described. In the *p*H range from 0.8 to 3.0, the reduction occurred in two steps. The first wave, corresponding to reduction to iodate, occurred at a mixed potential. The half-wave potential of the second wave, which corresponded to reduction of iodate to iodide, varied with the *p*H, but it was independent of the drop time and the concentration of periodate.

Gelatin was effective in shifting the half-wave potential of the iodate wave in a manner similar to that exhibited when complexes are formed.

Equations have been derived to express the changes in the iodate half-wave potential due to *p*H and gelatin.

The accuracy of the analytical application of the polarographic reduction of periodate has been mentioned.

STANFORD UNIV., CALIFORNIA RECEIVED JUNE 12, 1948

[CONTRIBUTION FROM EDWARD DAVIES CHEMICAL LABORATORIES, UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH]

The Conductance of Potassium Iodate at 25°, and Comments on the Conductances of Some Salts of Oxyacids

BY C. B. MONK

Conductance measurements on potassium iodate at 25° have been made by several workers; a review and discussion of these has been given by Krieger and Kilpatrick,[1] who report fresh data. A closer examination of their results for the more dilute solutions suggested that a further study of these concentrations might be worth while. Accordingly fresh measurements have been made and the extrapolation method of Owen[2] applied. This method is found to give satisfactory results in certain cases where the method of Shedlovsky[3] fails. Some other reported measurements[4] have been similarly analysed and, using these fresh results, dissociation constants have been calculated by the method of Davies.[5]

Experimental

"AnalaR" grade potassium iodate was purified and dried as described before.[1] A fused quartz conductivity cell was used, the apparatus and technique being similar to that described elsewhere.[6] The cell constant was obtained by measurements on potassium chloride solutions in the concentration range 0.0001 to 0.002 gram equivalent per liter and employing equation (2) in the paper just quoted. This, in effect, is a method of finding cell constants on the Jones and Bradshaw standard[7] for cells used in measurements on very dilute solutions. The thermometer was checked against one recently calibrated at the National Physical Laboratory. Table I contains the data. In this table C is the concentration in gram equivalents per liter, Λ is the conductance of the solution corrected for that of the water,[8] and K is the dissociation constant of the potassium iodate calculated in the manner described below. The conductances, together with those of Krieger and Kilpatrick[1] which cover the same range, are plotted in Fig. 1, against the square root of C.

TABLE I

Run	C	$\sqrt{C}$	Λ	K
a	0.00018265	0.01352	113.07	1.1
a	.00035295	.01879	112.61	2.0
a	.00070430	.02624	111.91	1.9
a	.00099845	.03160	111.45	1.8
b	.0017117	.04137	110.55	1.7
b	.0025362	.05037	109.78	...
b	.0032859	.05732	109.19	...
b	.0039118	.06255	108.78	...

Specific conductance of water, ohm^{-1} × 10^{-7} (a) 2.39, (b) 2.38.

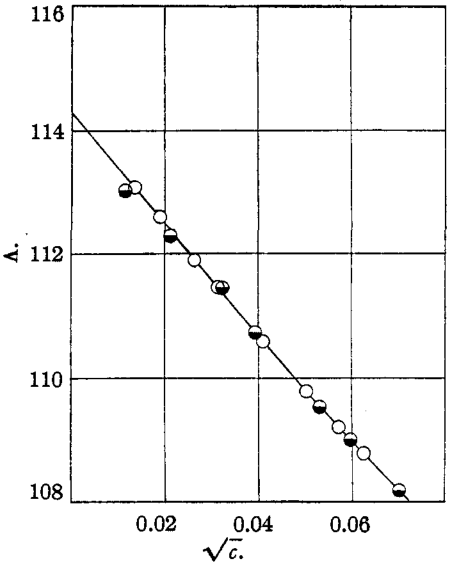

Fig. 1.—Conductivity of potassium iodate: ○, present data; ◒, ref. 1.

Discussion

Examination of the experimental curve in Fig. 1 shows that while excellent agreement is obtained

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(1) Krieger and Kilpatrick, THIS JOURNAL, **64**, 7 (1942).

(2) Owen, *ibid.*, **61**, 1393 (1939).

(3) Shedlovsky, *ibid.*, **55**, 1405 (1932).

(4) (a) J. H. Jones, *ibid.*, **66**, 1115 (1944); (b) **67**, 855 (1945); (c) **68**, 240 (1946); (d) **69**, 2065 (1947).

(5) Davies, *Trans. Faraday Soc.*, **23**, 351 (1927).

(6) Davies, *J. Chem. Soc.*, 432 (1937).

(7) Jones and Bradshaw, THIS JOURNAL, **55**, 1780 (1933).

(8) Davies. "Conductivity of Solutions," Chapman and Hall Ltd., London, p. 72.

between Krieger and Kilpatrick's figures and the present ones at concentrations greater than 0.001, in the more dilute regions the former workers' figures show some scattering. The present figures are consistently higher, and the slope of the line a little steeper than that indicated by the other results. A possible cause of this scattering is the adsorption effect which takes place in weak solutions of potassium iodate. It was noticed that the resistance readings drifted steadily, but that the effect could be overcome by shaking the cell and taking readings very quickly, *i. e.*, within three or four seconds. In this way consistent readings could be obtained irrespective of the extent of the drift which had previously occurred. A borosilicate cell, which was used for a separate run, besides showing this effect, gave readings which showed a very slow but definite increase of resistance with time, although this was negligible above $C = 0.002$. A few other salts have been found to show similar behavior.[9] Krieger and Kilpatrick[1] tried several methods of evaluating Λ_0. The result of plotting Λ against $\sqrt{C}$ was carried out by them with the figures obtained at concentrations less than 0.005. Examination of the present data, however, shows that at concentrations greater than 0.0025 the plot begins to show systematic curvature. A straight line can be drawn through the points at concentrations less than 0.0025, and leads to $\Lambda_0 = 114.3 \pm 0.05$, instead of the quoted value[1] of 113.96.

The second extrapolation method tried by them was that of Shedlovsky,[3] but they found that the plot was not linear, being convex to the C axis. This behavior was noticed by Shedlovsky[3] with some other uni-univalent salts, *e. g.*, potassium nitrate, the chlorates, iodates and thallium salts. He suggested that such salts are not completely dissociated in solution.

A method of extrapolation which was not tried by Krieger and Kilpatrick is that put forward by Owen.[2] This has been found by him to be of value for all salts where the dissociation constant is not less than 0.005, provided concentrations not greater than 0.005 are considered. Where the dissociation constant is larger, a higher limit is set to the concentration which can be taken for extrapolation. Application of this method to the present data gives a Λ_0 value of 114.27. An error of as little as 0.01 unit in the choice of Λ_0 produces distinct curvature at concentrations less than 0.001, so that it is possible to place a reasonable limit of 0.02 unit on the Λ_0 value obtained by this method. This extreme sensitivity has been found to be generally true for other similar salts, such as are discussed below. A consequence of this sensitivity is that any scattering of the measurements is easily apparent. On the basis $\Lambda_0 = 114.27$, and taking the conductance of the potassium ion as 73.52[10] (corrected to the Jones and Bradshaw standard[7]), the conductance of the iodate ion is 40.75 ± 0.02, which is in reasonably good agreement with the value of 40.93 suggested by MacDougall and Davies[11] from the data of Kraus and Parker[12] on iodic acid, and is rather greater than Krieger and Kilpatrick's figure of 40.48 ± 0.05. The limiting slope thus obtained is -89.6. This is slightly greater than the value of -87.29 obtained from the theoretical Onsager equation,[13] which, using the latest available data for the constants[14] involved, becomes, for uni-univalent electrolytes in water at 25°

$$\Lambda = \Lambda_0 - (0.2289\Lambda_0 + 60.14)\sqrt{C}$$

Krieger and Kilpatrick report the figures as -83.88 and -86.42, respectively. An experimental slope that is slightly steeper than the theoretical slope is quite common for uni-univalent salts of oxyanions (see for instance Robinson and Davies[15]; other cases are discussed below). The difference between the theoretical and experimental slopes can be attributed to slight ion-association, and the data can be used to calculate the dissociation constant of potassium iodate. The method of Davies[5] was used, up to the concentrations where the experimental slope begins to show curvature. The figures are shown in Table I, and give an average value of 1.7, which is in good agreement with the figure of 2.0 suggested by Davies.[16]

Calculations on Some Other Salts.—Several series of measurements on the conductances of uni-univalent salts of oxyanions, particularly those of potassium, have been reported in recent volumes of This Journal by Jones.[4] In all cases he found that the Shedlovsky[3] method of extrapolation, when applied to the potassium salts, showed more or less curvature in the dilute regions. Accordingly these results have been recalculated using the Owen[2] method, and dissociation constants calculated from those points which are not too scattered, and which lie on the linear part of the $\Lambda - \sqrt{C}$ curve.

Potassium Bromate.[4a]—Λ_0 obtained $= 129.36 \pm 0.03$, giving 55.84 ± 0.03 for the bromate ion, in good agreement with the figure of 55.78 ± 0.05 obtained by Jones.[4a] Dissociation constants calculated from the second, third, fourth and fifth most dilute points, respectively, are 2.7, 5.5, 4.4, 4.4, averaging 4.0.

Potassium Perchlorate.[4b]—Λ_0 obtained $= 140.83 \pm 0.03$, giving 67.31 ± 0.03 for the perchlorate ion, in very close agreement with the figure of 67.32 ± 0.06 obtained by Jones. Dis-

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[9] Hartley and Donaldson, *Trans. Faraday Soc.*, **33**, 467 (1937); Swift, This Journal, **60**, 728 (1938); J. C. James, Thesis, London University, 1947.

[10] MacInnes, Shedlovsky and Longsworth, This Journal, **54**, 2758 (1932).

[11] MacDougall and Davies, *J. Chem. Soc.*, 1417 (1935).

[12] Kraus and Parker, This Journal, **61**, 2429 (1922).

[13] Onsager, *Physik. Z.*, **27**, 388 (1926); **28**, 277 (1927).

[14] Birge, *Rev. Mod. Phys.*, **13**, 233 (1941).

[15] Robinson and Davies, *J. Chem. Soc.*, 574 (1937).

[16] Davies, *J. Chem. Soc.*, 2410 (1930).

sociation constants from the second, fourth, fifth, and sixth most dilute points are, respectively, 1.7, 2.9, 4.0 and 3.3, averaging 3.0.

Potassium Metaperiodate.[4c]—Λ_0 obtained = 128.05 ± 0.02, giving 54.53 ± 0.02 for the metaperiodate ion. This is somewhat higher than the value of 54.38 given by Jones. Dissociation constants from the third, fourth and fifth most dilute points are, respectively, 0.55, 0.56 and 0.59, averaging 0.57.

Potassium Perrhenate.—[4c]Λ_0 obtained = 128.47 ± 0.02, giving 54.95 ± 0.02 for the perrhenate ion, again somewhat higher than the quoted value of 54.68. Dissociation constants from the four most dilute points are 0.15, 0.17, 0.21 and 0.23, respectively, averaging 0.19.

Silver Chlorate.[4d]—Λ_0 obtained = 126.50 ± 0.02, giving 64.58 ± 0.02 for the chlorate ion (based on 61.92 for the silver ion,[10] corrected to the standard of Jones and Bradshaw[7]); this is somewhat lower than the quoted value of 64.65. Dissociation constants calculated from the first, second and fourth most dilute points are 0.54, 0.57 and 0.71, respectively, averaging 0.6.

Summary

The conductance of potassium iodate has been measured over the range 0.0002 to 0.004 molar at 25°. The Owen method[2] of extrapolation has been found to be satisfactory in this and some other cases where the Shedlovsky method[3] fails. The dissociation constants of this and some other salts are reported. From the results the following anion conductances are evaluated: iodate = 40.75, bromate = 55.84, perchlorate = 67.31, metaperiodate = 54.53, perrhenate = 54.95 and chlorate = 64.58, all within 0.02 to 0.03 unit. The following dissociation constants were obtained using the method of Davies[5]: potassium iodate = 1.7, potassium bromate = 4.0, potassium perchlorate = 3.0, potassium metaperiodate = 0.57, potassium perrhenate = 0.19 and silver chlorate = 0.6.

ABERYSTWYTH, WALES RECEIVED MAY 25, 1948

[CONTRIBUTION FROM GULF RESEARCH & DEVELOPMENT COMPANY]

Influence of Solvent, Hydrogen Bonding, Temperature and Conjugation on the Ultraviolet Spectra of Phenols and Aromatic Hydrocarbons[1]

BY NORMAN D. COGGESHALL AND ELEANOR M. LANG[1a]

It is well known that for some ultraviolet absorbing compounds the absorption spectra are dependent on the nature of the solvents used. For example, the spectrum obtained from a simple phenol in a paraffin solvent will be considerably different for that obtained with ethyl alcohol as the solvent. For the latter the spectrum is changed in shape from the former and shifted to the red. This phenomenon is quite general among the polar substituted aromatics.

It has been assumed that highly polar structures make a greater contribution to the excited than to the ground states of such compounds as polar substituted aromatics.[2] From this it follows that any factors which stabilize these structures will decrease the energy of transition and shift the absorption bands to longer wave lengths. The shifts to longer wave lengths that occur for such compounds when examined in a polar solvent as compared to similar data obtained for a neutral solvent may then be explained on this basis.

The present investigation was concerned with some of the factors expected to be effective in stabilizing the excited polar structures. Such stabilization would result from electrostatic or dipole interaction of the hydrogen bonding type, between the ionic structure of the excited state of the solute molecule and the polar component of the solvent molecule. Recent studies, by infrared absorption, of steric hindrance to hydrogen bonding in substituted phenols[3] furnish useful information for the correlation of these spectral shifts with the known hydrogen bonding characteristics of the phenols. It was shown from the infrared data that large alkyl groups such as *t*-butyl on one or both the ortho positions of a phenol are effective in hindering inter-molecular hydrogen bonding. These studies gave a classification of phenols into three classes: hindered, partially hindered, and unhindered. The same series of phenols were studied in this investigation.

Errera and Sack[4] found that the population of intermolecular complexes between ethyl alcohol and dioxane in a carbon tetrachloride solution is very strongly reduced by a change in temperature from 20 to 55°. From the infrared spectral changes it is believed that the energy per complex for association between a phenol and an alcohol solvent will be of the same order of magnitude as for the type of complex studied by Errera and Sack. Consequently, the ultraviolet spectra of the phenols in alcohol solution as a function of temperature should clarify the role of stable com-

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(1) Presented in part before the Division of Physical Chemistry at the 112th American Chemical Society meeting, New York, September, 1947.

(1a) Now at Camp Detrick, Frederick, Maryland.

(2) C. Curran, Paper P6, American Chemical Society meeting, Chicago, September, 1946.

(3) N. D. Coggeshall, THIS JOURNAL, **69**, 1620 (1947).

(4) J. Errera and H. Sack, *Trans. Faraday Soc.*, **34**, 728 (1938).