118. *Electrical Conductivities of Dilute Solutions of Sodium Dodecyl Sulphate in Ethyl Alcohol–Water Mixtures at 20°.*

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The conductivity of a salt with a large, highly unsymmetrical ion, *viz.*, sodium dodecyl sulphate, has been measured at low concentrations in ethyl alcohol–water mixtures. The equivalent conductances at infinite dilution have been derived. Although there is considerable variation in the product $\Lambda_0\eta$ for the salt, Walden's rule is approximately obeyed by the dodecyl sulphate ion. Results are compared with those for other large organic ions. The solvation of the ions has been estimated by various methods.

Straight lines for Λ plotted against $\sqrt{c}$ show agreement with the Kohlrausch equation in all solutions at sufficiently low concentrations. The slopes of the lines have been compared with theoretical values according to Onsager's equation. Reasonable agreement is found except for mixtures from 80 to 100% of alcohol, where the sodium dodecyl sulphate is incompletely ionised, and from 10 to 50% of alcohol, where the experimental slopes are abnormally low. In this same range, the solubility of sodium dodecyl sulphate rises to extremely high values. An explanation has been suggested to correlate these abnormalities, based on the dual nature of the dodecyl sulphate ion and its interaction with solvent molecules.

The conductivities of electrolytes in many non-aqueous solvents have been measured by Walden and various co-workers since 1906. The electrolytes used have been mainly alkyl-substituted ammonium salts with large, symmetrical ions, and also some simple salts. Since the development of the Debye–Hückel theory of strong electrolytes and the modification of the equations by Onsager (*Physikal. Z.*, 1927, **28**, 277) many investigations have been carried out to see how closely these equations agree with experiment for non-aqueous solvents. If a series of mixtures of water and an organic solvent are used, the gradual transition from the behaviour of the electrolyte in water to that characteristic of the other solvent may be followed.

The present work was undertaken to study the behaviour of a large, unsymmetrical ion in water and ethyl alcohol and in mixtures of these. Sodium dodecyl sulphate is very suitable for this purpose. Its conductivity in water at various temperatures has been measured by Lottermoser and Püschel (*Kolloid.-Z.*, 1933, **63**, 175) and Howell and Robinson (*Proc. Roy. Soc.*, 1936, *A*, **155**, 386). Although this salt behaves in aqueous solution as a colloidal electrolyte at high concentrations, it is completely dissociated into simple ions at very low concentrations. The absence of hydrolysis makes possible accurate measurement even in great dilution.

Conductivities had to be measured at concentrations low enough for the Onsager equation to be valid and for the equivalent conductance at infinite dilution to be deducible. Concentrations from about 0·0001N to 0·01N were used.

EXPERIMENTAL.

Cells.—Two quartz cells were used. The cell constants were determined with several solutions of Kahlbaum's potassium chloride, of which the specific conductances were of the same order as those of the solutions for which the cells were used, according to the method of Frazer and Hartley (*Proc. Roy. Soc.*, 1925, *A*, **109**, 351). The values of the constants were 0·02902 and 0·01355. The stoppers carrying the electrodes were fitted into the cells in exactly the same position each time. The variation of cell constant with volume of solution in the cell was found, and the cell was always filled sufficiently so that the cell constant no longer varied with the volume. The electrodes were lightly platinised, and it was shown that they caused no catalytic oxidation of the alcohol, for the resistance did not alter with time (cf. Walden, Ulich, and Laun, *Z. physikal. Chem.*, 1925, **114**, 275; Brownson and Cray, J., 1925, **127**, 2923). Between experiments, the cells were washed for about 24 hours with running hot water. The solutions were maintained at 20° ± 0·01°.

Electrical Apparatus.—The method of Howell and Handford (*Trans. Faraday Soc.*, 1933, **29**, 640) was used, with slight modifications. A valve oscillator gave alternating current of the sine-wave form (the frequency used was about 2000 cycles). The null-point was determined with a valve amplifier and telephones. A Tinsley non-inductive resistance box with six dials and Tinsley ratio arms formed the bridge, and similar ratio arms were used for the Wagner earth (*Elektrochem. Z.*, 1911, **32**, 1001). A variable capacity was used in parallel with the resistance box. Adjustment of this allowed the minimum sound at the null-point to be reduced to complete silence and increased the sensitivity. The author is very grateful to Dr. O. R. Howell for the loan of this apparatus.

Materials.—Sodium dodecyl sulphate. It was essential for this to be prepared completely free from other salts. Chlorosulphonic acid (190 g.) was added slowly to pure dodecyl alcohol (280 g.) (from Ronsheim and Moore, m. p. 22·8—23·3°), the temperature being kept between 40° and 45°. The product was poured slowly into sodium hydroxide solution (75 g. in 750 c.c.) cooled in ice, with vigorous stirring. The crude sodium salt was filtered off (yield 415 g.), crystallised twice from water, twice from ethyl alcohol, extracted (Soxhlet) with light petroleum (b. p. 40—60°) for 5 hours, and further crystallised three times from alcohol, the temperature being kept below 60° always. It was washed with light petroleum and kept for several months in a desiccator over phosphoric oxide and paraffin wax; yield 150 g. The sodium was estimated by ignition with sulphuric acid to sodium sulphate, and the hydrolysable sulphur by hydrolysing with hydrochloric acid and measuring the extra acidity due to the sodium hydrogen sulphate produced (Found: Na, $7{\cdot}97_3$; hydrolysable SO_3, $27{\cdot}6_4$. Calc. for $C_{12}H_{25}O_4SNa$: Na, 7·979; SO_3, 27·77%).

Water.—This was obtained by fractional condensation in a silver condenser, Howell and Robinson's apparatus (*loc. cit.*) being used. The specific conductance was about $0{\cdot}5 \times 10^{-6}$ reciprocal ohm. The water was collected and stored in silica vessels, and protected from carbon dioxide.

Absolute alcohol. Ordinarily pure absolute alcohol was distilled from lime, and the middle fraction collected. A little of this was refluxed with calcium shavings for one day, until a gel of calcium ethoxide was formed. To this was added the rest of the alcohol, and the whole refluxed for a further day. The alcohol was distilled directly into a silica bottle. This specimen was considerably purer than those usually employed for conductivity measurements. The specific conductance was only $0{\cdot}05 \times 10^{-6}$ reciprocal ohm, compared with values from $0{\cdot}15 \times 10^{-6}$ to $0{\cdot}36 \times 10^{-6}$ for the alcohol used in similar investigations (for review of data, see Walden, Ulich, and Laun, *loc. cit.*). Kraus and Callis (*J. Amer. Chem. Soc.*, 1923, **45**, 2624) obtained small quantities of alcohol with a specific conductance of $0{\cdot}03 \times 10^{-6}$ by a lengthy procedure.

Alcohol–water mixtures. Rectified spirit, several times distilled, was diluted with conductivity water, and the composition found from measurements of specific gravity and reference to tables. In addition to the mixture in the proportions found in the rectified spirit itself, mixtures were made with approximately 10%, 20%, 30% (by weight), etc., of ethyl alcohol.

The exact values of the composition of the mixtures are given below, together with the average specific conductance.

EtOH, % by wt. ...	9·91	20·02	29·78	39·60	49·94	59·37	69·23	80·15	93·04
$\kappa \times 10^6$, mho	0·33	0·21	0·16	0·12	0·12	0·11	0·12	0·12	0·10

These mixtures will subsequently be referred to by the nearest whole number in the percentage of alcohol.

Procedure.—The pure solvent was weighed in the cell, and its conductance measured. Known weights of a solution of suitable concentration were added successively to the cell from a weight pipette of borosilicate glass. With this method, due to Whetham (*Phil. Trans.*, 1900, *A*, **194**, 321), the concentration and the solvent correction are known more definitely than with the Ostwald–Arrhenius dilution method. The solvent correction was made by subtracting the conductance of the solvent from that of the solution. At all stages precautions were taken to prevent the access of carbon dioxide.

The concentrations were known originally in weight normalities. For comparisons between solutions in different solvents it was essential to convert these into volume normalities. For this purpose the densities of the solutions were taken as being the same as those of the corresponding solvents : determination of a number of densities showed that the greatest error introduced by this assumption at the highest concentrations used was about 2 parts per 1000.

TABLE I.

Water.			9·91% *Alcohol.*			20·02% *Alcohol.*			29·78% *Alcohol.*		
Λ_0 = 65·46; *a* = 52·4.			Λ_0 = 48·36; *a* = 41·2.			Λ_0 = 35·65; *a* = 11·0.			Λ_0 = 28·02; *a* = 7·8.		
$\sqrt{c}$.	Λ.	Λ, calc.	$\sqrt{c}$.	Λ.	Λ, calc.	$\sqrt{c}$.	Λ.	Λ, calc.	$\sqrt{c}$.	Λ.	Λ, calc.
0·01740	64·79	64·55	0·01225	47·79	47·86	0·01517	35·50	35·48	0·01421	27·97	27·91
0·02163	64·41	64·33	0·01903	47·50	47·58	0·01945	35·44	35·44	0·02181	27·89	27·85
0·02658	64·04	64·07	0·02564	47·31	47·30	0·02354	35·36	35·39	0·02894	27·74	27·79
0·03045	63·90	63·86	0·02826	47·20	47·20	0·02703	35·30	35·35	0·03750	27·74	27·73
0·03438	63·69	63·66	0·03769	46·79	46·81	0·03402	35·33	35·28	0·04540	27·63	27·67
0·04136	63·25	63·29	0·04351	46·62	46·57	0·03895	35·26	35·22	0·05331	27·64	27·60
0·04778	62·94	62·96	0·04915	46·36	46·33	0·04442	35·14	35·16	0·06564	27·54	27·51
0·05311	62·61	62·68	0·05529	46·13	46·08	0·05144	35·14	35·08	0·07698	27·40	27·42
0·05846	62·47	62·40	0·06536	45·60	45·67	0·05459	35·10	35·05	0·08788	27·33	27·33
0·06220	62·14	62·20				0·06363	34·97	34·95	0·09552	27·30	27·27
0·06836	61·82	61·88				0·07541	34·85	34·82	0·1021	27·23	27·22
0·07403	61·56	61·58				0·08570	34·79	34·71			
0·08143	61·20	61·19									

39·60% *Alcohol.*			49·94% *Alcohol.*			59·37% *Alcohol.*			69·23% *Alcohol.*		
Λ_0 = 25·46; *a* = 15·6.			Λ_0 = 24·84; *a* = 23·4.			Λ_0 = 25·08; *a* = 36·2.			Λ_0 = 25·65; *a* = 39·4.		
0·01105	25·30	25·29	0·01571	24·48	24·47	0·01888	24·41	24·40	0·01987	24·96	24·87
0·01788	25·16	25·18	0·02111	24·35	24·35	0·02752	24·08	24·08	0·02989	24·41	24·47
0·02560	25·09	25·06	0·02830	24·14	24·18	0·03470	23·81	23·82	0·03803	24·19	24·15
0·03379	24·92	24·93	0·03542	24·02	24·01	0·04117	23·53	23·59	0·04472	23·88	23·89
0·04038	24·79	24·83	0·04378	23·82	23·82	0·04629	23·37	23·41	0·05512	23·53	23·48
0·04645	24·76	24·74	0·05373	23·58	23·58	0·05182	23·22	23·20	0·06322	23·24	23·16
0·05136	24·68	24·66	0·07144	23·20	23·17	0·05992	22·95	22·91	0·07168	22·82	22·83
0·05508	24·60	24·60	0·08305	22·94	22·90	0·06892	22·62	22·58	0·08052	22·47	22·48
0·06452	24·47	24·45				0·07894	22·31	[22·22]	0·09059	22·05	22·08
0·07348	24·27	24·31				0·08984	22·05	[21·83]	0·1042	21·54	21·54
0·08228	24·19	24·18				0·1011	21·74	[21·42]			
0·09099	24·00	24·04									

80·15% *Alcohol.*			93·04% *Alcohol.*			*Absolute alcohol.*					
Λ_0 = 27·75; *a* = 62·0.			Λ_0 = 32·40; *a* = 125·4.			Λ_0 = 34·70; *a* = 209·0.					
0·01249	26·99	26·98	0·01462	30·53	30·57	0·01173	32·25	32·25	0·05565	23·87	—
0·02009	26·50	26·50	0·02156	29·77	29·71	0·02094	30·38	30·32	0·06761	22·36	—
0·02802	26·10	26·01	0·02858	28·82	28·83	0·03087	28·44	[28·25]	0·08748	19·93	—
0·03753	25·45	25·42	0·03643	27·86	27·85	0·03958	26·81	[26·42]	0·1156	17·38	—
0·04633	24·88	24·88	0·04702	26·51	26·52	0·04731	25·52	—			
0·05618	24·25	24·27	0·05564	25·49	25·44						
0·07125	23·41	[23·33]	0·07794	23·26	[22·66]						
0·08995	22·36	[22·17]	0·09559	21·87	[20·45]						

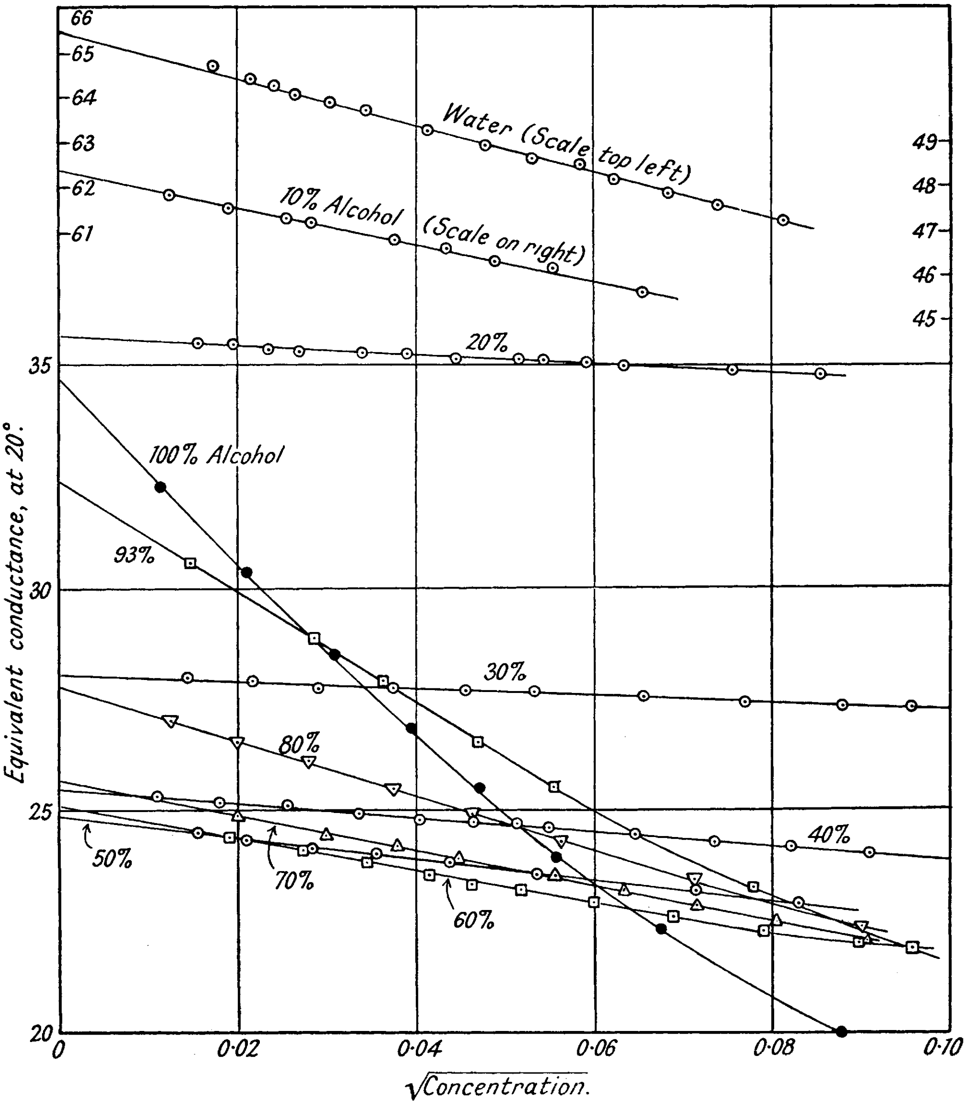
RESULTS AND DISCUSSION.

Values of the equivalent conductances (Λ) are collected in Table I for the various values of the concentration (*c*, in g.-equivs./l.) in the different solvent mixtures used.

In order to save space, results are not given for all the concentrations investigated, but only sufficient (about half) to show accurately the variation of Λ and agreement with Λ, calc. The results not shown agree excellently with those printed.

The conductances in aqueous solution agree with values extrapolated from the results of Lottermoser and Püschel at higher temperatures, but there is some divergence from the figures of Howell and Robinson. A systematic error has, however, been detected in the latter which will require the correction of their values for concentrations less than about 0·007N (Howell, private communication).

FIG. 1.

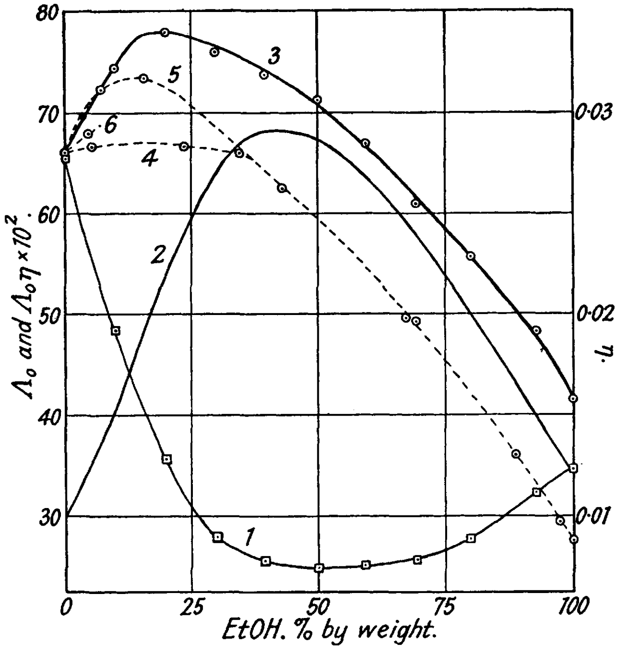


In Fig. 1, the equivalent conductances are plotted against $\sqrt{c}$. Straight lines are obtained, over part or all of the concentration range, for every solvent except absolute alcohol. This means that the Kohlrausch square-root law is obeyed, and the equivalent conductance is given by the equation $\Lambda = \Lambda_0 - a\sqrt{c}$. The values of Λ_0 shown in the table are obtained by graphical extrapolation to zero concentration from the curves in

Fig. 1. It is seen that, as the percentage of alcohol is increased, there is a rapid fall in the equivalent conductance at infinite dilution (Λ_0) from 65·46 for water to 24·84 for 50% alcohol, the lowest value obtained. As the percentage of alcohol is further increased, Λ_0 rises again to reach 34·70 for absolute alcohol. At the same time, there is a similar systematic alteration in the slope of the straight line, which reaches a minimum at about 30% of alcohol. The reasons for this are considered later.

Mobilities in Water and Alcohol.—Much evidence has been collected by Walden and his co-workers that the limiting equivalent conductance of an electrolyte in different solvents, or in a single solvent at different temperatures, is inversely proportional to the viscosity, but Walden's rule ($\Lambda_0\eta$ = constant) is not universally true. Aqueous solutions generally form an exception. The rule applies best to electrolytes with large symmetrical ions which are unlikely to be solvated (*e.g.*, tetraethylammonium picrate). In this case a value for $\Lambda_0\eta$ of 0·56 is obtained in all solvents at all temperatures investigated. Electrolytes with smaller ions may give a constant value of $\Lambda_0\eta$ at different temperatures in the same solvent, but different values on passing from one solvent to another. Simple inorganic salts, such as the alkali-metal halides, have values of $\Lambda_0\eta$ which vary with both temperature and solvent.

FIG. 2.



Curve 1 : Λ_0 *for sodium dodecyl sulphate.*
Curve 2 : *Viscosity of mixed solvent.*
Curve 3 : $\Lambda_0\eta$ *for sodium dodecyl sulphate.*
Curves 4, 5, *and* 6 : $\Lambda_0\eta$ *for* LiCl, KI, *and* NaCl, *respectively, multiplied by* ($\Lambda_0\eta$ NaD *in water*/$\Lambda_0\eta$ *salt in water*) (*from Connell, Hamilton, and Butler*).

Curve 1, Fig. 2. shows Λ_0 for sodium dodecyl sulphate plotted against the percentage of alcohol in the mixed solvents. Values of the viscosities of the mixtures are also given (curve 2). There is a general correlation between the two, but the maximum in the viscosity curve is not at the same concentration as the minimum value for Λ_0. The discrepancy is more obvious when values of $\Lambda_0\eta$ are plotted (curve 3, Fig. 2). This rises to a maximum at about 20% of alcohol, and beyond this concentration to 100% of alcohol there is a rapid fall.

Values of $\Lambda_0\eta$ for sodium dodecyl sulphate in water and alcohol may be compared with data for other typical compounds in Table II. The simpler the ions the greater is the difference between the values of $\Lambda_0\eta$ in the two solvents. An unusually small figure for $\Lambda_0\eta$ is explained by assuming solvation of the ions. No explanation has been given for the very large values for simple salts in water and also for solutions in liquid ammonia and in liquid sulphur dioxide. The values of $\Lambda_0\eta$ for sodium dodecyl sulphate are similar to those for sodium picrate, and are typical of a salt with a large organic ion and a small inorganic ion.

TABLE II.

	Water.			Ethyl alcohol.		
	$\Lambda_0\eta$.	l.	$l\eta$.	$\Lambda_0\eta$.	l.	$l\eta$.
Sodium dodecyl sulphate	0·661	—	—	0·414	—	—
Tetrapropylammonium picrate	0·486	—	—	0·490	—	—
Sodium picrate	0·729	—	—	0·512	—	—
Sodium chloride	1·15	—	—	0·477	—	—
$Na^{\cdot}$	—	45·6	0·460	—	20·3 or 17·0	0·242 or 0·203
D'	—	19·9	0·201	—	14·4 or 17·7	0·172 or 0·211
$NPr_4^{\cdot}$	—	21·8	—	—	18·7	—

Further information may be obtained by calculating the mobilities of the individual ions. Taking the mobility of the sodium ion in water ($l_{Na^{\cdot}}^{H_2O}$) to be 45·6 at 20°, we obtain 65·5 — 45·6 = 19·9 for that of the dodecyl sulphate ion ($l_{D'}^{H_2O}$). In ethyl alcohol the values are not so definite. Various estimates have been made of $l_{Na^{\cdot}}^{EtOH}$; Walden and Ulich (*Z. physikal. Chem.*, 1925, **114**, 297) give 22·2 at 25°, later modified to 22·3 ("Salts, Acids and Bases," p. 316). Barak and Hartley (*Z. physikal. Chem.*, 1933, *A*, **165**, 272), estimating the mobilities on a different basis, give rather higher values for the anions and correspondingly lower values for the cations, taking 18·7 for sodium. Although Ogston (*Trans. Faraday Soc.*, 1936, **32**, 1679) does not give a value for sodium, his estimates of mobilities in ethyl alcohol agree closely with those of Barak and Hartley. If these figure are converted to 20° by a viscosity correction, we obtain the values shown in Table II.

Walden's rule may be tested for individual ions by comparing the products $l\eta$ in different solvents. It is seen that the rule is approximately obeyed by the dodecyl sulphate ion but not by the sodium ion. The lack of constancy of the product $\Lambda_0\eta$ for sodium dodecyl sulphate is therefore due to the varying contribution of the sodium ion to the whole.

It is instructive to compare the mobilities of the $C_{12}H_{25}SO_4'$ ion and the tetrapropylammonium ion, $N(C_3H_7)_4^{\cdot}$, at 20° (Table II). These ions have almost exactly the same number of atoms, but the former is unsymmetrical and the latter symmetrical. The mobilities are similar in both solvents, but slightly lower values are found for the unsymmetrical ion. It is generally found that for isomeric ions, in most solvents, the most symmetrical have the greatest mobilities. Thus, for isomeric substituted-ammonium ions, the mobilities are in the order $NMe_4^{\cdot} > NH_2Et_2^{\cdot} > NH_3Bu^{\cdot}$.

Mobilities in Water–Alcohol Mixtures.—The variation in the value of $\Lambda_0\eta$ for sodium dodecyl sulphate is probably due to alteration in the solvation of the ions. Estimation of the effect of solvation in mixed solvents is more difficult than with single solvents, for the composition of the solvation layer will generally differ from that of the bulk of the mixture. Butler and Lees (*Proc. Roy. Soc.*, 1931, *A*, **131**, 382), from measurements of molar refractivities, have shown that water molecules in the solvation layer of lithium chloride do not begin to be replaced by ethyl alcohol molecules until there are 20 mols.% (*i.e.*, about 40% by weight) of alcohol in the solvent. Connell, Hamilton, and Butler (*ibid.*, 1934, *A*, **147**, 418) have measured conductivities of lithium chloride and potassium iodide in water–alcohol mixtures. Their values of $\Lambda_0\eta$ for these salts (at 25°) are plotted against the percentage by weight of alcohol in Fig. 2 (curves 4 and 5, broken lines). The values of $\Lambda_0\eta$ for the simple salts have been multiplied by suitable factors ($\Lambda_0\eta$ NaD in water/($\Lambda_0\eta$ salt in water)) so that the curves all leave the $\Lambda_0\eta$ axis at the same point (0·661) and comparison between the simple salts and the sodium dodecyl sulphate is easy.

There is a general similarity between the curves. The value of $\Lambda_0\eta$ for lithium chloride alters very little in the concentration range where the solvation layer is unchanged. The maxima obtained in this range for potassium iodide and sodium dodecyl sulphate may be due to alteration in the solvation, or, alternatively, the effective viscosity for an ion solvated with water molecules and moving in the mixed solvent may be different from the viscosity of the mixed solvent in bulk. Whether or not there is any alteration in the solvation of the sodium dodecyl sulphate up to 40—50% of alcohol, this most probably occurs with higher concentrations of alcohol. The fall in $\Lambda_0\eta$ for alcohol-rich mixtures is considerably larger than the initial rise.

Solvation of Ions in Water and Alcohol.—Various methods have been suggested by which the solvation may be calculated from conductivity measurements, but the results vary greatly because of the numerous assumptions which have to be made. The principle is that if the value of $\Lambda_0\eta$ (or $l\eta$ for a single ion) is smaller than would be expected from some empirical generalisation, this is because the solvation causes a lower mobility. These methods are not always applicable to aqueous solutions. By applying Walden's generalistion (*Z. Elektrochem.*, 1920, **26**, 65), that $\Lambda_0\eta\sqrt{M}$ = constant (where M = molecular weight of solute), the dodecyl sulphate ion is found to be solvated with 4—5 molecules of alcohol. Herzog's formula (*ibid.*, 1910, **16**, 1003) as developed by Walden (*loc. cit.*), *viz.*, $\Lambda_0\eta\sqrt[3]{V_m}$ = constant (where V_m = molecular volume of solute), gives 2—4 molecules of alcohol for the solvation of the dodecyl sulphate ion. The solvation of the sodium ion, as calculated by either of these methods, is 4—5 molecules of alcohol.

An alternative method is to calculate the radius of the solvated ion (r) from the mobility by means of Stokes's equation (Ulich, *Trans. Faraday Soc.*, 1927, **23**, 388). This gives $r = 8{\cdot}15 \times 10^{-9}/l\eta$ cm. If the volume of the "naked" ion is known, the number of molecules in the solvation layer can be calculated. The hydrocarbon chain of the dodecyl sulphate ion is probably tightly rolled up to present the minimum surface to the water. Manipulation of a three-dimensional scale model of the chain gave 180 A.^{3} as the minimum volume. Calculation of the solvation of the ion on this basis gave 2—3 molecules of alcohol or 4—7 molecules of water.

Slope of Curve for Λ *against* $\sqrt{c}$.—The Onsager equation for the conductivity of a completely dissociated uni-univalent electrolyte at 20° takes the form

$$\Lambda = \Lambda_0 - (162{\cdot}9\Lambda_0/\varepsilon^{3/2} + 4{\cdot}789/\eta\varepsilon^{1/2})\sqrt{c}.$$

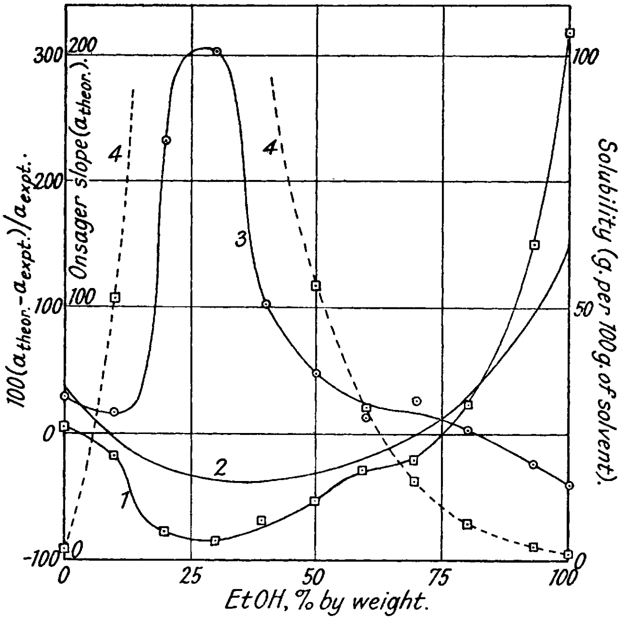
This equation is valid when certain fluctuation terms can be neglected as small, *i.e.*, at very low concentrations, and if the dielectric constant (ε) of the solvent is high enough. This means that a lower concentration must be reached in ethyl alcohol ($\varepsilon = 25{\cdot}07$) than in water ($\varepsilon = 80{\cdot}37$) before a straight line is obtained for Λ plotted against $\sqrt{c}$. At higher concentrations the equivalent conductance as measured is higher than the value calculated from the Onsager equation, so the curve is concave upwards, even for a completely dissociated electrolyte. Davies ("The Conductivity of Solutions," 1930, p. 32) gives the rule that when $\Lambda_0 - \Lambda$ amounts to 10% of Λ_0 the actual equivalent conductance is about 1% higher than the calculated. Walden (*Z. physikal. Chem.*, 1929, *A*, **140**, 104) finds that the concentration when the Λ–$\sqrt{c}$ curve deviates from a straight line is given by $\sqrt[3]{c} = \varepsilon/272$. These two methods give very similar estimates for the limiting concentration of sodium dodecyl sulphate in the water–alcohol mixtures, varying from about $\sqrt{c} = 0{\cdot}1$ in water to $\sqrt{c} = 0{\cdot}02$ in alcohol. It is seen from Fig. 1 that when $\sqrt{c}$ is greater than 0·02 a straight line is no longer obtained for the solution in alcohol. For solutions with smaller alcohol concentrations, the straight-line portions of the curves extend over increasing concentration ranges. In the measurements by Walden, Ulich, and Laun (*loc. cit.*) of equivalent conductances of ethyl alcohol solutions, deviations from the straight lines began at concentrations between $\sqrt{c} = 0{\cdot}02$ and $\sqrt{c} = 0{\cdot}04$.

In Table I, col. 3 gives values of Λ, calc., obtained from the equation Λ, calc. $= \Lambda_0 - a\sqrt{c}$. The values of Λ_0 and a given at the head of each part of the table have been obtained from the best straight lines drawn through the experimental points on a large-scale graph. It is seen that there is close agreement between the experimental values of Λ and those calculated from the Kohlrausch expression, over the appropriate concentration range.

Curve 1 in Fig. 3 shows how the slope a of the Λ–$\sqrt{c}$ lines varies with the percentage of alcohol in the solvent. The calculated values for the slope, according to the Onsager equation, are also plotted (curve 2). For the water-rich solvents the experimentally found slope is rather smaller than the theoretical, whereas for the mixtures rich in alcohol the experimental slope is the greater. The usual interpretation of a slope greater than the theoretical Onsager slope is that there is incomplete dissociation (or, alternatively, associated ion-pairs). Evidently, the dielectric constants of the mixtures from about 80% to 100% of alcohol are not sufficient to allow complete dissociation of the sodium dodecyl sulphate. The degree of dissociation decreases as the percentage of alcohol increases in this range. (The dielectric constant falls nearly linearly with increasing percentage of alcohol.)

Slopes greater than the Onsager theoretical are commonly found for solutions of electrolytes in ethyl alcohol. There is a greater variation among the deviations for different electrolytes in this solvent than in water, for the lower dielectric constant magnifies any tendency to form ion-pairs. The deviation for sodium dodecyl sulphate is about the same as that for the tetra-alkylammonium salts in ethyl alcohol (Barak and Hartley, *loc. cit.*) and considerably greater than for most simple inorganic electrolytes. For solutions in methyl alcohol, the deviations from the Onsager slope are generally very small (Unmack, Murray-Rust, and Hartley, *Proc. Roy. Soc.*, 1930, *A*, **127**, 228), but both positive and negative deviations are found. The ethyl alcohol–water mixture with a dielectric constant equal to that of methyl alcohol (about 85% EtOH) gives a slope for sodium dodecyl sulphate of nearly the theoretical value, indicating nearly complete dissociation.

FIG. 3.



Curve 1 : *Experimental slope.*
Curve 2 : *Theoretical Onsager slope.*
Curve 3 : *Percentage excess of theoretical over experimental slope.*
Curve 4 : *Solubility of sodium dodecyl sulphate at* 20°.

There is no explanation on Onsager's theory for a slope lower than the theoretical. Nevertheless, this is found with many substances, although they are a minority of those investigated. For example, for aqueous solutions at 18°, the following substances (Onsager, *loc. cit.*) give slopes lower than the Onsager value (given in parentheses after the experimental figure)—potassium iodide, 72·88 (79·9); cæsium chloride, 76·02 (80·5); potassium thiocyanate, 76·50 (77·8); potassium sulphate, 140·3 (159·5). The variation of the experimental slope for sodium dodecyl sulphate in the range 0—80% of alcohol gives a curve (Fig. 3) which is approximately parallel to the theoretical curve and about 10 units below it, except for a sharp dip between about 10% and 50% of alcohol. If a slope of about 10 units below the theoretical is accepted as normal for this salt, the rise from 80% to 100% and the dip between 10% and 50% of alcohol are evidently secondary effects superimposed. The slopes obtained for lithium chloride and potassium iodide in alcohol–water mixtures (Connell, Hamilton, and Butler, *loc. cit.*) follow the theoretical values fairly closely, except that potassium iodide shows the same evidence of association as does sodium dodecyl sulphate in alcohol-rich mixtures. When the concentration of alcohol is about 30% by weight, the experimental slopes are slightly lower than the theoretical values, but there is no abnormal dip such as occurs in the curve for sodium dodecyl sulphate in Fig. 3. This dip appears to be a specific effect caused by the dodecyl sulphate ion.

At higher concentrations of sodium dodecyl sulphate than those described here, aggregation of ions occurs in the water-rich solvents, with the formation of a colloidal electrolyte. This does not occur with alcohol-rich mixtures (Ward, Chemical Society Discussion on "Aggregation of Ions in Paraffin-chain Salt Solutions," *J. Soc. Chem. Ind.*, 1938, **58**, 1168; detailed account to be published shortly). The curves for Λ against $\sqrt{c}$, at higher salt concentrations where micelle formation occurs, do not show any anomalies which can be related to the abnormal dip in curve 1, Fig. 3. It is quite certain that no micelles are formed in any of the solutions at the concentrations considered in the present paper.

If the interaction of the ions with the solvent molecules were to cause an increase in the effect values of ε or η to figures higher than those characteristic of the solvents in bulk, then the experimental values for the slopes would be lower than the Onsager theoretical. It is unlikely that there is such an increase in the effective viscosity between the concentrations of 10% and 50% of alcohol. A decrease is more probable in view of the maximum in the value of $\Lambda_0\eta$ in this same range (Fig. 2). On the other hand, the dielectric constant might well be altered considerably by orientation of molecules in the solvation layer (Williams, *Chem. Reviews*, 1931, **8**, 303). This would make the application of Coulomb's law, on which the Onsager equation is based, only an approximation, and the effectively higher value for the dielectric constant might well explain the abnormally low values obtained for the slope.

Further experiments on the various properties of similar solutions in mixed solvents would be needed before this suggestion could be considered as proved, or the reason made clear why the abnormal decrease of the slope should occur only in the range of 10—50% of alcohol. A possible confirmation, however, is seen in the manner of variation of the solubility of sodium dodecyl sulphate in water–alcohol mixtures. Solubility depends ultimately on interaction between the molecules (or ions) of the solute and solvent—the same effect that is suggested as causing local increases in the dielectric constant. The solubility of sodium dodecyl sulphate has been measured in the various water–alcohol mixtures at 20°, and the values are plotted as a broken line in curve 4 in Fig. 3. For comparison, curve 3 shows the percentage excess of the theoretical slope over the experimental. There is a very close similarity between the two curves. Between 10% and 50% of alcohol the solubility is extremely high, so high that it is indeterminate. The solutions still remain unsaturated even at concentrations where they are so viscous as to be almost solid.

The reason why this increase in solubility occurs only over a certain range of alcohol concentrations depends most probably on the nature of the dodecyl sulphate ion. A hydrophilic and a hydrophobic group are combined together. When suitable concentrations of both water and alcohol are present, with specific attractions for the respective groups, the solubility should be greater than in either solvent alone. The question of the solubility is complicated in detail because at higher concentrations there are ionic micelles in equilibrium with the single ions, but the general considerations still apply.

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