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Determination of Magnetic Moments of Copper Ions in Water by the Viscometer Method

Toshio IKEDA

Department of Chemistry, Shizuoka University, Shizuoka

and Kazuo SUEOKA

Department of Chemistry, Johsai University, Sakado, Saitama

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The viscometer method was applied to determine the magnetic susceptibilities of aqueous solutions of cupric salts. The effective magnetic moments of the cupric ions obtained were in agreement with values in literature, except for cupric nitrate and acetate. The former showed a relatively high value and the latter gave variable values, which suggest some dimerization effect occuring in aqueous solution with increasing concentration.

Recently, one of the authors reported the viscometer method[1] to determine the magnetic susceptibility of liquids by measuring the time of flow of liquids through the capillary of a viscometer in an external magnetic field. This method was applied to determine the magnetic moments of copper ions in aqueous solutions.

General Scheme

A capillary viscometer of the Ostwald type is placed in a magnetic field so that its bulb part is in the homogeneous part near the center of the pole gap of an electromagnet, while its capillary part extends vertically, through the inhomogeneous part, outside the field. In this case, the Hagen-Poiseuille expression for the time, t, of flow of a liquid of volume v through the capillary of the viscometer is reduced as follows ignoring the magnetostrictive effect.[1]

$$1/t_0 - 1/t = \kappa H^2/2\rho g h t_0 \tag{1}$$

where t_0 is the time of flow in the absence of an external magnetic field; H denotes the local magnetic field in the liquid medium in the homogeneous magnetic field near the center of the pole gap of the magnet. This can be replaced by the intensity of an externally applied magnetic field; κ and ρ are the volume magnetic susceptibility and the density of the liquid, respectively; g is the gravity constant; h is the vertical height of the capillary part of the viscometer. We see from Eq. (1) that the liquid is identified as diamagnetic or paramagnetic according to whether time t is shorter or longer than t_0. A similar equation can be written also for water. Adopting water as a reference substance for calibration, we can calculate the mass magnetic susceptibility χ ($\kappa=\rho\chi$) of the solution in terms of the mass magnetic susceptibility of water χ_w as follows.

$$\chi = \frac{t_w(t-t_0)}{t(t_w-t_{w0})}\chi_w \tag{2}$$

where t_w and t_{w0} are respectively the time of flow of water through the viscometer in the presence and absence of the magnetic field under the same field strength as applied in the solution.

Experimental

Materials. Aqueous solutions of cupric chloride, cupric nitrate, cupric sulfate, and cupric acetate were prepared by using Guaranteed Reagent grade chemicals obtained from Wakō Pure Chemicals and distilled oxygen-free water. Iron was found to be the only paramagnetic impurity involved in cupric chloride, cupric nitrate, and cupric sulfate in quantities below 0.0002, 0.02, and 0.005%, respectively. The content of copper in solutions was determined by electroanalysis.

Apparatus and Measurements. A Bitter type 500 kg electromagnet of Tokyo Denki Seiki Co. was used to produce a magnetic field of strength up to 20 kG with a relative fluctuation of 10^{-4} using a well stabilized d.c. source, where the pole pieces of the magnet were set at a distance 21 mm apart. A capillary viscometer of the Ostwald type, equipped with a thermostat water jacket, was inserted vertically between the pole gap of the magnet so as to have its upper reservoir (18 mm diameter) come within the homogeneous magnetic field formed in the central circular region (about 30 mm diameter) inside the 60 mm diameter pole pieces. The details of the apparatus were described previously.[1] The time of flow of liquids was measured with a stopwatch of 0.1 sec division, down to 0.01 sec by visual estimation, at 25° ± 0.05°C.

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[1] T. Ikeda and H. Yoshioka, *J. Phys. Chem.*, **72**, 4392 (1968).

Calculation. The mass magnetic susceptibility, χ_s, of cupric salts was calculated from the data of χ of the solution by means of the Wiedemann additivity law, $\chi = p\chi_s + (1-p)\chi_w$, where p is the weight fraction of cupric salt in aqueous solution. The value -0.722×10^{-6} emu/g was adopted for χ_w in the present work.[2] The molar magnetic susceptibility χ_+ of the cupric ion was obtained from the molar susceptibility of cupric salt, making correction for the diamagnetic contribution from the anion constituent in aqueous solution: *i e.*, −28 for Cl^-, −23.5 for NO_3^-, −38 for SO_4^{2-} and $CH_3CO_2^-$ (in 10^{-6} emu/mol).[3] The effective Bohr magneton number, μ_{eff}, of copper(II) ion was calculated by using the Langevin equation as follows.

$$\mu_{eff} = 2.828\sqrt{\chi_+ T} \text{ B.M.}$$

where B.M. is the Bohr magneton unit, 0.9273×10^{-20} erg/G, and T is the absolute temperature. The diamagnetic correction for the cupric ion was not made.

TABLE 1. TIME OF FLOW OF WATER THROUGH THE CAPILLLARY OF VISCOMETER AT DIFFERENT MAGNETIC FIELDS AT 25°C

Magnetizing current (A)	Magnetic field[a] H (kG)	Time of flow[b] t_w (sec)
0	0	221.01
5	4.16	220.88
10	8.20	220.50
15	12.27	219.86
20	16.05	219.06
25	19.05	218.27
28	20.15	217.95

a) Measured with a TOSHIBA HM-3 Hall element magnetic field meter at the center of the pole gap of electromagnet.
b) Mean of seven measurements.

Results and Discussion

The results are shown in Tables 1, 2, and 3. When measurements are carried out with solutions of low concentration in a low magnetic field, the resulting magnetic moments might suffer an appreciable error, because a small difference between two large figures, t and t_0, and t_w and t_{w0}, seriously influences the value of magnetic susceptibility. This

TABLE 2. EFFECTIVE MAGNETIC MOMENTS OF Cu^{2+} IN AQUEOUS SOLUTIONS OF COPPER SALTS AT 25°C

Salt	$CuCl_2$				$Cu(NO_3)_2$				$CuSO_4$			
Wt%	23.80		40.36		20.98		35.15		14.89		18.00	
Current[a] (A)	t (sec)	μ_{eff} (B.M.)	t (sec)	μ_{eff} (B.M.)	t (sec)	μ_{eff} (B.M.)	t (sec)	μ_{eff} (B.M.)	t (sec)	μ_{eff} (B.M.)	t (sec)	μ_{eff} (B.M.)
0	371.40	—	655.52	—	353.66	—	743.76	—	374.54	—	432.01	—
5	372.18	2.1	658.07	2.1	354.12	2.2	746.03	2.3	374.90	2.2	432.19	1.6
10	373.97	1.94	664.31	1.94	355.62	2.2_3	751.82	2.2_3	375.58	1.9_7	433.69	1.9_7
15	377.22	1.94	675.77	1.94	358.14	2.24	761.90	2.21	376.70	1.92	435.57	1.93
20	381.34	1.93	690.39	1 93	361.33	2.23	775.73	2.23	378.40	1.94	438.01	1.92
25	385.59	1.93	705.85	1.93	364.63	2.24	788.42	2.20	379.68	1.91	440.82	1.94
28	387.41	1.93	712.10	1.93	365.66	2.22	795.04	2.22	380.30	1.91	441.59	1.93
μ_{eff} (B.M.)[b]	1.930				1.920—1.961				1.93—1.95			

a) The magnetizing current: refer to a) in Table 1.
b) Landolt-Börnstein, "Zahlenwerte und Funktionen aus Naturwissenschaften und Technik," New Series, Group II, Vol. 2, Springer Verlag, Berlin (1966).

TABLE 3. EFFECTIVE MAGNETIC MOMENTS OF Cu^{2+} IN AQUEOUS SOLUTIONS OF CUPRIC ACETATE AT 25°C

Wt%	2.059		3.071		4.068		5.061		6.307		9.375	
Current[a] (A)	t (sec)	μ_{eff} (B.M.)	t (sec)	μ_{eff} (B.M.)	t (sec)	μ_{eff} (B. M.)	t (sec)	μ_{eff} (B.M.)	t (sec)	μ_{eff} (B.M)	t (sec)	μ_{eff} (B.M.)
0	247.96	—	253.68	—	263.39	—	273.66	—	278.15	—	277.40	—
15	247.00	1.9_4	252.86	1.9_4	262.61	1.7_9	272.92	1.6_8	277.69	1.8_1	—	—
20	246.37	2.01	252.31	1.96	262.14	1.85	272.41	1.69	277.13	1.67	276.81	1.5_5
25	245.69	1.97	251.72	1.93	261.59	1.83	272.06	1.78	276.68	1.65	—	—
28	245.41	1.95	251.51	1.95	231.33	1.80	271.85	1.77	276.50	1.65	276.43	1.54

a) The magnetizing current: refer to a) inTable 1.

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[2] H. Auer, *Ann. Phys.*, **18**, 593 (1933).
[3] Landolt-Börnstein, "Zahlenwerte und Funktionen aus Physik, Chemie, Astrophysik, Geophysik und Techik," 6th Ed., Vol. I, Sect. 1, Springer Verlag, Berlin (1950), pp. 396—397.

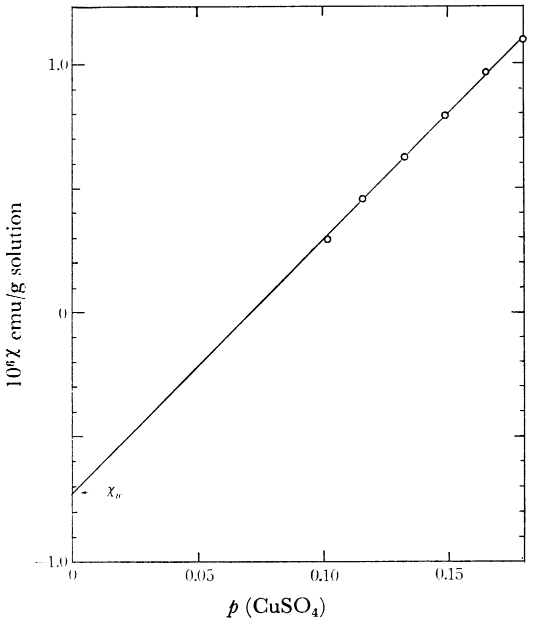

Fig. 1. The Wiedemann relation for aqueous solution of $CuSO_4$ at 25°C, representing the values measured at the magnetic field strength of 20.15 kG.

effect is actually seen in the Tables. Thus, in order to get reliable results, measurements should be carried out with solutions of higher concentration in as high a magnetic field as possible, particularly in the case of a solution involving a weak paramagnetic ion species such as Cu^{2+}: In the present method, a magnetic field of a strength higher than 12 kG gives results with tolerable accuracy.

Magnetic susceptibilities of aqueous solutions of cupric salts, except for cupric acetate, were found to obey the Wiedemann law. The Wiedemann relation for cupric sulfate was found to be perfectly linear, intersecting, on extrapolation to concentration zero, the ordinate at -0.725×10^{-6} emu/g. This is in close agreement with the susceptibility of water (Fig. 1). From the slope of the line in Fig. 1 we obtain the effective magnetic moment 1.92 B.M. for Cu^{2+}. The magnetic moments of copper(II) ion were found in good agreement with literature values,[4] except for cupric nitrate and cupric acetate (Tables 2 and 3). Cupric nitrate exhibited a value, about 15% higher than the literature values 1.92—1.96 B.M.[4] The magnetic moment we obtained seems to involve an error of 2—3%. The paramagnetic cation found as impurity in cupric nitrate was exclusively iron contained in such a minute quantity below 0.02% which can cause a deviation 0.15% at most from the accepted value of the magnetic moment of cupric ion. There might be some reason to cause such a large deviation of 15% in the case of cupric nitrate.

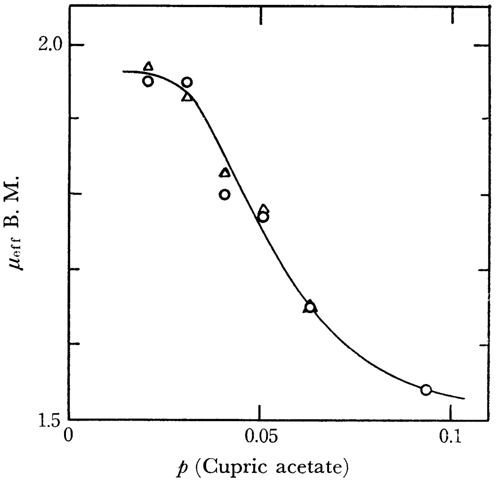

Fig. 2. Relation between the apparent magnetic moments of Cu^{2+} and the weight fraction, p, of cupric acetate in aqueous solutions at 25°C, Δ, measured at 19.05 kG; ○, measured at 20.15 kG.

The apparent magnetic moments of Cu^{2+} observed in aqueous solutions of cupric acetate appeared to depend on the concentration (Table 3 and Fig. 2): A value of 1.95 B.M. found at lower concentration is in agreement with the literature value.[4] However, it decreased with increasing concentration towards a value 1.42 B.M. found in the crystalline state where the dimerization of cupric acetate through a weak copper-copper bond formation was concluded.[5] This fact suggests a similar association of cupric acetate occuring also in aqueous solution with increasing concentration.

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[4] Landolt-Börnstein, "Zahlenwerte und Funktionen aus Naturwissenschaften und Technik," New Series, Group II, Vol. 2. Springer Verlag, Berlin (1966).

[5] B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, **1956**, 3837.