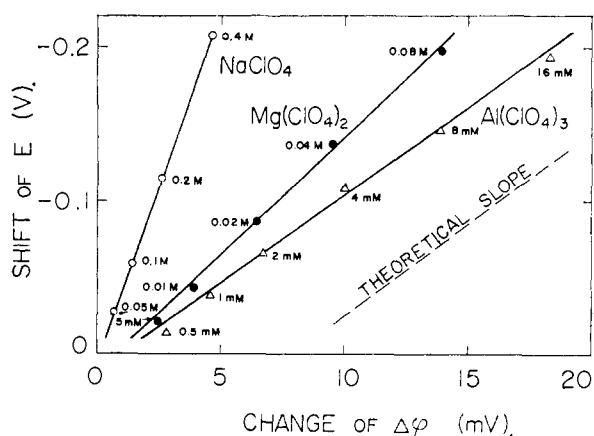


Fig. 4.—Shift of potential, as read on the Tafel plot for a current density of 10 microamp. cm^{-2} , with the change of potential across the diffuse double layer for reduction of $1 mM Ga^{+3}$ in $20 mM HClO_4$ and a varying concentration of salt (indicated for each point). The theoretical slope is for $z = 3$ and $\alpha n = 0.23$.

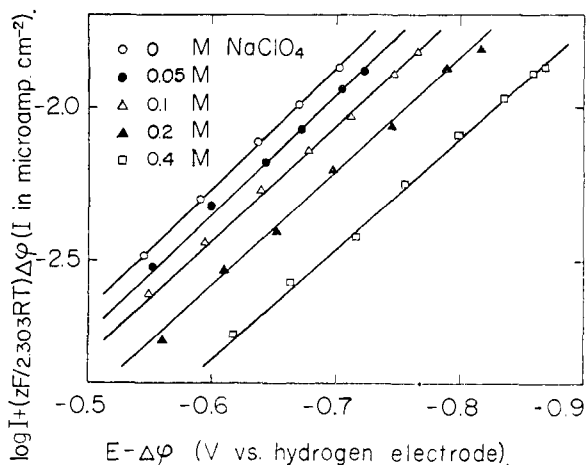


Fig. 5.—Corrected Tafel plot for the reduction of $1 mM Ga^{+3}$ in $20 mM HClO_4$ on mercury at 25° for a varying concentration of $NaClO_4$.

Several possible causes for the failure of theory will be considered: specific adsorption, formation of ion pairs in the double layer, complex discharge mechanism, spurious effects of impurities and shift of the point of zero charge as a result of gallium deposition. The latter effect was already ruled out in the discussion of the Al^{+3} case. Specific adsorption of Mg^{+2} or Na^+ could not be detected from the electrocapillary curves for $0.1 M HClO_4$ plus $0.08 M MgClO_4$ or $0.4 M NaClO_4$. Substantial ion pair formation in the diffuse double layer¹⁵ would invalidate the calculation of $\Delta\phi$ and change the value of z for the discharged species. One does not see, however, how to reconcile such an interpretation with the agreement between theory and experiment for Al^{+3} unless some compensation of errors is postulated for Al^{+3} . Likewise, complexity of the discharge mechanism would affect the results for Al^{+3} as well as Na^+ and Mg^{+2} .

since, in general, corrected values of αn are quite independent of salt concentration.

(15) Cf., e.g., A. N. Frumkin, *Trans. Faraday Soc.*, **55**, 156 (1959).

Spurious effects of impurities are unlikely in view of the care that was taken and the use of a dropping electrode with a continuously renewed surface.

Other Possible Cases of Local Field Effect

This study dealt with the case in which the discharged species is attracted in the diffuse double layer and the absolute value of the ionic valence ($|z|$) of the discharged ion is larger or equal to that of the ion of the indifferent electrolyte which is attracted in the diffuse double layer. Other possible cases should be considered, e.g.: (a) attraction of the discharged species but with $|z|$ for the discharged species smaller than for the ion of the indifferent electrolyte being attracted in the diffuse double layer; (b) repulsion of a discharged species with $|z|$ larger for the discharged species than for the ion of the indifferent electrolyte being attracted in or repelled from the diffuse double layer; and (c) repulsion of a discharged species having a $|z|$ smaller than the ion of the indifferent electrolyte (attraction in or repulsion from the diffuse double layer). Some evidence of a local field effect for case *a* may possibly be found by comparison of the effect of KCl on H⁺ discharge on mercury, as studied by Bagotskii and Yablokova,^{4b,16} with the effect of LaCl₃ on this reaction, as investigated by Levina and Sarinsky.^{4b,17} The agreement between theory and experiment was very good for KCl but poorer for LaCl₃. Further work on some of the above cases is now under way.

Conclusion

Results for the discharge of Ga⁺³ in presence of Na⁺, Mg⁺² or Al⁺³ suggest that the double layer

(16) V. S. Bagotskii and I. E. Yablokova, *Zhur. fiz. Khim.*, **23**, 413 (1949).

(17) S. Levina and V. Sarinsky, *Acta Physicochim. U.S.S.S.*, **7**, 485 (1937).

correction in electrode kinetics may fail in the absence of specific adsorption in the following case: the ion being discharged is attracted in the diffuse double layer; and the ion of the indifferent electrolyte, which is attracted in the diffuse double layer, has an ionic valence of the same sign as the discharged species but of different value. This failure is attributed to the local field effect *though other causes of departure from theory such as difference in solvation, etc., are not ruled out.*¹⁸ The local field effect results from the *discrete* nature of ions in the plane of closest approach and recalls, though the problem is not the same, the effect of the discrete nature of specifically adsorbed ions¹⁹⁻²¹ How general the local field effect is remains to be determined by further work.

Acknowledgments.—This investigation was supported in part by the National Science Foundation. One of us (A.K.S.) is indebted to the International Coöperation Administration, Washington, D. C., for a fellowship which made possible his stay in this Laboratory.

(18) Cf., e.g., the difference on the effect of alkali metals in the reduction of peroxydisulfate studied by Frumkin and co-workers; see A. N. Frumkin, *Z. Elektrochem.*, **59**, 807 (1955).

(19) (a) O. A. Esin and B. F. Markov, *Acta Physicochim., U.S.S.R.*, **10**, 353 (1939); (b) O. A. Esin and V. Shikov, *Zhur. fiz. Khim.*, **17**, 236 (1943).

(20) B. V. Ershler, *ibid.*, **20**, 679 (1946).

(21) (a) D. C. Grahame, *Z. Elektrochem.*, **62**, 264 (1958); *J. Am. Chem. Soc.*, **80**, 4201 (1958). (b) See ref. 2 for a review.

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNSYLVANIA]

Conductance of Solutions of Water, Acetic Anhydride and Acetyl Chloride in Acetic Acid

BY THOMAS B. HOOVER¹ AND A. WITT HUTCHISON

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The electrical conductances of solutions of water, acetic anhydride and acetyl chloride in acetic acid have been measured at 25°. The solvent employed was purified by careful fractional distillation and samples exhibiting specific conductances in the range of 2.4 to 3.0×10^{-9} mho were consistently obtained. The results showed water to be an exceedingly weak electrolyte in acetic acid; the specific conductance of a 0.1 molal solution was only a little more than twice that of the solvent itself. With increasing concentrations of water, the conductance increased more rapidly. Acetic anhydride increased the conductance of the solvent similarly in dilute solutions. Acetyl chloride solutions were much more conducting and resembled solutions of hydrogen chloride in this solvent. A few measurements were made of the conductance of acetic anhydride and of dilute solutions of acetic acid in this liquid.

Introduction

The objective of the investigation was to contribute to the knowledge of the electrolytic dissociation of solutes which have little ionic character, in a solvent where short range interionic attractions are an additional factor. The two-stage nature of the dissociation of ionogens in acetic acid (or solvents of similarly low dielectric constant) has been discussed in detail by Kolthoff and Bruckenstein.² These authors consider first, the primary ionization of the solute, involving the transformation of a partially covalent bond to a purely electrostatic attraction in the ion pair, and second,

the dissociation of the ion pair to free ions subject only to long range interactions.

Several investigations³ have been made of the conductance behavior of the binary system water-acetic acid but, in general, these did not provide measurements in dilute solutions. Kolthoff and Willman^{3a} reported consistent conductance measurements of solutions of water extending to concentrations as low as 0.02 molal in connection with an investigation of the effect of water on the conductance of other electrolytes in acetic acid. They

(1) Abstracted from a thesis by Thomas B. Hoover presented to the Graduate School in partial fulfillment of the requirements for the Ph.D. degree, June, 1960.

(2) I. M. Kolthoff and S. Bruckenstein, *J. Am. Chem. Soc.*, **78**, 1 (1956).

(3) (a) I. M. Kolthoff and A. Willman, *ibid.*, **56**, 1007 (1934). (b) W. R. Bousfield and T. M. Lowry, *J. Chem. Soc.*, **99**, 1432 (1911); W. C. Eichelberger and V. K. LaMer, *J. Am. Chem. Soc.*, **55**, 3635 (1933); A. A. Glagoleva, *Zhur. Obshchei Khim.*, **18**, 1005 (1948); A. N. Campbell and E. M. Kartzmark, *Can. J. Research*, **28B**, 43 (1950). (c) T. S. Brun, *Univ. i Bergen Årbok 1952, Naturvitenskap. Rekke No. 12*, 1 (1953).