557. *The Conductivity of Potassium Chloride in Mixed Solvents.*

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The conductivities of potassium chloride in mixtures of water with dioxan, acetone, or *iso*propanol as solvent have been determined. Theoretical and experimental Onsager slopes have been compared for the different dielectric constants. At dielectric constants above 60, the experimental Onsager slopes approach the theoretical slopes from above, whereas at dielectric constants below 50—60, the reverse occurs, suggesting that, at dielectric constants of this order, the onset of ion association first becomes apparent. The conductivities of solutions of constant electrolytic concentration were plotted against the dielectric constant. The results are considered from the point of view of solvation and the change in dielectric constant.

A new type of cell is described, together with a high-sensitivity detector and oscillator unit. A modified Jones and Joseph's bridge was employed.

IN recent years conductance measurements of many electrolytes in mixed solvents have been reported. Variations of conductance in these media have been accounted for satisfactorily by Bjerrum's ion-pair treatment, on a basis of variation of dissociation constants with change in the dielectric constant. Apart from the work of James (*J.*, 1950, 1094; 1951, 153, 2925), the majority of measurements appear to have been made with large ions, where no definite " solvent effect " has been encountered, as those large ions have presumably no solvation sheath. Comparative measurements employing different solvent media do not appear to have been carried out. In the present investigation, a simple uni-univalent electrolyte (potassium chloride) was used in three mixed solvents. The choice of dioxan, acetone, and *iso*propanol was determined by the desire to differentiate between the effect of dielectric-constant lowering and that due to the specific effect of the non-aqueous additions.

EXPERIMENTAL

The Bridge.—The Wagner ground was connected as suggested by Luder (*J. Amer. Chem. Soc.*, 1940, **62**, 89) to a modified Jones and Joseph's bridge (*ibid.*, 1928, **50**, 1049). The bridge components were shielded, and all the leads were screened, including those from the detector. In order to eliminate possible sources of eddy currents, the screening was connected to a common earth. The Wagner ground was fixed for given values of the ratio arms, resetting being unnecessary.

Detector.—The majority of detectors lack sensitivity at the higher resistance ranges, and since high resistances were being measured, a detector unit of the visual indicator type was used (Fig. 1). After amplification, by use of a high-gain valve V_1 (6J7), the signal was rectified, and fed to the grid of V_2 (6J5), which formed one arm of a direct-current bridge. Stability was improved by employing negative feed-back, the second arm of the bridge being used as the feedback resistance. Input to the amplifier was transformer-coupled. This enabled the detector to have a common chassis with that of the oscillator. A sensitivity potentiometer controlled the gain of the detector when the bridge was off balance. Zero control regulated the setting of the galvanometer needle on a suitable part of the scale. At maximum sensitivity the galvanometer needle indicated a variation of 1 ohm in 300,000.

Oscillator.—An oscillator (Fig. 2) capable of producing a good sinusoidal wave at the selected frequency was assembled from standard components. It was of the true Wien bridge type, consisting of a two-valve amplifier with feed-back through a resistance–capacitance network. This provided a rapid change of phase with frequency, giving positive feed-back, and hence causing oscillations at a fixed frequency. The frequency was varied from 300 to 5000 cycles per sec., by altering the resistance–capacitance network on five ranges. Negative feed-back was provided through a thermistor to give a pure sinusoidal wave-form. The oscillator was coupled to a small-power valve (6F6) operated as a cathode follower, the output being taken from the cathode through a potentiometer and transformer.

Conductivity Cell.—Jones and Bollinger (*J. Amer. Chem. Soc.*, 1931, **53**, **411**) indicated that the Parker effect (Parker, *ibid.*, 1923, **45**, 1366, 2017) can be eliminated by arranging the contact arms and the filling tubes of the cell as far apart as possible. The cell (Fig. 3) was intended to reduce this error still more, by employing only one filling tube. It could be used outside the cell, shorter leads to the bridge being then possible. Quick emptying and filling of the cell was facilitated. The cell was of Pyrex glass. The electrodes, 5 cm. apart, were backed with glass, and sealed into the walls, contact being made to the bridge through mercury cups.

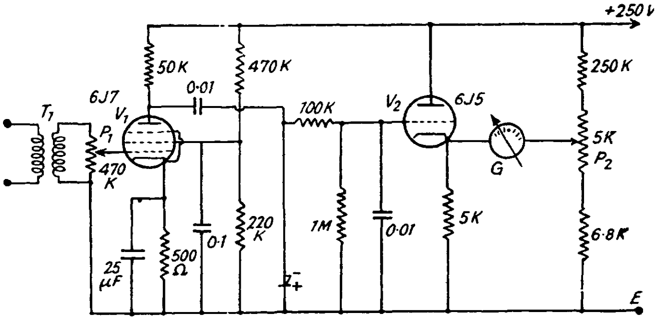


FIG. 1. *Circuit diagram of detector unit.*

T_1. Intervalve transformer (3 : 1).
P_1. Sensitivity control.
P_2. Zero-set potentiometer.

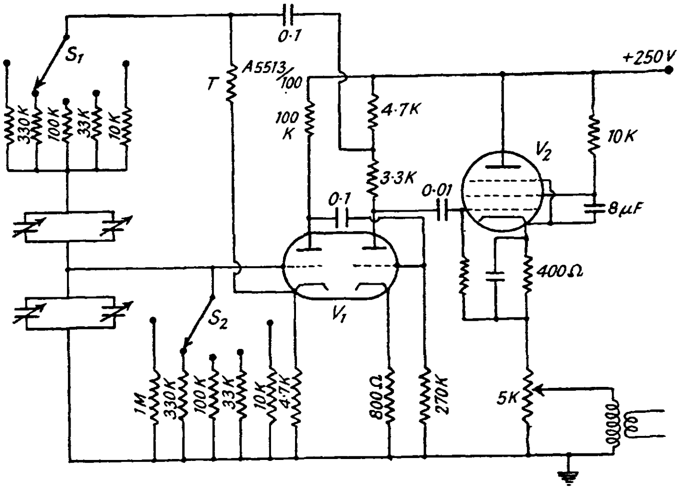
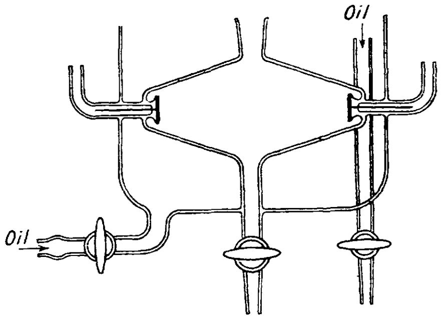


FIG. 2.

V_1. 6SN7.
V_2. 6F6.
T. Thermistor A5513/100.

The resistance and capacitance, shown to the right of V_1, are 270K and 25μF, respectively.

FIG. 3.



Surrounding the cell was a jacket through which oil was circulated from a thermostatic reservoir, by means of a rotary pump. The temperature of the solution in the cell was read directly from a thermometer, the presence of which in the cell did not interfere with the resistance of the solution being measured. Blacked electrodes were used in all measurements.

Thermostat.—This was of standard design, and a high-grade paraffin served as the thermostatic liquid. Measurements were made at 25° ± 0·05°. The thermostat was in operation continually, but when measurements were not actually being recorded, the stirring motor was switched in parallel with the heater.

Purification of Solvents and Solute.—Conductivity water. Water used in all measurements was prepared from a Pyrex still by fractional distillation in a counter-current of pure nitrogen (Vogel and Jeffrey, *J.*, 1931, 1201). The water was stored in well-seasoned flasks under nitrogen, and had a specific conductance of not more than $0{\cdot}5 \times 10^{-6}$ mho cm.$^{-1}$.

Dioxan. Commercial 1 : 4-dioxan was purified by Vogel's method (" Practical Organic Chemistry," Longmans Green and Co., London, 1948, p. 175). Physical constants are here compared with literature values (Ibert Mellan, " Industrial Solvents," Reinhold Publ. Corp., New York, 1950, 2nd edn. p. 674); given in parentheses : b. p. 101·5°/760 mm. (101·3°/760 mm.), n_D^{20} 1·4220 (1·4221), d_{20}^{20} 1·0482 (1·0356), κ—(2×10^{-8} mho).

Acetone. " AnalaR " acetone was refluxed over anhydrous copper sulphate, kept for 24 hr. over fresh anhydrous copper sulphate, and fractionally distilled. Its physical constants are compared here with literature values (*op. cit.*, p. 589) : b. p. 56·1°/760 mm. (56·1°/760 mm.), n_D^{20} 1·3590 (1·3584), d_{20}^{20} 0·7971 (0·790—0·793), κ—(6×10^{-8} mho).

iso*Propanol.* A batch of *iso*propanol was kept over freshly fired quicklime for 48 hr. and then fractionated. Distillate of b. p. 82—84° was further distilled from sodium at 82·4°. The constants are here compared with recorded values (*op. cit.*, p. 476) : b. p. 82·4°/759 mm. (82·4°/760 mm.), n_D^{20} 1·3778 (1·3776), d_{20}^{20} 0·7875 (0·7874), κ—$3{\cdot}5 \times 10^{-7}$ mho).

Potassium chloride. A stock sample of " AnalaR " salt was crystallised twice from freshly distilled water, and twice from conductivity water. It was then heated to dull redness in a platinum crucible, powdered, and kept in a thermostatic oven at 180° for 2 days. After spectroscopic examination, the stock was stored in a desiccator.

Determination of Cell Constant.—Shedlovsky's equivalent conductance data (*Trans. Electrochem. Soc.*, 1937, **66**, 165) and those of Davies (*J.*, 1937, 432) were used to calculate the cell constant, over a range of potassium chloride concentrations.

Conductivity Measurements in Mixed Solvents.—The determination of the conductance of the various solvents was followed immediately by conductance measurements with potassium chloride as the electrolyte. The results are tabulated, the equivalent conductance being corrected for that of the solvent. No difficulties were experienced in measurements with water–acetone and water–*iso*propanol, but during the water–dioxan measurements, fluctuations arose which were attributed to the formation of air bubbles.

Dielectric-constant data are taken from Akerlöf (*J. Amer. Chem. Soc.*, 1932, **54**, 4125) and Wyman and Ingalls (*ibid.*, 1936, **58**, 1241), and viscosity data are due to Geddes (*ibid.*, 1933, **55**, 4832) and Owen and Waters (*ibid.*, 1938, **60**, 2371). Viscosity measurements of *iso*propanol–water mixtures, carried out with a constant-pressure Ostwald viscometer, agreed with Whitman and Hurst's data (*ibid.*, 1930, **52**, 4766). The conductances of the pure solvents were not taken, but the literature values appear under physical constants for each solvent.

DISCUSSION

Conductivity data for potassium chloride in mixed solvents appear in Tables 1, 2, and 3. The dielectric constants of these media were chosen (by varying the concentrations of the non-aqueous additions) such that they were of comparable values. In Figs. 4, 5, and 6, both experimental and theoretical Onsager slopes have been obtained by using the equation for uni-univalent electrolytes as simplified to

$$\Lambda_0 - \Lambda = \sqrt{c}\left[\frac{158{\cdot}34}{D^{\frac{3}{2}}}\Lambda_0 + \frac{2{\cdot}3706}{D^{\frac{1}{2}}\eta}\right]$$

This use of the equation presupposes that the non-aqueous additions introduce no alteration in the mobilities other than those accounted for by changes in dielectric constant and viscosity. The values of Λ_0 have been obtained from large-scale plots of Λ against the square-root of the electrolyte concentration. Onsager (*Physikal. Z.*, 1927, **28**, 277) pointed out that completely dissociated electrolytes should approach the limiting slope asymptotically from above, whereas incompletely dissociated electrolytes should approach from below. At dielectric constants within the range of 50—60, it has been experimentally established that ion-association occurs, which is in agreement with Bjerrum's treatment (*Chem. Reviews*, 1935, **17**, 227). However, the dielectric-constant value at which ion-association occurs, varies in each medium.

In Fig. 7, the curves of equivalent conductances against the dielectric constant for each solvent medium exhibit a characteristic limiting slope. *iso*Propanol–water solvents cause most depression of the equivalent conductance (with respect to water as solvent), and dioxan–water solvents least, acetone–water being intermediate in value. Davies and Monk (*J.*, 1951, 2719), investigating the dissociation constants of silver acetate against changing dielectric constant, also found variations which were attributed to the nature of the solvent, and suggested that the effect may be explained by supposing that water molecules are being replaced in the solvation sheath of the ion by the organic solvent molecules. The latter workers report that, where silver acetate was used as the electrolyte, Walden's product, $\Lambda_0\eta$ remained approximately constant.

FIG. 4. *Dioxan–water media.*

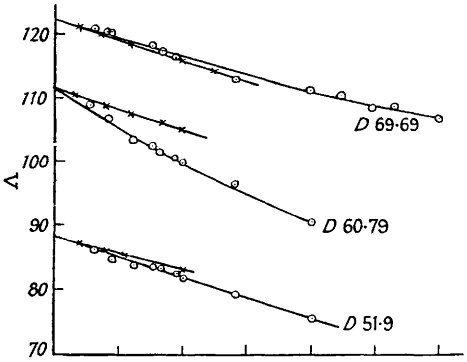
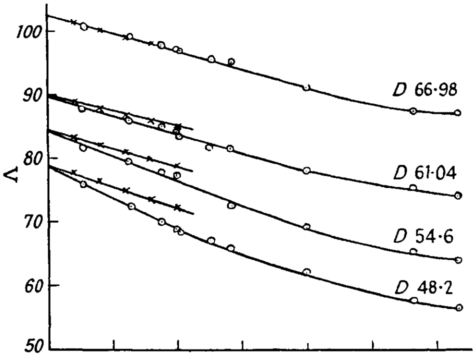
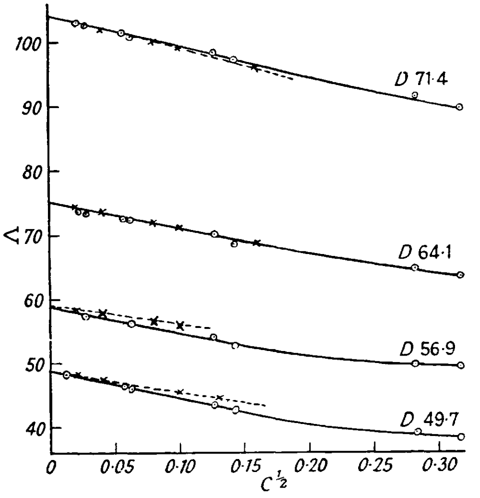


FIG. 5. *Acetone–water media.*



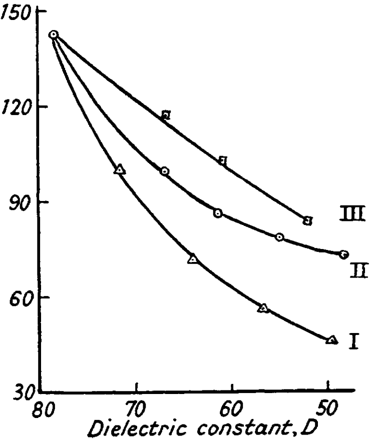
○ Experimental. × Theoretical (Onsager slopes).

FIG. 6. iso*Propanol–water media.*



○ Experimental.
× Theoretical (Onsager slopes).

FIG. 7. *Plot of equivalent conductance against dielectric constant* (0·004N-KCl *solution*).



I. *iso*Propanol–water.
II. Acetone–water.
III. Dioxan–water.

In this investigation, with the lower concentrations of non-aqueous additions, the values of $\Lambda_0\eta$ approximate to that of water, as solvent medium, but with higher non-aqueous concentrations $\Lambda_0\eta$ shows considerable variations. Values of Λ_0, η, and $\Lambda_0\eta$ are tabulated in Table 4. According to Stokes's law, an electric force XZe acting on a spherical ion of radius r, would maintain it at a velocity $v = XZe/6\pi\eta r$, where η is the viscosity of the medium. If it is assumed that a solvated ion moves as a single entity under an applied potential, then Stokes's law will give a direct measure of the primary solvation sheath

(Bockris, *Quart. Reviews*, 1949, **3**, 173). The variation of $\Lambda_0\eta$ in the different media can then be accounted for by a change in the ionic radius (caused by a change in the solvation sheath) which introduces a change in the velocity of the ion in different media. This can only occur by the organic solvent entering the solvation sheath, which is Debye's " salting effect " (Debye and McAulay, *Physikal. Z.*, 1925, **26**, 22). When an electrolyte is dissolved in a mixture of water and an organic solvent, the ions (particularly the cation) preferentially solvate water molecules (Shaw and Butler, *Proc. Roy. Soc.*, 1930, *A*, **129**, 519; Bockris and Egan, *Trans. Faraday Soc.*, 1948, **44**, 151).

TABLE 1. iso*Propanol–water media.*

	10%	20%	30%	40%
$10^6\kappa$, mho	1·657	1·13	0·92	0·74
D	71·4	64·1	56·9	49·7
Concn., N	Λ	Λ	Λ	Λ
0·10	89·53	63·30	49·19	38·22
0·08	91·25	64·53	49·44	39·27
0·02	96·89	67·86	52·77	42·91
0·016	98·10	69·82	54·10	43·69
0·004	100·39	71·91	56·11	45·61
0·0032	101·44	72·15	55·98	46·74
0·0008	102·33	73·02	57·05	—
0·00064	102·72	73·51	—	—
0·00016	—	—	—	48·47

TABLE 2. *Acetone–water media.*

	20%	30%	40%	50%
$10^6\kappa$, mho	1·92	1·76	1·65	0·74
D	66·98	61·04	54·6	48·2
Concn., N	Λ	Λ	Λ	Λ
0·1	87·09	74·16	64·11	56·47
0·08	87·39	75·66	65·23	57·90
0·04	91·05	78·01	69·30	62·04
0·02	95·20	81·97	72·72	66·08
0·016	95·50	81·63	77·04	67·17
0·012	96·97	83·24	—	68·62
0·01	97·11	84·48	77·14	68·89
0·008	97·89	85·00	77·92	70·00
0·004	99·01	85·99	79·43	72·87
0·0008	100·85	87·97	81·87	75·96

TABLE 3. *Dioxan–water media.*

	10%	20%	30%
$10^6\kappa$, mho	3·82	1·52	1·42
D	69·69	60·79	51·9
Concn., N	Λ	Λ	Λ
0·09	107·08	—	—
0·07	109·07	—	—
0·06	108·82	—	—
0·05	110·85	—	—
0·04	111·14	90·81	75·42
0·02	112·91	96·52	79·12
0·01	—	99·95	81·92
0·009	116·11	100·67	82·23
0·007	117·10	101·43	83·01
0·006	118·46	102·53	83·47
0·004	117·03	103·14	83·78
0·002	120·27	107·57	84·45
0·001	121·0	109·95	86·71

TABLE 4.

Solvent	Λ_0	$10^3\eta$	$\Lambda_0\eta$
Water	149·86	8·949	1·34
10% $C_4H_8O_2$	122·40	10·9	1·33
20%	111·11	12·9	1·43
30%	88·21	14·3	1·26
20% $COMe_2$	102·14	13·15	1·34
30%	90·0	13·60	1·22
40%	84·32	13·34	1·13
50%	78·92	12·30	0·97
Water	149·86	8·949	1·34
10% Pr^iOH	103·81	12·84	1·34
20%	75·22	18·47	1·38
30%	59·00	23·71	1·43
40%	48·91	27·95	1·37

Fig. 7 shows that there is less tendency for the dioxan–water curve than for the curve of the other two solvent media to pass through a minimum. Dioxan, owing to its low dipole moment and large molecular size, is less capable of entering the solvation sheaths of the ions, even at higher dioxan concentrations. This would account for the low solubility of potassium chloride in 40% dioxan. With acetone–water and *iso*propanol–water media, however, there is a tendency for inversion of the slopes over the range studied. This would suggest that, at higher concentrations of the non-aqueous solvent, both organic solvents enter the solvation sheath. Over the concentration range studied (as long as the non-aqueous additions are small) the dielectric-constant lowering is predominant, suggesting that hydration is little disturbed. However, with more non-aqueous solvent present, the latter enters into the solvation sheath, owing to decrease of dielectric constant.

As the dielectric constant of water is changed by non-aqueous additions, it is, unfortunately, accompanied by specific changes in the nature of the solvent. A quantitative treatment of the specific solvent effects due to organic solvent additions depends on (i) a more complete knowledge of the dielectric constant decrement, especially in the vicinity of an ion, (ii) organic solvent–water interactions, especially hydrogen bonding, and (iii) the solvation of ions in mixed solvents, which may lead to a diminution of mobility due to the reduction of potential of a central ion by dipole interaction with the solvation sheath. It is of interest that dioxan raises the relaxation time of water by a large factor, but hydrogen ions equally well raise the time (Magat, *J. Chem. Phys.*, 1948, **49**, 93); it is, however, impossible to generalise for other non-aqueous solvents.

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