Pakistan J. Sci. Ind. Res., 13, Nos 1—2 August 1970

A NEW TECHNIQUE FOR THE STUDY OF COPPER–ACETAMIDE SYSTEM IN AQUEOUS SOLUTION

SYED SHAMIM AHMED,* SHAMSHAD AHMED KHAN and ABDUL RASHEED KHAN

P.C.S.I.R., Laboratories, Karachi 32

(Received May 22, 1969; revised July 30, 1969)

The new technique called "continuous variation method", proved to be as reliable as the conventional monovariation method. The complex in the ratios 1:2 and 1:4 were observed. A reasonable structure for the complexes is also suggested.

A monovariation method is usually employed to study the interactions of metals with organic compounds in aqueous solution. But the study of complex formation by this method involves the preparation of a very large number of specimens and the standardization of instrument for each experiment. To avoid such tedious and time consuming experiments, a new technique, called "continuous variation method" has been adopted. In this, a small volume of concentrated metal solution is added in steps to a known volume of comparable dilute solution of ligand-forming compound to study the changes in the physical properties of the system. Physical properties like density, viscosity, surface tension and refractive index are studied. The results obtained by this method were verified by the conventional monovariation method.

Experimental

Standard solution of acetamide was prepared by dissolving chemically pure acetamide in twice distilled water. Stock solution of copper sulphate (B.D.H.) was prepared and its molar strength was determined idometrically.[1] All measurements were made at room temperature which was about 30°C.

Copper sulphate (1M solution, 0.01 ml) was added in steps to 4 ml of 0.05M acetamide solution. After each addition of copper sulphate solution, refractive index[2] was measured at 5460 Å using Pulfrich refractrometer. The instrument was standardized with distilled water and the accuracy of the observation was found to be ± 0.00002 units of refractive index.

For determining the density[3] changes, 0.32 ml copper sulphate solution was added in steps to 96ml of 0.1M acetamide solution. After each addition, the density was measured using Westphal balance. The instrument was standardized with distilled water. The mean of three observations was plotted which has an accuracy of ± 0.001 g/ml.

The viscosity[4] was measured by adding 0.04 ml standardized copper sulphate in steps to 12 ml 0.1M acetamide solution with Ostwald's viscometer which was standardized using distilled water. The results were accurate to $\pm 5 \times 10^{-2}$ c.p.

Lastly, following the principles of monovariation method, 1.0ml standardized copper sulphate solution was added in steps to the flasks containing 25 ml equimolar acetamide solution and making the volume to 100 ml in each case to measure the variation in density,[3] viscosity[4] and surface tension.[5]

Results and Discussion

The plots in Fig. 1 and 2 show two kinks at 0.25 and 0.5 $CuSo_4$/acetamide ratio, respectively. The refractive index composition curve in Fig. 3 shows only one kink at 0.5 ratio. The kink at 0.25 could not be detected because the change in refractive index with the change of components concentration is relatively small at lower concentrations and is not easily detectable with the instrument used.

The density, viscosity and surface changes measured by monovariation method are shown in Fig. 4, 5 and 6. The results are in agreement with the plots shown in Figs. 1,2 and 3 showing the reliability of our techniques. The sharp changes in physical properties at 0.25 and 0.5 show additive complexing of copper sulphate and acetamide molecule.

The coordination number[6,7,8,9] of copper is four and it has nine electrons in the *d* level (d^9) which may lead to formation of a square planner complex. In the present case, copper ion receives electron from nitrogen and the sharing of electrons pair through vacant obritals of copper(II) ions will lead to partial convalent nature of metal–ligand bond. If it is assumed that the two aceta-

* Department of Chemistry, University of Karachi.

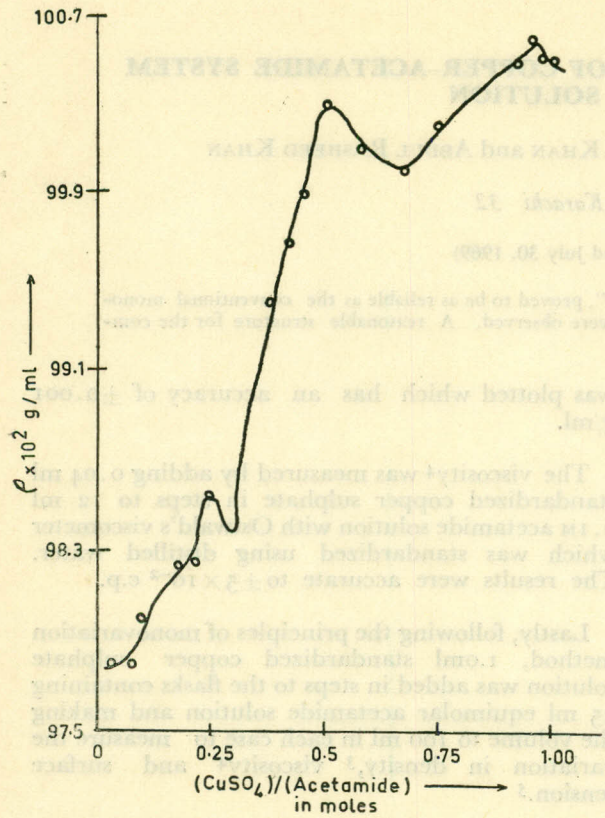


Fig. 1.—A plot of density (ρ) g/ml against mole ratio using continuous variation method.

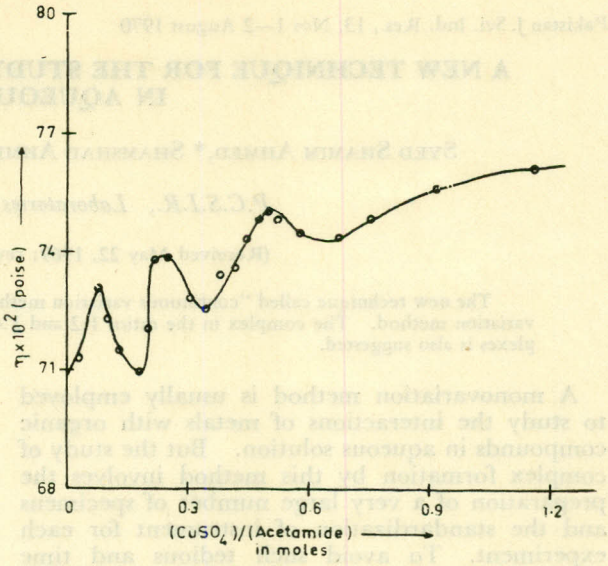


Fig. 2.—A plot of viscosity η poise against mole ratio using continuous variation method.

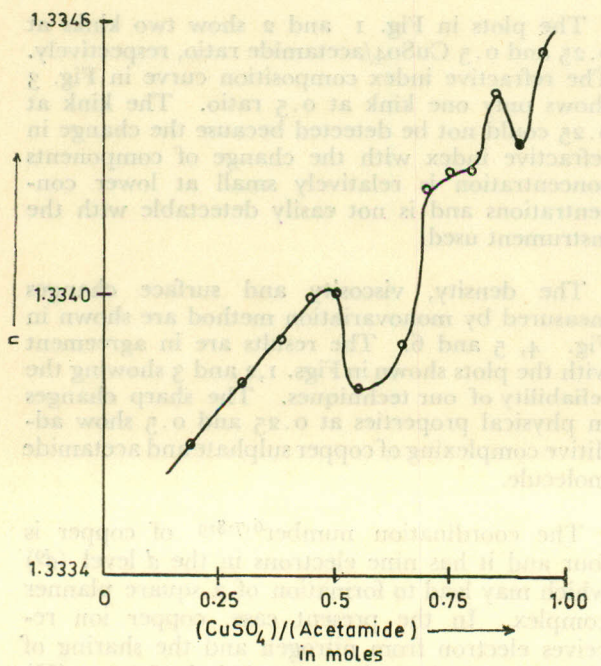


Fig. 3.—A plot of refractive index η against mole ratio using continuous variation method.

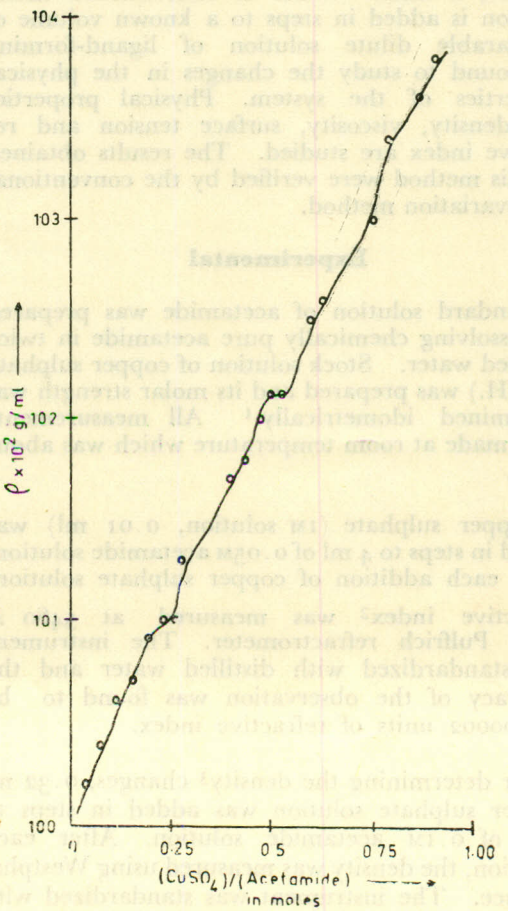


Fig. 4.—A plot of density (ρ) g/ml against mole ratio using monovariation method.

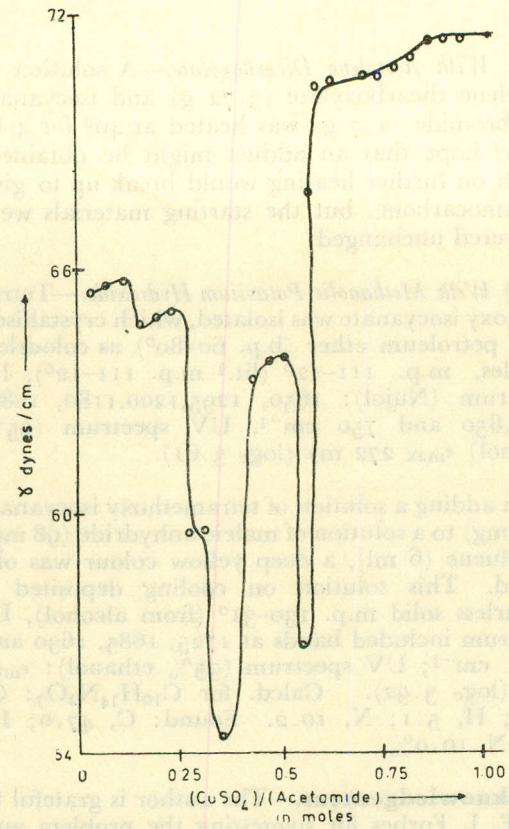


Fig. 5.—A plot of surface tension (γ) dynes/cm against mole ratio using monovariation method.

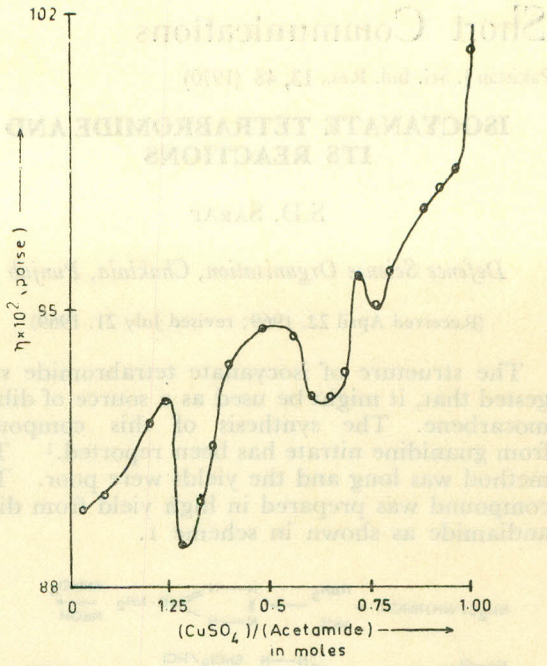
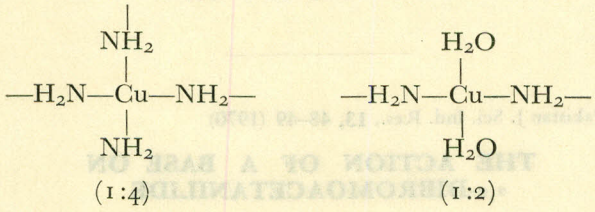


Fig. 6.—A plot of viscosity (η) poise against mole ratio using monovariation method.

mide groups are attached to Cu^{++}, the other two positions will be occupied by two water molecules. The possible structure will be



Acknowledgement.—The authors are thankful to Dr. S.A.K. Lodhi for his valuable suggestions.

References

1. A.I. Vogel, *A Text Book of Quantitative Inorganic Analysis* (Longmans Green, London, 1961), p. 358.
2. Alexander Findlay, *Practical Physical Chemistry* (Longmans Green, London, 1949).
3. Albert W. Davison, Henry S. Van Klooster and Walter H. Bauer, *Laboratory Manual of Physical Chemistry* (John Wiley, London; Chapman and Hall, London, 1950).
4. Adam, *Physics and Chemistry of Surfaces* (Oxford University Press, New York, 1942).
5. F. Daniels, J.H. Mathews, J.W. Williams Paul Bender and Robert A. Alberty, *Experimental Physical Chemistry*, 5th edition (McGraw-Hill, 1956), p. 350.
6. Linus Pauling, J. Am. Chem. Soc., **53,** 1391 (1931); *ibid.*, **54,** 988(1932).
7. P. Pfeiffer and Glaser H., J. Prakt. Chem., **151,** 145-59 (1938).
8. P. Ray and N.N. Ghosh, J. Indian Chem. Soc., **26,** 144 (1949).
9. J. Kleinberg, W. J. Argersinger and E. Griswold, *Inorganic Chemistry* (Heath, Boston, 1960), p. 232.