Discussion

In Fig. 1, the modified Longsworth function is plotted against ionic concentration for the two salts, and it is at once evident that it is linear in xC well within experimental precision, thus permitting an unambiguous extrapolation to infinite dilution. The resulting values of t_-^0 are 0.5187 and 0.5607 for NaCl and LiCl, respectively. The fact that such an extrapolation is possible here is encouraging, since it suggests that limiting transference numbers may be obtained in this way with other solvents where ion pair formation occurs without the necessity of making measurements at fantastic dilutions.

It should also be noted, in contrast to results in aqueous solution, that although the transference numbers are greater than one half, the limiting slope is approached in both cases from above. Potassium chloride in methanol showed similar behavior,[3a] and we believe that about the only generalization that can be made, based on the results in the three solvents, is that the deviation from the limiting law at finite concentrations is numerically least when the transference numbers are close to one-half.

Smisko and Dawson[10] have recently reported transference numbers for KCNS solutions in ethanol, based on measurements in an autogenic cell; a discussion of the correlation of their results with ours, and of the mutual consistency of our NaCl and LiCl data, is reserved for the accompanying paper.[4] Suffice it to say here that while the ethanol data are not of the precision obtained with water and methanol as solvents, they nevertheless fix a limiting conductance for chloride ion in ethanol which is probably reliable to a few hundredth's of a conductance unit.

In conclusion we wish to express our thanks to the National Research Council of Canada for the award to J. R. G. of two studentships.

[10] J. Smisko and L. R. Dawson, *J. Phys. Chem.*, **59**, 84 (1955).

TORONTO, ONTARIO, CANADA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TORONTO]

Equivalent and Ionic Conductances for Lithium, Sodium and Potassium Chlorides in Anhydrous Ethanol at 25°

BY J. R. GRAHAM, G. S. KELL AND A. R. GORDON

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The conductance of lithium, sodium and potassium chlorides in anhydrous ethanol has been determined for concentrations from 0.0001 to 0.0020 *N*. All three salts show definite ion-pair formation, the dissociation constants for the pairs (determined by the Shedlovsky procedure) being greatest as might be expected for LiCl and least for KCl. In conjunction with the transference numbers, the LiCl and NaCl results yield a limiting conductance for chloride ion of 21.85; this is probably reliable to 0.02 or 0.03 conductance units, and consequently should fix other limiting ion conductances within similar limits. The correlation of the ion conductances in ethanol with those in methanol and water is discussed.

If the transference measurements of the preceding paper[1] are to yield information as to ion conductances in ethanol solution, it is obvious that reliable equivalent conductances are necessary. Previous conductance studies of the alkali halides in ethanol have given an extraordinarily wide variation in conductance values. To take the case of Λ_0 for NaCl as an example, Goldschmidt and Dahll[2] give 46.5, Thomas and Marum[3] 43.0, and Barak and Hartley[4] 42.5. Admittedly, some of the spread is due to the methods of extrapolation employed (see below) but nonetheless such results indicate the necessity for measurements carried out under conditions much more carefully controlled than those obtaining in the earlier work. Here we report conductance data at 25° for lithium, sodium and potassium chlorides.

Experimental

The measurements were effected by the direct current method, developed in this Laboratory, employing the cells previously used with methanol[5] as solvent; their calibrations are based on the Jones and Bradshaw 25° 0.01 demal standard.[6] Bias potentials between the probe electrodes were in general no greater than in water and methanol, but great care had to be exercised, particularly in the more dilute solutions, to avoid the passage of any appreciable current through the probes as the result of significant off-balance in the initial setting of the potentiometer; if this occurred, the probes behaved erratically and had to be reanodized. It was also found impossible to determine the solvent conductance for ethanol by the direct current method; it was accordingly determined in a conventional conductance cell (cell factor 0.1005 cm.$^{-1}$) with an alternating current bridge. Work in methanol[5a] had shown that the two methods were in agreement to better than 1%.

The principal difficulty with ethanol is its preparation as a solvent with, at the same time, low water content and low specific conductance. The starting material was a Gooderham and Worts "anhydrous" alcohol, rectified by ethylene glycol distillation; it contained approximately 0.25% water, 0.01% esters and traces of aldehydes and acids, and its specific conductance was of the order 6 × 10^{-8} mho/cm. The procedure finally adopted was to reflux 4.5 l. of the starting material overnight under a 30-cm. Allihn condenser (condenser temperature 30°) while a slow stream of nitrogen (from which traces of oxygen, carbon dioxide and water vapor had been removed) bubbled through the charge; this removed the low-boiling impurities, which were taken off by a slight suction applied at the top of the condenser. The subsequent distillation was carried out under a slight positive pressure of the purified nitrogen, only a middle cut of 3 l. being retained. While this procedure left the water content unaltered, the specific conductance of the distillate was in general 0.5–0.8 × 10^{-8} mho/cm.

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[1] J. R. Graham and A. R. Gordon, THIS JOURNAL, **79**, 2350 (1957).

[2] H. Goldschmidt and P. Dahll, *Z. physik. Chem.*, **114**, 1 (1925).

[3] L. Thomas and E. Marum, *ibid.*, **143**, 191 (1929).

[4] M. Barak and H. Hartley, *ibid.*, **A165**, 272 (1933).

[5] (a) J. P. Butler, H. I. Schiff and A. R. Gordon, *J. Chem. Phys.*, **19**, 752 (1951); (b) R. E. Jervis, D. R. Muir, J. P. Butler and A. R. Gordon, THIS JOURNAL, **75**, 2855 (1953).

[6] G. Jones and B. B. Bradshaw, *ibid.*, **55**, 1780 (1933).

To remove the water, a modification of the Lunt and Bjerrum[7] method was used. Grignard quality magnesium turnings were cleaned by refluxing with ethanol and a few iodine crystals for three hours; the liquid was then decanted and discarded, and traces of iodine were removed by repeated washings of the turnings with ethanol. This preliminary cleaning and removal of the iodine are essential, in our experience, if a final product of low specific conductance is to be obtained. The magnesium was then refluxed under purified nitrogen for 24 hours with 1.5 l. of previously dried purified alcohol to permit the magnesium ethoxide to form; the center cut from the first distillation was added, refluxed for 12 hr., and distilled under nitrogen, a center cut of 3 l. being retained. The specific conductance was unaffected by this treatment, but the water content of the distillate, determined by Karl Fischer titration,[8] was reduced in general to 0.001–0.002 weight %. Acid and ester analyses, carried out by A.O.A.C. procedures modified for trace amounts[9] and checked by tests of samples containing known amounts of ester and acid, showed that the distillate was neutral and contained less than 0.002% esters. The mercuric cyanide test of Hartley and Raikes[10] showed negligible amounts of acetone and acetaldehyde, and a spectroscopic analysis for magnesium was negative.

The density of the distillate, determined by means of a Shedlovsky and Brown[11] type pycnometer, at 25.000° was $0.78503_9 \pm 0.00001_2$ g./ml. (8 determinations). Osborne, McKelvey and Bearce[12] report 0.78505_8 for what was almost certainly a somewhat wetter alcohol, and Brunel, Crenshaw and Tobin[13] give 0.78505 for the mean of several drying procedures. If one employs Osborne, McKelvey and Bearce's data for the effect of water on density, our value for the anhydrous alcohol would be 0.78503_5. Any significant study of the effect of solution concentration on density is precluded by the narrow concentration ranges available; however density measurements show that for the concentrations of interest here the solution densities are given within two or three units in the fifth decimal place by $d = 0.78504 + AX$ where X is the salt concentration in moles/kg. solution and A is 0.04, 0.05 and 0.06 for LiCl, NaCl and KCl, respectively.

The salts were prepared as previously described,[5] except that in the final stage they were heated to temperatures slightly below the melting point instead of being fused. This was necessary owing to the extreme slowness with which they dissolved in ethanol; in general, the weighed sample of salt had to be refluxed under purified nitrogen for from 3 to 6 hours in spite of the fact that the strongest stock solutions were only 0.0025 N, well below the values quoted for saturation. The dilution technique, in particular the precautions taken against evaporation losses and contamination with air or water vapor have been previously described.[5]

There is one additional complication with this solvent in that its specific conductance, regardless of the method of storage and of the fact that its water content does not change with time, shows a steady increase (for several days at any rate) of approximately 0.6×10^{-8} mho/cm. per day. Curiously enough, aged samples of pure solvent, refluxed under the conditions obtaining when the salt was dissolved, showed a small but definite decrease in conductance and, for this reason, solvent determinations had to parallel as closely as possible the conditions obtaining in the preparation of the stock solutions and the solvent used for dilution.

Hughes and Hartley[14] report that for exceedingly small additions of water, the viscosity increases by 4% per 1% added water. A series of measurements with 0.001 N NaCl solutions showed that up to approximately 0.015% water content, the conductance decreased per % added water by the same amount, *i.e.*, decrease in conductance for this range of water content is apparently a viscosity effect, as postulated by Hughes and Hartley. The decreases were so slight—at most of the order of 0.02 conductance unit and consequently not much greater than the reproducibility of the measurements—that a detailed presentation of the results is hardly justified, but the effect is unquestionably a real one.[15] For higher water contents, there is a minimum in Λ at about 0.04 wt. %, the minimum being some 0.03 conductance units below the "anhydrous" value, with a subsequent steady increase in Λ until with 0.2% water, Λ has risen to the anhydrous value again; as Hughes and Hartley suggest, this is possibly the result of decreased ion-pair formation. Bezman and Verhoek[16] found somewhat similar behavior with addition of water to ethanolic solutions of ammonium chloride, but their minimum occurs in the neighborhood of 2% water. In any event, with the water contents normally obtaining in our solvents, the water effect on the equivalent conductance is relatively negligible, amounting at most to a few thousandth's of a conductance unit; it has nevertheless been applied where necessary in arriving at the values in the tables.

Results

Owing to the large number of individual measurements, only mean values for round concentrations are recorded. To illustrate the method used in obtaining these, the experimental data for 0.0002 N NaCl are summarized in Table I. The first line gives the concentration in equivalents/liter, each solution being prepared from a different stock solution, and the second the equivalent conductance. The third gives the value of the Shedlovsky function[17]

$$\Lambda'_0 = (\Lambda + 2\sigma C^{1/2})/(1 - \vartheta C^{1/2}) \qquad (1)$$

TABLE I

CONDUCTANCE DATA FOR 0.0002 N NaCl

10^4C	1.9965	1.9983	1.9804	2.0102	2.1404
Λ	39.710	39.719	39.749	39.694	39.613
Λ'_0	41.756	41.766	41.788	41.748	41.732
Λ'_0, 0 = 0.0002	41.756	41.766	(41.785)	41.750	71.756

where $\vartheta = 1.330$ and $\sigma = 44.66$ (see below). It must be emphasized that the Shedlovsky function as defined in eq. 1 has no theoretical significance for a solvent where ion-pair formation occurs, but it does provide a convenient method of interpolation owing to its relatively slight variation with concentration. From a large scale plot of Λ'_0 *vs.* C, $d\Lambda'_0/dC$ at 0.0002 N is -0.17×10^4 for the concentration range of the table, and the resulting values of Λ'_0 for $C = 0.0002$ are given in the last line. Thus, if the bracketed entry be ignored, Λ'_0 for 0.0002 N is 41.757 with a mean average deviation of 0.004; this corresponds to $\Lambda = 39.709$. Table I is typical of the precision and reproducibility of the results entered in Table II. Each entry in Table II is the mean of four or more independent measurements, each involving a different stock solution. The spread covering the individual results for a given concentration is of the same order as that of Table I (or less) for the more concentrated solutions and is not significantly greater for 0.0001 N.

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(7) H. Lunt and J. Bjerrum, *Ber.*, **64**, 210 (1931).

(8) K. Fischer, *Z. angew. Chem.*, **48**, 394 (1935).

(9) Assoc. of Official Agric. Chemists "Official and Tentative Methods of Analysis," 6th ed., 1945, Chap. 16.

(10) H. Hartley and H. R. Raikes, *J. Chem. Soc.*, **127**, 524 (1925).

(11) T. Shedlovsky and A. S. Brown, THIS JOURNAL, **56**, 1066 (1934).

(12) N. S. Osborne, E. C. McKelvey and H. W. Bearce, *J. Wash. Acad. Sci.*, *II*, 95 (1912).

(13) R. F. Brunel, J. L. Crenshaw and E. Tobin, THIS JOURNAL, **43**, 561 (1921).

(14) O. L. Hughes and H. Hartley, *Phil. Mag.*, [7] **15**, 610 (1933).

(15) In estimating the effect, Λ was computed using the density data of Osborne, McKelvey and Bearce to correct for water content, and the Shedlovsky function Λ'_0 (see below) was then calculated. This has the advantage that Λ'_0 is relatively insensitive to the small variations in salt concentration inevitable in preparing a series of solutions.

(16) I. I. Bezman and F. H. Verhoek, THIS JOURNAL, **67**, 1330 (1945).

(17) T. Shedlovsky, *ibid.*, **54**, 1405 (1932).

TABLE II

EQUIVALENT CONDUCTANCE DATA IN ETHANOL AT 25°

10^4C	1	2	5	10	15	20
	LiCl, $\Lambda_0 = 38.90$, $K = 0.01795$					
Λ	37.360	36.695	35.300	33.780	32.650	31.770
ΛS	38.710	38.570	38.135	37.585	37.130	36.780
	NaCl, $\Lambda_0 = 42.16$, $K = 0.01250$					
Λ	40.450	39.710	38.095	36.300	34.970	33.910
ΛS	41.840	41.640	40.995	40.170	39.500	38.945
	KCl, $\Lambda_0 = 45.40$, $K = 0.00795$					
Λ	43.465	42.535	40.530	38.290	36.640	35.350
ΛS	44.890	44.500	43.455	42.135	41.090	40.260

To extrapolate the Shedlovsky procedure[18] was employed. By a short series of successive approximations

$$S = 1 + z + z^2/2 + z^3/8 \qquad (2)$$

is computed where $z = (\vartheta\Lambda_0 + 2\sigma)(C\Lambda)^{1/2}/\Lambda_0^{3/2}$, and $\vartheta = 8.204 \times 10^5/(DT)^{3/2}$, $\sigma = 41.21/(\eta \cdot (DT)^{1/2})$.[19] For a solvent of dielectric constant[20] 24.3 and viscosity[21] 0.01084 poise, ϑ and σ are thus 1.330 and 44.66. The degree of dissociation x is then given by

$$x = \Lambda S/\Lambda_0 \qquad (3)$$

ΛS is next plotted against $\Lambda^2S^2f^2C$, where f is the limiting law activity coefficient,[19] given by $\log f = -\alpha(xC)^{1/2}$; here $\alpha = 1.8246 \times 10^6/(DT)^{3/2} = 2.9585$. The plots should be linear, with intercept Λ_0 and a slope given by $-1/K\Lambda_0$, where K, the dissociation constant of the ion pairs is defined by

$$K = f^2x^2C/(1 - x) \qquad (4)$$

Table II gives the values of Λ and of ΛS for the three salts (rounded to the nearest 0.005 conductance unit) as well as the corresponding Λ_0 and K, while Fig. 1 shows the Shedlovsky plot of the data, the ordinates for economy of space being $(\Lambda S - \Lambda_0)$. The agreement is satisfactory, the individual points lying in general within 0.02 conductance unit (or better) of the lines as drawn; the only notable exception is for the most concentrated KCl solution where the discrepancy is 0.06 unit.

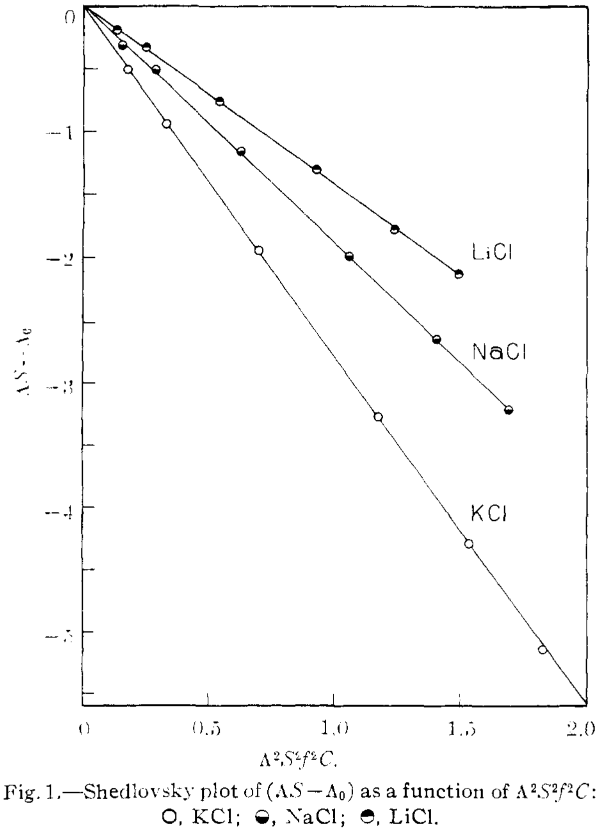

Fig. 1.—Shedlovsky plot of $(\Lambda S - \Lambda_0)$ as a function of $\Lambda^2S^2f^2C$: ○, KCl; ◒, NaCl; ◓, LiCl.

It should perhaps be noted that if Λ be plotted against $C^{1/2}$—a procedure frequently employed in the past, for example by Barak and Hartley[4]—the plot is definitely S-shaped. To take the case of NaCl as an example, a "best" straight line can be drawn representing the experimental data within 0.05 conductance unit or so, but the extrapolated Λ_0 is 42.35, a fifth of a unit in error. The result so obtained, however, agrees probably as closely as can be expected with Barak and Hartley's 42.5, and the slope, 190, is in reasonable agreement with the value, 197, quoted in their Table IV. Nevertheless, one must question the validity of conclusions as to ion-pair formation, etc., based on such a procedure.

TABLE III

LIMITING ION CONDUCTANCES AND CONDUCTANCE-VISCOSITY PRODUCTS AT 25°

	Li^+	Na^+	K^+	Cl^-
$\lambda^0_{\pm}$, C_2H_5OH	17.05	20.31	23.55	21.85
$(\lambda^0_{\pm} \cdot \eta)$, C_2H_5OH	0.185	0.220	0.255	0.237
$(\lambda^0_{\pm} \cdot \eta)$, CH_3OH	.217	.246	.285	.285
$(\lambda^0_{\pm} \cdot \eta)$, H_2O	.346	.448	.658	.683

TABLE IV

LIMITING ION CONDUCTANCE RATIOS

Solvent and temp., °C.	Li^+/Na^+	Na^+/K^+	Na^+/Cl^-	K^+/Cl^-
H_2O, 25	0.772	0.682	0.656	0.963
H_2O, 45	.786	.713	.679	.952
CH_3OH, 25	.881	.863	.863	1.000
C_2H_5OH, 25	.839	.862	.929	1.078

If the values of Λ_0 for NaCl and LiCl be combined with the t^0_- of the preceding paper,[1] one obtains 21.87 and 21.82, respectively, as the limiting conductance for chloride ion. The agreement is not as close as was obtained with methanol as solvent,[5a] but the mean, 21.85, is probably reliable to ±0.02 or 0.03 conductance unit. The corresponding λ^0_+ for the cations are summarized in Table III. Smisko and Dawson[22] have reported a limiting conductance for K^+ of 23.4; this is based on their value of t^0_+ for KCNS of 0.4612 and a Λ_0 for the salt of 50.8, computed by them from Barak and Hartley's data[4] by means of a Shedlovsky extrapolation; their result probably agrees with ours as closely as can be expected in view of the uncertainties of the conductance data they were forced to employ.

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[18] (a) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938); (b) R. M. Fuoss and T. Shedlovsky, This Journal, **71**, 1496 (1949).

[19] G. G. Manov, R. G. Bates, W. J. Hamer and S. F. Acree, *ibid.*, **65**, 1765 (1943).

[20] "Table of the Dielectric Constants of Pure Liquids," Nat. Bureau of Standards Circular No. 514, 1951, p. 8.

[21] H. Goldschmidt and H. Aarflot, *Z. physik. Chem.*, **112**, 371 (1926).

[22] J. Smisko and L. R. Dawson, *J. Phys. Chem.*, **59**, 84 (1955).

Discussion

Table III gives the limiting conductances and the conductance–viscosity products for the four ions.[23] It is at once apparent that while the Walden rule (as might be expected) is not obeyed, the variation in the product on passing from methanol to ethanol is considerably less than on passing from water to methanol, and is moreover not as great for the three cations as for chloride.

In Table IV are the limiting conductance ratios for the ions in water at 25 and 45° and in the two alcohols. It was earlier pointed[5b] out that viscosity effects on passing from one solvent to another should cancel to some extent in the ratio, if the ions compared were of the same sign and charge. A glance at Table IV shows at once, however, that no simple generalization as to the conductance ratio can be made. In all cases, there is an increase in the ratio of the conductance of the slower to the faster cation with rise in temperature, *i.e.*, with decrease in dielectric constant, and the same is true on going from water to methanol. On passing from methanol to ethanol, a solvent of still lower dielectric constant, however, the Na^+/K^+ ratio is unaltered, while that for Li^+/Na^+ actually decreases. Thus there does not seem any obvious dependence of the ratio on solvent dielectric constant, and this of itself would seem to bargain out any purely electrostatic picture of solvent dipole–cation interaction. It is true that the use of the macroscopic dielectric constant[24] as a rough measure of solvent–ion interaction and consequently of the ion size effective in transport is a gross and possibly unjustifiable simplification. A more sophisticated treatment such as that used by Gilkerson[25] in his recent study of the effect of solvent properties, in particular the dipole moment, on the ion-pair dissociation constant, however, does not seem hopeful, since it would involve assumptions as to the local dielectric constant effective in the interaction between the ion and the innermost layer of solvent dipoles. It should also be noted that while there is a definite trend in the ratio Na^+/Cl^-, this is not the case for K^+/Cl^-. If as relatively simple a quantity as the limiting conductance ratio for a pair of noble gas type ions, shows such individualistic behavior with three solvents as closely related as water and the two alcohols, it indicates (we believe) that any satisfactory answer to the problem of ionic mobility as a function of solvent properties is still remote.

Finally, it should be noted, however, that the ion-pair dissociation constants for the three salts lie in the order expected, *i.e.*, the salt with the smallest crystallographic and consequently the largest solvated radius for the cation shows the smallest tendency toward ion-pair formation.

In conclusion, we wish to express our thanks to the National Research Council of Canada for the award of studentships to J. R. G. and G. S. K.

[23] The water and methanol data are from Tables IV and V of ref. 5b; see also Benson and Gordon, *J. Chem. Phys.*, **13**, 473 (1945).

[24] P. Van Rysselberghe and R. M. Fristrom, THIS JOURNAL, **67**, 680 (1945).

[25] W. R. Gilkerson, *J. Chem. Phys.*, **25**, 1199 (1956).

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

Adsorption Kinetics and Electrode Processes

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The kinetics of adsorption on electrodes is studied for substances which are not reduced or oxidized at the electrode. Adsorption rates are derived for the plane electrode with control by semi-infinite linear diffusion, the streaming mercury electrode, and electrodes in stirred solution. Adsorption at the dropping mercury electrode is also considered briefly. To simplify the treatment it is assumed either (a) that the concentration of adsorbate is so low as to allow linearization of the isotherm, or (b) that the concentration of adsorbate is so large as to correspond to full coverage. In the range of concentrations in which the isotherm can be linearized, adsorption with diffusion control is a slow process and the equilibrium surface concentration is reached only after a long time (perhaps 30 min.). This conclusion is verified experimentally by differential capacity measurements for the adsorption of *n*-hexyl alcohol on a hanging mercury drop in 1 *M* potassium nitrate. Conversely, the streaming mercury electrode is essentially free of adsorbate. Implications are discussed for double layer capacity measurements, electrocapillary curves studies, electrochemical kinetics and polarography. Maxima and minima and other features of current–time curves during drop life in polarographic reductions in presence of an adsorbable species are accounted for; and the dependence of limiting currents on the head of mercury is interpreted. Experimental results are given for the reduction of Cu(II) in 0.5 *M* sodium citrate in presence of quinoline. Experimental methods are discussed, and a simple and accurate bridge for differential capacity measurements without isolation transformer is described.

Introduction

The characteristics of electrode processes often are affected by the adsorption of substances not directly involved in the electrode reaction. For instance, the exchange current and the transfer coefficient for the discharge of cadmium ion on cadmium amalgam vary when hexyl alcohol is added to the cadmium ion solution. The partial coverage of the electrode by the adsorbed substance causes an increase in actual current density and a concomitant increase in overvoltage. The variation of kinetic parameters and the increase in actual current density account for the distortion of current–potential curves which results from the addition of an adsorbable species such as a polar organic substance. If the exchange current is large enough, current–potential curves may not be altered because the decrease in the rate of the electrochemical reaction is not sufficient to cause a

[1] Paper presented at the 15th International Congress of Pure and Applied Chemistry, Lisbon, September 9–16, 1956.

[2] Predoctoral fellow 1955–1957.