Conductimetric Studies in Ketonic Solvents. Part I. Acetone as Solvent.

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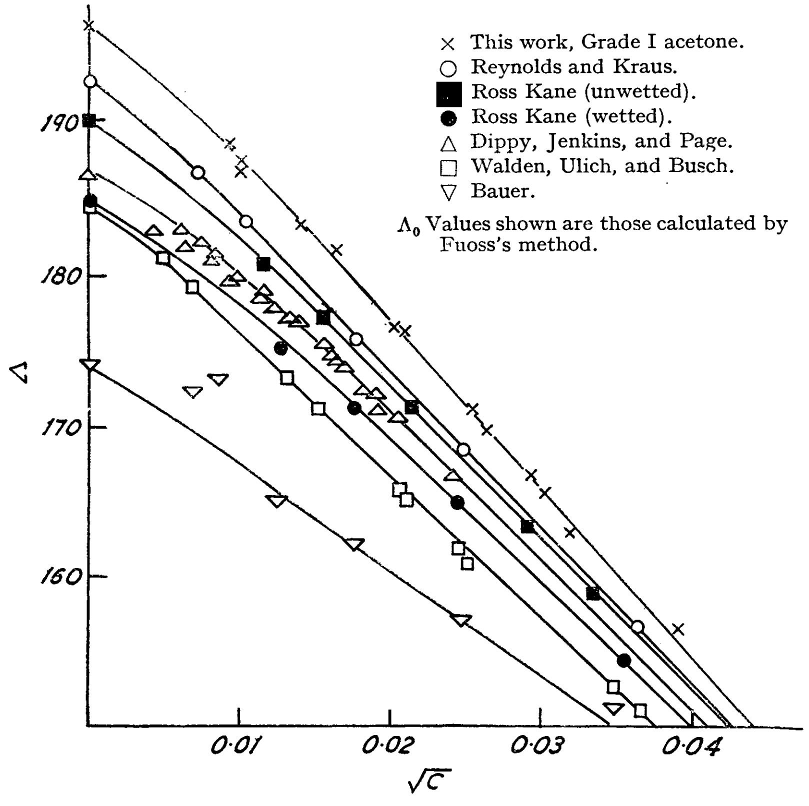
The literature reveals instances of serious lack of agreement in conductivity data for uni-univalent salts in acetone and these may be largely attributable to the variable water content of the specimens of solvent; this view is elaborated by an examination of the data relating to potassium iodide solutions. For some data Bjerrum's and Stokes's equations have been combined to allow estimates of the ionic radii of the solute to be made. It appears that, although a moderate total solvent correction is permissible, yet for valid conclusions to be reached from a comparison of conductivity data for acetone solutions, large divergence in solvent quality must be avoided.

Between 1926 and 1948 no less than six papers [Walden, Ulich, and Busch, *Z. physikal. Chem.*, 1926, **123**, 429; Bauer, *Ann. Physik*, 1930, **6**, 253; Hartley and Hughes (Ross Kane), *Phil. Mag.*, 1933, **15**, 610; Blokker, *Rec. Trav. chim.*, 1935, **54**, 975; Dippy, Jenkins, and Page, *J.*, 1939, 1386; Reynolds and Kraus, *J. Amer. Chem. Soc.*, 1948, **70**, 1709] have recorded the equivalent conductivity of potassium iodide in acetone at 25° as a function of concentration (see Fig.). The highest conductivities are due to Reynolds and Kraus, who claimed that their materials were of superior quality, in particular the solvent, for which new physical data were advanced. These authors deplore the use of a non-aqueous solvent of such a quality as to require a solvent correction; as their acetone had a specific conductance of 1—2 × 10^{-9} mho they seemed entitled to make this criticism, although all previous work (*loc. cit.*) had employed moderate total solvent corrections, for acetone whose conductance



Λ_0 Values shown are those calculated by Fuoss's method.

varied between 10^{-7} and 10^{-8} mho, with some apparent success. A further examination of this question has now been undertaken with special reference to potassium iodide (a solute common to the data of most workers) in acetone of different qualities, referred to as Grades I, II, and III.

Grade I acetone was prepared in an attempt to reproduce Reynolds and Kraus's data (*loc. cit.*), although their purification procedure (*viz.*, agitation with anhydrous calcium chloride followed by two distillations from activated alumina) was modified so as to use the alumina more effectively and to safeguard the product from atmospheric contamination. Nevertheless, our lowest specific conductance was 8×10^{-9} mho, and in no case after standing at 25° was a value less than $1{\cdot}5 \times 10^{-8}$ mho recorded. As, however, consistent values of Λ_{KI} were found with independent batches of solvent whose specific conductances ranged from $2{\cdot}09 \times 10^{-8}$ to $2{\cdot}36 \times 10^{-8}$ mho, it is considered that there is no serious objection to a moderate total solvent correction.

It is difficult to see why solvent and solute conductance should not be additive unless the former could be traced to some weak electrolyte showing an altogether phenomenal salt effect in the solvent of low dielectric constant. Furthermore, the uncorrected Λ values of most other authors remain below those of Reynolds and Kraus by amounts totally inexplicable on such a basis. The equivalent conductivities measured by us for potassium iodide in Grade I acetone (right-hand columns, Table 1) are, on the other hand, higher than those of any other workers. Determination of the densities of three samples of this acetone gave the smallest value hitherto recorded, *viz.*, 0·7840 ± 0·0001 (vacuum corrected) at 25° (cf. other values in Table 2).

TABLE 1. *The equivalent conductivities of potassium iodide in acetone of different qualities at* 25°.

Grade III acetone By Fuoss plot : $\Lambda_0 = 181{\cdot}8$; $K = 24{\cdot}2 \times 10^{-3}$			Grade II acetone By Fuoss plot : $\Lambda_0 = 188{\cdot}7$; $K = 12{\cdot}96 \times 10^{-3}$			Grade I acetone By Fuoss plot : $\Lambda_0 = 196{\cdot}6$; $K = 9{\cdot}13 \times 10^{-3}$		
$10^7\kappa$ (Solvent), mho	10^4C *	Λ corr.	$10^7\kappa$ (Solvent), mho	10^4C *	Λ corr.	$10^7\kappa$ (Solvent), mho	10^4C *	Λ corr.
1·6	0·1812	180·2	1·34	0·2909	184·7	0·236	0·8704	188·8
1·6	0·3040	180·1	1·34	0·6220	182·5	0·209	1·007	186·9
3·4	2·747	169·9	1·69	0·6348	183·8	0·213	1·055	187·7
2·9	3·863	166·6	1·34	0·8742	181·3	0·210	1·953	183·3
2·9	8·381	158·7	0·88	1·221	179·1	0·236	2·675	181·7
3·0	11·79	155·3	1·34	1·336	179·8	0·210	4·124	176·6
3·0	18·78	148·1	0·88	1·380	178·7	0·236	4·317	176·4
3·0	30·87 †	143·2	1·65	1·618	177·9	0·236	6·495	171·1
3·4	38·95 †	135·9	1·34	1·778	178·5	0·210	6·950	169·8
2·9	83·92 †	115·9	0·88	2·970	175·0	0·236	8·555	166·8
			0·88	5·321	169·4	0·210	9·189	165·6
			0·88	8·206	163·7	0·236	10·186	162·9
						0·236	15·370	156·7

* Concentrations, C, are in mole litre^{-1}.

† These concentrations are greater than the Fuoss critical concentration for acetone and are omitted in the calculation of Λ_0 and K.

Solvents having higher specific conductivities (Grades II and III) were obtained by drying acetone with anhydrous calcium chloride and anhydrous potassium carbonate, respectively, before fractionation, and had conductances of $0{\cdot}88$—$1{\cdot}69 \times 10^{-7}$ mho and $1{\cdot}6$—$3{\cdot}4 \times 10^{-7}$ mho. The equivalent conductivities of potassium iodide in solvents of Grades II and III are also set out in Table 1 ; those for Grade II resemble the data of Dippy, Jenkins, and Page, and those for Grade II the data of Walden, Ulich, and Busch. It is significant that within these moderate ranges of varying solvent conductance a total solvent correction gives self-consistent results for each grade.

EXPERIMENTAL

Measurement of Conductivity.—In essentials, the bridge network was based on the Jones and Josephs bridge (*J. Amer. Chem. Soc.*, 1928, **50**, 1067). The current was applied to the bridge from the push-pull outputs of the distant oscillator by means of two 5000-ohm potentiometers in series, with their junction earthed. The ratio arms of the bridge consisted of two 1000-ohm non-inductively wound resistances. The variable resistance arm consisted of two high-quality calibrated, low-inductance resistance boxes, one a single decade box of total resistance 1,000,000 ohms which was shorted out when not required, and the other a six-decade box having a total resistance of 111,111 ohms, adjustable to 0·1 ohm; two six-decade boxes were available for comparison. Variable capacitances of from 0·000025 μF to 0·02 μF could be applied across the resistance boxes or the conductivity cell, and also between earth and either end of the bridge, in each case by means of a variable 0·0005 μF air condenser and two banks of fixed mica condensers on decade switches. The method of obtaining balance was the same as described by Jones and Josephs.

The oscillator consisted essentially of two valves forming a resistance-capacity oscillator in which the frequency was determined by a Wien bridge network, the controlling element being a thermistor. Provision was made for coarse frequency control by means of switched condensers and for fine frequency control by means of a ganged wire-wound potentiometer. The output was fed into a pair of anode-follower valves, arranged to give a push-pull output. The high value of negative feedback in the output stages and the control exerted by the thermistor resulted in a highly stable, pure sine-wave and an extremely low hum level. The oscillator was set at 1000 cycles per sec. throughout this work.

The amplifier consisted of three pentodes, across the second of which could be switched a parallel T-filter. Negative feedback was then applied to the second valve at all frequencies other than that to which the filter was tuned. The output of the third pentode was fed to the grids of a double triode which gave an output on the headphones and on a cathode-ray tuning indicator. A signal of 0·1 microvolt could be detected in the headphones.

The cell employed in connection with acetone of Grades II and III was similar to that described by Dippy, Jenkins, and Page (*loc. cit.*), whereas a cell of the Erlenmeyer type, similar to that described by Reynolds and Kraus, having greyed platinum electrodes 1 cm. apart, was used for Grade I acetone. The cell constants were measured by the intermediate cell method, using a directly calibrated cell (constant 0·25926) also with greyed electrodes. Calibration with intermediate potassium chloride solutions of concentrations from M/500 to M/50,000 showed a constant ratio of cell constants as did series-parallel measurements with the two cells. The basic cell-constant was determined by using " AnalaR " potassium chloride (twice recrystallized from conductivity water and fused in a platinum dish) weighed on a microbalance and dissolved in " equilibrium " conductivity water of $\kappa = 0{\cdot}8 \times 10^{-6}$ mho. Jones and Prendergast's conductance data (*J. Amer. Chem. Soc.*, 1937, **59**, 731) were employed.

Materials and Solvent.—All acetone was initially of " AnalaR " quality, the dates of purchase being Grade III, 1947–48; Grade II, 1949–51; Grade I, 1951–53. The quality of these products as judged by distillation behaviour and conductivity, improved steadily over this period. After the drying treatment appropriate to the particular grade, acetone was fractionated in an all-glass still having a 20″ column packed with glass rings. Distillation was finely controlled by means of a regulated Thermomantle heater. Anhydrous potassium carbonate and calcium chloride, of reagent standard, were oven-dried at 140° before use. The alumina used for preparation of Grade I solvent was Spence's Type A (Harshaw's AL 4, as used by Reynolds and Kraus, was found to have no different effect). " AnalaR " potassium iodide was recrystallized twice from conductivity water, dried at 120°, and stored in a vacuum-desiccator.

In the preparation of Grade I acetone, Reynolds and Kraus's procedure (*loc. cit.*) was modified. " AnalaR " acetone, after being shaken over calcium chloride for 4 days, was filtered rapidly into a Pyrex flask containing fresh, cold alumina which had been baked out at 120°. After its contents had gently refluxed for 2—3 hr., the flask was closed whilst hot, and left in the dark for 7—10 days, after which, rapid filtration on to fresh alumina, refluxing, and standing were repeated. Before final fractionation, the acetone was filtered rapidly into the distillation flask previously baked out.

The receiving end of the still was encased in a " dry-space " consisting of a 12″ cubical Perspex box, constructed in part by Visijar Ltd. (Croydon), closed by a triple-beaded lid at one side to give an air-tight fit. The adaptor of the still, drilled above the nozzle to avoid spraying, was luted into the roof of this box. Manipulation within the dry-space was performed through surgical gloves let into one side, and renewed at regular intervals. A current of dry air was circulated in the box so as to maintain a continuous positive pressure. Distillation receivers, including the conductivity cell, and weighed stoppered tubes of solute were arranged on a tray resting on the floor of the box, which could be rotated to bring the objects into reach.

Conductivity Procedure.—Work in acetone of Grades II and III followed precisely the technique of Dippy, Jenkins, and Page (*loc. cit.*) but specialized procedure was needed in the case of Grade I acetone by reason of its extreme sensitivity to contamination. The cell was washed with distilled acetone, drained, and then conditioned in the dry-space for 30—40 min. before being capped. After being weighed, it was returned to the dry-space for 20—30 min. before receiving the appropriate middle fractions from the still (this was normally some 350 g. of acetone collected from two distillations). It was re-capped, left for *ca.* 30 min., and withdrawn for re-weighing, and the solvent conductivity then measured at 25° over a period of 1 hr.; a calibrated megohm shunt was used for the highest solvent resistance measurements. The cell (after its outside wall had been washed with distilled acetone) was returned to the dry-space together with sealed, weighed micro-tubes containing finely powdered potassium iodide. After 30 min. the cell was uncapped, and the contents of one or more of the micro-tubes added to it. The cell (re-capped) was placed in the thermostat (controlled within 0·005° by adjustment of the threshold heating) and the micro-tubes were re-weighed on a microbalance. The salt had dissolved after 1 hr. and the conductivity of the solution was then followed for a further hour.

The bottle used in the density determinations was manipulated within the dry-space (for Grade I acetone) and calibration was effected with conductivity water at 25°. All weighings were vacuum-corrected.

Karl Fischer Titrations.—The modified Karl Fischer reagent, for use with ketones, as specified by Mitchell and Smith (" Aquametry," Interscience Publ., 1948), was used in a burette protected from moisture. Titrations took place in a 175-c.c. conical flask fitted with an electromagnetic stirrer and sealed-in platinum electrodes which indicated the end-point potentiometrically by iodide depolarization; the flask was supplied with dry air during the titration. Calibration of the reagent was effected by means of Grade I acetone to which weight additions of conductivity water were made.

DISCUSSION

Owing to considerable association of salts in solvents of low dielectric constant, Onsager's expression takes the form

$$\Lambda = \alpha(\Lambda_0 - S_\Lambda\sqrt{\alpha C})$$

to which conductivity data may be fitted by Fuoss's procedure (*J. Amer. Chem. Soc.*, 1935, **57**, 489) to give consistent values of Λ_0 and the coulombic dissociation constant K. The equation provides for curvature of the Λ–$\sqrt{C}$ function in the low concentration region, although, with the exception of Hughes and Hartley (*loc. cit.*) and of Dippy, Jenkins, and Page (*loc. cit.*), few authors have noted this region and only in the latter case has extrapolation to Λ_0 been obtained through it. Before 1948 all data for the conductivity of potassium iodide in acetone were presented in the traditional Kohlrausch manner, and Λ_0 values obtained by simple linear extrapolation. With the exception of Dippy, Jenkins, and Page, all such authors obtained Λ_0 values which were some 1% high.

In order to compare the data of previous authors with those of Reynolds and Kraus, and with those reported here, it has been necessary to recalculate them after Fuoss's method. The outcome of this analysis is summarized in Table 2, which also includes

TABLE 2.

Authors	d_4^{25}	$10^3\eta_0^{25}$	Λ_0 (Fuoss)	Λ_0 (Kohlrausch)	10^3K
This work (Grade I)	0·7840	—	196·6	199·0	9·13
Reynolds and Kraus [1]	0·7845	3·040	192·8	194·5	8·02
Ross Kane (" unwetted " solvent) [2]	0·7850	3·075	190·1	192·1	11·93
Dippy, Jenkins, and Page [3]	—	—	186·8	186·0	18·6
Ross Kane (" wetted " solvent) [2] ...	0·7874	3·14	185·0	187·1	16·3
Walden, Ulich, and Busch	0·7862	3·158	184·4	185·6	9·30
Bauer [4]	0·79	—	173·9	176·0	29·7

[1] These workers analyzed their data by Fuoss's method, although it is interesting that their six points lie on a straight line both in this and in the Kohlrausch plot. The solvent correction could be neglected.

[2] Data, without details, released by Hartley and Hughes (*loc. cit.*). A solvent correction of $1{\cdot}8 \times 10^{-8}$ mho is employed throughout for the " unwetted " acetone. In this analysis, a dielectric constant of 20·88 was taken for the " wetted " acetone (0·769% added water).

[3] These authors, employing somewhat variable solvent corrections, publish 26 points, a feature absent from earlier work. The comparison between the Fuoss and Kohlrausch values of Λ_0 shows the extent to which the low-concentration data are consistent.

[4] This author's data are scanty and scattered. The density figure is mentioned in connection with a mathematical discussion and may not be experimental although it agrees markedly with his value for Λ_0.

density and viscosity data. Blokker's results (*loc. cit.*) have no place in this table as only one point (at 25°) is below the Fuoss critical concentration for acetone. This, however, lies very close to those obtained here for Grade I acetone and, had our density been employed, would have shown even greater agreement. It is noteworthy that Blokker's solvent was free from traces of methanol, and was intensively dried over calcium chloride before fractionation.

The data of Table 2, coupled with those derived from Table 1, reveal a trend which strongly suggests that the variable factor in these solvent grades is the water content. The effect of water on acetone solutions of potassium iodide has already been shown (Hughes and Hartley, *loc. cit.*) to be a preferential solvation of the potassium ion, increasing its effective radius. Such a factor, apart from reducing the value of Λ_0, should enhance the degree of dissociation of the salt in a medium of given dielectric constant, by reason of the reduced surface field of the cation. Examination of Table 2 shows this to be broadly the case.

Separate Stokes radii for the potassium and iodide ions may be derived in the cases of Reynolds and Kraus (who determined ion conductances by the method of Fowler and Kraus (*J. Amer. Chem. Soc.*, 1940, **62**, 2237) and of Walden, Ulich, and Busch, to whose measurements, presumably, the ion conductances of Ulich and Birr (*Z. angew. Chem.*, 1928, **41**, 443) relate. The sum of these is compared in Table 3 with the total ionic radii calculated from Bjerrum's expression (*Kgl. Danske Videnskab. Selsk.*, 1926, **7**, No. 9) for coulombic dissociation in dielectric media :

$$\log Q\ (b) = 3 \log D - (\log K + 6{\cdot}120)$$

and

$$\log (r_+ + r_-) = -(\log b + \log D + 5{\cdot}254)$$

TABLE 3.

	Stokes radii (Å)			Bjerrum sum (Å)
	r_{K^+}	r_{I^-}	$r_{K^+} + r_{I^-}$	$r_{K^+} + r_{I^-}$
Walden, Ulich, and Busch	3·67	2·23	5·90	5·70
Reynolds and Kraus	3·33	2·39	5·72	5·19

This comparison shows that there is no great incompatibility between radii given by Stokes's law and those obtained from Bjerrum's theory. On combining $\Sigma(1/r_i)$ (Stokes) with Σr_i (Bjerrum) a quadratic in r_i is obtained which, provided $(\Sigma r_i)^2 > 4\Sigma r_i/\Sigma(1/r_i)$, may be solved to give two unequal roots identifiable severally with r_{K^+} and r_{I^-}. The results of this analysis are shown in Table 4. In the case of Reynolds and Kraus, the roots are unreal, so their Stokes radii are given instead, in parentheses.

TABLE 4

	$10^{-8}\Sigma(1/r_i)$, cm.$^{-1}$ (Stokes)	$10^8\Sigma r_i$, cm. (Bjerrum)	r_{K^+}, Å	r_{I^-}, Å
This work, Grade I	0·7336	5·63	3·27	2·36
Reynolds and Kraus	0·7194	5·19	(3·33)	(2·39)
Ross Kane, " unwetted "	0·7174	6·79	4·84	1·96
This work, Grade II	0·7136	7·17	5·26	1·91
Dippy, Jenkins, and Page	0·7063	8·79	7·02	1·77
Ross Kane, " wetted "	0·7131	8·24	6·44	1·79
Walden, Ulich, and Busch	0·7153	5·70	3·48	2·22
This work, Grade III	0·7052	9·78	8·06	1·72
Bauer	0·6745	10·45	8·66	1·79

The iodide radius may be taken as relatively independent of solvent quality, whereas that of the potassium ion is more than doubled over the whole range of reported data. No special criticism of Reynolds and Kraus is implied by the failure of their data to conform to this analysis.

In order still further to test the view that variable water content has hitherto been the cause of discrepancies between conductivity data in acetone, the water impurity in our solvents was estimated by the modified Karl Fischer technique (see Experimental). This analysis was performed on samples of bulked Grade I acetone of known density, portions of which were used for a control experiment in which the equivalent conductivity of potassium iodide at 10^{-4} M-concentration was determined. Similar analyses were conducted upon two further specimens of bulked Grade I acetone (referred to as I*a*) to which additions of water had been made by weight. The following table relates water content to the other relevant data.

Source	Total wt. % of H_2O based on K. Fischer anlysis	d_4^{25}	Λ_{KI} at $c = 10^{-4}$
Grade I	0·18	0·7840	188·0
,, I*a*	0·22	0·7841	187·5
Reynolds and Kraus	—	0·7845	184·0
Ross Kane, " unwetted "	—	0·7850	182·2
I*a* + 0·65% of added H_2O	0·87	0·7861	184·0
Ross Kane, " wetted "	—	0·7874	178·0
I*a* + 1·43% of added H_2O	1·65	0·7882	178·5
Bauer	—	0·79	168·2

It may be concluded, therefore, that conductivity data for acetone solutions, in order to have comparative value, need not necessarily relate to the anhydrous medium (if that is attainable) but to comparable conditions of solvation of the ions concerned. In this connection it should be appreciated that traces of water will have a more profound influence upon ionic mobility than similar traces of electrolyte impurity.

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