128. *Conductimetric Studies in Ketonic Solvents. Part III.*[1] *Alkali Iodides and Salicylates in Ethyl Methyl Ketone and Acetophenone.*

By S. R. C. HUGHES.

Comparison of data for alkali-metal iodides in dry ketonic media gives little support to the idea that their cations are de-solvated by coulombic association, but the contrasting behaviour of alkali-metal salicylates in these solvents requires the presumption of considerable cation-desolvation.

WE have hitherto only studied the conductimetric behaviour of potassium iodide, selected as a suitable electrolyte common to most earlier work, to explore solvent qualities. Ethyl methyl ketone of the quality referred to in Part II [1] seems a suitable medium for comparing the behaviour of different electrolytes. Acetophenone is readily obtained and kept dry, as shown by the small ranges of its physical data in the literature.[2,3] Previous conductivity measurements in acetophenone [3,4] appear to have suffered from the application of inappropriate solvent corrections.

Measurements in these two solvents have therefore been carried out on alkali-metal iodides whose dissociation constants are high and closely grouped, and also on the corresponding salicylates, which are weakly dissociated to extents depending on the cation. The results are shown in Tables 1—3.*

TABLE 1. *Conductivities in dry ethyl methyl ketone at 25°.*

Solvent conductances (κ_s) from $4{\cdot}7 \times 10^{-8}$ to $0{\cdot}36 \times 10^{-8}$.

Sodium iodide ($\Lambda_0 = 147{\cdot}7$; $K = 2{\cdot}47 \times 10^{-3}$).

10^4c	Λ	10^4c	Λ	10^4c	Λ
0·6633	139·6	2·072	131·7	3·342	125·7
0·8424	139·5	2·631	129·3	4·465	122·5
1·060	138·4	3·205	126·4	5·053	120·7
1·368	135·2	3·225	127·0	5·359	119·6
1·922	131·7				

Lithium iodide ($\Lambda_0 = 147{\cdot}2$; $K = 2{\cdot}72 \times 10^{-3}$).

10^4c	Λ	10^4c	Λ	10^4c	Λ
0·7753	137·6	4·963	121·6	9·187	112·7
1·759	132·4	5·110	121·4	10·59	109·5
1·794	133·1	7·706	114·8	20·47	98·58
2·959	128·3				

Potassium salicylate ($\Lambda_0 = 129{\cdot}9$; $K = 3{\cdot}49 \times 10^{-5}$).

10^4c	Λ	10^4c	Λ	10^4c	Λ
0·3157	82·08	2·456	42·65	6·972	27·38
0·6816	66·28	3·709	36·19	9·253	24·18
1·198	55·69	4·729	32·33	9·519	24·14
2·333	42·99	5·652	30·55		

Sodium salicylate [$\Lambda_0 = 126{\cdot}8$ (indirect); $K = 4{\cdot}35 \times 10^{-6}$].

10^4c	Λ	10^4c	Λ	10^4c	Λ
0·6390	30·43	2·673	15·92	5·160	11·54
0·7432	29·37	3·586	13·78	6·837	10·08
1·356	21·80	3·804	13·48	7·320	9·815
2·321	17·05	5·159	11·66		

Lithium salicylate [$\Lambda_0 = 126{\cdot}3$ (indirect); $K < 5{\cdot}5 \times 10^{-7}$].

Kraus–Fuoss plot: $K = 4{\cdot}98 \times 10^{-7}$; $K_{32} = 3{\cdot}58 \times 10^{-4}$.

Wooster plot: $K = 3{\cdot}93 \times 10^{-7}$; $K_{31} = 0{\cdot}89 \times 10^{-4}$.

10^4c	Λ	10^4c	Λ	10^4c	Λ
0·9386	9·430	4·187	6·080	25·46	4·851
1·412	8·021	5·870	5·782	39·68	4·563
2·341	6·846	6·266	5·775	49·23	4·414
2·823	6·555	9·309	5·469	97·81	3·888
3·228	6·375	10·17	5·474	185·1	3·403
3·685	6·342	13·43	5·318	343·0	2·920

* Concentrations are in moles/litre. Percentages of water are w./w. The values of Λ_0 and K at the head of each column are from the Fuoss plot except where otherwise stated. K_{32} refers to bilateral ternary dissociation and K_{31} to unilateral ternary dissociation; in the former case Λ_{03} is taken arbitrarily as $\frac{1}{3}\Lambda_0$ and in the latter as $\frac{2}{3}\Lambda_0$.

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[1] Part II, *J.*, 1956, 998.

[2] Perkin, *J.*, 1896, **69**, 1025; Sugden, *J.*, 1933, 768; Guia and Guastalla, *Chimie et Industrie*, 1933, **29**, 268; Timmermans and Hennaut-Roland, International Conference (Brussels), *J. Chim. phys.*, 1935, **32**, 501.

[3] Morgan and Lammert, *J. Amer. Chem. Soc.*, 1924, **46**, 881.

[4] Dutoit and Nicollier, *Z. Elektrochem.*, 1906, **12**, 643.

TABLE 2. *Conductivities in wet ethyl methyl ketone at 25°.*

Potassium salicylate

Solvent containing 1·25% of water ($10^7\kappa_s$ = 0·92—0·73; Λ_0 = 120·0$_5$; K = 5·33 × 10^{-5}).

10^4c	Λ	10^4c	Λ	10^4c	Λ
0·3626	81·94	2·572	44·38	7·350	29·95
0·6294	71·09	3·930	36·09	9·495	27·07
0·9237	63·42	4·083	31·96	11·98	24·82
1·922	50·93	5·065	34·54	14·95	21·25

Solvent containing 1·83% of water ($10^7\kappa_s$ = 0·32 × 10^{-7}; Λ_0 = 116·1; K = 2·86 × 10^{-4}).

10^4c	Λ	10^4c	Λ
0·4923	98·07	4·985	56·48
1·730	78·09	8·960	47·10

Solvent containing 3·40% of water ($10^7\kappa_s$ = 1·087; Λ_0 = 113·0; K = 3·96 × 10^{-4}).

10^4c	Λ	10^4c	Λ
1·670	86·34	11·39	53·81
3·413	74·95	15·52	49·00
5·883	65·40		

Sodium salicylate

Solvent containing 1·25% of water [$10^7\kappa_s$ = 1·02—0·64; Λ_0 (indirect) = 119·5; K = 2·57 × 10^{-5}].

10^4c	Λ	10^4c	Λ	10^4c	Λ
0·0972	67·64	2·352	17·74	4·041	13·80
0·1599	56·10	2·662	16·89	6·419	11·01
1·040	25·09	3·011	15·80	9·886	9·19
1·917	19·23	3·016	15·71	10·16	8·90

Lithium salicylate

Solvent containing 1·25% of water [$10^7\kappa_s$ = 1·24—0·66; Λ_0 (arbitrary) = 115; K<8·43 × 10^{-7}].

Kraus–Fuoss plot; K = 7·78 × 10^{-7}; K_{32} = 5·99 × 10^{-4}.

Wooster plot: K = 7·59 × 10^{-7}; K_{31} = 2·34 × 10^{-4}.

10^4c	Λ	10^4c	Λ	10^4c	Λ
0·3833	16·03	1·855	8·037	8·116	5·087
0·6061	12·74	3·406	6·603	10·42	4·916
0·8835	11·08	4·254	6·099	16·80	4·794
1·277	9·262	5·124	5·745	32·82	4·444
1·331	9·160	6·963	5·421	78·07	4·144
1·826	7·911				

TABLE 3. *Conductivities in dry acetophenone at 25°.*

$10^7\kappa_s$ from 1·208 to 0·031.

Potassium iodide (Λ_0 = 38·13; K = 5·22 × 10^{-3}).

10^4c	Λ	10^4c	Λ	10^4c	Λ
0·7566	36·34	2·874	34·38	6·259	32·49
0·8189	36·29	3·795	33·79	6·270	32·44
1·081	36·04	4·442	33·50	6·303	32·51
1·857	35·17	4·637	33·15	6·722	32·26
2·058	35·01	4·767	33·09	8·385	31·40

Sodium iodide (Λ_0 = 37·55; K = 5·94 × 10^{-3}).

10^4c	Λ	10^4c	Λ	10^4c	Λ
0·8321	35·60	4·176	32·96	9·078	30·57
1·076	35·45	5·826	32·16	10·31	30·13
2·646	34·02	6·680	31·60	16·30	28·41
3·368	33·55				

Lithium iodide (Λ_0 = 35·27; K = 6·83 × 10^{-3}).

10^4c	Λ	10^4c	Λ	10^4c	Λ
1·179	33·32	4·604	31·35	10·78	28·66
2·114	32·60	5·622	30·38	13·12	28·50
2·591	32·89	7·012	30·16	18·88	26·97
3·368	31·59				

Potassium salicylate (Λ_0 = 27·62; K = 1·90 × 10^{-4}).

10^4c	Λ	10^4c	Λ	10^4c	Λ
0·4252	22·49	1·288	19·08	2·821	15·63
0·4828	21·48	1·299	19·23	4·123	13·70
0·6504	21·48	2·587	15·97	6·437	11·45
0·7263	20·65				

Sodium salicylate [Λ_0 (indirect) = 27·04; K = 1·01 × 10^{-5}].

10^4c	Λ	10^4c	Λ	10^4c	Λ
0·6106	9·718	2·552	4·976	5·573	3·755
0·9353	7·805	4·009	4·084	7·069	3·009
2·164	5·555	4·430	3·804		

Lithium salicylate [Λ_0 (indirect) = 24·76; K< 7·55 × 10^{-7}].

Kraus–Fuoss plot: K = 7·01 × 10^{-7}; K_{32} = 9·96 × 10^{-4}.

Wooster plot: K = 6·96 × 10^{-7}; K_{31} = 2·73 × 10^{-4}.

10^4c	Λ	10^4c	Λ	10^4c	Λ
1·575	1·613	8·191	0·9727	16·47	0·8354
1·824	1·589	8·217	0·9598	27·63	0·7705
3·700	1·201	15·56	0·8521	29·43	0·7509
3·760	1·166				

EXPERIMENTAL

Conductivity Measurements and Purification of Solvents.—These followed the procedure used [1] for ethyl methyl ketone. Acetophenone was purified by three fractional freezings followed by two distillations by dry-space procedure, d_4^{25} = 1·0238; η_0^{25} = 0·01675 (cf. refs. 2, 3). This solvent was protected from the light, and the conductivity cell enclosed in a light-proof jacket when containing it. Potassium iodide and potassium and sodium salicylates dissolved only slowly in acetophenone, precluding the exploration of wide concentration ranges.

Purification of Solutes.—Potassium iodide was purified as described in Part I.[5] Sodium iodide, after two recrystallisations from hot conductivity water, was baked to constant weight at 120° and stored in a desiccator. Lithium iodide was dehydrated by Hart and Partington's method;[6] all normally accepted desiccants rehydrated it. The manipulation of this salt and

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[5] Dippy and Hughes, *J.*, 1954, 953.

[6] Hart and Partington, *J.*, 1943, 104.

of sodium iodide was only possible within the dry-space. All iodides were analysed by Andrews's method,[7] the lithium iodide being simultaneously sampled for analysis with each set of conductivity measurements. The alkali salicylates were recrystallised twice from conductivity water with a high degree of rejection, the concentrated solutions being filtered through hardened filter-cones; the recrystallised salts were dried at 110° and stored in desiccators. They were analysed by ignition to constant weight with sulphuric acid.

DISCUSSION

Alkali-metal Iodides.—Our results and those reported by others [3,4,8,9] have been analysed by Fuoss's method to give the values of Λ_0 and K shown in Table 4. Except for Morgan and Lammert's data,[3] to which a uniform solvent correction was applied throughout, Λ_0 decreases in the order KI > NaI > LiI ascribed to solvation, and the dissociation constants in the reverse order.

TABLE 4. *Hydrodynamic and association data for alkali iodides in ketonic solvents.*

					Ionic radius parameters (Å)		
				Bjerrum parameter	Stokes–Bjerrum		Stokes cation
Solvent	Salt	Λ_0	10^3K	(Å)	mutual r_+	solution r_-	radius * r_+
Ethyl methyl ketone (dry) [a]	KI	150·8	2·13	3·65	—	—	4·13
	NaI	147·7	2·47	3·87	—	—	4·43
	LiI	147·2	2·76	3·96	—	—	4·49
Ethyl methyl ketone (water content 0·69%) [b]	KI	144·9	2·42	3·58	—	—	4·24
	NaI	137·0	3·98	4·32	—	—	5·07
Acetophenone (dry) [c]	KI	38·13	5·22	6·36	4·59	1·77	3·10
	NaI	37·55	5·94	6·94	5·21	1·73	3·25
	LiI	35·27	6·83	7·59	5·79	1·80	3·79
Acetophenone [d]	NaI	36·76	4·55	5·84	3·82	2·02	3·40
Acetophenone [e]	KI	39·37	4·51	5·80	4·03	1·78	2·88
	NaI	39·91	2·28	4·19	—	—	2·79

* Stokes's radius of I^- is taken as the crystallographic value (2·16 Å). Alternative arbitrary values lying between 1·73 Å and 2·36 Å (cf. Grade I acetone [5]) do not seriously disturb the parallelism between Stokes and Bjerrum radii in the dry solvents.

[a] Part I [5] and present work. [b] Ref. 9, recalculated. [c] Present work. [d] Ref. 4, recalculated. [e] Ref. 3, recalculated.

Data for acetophenone for all three salts can be treated by the quadratic-equation method [5] to give radii compatible with both Stokes's and Bjerrum's equations; those for ethyl methyl ketone do not conform to this analysis. The radii ascribed to the iodide ion in acetophenone are consistent, some 0·4 Å below the crystallographic radius, recalling those emerging from the data for potassium iodide in acetone.[5]

Cation radii, calculated by assuming a crystallographic iodide ion radius, are compared in the Figure, which shows that in each solvent the hydrodynamic parameters vary with the alkali metal in a manner parallel to the corresponding Bjerrum distances. Such relationships are strictly conventional and open to alternative interpretations. The simplest, that of rigidly solvated spheres, is subject to the errors inherent in Stokes's and Bjerrum's theories. Alternatively the theory of association-desolvation may be applied with the proviso that the degree of such desolvation is in almost constant proportion to the hydrodynamic radius.

Corresponding comparisons of potassium and sodium iodides in acetone,[8,10] while agreeing in the sequence of Λ_0 values KI > NaI, show dissociation constants decreasing in the same order. This may be ascribed to the effects of water in this solvent.[1]

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[7] Andrews, *J. Amer. Chem. Soc.*, 1903, **25**, 756.

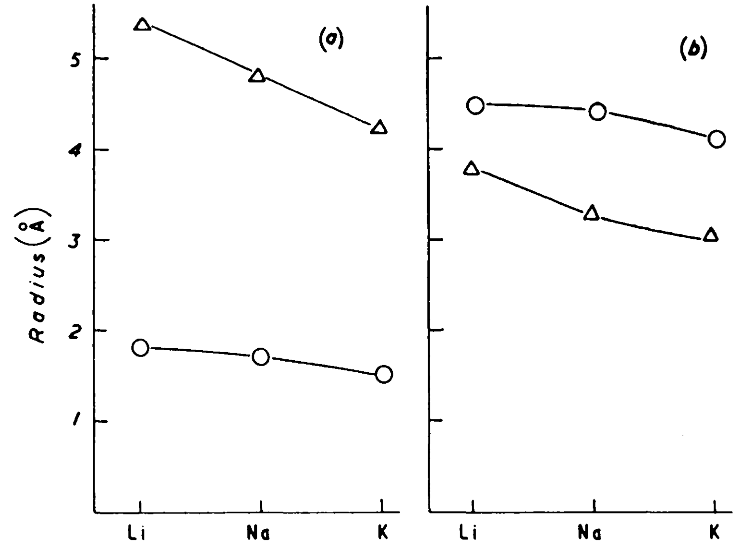
[8] Walden, Ulich, and Busch, *Z. phys. Chem.*, 1926, **123**, 429.

[9] Walden and Birr, *Z. phys. Chem.*, 1931, *A*, **153**, 1.

[10] Dippy, Jenkins, and Page, *J.*, 1939, 1386.

Alkali-metal Salicylates.—Fuoss analyses[11] of the data for potassium salicylate give both Λ_0 and K; Λ_0 for the sodium and lithium salts can then generally be obtained from the parallel iodide data. Sodium salicylate conforms to Fuoss analyses for K values but lithium salicylate gives plots of decreasing slope indicating ternary association. Up to 10^{-3}M application of Kraus and Fuoss's procedure[12] to the data for lithium salicylate supposes the bilateral formation of triple-ions; Wooster's[13] analysis applies to the unilateral process. There is a barely perceptible curvature in the plots obtained by assuming a bilateral process for all three media. The binary constants from both procedures agree closely with each other as do their upper limits estimated from the steepest portions of the Fuoss plots. Unilateral triple-ion formation seems the more probable basis of the effect.

Relative cation radii of alkali iodides based on the radius of the iodide ion = 2·16 Å.



a, Association radii; *b*, hydrodynamic radii.
○ Ethyl methyl ketone. △ Acetophenone.

TABLE 5. *Association parameters* (Å) *of alkali salicylates in ketonic solvents.*

Solvent	Water (% w./w.)	Binary parameters $C_7H_5O_3K$	$C_7H_5O_3Na$	$C_7H_5O_3Li$	Ternary parameters for $C_7H_5O_3Li$ Bilateral	Unilateral
Acetone[a]	0·68[b]	2·14[c]	1·73[d]	—	—	—
Ethyl methyl ketone[e] ...	—	1·95	1·65	1·43	0·797	0·746
	1·25	2·02	1·78	1·39	0·780	0·722
	1·83	2·30				
	3·40	2·14				
Acetophenone[e]	—	2·52	1·89	1·56	0·921	0·837

[a] Recalculated from ref. 10. [b] Estimated. $10^4K = 3{\cdot}17$; $\Lambda_0 = 151{\cdot}3$. [d] $10^5K = 4{\cdot}45$; Λ_0 (indirect) = 148·4. [e] Present work.

Although the dissociation constant of potassium salicylate is much increased by wetting the ethyl methyl ketone, the Bjerrum parameters (Table 5) derived by use of appropriately increased bulk dielectric constants are almost unchanged. The consequent suggestion that association of salicylates is electrostatic in character, despite earlier views,[10] is

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[11] Fuoss, *J. Amer. Chem. Soc.*, 1935, **57**, 488.

[12] Kraus and Fuoss, *J. Amer. Chem. Soc.*, 1933, **55**, 2387.

[13] Wooster, *J. Amer. Chem. Soc.*, 1937, **59**, 377; 1938, **60**, 1609.

supported by the accompanying decreases in Λ_0 which resemble those of potassium iodide in wet ethyl methyl ketone [1] when represented as fractions.

In a given medium, binary dissociation constants of salicylates decrease sharply in the order K > Na > Li, showing marked contrast to those of the iodides. Bjerrum parameters for salicylates follow the corresponding cation crystallographic radii and, in ethyl methyl ketone and acetone, show little dependence on the solvent or its water content. The values are slightly higher in acetophenone but still follow the bare cation radii. It is therefore suggested that in these media alkali cations are largely desolvated when in electrostatic association with salicylate anions.

Although little direct meaning can be read into ternary association parameters, which are based on arbitrary values of Λ_{03}, their small magnitudes for lithium salicylate (Table 5) suggest closer grouping of charge centres in the triple ions than would be given by linear configurations favoured in the Kraus and Fuoss [12] treatment. The chief interest here, however, lies in the small dependence of the ternary parameters in ethyl methyl ketone on the water content of the solvent, which supports the idea of cation-desolvation. The ternary parameter in acetophenone is somewhat larger.

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