

CCCXXIX.—*The Conductivity of Some Uni-univalent Salts in Ethyl Alcohol.*

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THE conductivity of a large number of uni-univalent salts has been measured in water and in methyl alcohol, but there are few accurate data available for ethyl alcohol. The purposes of this investigation were, first, to work out a convenient method of preparing pure ethyl alcohol suitable for conductivity measurements and, secondly, to determine the mobility of the perchlorate ion, in order to discover whether this was abnormally great compared with that of other anions, as has been found to be the case in methyl alcohol (see preceding paper). The conductivity of a few other salts was measured for purposes of comparison, but the choice of salts is more limited than in methyl alcohol, for many salts were found to be insufficiently soluble in dry ethyl alcohol. Since this work was completed, a more extensive investigation of the conductivity of salts in ethyl alcohol has been undertaken by M. Barak in this laboratory, and the results of this will be published shortly.

EXPERIMENTAL.

Purification of Ethyl Alcohol.—A method of purifying ethyl alcohol based on that used by McKelvey (*Bull. Bur. Standards*, 1913, 9, 327) has been worked out by one of us (E. D. C.). Most of the water was removed by refluxing for 24 hours with freshly fired lime, followed by distillation through a long fractionating column, and the last traces were removed by distillation from aluminium ethoxide made by warming the lime-dried alcohol with aluminium amalgam for some hours. The preliminary drying with lime was found to be necessary, as the aluminium amalgam would not react with the alcohol unless the water content was very small; in some cases when the alcohol was being recovered from residues containing a considerable amount of water, two distillations from lime were necessary before the amalgam would react. Volatile impurities were removed by refluxing for some hours in a current of pure air in the presence of a small quantity of anhydrous copper sulphate, followed by distillation into a siphon conductivity cell, which was fitted to the still so that the conductivity of each sample could be measured as it distilled. The average specific conductivity of the distillate was 0.003×10^{-6} mho. The water content of the alcohol was determined by measurements of its viscosity in an Ostwald viscometer. The increase of viscosity caused by the addition of

small quantities of water is proportional to the water content, and it was found that the addition of 0.1% of water raised the viscosity by about 0.4%, a value which is in agreement with the measurements of Goldschmidt and Aarflot (*Z. physikal. Chem.*, 1926, **122**, 371). The viscosity of the pure alcohol was taken to be 0.01078, as this was the lowest value that was consistently obtained. The carbide test used by Hartley and Raikes (*J.*, 1925, **127**, 524) for the determination of water in methyl alcohol was found not to be applicable to ethyl alcohol.

Preparation of Salts.—*Lithium chloride.* This was made by heating pure lithium nitrate several times to dryness with constant-boiling hydrochloric acid. It was recrystallised from water and dried to constant weight by heating in dry hydrogen chloride at 400° in a Richards bottling apparatus, followed by further heating in nitrogen. It was found unexpectedly difficult to obtain concordant results with different specimens of lithium chloride, and the final values are taken from the mean of five series of measurements (two of which were carried out by M. Barak in this laboratory) with three independent samples of salt.

Lithium nitrate. Measurements were made with a sample of Merck's pure lithium nitrate and also with a sample made from impure lithium chloride. The fluoride was precipitated by adding a solution of hydrogen fluoride to a boiling solution of lithium chloride and was converted into the nitrate by heating to dryness with nitric acid. The lithium nitrate was recrystallised from water, and dried to constant weight in an air-bath at 160°.

Lithium, sodium, and silver perchlorates. The samples used were those made by Copley and Hartley (see preceding paper) for the measurement of conductivities in methyl alcohol.

Potassium iodide. A sample of Merck's potassium iodide was recrystallised and dried to constant weight in an air-bath at 160°.

Silver nitrate. This was prepared from pure silver by treatment with nitric acid and was dried to constant weight in an air-bath at 110°.

Rubidium iodide and sodium bromide. The results for these salts are less accurate than for the other salts described, as they were known to contain a certain amount of impurity. The apparent equivalent weight of the rubidium iodide, determined by titration, was found to be 210.7 (Calc. for RbI : *M*, 212.4), and the results are calculated from this experimental value.

Measurement of Conductivity.—The conductivity was measured in a cell of the type described by Hartley and Barrett (*J.*, 1913, **103**, 789); successive additions of weighed amounts of solution were made to a known weight of solvent in the cell and the resistance

was determined after each addition. All measurements were made at 25°.

Results.—Table I shows the values of the equivalent conductivities at various concentrations. The concentrations are given

TABLE I.

	κ .	$c \times 10^4$.	$100\sqrt{c}$.	Λ_c .	Diff.
<i>Lithium chloride</i> : $\Lambda_0 = 39.2$; $x = 168$.					
Series A	0.028	1.457	1.207	37.07	-0.10
		3.005	1.733	36.22	-0.07
		4.988	2.234	35.38	-0.07
		7.509	2.741	34.54	-0.06
		10.479	3.237	33.69	-0.07
		14.173	3.767	32.82	-0.05
Series B (by M. Barak)	0.025	1.048	1.024	37.54	+0.09
		2.179	1.476	36.83	+0.11
		4.233	2.058	35.84	+0.09
		7.329	2.707	34.71	+0.06
		10.171	3.189	33.90	+0.05
		13.664	3.676	33.08	+0.05
Series C (by M. Barak)	0.024	1.036	1.018	37.42	-0.07
		2.054	1.433	36.76	-0.03
		4.412	2.100	35.62	-0.05
		8.950	2.992	34.10	-0.07
		13.964	3.736	32.88	-0.04
		19.654	4.433	31.76	+0.02
Series D	0.029	1.305	1.142	37.42	+0.11
		2.606	1.614	36.64	+0.16
		4.779	2.192	35.65	+0.13
		8.331	2.886	34.44	+0.09
		11.846	3.442	33.52	+0.11
		16.238	4.030	32.59	+0.17
Series E	0.022	1.462	1.205	37.26	+0.08
		2.780	1.667	36.47	+0.07
		5.245	2.290	35.39	+0.04
		9.190	3.031	34.10	-0.01
		13.098	3.619	33.17	-0.01
		17.064	4.195	32.26	+0.11
<i>Lithium nitrate</i> : $\Lambda_0 = 42.7$; $x = 171$.					
Series A	0.024	2.1935	1.450	40.25	+0.03
		4.0465	2.011	39.24	-0.02
		7.367	2.714	38.05	± 0.00
		12.854	3.585	36.52	-0.05
		17.128	4.139	35.60	-0.02
		24.074	4.906	34.39	+0.08
Series B	0.038	2.2091	1.486	40.18	+0.02
		4.4267	2.104	39.05	-0.05
		7.195	2.682	38.06	+0.08
		11.141	3.338	36.86	-0.13
		14.934	3.864	35.98	-0.01
		21.375	4.623	34.77	-0.03
Series C	0.068	2.2189	1.490	40.10	-0.05
		3.779	1.944	39.52	+0.14
		6.906	2.628	38.25	+0.04
		11.882	3.447	36.81	± 0.00
		16.860	4.106	35.69	+0.01
		23.676	4.866	34.49	+0.11

	κ .	$c \times 10^4$.	$100\sqrt{c}$.	Λ_c .	Diff.
<i>Lithium perchlorate</i> : $\Lambda_0 = 48.50$; $x = 162$.					
Series A	0.043	2.0202	1.421	46.07	-0.13
		3.6493	1.910	45.48	+0.07
		5.826	2.414	44.61	+0.02
		10.001	3.162	43.32	-0.06
		13.655	3.695	42.49	-0.02
	18.695	4.324	41.56	+0.06	
Series B	0.029	2.0027	1.415	46.29	+0.08
		3.806	1.951	45.34	± 0.00
		6.614	2.572	44.31	-0.02
		10.075	3.174	43.34	-0.02
		13.296	3.647	42.58	-0.01
	18.809	4.337	41.55	+0.08	
<i>Sodium perchlorate</i> : $\Lambda_0 = 52.45$; $x = 233$.					
Series A	0.046	1.6622	1.289	49.52	+0.07
		3.261	1.806	48.31	+0.07
		5.500	2.345	47.00	+0.01
		8.791	2.965	45.56	+0.02
		11.812	3.437	44.48	+0.04
	17.082	4.133	42.94	+0.12	
Series B	0.054	1.797	1.341	49.27	-0.06
		3.581	1.892	48.00	-0.04
		7.593	2.755	45.97	-0.06
		11.483	3.389	44.54	-0.01
		17.517	4.185	42.70	+0.11
<i>Silver perchlorate</i> : $\Lambda_0 = 51.2$; $x = 184$.					
Series A	0.075	1.791	1.338	49.22	+0.48
		3.755	1.938	47.67	+0.02
		5.492	2.344	46.90	+0.02
		8.446	2.906	45.78	-0.07
		12.550	3.543	44.57	-0.10
	18.823	4.339	43.20	-0.01	
Series B	0.038	1.952	1.397	48.45	-0.18
		3.705	1.925	47.63	-0.03
		6.981	2.642	46.35	+0.02
		11.352	3.369	45.02	+0.02
		15.760	3.970	43.96	+0.07
	21.191	4.603	42.91	+0.19	
Series C	0.020	1.894	1.376	48.78	+0.10
		3.993	1.998	47.51	+0.01
		7.492	2.737	46.02	-0.15
		10.149	3.186	45.20	-0.14
	14.042	3.747	44.17	-0.13	
<i>Silver nitrate</i> : $\Lambda_0 = 46.25$; $x = 336$.					
Series A	0.044	2.051	1.432	41.44	0.00
		3.904	1.976	39.59	-0.02
		6.668	2.582	37.54	-0.03
		9.174	3.029	36.08	+0.01
	13.791	3.714	33.77	+0.19	
Series B	0.061	2.139	1.463	40.96	-0.37
		4.078	2.019	39.29	-0.18
		9.175	3.029	36.02	-0.05
		12.545	3.542	34.37	+0.02
		17.073	4.132	32.69	+0.32

	κ .	$c \times 10^4$.	$100\sqrt{c}$.	Λ_c .	Diff.
<i>Sodium bromide</i> : $\Lambda_0 = 44.85$; $x = 192$.					
Series A	0.028	0.6246	0.790	43.26	-0.18
		1.2301	1.109	42.69	-0.03
		2.517	1.554	41.89	+0.02
		4.064	2.016	40.98	0.00
		5.420	2.328	40.37	-0.01
		7.864	2.805	39.45	-0.02
Series B	0.034	1.380	1.175	42.52	-0.07
		2.750	1.658	41.72	+0.05
		4.971	2.229	40.62	+0.05
		8.517	2.918	39.25	0.00
		10.954	3.310	38.55	+0.05
		14.161	3.763	37.66	+0.04
<i>Potassium iodide</i> : $\Lambda_0 = 50.8$; $x = 209$.					
Series A	0.059	1.696	1.302	48.04	-0.04
		3.361	1.833	46.96	-0.01
		6.741	2.596	45.38	0.00
		8.933	2.989	44.55	0.00
		13.612	3.628	43.20	-0.02
Series B	0.309	2.079	1.442	47.09	-0.70
		3.860	1.964	46.41	-0.29
		7.411	2.722	45.10	-0.01
		10.268	3.204	44.15	+0.05
		14.050	3.748	42.95	-0.02
Series C (by C. R. Bury)		0.773	0.867	48.72	-0.27
		1.679	1.293	48.16	+0.06
		3.358	1.832	47.09	+0.12
		6.725	2.593	45.47	+0.09
		10.465	3.235	44.09	+0.05
		13.602	3.688	43.16	+0.07
<i>Rubidium iodide</i> : $\Lambda_0 = 51.8$; $x = 228$.					
Series A	0.042	0.656	0.810	49.55	-0.40
		1.316	1.148	49.17	-0.01
		2.254	1.501	48.47	+0.09
		3.102	1.762	47.92	+0.13
		4.340	2.083	47.14	+0.09
Series B	0.022	0.842	0.918	49.33	-0.38
		1.592	1.261	48.88	-0.04
		2.761	1.661	47.99	-0.02
		3.763	1.940	47.38	0.00
		5.111	2.261	46.60	-0.05

in g.-equivs. per litre, the density of the solutions being assumed to be the same as that of the pure solvent ($D_4^{25} 0.7851$). All the salts obey the square-root relation $\Lambda_c = \Lambda_0 - x\sqrt{c}$, and the mean values for Λ_0 and x are given for each salt at the head of the appropriate section of the table. Col. 1 gives the value of κ , the specific conductivity of the solvent in reciprocal megohms, and the solvent correction was applied by subtracting this value from the specific conductivity of the solution in each case. Col. 2 gives the value of the concentration; col. 3, the value of $100\sqrt{c}$; col. 4, the observed equivalent conductivity Λ_c , and col. 5 the difference between the

observed value of Λ_c and that calculated from the given values of Λ_0 and x .

Discussion of Results.

The results when plotted show that the fall in conductivity is proportional to the square root of the equivalent concentration in accordance with the theory for strong electrolytes, and values of Λ_0 have been determined by direct extrapolation of these straight lines. A comparison of the slopes of the experimental lines with those calculated from theory is given in Table II: $x_{\text{obs.}}$ is the experimental slope, and $x_{\text{calc.}}$ is the value calculated from the Debye-Hückel-Onsager equation, which for uni-univalent electrolytes in ethyl alcohol reduces to the form

$$\Lambda_c = \Lambda_0 - (1.256\Lambda_0 + 87.8)\sqrt{c}.$$

The last column of the table gives the values of Δ , the percentage deviation of the observed values from the theoretical:

$$\Delta = 100(x_{\text{obs.}} - x_{\text{calc.}})/x_{\text{calc.}}$$

TABLE II.

Salt.	Λ_0 .	$x_{\text{obs.}}$	$x_{\text{calc.}}$	Δ .	Salt.	Λ_0 .	$x_{\text{obs.}}$	$x_{\text{calc.}}$	Δ .
LiCl ...	39.2	166	137	21	AgNO ₃	46.25	336	146	130
LiNO ₃ ...	42.7	171	141	21	NaBr ...	44.85	192	144	33
LiClO ₄	48.6	164	149	10	KI	50.8	209	152	38
NaClO ₄	52.45	232	154	52	RbI	51.8	228	153	49
AgClO ₄	51.45	195	152	28					

In all cases Δ has a positive value, indicating that the experimental slope is greater than the theoretical, as would be expected if there were any ionic association. It is seen that the lithium salts show the smallest deviation from theory, as is the case with methyl alcohol (Unmack, *Proc. Roy. Soc.*, 1930, *A*, 127, 228), but there are not sufficient data for a systematic comparison; this will be left until a later paper when the results of a more complete investigation of salts in ethyl alcohol will be published. The values of Λ_0 for the perchlorates show that, in this solvent as well as in methyl alcohol, the perchlorate ion has a larger mobility than the other anions and so is presumably less solvated.

One other point of interest is the large deviation shown by silver nitrate, which makes it probable that the value of Λ_0 found by direct extrapolation is too high, as the curve should be tangential to the theoretical slope at high dilutions. This view is supported by comparing the values for the difference $l_{0\text{Ag}^+} - l_{0\text{Li}^+}$ obtained from the nitrates with that from the perchlorates. The value of $\Lambda_{0\text{AgNO}_3} - \Lambda_{0\text{LiNO}_3}$ is 3.55, while $\Lambda_{0\text{AgClO}_4} - \Lambda_{0\text{LiClO}_4}$ is 2.85, and as the perchlorates have about the same slope, the latter value for the difference between the mobilities of the silver and lithium ions is the more trustworthy.

Among previous measurements of the salts described here, the most important are those with potassium iodide by Walden (*Z. physikal. Chem.*, 1905, **54**, 129) and by Philip and Courtman (*J.*, 1910, **97**, 1268), and those with sodium bromide by Goldschmidt and his pupils. The measurements with potassium iodide were made in more concentrated solutions than have been used in the present work, and neither series gives a straight line when Λ_c is plotted against \sqrt{c} . In the short range in which they overlap with our measurements, Walden's results are about 1% lower than ours, and Philip and Courtman's about 2% lower. Goldschmidt's early measurements with sodium bromide also do not give a straight line for the $\Lambda_c - \sqrt{c}$ relationship, but quite recently Thomas and Marum have repeated the work in dilute solution (*Z. physikal. Chem.*, 1929, **143**, 191); their individual points are rather more scattered than ours, but the mean line which they draw through them ($\Lambda_0 = 44.9$, $x = 192$) is in excellent agreement with our results.

Summary.

1. A method of preparing pure ethyl alcohol for conductivity work is described.
2. The electrical conductivity of solutions of nine uni-univalent salts in ethyl alcohol has been measured at 25° over a concentration range from $N/10,000$ to $N/500$.
3. The perchlorate ion is found to have a greater mobility than other anions in ethyl alcohol.

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