column then gives the electrocapillary curve of tenth-normal potassium chloride. There are no published data of high precision with which to compare these results.

Discussion of Results

A rather full treatment of the significance of electrocapillary data has been published in another place.[4] The data here presented differ from those already published for *sodium* chloride[4] by only a small amount, the differential capacities of the two chlorides being within 2% of one another at comparable potentials over the range of potentials $E = 0.01$ to 1.2 volts. This great similarity indicates that sodium and potassium ions are hydrated in the double layer, since otherwise their different radii would necessarily be reflected in their capacities. Investigations with other cations now under way also point to this conclusion.

A further interpretation of the data (beyond that given in reference 4) has been attempted, but since it is not the purpose of this paper to present an extensive theoretical treatment of the electrical double layer, this interpretation will be postponed. For the present we shall be content to show, in the following paper, how the differential capacity may be used in conjunction with other data to give a fairly precise value of the potential of the e. c. max.

Acknowledgment.—The author is grateful to the Research Corporation for a Frederick Gardner Cottrell grant of funds in support of this work.

Summary

1. Recent modifications in the author's apparatus for measurement of the capacity of the electrical double layer at a mercury surface in contact with aqueous salt solutions are described.

2. The differential capacity of the electrical double layer, the surface charge density, and the electrocapillary curve of mercury in tenth-normal potassium chloride are presented in tabular form.

AMHERST, MASS. RECEIVED FEBRUARY 23, 1949

[CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE]

The Potential of the Electrocapillary Maximum of Mercury

BY DAVID C. GRAHAME, ROBERT P. LARSEN[1] AND MARILYN A. POTH

The potential of the electrocapillary maximum (e. c. max.) of mercury in contact with aqueous solutions is of the first importance in any theoretical or experimental study of the electrical double layer at such an interface. In addition to its direct thermodynamic significance, it has interest in connection with the kinetic theory of the electrical double layer, and a knowledge of its value is indispensable if one wishes to make full use of the very extensive information provided by studies of the differential capacity of the electrical double layer. In particular, integration of the last-named quantity with respect to potential gives the magnitude of the surface electronic charge except for a constant of integration, which is *zero* if the integration is begun at the potential of the electrocapillary maximum.

To the authors' knowledge there are only four papers on this subject, plus a few incidental measurements of the potential of the e. c. max. to be mentioned later. The first paper of importance in this connection, by Paschen,[2] uses a technique which has not been successful in the hands of later workers (who have found it necessary to remove dissolved oxygen), and it therefore comes as a surprise to find, as a result of the present work, that Paschen's values are very nearly correct. The second paper is by Gouy,[3] whose values of the e. c. max. potential are often quoted, but which the authors now believe to be somewhat in error for reasons explained below. A third paper by Winkel and Siebert,[4] gives value which sometimes agree and sometimes disagree with those of Gouy. The fourth paper, by Erdey-Gruz and Szarvas,[5] is difficult to compare with the others because these authors employed a saturated potassium chloride salt bridge, unlike the rest, and so measured a somewhat different quantity. We have attempted to make the conversion in a few simple cases and find satisfactory agreement with our own results when this is done.

The present authors have measured the potential of the electrocapillary maximum of mercury in tenth-normal potassium chloride and sodium chloride by five more or less independent methods. It is the principal function of this paper to describe these methods and their results.

Principle of Experimental Methods I, II and III

It is desirable to describe first the main principle upon which the first three methods depends. These three methods are really only variants of a single method, but since the least certain measurement is carried out differently in the three variants, we regard them as essentially independent.

Suppose that one knows the differential capacity of the electrical double layer in the solution in

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[1] Present address: Department of Chemistry, Ohio Wesleyan University.

[2] Paschen, *Ann. Physik*, **43**, 568 (1891).

[3] Gouy, *Ann. chim. phys.*, [7] **29**, 145 (1903).

[4] Winkel and Siebert, *Z. Elektrochem.*, **44**, 127 (1938).

[5] Erdey-Gruz and Szarvas, *Z. physik. Chem.*, **A177**, 277 (1936).

question as a function of the potential relative to any convenient reference electrode. Suppose that one now assumes a value of the e. c. max. potential relative to the same electrode. By integrating the differential capacity from the assumed potential of the e. c. max. one obtains the corresponding values of the surface charge density of electrons, as has been done in the preceding paper.[6] A further integration starting from the same point gives the *shape* of the electrocapillary curve, but not the absolute magnitude of the interfacial tension at any point. This latter need not be known for the method we are describing. Results of this second integration are also given in the preceding paper.

A horizontal line drawn through the electrocapillary curve intersects it at two points of equal interfacial tension. The two potentials thus defined will be called isotension potentials. The average (or the sum) of these pairs of potentials will be a constant in the ideal case of an electrocapillary curve symmetrical about a vertical axis. In a typical real case (0.1 *N* potassium chloride) the sum or average changes by about 20% over the experimentally studied portion of the electrocapillary curve.

One can plot the sum of the isotension potentials against any convenient parameter, and as far as the methods we are discussing now are concerned, it would suffice to plot the sum against either one of the two components of the sum. In connection with another method (IV) to be described below, it is desirable to plot the sum against *both* components of the sum, and this has been done in Fig. 1. In Fig. 2 the same calculated points are shown, but in this case only the right-hand branch of the curve has been represented. In Figs. 1 and 2 the solid circles are taken from the electrocapillary curve calculated in the preceding paper.[6] It should be recalled that these points depend upon an assumed value of the potential of the e. c. max.

If one had assumed a value 1 mv. greater, the solid circles would have lain almost exactly 2 mv. above the ones shown and so on. Thus one can compute a *family* of curves, of which only one member is shown, corresponding to various assumed values of the e. c. max. These computations have been made. If the differential capacity measurements were in error by 1% over the range of potentials where such an error would have its greatest effect, an error of about 0.7 mv. would be introduced into the final result. A more likely estimate of the uncertainty arising on this account is ±0.3 mv.

It will be apparent that if one can observe a pair of isotension potentials on a capillary electrometer or otherwise, one can select from the family of curves that member corresponding to the correct value of the e. c. max. Three methods of observing isotension potentials will be described which, taken together with the above curves, constitute what we shall call methods I, II and III.

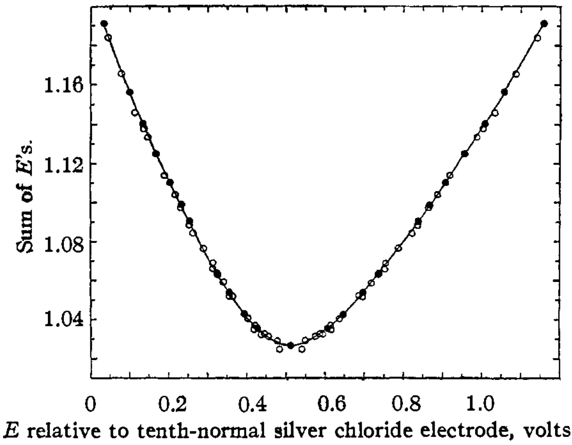

Fig. 1.—Sum of isotension potentials in tenth-normal potassium chloride *vs.* each one singly. Method I. Without the calculated points this figure is also used in method IV. The two lowermost points (really one point plotted twice) are of low accuracy and show how the experimental accuracy deteriorates near the potential of the e. c. max: calculated values, ●; observed by Method I, ○.

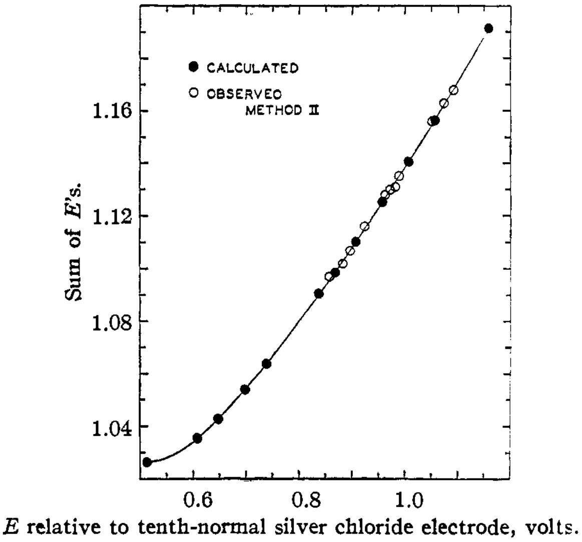

Fig. 2.—Sum of isotension potentials in tenth-normal potassium chloride *vs.* larger value of the pair, method II.

A fourth and fifth method of obtaining the e. c. max. potential are described below.

Experimental Methods

Method I.—We shall describe first the method developed last and considered by us to provide the most reliable results. In this method we determine isotension potentials with a capillary electrometer modeled after that used by Gouy[3] but improved and modified to take advantage of the increased accuracy made possible by the fact

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(6) Grahame, This Journal, 71, 2975 (1949).

that we do not need to measure the height of the mercury column but only to hold it constant. Our instrument is shown in Fig. 3. The solution to be investigated is deaerated either in the reservoir A or in the main body of the cell B. Two electrodes are used, a working electrode C and a primary standard D. In the work to be described in this paper, the latter was silver chloride in tenth-normal potassium chloride, prepared in the manner of Noyes and Ellis.[7] The working electrode was also of this type, except that the electrolyte was whatever chloride happened to be under investigation. By refilling the cell B with tenth-normal potassium chloride, the potential of the working electrode could be compared with that of the primary standard and checked for its proper operation.

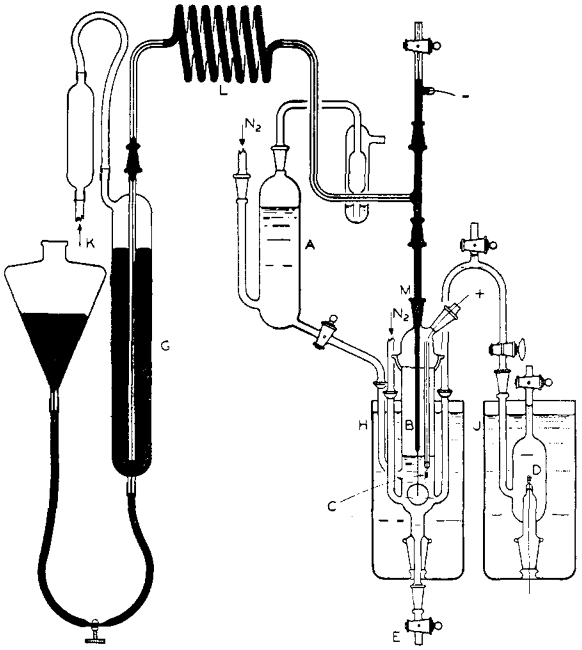

Fig. 3.—Differential capillary electrometer,

The capillary was drawn from Pyrex glass tubing and was approximately 1 mm. o. d. and 0.06 mm. i. d. The stopcock at the bottom of the cell was not greased for most of the measurements reported in this paper, but it was later found that Apiezon L grease could be used without deleterious effect, presumably because it was soon covered by mercury and was not in any case in intimate contact with the solution near the capillary. The ground-glass joints were not greased but were provided with mercury cups (not shown) except in the case of joint M, which was of the feed-through type, and therefore not susceptible to leakage. This construction made it easy to remove the capillary for cleaning whenever that became necessary.

The flexible tubing which connects the leveling bulb to the vertical reservoir was of Tygon tubing (a flexible semi-transparent plastic).[8] The rubber tubing K connects to a mouthpiece which can be used to oscillate the mercury in the capillary in the manner recommended by Gouy.[3] This is an indispensable feature of the apparatus. Two water jackets, H and J, were used to control the temperature of the cells, although temperature control is hardly necessary, since the temperature coefficient of the effect being measured is very small.

The main body of the cell and also the water jacket were provided with windows of optically flat glass. The former was fused into the cell, the latter was held on with picein wax. A cathetometer with a short travel, but with high magnification, made it possible to observe differences in level of the mercury in the capillary of the order of 0.002 mm.

The treatment of the capillary has been given much attention by those who have worked in this and similar fields. We have found it possible and desirable to clean the capillaries in very hot cleaning solution (sulfuric acid + sodium chromate). The subsequent rinsing is done in such a manner as to prevent dust-laden air from being drawn through the capillary. When this was not done, bits of lint lodged in the capillary could be seen under the microscope. It was not necessary to dry the capillary. Sometimes this treatment did not suffice to produce a clean capillary. In these cases a very brief (five seconds) treatment with 50% hydrofluoric acid always sufficed to overcome the difficulty. The enlargement of the capillary was not noticeable, nor was it rendered translucent. This cleaning of the capillary with hydrofluoric acid was sometimes done without removing it from the cell. For this purpose equal parts of 0.2 *N* potassium chloride and 50% hydrofluoric acid were mixed and introduced into the cell in order to avoid "shocking" the silver chloride working electrode. No damage to the cell, the optical flats, the stopcocks or the electrode was noted. Sometimes tenth-normal hydrochloric acid alone would suffice to clean the capillary *in situ* in case it had become contaminated with the hydroxides of the heavy metals when solutions of their chlorides were introduced.

Theoretical considerations indicate that the capillary should be very slightly tapered in order to achieve stability. The sensitivity depends upon the magnitude of the taper. Apparently some taper is always achieved when the capillary is drawn, but the behavior of seemingly identical capillaries might be found to be very different depending upon the amount of taper present.

The glass spiral L is intended to give flexibility to the top piece so that it can be removed and replaced.

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(7) Noyes and Ellis, THIS JOURNAL, **39**, 2532 (1917).

(8) In a later model (not used in the measurements here reported and therefore not represented in the figure) we have eliminated the clamp, which causes incipient cracking of the tubing, by connecting the top of the leveling bulb to the top of the vertical reservoir by another piece of Tygon tubing.

It was found by experiment that the same results were obtained whether the solutions were deaerated or not.[9] Deaeration is desirable as a means of reducing the current flow (and thus protecting the working electrode) when mercury droplets are expelled from the tip. It would also seem to be desirable to prevent the products of the reduction of oxygen from accumulating at the mercury surface where measurements are being taken, but, very surprisingly, no effect traceable to this cause has been observed.

Two calibrated Leeds and Northrup student potentiometers were employed to fix the potential. These were wired in the usual manner and provided with a switch which made it possible to change over rapidly from one to the other. Thus the interfacial tension at two potentials could be the more readily compared. The technique employed in making measurements was as follows: The potential of the mercury in the capillary would be brought to such a value on the descending (cathodic) branch of the electrocapillary curve that the equilibrium position of the mercury would lie approximately one mm. from the tip of the capillary. In order to be sure that the mercury surface was clean, a droplet of mercury would be expelled by blowing gently upon the mouthpiece attached to the rubber tube K. There was usually no difficulty in obtaining reproducible values on this branch of the curve. Another droplet of mercury would then be expelled, and with the mercury flowing, the potential would be switched to a value on the ascending branch thought to have the same interfacial tension. The mercury flow would be arrested by sucking momentarily on the mouthpiece, whereupon the mercury came to its new equilibrium position. If this position was the same as that found at the other potential, the values so found corresponded to the same interfacial tension (isotension potentials). If not, it was found necessary to repeat the measurement at the higher (cathodic) potential before repeating the measurement (with a new potential) on the low side. The reason for this is not clear except that the mercury is apparently not completely freed from capillary-active impurities on the low potential side even after one or more droplets have been expelled. On the high potential side, this is not so. The equilibrium position on the low side usually does not persist for more than five or ten seconds, at best, after which a steady fall of the meniscus attests to the adsorption of impurities from the solution. It is remarkable that the most carefully purified solutions did not differ in this or in any other observable respect from solutions made up from ordinary C.P. salts. The measurements reported in this paper were all carried out with purified solutions, however.

The results obtained by this method for tenth-normal potassium chloride at 25° are shown by the open circles in Fig. 1. They are seen to agree with the calculated curve with an accuracy of ±1 mv., which represents an uncertainty in the e. c. max. potential of not over half a millivolt for any one reading, except near the e. c. max., where the rate of change of interfacial tension with potential is approaching zero, and the accuracy of the measurements is accordingly much diminished. Such points were not taken into account in selecting a "best" fit from the family of curves.

The "best" curve, which is the only one shown, corresponds to an e. c. max. potential of 0.506_0 volt relative to a normal calomel electrode or 0.559_0 volt relative to a tenth-normal calomel electrode or 0.513_6 volt relative to a tenth-normal silver chloride electrode. These values are considered correct within ±0.5 mv.

The method we are here discussing does not give satisfactory results in hundredth-normal solutions of chlorides (the only salts we have tried at this dilution). Not only are the results in disagreement with all curves in the family of curves calculated from the differential capacity, but they are in disagreement with other methods, and also with all reasonable expectation. The difficulty is undoubtedly associated with the fact that the equilibrium position in the capillary is achieved only slowly, by which time the mercury surface could have and generally would have become contaminated. Method V, to be discussed below, is believed to be the best of the five in more dilute solutions.

The only values of the e. c. max. potential to be found in the literature for tenth-normal potassium chloride are two very old values, one by Paschen,[2] who arrives at a result 6 mv. lower than ours, and another by Smith,[10] whose final result is 9 millivolts higher than ours.

Method II.—It was found that when the head of mercury which caused mercury to flow from the capillary tip in the apparatus shown in Fig. 3 was barely sufficient to maintain the flow, a gradual change of the potential toward that of the e. c. max. caused a fairly abrupt cessation of flow. More accurately stated, as the potential was changed, there would appear a point when there was a monentary pause, amounting to perhaps five-tenths of a second at first, between the fall of one droplet and the beginning of the formation of the next. This phenomenon could be observed directly or by watching a galvanometer in series with the capillary.[11] It was suspected that the arrest potential corresponded to a definite interfacial tension, depending upon the

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[9] This is not to be confused with the statement made earlier that the method used by Paschen is generally considered to require deaeration for its successful execution. The method here described differs entirely from that used by Paschen.

[10] Smith, *Phil. Trans. A*, **193**, 47 (1899); quoted by Smith and Moss, *Phil. Mag.*, [6] **15**, 478 (1908).

[11] The galvanometer swings as the mercury droplet begins to flow, even in the absence of air, because of the charging current familiar in polarographic measurements. It swings abruptly back to zero when the mercury droplet falls unless a new droplet immediately begins to form.

head of mercury and the diameter of the capillary, and that two such arrest points on opposite sides of the e. c. max. potential would constitute a pair of isotension potentials. This expectation was tested and found to be valid in tenth-normal solutions. Figure 2 illustrates the kind of agreement obtained. The "best" value is not perceptibly different from that found by method I, although the uncertainty is about twice as great. In more dilute solutions there is some evidence that method II may constitute a more accurate method of estimating isotension potentials than method I.

Method III.—Measurements of drop weight have long been popular as a means of measuring surface tension or interfacial tension. In a modification of this method we have sought pairs of potentials having the same drop *time*. The apparatus is the same. An interval timer accurate to 0.01 sec. is used to measure the drop time. Usually five droplets are counted at each potential setting and a great many sets of values are taken alternately until a pair of potentials with the same drop time is found. One such pair is sufficient to fix the potential of the e. c. max. By this method, taking only one pair, we arrive at a value one millivolt higher than our "best" value quoted above. This method has not been explored to the fullest extent in our laboratory. It is very laborious, but may be advantageous under some circumstances.

Method IV.—All of the above methods demand a knowledge of the differential capacity, which may not be available in some cases. However, one knows that if the data were available, the family of curves would be qualitatively similar to those found for, say, potassium chloride. In particular, it is a necessary consequence of the method of calculation that the curves should have a minimum ordinate at the abscissa of the assumed value of the e. c. max. potential and that this minimum ordinate should be twice the e. c. max. potential. This fact can be understood by remembering that we are plotting twice the abscissa of the diameter of the electrocapillary curve against the abscissas of each of the two points of intersection of a horizontal transversal. Obviously all three abscissas coincide at the e. c. max.

Accordingly it is possible to obtain a fairly good estimate of the potential of the electrocapillary maximum by plotting the isotension potentials as before and interpolating the flat minimum portion without the aid of any theoretical curves, except insofar as one knows that the curve cannot bend sharply at any point. Half the ordinate of the minimum is then taken as the desired value of the e. c. max. potential.

Experience with this method indicates that an accuracy of ± 1 mv. is attainable by a very skillful operator in tenth-normal solutions of chlorides. This method may lead to very large errors, however, if it is not corroborated with independent evidence for at least some of the electrolytes under test. The values here given for tenth-normal potassium chloride can serve for such corroboration in future work. The method cannot be recommended, however, in view of the extreme skill required of the operator and the consequent danger of error in particular cases.

Method V.—This method is not new to this paper. It consists of allowing a stream of mercury to flow into a carefully purified and deaerated solution of the electrolyte under test and measuring its potential relative to some electrode. It has been used by Paschen, Palmaer, Smith and Moss, Erdey-Gruz and Szarvas, and perhaps by others. We have investigated the method thoroughly in this Laboratory and consider it to be the most reliable of the methods available for more dilute solutions than those mentioned in this paper. It can be carried out in the apparatus already described with the following changes: A short jagged fine-tipped capillary is used and arrangements are made for increasing the pressure on the mercury column. This may be done with a compressed gas and a commercial pressure regulator since only very rough control of the pressure is needed. Pressures of from 5 to 20 lb. per sq. in. are generally needed to reach a "plateau" in the readings, and only readings obtained on a good "plateau" may be regarded as valid. Because of the difficulty of removing reducible substances, and perhaps for other reasons of which we are not fully aware, it is not as highly reproducible as the sensitivity of the meter readings suggests. Moreover, in tenth-normal potassium chloride it gives values about 3 mv. lower than the other methods, which we consider the more reliable at this concentration. This amount of error would not be objectionable for many purposes, but it would be desirable to find its source before depending too heavily upon values obtained in this manner.

By the use of method V we find a temperature coefficient of -0.0705 mv./deg. for the potential of the e. c. max. of tenth-normal potassium chloride in the neighborhood of room temperature. This is for the case where the reference electrode (calomel or silver chloride) is in the same solution at the same (variable) temperature.

The results obtained by these five methods are summarized in Table I, along with other results discussed below.

Measurements with Tenth-Normal Sodium Chloride.—For a further check on our methods we have measured the potential of the e.c. max. in tenth-normal *sodium* chloride relative to an electrode in sodium chloride and again relative to an electrode in potassium chloride. This was done because more work has been reported on sodium chloride than on any other electrolyte and because the results have sometimes been reported relative to an electrode in potassium

TABLE I

POTENTIAL OF THE ELECTROCAPILLARY MAXIMUM IN TENTH-NORMAL SODIUM OR POTASSIUM CHLORIDE RELATIVE TO A TENTH-NORMAL CALOMEL ELECTRODE IN THE SAME ELECTROLYTE

Method	Source	Potential, volts NaCl	KCl
I	This work	0.5585	0.5590
II	This work	.562	.559
III	This work	.560	.560
IV	This work	.5585	.5595
V	This work	.558	.556
V	Paschen	.557	.553
V	Erdey-Gruz and Szarvas	.551	
	Gouy	.58	
I	Gouy + this work	.56	
	Smith		.57
V	Palmaer		.573

chloride. No two authors have done exactly the same thing, and in order to make a comparison, we have made the best conversions we could to a single standard. Values given in Table I for tenth-normal sodium chloride are expressed relative to a calomel electrode in the *same* solution.

Except for the value by Gouy, these measurements are in reasonably good accord. Gouy obtained his result by extrapolation of the diameters of the electrocapillary curve, and close examination of his data reveals that the extrapolation was a long one, especially in this case. If one combines his interfacial tension measurements with our differential capacity data as in method I, thus eliminating the extrapolation, the disagreement with our "best" value disappears to within less than the accuracy to which Gouy's values are reported. This corrected value is entered along with the others in Table I.

Acknowledgment.—We are grateful to the Research Corporation for two grants from the Frederick Gardner Cottrell fund in support of this work.

Summary

1. Three techniques are described for the determination of "isotension potentials," pairs of potentials at which the interfacial tension is the same on the two branches of the electrocapillary curve.

2. A method is described for the determination of the potential of the electrocapillary maximum by combining isotension potential data with measurements of the capacity of the electrical double layer.

3. Values of the potential of the e. c. max. in tenth-normal potassium and sodium chlorides are obtained by these three methods and also by two other methods of which one is new. Good agreement is obtained.

4. A value of 0.559_0 volt is obtained for the e. c. max. potential of tenth-normal potassium chloride relative to a tenth-normal calomel electrode, both at 25°.

5. Essentially the same value is obtained for tenth-normal sodium chloride relative to a tenth-normal calomel electrode in sodium chloride. This value is compared with previously published values.

6. A temperature coefficient of −0.0705 mv./deg. is found for the e. c. max. potential in tenth-normal potassium chloride.

AMHERST, MASS. RECEIVED NOVEMBER 29, 1948

[CONTRIBUTION FROM METCALF RESEARCH LABORATORY, BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XLIII. Effect of Ammonia and Water on the Conductance of Lithium, Sodium and Silver Ions in Pyridine at 25°[1]

BY CHARLES J. CARIGNAN[2] AND CHARLES A. KRAUS

I. Introduction

Burgess has shown that the conductance of tetrabutylammonium picrate in pyridine is changed but little on addition of ammonia. The observed effect may be accounted for by the viscosity change of the solvent; the dissociation constant of the salt remains unchanged. However, when ammonia is added to a solution of sodium picrate, the conductance of the salt is greatly increased. In view of the fact that the conductance of the quaternary ammonium picrate remains constant (except for viscosity effect), it may be concluded that the increased conductance of sodium picrate is due to an increase in the conductance of the sodium ion.

It seemed worth while to investigate this phenomenon in somewhat greater detail. Accordingly, we have measured the conductance of lithium picrate at five different concentrations of ammonia, sodium picrate at two concentrations, and sodium iodide and silver nitrate, each at one concentration of ammonia. In addition, we have measured the conductance of sodium picrate at three different concentrations of water.

II. Experimental

1. Materials.—Pyridine was purified according to the procedure of Luder[3] and Burgess[4]

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[1] This paper is based on a portion of a thesis presented by Charles J. Carignan in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University, June, 1947.

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[3] Luder and Kraus, THIS JOURNAL, **69**, 2481 (1947).

[4] Burgess and Kraus, *ibid.*, **70**, 706 (1948).