On the Isopropoxyacetate and (Isopropylthio)acetate Complexes of Copper(II)

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The formation of isopropoxyacetate and (isopropylthio)acetate complexes of Cu^{2+} in aqueous solution has been investigated at 25.0°C by indirect determination of the concentration of free ligand in the complex solutions.

In both systems, the formation of three mononuclear complexes was indicated, the third complex in the isopropoxyacetate system, however, rather ambiguously. The following gross stability constants were calculated:

Cu^{2+}/isopropoxyacetate: $\beta_1 = (59.8 \pm 0.3)$ M^{-1}, $\beta_2 = (780 \pm 20)$ M^{-2}; Cu^{2+}/(isopropylthio)acetate: $\beta_1 = (307 \pm 3)$ M^{-1}, $\beta_2 = (5.91 \pm 0.07) \times 10^4$ M^{-2}, $\beta_3 = (1.3 \pm 0.2) \times 10^5$ M^{-3}.

The acid constant for isopropoxyacetic acid was determined to $(2.59 \pm 0.05) \times 10^{-4}$ M and for (isopropylthio)acetic acid to $(2.22 \pm 0.05) \times 10^{-4}$ M.

The constants refer to the ionic strength 1.0 M ($NaClO_4$).

The results are interpreted as an indication that chelates are formed to a higher degree in the (isopropylthio)acetate than in the isopropoxyacetate complexes of Cu^{2+}.

The principal features of the numerical method used in calculating the stability constants are presented.

The formation of copper(II) complexes in aqueous solution with ethoxyacetate and (ethylthio)acetate has earlier been investigated.[1] The results indicated that chelates are formed to a much greater extent by the (ethylthio)-acetate than by the ethoxyacetate. This should imply that the copper(II) ion is more strongly bonded to the ether sulphur than to the ether oxygen in this type of compound.

Suzuki and Yamasaki[2] report, however, that such a conclusion cannot be drawn from the results of their investigation of the phenoxy- and (phenylthio)-acetate complexes of copper(II).

To broaden the knowledge of this class of compounds, the formation of copper(II) complexes in aqueous solution with isopropoxyacetate and (isopropylthio)acetate ion has been studied by the present author. The two

systems were investigated by the same method, *viz.* indirect determination of free ligand in buffer solutions by means of a glass electrode.

SYMBOLS AND CALCULATIONS

The following symbols are used.

C_M = total concentration of Cu^{2+}-ion

[M]   = concentration of free Cu^{2+}-ion

α = proportionality factor. The excess of acid in the copper(II) perchlorate stock solution is $\alpha\,C_M$

C_L' = stoichiometric total concentration of ligand L

C_L = corrected total concentration of ligand L

δ = buffer quotient in the ligand buffer. The stoichiometric concentration of the acid HL is $\delta\,C_L'$

[L]   = concentration of free ligand

K_a = $[H_3O^+][L]/[HL]$

N = maximum coordination number

β_n = $[ML_n]/([M][L]^n)$ = gross stability constant

K_n = $[ML_n]/([ML_{n-1}][L])$ = stepwise stability constant

X = $1 + \sum\limits_{n=1}^{N} \beta_n[L]^n$

X' and X'' = $dX/d[L]$ and $dX'/d[L]$

$\bar{n}$ = $(C_L - [L])/C_M$ = the ligand number

$\bar{n}/[L]$ = X'/X

X_i = $(X_{i-1} - \beta_{i-1})/[L]$; $(1 \le i \le N; X_0 = X; \beta_0 = 1)$

h_M and h_0 = $[H_3O^+]$ in solutions with the same C_L'-value, h_0 referring to a solution with $C_M = 0$

h_R = $[H_3O^+]$ in a reference solution

E_M and E_0 = 59.16 $\log(h_M/h_R)$ mV and 59.16 $\log(h_0/h_R)$ mV

E_L = $E_M - E_0$ = 59.16 $\log(h_M/h_0)$ mV

h_s = concentration of free acid in the sodium perchlorate stock solution

With F/RT denoted by K, the concentration of free ligand is obtained from

$$[L] = \exp(-E_L K)(C_L' - s_0 + h_0)\,\frac{\delta\,C_L' + \alpha\,C_M + s_M - h_M}{\delta\,C_L' + s_0 - h_0} \tag{1}$$

where s_0 and s_M are due to the excess of free acid in the stock solution of sodium perchlorate. In the present case they are obtained from

$$s_0 = h_s\,(1 - C_L') \quad \text{and} \quad s_M = h_s\,(1 - C_L' - 3C_M)$$

The ligand number $\bar{n}$ is calculated from

$$\bar{n} = (C_L' - \alpha\,C_M - s_M + h_M - [L])/C_M \tag{2}$$

The stability constants were calculated both graphically and numerically.

The graphical method. In this case the method of Fronæus [3],[4] was used. Thus a smooth curve was drawn to fit the plot of $\bar{n}/[L]$ against [L]. From this

curve, corresponding values of X and [L] were obtained by graphical integration. Graphical extrapolation of the X_n-functions to [L] = 0 gave estimates of β_n. The procedure was repeated on upper and lower limiting curves to the $\bar{n}$/[L]-plot. In this way, estimates were obtained of the errors of the graphically determined β_n-values. With the (isopropylthio)acetate system, however, the graphical integration was difficult to carry out with precision, since the $\bar{n}$/[L]-plot appeared to have a maximum at [L] $\approx$ 1 mM (see Fig. 2). To check the β-values, a numerical method was developed according to the following principles.

The numerical method. The calculations were based on the expression

$$G = \bar{n} + \sum_{k=1}^{N} \beta_k [L]^k (\bar{n} - k) = 0 \tag{3}$$

which is easily obtained from the equation $\bar{n}$/[L] = X'/X. In eqn. (3), G is a function of the two variables [L] and $\bar{n}$.

Estimates of the stability constants β_k were obtained by minimizing the sum of squares

$$S = \sum_i w_i (\bar{n}_i + \sum_{k=1}^{N} \beta_k [L]_i^k (\bar{n}_i - k))^2 \tag{4}$$

According to Guest,[5] a reasonable value of the weight w_i should be obtained from

$$1/w_i = c \, \text{var}(\bar{n}_i) \left(\frac{\partial G}{\partial \bar{n}} \right)_i^2 + c \, \text{var}([L]_i) \left(\frac{\partial G}{\partial [L]} \right)_i^2 \tag{5}$$

where c is an arbitrary constant. The symbols var($\bar{n}_i$) and var([L]$_i$) are the variances of $\bar{n}_i$ and [L]$_i$. Instead of these variances, which are not known, the squares of estimates of the maximum errors in $\bar{n}_i$ and [L]$_i$ were used. These estimates, $\Delta\bar{n}_i$ and Δ[L]$_i$, were obtained in the following way.

Rewriting, for brevity's sake, eqn. (1) as

$$[L] = \exp(-E_L K) \, PQ/U \tag{6}$$

and differentiating the logarithm of both members, gives the result

$$d[L]/[L] = -K \, dE_L + dP/P + dQ/Q - dU/U \tag{7}$$

If the differentials are replaced by estimates of the maximum experimental errors, and if the values of C_L', δ, α, C_M, s_0, and s_M are considered error-free, then the following estimate of Δ[L] is obtained

$$\Delta[L] = [L](K|\Delta E_L| + |\Delta h_0|/P + |\Delta h_M|/Q + |\Delta h_0|/U) \tag{8}$$

Since $E_0 K = \ln(h_0/h_R)$, and $E_M K = \ln(h_M/h_R)$, one obtains in a similar way, if h_R is considered free from error,

$$|\Delta h_0| = h_0 \, K|\Delta E_0|, \quad \text{and} \quad |\Delta h_M| = h_M \, K|\Delta E_M| \tag{9}, (10)$$

Empirically it was found that $|\Delta E_0| = |\Delta E_M|$. With $\Delta E_L = |\Delta E_M| + |\Delta E_0|$, eqn. (8) can be written

$$\Delta[L] = c \, [L](2 + h_0/P + h_M/Q + h_0/U) = c \, Z \tag{11}$$

An estimate of $\Delta \bar{n}$ was obtained from eqn. (2) by an analogous discussion, resulting in

$$\Delta \bar{n} = c \ (h_{\mathrm{M}} + Z)/C_{\mathrm{M}} \tag{12}$$

The calculations were performed iteratively. The estimates of β_n obtained in one cycle were used in the next one in calculating $\partial G/\partial \bar{n} = \mathrm{X}$ and $\partial G/\partial[\mathrm{L}] = ((\mathrm{X}')^2/\mathrm{X} - \mathrm{X}'')[\mathrm{L}] - \mathrm{X}'$. Practical tests showed that the calculations converged rapidly and were very little influenced by the initial values chosen for β_n. Therefore, the starting values of all β_n were simply put equal to $\bar{n}/[\mathrm{L}]$ for some small [L]-value.

To find the normal equations and to write a suitable computer program is an essentially trivial task that is not commented on here.

In the present paper, the limits of error ascribed to estimates, obtained by numerical methods, are calculated 99 % confidence limits.

EXPERIMENTAL

Chemicals

Crystallized *copper(II) perchlorate* was delivered by The G. Frederick Smith Chemical Co., Columbus, Ohio. The salt was dissolved in pure water and the solution filtered through 0.22 μ Millipore. The copper content was determined by electrodeposition. The solution was tested for impurities by means of $AgNO_3$, $NaCl$, $BaCl_2$, and Na_2SO_4. No precipitations were observed.

Isopropoxyacetic acid was synthesized from monochloroacetic acid, 2-propanol and sodium metal according to a method [6] originally intended for the preparation of ethoxy-acetic acid. *(Isopropylthio)acetic acid* was prepared from freshly distilled mercaptoacetic acid and 2-bromopropane.[7] Both acids were purified by repeated vacuum distillation. The final portion of isopropoxyacetic acid was collected at 104°C and 14 mbar, and of (isopropylthio)acetic acid at 120°C and 12 mbar. Within the experimental error, the theoretical equivalent weight was found with both acids. Buffer solutions were prepared from carbonate-free sodium hydroxide and the constant-boiling fractions of the acids. The buffers were analysed by the aid of a cation exchange resin.

The same *sodium perchlorate* was used as in an earlier investigation.[8] In this preparation, the concentration of protolytic impurities could be neglected.
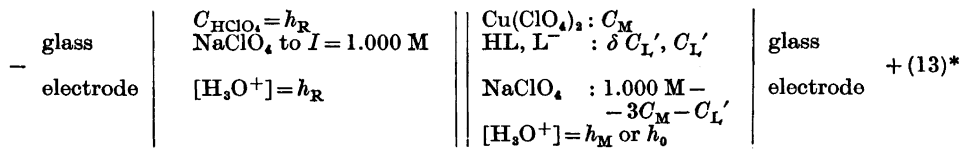
All other chemicals used were of *p.a.* grade.

Method

In order to suppress the hydrolysis of the copper(II) ion [9] the measurements were made in buffers of the ligand and its corresponding acid.

The measurements were carried out as potentiometric titrations, C_{M} being kept constant and C_{L}' varied during a titration.

The calculations are based on the emf, E_{M} or E_0, of cells of the type (13).

| glass electrode | $C_{\mathrm{HClO_4}} = h_{\mathrm{R}}$ $NaClO_4$ to $I = 1.000$ M $[H_3O^+] = h_{\mathrm{R}}$ | $Cu(ClO_4)_2 : C_{\mathrm{M}}$ $HL, L^- : \delta\ C_{\mathrm{L}}', C_{\mathrm{L}}'$ $NaClO_4 : 1.000$ M $-$ $-3C_{\mathrm{M}} - C_{\mathrm{L}}'$ $[H_3O^+] = h_{\mathrm{M}}$ or h_0 | glass electrode | $+ (13)*$ |

* In the present paper, the double lines symbolize a salt bridge with 1.000 M $NaClO_4$.

In practice, each of the half-cells were combined with an Ag,AgCl reference electrode. From the emf of these cells the emf of (13) was calculated.

The emf was measured by a Radiometer PHM4 potentiometer. The glass electrode, a Jena Type U, had the theoretical slope in the pH-region in question. The Ag,AgCl reference electrode was prepared according to Brown.[10]

A magnetic stirrer was used during the titrations. Within a few minutes after addition of titrant, the emf reached a stable value, which was not affected by the speed of the magnetic stirrer.
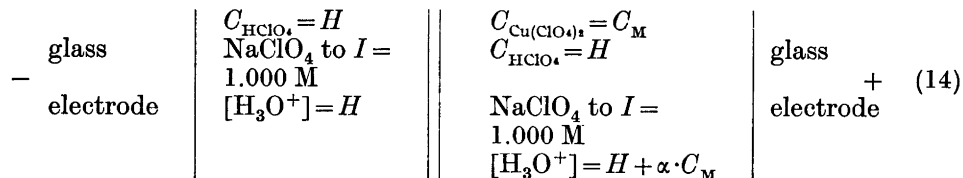
With solutions containing (isopropylthio)acetate, the same emf readings were obtained, whether the solutions were swept free from oxygen or not.

All titrations were carried out at least twice. The reproducibility of the emf readings was $0.1-0.2$ mV.

The cells were kept at $(25.00 \pm 0.05)°C$ by means of a water thermostat.

MEASUREMENTS AND RESULTS

The copper(II) perchlorate. The value of α was determined from the emf of cell (14).

$$
-\
\begin{array}{|c|}
\text{glass} \\
\text{electrode}
\end{array}
\left|\begin{array}{l}
C_{\text{HClO}_4} = H \\
\text{NaClO}_4 \text{ to } I = \\
1.000 \text{ M} \\
[\text{H}_3\text{O}^+] = H
\end{array}\right|\left|\begin{array}{l}
C_{\text{Cu(ClO}_4)_2} = C_{\text{M}} \\
C_{\text{HClO}_4} = H \\ \\
\text{NaClO}_4 \text{ to } I = \\
1.000 \text{ M} \\
[\text{H}_3\text{O}^+] = H + \alpha \cdot C_{\text{M}}
\end{array}\right|
\begin{array}{c}
\text{glass} \\
\text{electrode}
\end{array}\ +\quad (14)
$$

At sufficiently low pH, the emf, E, of this cell can be written

$$E = E_1 + RT/F \ln(1 + \alpha\ C_{\text{M}}/H) \tag{15}$$

which can be transformed into

$$\exp(K\ E) = \exp(K\ E_1) + \exp(K\ E_1)\ \alpha\ C_{\text{M}}\ H^{-1} \tag{16}$$

In the measurements, C_{M} was 60.0 mM and H was varied between 1.792 mM and 18.64 mM. In accordance with theory, a straight line was obtained by plotting $\exp(K\ E)$ against H^{-1}. From this line, E_1 was estimated to (0.46 ± 0.03) mV and α to $(-1.7 \pm 0.1) \times 10^{-3}$.

The copper(II) isopropoxyacetate system. A buffer with $\delta = 0.204$ was used in the main part of the investigation. The experimental data are collected in Table 1. As illustrated in Fig. 1, $\bar{n}/[\text{L}]$ was independent of C_{M}, which is in accordance with theory if only mononuclear complexes are formed.[4]

By titrations with $C_{\text{M}} = 40.0$ mM and a buffer with $\delta = 0.433$, it was found that $\bar{n}/[\text{L}]$ was independent of δ (see Fig. 1).

Since $\bar{n}/[\text{L}]$ was independent of both C_{M} and δ, it was concluded that the protolysis of the hydrated copper(II) ion could be neglected under the experimental conditions, and that no complex was formed between Cu^{2+} and HL.

The plot of X_1 *versus* $[\text{L}]$ was perfectly linear for $[\text{L}] < 35$ mM ($\bar{n} < 1.0$, $C_{\text{L}}' < 100$ mM). From this plot, β_1 and β_2 could be determined with good precision. The numerical treatment of the experimental data from this region resulted in estimates of β_1 and β_2 which agreed well with those obtained by the graphical method.

Table 1. Determination of corresponding values of [L] and $\bar{n}$/[L] in the copper(II) iso-propoxyacetate system. Buffer with $\delta = 0.204$. The values of E_0 refer to $h_R = 3.88 \times 10^{-3}$ M.

| C_L' (mM)	$-E_0$ (mV)	$C_M = 70.0$ mM			$C_M = 50.0$ mM			$C_M = 30.0$ mM		
		E_L (mV)	[L] (mM)	$\bar{n}$/[L] (M⁻¹)	E_L (mV)	[L] (mM)	$\bar{n}$/[L] (M⁻¹)	E_L (mV)	[L] (mM)	$\bar{n}$/[L] (M⁻¹)
3.75	112.5	30.5	0.787	58.8	26.3	1.037	56.5	20.3	1.460	55.9
4.72	112.1	32.3	0.995	57.7	27.8	1.295	56.4	21.1	1.836	55.3
5.78	111.9	33.9	1.206	57.8	28.9	1.577	56.3	21.8	2.24	55.3
7.06	111.7	35.1	1.467	57.5	29.7	1.925	55.9	22.2	2.74	54.7
8.86	111.5	36.2	1.836	57.2	30.4	2.42	55.3	22.5	3.45	53.8
11.09	111.3	36.8	2.32	56.0	30.7	3.06	54.0	22.4	4.40	52.0
13.61	111.2	37.3	2.86	55.3	30.9	3.80	53.1	22.3	5.48	50.5
16.73	111.1	37.4	3.58	53.9	30.8	4.75	51.5	22.0	6.87	48.7
20.53	111.1	37.4	4.47	52.5	30.6	5.94	49.9	21.5	8.66	46.4
25.38	111.1	37.3	5.62	51.1	30.1	7.57	47.7	20.9	11.02	43.9
31.25	111.1	36.7	7.17	48.7	29.3	9.70	44.9	20.0	14.12	40.8
37.0	111.2	36.1	8.76	46.6	28.6	11.86	42.8	19.3	17.23	38.6
42.7	111.3	35.5	10.40	44.8	28.0	14.07	41.0	18.4	20.6	35.9
48.2	111.4	35.0	12.02	43.4	27.3	16.37	39.2	17.7	24.0	33.9
53.6	111.6	34.4	13.73	41.8	26.6	18.74	37.4	17.1	27.3	32.2
58.8	111.7	33.7	15.51	40.1	25.9	21.2	35.8	16.5	30.7	30.6
64.0	111.8	33.0	17.39	38.5	25.2	23.7	34.2	16.0	34.1	29.3
73.9	111.9	31.8	21.1	35.9	23.9	28.9	31.4	14.7	41.5	26.2
83.3	112.0	30.4	25.2	33.1	22.7	34.1	28.9	13.7	48.7	23.8
96.8	112.3	29.0	31.0	30.5	21.2	42.1	26.1	12.7	58.8	21.6
109.4	112.6	27.6	37.0	28.0	19.9	50.1	23.7	11.9	68.6	19.9
121.2	112.8	26.1	43.5	25.6	18.8	58.0	21.9	11.1	78.5	18.2
139.4	113.1	24.2	54.0	22.7	17.2	71.1	19.3	10.1	93.9	16.2
159.1	113.6	22.5	65.9	20.2	15.8	85.7	17.2	9.3	110.6	14.7
179.5	113.9	20.8	79.5	18.0	14.6	101.4	15.4	8.4	129.2	13.0
202.4	114.5	19.3	95.1	16.1	13.4	119.8	13.8	7.8	149.2	11.9
230.2	114.9	17.2	117.5	13.7	12.0	144.0	12.0	6.9	175.8	10.3
258.1	115.6	15.7	139.7	12.1	11.1	167.2	10.9	6.4	201	9.5
285.7	116.1	14.4	162.7	10.8	10.2	191.8	9.8	5.9	227	8.7
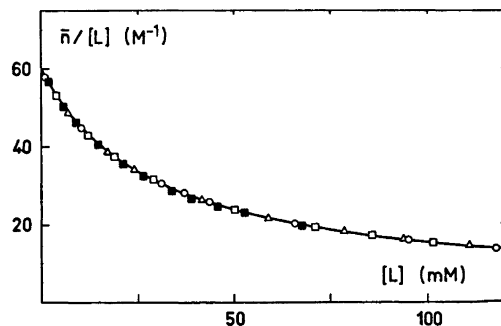
Fig. 1. Some $\bar{n}$/[L]-values for [L] < 120 mM in the copper(II) isopropoxyacetate system. The main investigation ($\delta = 0.204$): $C_M = 70$ mM (○), $C_M = 50$ mM (□), $C_M = 30$ mM (△). Buffer with $\delta = 0.433$, $C_M = 40$ mM (■). The full curve is calculated by means of the three stability constants obtained by the numerical method.

Table 2. Some representative values from the graphical determination of the X_n-functions in the copper(II) isopropoxyacetate system.

[L] (mM)	X_1 (M^{-1})	X_2 (M^{-2})	[L] (mM)	X_1 (M^{-1})	X_2 (M^{-2})
0	*59.8*	*800*			
			20.0	75.8	800
1.00	60.5		24.0	79.1	805
2.00	61.4		28.0	82.3	805
3.00	62.3		34.0	87.2	805
4.00	63.1		42.0	93.9	810
5.00	63.9		50.0	100.6	815
6.00	64.7		58.0	107.3	820
8.00	66.3		68.0	116.0	825
10.00	67.8	800	80.0	126.9	840
12.00	69.4	800	92.0	138.2	850
14.00	71.0	800	110.0	155.4	870
16.00	72.6	800	130.0	175.1	885
18.00	74.2	800	150.0	195.4	905

The general shape of the X_2-plot indicated that a relatively weak third complex was formed in small amounts within the [L]-range covered in the present investigation. The value of β_3, however, could only be estimated within wide limits of error.

Estimates of the β_n-values were also calculated by applying the numerical method to the entire experimental material.

The following results were obtained in the different calculations.

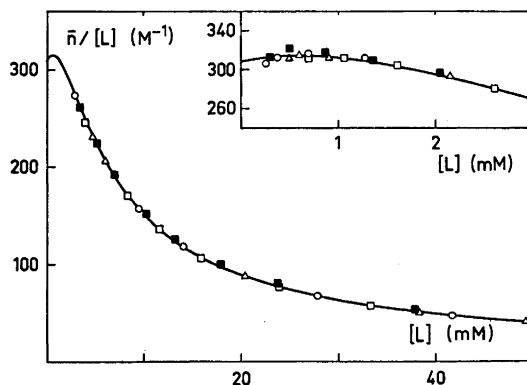|	Graphical	Numerical $\bar{n} \leq 1.0$	Numerical All data	
β_1	60 ± 1	59.8 ± 0.4	59.8 ± 0.3	M^{-1}
β_2	800 ± 20	780 ± 40	780 ± 20	M^{-2}
β_3	800 ± 400		700 ± 300	M^{-3}

Fig. 2. Some $\bar{n}/[L]$-values for [L] < 50 mM in the copper(II) (isopropylthio)acetate system. The main investigation ($\delta = 0.253$): $C_M = 50$ mM (O), $C_M = 40$ mM (□), $C_M = 30$ mM (△). Buffer with $\delta = 0.397$, $C_M = 40$ mM (■). The full-drawn curve is calculated from the β_n-values listed in Table 5.

Table 3. Determination of corresponding values of [L] and $\bar{n}/$[L] in the copper(II) (isopropylthio)acetate system. Buffer with $\delta = 0.253$. The E_0-values refer to $h_R = 3.88 \times 10^{-3}$M.

$C_L{}'$ (mM)	$-E_0$ (mV)	$C_M = 50$ mM			$C_M = 40$ mM			$C_M = 30$ mM		
		E_L (mV)	[L] (mM)	$\bar{n}/$[L] (M^{-1})	E_L (mV)	[L] (mM)	$\bar{n}/$[L] (M^{-1})	E_L (mV)	[L] (mM)	$\bar{n}/$[L] (M^{-1})
3.75	110.8	52.2	0.260	306	49.7	0.319	302	46.7	0.398	312
4.72	110.5	55.3	0.319	310	52.4	0.393	306	48.8	0.495	311
5.78	110.2	57.7	0.383	312	54.5	0.472	309	50.5	0.598	313
7.06	109.9	59.7	0.463	313	56.2	0.571	308	51.9	0.724	313
8.86	109.8	61.9	0.570	315	58.1	0.703	311	53.3	0.901	312
11.09	109.7	63.7	0.704	316	59.6	0.870	311	54.5	1.118	312
13.61	109.7	65.1	0.856	316	60.8	1.058	312	55.2	1.377	309
16.73	109.7	66.3	1.044	316	61.7	1.297	310	55.6	1.711	303
20.53	109.7	67.1	1.285	312	62.1	1.614	304	55.6	2.15	293
25.38	109.7	67.3	1.627	302	62.2	2.04	295	55.0	2.78	278
31.25	109.7	67.3	2.06	292	61.7	2.61	280	53.7	3.66	256
37.0	109.9	67.6	2.44	290	60.7	3.27	263	51.8	4.72	231
42.7	110.0	67.0	2.93	277	59.4	4.02	245	49.5	6.01	206
48.2	110.1	66.1	3.46	263	57.9	4.85	226	46.8	7.60	180
53.6	110.2	64.9	4.07	247	56.2	5.80	208	43.9	9.51	156
58.8	110.4	63.8	4.69	234	54.2	6.92	189	41.1	11.68	135
64.0	110.5	62.4	5.43	218	51.9	8.28	170	38.0	14.39	116
73.9	110.7	59.1	7.19	187	47.2	11.56	136	32.8	20.42	88
83.3	110.9	55.3	9.47	157	42.2	15.91	106	28.4	27.39	68
96.8	111.2	49.1	14.10	118	35.7	23.9	76	23.7	38.3	51
109.4	111.5	42.9	20.4	88	30.4	33.3	57	20.4	49.3	41
121.2	111.8	37.5	27.9	67	26.7	42.7	46	18.2	59.5	35
139.4	112.3	30.9	41.7	47	22.4	58.1	35	15.7	75.5	28
159.1	112.8	25.9	57.8	35	19.1	75.4	28	13.5	93.9	23
179.5	113.3	22.1	75.7	27	16.6	93.9	23	11.9	112.8	20
202.4	113.8	19.0	96.4	22	14.3	115.8	19	10.5	134.3	17
230.2	114.6	16.2	122.3	18	12.6	140.8	16	9.3	160.1	15
258.1	115.4	14.2	148.3	15	11.3	166.0	14	8.4	186.0	13
285.7	116.1	12.7	174.0	13	10.2	191.9	12	7.6	212	12
333	117.4	10.8	219	10	8.8	236	10	6.7	257	10

The copper(II) (isopropylthio)acetate system. The experimental data from the main investigation, in which a ligand buffer with $\delta = 0.253$ was used, are collected in Table 3. Some titrations were also carried out at $C_M = 40.0$ mM using a buffer with $\delta = 0.397$. As illustrated in Fig. 2, $\bar{n}/$[L] was independent of both C_M and δ, which indicated that only mononuclear complexes were formed, and that the free acid HL did not act as a ligand.

Representative data from the graphical procedure are collected in Table 4. The values of β_1 and β_2 were obtained from the X_1-plot, which was linear for [L] < 10 mM ($\bar{n} < 1.6$). The X_2-plot indicated that a third mononuclear complex was formed. The β_3-value was calculated from the slope of the X_2-graph. The β_2-value obtained from the X_2-plot agreed well with that obtained from the X_1-plot.

Table 4. Some representative values from the graphical determination of the X_n-functions in the copper(II) (isopropylthio)acetate system.

[L] (mM)	$X_1 \times 10^{-2}$ (M^{-1})	$X_2 \times 10^{-4}$ (M^{-2})	[L] (mM)	$X_1 \times 10^{-2}$ (M^{-1})	$X_2 \times 10^{-4}$ (M^{-2})	$X_3 \times 10^{-5}$ (M^{-3})
0	*3.05*	*6.0*				
			8.00	7.90	6.1	
0.50	3.34		10.00	9.12	6.1	
1.00	3.65		15.00	12.25	6.1	
1.50	3.96		20.0	15.4	6.2	
2.00	4.26		26.0	19.25	6.2	
2.50	4.57		34.0	24.6	6.3	
3.00	4.87		46.0	32.8	6.5	
3.50	5.18		60.0	42.8	6.6	
4.00	5.48		75.0	54.1	6.8	
4.50	5.78		90.0	66.3	7.0	
5.00	6.08		110.0	84	7.4	1.3
6.00	6.68	6.1	140.0	113	7.8	1.3
7.00	7.29	6.1	190.0	168	8.7	1.4

The stability constants were also calculated by the numerical method. The different calculations gave the following results.

	Graphical	Numerical $\bar{n} < 1.6$	Numerical All data	
β_1	305 ± 5	305 ± 4	307 ± 3	M^{-1}
β_2	$(6.0 \pm 0.2) \times 10^4$	$(6.0 \pm 0.1) \times 10^4$	$(5.91 \pm 0.07) \times 10^4$	M^{-2}
β_3	$(1.0 \pm 0.3) \times 10^5$		$(1.3 \pm 0.2) \times 10^5$	M^{-3}

The acid constants. With both acids, the K_a-values calculated from E_0 were approximately constant at low buffer concentration ($C_L' < 30$ mM). The values obtained in this way were 2.57×10^{-4} M for the isopropoxyacetic acid and 2.19×10^{-4} M for the (isopropylthio)acetic acid. With increasing
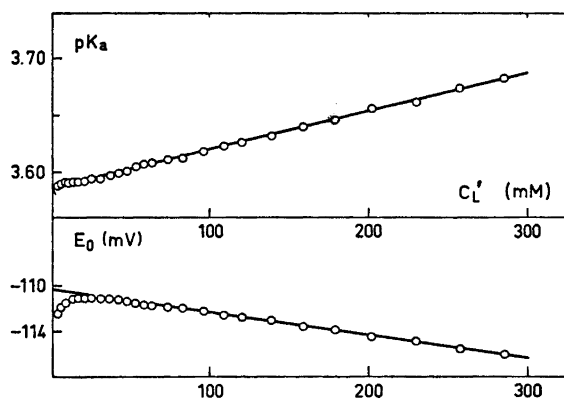

Fig. 3. The dependence of E_0 and pK_a on C_L' with the isopropoxyacetate buffer.

C_L', the E_0-values decreased continuously, causing a corresponding decrease in the calculated K_a-values.

With the *isopropoxyacetate* buffer, the plot of E_0 against C_L' was found to be linear at $C_L' > 75$ mM (see Fig. 3).

$$E_0 = E_K + q\,C_L' \tag{17}$$

Assuming, for the sake of simplicity, the activity coefficients to be constant, then qC_L' should represent the variation of the liquid junction potential caused by the exchange of sodium perchlorate for buffer. If the liquid junction potential of the cell (13) at $C_L' = 0$ is neglected, then E_K should be 59.16 $\log(\delta K_a/h_R)$ mV. (When $C_L' > 75$ mM, h_0 can be put equal to δK_a well within experimental reproducibility.) Applying the principle of least squares the following estimates were obtained: $E_K = -(110.3 \pm 0.2)$ mV, $q = -(20.2 \pm 0.8)$ mV/M. The K_a-value calculated from E_K was $(2.60 \pm 0.02) \times 10^{-4}$ M.

Assuming the estimate of q to be valid also for $C_L' < 75$ mM, the calculation of K_a in this region from the corrected E_0-values gave the result $(2.594 \pm 0.003) \times 10^{-4}$ M.

Finally, the pK_a-values, obtained from the uncorrected E_0-values, were plotted against C_L'. This plot was found to be linear (see Fig. 3). Fitting the best straight line (least squares criterion) resulted in $K_a = (2.594 \pm 0.005) \times 10^{-4}$ M.

With the *(isopropylthio)acetate* buffer, the plot of E_0 against C_L' showed a slight curvature at $C_L' > 80$ mM, in which region h_0 should be equal to δK_a within the limits of experimental precision. Fitting the best polynomial of the second degree

$$E_0 = E_K + q\,C_L' + r\,(C_L')^2 \tag{18}$$

resulted in the estimates: $E_K = -(108.9 \pm 0.2)$ mV, $q = -(23 \pm 3)$ mV/M, and $r = -(8 \pm 6)$ mV/M². The K_a-value obtained from E_K was $(2.21 \pm 0.02) \times 10^{-4}$ M and from the corrected E_0-values at $C_L' < 80$ mM $(2.217 \pm 0.008) \times 10^{-4}$ M.
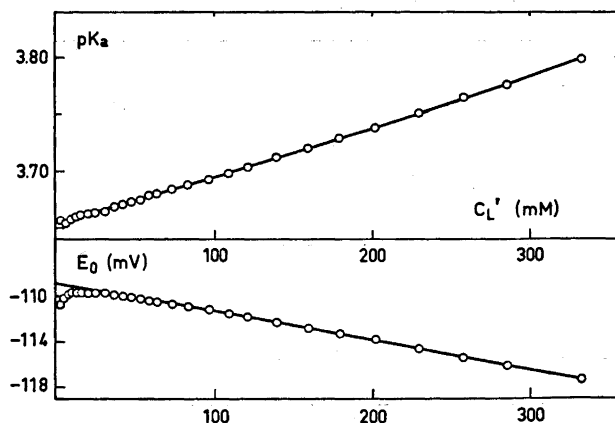

Fig. 4. The dependence of E_0 and pK_a on C_L' with the (isopropylthio)acetate buffer.

The plot of the pK_a-values, obtained from the uncorrected E_0-values, against C_L' also showed a slight curvature (see Fig. 4). Fitting the best polynomial of the second degree to the plot gave $K_a = (2.217 \pm 0.003) \times 10^{-4}$ M.

Collecting the results from the different methods of calculation, the acid constants in the medium in question should be: for the *isopropoxyacetic acid* $(2.59 \pm 0.05) \times 10^{-4}$ M and for the *(isopropylthio)acetic acid* $(2.22 \pm 0.05) \times 10^{-4}$ M. The limits of error are subjectively estimated to cover the analytical errors of δ and h_R, and the error made in neglecting the liquid junction potential of cell (13) at $C_L' = 0$.

DISCUSSION

As illustrated in Figs. 5 and 6, $\bar{n}$ reached a value of about 1.9 in the isopropoxyacetate system, and 2.4 in the (isopropylthio)acetate system. Hence it follows that at least two complexes should be present in the former system, and three in the latter, at [L]-values covered by the investigation. The form of the complex formation curve in Fig. 6 indicates a wide range of existence for the second complex in the (isopropylthio)acetate system.
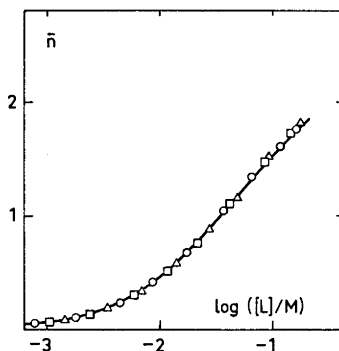

Fig. 5. Some experimentally obtained $\bar{n}$-values in the copper(II) isopropoxyacetate system. $C_M = 70$ mM (O), 50 mM (□), 30 mM (△). The curve is calculated from the three stability constants obtained by the numerical method.
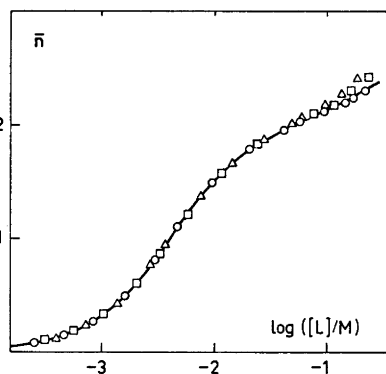
Fig. 6. Some experimentally obtained $\bar{n}$-values in the copper(II) (isopropylthio)-acetate system. $C_M = 50$ mM (O), 40 mM (□), 30 mM (△). The full curve is calculated by means of the stability constants obtained by the numerical method.

A closer examination of the data indicated that three complexes were formed in both systems. The results are collected in Table 5.

In both systems, the calculation of the stability constant of the third complex had to be based on measurements at rather high C_L-values. The unknown variations in the liquid junction potential and in the activity coefficients, caused by the complex formation, give rise to a systematic error in the calculations based on E_L. This error is likely to increase with increasing C_M and increasing C_L in a given complex system. In the (isopropylthio)acetate

system, the $\bar{n}$-values increased with decreasing C_M at [L] > 60 mM, which can be found from Fig. 6, and is still more evident if all data in Table 3 are taken into consideration. This should indicate that correct $\bar{n}$-values could be obtained by extrapolation to $C_M = 0$. In practice, however, such an extrapolation is hazardous, since the random error of $\bar{n}$ increases rapidly with decreasing C_M in this region. Therefore, in the numerical calculation, the $\bar{n}$-values were treated as being scattered at random. In the plot of $\bar{n}/[L]$ versus [L], upon which the graphical treatment was based, no dependence upon C_M was observed even at the highest [L]-values.

Table 5. The stability constants. The constants of the ethoxyacetate and (ethylthio)-acetate systems refer to 20.0°C (see Ref. 1).

System	β_1 (M^{-1})	β_2 (M^{-2})	β_3 (M^{-3})	K_1 (M^{-1})	K_2 (M^{-1})	K_3 (M^{-1})	$\dfrac{K_1}{K_2}$	$\dfrac{K_2}{K_3}$
Cu^{2+}/i-C$_3$H$_7$·O·CH$_2$COO$^-$	59.8	780	(700)^a	59.8	13.0	(1)	4.6	(13)
Cu^{2+}/i-C$_3$H$_7$·S·CH$_2$COO$^-$	307	59 100	130 000^a	307	192	2.2	1.6	90
Cu^{2+}/C$_2$H$_5$·O·CH$_2$COO$^-$	62	740	1 600	62	11.9	2	5.2	5
Cu^{2+}/C$_2$H$_5$·S·CH$_2$COO$^-$	365	58 000	70 000	365	160	1.2	2.3	130

^{a} cf. Discussion.

In the isopropoxyacetate system, no dependence of $\bar{n}$ and $\bar{n}/[L]$ upon C_M was observed. In this system, however, the maximum concentration of the third complex was too small to enable the calculation of a reliable β_3-value.

Thus it must be concluded that, owing to the sources of systematic error, the stability constants of the comparatively weak anionic complexes may be less significant than expressed by the 99 % confidence limits, which of course refer to a random scatter in the data. In the isopropoxyacetate system, it seems even possible to obtain a sufficiently good agreement with the experimental data by the assumption that only the complexes ML and ML$_2$ are formed.

Regarding the formation of the first and second complexes in the systems under investigation, the situation is a close parallel to that earlier found[1] with the ethoxyacetate and (ethylthio)acetate complexes of copper(II). The stability constants K_1 and K_2 are much larger in the (alkylthio)acetate systems than in the alkoxyacetate systems. This indicates that chelates are formed to a larger extent in the (alkylthio)acetate complexes than in the alkoxyacetate complexes of copper(II). The predominance of the second complex in the (alkylthio)acetate systems is reflected in the values of the quotients K_1/K_2 and K_2/K_3 (see Table 5).

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