

## *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 0.1N. The attempts of Falkenhagen and Leist<sup>1</sup>, Robinson and Stokes<sup>2</sup>, Wishaw and Stokes<sup>3</sup>, and Leist<sup>4</sup>, are the most notable contributions in recent times in this direction.

Suryanarayana and Venkatesan<sup>5,6</sup> re-

cently formulated the equation,

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

where

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

$$\Lambda_s = \frac{\text{specific conductance at saturation } (K_s) \times 1000}{c_p = 1}$$

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

of course, at saturation  $c_p = 1$

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

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).

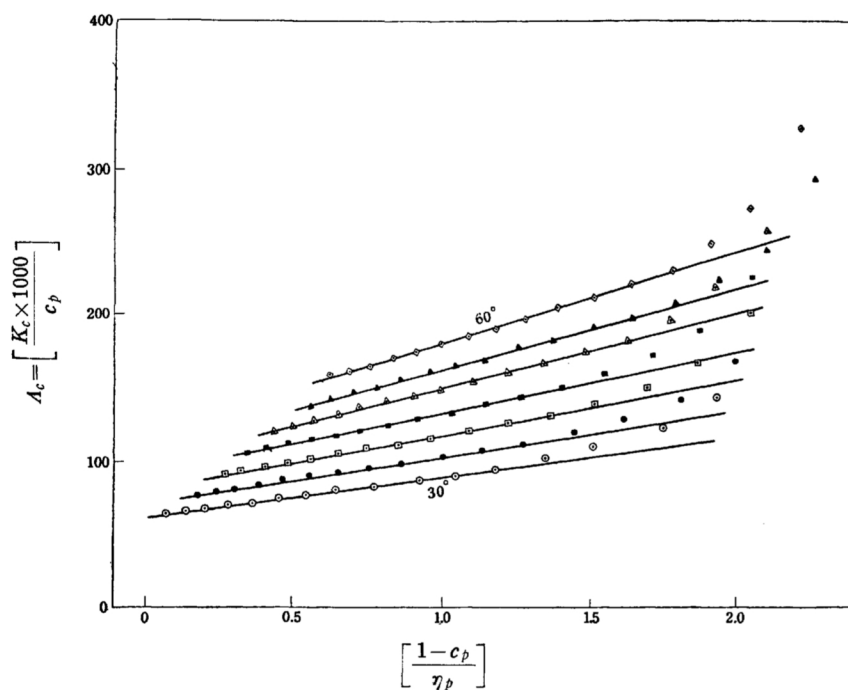


Fig. 1.

TABLE I  
TEMPERATURE 30°C

| Molality          | Specific conductance<br>$K_c \times 10^2$ | Density | Relative viscosity | $c_p$  | $\eta_p$ | $A_c$ | $\left[ \frac{1-c_p}{\eta_p} \right]$ |
|-------------------|-------------------------------------------|---------|--------------------|--------|----------|-------|---------------------------------------|
| 0.0992            | 0.9661                                    | 1.011   | 1.042              | 0.0673 | 0.4818   | 143.5 | 1.936                                 |
| 0.1965            | 1.638                                     | 1.027   | 1.070              | 0.1332 | 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<br>(Satd.) | —                                         | 1.223   | 2.162              | 1.0000 | 1.0000   | —     | —                                     |

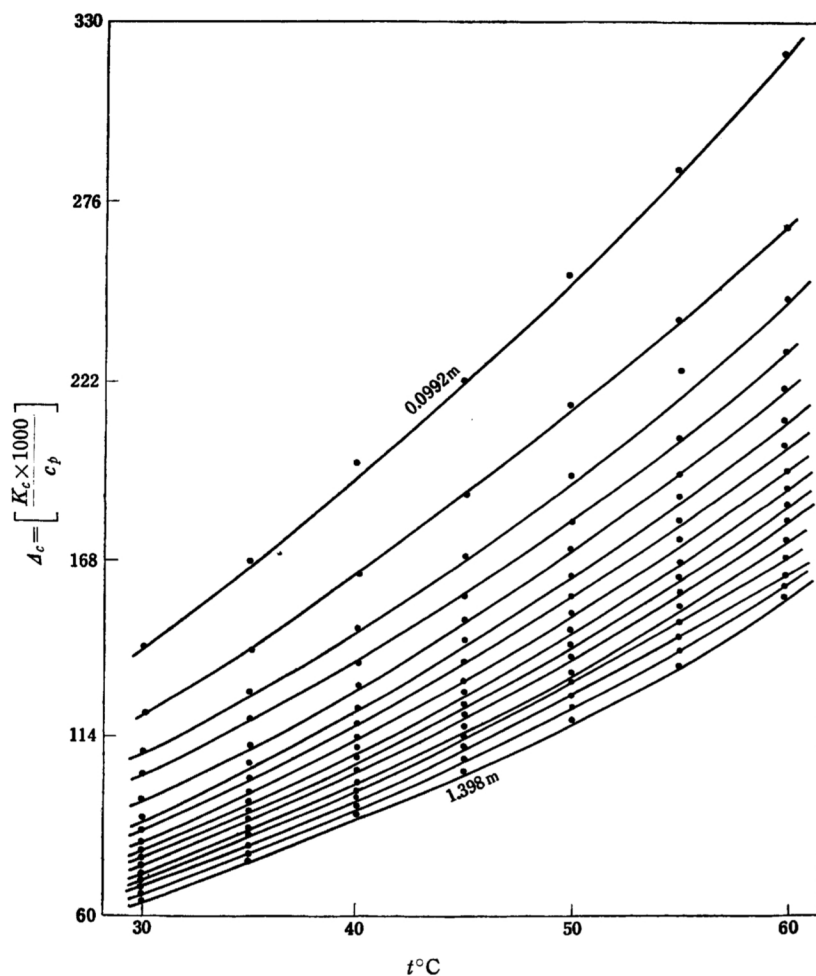


Fig. 2.

TABLE II  
TEMPERATURE 35°C

| Molality          | Specific<br>conductance<br>$K_c \times 10^3$ | Density | Relative<br>viscosity | $c_p$  | $\eta_p$ | $A_c$ | $\left[ \frac{1-c_p}{\eta_p} \right]$ |
|-------------------|----------------------------------------------|---------|-----------------------|--------|----------|-------|---------------------------------------|
| 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<br>(Satd.) | —                                            | 1.249   | 2.217                 | 1.0000 | 1.0000   | —     | —                                     |

TABLE III  
TEMPERATURE 40°C

| Molality          | Specific<br>conductance<br>$K_c \times 10^2$ | Density | Relative<br>viscosity | $c_p$  | $\eta_p$ | $A_c$ | $\left[ \frac{1-c_p}{\eta_p} \right]$ |
|-------------------|----------------------------------------------|---------|-----------------------|--------|----------|-------|---------------------------------------|
| 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<br>(Satd.) | —                                            | 1.251   | 2.266                 | 1.0000 | 1.0000   | —     | —                                     |

TABLE IV  
TEMPERATURE 45°C

| Molality          | Specific<br>conductance<br>$K_c \times 10^2$ | Density | Relative<br>viscosity | $c_p$  | $\eta_p$ | $A_c$ | $\left[ \frac{1-c_p}{\eta_p} \right]$ |
|-------------------|----------------------------------------------|---------|-----------------------|--------|----------|-------|---------------------------------------|
| 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<br>(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  $\eta_p$  has already been given<sup>7)</sup>.

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-valent salt with complications regarding ionic hydration in solution, and owing to uncertainty regarding the actual value of the mean distance of closest approach ' $\bar{a}$ ', 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

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

TABLE V  
TEMPERATURE 50°C

| Molality | Specific conductance<br>$K_c \times 10^2$ | Density | Relative viscosity | $c_p$  | $\eta_p$ | $A_c$ | $\left[ \frac{1-c_p}{\eta_p} \right]$ |
|----------|-------------------------------------------|---------|--------------------|--------|----------|-------|---------------------------------------|
| 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   | —                                         | 1.285   | 2.296              | 1.0000 | 1.0000   | —     | —                                     |

(Satd.)

TABLE VI  
TEMPERATURE 55°C

| Molality | Specific conductance<br>$K_c \times 10^2$ | Density | Relative viscosity | $c_p$  | $\eta_p$ | $A_c$ | $\left[ \frac{1-c_p}{\eta_p} \right]$ |
|----------|-------------------------------------------|---------|--------------------|--------|----------|-------|---------------------------------------|
| 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   | —                                         | 1.302   | 2.360              | 1.0000 | 1.0000   | —     | —                                     |

(Satd.)

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 Drug House) variety of copper sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ). A Jones and Bollinger type cell<sup>8</sup> 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

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

TABLE VII  
TEMPERATURE 60°C

| Molality          | Specific conductance<br>$K_c \times 10^2$ | Density | Relative viscosity | $c_p$  | $\eta_p$ | $A_c$ | $\left[ \frac{1-c_p}{\eta_p} \right]$ |
|-------------------|-------------------------------------------|---------|--------------------|--------|----------|-------|---------------------------------------|
| 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<br>(Satd.) | —                                         | 1.319   | 2.394              | 1.0000 | 1.0000   | —     | —                                     |

range of measurement of resistance the instrumental error was  $\pm 2.00\%$ . The conductivity cell was immersed in a Gallenkamp b-12210 thermostat giving an accuracy of  $\pm 0.05^\circ\text{C}$ .

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<sup>9</sup>.

Results obtained are given in the tables.

### Discussion

A test of equation 1 consists in obtaining a linear plot when  $A_c$  is plotted against  $(1-c_p)/\eta_p$ . Fig. 1 shows that such a plot is a straight line at all the temperatures between  $30^\circ$  and  $60^\circ\text{C}$ , 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 0.3862M to saturation (1.5 to 2.5M). 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  $A_c$  with that found experimentally

owing to the limitations of the instrument used. This aspect is postponed to a future date.

Pearce and Pumplin<sup>10</sup> found out the partial molal volumes of copper sulfate in aqueous solutions upto saturation at  $25^\circ\text{C}$ . 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<sup>11</sup> 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.

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  $\Lambda_c$  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  $\Lambda_c$  against temperature.

Equation 1 was originally 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<sup>12)</sup>

and the above mentioned observations show that equation 1 holds well even with a bivalent 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.