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The Role of the Tosyl Group on the Coordination Ability of N-Protected Amino Acids. 2. Behavior of the Copper(II) Ion–*N*-Tosylglycinate System in Aqueous Solution

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Abstract: The formation reactions of complexes of *N*-tosylglycine with the copper(II) ion were investigated by polarographic measurements in aqueous solution at different ligand concentrations and pH values to identify the number and type of complex species present in aqueous solution, to establish the equilibria in which they are involved, and to calculate their stability constants. A polarographic, pH-metric, and spectrophotometric study of the ligand was also performed to determine its pK_A values (3.5 and 11.6). Until pH 5 no formation of complexes is observed; in the 5–7.5 pH range the polarographic analysis reveals the presence of a wave and in the 7.5–13 pH range a second wave also appears; this second wave does not appear when a large ligand excess is present. The analysis of the two waves shows that different complexes prevail in the different ranges of pH: in the 5–7.5 pH range only the $Cu(TsglyH)_2$ complex is present, and in the 8–10 pH range $Cu(TsglyH)_2$, $[Cu(Tsgly)_2]^{2-}$, and $[Cu(Tsgly)(OH)]^-$ are present. In the $Cu(TsglyH)_2$ complex the ligand seems to coordinate through the O atoms of the carboxylate group, while in the other complexes it does so through N,O atoms of the sulfonyl and carboxylate groups. In the 10–13 pH range the $[Cu(Tsgly)_2(OH)_2]^{4-}$ and $[Cu(Tsgly)(OH)_2]^{2-}$ complexes prevail. The overall equilibria as a function of the pH are also proposed. The results are compared with those previously performed on the solid-state copper(II) complexes of *N*-tosylglycine.

In the solid- and solution-state complexes of metal ions with L-α-amino acids, the acids coordinate through the amino and carboxylate groups.[2] A substituent, such as a benzoyl or an acetyl group, directly introduced on the amino group, diminishes the affinity of this group for the metal ions and since the acids coordinate solely through the carboxylate group, as found in the solid complexes,[3] they are unable to coordinate with the metal ions in aqueous solution.[4]

To investigate the effects of the substituents on the amino group, we previously examined the coordination properties of *N*-tosylglycine ($TsglyH_2$ = *N*-tosylglycine; $TsglyH^-$ = *N*-tosylglycinate anion; $Tsgly^{2-}$ = *N*-toslyglycinate dianion) with the copper(II) ion.[5] This investigation, performed on four solid-state complexes separated from aqueous solution at different pH values, showed that the ligand has the properties of both the L-α-amino acids and their acetyl or benzoyl derivatives, since it may act as monodentate through the carboxylate group or bidentate through the oxygen of the carboxylate group and the nitrogen of the sulfonyl group. Sometimes the SO_2 group may also be involved in the metal ion coordination.

Since the separation of four different solid complexes from aqueous solution indicated the presence of strongly complicated equilibria in solution, in order to rationalize it we have now studied the behavior of the copper(II) ion–*N*-tosylglycinate system in aqueous solution at different ligand concentration and pH values by means of polarographic, pH-metric, and spectrophotometric measurements. The aim of this work is to determine type, number, and stability constants of the complexes present in solution and their relationship with the complexes separated in the solid state.

Experimental Section

Using an Amel Multipolarograph Model 471 the polarographic measurements were performed at 25 ± 0.1 °C and at dropping times of 2, 3, 4, and 6 s; all half-wave potential values are referred to a saturated calomel electrode (SCE) which was used as reference. The solutions were prepared by dissolving the solid complexes or adding copper(II) perchlorate hexahydrate to the sodium salt of *N*-tosylglycine in doubly distilled water; sodium perchlorate (0.1 $mol{\cdot}dm^{-3}$) was used as base electrolyte and the ionic strength was kept constant ($\mu = 0.1$). The pH solution values were obtained by adding an aqueous NaOH solution (0.1 $mol{\cdot}dm^{-3}$) and the ligand concentrations were changed by adding an aqueous sodium *N*-tosylglycinate solution (0.1 $mol{\cdot}dm^{-3}$). All the solid complexes were prepared as previously reported.[5] The pH-metric measurements were determined with a Praizious pH-meter KNICK with an Ingold B7213 glass electrode (0–14 pH range). The electronic spectra were recorded with a Beckman DK2 spectrophotometer. The pH solutions for the spectrophotometric analyses were made constant with buffer "Normex" solutions. All measurements were performed at 25 ± 0.1 °C.

Results and Discussion

Behavior of *N*-Tosylglycine in Aqueous Solution. The physical and chemical properties of *N*-tosylglycine—low melting point (149–50 °C), slight solubility in water, great solubility in organic solvents, electronic bands (λ_{max} at 227 and 267 nm with log ε of 4.1 and 2.8, respectively) very similar in shape and position to those found in 4-benzenesulfonamide ($CH_3C_6H_4SO_2NH_2$) (λ_{max} at 227 and 264 nm with log ε of 4 and 2.5, respectively),[6] absence of a broad band around 3000–2800 cm^{-1} in its infrared spectrum[7]—exclude for this ligand any type of zwitterionic

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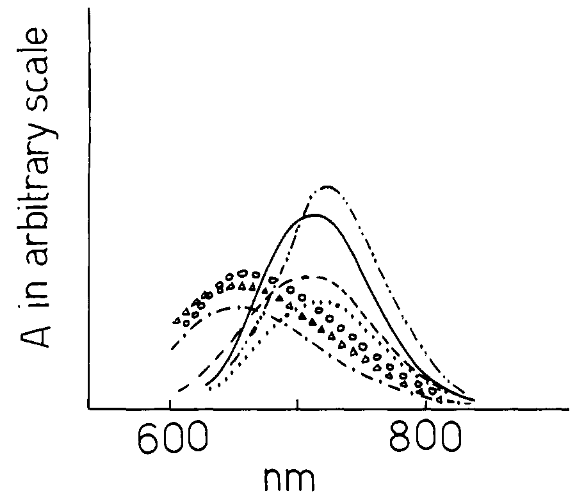

Figure 1. Electronic spectra of the $Cu(TsglyH)_2 \cdot 4H_2O$ complex in the solid state (-···-) and in aqueous solution at pH 4 (···), 7 (---), 9 (O), 11 (Δ), and 12 (-··) and of the $Cu(ClO_4)_2 \cdot 6H_2O$ salt in aqueous solution at pH 2 and 4 (—).

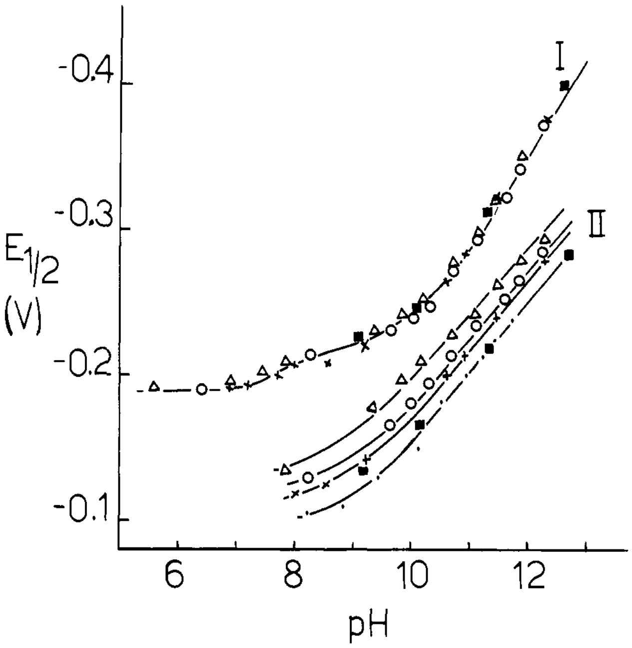

Figure 2. Plots of $E_{1/2}$ vs. pH for wave I and wave II of the copper(II) ion-*N*-tosylglycinate system at increasing *N*-tosylglycinate concentration: (•) = 2×10^{-4} mol·dm^{-3}; (×) = 9×10^{-4} mol·dm^{-3}; (O) = 1.2×10^{-3} mol·dm^{-3}; (Δ) = 2.2×10^{-3} mol·dm^{-3}; (■) $K_2[Cu(Tsgly)_2]$ = 5×10^{-4} mol·dm^{-3} at increasing pH values.

Table I. Polarographic Results of the Copper(II)-*N*-Tosylglycinate System[a]

pH	$-(E_{1/2})^{II}$/ V	$-(E_{1/2})^{I}$/ V	i_d^{II}/ μA	i_d^{I}/ μA	i_{tot}/ μA	i_d^{II}/i_{tot}	i_d^{I}/i_{tot}
7.4		0.187		1.18	1.18		
8.2	0.105	0.205		1.32	1.32		
8.8	0.110	0.215	0.89	1.28	2.17	0.41	0.59
9.4	0.130	0.220	0.92	1.34	2.26	0.41	0.59
9.5	0.135	0.225	0.90	1.38	2.28	0.39	0.61
10.1	0.150	0.240	0.99	1.12	2.11	0.47	0.53
10.5	0.182	0.258	1.27	0.98	2.16	0.59	0.41
10.9	0.200	0.280	1.16	0.97	2.13	0.54	0.46
11.2	0.214	0.295	1.20	1.15	2.35	0.51	0.49
11.4	0.224	0.316	0.76	0.76	1.52	0.50	0.50
11.7	0.238	0.330	0.82	0.72	1.54	0.53	0.47

[a] $|Cu(TsglyH)_2| = 5 \times 10^{-4}$ mol dm^{-3}; $|NaTsglyH| = 2 \times 10^{-4}$ mol dm^{-3}; dropping time = 2 s; I and II refer to wave I and wave II; i_d = diffusion current.

Table II. Polarographic Results of the Copper(II)-*N*-Tosylglycinate System[a]

pH	$-(E_{1/2})^{II}$/ V	$-(E_{1/2})^{I}$/ V	i_d^{II}/ μA	i_d^{I}/ μA	i_{tot}/ μA	i_d^{II}/i_{tot}	i_d^{I}/i_{tot}
6.8		0.195		1.13	1.13		
7.7		0.200		1.14	1.14		
8.2	0.120	0.205	1.28	1.12	2.40	0.53	0.47
8.5	0.125	0.208	1.20	1.30	2.50	0.48	0.52
9.2	0.143	0.220	1.19	1.30	2.49	0.48	0.52
10.6	0.200	0.265	1.13	1.37	2.50	0.45	0.55
10.9	0.214	0.284	1.16	1.36	2.52	0.46	0.54
11.4	0.240	0.322	1.12	1.42	2.54	0.44	0.56
12.3	0.280	0.378	1.44	1.88	3.32	0.43	0.57

[a] $|Cu(TsglyH)_2| = 5 \times 10^{-4}$ mol dm^{-3}; $|NaTsglyH| = 9 \times 10^{-4}$ mol dm^{-3}; dropping time = 2 s.

Table III. Polarographic Results of the Copper(II)-*N*-Tosylglycinate System[a]

pH	$-(E_{1/2})^{II}$/ V	$-(E_{1/2})^{I}$/ V	i_d^{II}/ μA	i_d^{I}/ μA	i_{tot}/ μA	i_d^{II}/i_{tot}	i_d^{I}/i_{tot}
7.0		0.206		1.19	1.19		
8.2	0.130	0.215	1.32	1.62	2.94	0.45	0.55
9.6	0.165	0.230	1.32	1.34	2.66	0.50	0.50
10.0	0.180	0.237	1.26	1.38	2.64	0.48	0.52
10.3	0.192	0.247	1.34	1.42	2.76	0.48	0.52
10.7	0.215	0.273	1.34	1.32	2.66	0.50	0.50
11.1	0.234	0.294	1.30	1.42	2.72	0.48	0.52
11.6	0.252	0.325	1.28	1.40	2.68	0.48	0.52
11.8	0.265	0.338	1.20	1.32	2.52	0.48	0.52
12.2	0.283	0.372	1.18	1.36	2.54	0.46	0.54

[a] $|Cu(TsglyH)_2| = 5 \times 10^{-4}$ mol dm^{-3}; $|NaTsglyH| = 1.2 \times 10^{-3}$ mol dm^{-3}; dropping time = 2 s.

Table IV. Polarographic Results of the Copper(II)-*N*-Tosylglycinate System[a]

pH	$-(E_{1/2})^{II}$/ V	$-(E_{1/2})^{I}$/ V	i_d^{II}/ μA	i_d^{I}/ μA	i_{tot}/ μA	i_d^{II}/i_{tot}	i_d^{I}/i_{tot}
5.60		0.190		0.80	0.80		
6.94		0.194		1.10	1.10		
7.45	0.130	0.200	1.00	1.20	2.20	0.45	0.55
7.85	0.135	0.210	0.97	1.13	2.10	0.46	0.54
9.35	0.180	0.229	1.16	1.41	2.57	0.45	0.55
9.84	0.195	0.241	1.15	1.40	2.55	0.45	0.55
10.2	0.210	0.252	1.15	1.40	2.55	0.45	0.55
10.7	0.228	0.277	0.99	1.48	2.47	0.40	0.60
11.1	0.243	0.296	1.24	1.24	2.48	0.50	0.50
11.5	0.263	0.322	1.24	1.14	2.38	0.52	0.48
11.9	0.279	0.350	1.31	1.08	2.39	0.55	0.45
12.3	0.294	0.374	1.28	1.09	2.37	0.54	0.46

[a] $|Cu(TsglyH)_2| = 5 \times 10^{-4}$ mol dm^{-3}; $|NaTsglyH| = 2.2 \times 10^{-3}$ mol dm^{-3}; dropping time = 2 s.

character. Therefore its dissociation equilibria at increasing pH values may be represented as follows:

$$CH_3C_6H_4SO_2NHCH_2COOH \xrightleftharpoons{pK_{1A}}$$

$$CH_3C_6H_4SO_2NHCH_2COO^- \xrightleftharpoons{pK_{2A}} CH_3C_6H_4SO_2\bar{N}CH_2COO^-$$

The pK_{1A} and pK_{2A} values, potentiometrically and spectrophotometrically determined, are 3.5 and 11.6, respectively.

Behavior of the Complexes in Aqueous Solution. Since the polarographic analysis of the $Cu(TsglyH)_2 \cdot 4H_2O$ complex in aqueous solution shows a reduction wave, corresponding to the aqueous copper(II) ion reduction,[8] and its aqueous solution electronic spectrum strongly resembles that of the $Cu(ClO_4)_2 \cdot 6H_2O$ in the same experimental conditions (Figure 1), this complex may be considered completely dissociated. On increasing the pH of the solution by adding NaOH (0.1 mol·dm^{-3}), at pH greater than 5, when the carboxylate group is completely dissociated, the first evidence of a complex in solution is found. In these conditions

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[8] "Encyclopedia of Electrochemistry of the Elements"; Bard, A. J., Ed.; Marcel Dekker, Inc.: New York, 1974; Vol. II, p 387.

a new wave (wave I) appears, which has a more negative $E_{1/2}$ value than that of the free copper(II) ion[8] and which shows an increasing limiting current value at increasing pH, while the free copper(II) ion reduction wave decreases until it disappears.

The $E_{1/2}$ value of wave I does not depend on the ligand concentration in the whole pH range (Tables I, II, III, and IV) and does not depend on the pH in the 5–7.5 pH range alone. The total dependence of $E_{1/2}$ on the pH is reported in Figure 2; furthermore, the $E_{1/2}$ value is also independent of the starting complex concentration.

At pH greater than 7.5 another wave (wave II) appears, the $E_{1/2}$ values of which are slightly more positive than those of wave I, decreasing at increasing ligand concentration and pH values (Figure 2). The ratio of the limiting current values between wave II and wave I increases with the pH until it becomes constant and nearly equal to 1. At ligand concentrations greater than 5×10^{-3} mol·dm^{-3} wave II does not appear.

An essentially octahedral environment of the copper(II) ion in the 5–7.5 pH range, due to the presence of the CuO_6 chromophore and an amino acid coordination through the carboxylate group, may be suggested for the complex in solution on the basis of the strict similarity of its electronic spectrum with those of the $Cu(H_2O)_6^{2+}$ cation and of the solid $Cu(TsglyH)_2 \cdot 4H_2O$ complex[5] (Figure 1).

The blue shift of the d–d band maximum (Figure 1) in the 7.5–9 pH range may be attributed to a change in the ligand coordination from an O coordination through the carboxylate group to an N,O coordination through the sulfonyl and carboxylate groups, the hydrogen atom of the NH group being dissociated. This may be confirmed since the spectrum does not change at pH values greater than 9, and it also explains the step observed in the plot of $E_{1/2}$ vs. pH of wave I at around pH 7.5 (Figure 2).

The dissociation of the NH group at lower pH than that corresponding to the ligand pK_{2A}, in agreement with that found in the solid N-tosylglycinate complexes[5] and in some glycine peptide complexes,[9,10] may depend on the presence of the copper(II) ion coordinated to the ligand via the carboxylate group, which increases the acidic character of the NH group.

The pH-metric titration of the complex in aqueous solution with NaOH (0.1 mol·dm^{-3}) shows two steps, one in the same pH range in which the first polarographic wave appears and the other in the same pH range in which the greatest changes of λ_{max} are observed; this also supports the hypothesis of a coordination change of the ligand. The polarographic analysis of the titrated solution at pH 12.5 shows two waves with $E_{1/2}$ values identical with those previously determined in the same conditions and with current ratio equal to one.

An important suggestion may derive from comparison of the polarographic behavior with the spectrophotometric and potentiometric ones. In fact, while $E_{1/2}$ values decrease at increasing pH values until pH 13, λ_{max} and the potentiometric curve do not change at pH greater than 11. This may be explained by the formation of mixed complexes in which the hydroxide group (OH^-) could be involved in the metal ion coordination.

The semilogarithmic analysis of the two polarographic waves shows that they both correspond to a reversible, bielectronic reduction process and the study at different dropping times and depolarizer concentrations indicates that each wave is diffusion controlled [$i_d/h^{1/2}$ and i_d/C are constant (i_d = diffusion current; h = height of the mercury head; C = depolarizer concentration)]; therefore the species reduced on the electrode derive from reactions that take place in the bulk of the solution. The $E_{1/2}$ values are proportional to the standard potential of the redox process, thus they are used to determine type, number, and stability constants of the complexes and the pH range in which each complex prevails.

The polarographic behavior of the $K_2[Cu(Tsgly)_2]$ complex in aqueous solution (initial pH 9) strictly resembles that found for the $Cu(TsglyH)_2 \cdot 4H_2O$ complex at the same pH values (Figure 2), further confirming that at pH greater than ~8 the ligand acts as bidentate via N,O atoms. Its reduction shows two waves, whose $E_{1/2}$ values correspond to those determined for the solutions of $Cu(TsglyH)_2 \cdot 4H_2O$ complex at the same pH values.

Table V. Values of *A*, *B*, and *C* at Different *N*-Tosylglycinate Concentrations and of Stability Constants Calculated by the Schaap and McMasters Method[13]

	[NaTsglyH]				stability constants
	2.0×10^{-4}	0.9×10^{-3}	1.2×10^{-3}	2.2×10^{-2}	
A	3.0×10^{2}	8.0×10^{2}	1.2×10^{3}	2.2×10^{3}	$\beta_{1,0} = 8.0 \times 10^{5}$
B	3.0×10^{8}	2.1×10^{9}	3.7×10^{9}	1.5×10^{10}	$\beta_{1,1} = 5.0 \times 10^{12}$
C	1.1×10^{12}	7.0×10^{12}	10.0×10^{12}	2.1×10^{13}	$\beta_{1,2} = 7.0 \times 10^{15}$

Analysis of Wave I at Different pH Ranges. (a) Since in the 5–7.5 pH range half-wave potentials ($E_{1/2}$) and diffusion current (i_d) values are independent of the ligand concentration and of the pH of the solution, it suggests the presence of two molecules of ligand coordinated to the copper(II) ion. The ligand coordination through the carboxylate group agrees with the "normal" behavior of the N-protected amino acids already investigated.[3,4]

The overall electrodic process, determined by the reversible reduction of the complex, may be represented as follows:

$$Cu(TsglyH)_2 + 2e^- \overset{Hg}{\rightleftharpoons} Cu(Hg) + 2TsglyH^-$$

Its stability constant may be determined by using the equation[11]

$$(E_{1/2})_S{}^r - (E_{1/2})_C{}^r = \frac{RT}{nF} \ln \beta_2$$

where $(E_{1/2})_S{}^r$ is the reversible half-wave potential of the uncomplexed metal ion [$(E_{1/2})_S{}^r = -0.02$ V vs. SCE[8]] and $(E_{1/2})_C{}^r$ that of the complexed metal ion and β_2 is the stability constant itself, the calculated average value of which is $\sim 10^6$.

(b) In the 7.5–9 pH range the step observed on the plot of $E_{1/2}$ vs. pH, may be attributed to a coordinative rearrangement of the ligand from an O coordination to an N,O coordination, as is suggested above by the spectrophotometric and pH-metric studies. Therefore the step may be associated with the following equilibrium reaction:

$$Cu(TsglyH)_2 \rightleftharpoons [Cu(Tsgly)_2]^{2-} + 2H^+$$

(c) In the 10–13 pH range the $E_{1/2}$ values are independent of the ligand concentration and depend on the pH (Figure 2); this suggests that a variable number of hydroxide ions are bonded to the copper(II) ion in the $[Cu(Tsgly)_2]^{2-}$ complex.

As the plot of $E_{1/2}{}^r$ vs. pH is a bent line, the DeFord–Hume method[12] can be applied with the equation:

$$\operatorname{antln}\left[\frac{nF}{RT}\Delta E_{1/2}{}^r + \ln\frac{I_M}{I_C}\right] = \beta_{2,0} + \beta_{2,1}[OH^-] + \beta_{2,2}[OH^-]^2 + \ldots = F_{0,0}$$

where $\beta_{2,0}$ is the formation constant of the $[Cu(Tsgly)_2]^{2-}$ complex and the other symbols have their usual meaning.

It has been calculated by graphical interpolation (Figure 3) that three complexes, $[Cu(Tsgly)_2]^{2-}$, $[Cu(Tsgly)_2(OH)]^{3-}$, and $[Cu(Tsgly)_2(OH)_2]^{4-}$, are present in solution, the stability constants of which are reported in Table VI.

Since the reduction process is reversible, it is not possible to determine the species involved in the electrodic reduction process; therefore, the overall reduction process may be represented as follows:

$$\begin{array}{c} \underbrace{[Cu(Tsgly)_2]^{2-} \overset{OH^-}{\rightleftharpoons} [Cu(Tsgly)_2(OH)]^{3-} \overset{OH^-}{\rightleftharpoons} [Cu(Tsgly)_2(OH)_2]^{4-}} \\ \mathrm{Hg}\Big\downarrow\!\Big\uparrow 2e^- \\ Cu(Hg) \end{array}$$

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(9) Freeman, H. C. In "Inorganic Biochemistry"; Eichorn, G. L., Ed.; Elsevier: Amsterdam, 1973; Vol. 1, p 121 and references cited therein.

(10) Bell, J. D.; Freeman, H. C.; Wood, A. M.; Driver, R.; Walker, W. R. *J. Chem. Soc., Chem. Commun.* **1968**, 1441.

(11) Heyrovsky, J.; Kuta, J. In "Principles of Polarography"; Publishing House of the Czechoslovak Academy of Sciences: Prague, 1965; pp 147–160.

(12) Crow, D. R. In "Polarography of Metal Complexes"; Academic Press: New York, 1969; Chapter IV and references cited therein.

Table VI. Types of Complexes Present in Aqueous Solution at Different Ranges of pH and Their Stability Constant Values[a]

wave I			wave II
$5 < pH < 7.5$	$8 < pH < 10$	$10 < pH < 13$	$8 < pH < 13$
$\beta_{Cu(TsglyH)_2} = 1.0 \times 10^6$	$\beta_{Cu(TsglyH)_2} = 1.0 \times 10^6$	$\beta_{[Cu(Tsgly)_2]^{2-}} = 2.5 \times 10^7$	$\beta_{Cu(Tsgly)} = 8.0 \times 10^5$
	$\beta_{[Cu(Tsgly)_2]^{2-}} = 2.5 \times 10^7$	$\beta_{[Cu(Tsgly)_2(OH)]^{3-}} = 1.5 \times 10^{11}$	$\beta_{[Cu(Tsgly)(OH)]^-}$[b] $= 5.0 \times 10^{12}$
		$\beta_{[Cu(Tsgly)_2(OH)_2]^{4-}} = 2.1 \times 10^{15}$	$\beta_{[Cu(Tsgly)(OH_2)]^{2-}} = 7.0 \times 10^{15}$

[a] The complexes, which prevail in each range of pH, are underlined. [b] This complex prevails until pH <10.

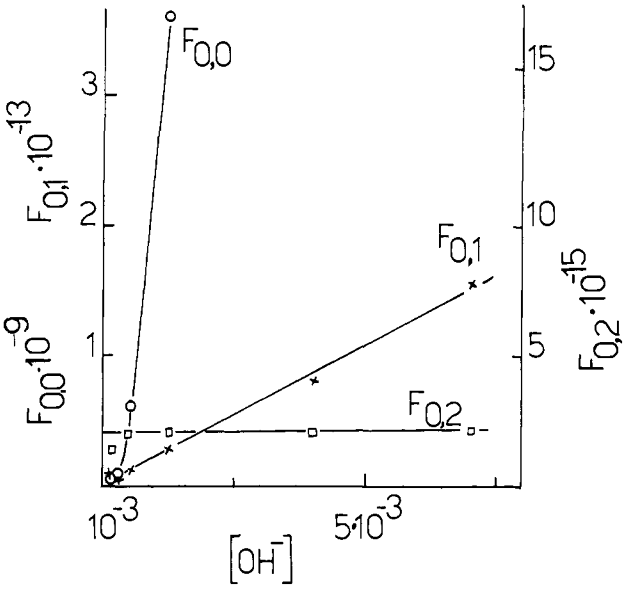


Figure 3. Plot of $F_J(X)$ vs. $[OH^-]$ for wave I in the 10–13 pH range.

Analysis of Wave II. The $E_{1/2}$ values of this wave depend on the ligand concentration and on the pH of the solution (Figure 2). Since at a constant pH value the plot of $E_{1/2}$ vs. log C is a straight line (Figure 4), it has been calculated from the slope that only one N-tosylglycinate ion is coordinated with the copper(II) ion.[12] As shown above, the ligand acts as bidentate through a carboxylate oxygen and the sulfonyl deprotonated nitrogen atoms.

At a constant value of ligand concentration the plot of $E_{1/2}$ vs. pH is a bent line; therefore in solution mixed-hydroxy complexes are present, the stability constants of which may be evaluated by using the Schaap–McMasters method;[13,14] this method represents an extension for mixed complexes of the original DeFord–Hume method. The formation reactions of these complexes may be represented as follows:

$$M^{n+} + I(OH)^- + J(Tsgly)^{2-} \rightleftharpoons [M(Tsgly)_J(OH)_I]^{n-(I+2J)}$$

The stability constants ($\beta_{I,J}$) are determined from the shifts of the $E_{1/2}$ values by using the following equation,[13] in which all terms on the far right are readily evaluated from the polarographic wave:

$$F_{0,0}(Tsgly^{2-},OH^-) = \sum_{O}^{N} \beta_{I,J}[OH^-]^I[Tsgly^{2-}]^J = \text{antln}\left[\frac{nF}{RT}((E_{1/2})_S{}^r - (E_{1/2})_C{}^r) + \ln\frac{I_S}{I_C}\right]$$

In our system only OH^- and $Tsgly^{2-}$ ions are coordinated with the copper(II) ion and two species $Cu(OH)^+$ and $Cu(OH)_2$ are considered absent, since the first has a small formation constant[15] and the second is also very scarcely soluble.[15] Therefore the function $F_{0,0}(Tsgly^{2-},OH^-)$ at a constant N-tosylglycinate concentration can be expressed as follows:

$$F_{0,0}(Tsgly^{2-},OH^-) = \{1 + \beta_{1,0}[Tsgly^{2-}] + \beta_{2,0}[Tsgly^{2-}]^2\} + \{\beta_{1,1}[Tsgly^{2-}] + \beta_{2,1}[Tsgly^{2-}]^2\}[OH^-] + \{\beta_{1,2}[Tsgly^{2-}]\}[OH^-]^2 = A + B[OH^-] + C[OH^-]^2$$

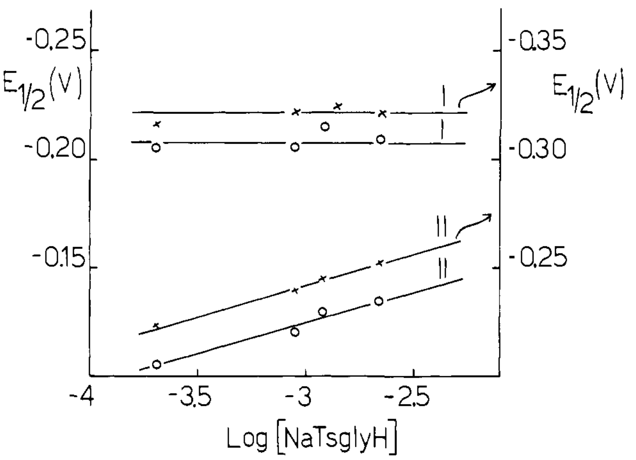
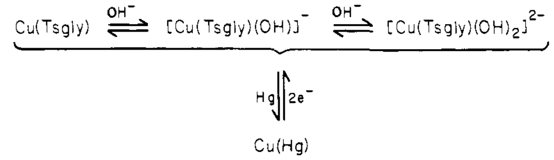


Figure 4. Plots of $E_{1/2}$ vs. log [NaTsglyH] of the two polarographic waves at two different pH values: (O) pH 8.2; (×) pH 11.4.

At every N-tosylglycinate concentration constant, the A, B, and C are constant and their values may be evaluated from graphical interpolation; but A, B, and C strictly depend on the N-tosylglycinate concentration, so it is possible to determine the presence of the Cu(Tsgly), $[Cu(Tsgly)(OH)]^-$, and $[Cu(Tsgly)(OH)_2]^{2-}$ complexes in solution and to calculate their values of β. All these values are reported in Table V.

The overall reduction process, corresponding to the second polarographic wave, can be represented as follows:



Conclusion

(a) The overall equilibria in aqueous solution as a function of the pH values can represented as follows:

$$Cu(aq)^{2+} + 2TsglyH^- \xrightleftharpoons{5 \le pH \le 7.5} Cu(TsglyH)_2 \xrightleftharpoons{7.5 \le pH \le 9} [Cu(Tsgly)_2]^{2-}$$

$$[Cu(Tsgly)_2]^{2-} + OH^- \xrightleftharpoons{\text{wave 1}} [Cu(Tsgly)_2(OH)]^{3-} \xrightleftharpoons{OH^-} [Cu(Tsgly)_2(OH)_2]^{4-} \xrightleftharpoons[-Tsgly^{2-}]{\text{wave 11}} [Cu(Tsgly)(OH)]^- \xrightleftharpoons{OH^-} [Cu(Tsgly)(OH)_2]^{2-}$$

From the linear plots of $E_{1/2}$ vs. pH (Figure 2), at pH greater than 11, it has been possible to determine, using the Lingane equation,[12] that the $[Cu(Tsgly)_2(OH)_2]^{4-}$ and $[Cu(Tsgly)(OH)_2]^{2-}$

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Table VII

solution complexes	pH range in which each complex prevails	solid complexes	pH formation value
$Cu(TsglyH)_2$	$5 \leq pH \leq 7.5$	$Cu(TsglyH)_2 \cdot 4H_2O$	pH <5
$[Cu(Tsgly)(OH)]^-$	$8 \leq pH \leq 10$	$[Cu(Tsgly)(H_2O)_3]$	pH >5
$[Cu(Tsgly)(OH)_2]^{2-}$	$8 \leq pH \leq 13$		
$[Cu(Tsgly)_2(OH)_2]^{4-}$	$10 \leq pH \leq 13$	$K_2[Cu(Tsgly)_2]$	pH >10

complexes are prevalent. The stability constant values of these last two complexes, very similar to one another, justify their simultaneous presence in solution and the unitary ratio of the diffusion currents of their polarographic waves.

In Table VI all the complexes present in solution and their stability constants are reported and the complexes which prevail in each pH range are underlined.

The types of complexes are in accordance with expectations on the formation of mixed copper(II) complexes in the different pH ranges.[16]

(b) The complexes that prevail in solution are the same ones as are isolated in the solid state in about the same condition of pH as shown in Table VII. This quite similar behavior also supports the assignments of the coordination of the ligand in solution on the basis of the information on the structure of the solid complexes which has been previously reported.[5]

The variety of the copper(II) ion geometries in the solid complexes is not observed in solution complexes. The electronic spectra of the latter may reasonably suggest elongated octahedral geometries since water molecules present in large excess (mass effect) may occupy the coordination positions of the metal ion free from *N*-tosylglycinate or OH^- ions.

In solution the excess of water molecules enables the involvement of the SO_2 group in the copper(II) ion coordination to be excluded, since it is probably involved in strong hydrogen bonding. Its presence in the solid state may be justified as imposed by metal ion geometry or crystal packing or other causes.

However, the presence of the SO_2 group on the ligand is of fundamental importance to determining the variable coordinative ability, which permits the existence of a greater number of complexes both in solution and in the solid state. Since the sulfonyl group has a strong inductive electrophilic effect, the anion of the sulfonamide group becomes an excellent nucleophile and the substituted amino group can react further.[17,18]

Registry No. *N*-Tosylglycine, 1080-44-0.

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Formation Constants of Complexes between Crown Ethers and Alkali Picrates in Apolar Solvents. Application of Crown Ether Network Polymers

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Abstract: Benzo-18-crown-6 and benzo-15-crown-5 ligands anchored to cross-linked polystyrene resins were utilized to obtain quantitative information on the complexation of soluble crown ether ligands (including linear polycrown ethers) to sodium and potassium picrate in dioxane and toluene. The constant K describing the competition equilibrium $Pi^-,M^+,Cr^* + L \rightleftarrows Pi^-,M^+,L + Cr^*$ (where L is a soluble ligand and Cr^* the immobilized crown ether) was determined spectrophotometrically. The formation constants, K_L, of the soluble Pi^-,M^+,L complexes were then computed from the expression $K_L = KK_N$, where K_N denotes the known binding constant of the picrate salt to the particular crown network used. K_N, and, therefore, K_L, cannot be obtained in toluene, but the measured K values still furnish a relative scale of ligand affinities toward the picrate salt in this solvent. Use of different networks to obtain K_L and direct measurement of K_L for some of the ligands have established the reliability of the competition method as a way to obtain quantitative information on ligand interaction with ion pairs in apolar media. Values obtained for K and K_L demonstrate the sensitivity of such interactions with solvent and counterion. It is argued that the competition method is a versatile tool for studying interactions of ionic solutes with different types of ligands in apolar solvents.

Soluble as well as immobilized crown ethers, cryptands, and other cation-binding ligands have been extensively employed in studies of mediated ion transport, solute separations, and anion-activated catalysis.[1-6] Chloroform, toluene, dioxane, or similar apolar solvents are frequently chosen as the reaction medium. In these solvents, formation constants of the ligand–ion or –ion pair complexes may easily exceed values of 10^6 M^{-1}. When complexation to an ion pair causes a significant change in its absorption spectrum, binding constants can be obtained spectrophotometrically. Such changes are sometimes observed when tight ion pairs are modified on complexation to ligand-separated ion pairs, for example, with fluorenyl and picrate salts.[7,8] When complexation results in increased formation of free ions, conductometry can be

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