Since the equilibrium constants for the two solutions are evidently equal, the concentration of bromine in solution 1 can be calculated. Applying this correction to equations (2) and (3), a better value for x and hence for the degree of dissociation can be calculated.

Mean value of the degree of dissociation obtained from the data given in Table I was 5.9% with the average deviation of 1.5%. This figure is somewhat lower than the one given by Yost, *et al.*,[1] but is of the same order of magnitude.

Due to the fact that the dissociation is small, and does not increase with dilution, and that at no wave length bromine or iodine absorb strongly while the remaining species absorb very little, one is forced to analyze for small quantities as differences of large quantities. It is thus quite difficult to decrease the experimental error.

Acknowledgment.—The authors wish to express their appreciation to Dr. Harold Boaz for helpful discussions on this problem.

IOWA CITY, IOWA RECEIVED JULY 13, 1950

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

Electrical Conductance and Viscosity in the System Tetra-*n*-butylammonium Picrate–*n*-Butyl Alcohol at 91°

BY RALPH P. SEWARD

Densities, viscosities and conductances have been measured over the whole range of composition in the homogeneous liquid system tetra-*n*-butylammonium picrate–*n*-butyl alcohol at 91°. The limiting equivalent conductance has been evaluated. The product of the limiting equivalent conductance and viscosity is shown to be substantially equal to the equivalent conductance–viscosity product for the pure salt. At low concentrations the salt behaves like a weak electrolyte but appears to become a strong electrolyte at high salt concentrations.

Although the nature of dilute solutions of electrolytes in many solvents has been studied in a multitude of investigations, solutions of non-electrolytes in fused salts have been little explored. The high melting points of most salts, making experimental work more difficult, and perhaps a feeling that such solutions are intrinsically more complex, seems to account for their being neglected. In view of the lack of information in this field it was thought worth while to measure the electrical conductance in a binary system consisting of a non-electrolyte and a salt, over the whole range from zero to one hundred per cent. salt at a constant temperature. The results of the investigation are presented below.

The salt chosen was tetra-*n*-butylammonium picrate, because it is easily prepared and melts at about 90°. The non-electrolyte, *n*-butyl alcohol, was chosen on the basis of its showing complete miscibility with the salt and its relatively low volatility at the melting point of the salt. The temperature, 91°, was chosen as being just above the melting point. Viscosities in the system were measured since the viscosity is a major factor in determining electrical conductance. Densities were measured because they were required in calculating the viscosities and the equivalent conductances. Conductance measurements were made on a series of dilute solutions of the picrate in butanol in order to establish the limiting conductance and the nature of the salt in dilute solution.

Experimental

Tetra-*n*-butyl picrate was prepared by neutralization of aqueous tetra-*n*-butylammonium hydroxide with picric acid, recrystallization of the picrate several times from methanol, and drying at about 50°. Its m.p. was 89.4°.

A reagent grade of *n*-butyl alcohol was refluxed several hours with lime and distilled through a column equivalent to about six theoretical plates. Material boiling at 117.3–117.5° was used. Its specific conductance was 3.0×10^{-7} mho at 91°. Measurement of densities, viscosities and conductances were made in an oil filled constant temperature bath held at 91°. Although no effort was made to obtain an absolute value for the temperature to this accuracy, the temperature was held constant to ±0.02°. The various mixtures were made up by weight. The densities were determined with a Westphal balance. The viscosities were measured in Cannon and Fenske[1] type viscometers.

The conductances were measured in a cell, Fig. 1, of Pyrex glass with a mixing chamber of about 25-ml. capacity connected to a smaller chamber containing the electrodes into which the solutions were drawn for the resistance measurements. Solutions were made by adding known weights of material directly into the apparatus. The electrodes were platinized. The cell constant was determined with 0.015 *N* KCl at 25° as 2.00. It was assumed that no change in cell constant within the expected precision occurred on operation at 91°. For the dilute solutions (below 0.008 molar), a Freas type cell (Central Scientific Co. No. 70004) was used, having a cell constant of 0.356.

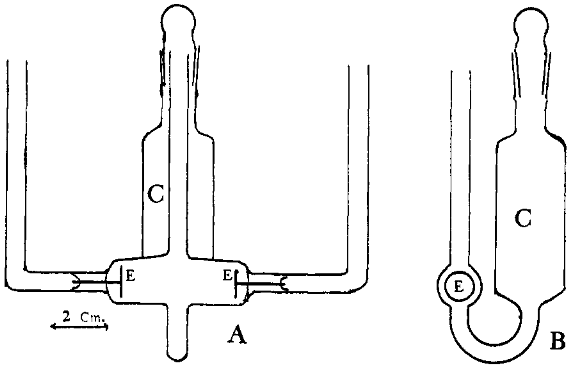

Fig. 1.—Conductance cells, A front, B side, E electrodes, C mixing chamber.

Resistances were measured with the use of an oscillator of variable frequency, a Leeds and Northrup Campbell-Shakelton ratio box, shielded a.c. resistance box and amplifier. An adjustable capacitance was connected in parallel with the resistance box.

Results

The density and viscosity measurements are shown in Table I; the viscosity is in poises, density

[1] M. R. Cannon and M. R. Fenske, *Ind. Eng. Chem., Anal. Ed.*, **10**, 297 (1938).

in g./ml. and composition in weight per cent. tetrabutyl picrate.

TABLE I

VISCOSITY AND DENSITY IN THE SYSTEM *n*-BUTYL ALCOHOL–TETRA-*n*-BUTYLAMMONIUM PICRATE AT 91°

% picrate	$\eta \times 10^3$	d
0.00	6.09	0.758
11.39	8.11	.790
25.14	11.55	.838
41.29	19.33	.894
61.47	37.0	.949
75.23	74.3	1.014
86.41	146.3	1.050
93.36	268	1.076
97.72	403	1.093
100.0	581	1.105

The viscosities and densities employed in treating the conductance data were obtained by interpolation from plots of the viscosities and densities of Table I against weight composition. The conductance data are shown in Table II; κ the specific and Λ the equivalent conductance in mho, c the concentration of picrate in moles per liter solution.

For the dilute solutions of the salt in butyl alcohol the data shown in Table III were obtained.

Comparison with published data is possible only for the pure salt. Walden and Birr[2] give 1.105 for the density and 0.001803 for the specific conductance at 90° which seem in reasonable agreement.

Discussion

Inspection of Table II shows that with increasing salt content the specific conductance rises to a maximum at about 60% salt and then falls, finally reaching a value for the pure salt which is roughly one-fifth of the value at the maximum.

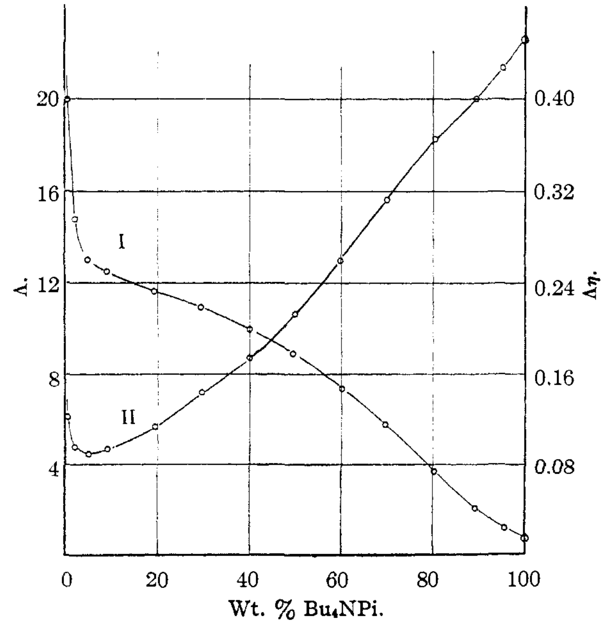

Fig. 2.—Electrical conductance in the system tetra-*n*-butylammonium picrate–*n*-butyl alcohol at 91°: I, equivalent conductance; II, conductance–viscosity product.

TABLE II

ELECTRICAL CONDUCTANCE IN THE SYSTEM *n*-BUTYL ALCOHOL–TETRA-*n*-BUTYLAMMONIUM PICRATE AT 91°

Wt. % picrate	c	$\kappa \times 10^3$	Λ	$\Lambda\eta$
0.000	0.000	0.000	71.5	435
0.50	.008	0.162	20.08	127
2.09	.034	0.501	14.77	94.7
5.04	.083	1.078	13.03	92.1
9.11	.152	1.892	12.50	95.0
19.13	.334	3.914	11.71	114.6
29.60	.538	5.917	10.99	143
39.81	.751	7.518	10.00	175
49.69	.975	8.680	8.90	217
60.31	1.230	9.007	7.32	252
69.70	1.471	8.463	5.75	314
80.75	1.773	6.622	3.74	366
89.42	2.022	4.357	2.15	400
96.26	2.226	2.721	1.22	427
100	2.342	1.821	0.778	452

TABLE III

THE CONDUCTANCE OF DILUTE SOLUTIONS OF TETRA-*n*-BUTYLAMMONIUM PICRATE IN *n*-BUTYL ALCOHOL AT 91°

$c \times 10^4$	80.72	40.00	19.78	9.768	4.801	2.351	1.145
Λ	19.81	24.07	29.47	35.85	42.84	50.35	56.61

Figure 2 shows the equivalent conductance as a function of weight composition. There is an initial rapid decrease followed by a more gradual decrease to the pure salt. Although there is evidence of incomplete dissociation, the minimum and maximum found by Strong and Kraus[3] for similar electrolytes in benzene do not appear. Presumably the higher dielectric constant of the alcohol and higher temperature account for the difference.

Since the low conductances observed at high salt concentrations must reflect the effect of greatly increased viscosity, the products of conductance and viscosity, which should represent a measure of conductance compensated for this effect, were calculated and plotted in Fig. 2. This curve shows a minimum at about 5% salt, followed by increasing values all the way to the pure salt. Although it is conceded that the conductance viscosity product is not quantitatively a measure of the number of current carrying particles, it does suggest that the number of free ions reaches a minimum in the neighborhood of 5% salt (0.083 molar).

Only in dilute salt solutions do we have adequate theories to explain conductance. In order to establish the nature of dilute solutions of the tetra-*n*-butyl ammonium picrate, a plot of Λ *versus* the square root of the concentration was made. It showed no evidence of approaching linearity and its slope was always much greater than the Debye–Onsager theoretical slope. When the conductances were treated by the method of Fuoss[4] for incompletely dissociated electrolytes, a very good linear plot was obtained. The value of 9.8 was taken as the dielectric constant of butyl alcohol[5] at 91°. From this plot values of 71.5

---

[2] P. Walden and E. J. Birr, *Z. physik. Chem.*, **A160**, 50 (1932).

[3] L. E. Strong and C. A. Kraus, THIS JOURNAL, **72**, 166 (1950).

[4] R. M. Fuoss, *ibid.*, **57**, 488 (1935).

[5] C. P. Smyth and W. N. Stoops, *ibid.*, **51**, 3318 (1929).

for the limiting conductance and of 3.2×10^{-4} for the dissociation constant were obtained. Since the specific conductance of the solvent, which was subtracted, amounted to 5% of the total conductance in the most dilute solution, these numerical values may not be very accurate. However, the treatment did indicate that the salt was not completely dissociated in dilute solution. Furthermore, the product of limiting conductance and viscosity, 0.435, is substantially equal to the conductance–viscosity product of the pure salt, 0.452. Walden[3] has shown that this agreement is quite general, but this is the first demonstration of it where the dilute solution and the fused salt have been treated at the same temperature. Mead and Fuoss[6] report a value of 0.4508 for the limiting conductance–viscosity product of tetra-*n*-butylammonium picrate in ethylene chloride (*D* 10.23) at 25°.

The data appear to indicate that tetra-*n*-butylammonium picrate is a weak electrolyte when at low concentrations in butyl alcohol but that it becomes a strong electrolyte at high concentrations. Extension of the experiments, with variation of both components, is planned.

[6] D. J. Mead with R. M. Fuoss, THIS JOURNAL, **61**, 2051 (1939).

STATE COLLEGE, PA. RECEIVED AUGUST 21, 1950

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF WISCONSIN]

Moving Boundary Systems Formed by Weak Electrolytes. Study of Cadmium Iodide Complexes[1]

BY ROBERT A. ALBERTY AND EDWARD L. KING

It has been shown that the moving boundary method may be used to study complex ion equilibria. The constituent mobility of cadmium has been determined at 0° over a range of iodide concentrations from 0.003 to 0.4 *N*. The constituent mobility of iodide in a solution containing 0.010 mole/liter of iodide has been determined over a range of cadmium concentration of 0.03 to 0.07 mole/liter. The equilibrium constants for the formation of the complexes CdI^+, CdI_2, CdI_3^- and $CdI_4^{=}$ have been calculated from these data.

Numerous types of experimental data indicate that cadmium iodide in aqueous solution is not a strong electrolyte. Studies of the transference number of cadmium in solutions of cadmium iodide carried out by both the Hittorf method[2] and the differential moving boundary method[3] indicate that the cation transference number of cadmium decreases with increasing concentration, becoming negative at a concentration of 0.25 mole/liter. The activity coefficient of this substance is very low, even in relatively dilute solution.[4] The existence in solutions of cadmium iodide of species with some covalent bond character is demonstrated by the Raman lines which are observed.[5] Various complex species of cadmium and iodide have been proposed to explain the observed phenomena; it appears likely that all of the species, Cd^{++}, CdI^+, CdI_2, CdI_3^- and $CdI_4^{=}$, are present in solutions containing cadmium ion and iodide ion.[6]

It appears worthwhile to study, by the moving boundary method, solutions containing cadmium and iodide ions. The data are mainly of interest in connection with recent studies of weak electrolyte moving boundary systems[7] and are also of value in the further elucidation of the complex ion equilibria which exist in solutions containing cadmium and iodide. Svensson, Benjaminsson and Brattsten[8] have shown that the ionization constants of amino acids may be determined from moving boundary experiments with solutions of different *p*H.

As pointed out by Longsworth[3] it is doubtful if the direct moving boundary method could be applied to solutions of cadmium iodide owing to the difficulty of finding sufficiently slow indicator ions. In the present study the mobility of the cadmium and iodide constituents have been determined by means of moving boundary systems similar to those used in the electrophoresis of proteins, *e. g.*, a cadmium salt is dissolved in an electrolyte which extends throughout the U-tube. This method has the advantage that it is unnecessary to find an indicator electrolyte and the ratio of iodide concentration to cadmium concentration may be varied over a wide range.

It will be assumed provisionally that all of the species Cd^{++}, CdI^+, CdI_2, CdI_3^-, $CdI_4^{=}$ exist. The equilibria which are established very rapidly in solution are

$$Cd^{++} + nI^- \rightleftarrows CdI_n^{+2-n} \qquad n = 1, 2, 3, 4 \quad (1)$$

for which the corresponding concentration equilibrium constants are

$$K_n = (CdI_n^{+2-n})/(Cd^{++})(I^-)^n \quad n = 1, 2, 3, 4 \quad (2)$$

The moving boundary experiments in which cadmium disappears across the boundary lead to a direct evaluation of the cadmium constituent mobility.[7] This is the average mobility of the cadmium in solution and is given by the equation

$$\bar{u}_{Cd} = \frac{(Cd^{++})u_0 + (CdI^+)u_1 + (CdI_2)u_2 + (CdI_3^-)u_3 + (CdI_4^{=})u_4}{(Cd^{++}) + (CdI^+) + (CdI_2) + (CdI_3^-) + (CdI_4^{=})} \quad (3)$$

---

[1] Presented at the Chicago Meeting of the American Chemical Society, September, 1950.

[2] Redlich and Bukschnewski, *Z. physik. Chem.*, **37**, 673 (1901).

[3] Longsworth, THIS JOURNAL, **65**, 1755 (1943).

[4] Robinson and Wilson, *Trans. Faraday Soc.*, **36**, 738 (1940); Bates and Vosburgh, THIS JOURNAL, **59**, 1583 (1937).

[5] Delwaulle, Francois and Wiemann, *Compt. rend.*, **208**, 184 (1939).

[6] Leden, *Z. physik. Chem.*, **188A**, 160 (1941).

[7] Svensson, *Acta Chem. Scand.*, **2**, 855 (1948); Alberty and Nichol, THIS JOURNAL, **70**, 2297 (1948); Brattsten and Svensson, *Acta Chem. Scand.*, **3**, 359 (1949); Alberty, THIS JOURNAL, **72**, 2361 (1950); Nichol, *ibid.*, **72**, 2367 (1950).

[8] Svensson, Benjaminsson and Brattsten, *Acta Chem. Scand.*, **3**, 307 (1949).