Electrical Conductance of Concentrated Aqueous Solutions of Copper Sulfate

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Numerous attempts have been made to extend the Debye-Hückel theory to electrolyte solutions of higher concentrations than 0.1 N. The attempts of Falkenhagen and Leist[1], Robinson and Stokes[2], Wishaw and Stokes[3], and Leist[4], are the most notable contributions in recent times in this direction.

Suryanarayana and Venkatesan[5,6] recently formulated the equation,

$$\Lambda_c = \Lambda_s + A\frac{(1-c_p)}{\eta_p} \tag{1}$$

where

$$\Lambda_c = \frac{\text{specific conductance } (K_c)\times 1000}{c_p}$$

Λ_s = specific conductance at saturation $(K_s)\times 1000$

$$c_p = \frac{\text{mole fraction at a given concn.}}{\text{mole fraction at saturation at the same temp.}}$$

of course, at saturation $c_p = 1$

$$\eta_p = \frac{\text{viscosity at a given concn.}}{\text{viscosity at saturation}}$$

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[1] H. Falkenhagen and M. Leist, *Naturwiss.*, **41**, 570 (1954).

[2] R. A. Robinson and R. H. Stokes, *J. Am. Chem. Soc.*, **76**, 1991 (1954).

[3] B. F. Wishaw and R. H. Stokes, ibid., **76**, 2065 (1954).

[4] M. Leist, *Z.phys.Chem.*, **205**, 16 (1955).

[5] C. V. Suryanarayana and V. K. Venkatesan, *Nature*, **178**, 1461 (1956).

[6] C. V. Suryanarayana and V. K. Venkatesan, *Acta. Chim. Hung.*, **17**, 327 (1958).

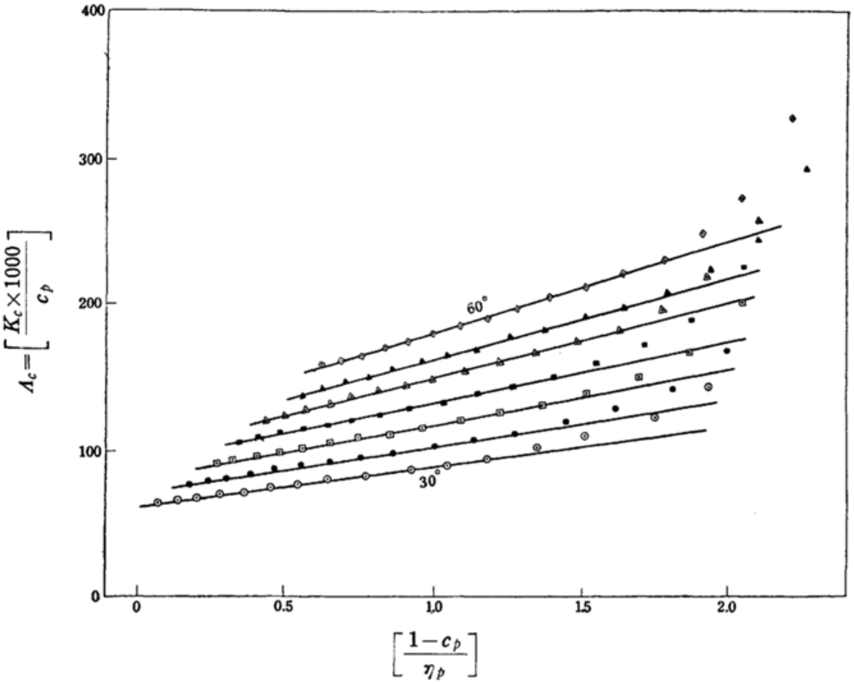

Fig. 1.

TABLE I

TEMPERATURE 30°C

Molality	Specific conductance $K_c \times 10^2$	Density	Relative viscosity	c_p	η_p	Λ_c	$\left[\frac{1-c_p}{\eta_p}\right]$
0.0992	0.9661	1.011	1.042	0.0673	0.4818	143.5	1.936
0.1965	1.638	1.027	1.070	1.1332	0.4946	122.9	1.752
0.2921	2.179	1.042	1.131	0.1977	0.5231	110.2	1.508
0.3862	2.673	1.057	1.182	0.2609	0.5468	102.4	1.352
0.4785	3.042	1.071	1.246	0.3228	0.5762	94.26	1.175
0.5693	3.413	1.085	1.288	0.3833	0.5958	89.04	1.035
0.6586	3.842	1.098	1.326	0.4428	0.6132	86.76	0.9088
0.7463	4.075	1.110	1.403	0.5009	0.6488	81.34	0.7693
0.8326	4.482	1.124	1.485	0.5581	0.6869	80.32	0.6433
0.9175	4.719	1.136	1.539	0.6141	0.7117	76.85	0.5423
1.0010	5.003	1.149	1.602	0.6688	0.7408	74.82	0.4471
1.0830	5.253	1.161	1.675	0.7231	0.7747	72.64	0.3575
1.1640	5.502	1.172	1.738	0.7759	0.8037	70.92	0.2788
1.2440	5.650	1.184	1.827	0.8273	0.8448	68.28	0.2044
1.3210	5.825	1.195	1.908	0.8780	0.8824	66.34	0.1382
1.3980	5.977	1.205	2.009	0.9281	0.9290	64.40	0.0774
1.5100 (Satd.)	—	1.223	2.162	1.0000	1.0000	—	—

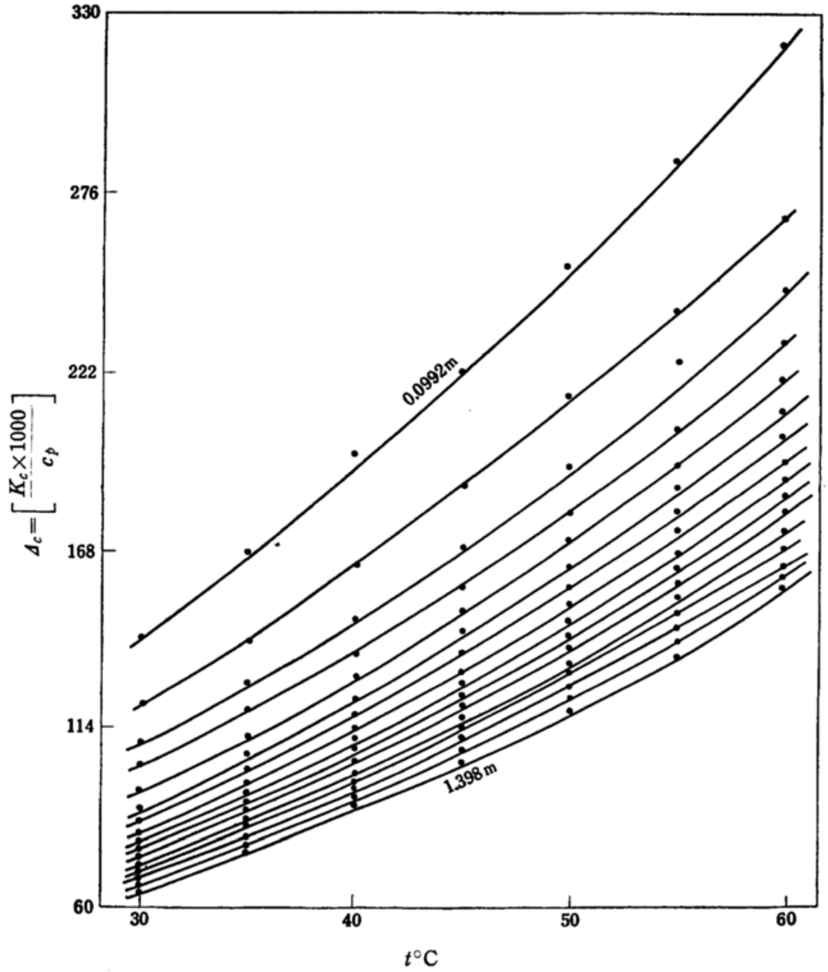

Fig. 2.

TABLE II
TEMPERATURE 35°C

Molality	Specific conductance $K_c\times 10^2$	Density	Relative viscosity	c_p	η_p	Λ_c	$\left[\frac{1-c_p}{\eta_p}\right]$
0.0992	1.041	1.009	1.047	0.0618	0.4722	168.6	1.9870
0.1965	1.738	1.025	1.078	0.1222	0.4863	142.2	1.8050
0.2921	2.343	1.040	1.124	0.1813	0.5069	129.2	1.6150
0.3862	2.874	1.054	1.172	0.2393	0.5286	120.0	1.4390
0.4785	3.321	1.068	1.225	0.2961	0.5525	112.1	1.2750
0.5693	3.778	1.082	1.273	0.3517	0.5741	107.4	1.1290
0.6586	4.151	1.095	1.318	0.4061	0.5944	102.2	0.9993
0.7463	4.482	1.109	1.385	0.4595	0.6247	97.54	0.8652
0.8326	4.872	1.121	1.442	0.5119	0.6504	95.17	0.7504
0.9175	5.172	1.133	1.502	0.5632	0.6775	91.83	0.6443
1.0010	5.508	1.146	1.555	0.6135	0.7013	89.78	0.5512
1.0830	5.821	1.158	1.619	0.6633	0.7318	87.76	0.4601
1.1640	6.009	1.170	1.687	0.7117	0.7608	84.43	0.3789
1.2440	6.169	1.181	1.760	0.7590	0.7938	81.28	0.3036
1.3210	6.341	1.192	1.830	0.8054	0.8254	78.74	0.2357
1.3980	6.528	1.203	1.914	0.8513	0.8632	76.67	0.1723
1.6500 (Satd.)	—	1.249	2.217	1.0000	1.0000	—	—

TABLE III
TEMPERATURE 40°C

Molality	Specific conductance $K_c \times 10^2$	Density	Relative viscosity	c_p	η_p	Λ_c	$\left[\frac{1-c_p}{\eta_p}\right]$
0.0922	1.143	1.007	1.047	0.0568	0.4619	201.3	2.042
0.1965	1.867	1.023	1.084	0.1123	0.4784	166.3	1.856
0.2921	2.504	1.038	1.119	0.1667	0.4937	150.2	1.689
0.3862	3.063	1.052	1.163	0.2200	0.5133	139.2	1.520
0.4785	3.576	1.066	1.207	0.2721	0.5325	131.4	1.367
0.5693	4.062	1.080	1.259	0.3232	0.5555	125.7	1.218
0.6586	4.482	1.093	1.305	0.3734	0.5757	120.0	1.088
0.7463	4.872	1.106	1.362	0.4224	0.6009	115.3	0.961
0.8326	5.253	1.119	1.417	0.4706	0.6252	111.6	0.847
0.9175	5.650	1.131	1.467	0.5177	0.6474	109.1	0.745
1.0010	5.942	1.143	1.520	0.5639	0.6707	105.4	0.650
1.0830	6.169	1.155	1.580	0.6096	0.6972	101.2	0.560
1.1640	6.441	1.167	1.640	0.6542	0.7236	98.47	0.478
1.2440	6.691	1.179	1.708	0.6976	0.7536	95.92	0.401
1.3210	6.901	1.190	1.771	0.7403	0.7814	93.22	0.332
1.3980	7.078	1.200	1.850	0.7807	0.8164	90.65	0.269
1.8000 (Satd.)	—	1.251	2.266	1.0000	1.0000	—	—

TABLE IV
TEMPERATURE 45°C

Molality	Specific conductance $K_c \times 10^2$	Density	Relative viscosity	c_p	η_p	Λ_c	$\left[\frac{1-c_p}{\eta_p}\right]$
0.0992	1.191	1.005	1.039	0.0525	0.4625	226.7	2.0480
0.1965	1.977	1.021	1.080	0.1040	0.4808	190.2	1.8630
0.2921	2.668	1.035	1.110	0.1543	0.4942	172.9	1.7120
0.3862	3.248	1.050	1.152	0.2036	0.5130	159.5	1.5520
0.4785	3.820	1.064	1.195	0.2519	0.5321	151.7	1.4060
0.5693	4.338	1.077	1.242	0.2991	0.5530	145.0	1.2680
0.6586	4.803	1.091	1.289	0.3455	0.5740	139.0	1.1400
0.7463	5.172	1.104	1.339	0.3909	0.5962	132.3	1.0220
0.8326	5.650	1.116	1.389	0.4355	0.6186	129.7	0.9126
0.9175	6.032	1.129	1.436	0.4792	0.6393	125.9	0.8147
1.0010	6.339	1.141	1.490	0.5219	0.6634	121.4	0.7206
1.0830	6.658	1.153	1.542	0.5643	0.6866	118.0	0.6346
1.1640	6.947	1.165	1.592	0.6054	0.7089	114.8	0.5567
1.2440	7.269	1.176	1.656	0.6457	0.7374	112.6	0.4805
1.3210	7.458	1.188	1.717	0.6852	0.7643	108.8	0.4118
1.3980	7.598	1.198	1.786	0.7243	0.7952	104.9	0.3466
1.9500 (Satd.)	—	1.268	2.246	1.0000	1.0000	—	—

A = a constant whose value is a function of temperature and dielectric constant of the medium.

The basis of the formulation of the concepts c_p and η_p has already been given[7].

In the present investigations the data collected for copper sulfate solutions are sought to be fitted into equation 1. We hoped to verify the equation of Wishaw and Stokes (loc. cit.) with the same data. Unfortunately, copper sulfate being an "intermediate electrolyte" and a bi-bivalent salt with complications regarding ionic hydration in solution, and owing to uncertainty regarding the actual value of the mean distance of closest approach '$\mathring{a}$', we could not test Wishaw and Stokes' equation or even that of Falkenhagen and Leist (loc. cit.). Equation 1 involves no such uncertain parameters since the very

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[7] C. V. Suryanarayana and V. K. Venkatesan, This Bulletin 31, 442 (1958).

TABLE V

TEMPERATURE 50°C

Molality	Specific conductance $K_c\times10^2$	Density	Relative viscosity	c_p	η_p	Λ_c	$\left[\frac{1-c_p}{\eta_p}\right]$
0.0992	1.254	1.003	1.042	0.0485	0.4535	258.7	2.0980
0.1965	2.094	1.019	1.082	0.0959	0.4710	218.4	1.9200
0.2921	2.802	1.033	1.113	0.1423	0.4844	196.9	1.7710
0.3862	3.448	1.047	1.149	0.1878	0.5001	183.6	1.6240
0.4785	4.051	1.061	1.191	0.2324	0.5184	174.4	1.4800
0.5693	4.605	1.075	1.239	0.2759	0.5393	166.9	1.3430
0·6586	5.093	1.088	1.282	0.3187	0.5581	159.8	1.2210
0.7463	5.556	1.101	1.330	0.3606	0.5790	154.1	1.1040
0.8326	6.003	1.114	1.382	0.4017	0.6016	149.5	0.9945
0.9175	6.343	1.127	1.418	0.4420	0.6172	143.5	0.9040
1.0010	6.733	1.139	1.468	0.4814	0.6392	139.8	0.8114
1.0830	7.191	1.150	1.519	0.5205	0.6612	138.1	0.7252
1.1640	7.401	1.162	1.565	0.5585	0.6813	132.5	0.6480
1.2440	7.640	1.173	1.628	0.5955	0.7086	128.3	0.5709
1.3210	7.854	1.185	1.690	0.6320	0.7357	124.3	0.5001
1.3980	8.004	1.195	1.753	0.6680	0.7630	119.8	0.4351
2.1200 (Satd.)	—	1.285	2.296	1.0000	1.0000	—	—

TABLE VI

TEMPERATURE 55°C

Molality	Specific conductance $K_c\times10^2$	Density	Relative viscosity	c_p	η_p	Λ_c	$\left[\frac{1-c_p}{\eta_p}\right]$
0.0992	1.311	1.001	1.039	0.0448	0.4401	292.5	2.1700
0.1965	2.172	1.016	1.076	0.0886	0.4560	245.0	1.9980
0.2921	2.936	1.030	1.108	0.1316	0.4693	223.1	1.8500
0.3862	3.634	1.045	1.140	0.1737	0.4831	209.2	1.7110
0.4785	4.241	1.059	1.180	0.2148	0.5000	197.4	1.5700
0.5693	4.838	1.073	1.223	0.2552	0.5182	189.5	1.4370
0.6586	5.379	1.086	1.266	0.2947	0.5365	182.5	1.3140
0.7463	5.898	1.098	1.311	0.3334	0.5555	176.9	1.2000
0.8326	6.284	1.111	1.355	0.3715	0.5741	169.2	1.0950
0.9175	6.723	1.124	1.398	0.4087	0.5926	164.5	0.9979
1.0010	7.145	1.136	1.437	0.4451	0.6088	160.5	0.9104
1.0830	7.471	1.148	1.486	0.4812	0.6298	155.2	0.8237
1.1640	7.782	1.160	1.530	0.5164	0.6483	150.7	0.7457
1.2440	8.082	1.170	1.582	0.5507	0.6705	146.8	0.6701
1.3210	8.289	1.182	1.641	0.5843	0.6953	141.9	0.5977
1.3980	8.405	1.192	1.702	0.6177	0.7206	136.1	0.5306
2.3000 (Satd.)	—	1.302	2.360	1.0000	1.0000	—	—

approach in its derivation was from a new angle (loc. cit.). Hence, equation 1 is now tested with the data of copper sulfate.

Experimental

All solutions were made by weight using "Analar" (British Drag House) variety of copper sulfate ($CuSO_4\cdot5H_2O$). A Jones and Bollinger type cell[8] of cell constant 0.6723 was used for conductivity determinations for all concentrations at different temperatures. The measurement of conductance was made by a Philip's GM 4249/01 bridge at a frequency of 1000 cycles/sec. Owing to the high concentration range in which measurements were made, the correction for conductance of pure solvent was quite negligible owing to high specific conductance in all the solutions and the correction was ignored. All connecting wires were heavily insulated, rigid, and well separated so that errors of poor insulation and induction effect were avoided. In the

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8) G. Jones and G. M. Bollinger, *J. Am. Chem. Soc.*, 53, 411 (1931).

TABLE VII
TEMPERATURE 60°C

Molality	Specific conductance $K_c\times10^2$	Density	Relative viscosity	c_p	η_p	Λ_c	$\left[\frac{1-c_p}{\eta_p}\right]$
0.0992	1.367	0.9988	1.034	0.0415	0.4319	329.3	2.219
0.1965	2.256	1.014	1.076	0.0822	0.4495	274.7	2.042
0.2921	3.063	1.028	1.099	0.1220	0.4592	251.1	1.912
0.3862	3.757	1.042	1.131	0.1609	0.4725	233.4	1.776
0.4785	4.438	1.056	1.169	0.1991	0.4884	222.9	1.640
0.5693	5.036	1.070	1.210	0.2364	0.5055	213.0	1.510
0.6586	5.603	1.083	1.251	0.2731	0.5225	205.1	1.391
0.7463	6.112	1.095	1.293	0.3089	0.5401	197.8	1.279
0.8326	6.560	1.109	1.331	0.3442	0.5560	190.5	1.180
0.9175	7.078	1.121	1.368	0.3787	0.5715	186.9	1.087
1.0010	7.521	1.133	1.411	0.4125	0.5893	182.4	0.997
1.0830	7.818	1.144	1.457	0.4460	0.6087	175.3	0.910
1.1640	8.175	1.157	1.502	0.4785	0.6275	170.8	0.831
1.2440	8.405	1.168	1.552	0.5102	0.6483	164.7	0.755
1.3210	8.735	1.180	1.600	0.5416	0.6683	161.3	0.686
1.3980	9.086	1.190	1.654	0.5724	0.6910	158.8	0.619
2.4900 (Satd.)	—	1.319	2.394	1.0000	1.0000	—	—

range of measurement of resistance the instrumental error was ±2.00%. The conductivity cell was immersed in a Gallenkamp b-12210 thermostat giving an accuracy of ±0.05°C.

The viscosities were determined using an Ostwald viscometer immersed in the same thermostat. After attainment of equilibrium the saturated solution was sucked through a tube plugged with cotton wool into a pipette which was kept at the same temperature as the thermostat to avoid crystallization of the saturated solution and transferred into the viscometer. The densities of all the solutions were also measured. Solubility data were obtained from Seidell[9].

Results obtained are given in the tables.

Discussion

A test of equation 1 consists in obtaining a linear plot when Λ_c is plotted against $(1-c_p)/\eta_p$. Fig. 1 shows that such a plot is a straight line at all the temperatures betweem 30° and 60°C, with a few points (right hand side)toward low concentrations going off the straight line at each temperature. This indicates that equation 1 is valid in the range of concentrations from 0.3862 M to saturation (1.5 to 2.5 M). Since the actual resistance measured at saturation at different temperatures happened to be small, attempt is not made here to compare the extrapolated value of Λ_s with that found experimentally owing to the limitations of the instrument used. This aspect is postponed to a future date.

Pearce and Pumplin[10] found out the partial molal volumes of copper sulfate in aqueous solutions upto saturation at 25°C. They observed that the data on copper sulfate solutions are especially interesting because of the negative values of the partial molal volumes in dilute aqueous solutions, quite similar to the phenomenon observed for lithium hydroxide, sodium hydroxide and magnesium sulfate solutions. The very low values in general for copper sulfate indicate a very large amount of electrostriction of the solvent produced by the cupric ion, the water dipoles being compressed around the cupric ion by the intense electrostatic field produced by the high charge density of the ion. Absence of any discontinuity in the curve and a constancy of the law of variation throughout the curve upto saturation indicate that no sudden changes occur either in the total number of water molecules surrounding the ion or the type of bonding between the ion and the water molecules. Stewart[11] observed that the variation of the partial molal volume of ions with concentration is closely linked with the change in structure of water in the same solutions, as revealed by X-ray studies.

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9) Seidell "Solubilities of Organic and Inorganic Compounds," Van Nostrand Co., New York (1940), Vol. I.

10) J. N. Pearce and G. G. Pumplin, *J. Am. Chem. Soc.*, **59**, 1221 (1937).

11). G. W. Stewart, *J. Chem. Phys.*, **7**, 869 (1939).

Fig. 2 shows the temperature variation of Λ_c for all the sixteen concentrations of copper sulfate solutions investigated upon. The curves are not perfect straight lines but are slightly bent convex toward the X-axis. Usually the two factors that determine the form of the temperature conductance curve are: (1) the increase in the viscosity of the solution, and the corresponding decrease in the mobility of the ions, with decreasing temperature; and (2) the effect of temperature on association of ions. With complications of ionic hydration and uncertainties regarding the predominance of one or the other of the above two factors, it is difficult to explain the non-linear variation of Λ_c against temperature.

Equation 1 was originially derived for fully dissociated strong electrolytes based on the principle that the difference in the mobilities of an ion at two different concentrations is a function of the difference in the respective internal pressures at the two concentrations. Copper sulfate is known to be an intermediate electrolyte[12] and the above mentioned observations show that equation 1 holds well even with a bibivalent electrolyte like copper sulfate.

Summary

The electrical conductance of aqueous solutions of copper sulfate has been measured over a wide range of concentrations up to saturation. The equation connecting conductance and concentration in the range of high concentrations recently formulated by Suryanarayana and Venkatesan has been tested with the data obtained for copper sulfate solutions. The equation is found to be valid over a wide range of concentration from 0.3862 M to saturation at temperatures ranging from 30° to 60°C. Slight deviations have been observed at lower concentrations.

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[12] S. Glasstone, "The Electrochemistry of Solutions", Methuen and Co., London (1945), p. 67.