Spectrophotometric Studies on Copper and Iron Dinitrosoresorcinol Sulfonate Complexes

Mamdouh S. Masoud,* Tahany M. Salem, and Mohiy M. Elessawy
Chemistry Department, Faculty of Science, Alexandria, Egypt

Dinitrosoresorcinol sulfonate was found to form two copper complexes (1:1 and 1:2) and three ion complexes (1:1, 1:2, and 1:3). The p*K* values for the complexes were determined. The ligand could be used to determine low concentrations of these ions under the optimal conditions of analysis.

Considerable interest has been emerging on some potential ligands containing the "hard" atoms nitrogen and oxygen in nitroso compounds (*1, 2, 4, 5, 9–12, 15, 18, 19*). In the present investigation we sought to use the new dinitrosoresorcinol sulfonate ligand (DNRS) to determine low concentrations of copper and iron under the optimal conditions established in this study.

Experimental Section

The reagent (*14*) was prepared by heating resorcinol and concentrated H_2SO_4 for 3 h at 130 °C. The cold material was neutralized by adding 3 M NaOH and a small amount of concentrated ammonia. $NaNO_2$ was then stirred (weight equivalent of two nitroso groups) and was kept in a thermostat below 10 °C. Acetic acid was then added stepwise while stirring until the mixture was acidic. Several milliliters of HCl was added to complete the reaction. The product was filtered by suction, washed with ice water and dried at 100 °C. The analyses of this compound proved the molecular formula to be $C_6H_3O_7N_2SNa$. An aqueous 0.1% (w/v) solution was prepared from the pure material. The solution was stable for several months.

Stock copper(II) and iron(II) solutions were prepared from the metal chlorides.

All the other reagents used were made from high-purity materials or purified reagents, and all solutions were prepared with deionized water.

Absorbance curves were measured with a Model SP 800 Unicam recording spectrophotometer with 1-cm matched quartz cells. A Radiometer 28 pH meter type and a Pye conductometric bridge of the magic eye type were employed.

Results and Discussion

Absorption Spectra of the Ligand. In the pH range of 2.6–6 the spectrum of 1×10^{-4} M DNRS is composed of two bands, one in wavelength range 240–260 nm and the second between 320 and 350 nm. For pH >9, only one spectral band with λ_{max} at 330 nm is observed. This band suffers red shifts with increasing pH, Figure 1, which are related to the presence of tautomeric equilibria between the nitrosophenol and keto-oxime forms. This is verified by the presence of an isosbestic point at 310 nm. The A_s–pH plot, Figure 2A, illustrates that the compound under investigation behaves as a dibasic acid. On applying the relation (*13*)

$$\mathrm{pH} = \mathrm{p}K + \log((\epsilon_1/\epsilon_2)\gamma) + \log A_s/((A_s)_{max} - A_s)$$

(the above terms have the usual meanings) and plotting the logarithmic absorbance ratio against pH, Figure 2B, $\mathrm{p}K_1$ and $\mathrm{p}K_2$ were found to be 4.20 and 9.20, respectively.

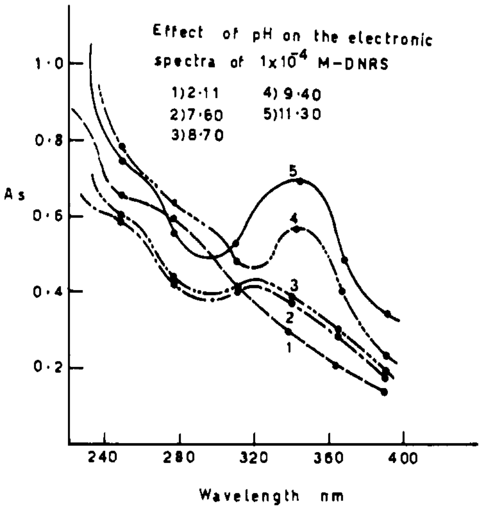

Figure 1. Absorbance–wavelength relationship for dinitrosoresorcinol sulfonate at different pHs.

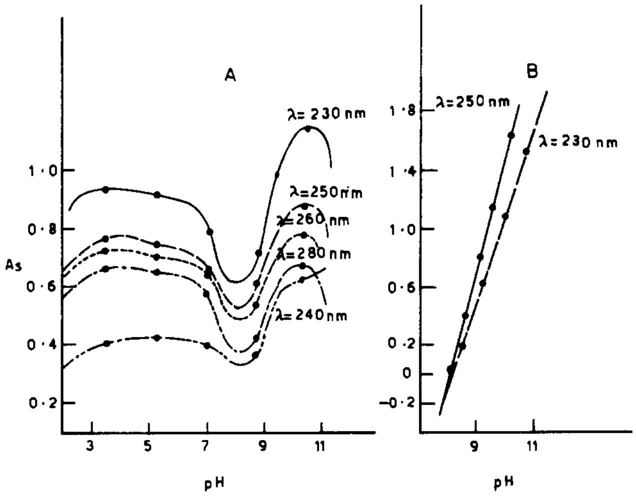

Figure 2. (A) Absorbance–pH relationship for dinitrosoresorcinol sulfonate at different wavelengths. (B) Log $A_s/((A_s)_{max} - A_s)$–pH relationship for dinitrosoresorcinol sulfonate.

Absorption Spectra of Copper and Iron Complexes. Figure 3 shows the characteristic bands for copper and iron complexes in the wavelength range 300–825 nm. For the yellowish copper system, only one sharp band is apparent at 370 nm. In the bright green iron system, two bands are formed: a sharp one at 385 nm and a broad one at ~675 nm.

The effect of pH on the electronic spectra of both systems is depicted in Figure 4. It shows that the absorbance increases stepwise until saturation in absorbance at pH ~5.5 in the copper system and at pH ~6.0 for the iron system. So, the suitable media for complexation are weakly acidic.

Applications. The characteristics of copper and iron dinitrosoresorcinol sulfonate complexes make it suitable for the determination of the elements in the presence of one another. The large separation between the two maxima (λ_{max} for the copper system is 370 nm and that for the iron system is 675 nm)

---

* To whom correspondence should be addressed at King Abdul Aziz University, P.O. Box 1540, Jeddah, Saudi Arabia.

0021-9568/78/1723-0012$01.00/0

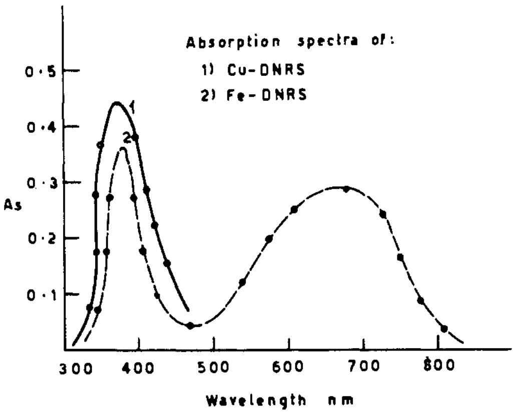

Figure 3. Absorbance-wavelength relationship for (1) the copper-dinitrosoresorcinol sulfonate system and (2) the iron-dinitrosoresorcinol sulfonate system.

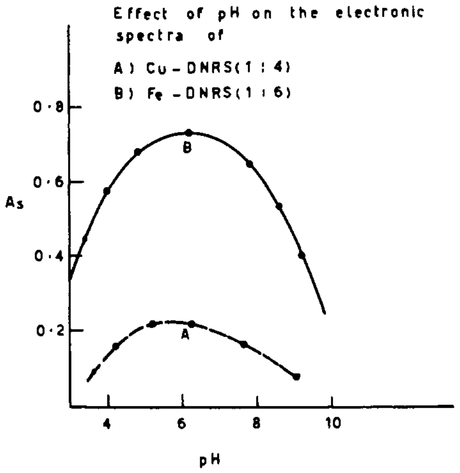

Figure 4. Absorbance-pH relationship for (A) the copper-dinitrosoresorcinol sulfonate system and (B) the iron-dinitrosoresorcinol sulfonate system.

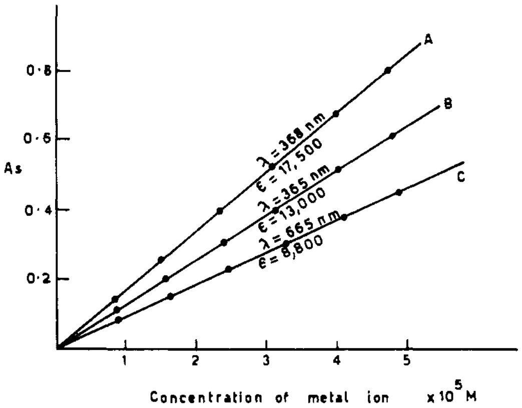

Figure 5. The use of dinitrosoresorcinol sulfonate for the determination of copper and iron.

Table I. Effect of Diverse Ions on 1 ppm Fe^{2+}

Ion	Concen, ppm	% deviation	Ion	Concen, ppm	% deviation
K^+	1000	4.4	Cl^-	1000	4.5
Na^+	500	3.4	SO_4^{2-}	380	2.0
Mg^{2+}	25	2.5	NO_3^-	350	−1.5
Zn^{2+}	20	2.0	Acetate	300	−2.0
Ca^{2+}	15	6.5	NO_2^-	500	−41.5
Cd^{2+}	10	−12	Tartrate	500	−3.5
Ba^{2+}	1	−13	Citrate	200	−32

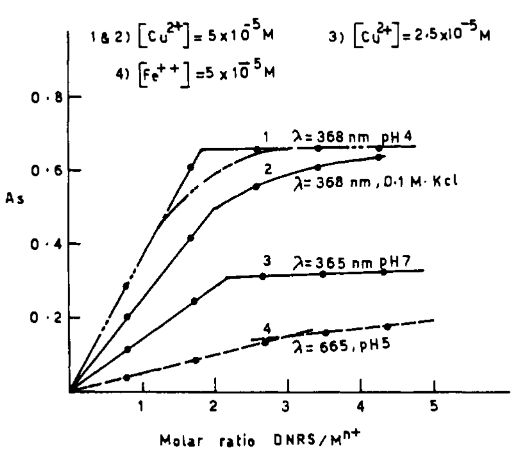

Figure 6. Stoichiometry of the complexes using the molar ratio method.

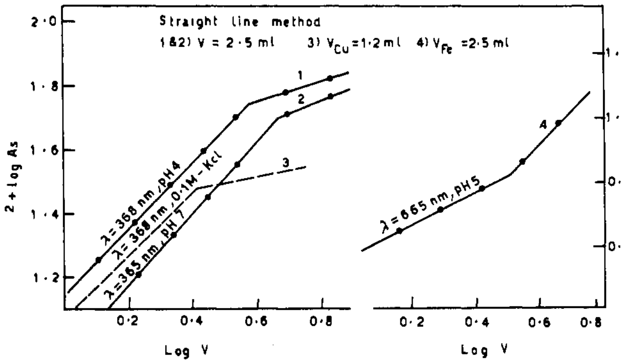

Figure 7. Stoichiometry of the complexes using the straight line method.

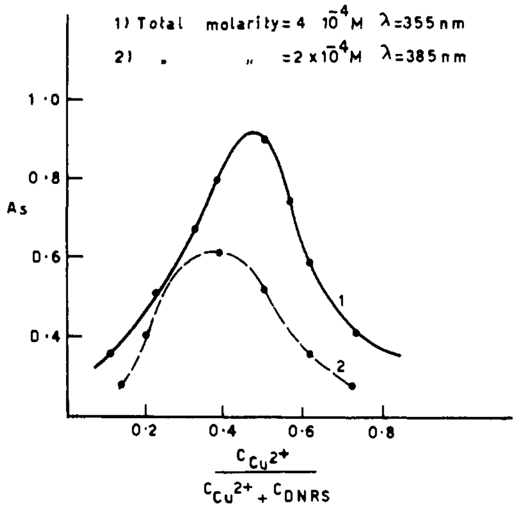

Figure 8. Stoichiometry of the complexes using the continuous variation method.

and the high molecular extinction coefficients of the complexes, Figure 5 curves A, B, and C, provide an advantage for determination of both elements with fair accuracy (0.13–3.30 ppm iron and 0.15–3.25 ppm copper).

It was found that apparent interference occurred with 1 ppm Fe^{2+} solutions containing K^+, Na^+, Li^+, Zn^{2+}, Cl^-, SO_4^{2-}, NO_3^-, acetate, and tartrate within the concentrations given in Table I. Cd^{2+}, Ca^{2+}, and Ba^{2+} caused serious deviations (~ ±20%) resulting in a decrease in the effective ligand concentration for ion. Al(III) formed a precipitate and the supernatant liquid was slightly colored indicating that some of the iron had been re-

Table II. p*K* Values of the Formed Complexes

Complexes	p*K*	ϵ_0
(1:1) iron	5.15 ± 0.21	12924
(1:2) iron	4.79 ± 0.05	8102
(1:3) iron	4.23 ± 0.31	3224
(1:1) copper	5.63 + 0.34	5026
(1:2) copper	11.34 ± 0.03	13012

moved by the aluminum. Citrate and nitrite ions caused high negative deviations.

Nature of the Complexes. pH and the conductometric titration of Cu^{2+} against DNRS resulted in a decrease in the pH with an increase in conductance due to hydrogen liberation with the formation of 1:1 and 1:2 complexes. These two tools permit the tracing of 1:1, 1:2, and 1:3 iron complexes. In the molar ratio method, Figure 6, in which the metal ion concentration was kept constant while that of the ligand was varied, bis copper and tris iron complexes were shown to exist. The straight line method (*3*), Figure 7, by plotting log A_s vs. log V (V was the volume of the ligand added per constant volume of the metal ion) proved the existence of a mono complex in both systems. However, the continuous variation method (*16*) for the iron system did not give reliable results due to the formation of colloidal particles at different pHs even in dilute solutions at 4×10^{-5} M. By plotting the A_s vs. the mole fraction of Cu^{2+}, Figure 8, different complexes were traced depending on the total molar concentrations of Cu^{2+} and the wavelength of the measurements. Solutions with a total molar concentration of 4×10^{-4} M in aqueous media at wavelength 355 nm, gave a sharp maximum at 0.5 mole fraction of Cu(II) indicating the formation of a complex of copper in which the metal:ligand ratio is 1:1. When this experiment was performed at pH 4 with a total molar concentration of 2×10^{-4} M and a wavelength 385 nm, another complex with the mole fraction of 0.33 was traced, indicating the formation of a 1:2 complex.

Determination of the Dissociation Constant of the Complexes. The molar ratio (*17*), the straight line (*3*), and the continuous variation methods (*16*) were used to evaluate the p*K* values of the complexes, based on assuming the reaction to take place as follows (*6–8*).

$$\mathrm{M} + \mathrm{L} \rightleftharpoons \mathrm{ML}$$

$$K = [\mathrm{ML}]/((\mathrm{M}^0 - [\mathrm{ML}])(\mathrm{L}^0 - [\mathrm{ML}]))$$

and

$$A_s = (\mathrm{M}^0 - [\mathrm{ML}])\epsilon_\mathrm{M} + (\mathrm{L}^0 - [\mathrm{ML}])\epsilon_\mathrm{L} + [\mathrm{ML}]\epsilon_\mathrm{C}$$

M, L, and C denotes metal, ligand, and complex, respectively. Hence

$$\frac{\mathrm{M}^0\mathrm{L}^0}{A_s - \epsilon} + \frac{A_s - \epsilon}{{\epsilon_0}^2} = \frac{\mathrm{M}^0 + \mathrm{L}^0}{\epsilon_0} + \frac{1}{K\epsilon_0}$$

Where $\epsilon = \mathrm{M}^0\epsilon_\mathrm{M} + \mathrm{L}^0\epsilon_\mathrm{L}$ and $\epsilon_0 = \epsilon_\mathrm{C} - [\epsilon_\mathrm{M} + \epsilon_\mathrm{L}]$. On plotting $\mathrm{M}^0\mathrm{L}^0/(A_s - \epsilon_0)$ against $\mathrm{M}^0 + \mathrm{L}^0$ a straight line is obtained with a slope $= 1/\epsilon_0$ and an intercept equals $1/K\epsilon_0$. So, the K and ϵ_0 of the reaction can be evaluated. The results are collected in Table II.

Literature Cited

(1) Abbasi, S. A., Bhat, B. G., Singh, R. S., *Indian J. Chem.*, **14A**, 215 (1976).
(2) Aly, M., Makhyoun, M., El-Ezaby, S., *J. Inorg. Nucl. Chem.*, **35**, 2727 (1973).
(3) Asmus, Z., *Z. Anal. Chem.*, **104**, 178 (1960).
(4) Banergee, A. K., Layton, A. J., Nyholm, R. S., Truter, M. R., *J. Chem. Soc.*, 2536 (1969).
(5) Boll, P., *Acta Chem. Scand.*, **12**, 1777 (1958).
(6) Chattopadhyaya, M., Singh, R., *Indian J. Chem.*, **10**, 850 (1972).
(7) Chattopadhyaya, M., Singh, R., *Anal. Chim Acta*, **70**, 49 (1974).
(8) Chattopadhyaya, M., *J. Inorg. Nucl. Chem.*, **38**, 509 (1976).
(9) Dyressen, D., Johsson, E., *Acta Chem. Scand.*, **9**, 763 (1955).
(10) El-Khadem, H., Orabi, W. M., *Z. Anorg. Allg. Chem.*, **362**, 210 (1968).
(11) El-Khadem, H., Orabi, W. M., *Z. Anorg. Allg. Chem.*, **465**, 315 (1969).
(12) Herfeld, H., Gerngross, O., *Anal. Chem.*, **14**, 7 (1933).
(13) Ibrahim, N. A., Issa, R. M., *J. Prakt. Chem.*, **315**, 202 (1973).
(14) Peach, S. M., *J. Chem. Educ.*, 42, 437 (1965).
(15) Shimpan, W. H., Fori, S. C., Simon, W., *Anal. Chem.*, **27**, 1240 (1955).
(16) Vosbourgh, W. C., Coopers, E. R., *J. Am. Chem. Soc.*, **64**, 437 (1941).
(17) Yoe, J. H., Jones, A. L., *Ind. Eng. Chem.*, **65**, 111 (1944).
(18) Zayan, S., Issa, R., El-Dessoky, M., Iskander, M., *Z. Phys. Chem.*, **233**, 313 (1966).
(19) Zayan, S., Ebrahim, N., Masoud, M. S., *Bull. Fac. Sci., Alexandria*, **3**, 185 (1971).

Received for review March 14, 1977. Accepted July 27, 1977.

Viscosity of Molten $LiNO_3$

George J. Janz,* Stephen W. Lurie, and Gary L. Gardner
Rensselaer Polytechnic Institute, Molten Salts Data Center, Troy, New York 12181

A precise and accurate reinvestigation of the viscosity of molten $LiNO_3$ is reported, together with additional results for molten KNO_3, using an Ostwald capillary viscometer modified for molten salts studies. The temperature dependence of the results for $LiNO_3$ may be expressed by the equation $\eta = (7.283 \times 10^{-2}) \exp(4578/RT)$, and the accuracy is better than ±1.5%. The previously reported Dantuma (1928) results are found to be seriously in error, and the NSRDS recommendation based on the Dantuma data should be revised.

Viscosity techniques are generally classified into four main groups: capillary flow, oscillational, falling body, and rotational methods. The former two methods have found extensive application to ionic melts where the viscosities fall in the range 0.5–10 cP. The falling body methods are suited for liquids of higher viscosities (>40 cP) and the rotational technique, although having been used for melts with viscosities as low as 5 cP, is in general only feasible for systems of high viscosities. Capillary techniques, using both the Ostwald and Ubbelohde design, have had rather limited application at moderately high temperatures (400–900 K), the primary difficulties being the need for capillaries of known and stable dimensions and inertness to attack by molten ionic compounds.

In principle the viscosity data from these four methods should be in exact agreement, and indeed this has been shown to be possible for selected molten salts. Thus for molten KNO_3 for which some 13 independent investigations are known, an intercomparison of the capillary and oscillational techniques shows the results generally in good agreement (±1.5% agreement). With reference to $LiNO_3$, value judgments were advanced (*7*)

0021-9568/78/1723-0014$01.00/0