April, 1988] *Bull. Chem. Soc. Jpn., 61, 1159—1162 (1988)*

Interfacial Adsorption of 1,10-Phenanthroline Complexes in Solvent Extraction Systems

Hitoshi WATARAI,* Yoko HORII, and Mitsuaki FUJISHIMA
Department of Chemistry, Faculty of Education, Akita University, Akita 010

(Received August 8, 1987)

A significant adsorptivity of tris(1,10-phenanthroline)iron(II), $[Fe(phen)_3]^{2+}$, at the interface of chloroform or carbon tetrachloride/0.1M aqueous sodium chloride systems was determined by means of interfacial tension measurements at 25 °C. In the distribution systems of phen containing Zn(II) or Cu(II), a characteristic interfacial tension lowering was observed and interpreted in terms of an interfacial adsorption of metal-phen complexes.

Ion-association extraction of Fe(II) with 1,10-phenanthroline, phen, has been extensively studied not only for a colorimetric determination of iron itself, but also for an indirect determination of a variety of organic and inorganic anions which are extractable with $[Fe(phen)_3]^{2+}$.[1,2] Although the stoichiometry of the overall extraction equilibrium between bulk phases has been established, there is no available information concerning the role of the interface in an extraction with phen and its derivatives, except those which we reported recently. In this case the interfacial adsorption of protonated phen derivatives in the chloroform/acidic aqueous phase[3] and of Cu(II) and Zn(II) 4,7-diphenyl-1,10-phenanthroline complexes in the chloroform/aqueous phase systems[4] were determined by means of a high-speed stirring method. Also, a significant role of the interface was demonstrated. For the elucidation of a realistic mechanism of ion-association extraction, which should include a rational assessment on interfacial reactions, further extensive studies concerning interfacial phenomena are required.

In the present study, first the interfacial adsorptivity of $[Fe(phen)_3]^{2+}$, a very stable tris(phen) complex, was examined by means of interfacial tension measurements. Secondly, the interfacial tension in the systems containing both phen and Zn(II) or Cu(II), which include mono, bis, and tris(phen) complexes, was measured; the adsorptivity of each complex, especially of the tris(phen) complexes, is discussed based on the results of $[Fe(phen)_3]^{2+}$ system.

Experimental

Chemicals. phen, wako G.R., was used as purchased. $[Fe(phen)_3]Cl_2$ and $[Fe(phen)_3](ClO_4)_2$ were synthesized by the conventional methods and purified by recrystallization from an aqueous solution. Chloroform, Wako G.R., was washed with an equal amount of water three times prior to use. Carbon tetrachloride, Nakarai G.R., was shaken with sulfuric acid, washed with water and then fractionally distilled. Other chemicals used were of all G.R. grade. Stock solutions of Zn(II) and Cu(II) were prepared by dissolving pure zinc powder and $CuCl_2 \cdot 2H_2O$ in hydrochloric acid solution, respectively. The ionic strength of the aqueous solution was adjusted to 0.1 by sodium chloride, and the pH was controlled by hydrochloric acid and sodium acetate (0.002 M, 1 M=1 mol dm^{-3}). The use of sodium chloride completely depressed the ion-association extraction of metal-phen complexes and made conspicuous the interfacial adsorption of the complexes.

Interfacial Tension Measurements. Measurements of the interfacial tension, γ, were carried out by means of a drop-volume method at 25±1 °C. The apparatus used is schematically shown in Fig. 1. The organic and aqueous phases, 10 ml each, were shaken for 30 min and equilibrated prior to the measurements. The aqueous drop produced on the end of a glass capillary (6 mm o.d.) was slowly released after 5 min equilibration, and the volume of a detached drop was measured using a Gilmont micrometer pipet s1200 (2 μl smallest division) or s4200 (0.1 μl smallest division). The volume of one drop was determined as an average of at least 5 drops. The interfacial tension was then calculated by using the interfacial tension values of 31.5 dyn cm^{-1} and 44.55 dyn cm^{-1} for $CHCl_3$/water and CCl_4/water systems, respectively, and by applying the Lando-Oakley's equation.[5]

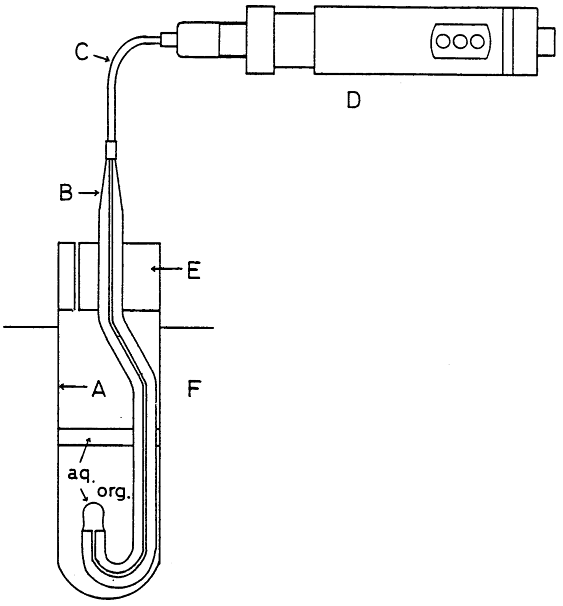

Fig. 1. Apparatus for interfacial tension measurements by drop-volume method in halomethane/water system: A, glass vessel; B, glass capillary; C, teflon tube; D, digital micrometer pipet; E, stopper with a hole; F, thermostated water bath.

Distribution of phen. Distribution constants of phen in

$CHCl_3$/0.1 M NaCl and CCl_4/0.1 M NaCl systems were determined by a batch method. An aqueous solution of phen, 5 ml or 10 ml, was shaken with 5 ml organic solvent for 30 min by means of a mechanical shaker. The pH of the aqueous phase was controlled to higher than 6.2. From the absorbances at 265 nm of the aqueous phases before and after distribution, the distribution constant, K_D, was calculated, as listed in Table 1. Absorbance measurements were carried out by means of a Hitachi 200-20 or UVIDEC 430 spectrophotometer. The value of K_D was employed for the calculation of the concentrations of mono, bis, and tris(phen) complexes in the aqueous phases of $CHCl_3$/aqueous systems containing phen, and Zn(II) or Cu(II). An NEC PC-microcomputer was used for both calculations of the concentrations and the interfacial tensions.

Results and Discussion

Interfacial Adsorption of $[Fe(phen)_3]^{2+}$. The interfacial tension in an $CHCl_3$/0.1 M NaCl solution decreased upon the addition of $[Fe(phen)_3]^{2+}$ above a concentration of 10^{-6} M, as shown in Fig. 2. The substitution of $[Fe(phen)_3]Cl_2$ by $[Fe(phen)_3](ClO_4)_2$ did not seriously affect γ under the present conditions. When the organic solvent was changed from $CHCl_3$ to CCl_4, the concentration at which γ began to decrease was shifted to a value about 100-times higher than that in the $CHCl_3$ system (see Fig. 2).

The observed lowering in γ is attributable to an interfacial adsorption of $[Fe(phen)_3]^{2+}$, which is usually analysed according to the Gibbs equation or the Langmuir isotherm. The interfacial excess Γ of a solute is defined by the Gibbs equation:

$$\Gamma = -\frac{1}{RT}\frac{\partial\gamma}{\partial \ln C}, \tag{1}$$

where C refers to the solute concentration in aqueous phase. However, according to the Langmuir isotherm, the interfacial concentration of the solute, C_i, can be represented by

$$C_i = \frac{aK'C}{a+K'C}, \tag{2}$$

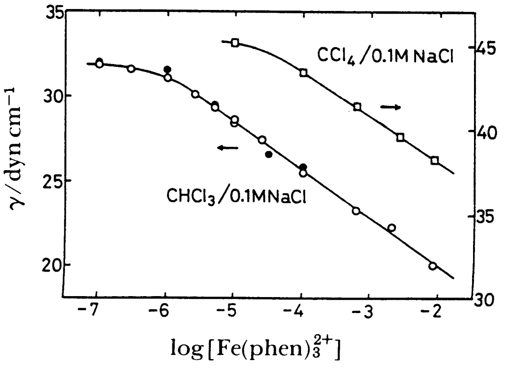

Fig. 2. Interfacial tension lowering by addition of $[Fe(phen)_3]Cl_2$ (○) or $[Fe(phen)_3](ClO_4)_2$ (●) in $CHCl_3$/0.1 M NaCl (pH=6.2) and CCl_4/0.1 M NaCl (pH=6.2).

where a refers to the interfacial concentration at saturation and K' to the equilibrium constant for adsorption of the solute from aqueous phase to interface at infinite dilution. By combining Eqs. 1 and 2 by approximating $\Gamma = C_i$, and integrating the combined equation over a concentration range from zero to C, corresponding to the interfacial tension from γ_0 to γ, one obtains

$$\gamma = \gamma_0 - aRT \ln\left(1+\frac{K'C}{a}\right). \tag{3}$$

When $C \gg a/K'$, Eq. 3 becomes,

$$\gamma = \gamma_0 - aRT \ln\frac{K'}{a} - aRT \ln C. \tag{4}$$

Equation 4 represents a linear relationship between γ and log C, as observed in a higher-concentration region in Fig. 2; the slope of the straight line refers to $-2.303aRT$. In addition, the concentration C^*, at which the straight line of Eq. 4 and another straight line of $\gamma=\gamma_0$ crosses, is found to be equal to a/K'. The application of these analyses to $[Fe(phen)_3]^{2+}$ systems yields parameters a and K' for the two-solvent systems listed in Table 1. The values of the interfacial concentration at the saturation or interfacial area occupied by a single complex ion does not differ very much in two-solvent systems (see Table 1). As for the values of C^*, however, as well as those of K', there is a strong solvent dependence: K' in $CHCl_3$ system is 86-times larger than that in the CCl_4 system; this means that the $[Fe(phen)_3]^{2+}$ ion is much more adsorbable to the $CHCl_3$/water interface than the CCl_4/water interface. Ozeki et al. recently reported that $[Fe(phen)_3]^{2+}$ is never surface-active from the fact that the surface tension of a 5.0×10^{-4} M $[Fe(phen)_3](ClO_4)_2$ solution was 71.93±0.1 dyn cm^{-1}, agreeing with that of pure water.[6] Consequently, the interfacial adsorptivity of $[Fe(phen)_3]^{2+}$ observed in the present systems should be ascribable to a lipophilic interaction between phen molecules coordinated to Fe(II) and the organic solvent at the interface. This idea is supported by the fact that the distribution constant of phen, which is a measure of the lipophilic interaction, is much larger in the $CHCl_3$ system (see Table 1). From the above discussion, it is concluded that tris(phen) complexes are strongly

Table 1. Parameters in the Interfacial Adsorption of $[Fe(phen)_3]^{2+}$ at 25 °C

Parameter	Organic solvent	
	CCl_4	$CHCl_3$
a/mol cm^{-2}	4.80×10^{-11} (346)[a]	4.98×10^{-11} (333)
C^*/mol l^{-1}	4.50×10^{-5}	5.40×10^{-7}
K'/l cm^{-2}	1.07×10^{-6}	9.23×10^{-5}
K_D(phen)	1.14±0.07	723±18

a) Values in parentheses refer to an area (Å^2) per molecule.

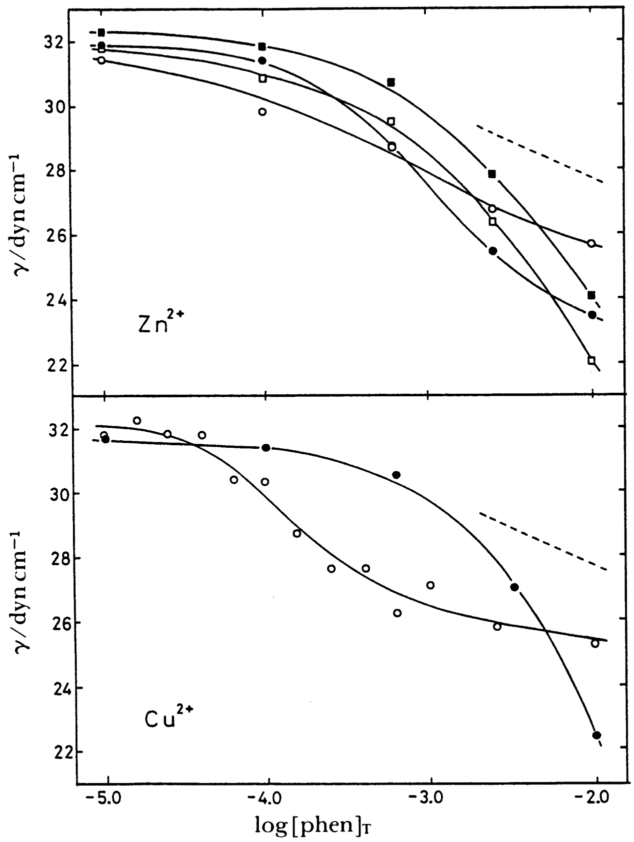

Fig. 3. Effects of zinc(II) and copper(II) on the interfacial tension of phen-$CHCl_3$/0.1 M NaCl systems: no metal ion (-----); $[Zn^{2+}]_T=1.0\times10^{-4}$ M, pH=6.06 (○), 1.0×10^{-3} M, pH=5.33 (●), 5.0×10^{-3} M. pH=3.44 (□), 1.0×10^{-2} M, pH=2.68 (■); $[Cu^{2+}]_T=1.0\times10^{-4}$ M, pH=6.28 (○), 1.0×10^{-3} M. pH=6.03 (●).

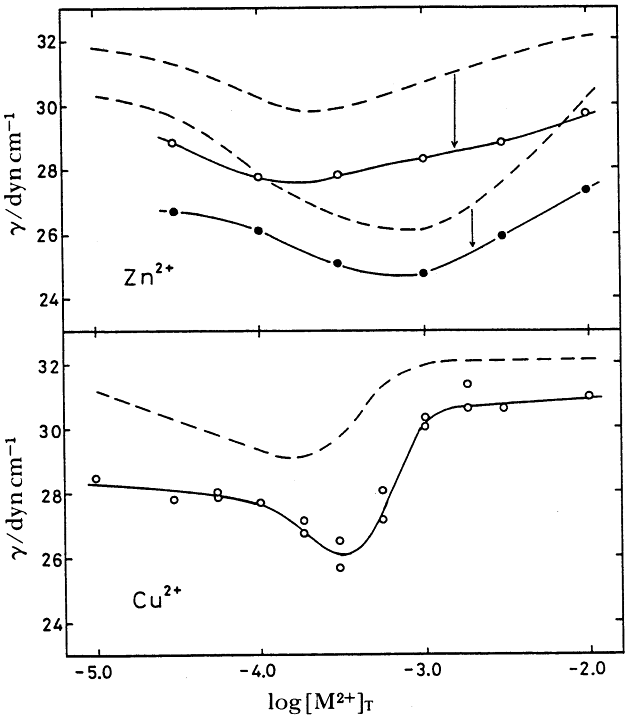

Fig. 4. Dependence of interfacial tension in $CHCl_3$ system on the zinc(II) and copper(II) concentrations at a constant phen concentration: $[phen]_T=6.21\times10^{-4}$ (○), 2.49×10^{-3} M (●), pH=6.1 in Zn(II) systems; $[phen]_T=6.24\times10^{-4}$ M (○), pH=3.91—6.02 in Cu(II) systems.

adsorbable at the $CHCl_3$/water interface.

Interfacial Adsorption of Zn(II)-phen and Cu(II)-phen Complexes. The interfacial tension in phen-$CHCl_3$/0.1 M NaCl systems containing Zn(II) or Cu(II) ions depended on both the concentrations of phen and the metal ion. In Fig. 3, the effect of the metal ions on plots of γ vs. the logarithm of the total phen concentration, log $[phen]_T$, is shown. In both systems, the following tendencies are observed: in a lower phen concentration, the lowering of γ is larger in a lower metal concentration than that in a higher metal concentration, while in a higher phen concentration the situation is reversed, more obviously in Cu(II) systems. In the region $[phen]_T=10^{-4}$—10^{-3} M, the values of γ in $[Cu^{2+}]_T=10^{-4}$ M are lower than those in $[Cu^{2+}]_T=10^{-3}$ M. This means that the species formed under the condition $[phen]_T>[Cu^{2+}]_T$ is more adsorbable than those formed under $[phen]_T<[Cu^{2+}]_T$, suggesting a preferencial adsorptivity of a bis or tris(phen) complex than a mono(phen) complex. When the total phen concentration was fixed, the plots of γ vs. log $[M^{2+}]_T$ showed a minimum that depended on the phen concentration, as shown in Fig. 4. It is noted in Fig. 4 that the Zn(II) concentration, showing a minimum in γ, shifted toward a higher region when $[phen]_T$ was increased. These interfacial tension lowering characteristics are thought to be ascribable to the adsorption of Zn(II) or Cu(II)-phen complexes, since the adsorptivity of phen is very low.[3] In order to discuss which type of the complex is most responsible for the lowering of γ, the concentrations of mono-, bis-, and tris(phen) complexes in the aqueous phase under the given total concentrations of metal ion and phen were calculated using

$$[M^{2+}]_T = [M^{2+}](1+\beta_1[L]+\beta_2[L]^2+\beta_3[L]^3) \qquad (5)$$

and

$$[L]_T = (1+\frac{[H^+]}{K_a}+K_D)[L] + [M^{2+}](\beta_1[L]+2\beta_2[L]^2+3\beta_3[L]^3), \qquad (6)$$

where $[M^{2+}]$ and $[L]$ refer to the concentrations of the free metal ion and the free ligand phen, respectively; the subscript T denotes the total concentration of the metal ion or phen. The value of the formation constants used for the calculation are log β_1=6.30, log β_2=11.95, and log β_3=17.05 for Zn(II)-phen system and log β_1=8.82, log β_2=15.39, and log β_3=20.41 for Cu(II)-phen system.[7] A calculation of $[M^{2+}]$, $[ML^{2+}]$

$[ML_2^{2+}]$, and $[ML_3^{2+}]$ was carried out by determining the best value of [L] so that the $[M^{2+}]_T$ and $[L]_T$ calculated by Eqs. 5 and 6 would agree with the experimental concentrations. The contribution of $[LH^+]$ in Eq. 6 was not serious in almost systems studied here, since $pK_a=4.98$ for phen.[7] Because a preliminary comparison between the calculated results and Figs. 3 and 4 suggested a significant contribution of ML_3^{2+}, a semiquantitative comparison was attempted between the observed γ values and the estimated values using

$$\gamma = 32.1 - 1.24 \ln\left(1 + \frac{[ML_3^{2+}]}{5.40 \times 10^{-7}}\right), \qquad (7)$$

which is determined for the $[Fe(phen)_3]^{2+}$ system, assuming that the adsorptivity of ML_3^{2+} is the same as that of $[Fe(phen)_3]^{2+}$. The broken lines in Fig. 4 show the γ estimated using the calculated $[ML_3^{2+}]$ and Eq. 7. Although a quantitative agreement between the calculated and observed γ's is not satisfactory, the features of the γ vs. log $[M^{2+}]_T$ profile are well-reproduced, especially in Zn(II) systems. The observed minima in Zn(II) systems correspond to the situation where $[M^{2+}]_T$: $[L]_T=1:3$. These results confirm that a predominant species at the interface in Zn(II) systems is $[Zn(phen)_3]^{2+}$. In Cu(II) systems, the minimum point in Fig. 4 is close to $[M^{2+}]_T:[L]_T=1:2$. Hence, the adsorption of $[Cu(phen)_2]^{2+}$ as well as $[Cu(phen)_3]^{2+}$ may take place in higher Cu(II) concentration.

The authors wish to thank the Ministry of Education, Science and Culture for a financial support, a Grant-in-Aid for Scientific Research to H.W. (No. 61470034).

References

1) Y. Yamamoto, T. Tarumoto, and E. Iwamoto, *Anal. Chim. Acta*, **64**, 1 (1973).

2) K. L. Cheng, K. Ueno, and T. Imamura, "Handbook of Organic Analytical Reagents," CRC Press, Inc., Florida, USA (1982).

3) H. Watarai, *J. Phys. Chem.*, **89**, 384 (1985).

4) H. Watarai, *Talanta*, **32**, 817 (1985).

5) J. L. Lando and H. T. Oakley, *J. Colloid Interface Sci.*, **25**, 526 (1967).

6) S. Ozeki, S. Tachiyashiki, S. Ikeda, and H. Yamatera, *J. Colloid Interface Sci.*, **91**, 439 (1983).

7) H. Irving and D. H. Miller, *J. Chem. Soc.*, **1962**, 5222.