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Transference Numbers in Aqueous Cupric Sulfate Solution: Effect of Concentration and Temperature at Constant pH

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Transference numbers of aqueous cupric sulfate solutions of various concentrations have been measured at constant pH by the Hittorf method. The cation transference numbers increase with increase in concentration (of electrolyte) as well as with temperature. An attempt has been made to account for such unusual variation.

Even though measurements of transport numbers of ions in solutions have been the subject of numerous investigations, data on 2-2 electrolytes in aqueous solution and their dependence on temperature and concentration are limited (*1-8*). A diligent literature search shows that most of the earlier researchers, on the basis of their data on 1:1 electrolytes of low concentrations, felt that cation transference numbers decrease with an increase in concentration of electrolytes and tend to approach 0.5 with increase in temperature (*9*). However, in some cases the trend seems to be the opposite (*1*, *2*, *10*). It is therefore considered worthwhile to carry out a systematic study of the effect of concentration and temperature on transport numbers of 2-2 electrolytes. In this paper, we report the findings on the effect of concentration (>0.1 *m*) as well as temperature on the transport number of the cupric ion in aqueous cupric sulfate solutions.

Materials and Methods

Analytical grade copper sulfate was further purified by crystallization from its saturated solution. Deionized water distilled once was used for preparing the solutions of the desired strength. The pH of copper sulfate solution varies with concentration (*11*, *12*). In order to study the effect of concentration and temperature on the transport number of the cupric ion, t_+, the pH of the solutions was maintained constant (3.2).

In spite of the fact that the Hittorf method of determining transference numbers presents some difficulties in chemical analysis (when high precision is required), we chose it since it is valid at any concentration and the spectral method (using PAR, 4-(2-pyridylazo)resorcinol monosodium salt, as reagent for estimating Cu by converting it into $[Cu(PAR)_2]^{2+}$ complex and measuring the absorbance of the complex at 510 nm (*13*)) is quite sensitive. The transport numbers were determined by using platinum electrodes and the detailed experimental procedures are given elsewhere (*14*, *15*). The temperature of the thermostated solutions could be controlled with an accuracy of ±0.01 °C. The experiments were repeated thrice and the results were reproducible within an error limit of ±0.0005. A nonlinear least-squares program was used to analyze the data.

Results and Discussion

The results of measurements of transport numbers of copper sulfate solutions of various concentrations at different temperatures are summarized in Table I. It is quite interesting to note that aqueous copper sulfate solution is acidic and its pH decreases from 4.5 to 3.2 as the concentration increases from 0.1 to 1.0 *m*. It can be seen from the table that, when the concentration of copper sulfate solution was increased from 0.1 to 1.0 *m*, the apparent cupric transport number, t_+, increased from 0.3255 to 0.3737 (at 25 °C) and this unusual trend, i.e., increase of t_+ with the increase in concentration of cupric sulfate solution, was also observed at the other temperatures, 35, 45, and 55 °C. It is to be noted that most of the earlier workers had restricted their work to very low concentrations of electrolyte (neglecting the effect of change of pH) and they had attempted to fit the experimentally observed data to a theoretical equation (*1-6*,*8*). For the case of completely dissociated symmetrical electrolytes, the Onsager (*16*, *17*) limiting law, that is

$$\Lambda = \Lambda_i^0 - (\alpha\Lambda_i^0 + B/2)c^{1/2} \quad (1)$$

was applied to obtain transference number of either cation or anion (*18*)

$$t_\pm = t_\pm^0 + (t_\pm^0 - 0.5)Bc/\Lambda' \quad (2)$$

where

$$\Lambda' = \Lambda_0 - (\alpha\Lambda_0 + B)c^{1/2}$$

Subsequent treatments using the Fuoss-Onsager (*19*, *20*) equation (which were based on the electrostatic system to allow direct comparison with the published literature (8)) eliminate the relaxation term, α, so that Λ' in eq 2 is replaced with Λ_0

$$t_\pm = t_\pm^0 + (t_\pm^0 - 0.5)Bc^{1/2}/\Lambda_0 \quad (3)$$

At very low concentrations, the transference number varies with the concentration in accordance with the equation

$$\frac{dt_\pm}{d(c)^{1/2}{}_{c\to 0}} = \frac{(t_\pm^0 - 0.5)B}{\Lambda_0} \quad (4)$$

The above equation shows that t_+ should decrease with increasing concentration of electrolytes.

It is worth noting that eq 4 is applicable (i) to 1:1 electrolytes and (ii) at very low concentration ranges. It has been reported in the literature that, in the case of 1:1 electrolytes, like KNO_3 and $AgNO_3$, the cation transference numbers increase with increase in concentration of electrolytes (*1*, *2*, *5*). In the absence of any alternate theory for bivalent electrolytes and that too at higher concentration (*8*), one probably assumes that an equation similar to (4) may be applicable to the salts of higher valence types (like $CuSO_4$) and at higher concentrations. However, Longsworth (*1*, *2*, *10*) had reported that in K_2SO_4 (unibivalent electrolyte) the cation transport number t_+ increased from 0.4829 to 0.4909 when the concentration of K_2SO_4 was increased from 0.01 to 0.5N. So our present experimental results suggesting that $t_\pm$ increases with an increase in concentration (at constant pH) supports the earlier views that, for salts of higher valence and at higher concentrations, eq 2 and 4 may not be applicable. As mentioned earlier, copper sulfate solution is acidic and with an increase in its concentration, hydrogen ion concentration increases. So, the solution which is being electrolyzed contains H^+, in addition to Cu^{2+} (cations) and SO_4^{2-} (anions). Therefore, such a cupric sulfate solution should be treated as a "mixture of electrolytes" and not as a single electrolyte. During electrolysis of such mixed

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Table I. Dependence of the Cationic Transport Number[a] of Aqueous Cupric Sulfate on Concentration and Temperature

		temp, °C			
concn, *m*	pH	25	35	45	55
0.0		0.3201[b]	0.3409[b]	0.3595[b]	0.3760[b]
0.1	4.51	0.3255 (0.373 (a), 0.355 (b))[c]	0.3446	0.3630	0.3785
0.2	4.05	0.3287 (0.361 (a))	0.3490	0.3668	0.3810
0.3	3.81	0.3325 (0.329 (b))	0.3583	0.3706	0.3834
0.4	3.65	0.3377	0.3573	0.3744	0.3860
0.5	3.51	0.3445 (0.327 (b))	0.3609	0.3780	0.3886
0.6	3.43	0.3495	0.3655	0.3805	0.3912
0.7	3.37	0.3558	0.3703	0.3840	0.3938
0.8	3.30	0.3620	0.3749	0.3875	0.3964
0.9	3.25	0.3680	0.3794	0.3911	0.3996
1.0	3.20	0.3737	0.3840	0.3945	0.4018
RMSD		8.6569×10^{-4}	2.9097×10^{-4}	3.6057×10^{-4}	1.6464×10^{-4}

[a] Error limit, ±0.0005. [b] Obtained by using the equation $Y = a + bX + cX^2$. [c] The values in parentheses refer to literature data: (a) ref *3*; (b) ref 7.

electrolytes, H_3O^+ moves out of the anodic compartment along with Cu^{2+}. So, the increase in concentration in the cathodic compartment is naturally less than that found in the case of neutral cupric sulfate solution of the same concentration and this difference between the expected and observed values should increase with an increase in the concentration of H^+, i.e., with an increase in the concentration of copper sulfate. Here it should be noted that even though the concentration of H^+ is very small, compared to that of Cu^{2+} the contribution of the former in carrying current cannot be overlooked due to its high mobility. Therefore in order to minimize the effect of variation of H^+ concentration on t_+, we kept the concentration of H^+ constant (i.e., pH 3.2, as the pH of 1.0 *m* cupric sulfate solution is 3.2) in our experiments. As the concentration of H^+ is constant (assuming that the other factors remain constant), we feel that the increase of t_+, with an increase in concentration of the electrolyte, is more reasonable than the earlier literature data. Of course, we should not forget that the observed transference number is an "apparent" number and not the "true" number of Cu^{2+}. So, we feel that the existing theories which were developed for uni-univalent electrolytes may not be adequate to explain the behavior of 2:2 electrolytes especially at higher concentrations. (Here it should be noted that Spiro (*8*) is of the opinion that transference numbers at higher concentrations are likely to provide the best evidence for the existence of complex ions, once the interionic theories have been developed.)

The transport numbers were determined at various temperatures. It can be seen from the table that, as expected, t_+ increases with an increase in temperature. The dependence of the transference number on concentration decreases as the temperature is increased and it looks as if all of them may merge at higher concentration, which is difficult to explain on the basis of solvation and incomplete dissociation. Spiro (*8*) has rightly pointed out that the temperature dependence of transference numbers cannot be accounted for by any theoretical treatment at present.

From the above observations, it is evident that, at constant pH, the transport number of Cu^{2+} increases with an increase in concentration of copper sulfate as well as with temperature, which is not possible to explain on the basis of the existing theories which were developed for 1:1 electrolytes. However, before making an attempt to modify the existing theories one must have more reliable experimental data of transport numbers of 2-2 electrolytes (which are lacking) at low as well as high concentrations in aqueous as well as nonaqueous media at various temperatures.

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Literature Cited

(1) Longsworth, L. G. *J. Am. Chem. Soc.* **1932**, *54*, 2742.
(2) Longsworth, L. G. *J. Am. Chem. Soc.* **1935**, *57*, 1185.
(3) Hartley, G. S.; Donaldson, G. W. *Trans. Faraday Soc.* **1937**, *33*, 457.
(4) Noyos, A. A.; Falc, K. G. *J. Am. Chem. Soc.* **1911**, *33*, 1436.
(5) Hittorf, W. *Pogg. Ann.* **1853**, *89*, 177.
(6) Fritz, J. J.; Fuget, C. R. *J. Phys. Chem.* **1958**, *62*, 303.
(7) Pikal, M. J.; Miller, D. G. *J. Chem. Eng. Data* **1971**, *16*, 226.
(8) Lima, M. C. P.; Kumarsinghe, S.; Spiro, M. *Trans. Faraday Soc.* **1978**, *74*, 1036.
(9) Glasstone, S. *Introduction to Electrochemistry*: Van Nostrand: New York, 1942.
(10) Longsworth, L. G.; MacInnes, D. A. *J. Am. Chem. Soc.* **1938**, *60*, 3070.
(11) Dye, J. L.; Faber, M. P.; Karl, D. S. *J. Am. Chem. Soc.* **1960**, *82*, 314.
(12) Dye, J. L.; Faber, M. P.; Karl, D. S. *J. Am. Chem. Soc.* **1961**, *83*, 5047.
(13) Anderson, R. G.; Nickles, G. *Analyst* **1967**, *92*, 207.
(14) Shedbalkar, V. P.; Bhat, S. N. *Electrochim. Acta* **1983**, *28*, 359.
(15) Dwivedi Rajeev; Bhat, S. N. *Proc. Indian Acad. Sci.* **1980**, *89*, 337.
(16) Onsager, L. *Z. Phys.* **1926**, *27*, 388.
(17) Onsager, L. *Z. Phys.* **1927**, *28*, 277.
(18) Spiro, M. *Conductance and Transference Numbers*; *Part 2*; *Transference Number in Physical Chemistry of Organic Solvent Systems*; Covington, A. K., Dickson, T., Eds.; Plenum: London, 1973.
(19) Fuoss, R. M.; Onsager, L. *J. Phys. Chem.* **1957**, *61*, 668.
(20) Fuoss, R. M.; Onsager, L.; Skinner, J. F. *J. Phys. Chem.* **1965**, *69*, 2581.

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