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Tensammetric Study of the Adsorption of Brucine

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This paper will present two results of experiments concerning the adsorption of brucine. We will first discuss the adsorption of brucine on D. M. E. studied tensammetrically. Brucine was found to give a tensammetric wave with two peaks, at +0.10 V and −1.15 V *vs.* SCE. The positive tensammetric peak can be ascribed to the usual adsorption process. The second peak, however, behaved differently from the first, probably due to the reformation of adsorbed brucine film involving the protonation and the reorientation of brucine. Secondly, we will present experimental facts concerning the depressive effects of brucine on the reduction waves of copper(II).

Brucine has been reported to produce a catalytic wave in the pH range from 5.0 to 12.0.1) In previous papers,2,3) we studied chronopotentiometrically the perturbation effect of adsorbed

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1) H. F. Kirkpatrick, *Quart. J. Pharm. Pharmacol.*, **19**, 127 (1946).

2) M. Kodama and R. W. Murray, *Anal. Chem.*, **37**, 1638 (1965).

3) R. W. Murray and M. Kodama, *ibid.*, **37**, 1759 (1965).

brucine on the electroreduction of copper(II) in a tartrate medium and the discriminative effects of the brucine film toward the electroactive-metal-complex enantiomers. In the absence of brucine, the chronopotentiometry of copper(II) tartrate shows a diffusion-controlled character and the behavior of copper tartrate *d*- and *l*-enantiomers is identical. In the presence of brucine, however, the electrolysis is no longer diffusion-controlled and the product, $i\cdot\tau^{1/2}$, of the chronopotentiometric wave of copper(II) decreases linearly with an increase in the applied current. A measurable difference in $i\cdot\tau^{1/2}$ value between the copper(II) complex of *d*-tartrate and that of *l*-tartrate was also observed. These facts were ascribed to the interaction between the copper tartrate complex and the adsorbed brucine film, but no precise description of the nature of the surface interaction of brucine film with the electroactive species was given.

In view of all this, it is worthwhile to study the nature of the adsorbed brucine film. In the present paper, we will discuss our study of the adsorption of brucine on DME using the tensammetric method.

Experimental

Reagents. The tartaric acid and brucine sulfate used were of an analytical reagent grade (Tokyo Kasei). All the other chemicals were of an analytical reagent grade and were used without further purification.

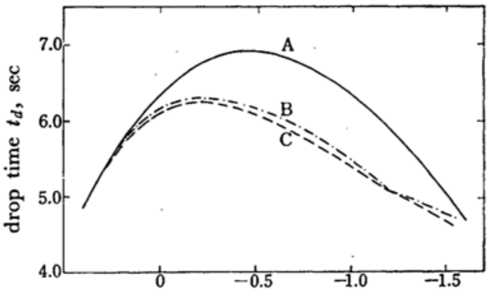
Apparatus. The tensammetric waves of brucine were measured with a Yanagimoto PA-102 Pen-recording Polarograph either manualy or automatically. The d.c. potentials appllied were determined by using a Shimadzu K-2 potentiometer.

The flow rate of mercury, *m*, and the drop time, t_d, of the dropping mercury electrode (DME) were measured and found to be 1.24_8 mg/sec and 6.30 sec respectively in an air-free 0.10 M acetate buffer solution of pH 4.80, with an open circuit at 60 cm of a mercury column at 25°C. A saturated calomel electrode (SCE) of a large area was used as a reference electrode and connected to the cell solution through a Hume and Harris type salt bridge. In a. c. polarographic measurements, a 200-μF condenser was used to minimize the effect of cell resistance.[4] The pH of the solution was measured with a glass electrode pH meter (Hitachi-Horiba Model M-4).

All the polarographic studies were carried out at 25°C in solutions of 1.50 ionic strength, which was adjusted by adding appropriate amounts of sodium sulfate. The oxygen dissolved in the sample solution was removed by bubbling pure nitrogen gas through the solution.

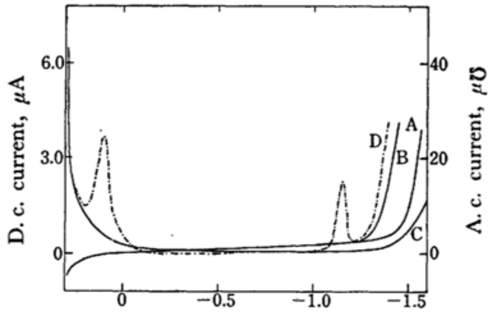
Results and Discussion

Tensammetric Behaviors of Brucine. As is obvious from the curves in Fig. 1, brucine lowers the surface tension at the interface of a mercury-electrolyte solution and changes the electrocapillary



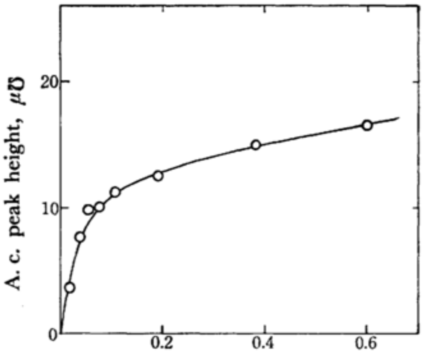
Potential, *E*, V *vs.* SCE

Fig. 1. Electrocapillary curves.
A pH=4.0, 0.50 M sodium sulfate
B pH=2.0, 0.50 M sodium sulfate, 1.0 mM brucine
C pH=7.0, 0.50 M sodium sulfate, 1.0 mM brucine



Potential, *E*. V *vs.* SCE

Fig. 2. D. c. and a. c. base-currents.
pH=4.0, 0.50 M sodium sulfate
A d. c. base-current, no brucine
B d. c. base-current, 1.0 mM brucine
C a. c. base-current, no brucine
D a. c. base-current, 1.0 mM brucine



Concentration of brucine, mM

Fig. 3. The peak-height of the first a. c. polarographic wave and the concentration of brucine. pH=4.0, 0.50 M sodium sulfate

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[4] B. Breyer, F. Gutmann and S. Hacobian, *Australian J. Sci. Res., Ser. A*, **4**, 595 (1951).

curve considerably. The top part of the electrocapillary curve becomes very flat. The surface-tension lowering by brucine was found to be independent of the pH value of the solution and of the nature of the supporting electrolyte (Fig. 1). The lowering of the a.c. base current and the appearance of an a.c. polarographic wave due to the presence of brucine are also shown in Fig. 2. The a.c. polarographic wave, with summit potentials at +0.10 V and −1.15 V *vs.* SCE, can be considered to be tensammetric in nature, because it is not accompanied by a corresponding d.c. step (Fig. 2). The maximum depression of the a.c. base-current was shown to occur at the potential around the e.c.m. (electrocapillary maximum). The surface-tension lowering and the a.c. base-current lowering become greater with an increase in the concentration of brucine in the bulk solution. The dependence of the peak height of the positive tensammetric wave on the brucine concentration is shown in Fig. 3. The peak height increases with the concentration up to 0.1 mM and reaches a limiting height above concentration of 0.2 mM following a typical Langmuir-type relation.

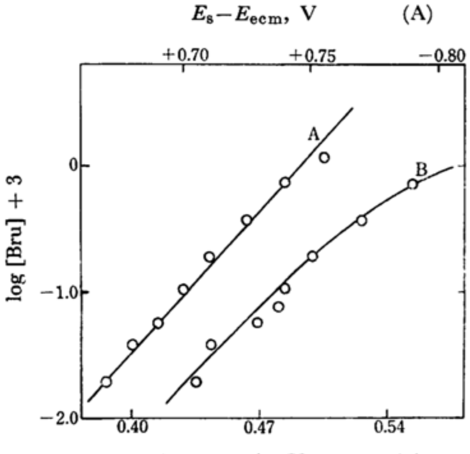

Fig. 4. Relation between log [Brucine] and $E_{ecm}-E_s$ or $(E_{ecm}-E_s)^2$ for the first peak-height. pH=2.00, 0.50 M sodium sulfate
A: $E_{ecm}-E_s$, B: $(E_{ecm}-E_s)^2$

The positive tensammetric peak was found to shift slightly to the more positive potential with an increase in the pH value and to disappear at pH values higher than 7.0, merging with the mercury dissolution wave. As Fig. 4 shows, it was also found to shift to the more positive potential with an increase in the brucine concentration in all the supporting electrolytes tested (sulfate and tartrate) according to the following relation, given by Breyer and Bauer.⁵⁾

$$E_s - E_{ecm} = K_1 - K_2 \log C_{Bru}{}^{5)}$$

where E_s represents the summit potential; E_{ecm}, the electrocapillary zero potential (−0.50 V *vs.* SCE), and C_{Bru}, the bulk concentration of brucine, and where K_1 and K_2 are constants.

The above experimental results clearly indicate that the positive tensammetric peak arises from the usual adsorption process involving the neutral form of brucine. This conclusion could also be confirmed by examining the effect of adsorbed brucine on the d.c. polarograms of copper(II). As Fig. 5 illustrates, the minimum occurs in the region of the e.c.m., showing the maximum adsorbability and the maximum depression action of brucine at this potential range.⁶⁾ At potentials more negative than the e.c.m., the depression of the limiting current becomes less pronounced with an increase in the negative potential; the wave height reaches its full height again at potentials more negative than −0.90 V *vs.* SCE.

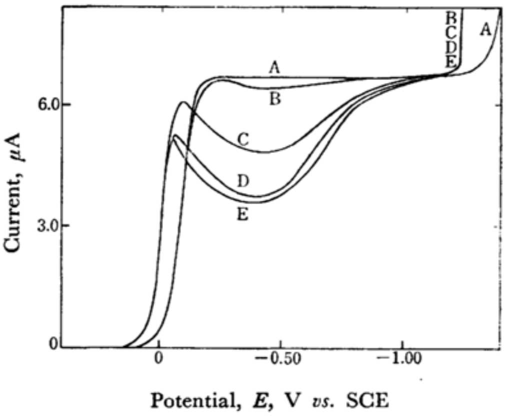

Fig. 5. Depressive effect of brucine on the reduction wave of copper(II), at ionic strength=1.50.

A	0.50 M tartrate, no brucine, pH=3.0
B	0.50 M tartrate, 1.0 mM brucine, pH=3.0
C	0.10 M tartrate, 1.0 mM brucine, pH=3.0
D	0.01 M tartrate, 1.0 mM brucine, pH=3.0
E	0.50 M Na_2SO_4, 1.0 mM brucine, pH=2.10

Conversely, the negative tensammetric peak differs considerably from the usual tensammetric wave involving the adsorption-desorption processes, in which, even at the potential where the negative peak appears, a lowering of the surface tension can still be observed (Fig. 1) and in which neither the plot of E_s-E_{ecm} nor that of $(E_s-E_{ecm})^{2,5)}$ against log C_{Bru} gives a linear relation, as is shown in Fig. 6.

The kink appearing in the electrocapillary curve shown in Fig. 1 corresponds exactly to the second summit potential, and a rise in the a.c. base-current can be observed on the negative side of the second wave. It is also interesting that the second tensammetric wave was always found to be accompanied by

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5) B. Breyer and H. H. Bauer, "Alternating Current Polarography and Tensammetry," Interscience Publishers, New York (1963), p. 89.

6) *Ibid.*, p. 86.

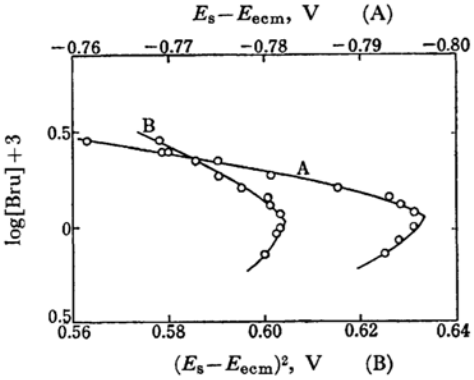

Fig. 6. Relation between log[Brucine] and $E_{ecm}-E_s$ or $(E_{ecm}-E_s)^2$ for the second peak-height.
pH=3.0, 0.50 M sodium sulfate
A: $E_{ecm}-E_s$, B: $(E_{ecm}-E_s)^2$

a catalytic wave (presumably due to the catalytic hydrogen discharge) in the pH range from 3.0 to 8.5 (contrary to the findings by Kirkpatrick[1]). At low concentrations of brucine, the catalytic wave occurs at a potential very close to the second summit potential. However, as the concentration of brucine increases, the separation between the second summit potential and the potential at which a catalytic wave occurs becomes greater.

Since the catalytic effect is generally influenced by the orientation of the catalytically-active species, and since the adsorption of positively-charged species must be advantageous compared with that neutral one at potential sufficiently negative with respective to the e.c.m., we can assume that the second tensammetric peak corresponds to a process such as the reformation of adsorbed brucine film involving the protonation and the reorientation of brucine. Here, the resulting brucine film with a relatively loose structure may be catalytically more active than that with a compact structure which is expected at high brucine concentrations.

The dependence of the peak height on the temperature was also examined in the temperature range from 15°C to 35°C. In this temperature range, both peak heights were found to decrease slightly with an increase in the temperature. On the other hand, it was also found that the peak height is little affected by the addition of 5×10^{-4} M LEO (Polyoxyethylene-Lauryl-Ether). From these results, we can deduce that brucine is firmly adsorbed on DME under the experimental conditions employed.

Strychnine was also found to be adsorbed on DME and to show exactly the same tensammetric behavior as brucine.

The Blocking Effect of Brucine on D. C. Polarographic Waves of Copper(II). Brucine was found to exert a depressive effect on the reduction waves of copper(II) in both sulfate and tartrate solutions. As has been described previously, the maximal depression of the limiting current occurs around the e. c. m.

In contrast to the sulfate system, the depressive effect of brucine on the reduction wave of copper(II) was demonstrated to become less pronounced in a tartrate solution upon an increase in the concentration of tartrate over the pH range from 2.0 to 5.0 (Fig. 5). Copper(II) has been reported to form a variety of complexes, depending on the pH value in solution and the concentration ratio between tartrate and copper(II). At a pH higher than 6 under a low ratio, mixed hydroxy-tartrate complexes have been reported.[7] A low pH value may be responsible for the formation of such a protonated

TABLE 1. FRACTION OF COPPER(II) PRESENT AS VARIOUS COMPLEX SPECIES IN 0.50 M AND 0.10 M TARTRATE SOLUTIONS

pH	Total concentration of tartrate, M	Fraction				
		Cu^{2+}	CuT	CuT_2^{2-}	CuT_3^{4-}	CuT_4^{6-}
1.20	0.10	0.998	0.002	—	—	—
	0.50	0.992	0.008	—	—	—
2.00	0.10	0.946	0.054	—	—	—
	0.50	0.786	0.211	0.003	—	—
3.00	0.10	0.207	0.687	0.106	—	—
	0.50	0.033	0.517	0.421	0.019	0.010
4.00	0.10	0.007	0.300	0.673	0.008	0.012
	0.50	—	0.057	0.623	0.040	0.280
5.00	0.10	0.001	0.113	0.744	0.027	0.115
	0.50	—	0.006	0.194	0.037	0.763
6.00	0.10	—	0.091	0.714	0.032	0.160
	0.50	—	0.003	0.145	0.033	0.819
7.00	0.10	—	0.091	0.711	0.032	0.166
	0.50	—	0.003	0.141	0.032	0.824

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[7] A. S. Tikhonov and V. P. Bel'skaya, *Obachxhei Khim., Akad. Nauk. S.S.S.R.,* **2**, 1211 (1953).

complex as $CuHT^+$.[8] At a low pH, in addition, a series of complexes expressed by $CuT_x{}^{2-2x}$ may be expected, where $x=1$ to 4. From the step-by step formation constants for this series, reported to be 3.20, 1.91, −0.34, and 1.71 in logarithm value respectively,[9] the equilibrium compositions can be calculated. Table 1 shows the expected compositions in solution with various pH values. In a 0.50 M tartrate solution, the predominant species in the pH range from 3.0 to 7.0 are $CuT_2{}^{2-}$ and $CuT_4{}^{6-}$. At pH 2.0, the major component is Cu^{2+}, while CuT is present in a small equilibrium concentration of 21%. Considering that the reported values may differ by several tenths from the logarithm values of true formation constants which can be safely used in the calculation, it can be concluded that there is no close relation between the composition of the tartrato-copper(II) complex and the minimizing action of the tartrate ion, but that the complex formation between copper(II) and the tartrate ion is essential. This conclusion is confirmed by the fact that, in a 0.10 M tartrate solution of pH 2.0, where almost all copper(II) ions were present in the form of Cu^{2+}, a pronounced depressive effect of brucine is observed. The importance of the complex formation in minimizing the depressive effect of brucine can also be seen by examining the effect of brucine on the limiting current of copper(II)-nitrilotriacetate complexes (a graph is not shown here). The depressive effect of brucine is eliminated completely by the addition of 10 mM nitrilotriacetate to 2.0 mM copper(II) at pH 4.0. Although the solution components in a 0.50 M tartrate solution of pH 6.0 are quite similar to those in the pH 5.0 solution, the effect of brucine was observed to be greater in the former solution. This clearly indicates that hydrogen ions also play an important role in the minimizing action performed the tartrate ion.

Though the detailed roles that tartrate and hydrogen ions play in the minimization of the depressive effect of brucine on the reduction of copper(II) in a tartrate solution could not completely explained in this study, and since, hence, further systematic investigations must be conducted to describe the characteristic nature of adsorbed brucine film precisely, we hope the results discussed here will provide suggestive clues for the explanation of the interaction between the adsorbed film and the electroactive substance at the electrode surface.

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8) H. Flashka, J. Butcher and R. Speights, *Talanta*, **8**, 400 (1961).

9) S. Froneaus, Dissertation Lund (Sweden), 1948.