296. *The Electrical Conductivity of Uni-univalent Salts in Acetone.*

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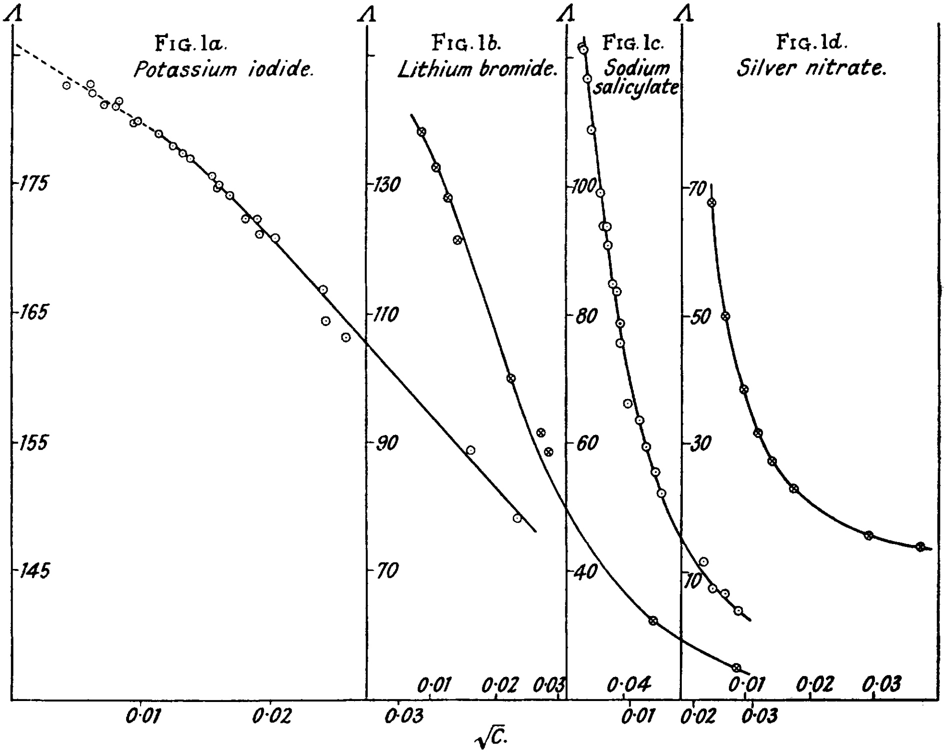
Conductivity measurements have been made upon seven uni-univalent salts in acetone, and a diversity of results has been obtained. The Λ–$\sqrt{c}$ curves for sodium and potassium iodides show good agreement with Onsager's prediction at low concentrations, and Λ_0 values have been derived by extrapolation. With other salts, *e.g.*, sodium and potassium salicylates, curves of entirely different type have been obtained. The results as a whole are believed to be consistent with the general conductivity curve whose form is determined by considerations of interionic attraction and ion association. Calculations involving the data for the less highly dissociated salts show that here ion-duplet formation is governed largely by the mass-action law.

MOST of the earlier work on the conductivities of uni-univalent salts in acetone was done upon relatively concentrated solutions, and the procedure was not refined (*e.g.*, the method of successive dilution was usually employed), but the more recent work of Walden, Ulich, and Busch (*Z. physikal. Chem.*, 1926, **123**, 429), Bauer (*Ann. Physik*, 1930, **6**, 253), and Ross Kane (mentioned by Hartley *et al.*, *Ann. Reports*, 1930, **27**, 240; complete details of this work have not yet appeared) has provided certain trustworthy data.

The uni-univalent salts selected for the present investigation have exhibited a diversity of behaviour, and although the series is not extensive it reveals a number of noteworthy features. Solutions of sodium and potassium iodides are relatively highly conducting; the slope of the curve connecting Λ with $\sqrt{c}$ for each salt falls off very gradually as c diminishes, although over an appreciable range it appears to be almost constant, and ultimately it approaches the theoretical value ($1{\cdot}627\ \Lambda_0 + 326{\cdot}7$) for a uni-univalent salt in acetone solution at 25°, a number of experimental points being actually situated in this region (see Fig. 1*a*, where the broken line indicates the theoretical slope); this is an improvement on previous data for acetone solutions. In order to evaluate Λ_0 we have relied on the points for the very dilute solutions, where it would appear that interionic attraction effects are alone operative. Ammonium iodide gives a curve of similar form to those of the foregoing salts but is exceptional in that the experimental slope falls considerably below the theoretical value.

FIG. 1.



The limited region of ideal behaviour may be called " Zone 1 " in order to distinguish it from the more extensive region of high slope which we describe as " Zone 2," where ion-association into duplets, a process believed to be governed by the law of mass action (compare Martin, J., 1928, 3270), is considered to occur (Onsager, *Physikal. Z.*, 1927, **28**, 277). The plot lying within this zone is frequently a straight line for the greater part, and according to Kraus and Fuoss (*J. Amer. Chem. Soc.*, 1933, **55**, 476) this is to be expected as an approximation in certain circumstances; thus the Kohlrausch law would seem to be obeyed, with the result that earlier workers in non-aqueous solvents almost invariably extrapolated the line, and so derived only " apparent " values of Λ_0.

The Λ–$\sqrt{c}$ curves for sodium and potassium salicylates and silver nitrate present a contrast to those of the alkali-metal iodides (see Fig. 1). Here the equivalent conductivities are very much smaller and for a considerable range increase only slowly with increasing dilution but then undergo a sudden rise which continues very rapidly; computation of Λ_0 is impossible here, for inspection shows that Zone 1 is completely absent. Sêrkov (*J. Russ. Phys. Chem. Soc.*, 1909, **41**, 9), working with concentrated solution, failed to observe this sudden rise and so obtained an absurdly low value of Λ_0 (76·6) for the sodium salt. The curves for the salicylates and silver nitrate (Figs. 1*c* and 1*d*) also represent Zone 2 of the general conductivity scheme, although a point of inflexion must lie between this portion of the zone and that represented by the steep section of the potassium iodide and sodium iodide plots. Support for the claim that these curves are comparable and have a form attributable to simple ion-association is provided by the fact that the data they represent are capable of furnishing satisfactory dissociation constants; *e.g.*, a constant of 2·05 × 10^{-2} can be calculated for potassium iodide by means of Onsager's approximation (*loc. cit.*), *viz.*, $\Lambda_0 - \Lambda_0 c/K = \Lambda + xc^{\frac{1}{2}}$; again, for sodium and potassium salicylates the values calculated on the basis of the Ostwald dilution formula are reasonably constant, data for a typical run on sodium salicylate being :

10^6c	69·66	94·48	127·7	156·2	192·3	224·0	
Λ_c	75·41	66·01	63·53	59·26	55·08	52·00	
10^5K	2·46	2·33	2·84	2·91	2·99	3·02	Mean 2·76

The slight drift in K is probably due to variations in the mobilities of the ions with changing concentration, and to the fact that the value of Λ_0 (170) was estimated from Walden's rule and by assuming the salicylate-ion mobility in water to be that of the *o*-methoxybenzoate ion [compare Walden, Ulich, and Busch, *loc. cit.*, and Walden and Birr, *Z. physikal. Chem.*, 1931, *A*, **153**, 1, who obtained good stoicheiometric constants (10^{-5}) for alkylammonium halides and picrates in acetone and methyl ethyl ketone]. Potassium salicylate gives a higher mean dissociation constant, *viz.*, *ca.* 2·0 × 10^{-4}.

The foregoing claim is supported by a comparison of Figs. 1 and 2, which show the similarity of the curves for potassium iodide in acetone and 6-nitro-*o*-toluic acid in water and also the analogy between sodium salicylate in acetone and *p*-ethylbenzoic acid in water. The two acids, investigated by Dippy and Page (J., 1938, 357) and Baker, Dippy, and Page (J., 1937, 1774), may be regarded as typical and possess approximate strengths of 10^{-2} and 10^{-5} respectively (in water), thus being comparable in extent of dissociation to these particular salts in acetone.

The curves for lithium bromide, ammonium iodide, and sodium iodide (to a less marked extent) incorporate the inflexion referred to above; the first curve (Fig. 1*b*) cannot be extrapolated and presents a type intermediate between the salicylates on the one hand and sodium and potassium iodides on the other.

Kraus and Fuoss (*J. Amer. Chem. Soc.*, 1933, **55**, 21, 2387) stated that analysis of the usual Λ–$\sqrt{c}$ curves for a variety of solvents, covering a wide range of chemical constitution and dielectric constant, indicates the existence of four well-defined regions, and they postulate that all solutions of electrolytes conform to a general conductivity curve. Although the first of these regions is the same as Zone 1, the second region differs from our Zone 2 in that it extends only to the inflexion point; we believe that the region of simple ion-association to neutral duplets reaches beyond this point, well into Kraus and Fuoss's third arbitrary section. It would seem, therefore, that altogether there exist only three distinct zones

TABLE I.

	Λ_0.			
Salt.	Present work.	Walden, Ulich, and Busch.	Ross Kane.	Bauer.
Sodium iodide	182·5	184·6	190	—
Potassium iodide	186	185·6	192	176
Ammonium iodide	162	—	208	—

in the complete conductivity curve (this includes, as Zone 3, the neighbourhood of the minimum, where triple-ion formation intervenes).

The low mobility of the ammonium ion indicated by our measurements is in contrast to that due to Ross Kane (Table I); his Λ_0 data are all considerably higher than ours, but not sufficiently so to account for a difference of 46 in the values for ammonium iodide. Our data agree reasonably well with those of Walden, Ulich, and Busch for sodium and potassium iodides; but if these workers had been able to show that at high dilutions the curve conformed to the predictions of Onsager, they would have got lower values of Λ_0. The mobility of the potassium ion is again found to be greater than that of sodium, a feature now well established for these ions in a number of solvents, not only those of a hydroxylic character.

FIG. 2

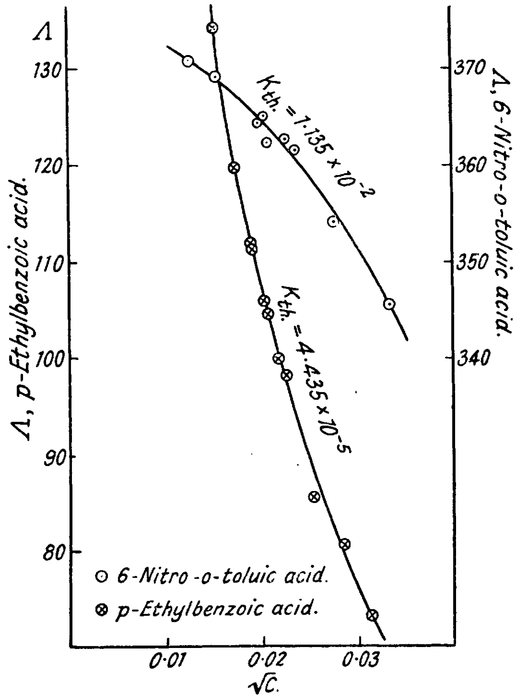
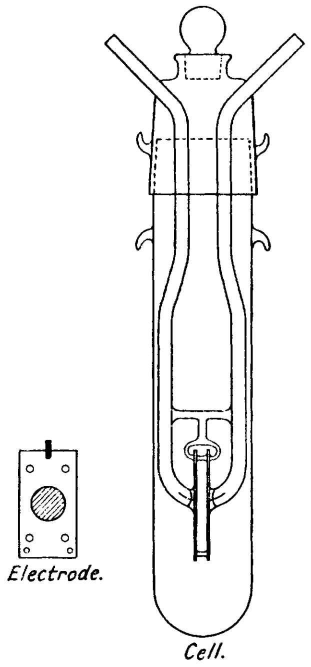
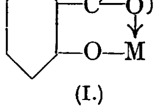


FIG. 3.



The scope of our work was limited by solubility difficulties, for, apart from the tetra-alkyl ammonium halides, etc., the only uni-univalent salts found to dissolve sufficiently in acetone are those described here. The ease with which sodium and potassium salicylates dissolve contrasts sharply with the relative insolubility of the corresponding salts of other common carboxylic acids. The intervention of such a structure as (I) might be a factor contributing to this (cf. Sidgwick, "The Electronic Theory of Valency," 1929, p. 242); the suggestion implies that the alkali metal is, at least partly, associated with phenolic oxygen. The existence of such a covalent form would account, not only for the abnormal solubility, but also for the low degree of dissociation of these salts; the marked difference in ionisation between potassium iodide and salicylate must be attributed to the constitution of the anion.



(I.)

EXPERIMENTAL.

The Wheatstone bridge network consisted of a 1-m. wire of constantin carrying extension resistances which served to increase ten-fold the effective length of the wire. The Cambridge standard decade resistances were of low inductance quality and extended to a maximum of 1 megohm. Where cell resistances exceeded 10,000 ohms, the telephones were replaced by a three-valve amplifier of the usual transformer-coupled type which operated a moving-coil loud-speaker of the kind used in radio receiving sets. A variable air-condenser (maximum capacity — 0·002 μF) was connected in parallel with the standard resistance of the bridge circuit in order to balance out the difference in capacity between the conductivity cell and the standard resistance; in this way it was possible to secure satisfactory end-points with a sharp minimum of sound in measuring up to 250,000 ohms.

The conductivity cell (Fig. 3), of Pyrex glass, is considered to be an improvement on that described by Walden, Ulich, and Laun (*Z. physikal. Chem.*, 1925, **114**, 275). The cylindrical body has a capacity of approximately 200 ml. and possesses an externally-ground neck covered by a closely-fitting glass cap carrying the dipping electrodes. The perforated platinum plates, each of 8 sq. cm. area and of 24 (wire) gauge thickness, are situated 3 mm. apart, and held rigidly by their respective glass tubes and secured further by glass struts. The electrodes are covered with grey platinum so as to minimise the effects of polarisation (Whetham, *Phil. Trans.*, 1900, **194**, 321); in a cell designed for non-aqueous work the plates must be of a greater area so as to provide reasonable resistances, consequently the polarisation factor becomes more serious. Walden, Ulich, and Laun (*loc. cit.*) endeavoured to overcome the difficulty by giving the electrodes only a light coating of black platinum, but grey platinum affords a more stable surface, for the cell constant (0·01950) did not alter perceptibly

TABLE II.

Potassium iodide.

	10^4C.	Λ_u.	Λ_c.
a	0·1770	184·9	182·5
b	0·3687	184·8	182·7
a	0·3890	184·0	182·0
a	0·5040	183·0	181·2
a	0·6508	182·0	181·1
b	0·6993	182·5	181·5
c	0·8650	180·7	179·8
d	0·9448	180·7	179·9
c	1·297	179·4	178·7
e	1·375	179·8	(179·3)
d	1·500	178·4	177·9
c	1·766	177·7	177·2
e	1·920	177·3	177·0
e	2·433	175·9	175·6
b	2·581	175·4	174·9
c	2·675	174·8	174·5
e	2·873	174·4	174·2
e	3·270	172·6	172·4
c	3·603	172·6	172·3
e	3·690	171·2	171·1
c	4·217	170·8	170·7
c	5·784	166·8	166·8
d	5·886	164·4	164·4
d	6·686	163·0	163·0
c	12·68	154·4	154·4
d	16·21	149·2	149·2

κ for solvent: (a) 0·0670; (b) 0·0800; (c) 0·0195; (d) 0·0195; (e) 0·0670.

Silver nitrate.

	10^4C.	Λ_u.	Λ_c.
c	0·2285	67·71	67·21
a	0·4906	50·17	49·65
a	0·8909	38·62	38·30
a	1·375	31·51	31·30
a	1·985	27·10	27·00
a	3·014	22·95	22·95
a	8·475	15·39	15·39
b	13·77	14·01	14·01

κ for solvent: (a) 0·0880; (b) 0·0640; (c) 0·1410.

Sodium iodide.

	10^4C.	Λ_u.	Λ_c.
a	0·2926	181·5	180·0
a	0·4102	177·7	177·2
a	0·6435	177·5	177·1
b	0·8120	176·5	176·0
a	0·9829	176·6	176·3
b	1·250	175·4	175·1
c	2·477	168·7	168·5
c	2·961	168·3	168·1
c	3·726	165·7	165·6
c	5·570	161·2	161·1
a	10·95	151·8	151·8
a	16·81	146·1	146·1
b	17·81	144·6	144·6

κ for solvent: (a) 0·098; (b) 0·110; (c) 0·130.

Lithium bromide.

	10^4C.	Λ_u.	Λ_c.
a	0·7663	139·4	138·0
a	1·148	133·8	132·7
a	1·525	128·9	128·0
a	2·057	122·0	121·2
a	5·096	100·7	100·0
b	7·561	92·00	91·52
a	8·025	89·30	88·70
a	24·11	62·66	62·39
b	33·23	55·61	55·51

κ for solvent: (a) 0·1000; (b) 0·0670.

Ammonium iodide.

	10^4C.	Λ_u.	Λ_c.
a	0·4830	161·3	160·7
a	0·8360	160·6	160·0
a	1·635	160·0	159·7
a	2·146	159·5	159·3
b	2·360	158·0	157·6
b	3·313	153·7	153·3
b	5·665	141·9	141·6
b	15·95	112·6	112·5

κ for solvent: (a) 0·130; (b) 0·0980.

Sodium salicylate.

	10^4C.	Λ_u.	Λ_c.
a	0·05063	137·1	121·1
b	0·06383	136·8	121·2
b	0·09913	127·4	116·9
b	0·1601	114·8	108·4
b	0·2810	102·4	98·91
b	0·3497	97·18	94·32
a	0·4041	96·25	93·78
b	0·4149	93·03	90·59
b	0·5299	86·62	84·72
a	0·5988	85·19	83·52
b	0·6905	79·66	78·20
c	0·6966	76·83	75·41
c	0·9448	67·07	66·01
c	1·277	64·31	63·53
c	1·562	59·89	59·26
c	1·923	55·62	55·08
c	2·240	52·46	52·00
d	4·564	42·10	41·82
c	5·274	37·73	37·51
d	6·099	37·01	36·80
d	7·213	34·26	34·06

κ for solvent: (a) 0·0975; (b) 0·0655; (c) 0·0975; (d) 0·0975.

Potassium salicylate.

	10^4C.	Λ_u.	Λ_c.
a	0·4062	136·9	133·2
b	0·4211	147·3	131·5
b	0·5468	140·0	127·7
b	0·7326	134·4	125·3
a	1·008	121·9	120·2
b	1·075	125·5	119·3
b	1·479	116·4	111·9
a	1·693	109·9	108·8
b	2·834	101·2	98·90
a	3·306	93·01	92·51
b	7·360	76·00	73·72
a	11·07	64·12	64·03

κ for solvent: (a) 0·1760; (b) 0·6700.*

* Although the acetone employed in run (b) had a much higher conductivity than usual, the points representing runs (a) and (b) lie uniformly on a smooth curve. This can be taken as evidence of the satisfactory nature of the solvent correction employed.

throughout our work. Calibration of the cell was effected by the "intermediate cell" method (Davies, "The Conductivity of Solutions," 1933, p. 60), comparison being made with a cell of constant *ca.* 0·07 (determined accurately by using Jones and Prendergast's data, *J. Amer. Chem. Soc.*, 1937, **59**, 731), and an aqueous solution of potassium chloride of approximate concentration 0·001N (cf. Davies, J., 1937, 432). All measurements were carried out at 25° ± 0·01°.

Acetone of conductivity quality was required in large amounts, but as it was essential that its conductivity should not alter sensibly during the course of a run, intensive drying such as that carried out by Carvallo (*Compt. rend.*, 1913, **156**, 1757; *Ann. Physique*, 1914, **1**, 171; **2**, 142) ($\kappa = 0{\cdot}00012$ gemmho) was not contemplated. A preliminary examination of the efficiency of various drying agents was therefore conducted upon "AnalaR" acetone. Phosphoric oxide had serious disadvantages, for upon addition to acetone in the cold it quickly produced a brown colour and heat was generated; after some time the presence of acetaldehyde was noticed and mesitylene suspected. Anhydrous potassium carbonate, sodium sulphate, and magnesium sulphate were not efficient, but calcium chloride proved suitable from a conductimetric point of view, and the following procedure was adopted. "AnalaR" Acetone was kept over finely-ground, fused calcium chloride and a little anhydrous potassium carbonate for at least two weeks (excessive standing must be avoided, however, as acetone slowly combined with the former salt), then distilled from a Pyrex flask connected to a 3-foot fractionating column packed with glass-beads and lagged with cotton-wool. All corks in the apparatus were covered with tin-foil. The first runnings were always rejected, and the reserved acetone usually had $\kappa = 0{\cdot}06$—$0{\cdot}13$ gemmho at 25°. The success of this method depends, however, on the use of acetone of "AnalaR" quality; it was found to be much superior to bisulphite-purified acetone as starting material.

Various workers have suggested that the conductivity of acetone is affected by exposure to light. Dutoit and Levier (*J. Chim. physique*, 1905, **3**, 628) state that the conductivity is decreased, whereas Jones and Mahin (*Z. physikal. Chem.*, 1909, **69**, 402) claim that it increases. We found no alteration in the conductivity of dried acetone, but that of "AnalaR" acetone diminished with time, although only while standing in the cell, and this is attributed to adsorption of impurities by the platinised electrodes; no such behaviour was observed with conductivity acetone. In the present work all flasks containing acetone were covered with black cloths, and the thermostat was enclosed with a black hood.

In each run the procedure was to add a known weight of acetone to the dry cell so as completely to cover the electrodes, and the conductivity determined accurately for solvent-correction purposes. A small quantity of stock salt solution (*ca.* N/100) was then added from a weight-burette (see below) to the cell by removing the stopper in the cap, and the contents were stirred by rotating the electrodes. The concentration (wt./vol.) of the resultant solution can be calculated by assuming the density of the solution to be that of acetone (a usual assumption in such work), the concentration of the stock solution (wt./wt.) being known accurately (about 500 g. are made up). Before measurement was made, the cell was kept in the thermostat for 15 minutes. By adding further quantities of stock solution from the weight-burette a series of dilutions were obtained. The values of Λ_c quoted in the Table II have been derived by subtracting the specific conductivity of the solvent from that of the solution in each case (Λ_u signifies uncorrected equivalent conductivity); κ is recorded in gemmhos, and C is g.-equivs./l.

The weight-burette, of 60 ml. capacity, was fitted with a vertical tap at the lower end, the jet of which could be closed by a well-fitting ground-glass drip-tube. The amount run into the cell was determined by weighing the burette before and after each operation. The tap was lubricated with a special mixture of white vaselin and paraffin-wax previously washed with acetone (after examining several substances this was found to be the most efficient lubricant). All other ware was of Pyrex glass dried at 130° in an electric oven; "AnalaR" acetone was used for all rinsings. The balances and other equipment, such as the valve oscillator (frequency, 1000 cycles/sec.), were those already described by Dippy and Williams (J., 1934, 161).

The salts, from British Drug Houses, were all further purified by crystallisation from conductivity water, except the salicylates, which were treated like other organic salts (see Dippy and Williams, *loc. cit.*). Filtration was conducted on a hardened filter-paper in a glass Buchner funnel, and drying effected in a vacuum desiccator in the dark.

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