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A New Method for Measuring 1:1 Association Constants Based on Releasing Rate of Free Ligand from Aqueous into Gaseous Phase, Applied to Determining Formation Constants of Metal Acetylacetonate Complexes

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A simple method is presented that allows estimation of 1:1 association constants between volatile and nonvolatile solutes in aqueous medium. On introducing an inert gas at a constant flow rate into the aqueous phase, the volatile solute is expelled from the solution, and the amount of the released solute is measured as a function of aeration time. Measurements are made in two separate runs at the same inert gas flow rate, one in the absence and the other in the presence of nonvolatile solutes. The releasing rate of the volatile solute is reduced with increasing association between both the solutes in the aqueous medium. The method was used to estimate formation constants of 1:1 acetylacetone complexes with metal ions, Cu(II), Ni(II), Co(II), Mg(II), Fe(II), Fe(III), and Al(III), at 25.0 °C and I=0.1 ($NaClO_4$), results being compared with literature values.

It has been shown that the disproportionation constant of mercury(I) in aqueous medium, i.e., the equilibrium constant for $Hg_2^{2+} \rightleftharpoons Hg^{2+} + Hg$, can be determined by combining two rate constants obtained from two independent experiments: one is concerned with measurement of the disproportionation rate while the equilibrium is caused to shift to the right by introducing nitrogen gas at a constant flow rate into the solution containing Hg(I) to expel Hg, and the other is concerned with measurement of the releasing rate of metallic mercury in the absence of Hg(II) at the same N_2 gas flow rate.[1] The present work was undertaken to demonstrate that the method might be applicable widely to systems where association occurs in aqueous medium between volatile and nonvolatile solutes.

In this work we are concerned with measurement of 1:1 formation constants of metal complexes. Acetylacetone was selected because this ligand is volatile[2] and because formation constants for a wide variety of metal ions are available from published compilations.[3] Various methods such as spectrophotometry, potentiometry, polarography, calorimetry, and solvent extraction have so far been used to determine formation constants for metal acetylacetonates.[3-8] Compared with these techniques, the present method is simple and not specific for the metal ions to be studied.

Experimental

Reagents and Materials. Distilled deionized water was used throuhout. Acetylacetone was of analytical reagent grade from Wako Pure Chemical. Stock solutions of 0.1 or 0.2 M (1 M=1 mol dm^{-3}) metal ions were prepared by dissolving their salts (ammonium iron(III) sulfate, aluminium potassium sulfate, sulfate and chloride for Cu(II), and chlorides for the other metals) in 0.01 M $HClO_4$, and standardizing gravimetrically (Fe: Fe_2O_3 converted to hydroxide; Al: 8-quinolinolate; Ni: dimethylglyoximate; Co: Co_3O_4 converted to α-nitroso-β-naphtholate) or titrimetrically (Mg: EDTA; Cu: iodometry). Amberlite XAD-2 resin, 20—50 mesh (Rohm and Hass), was ground in an agate mortar, a 50—80 mesh portion was collected and washed with ethanol by decantation until the supernatant became clear.

Preparation of Sample Solutions. A known amount of acetylacetone (5 to 50 μL) was added with a 25 or 100 μL micropipet to ca. 50 cm^3 of 0.1 M $NaClO_4$, a known volume of a metal ion stock solution was added, the pH was adjusted with a suitable buffer solution, and finally the solution was diluted to 100 cm^3 with 0.1 M $NaClO_4$ (the acetylacetone concentration was in the range of 4.87×10^{-4} to 4.87×10^{-3} M and the metal ion concentration was in the range indicated in Tables 1—3). The buffer solutions used are as follows: 0.2 M acetic acid–0.2 M sodium acetate (pH=3—6), 0.1 M sodium dihydrogenphosphate–0.1 M sodium hydroxide (pH=6—7.5), and 0.2 M boric acid–0.2 M potassium chloride–0.2 M sodium hydroxide (pH=7.5—10). For pHs lower than 3, perchloric acid (0.1 M) was used. The amount of the buffer or $HClO_4$ solution added to an aqueous solution containing both acetylacetone and metal ion was moderated so that the contribution of buffer salts to the increase in ionic strength was less than 0.01. The pH was measured with a Horiba Type F-7 pH meter to 0.01 pH unit.

Apparatus and Procedures. A 25 cm^3 portion of sample solution was transferred into a 100 cm^3 Erlenmeyer flask with a ground glass joint, the flask being immersed in a thermostated bath at 25.0±0.1 °C. A gas-inlet-type adaptor was mounted on the flask and nitrogen gas was dispersed through the solution via a sintered glass ball at a constant flow rate of 895 cm^3 min^{-1}. The N_2 gas flow rate was adjusted by means of a needle valve and monitored during the aeration by a flow meter (Ueshima Brooks Rotameter); a deviation within 2% was observed around the adopted flow rate. The N_2 gas leaving the sample solution was passed through a 5 mm×5 cm glass column which contained XAD-2 resin beads 3.5 cm in length and had its exit end plugged with glass wool. After a fixed time, the N_2 gas stream was interruted, the XAD column was replaced by another one, and the introduction of N_2 gas was resumed. This operation was repeated at regular time intervals. The acetylacetone adsorbed on the resin was completely eluted out with a 5 cm^3 ethanol, and the amount expelled from the solution during the fixed time was determined spectrophotometrically at 272 nm by reference to a calibration curve prepared in advance with acetylacetone–ethanol solutions of known concentrations. The XAD column, after subjected to elution with ethanol and air-dried, could be used repeatedly.

After completion of each aeration run, the pH of the sample solution was checked; no appreciable change in pH was found before and after aeration.

Results

Derivation of an Equation That Allows Estimation of 1:1 Metal Acetylacetonate Complex Formation Constants. The equilibria among the species that should be taken into account are

$$\mathrm{acac}^- + \mathrm{M}^{n+} \rightleftharpoons \mathrm{M(acac)}^{n-1},\ K_1, \tag{1}$$

$$\mathrm{Hacac} \rightleftharpoons \mathrm{H}^+ + \mathrm{acac}^-,\ K_a, \tag{2}$$

$$\mathrm{Hacac(aq)} \longrightarrow \mathrm{Hacac(gas)},\ k, \tag{3}$$

where K_1, is the formation constant of 1:1 metal acetylacetonate complex, K_a is the acid dissociation constant of acetylacetone (Hacac), and k is the rate constant for the expulsion of Hacac molecules from the aqueous into the gaseous phase. For convenience, symbol L^- will hereafter be used to denote species acac$^-$.

The solute HL expelled into the gaseous phase is to be trapped successively by XAD-2 columns, and the amount, Q_{HL}, trapped during a fixed time is measured as a function of aeration time, t. Here, we assume that the releasing rate of HL at a constant N_2 gas flow rate is of first-order dependence on the concentration of this species present in the solution, and thus

$$\mathrm{d}Q_{HL}V^{-1}/\mathrm{d}t = k[\mathrm{HL}], \tag{4}$$

where V is the volume of the aqueous phase. We have mass-balance equations

$$C_M = [\mathrm{M}^{n+}] + [\mathrm{ML}^{n-1}], \tag{5}$$

$$\begin{aligned} C_{HL} &= [\mathrm{HL}] + Q_{HL}V^{-1} + [\mathrm{ML}^{n-1}] + [\mathrm{L}^-] \\ &= [\mathrm{HL}] + Q_{HL}V^{-1} + K_1[\mathrm{L}^-][\mathrm{M}^{n+}] + [\mathrm{L}^-] \\ &= [\mathrm{HL}] + Q_{HL}V^{-1} + (K_1[\mathrm{M}^{n+}]+1)K_a[\mathrm{HL}][\mathrm{H}^+]^{-1}, \end{aligned} \tag{6}$$

where C_M and C_{HL} indicate the total concentration of metal ions and that of acetylacetone, respectively. Substitution of Eq. 6 into Eq. 4 yields

$$\begin{aligned} \mathrm{d}Q_{HL}V^{-1}/\mathrm{d}t = k(C_{HL} - Q_{HL}V^{-1})/(1 + K_a[\mathrm{H}^+]^{-1} \\ + K_1K_a[\mathrm{M}^{n+}][\mathrm{H}^+]^{-1}), \end{aligned} \tag{7}$$

which becomes, on integration and with $Q_{HL}=0$ at $t=0$,

$$\begin{aligned} \ln (C_{HL} - Q_{HL}V^{-1}) = -kt/(1 + K_a[\mathrm{H}^+]^{-1} \\ + K_1K_a[\mathrm{M}^{n+}][\mathrm{H}^+]^{-1}) + \ln C_{HL}. \end{aligned} \tag{8}$$

Plots of $\ln(C_{HL}-Q_{HL}V^{-1})$ vs. t will give a straight line with a slope which corresponds to $-k/(1+K_a[\mathrm{H}^+]^{-1}+K_1K_a[\mathrm{M}^{n+}][\mathrm{H}^+]^{-1})$ or to $-k/(1+K_a[\mathrm{H}^+]^{-1})$ in the absence of metal ions. Under the condition that the total concentration of metal ions is sufficiently large compared to the concentration of the metal complex formed, that is, $C_M \gg [\mathrm{ML}^{n-1}]$, we can set $[\mathrm{M}^{n+}]$ in Eq. 8 equal to C_M.

Estimation of k and K_a. The constants k and K_a were determined from runs in the absence of metal ions. Figure 1 shows some plots constructed with the aid of Eq. 8. It is found that these plots give straight lines up to ca. 70% release of the acetylacetone initially present in the solution. This linearity verifies the validity of the assumption that the releasing rate of HL is first order in this species at a constant aeration rate. It can be seen from Fig. 1 that when the total concentration of HL is the same, the

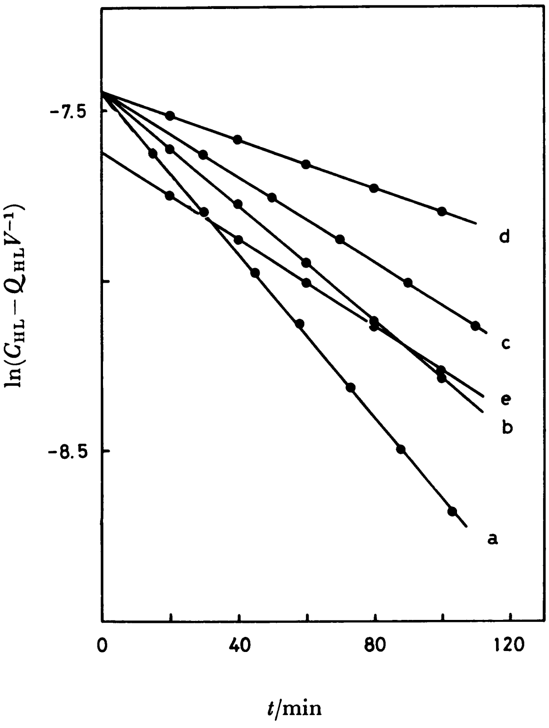

Fig. 1. The plots of ln $(C_{HL}-Q_{HL}V^{-1})$ vs. t in the absence of metal ions. pH 2.30; N_2 gas flow rate: (a) 895, (b) 640, (c) 460, (d) 255, (e) 460 cm^3 min^{-1}; C_{HL}: (a)—(d) 5.85×10^{-4}, (e) 4.87×10^{-4} mol dm^{-3}.

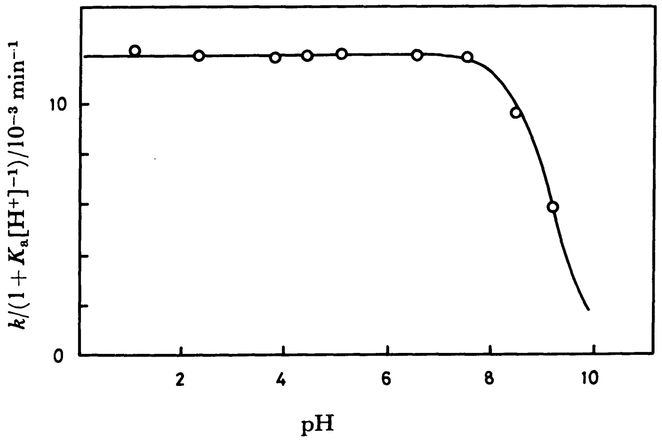

Fig. 2. The plots of $k/(1+K_a[H^+]^{-1})$ vs. pH in the absence of metal ions. N_2 gas flow rate 895 cm^3 min^{-1}; C_{HL} 5.85×10^{-4} mol dm^{-3}. The curve calculated using $k=1.20\times10^{-2}$ min^{-1} and pK_a=9.17 is depicted in a solid line.

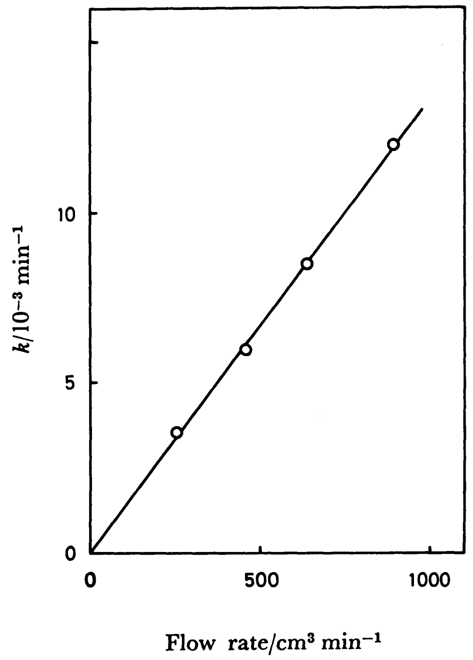

Fig. 3. k as a function of N_2 gas flow rate in the absence of metal ions. pH 2.30; C_{HL} 5.87×10^{-4} mol dm^{-3}.

slopes coincide with one another at the same aeration rate. This also supports the validity of Eq. 4.

At a constant N_2 gas flow rate, the slope of the straight line is almost constant in the acidic region, but steeply decreases in higher pH solutions, as seen from the plots of $k/(1+K_a[H^+]^{-1})$ vs. pH shown in Fig. 2. A least-squares calculation has revealed that k is 1.20×10^{-2} min^{-1} at an aeration rate of 895 cm^3 min^{-1} and that pK_a is 9.17. The K_a value thus determined is about half the reference one, 8.82 as pK_a,[9] reported at 25 °C and I=0.1(Na$^+$, H$^+$)ClO$_4$. The rate constant, k is proportional directly to the N_2 gas flow rate in the range of 250 to 895 cm^3 min^{-1} studied, as shown in Fig. 3. In the subsequent runs, the flow rate was fixed at 895 cm^3 min^{-1} to reduce the time required for completing a single run.

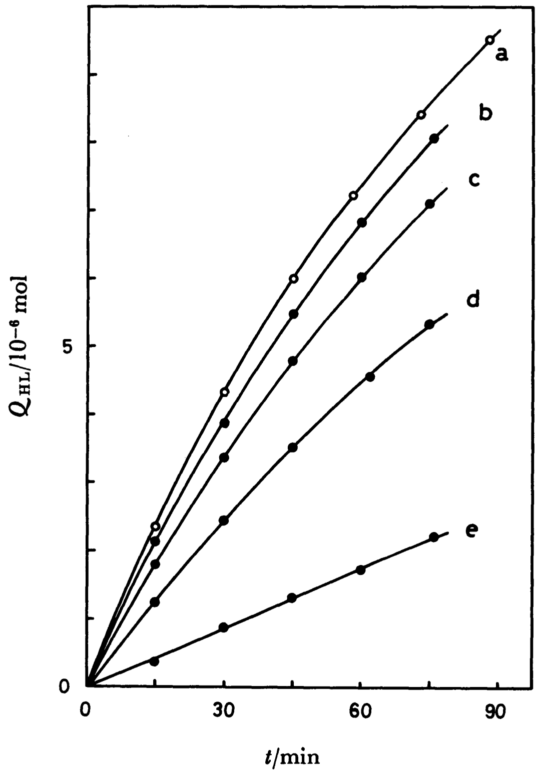

Fig. 4. The plots of Q_{HL} vs. t in the absence and presence of metal ions. N_2 gas flow rate 895 cm^3 min^{-1}; C_{HL} 5.85×10^{-4} mol dm^{-3}; (a): $C_M=0$, pH=2.30, (b): $C_{Mg}=2.05\times10^{-3}$ mol dm^{-3}, pH=7.37, (c): $C_{Ni}=9.85\times10^{-3}$ mol dm^{-3}, pH=4.76, (d): C_{Cu}(sulfate) = 1.98×10^{-3} mol dm^{-3}, pH=3.68, (e): $C_{Fe(III)}=4.02\times10^{-3}$ mol dm^{-3}, pH=1.82.

Estimation of K_1. The amount of acetylacetone released into the gaseous phase was plotted against aeration time to give a parabolalike curve. Results for some metals are shown in Fig. 4, in which the result obtained in the absence of metal is included for comparison. Plots constructed with the aid of Eq. 8 gave straight lines for each run over the aeration time range investigated. Insofar as sample solutions are sufficiently acidic that the term $K_a[H^+]^{-1}$ can be neglected compared to unity, and provided also that the total concentration of metal ions is sufficiently large compared with the ligand concentration, the slope of the straight line can be taken as $-k/(1+K_1K_aC_M[H^+]^{-1})$. The effect of C_M and pH on the slope was examined for Cu and Ni. The results are shown in Fig. 5 ($C_{Ni}=1.97\times10^{-3}$—4.93×10^{-2} M, $C_{HL}=5.85\times10^{-4}$ M, and pH almost constant around 4.8) and in Fig. 6 ($C_{Cu}=1.98\times10^{-3}$ M, $C_{HL}=5.85\times10^{-4}$ M, and pH=1.02—4.89). As expected, the gradient of the straight line decreases as either C_M or pH increases.

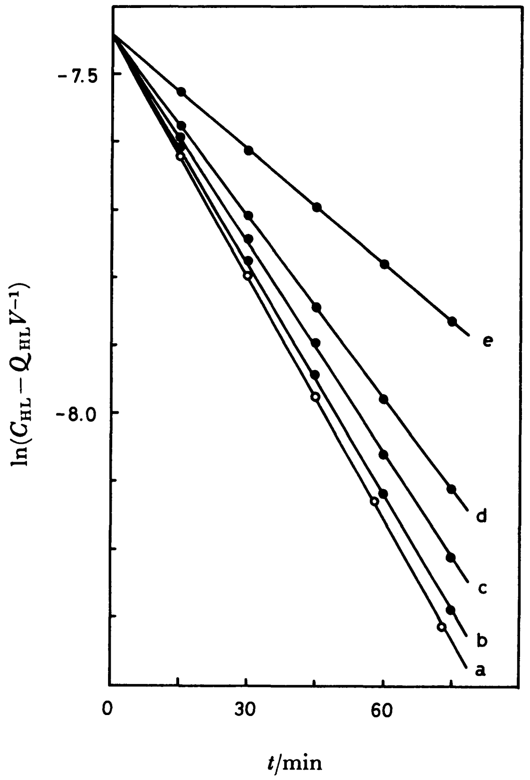

Fig. 5. The effect of C_M on the plots of $\ln(C_{HL}-Q_{HL}V^{-1})$ vs. t. N_2 gas flow rate 895 cm^3 min^{-1}; C_{HL} 5.85 $\times 10^{-4}$ mol dm^{-3}; (a): $C_M=0$, pH=2.30, (b): $C_{Ni}=1.97\times10^{-3}$ mol dm^{-3}, pH=4.80, (c): $C_{Ni}=4.93\times10^{-3}$ mol dm^{-3}, pH=4.80, (d): $C_{Ni}=9.85\times10^{-3}$ mol dm^{-3}, pH=4.76, (e): $C_{Ni}=4.93\times10^{-2}$ mol dm^{-3}, pH=4.63.

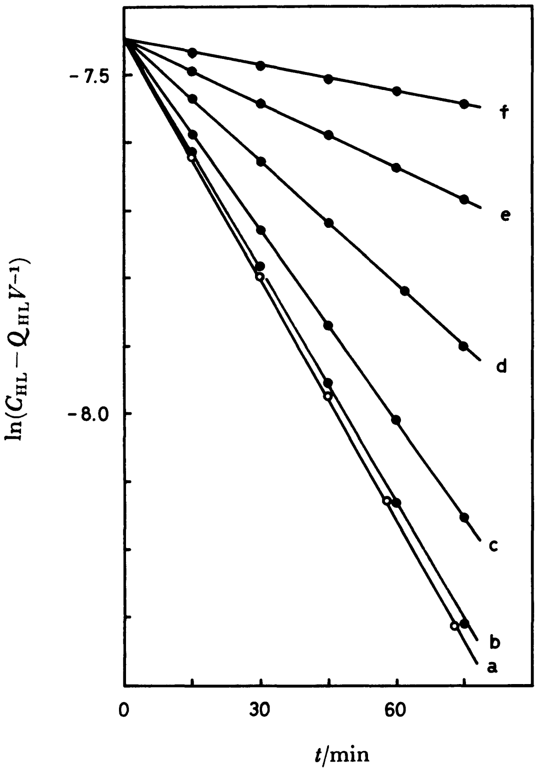

Fig. 6. The effect of pH on the plots of $\ln(C_{HL}-Q_{HL}V^{-1})$ vs. t. N_2 gas flow rate 895 cm^3 min^{-1}; C_{HL} 5.85$\times10^{-4}$ mol dm^{-3}; C_{Cu}(sulfate): (a) 0, (b)—(f) 1.98$\times10^{-3}$ mol dm^{-3}; pH: (a) 2.30, (b) 1.02, (c) 3.00, (d) 3.68, (e) 4.28, (f) 4.89.

The k and K_a values being known from the runs undertaken in the absence of metal, we can evaluate K_1 for each metal from the slope of the straight line. The K_1 values thus determined for Cu and Ni under various C_M and pH conditions are given in Table 1, and those for the other seven metals studied are summarized in Table 2, in which the K_1 values evaluated by using the reference pK_a(=8.82) are also listed together with those reported in the literature.[4–8] The K_1 values obtained by the present method are in reasonable agreement within 0.1 to 0.2 in the log unit with the literature values except for Al(III), which case differs by ca. 0.4 log unit.

Discussion

There are various factors which affect the precision and accuracy of the method proposed here for evaluating association constants between volatile and nonvolatile solutes. As was noted in a previous paper,[1] it is a requirement to carry out two separate runs, one in the absence and the other in the presence of nonvolatile solutes, under the same aeration conditions. To meet this requirement, the same sintered glass ball should be used in common, and the N_2 gas flow rate should be controlled to be as identical with each other as possible. Indeed, the rate constant, k, the absolute value of which is of no significance, is a function of the aeration rate (Fig. 3). In addition, the ionic strength and the kind of the electrolyte used to adjust it should be the same for the two runs, because the so-called salting-out effect may influence the volatility of the solute of interest, and hence the k value.

Particular attention should be paid to the presence of such electrolytes as may cause association with the nonvolatile solute to be studied, since this also affects the accuracy of the present method. For instance, the K_1 value for Cu decreases step by step as C_M increases, as can be seen from Table 1, when the sulfate salt is used; we first thought this arose from the salting-out of SO_4^{2-} ions, but it now seems more reasonable to consider ion-pair formation between Cu^{2+} and SO_4^{2-}.[10] The K_1 value of Cu(II) for the chloride salt is employed for this reason. Incidentally, the ion-pair formation constant has been reported to be ca. 200 at 25 °C and at ionic strengths corrected to zero.[3] The K_1 value of Cu(II) for the sulfate salt is to be underestimated unless the free metal ion concentration, $[M^{n+}]$, in the experimentally determined slope, $-k/(1+K_1K_a[M^{n+}][H^+]^{-1})$, is corrected for the

Table 1. Effects of the Total Concentration of Metal Ion and pH of Aqueous Solution on the Estimation of Formation Constants of Cu(II) and Ni(II) Acetylacetonate Complexes[a)]

Metal ion[b)]	$10^3\times C_M$/mol dm^{-3}	pH	log K_1[c)]
Cu(II), SO_4^{2-}	1.98	3.00	8.3
	4.96	3.00	8.2
	9.92	3.00	8.2
	49.6	3.08	8.0
	1.98	1.02	9.4[d)]
	1.98	3.68	8.2
	1.98	4.28	8.0
	1.98	4.89	7.9
Cu(II), Cl^-	1.96	2.92	8.3
	4.90	2.88	8.3
	9.80	2.85	8.2
	49.0	2.79	8.2
Ni(II), Cl^-	1.97	4.80	5.9
	4.93	4.80	5.9
	9.85	4.76	6.0
	49.3	4.63	5.9
	1.97	3.80	6.5[d)]
	1.97	5.56	5.9
	1.97	6.36	5.7

a) The total concentration of acetylacetone is 5.85×10^{-4} mol dm^{-3}, temperature is 25.0±0.1 °C, and $I=0.1$ ($NaClO_4$). b) The counter anion is specified. c) Estimated with p$K_a=9.17$. d) See the text.

Table 2. Formation Constants, K_1, of Matal Acetylacetonates at 25.0±0.1 °C and $I=0.1$($NaClO_4$)

Metal ion[a)]	$10^3\times C_M$ / mol dm^{-3}	pH	log K_1	
			This work[b)]	Literature
Cu(II)	1.96—49.0	2.79—2.92	8.3(7.9)[c)]	8.16[d)]
Ni(II)	1.97—49.3	4.63—6.36	5.9(5.5)[c)]	5.72[d)]
Co(II)	2.02	5.58	5.3(5.0)	5.10[e)]
Mg(II)	2.05	7.37	3.5(3.1)	3.34[e)]
Fe(II)	6.44	5.30	5.2(4.9)	5.07[f)]
Fe(III)	4.02	1.82	10.5(10.2)	9.27[g)], 10.5[h)]
Al(III)	4.98	2.00	8.7(8.3)	8.25[g)]

a) Chloride salt except for Fe(III) (ammonium iron(III) sulfate) and Al(III) (aluminium potassium sulfate). b) The total concentration of acetylacetone is 5.85×10^{-4} mol dm^{-3}, and the value are derived based on pK_a =9.17 estimated in this work, those on pK_a=8.82 (the literature value, Ref. 9) being given in the parentheses. c) The average of the chloride salts given in Table 1 (the value for Ni with the superscript d in Table 1 is excluded). d) Ref. 4, 25 °C, $I=0.1$($NaClO_4$). e) Recommended values cited in Ref. 5, 25 °C, $I=0.1$(Na^+, H^+)ClO_4^-. f) Ref. 6, 30 °C, $I=0$. g) Ref. 7, 25 °C, low ionic strength. h) Ref. 8, 25 °C, $I=1.0$.

ion-pair formation, that is, $[Cu^{2+}]=C_{Cu}-[Cu^{2+}SO_4^{2-}]$.

The choice of proper pK_a value is essential in estimating K_1. We have listed the two K_1 values in Table 2, one being evaluated based on pK_a=9.17 and the other on pK_a=8.82 reported in the literature. Although the K_a value determined in this work is appreciably lower, we are of the opinion that the use of this value leads to a better K_1 value since the same procedure employed to evaluate both pK_a and K_1 tends to compensate for systematic errors inherent in the present method.

An important point to keep in mind is the magnitude of the product, $K_1K_aC_M[H^+]^{-1}$. The value of K_1, cannot be evaluated accurately or at all when the term is too small compared with unity. This may be responsible for the unusual values observed for Cu at pH=1.02 and for Ni at pH=3.80 (Table 1). To get more reliable K_1, the solution pH and/or C_M should desirably be high for metals with relatively small stability constants. The choice of the solution pH, however, may be limited for metals subject to hydrolysis. For metals with large stability constants, on the other hand, these conditions are not necessarily desirable, because it takes a prolonged time to expel the free ligand from the aqueous phase.

When it is necessary to consider hydrolysis of metal ions, the concentration of M^{n+} should be modified by using $\alpha_{M(OH)}$, a side reaction coefficient, into $[M^{n+}]=C_M/\alpha_{M(OH)}$; with correction for the hydrolysis reaction, $M^{n+}+H_2O \rightleftharpoons M(OH)^{n-1}+H^+$, the complex formation constant, $K_{1,\text{correct}}$, can be written as

$$\log K_{1,\text{correct}} = \log K_1 + \log \alpha_{M(OH)},$$

including the second term of the right hand side of the equation as a correction term. This correction term, however, is negligibly small at the solution pH adopted here except for Fe(III). The K_1 value of Fe(III) listed in Table 2 has been corrected by 0.1 in the logarithmic unit; for Fe(III) the literature value of −2.55 was used as $\log K_{\text{hydrol}}$, where K_{hydrol} is the hydrolysis constant and can be converted into the side reaction coefficient by the relationship, $\alpha_{M(OH)}=1+K_{\text{hydrol}}[H^+]^{-1}$.

An attempt was made to evaluate 1:2 formation constants for some metal acetylacetonato complexes on the basis of the equilibration

$$acac^- + M(acac)^{n-1} \rightleftharpoons M(acac)_2^{n-2},\ K_2 \qquad (9)$$

It is difficult in this case to derive a rate equation like Eq. 7 under the experimental condition $C_{HL}>C_M$ or $C_{HL}\approx C_M$. We therefore tried to estimate K_2 through the following three successive steps. The first step: $\log(Q_{HL}/V)$ is plotted vs. $\log t$ to give a straight line for each run, and the intercept, $\log a$, and the slope, b, are derived. The second step: on the assumption $Q_{HL}/V=a\,t^b$, $dQ_{HL}V^{-1}/dt$ is calculated at a selected aeration time, t, and then, the concentration of free

HL present in the solution at t is obtained based on the rate equation, Eq. 4. The third step: from the mass-balance equations

$$C_{HL} = [HL] + Q_{HL}/V + [L^-] + [ML^{n-1}] + 2[ML_2{}^{n-2}],$$
$$C_M = [M^{n+}] + [ML^{n-1}] + [ML_2{}^{n-2}],$$

we can derive

$$C_{HL} = [HL] + Q_{HL}/V + K_a[HL][H^+]^{-1} + 2C_M - [M^{n+}](2+K_1K_a[HL][H^+]^{-1}),$$

which allows us to estimate $[M^{n+}]$ by using the K_a and K_1 values evaluated by the present method, and in turn, $[ML^{n-1}]$ and $[ML_2{}^{n-2}]$ can be determined from the mass-balance relationships, from which K_2 is to be derived. The values thus determined are given in Table 3. Again, if it is necessary to make correction for the hydrolysis of metal ions, the product $[M^{n+}]\alpha_{M(OH)}$ must be employed instead of the simple $[M^{n+}]$; this correction was applied only to Fe(III).

Table 3. Change in Concentration of Free Ligand and Metal Complexes as a Function of Aeration Time and the Tentatively Estimated Formation Constants, K_2, of Metal Acetylacetonates at 25.0±0.1 °C, I=0.1(NaClO$_4$)

Aeration time/min	Concentration/10^{-4} mol dm^{-3}					log K_2
	Q_{HL}/V	HL	M^{n+}	ML^{n-1}	$ML_2{}^{n-2}$	
Cu(II)[a]						
15	1.71	8.26	0.83	6.51	2.46	6.9
30	3.23	7.45	0.98	6.92	1.90	6.9
45	4.53	7.01	1.13	7.49	1.19	6.6
60.5	5.73	6.71	1.27	8.10	0.43	6.2
76.5	6.77	6.49	1.41	8.65		
					Average	6.7
					Literature value[b]	6.84
Ni(II)[c]						
15	1.89	9.12	1.77	5.82	2.26	4.9
30	3.54	8.25	2.04	6.06	1.76	4.9
45	4.99	7.78	2.31	6.49	1.05	4.7
60	6.29	7.47	2.58	6.94	0.33	4.1
75	7.45	7.23	2.82	7.37		
					Average	4.8
					Literature value[d]	4.45
Fe(III)[e]						
15	2.25	11.08	6.43	20.08	11.31	9.7
30	4.28	10.01	6.96	19.63	11.03	9.7
45	6.09	9.43	7.40	19.66	10.40	9.7
60	7.83	9.03	7.80	10.85	9.67	9.7
75	9.43	8.74	8.15	20.07	8.96	9.7
90	10.93	8.51	8.49	20.36	8.21	9.7
					Average	9.7
					Literature value[b]	8.71
Al(III)[f]						
15	2.11	10.02	3.27	4.11	2.58	8.4
30	3.97	8.95	3.67	4.11	2.19	8.4
45	5.53	8.37	4.07	4.27	1.16	8.3
60	6.85	7.98	4.45	4.45	1.06	8.1
75	8.06	7.70	4.82	4.64	0.50	7.7
					Average	8.2
					Literature value[b]	7.35

a) As the chloride salt, $C_{Cu}=9.80\times10^{-4}$ mol dm^{-3}, $C_{HL}=2.14\times10^{-3}$ mol dm^{-3}, pH=4.89, and the data used are pK_a=9.17 and log K_1=8.3. b) Ref. 7. c) $C_{Ni}=9.85\times10^{-4}$ mol dm^{-3}, $C_{HL}=2.14\times10^{-3}$ mol dm^{-3}, pH=6.86, and the data used are pK_a=9.17 and log K_1=5.9. d) Ref. 5. e) $C_{Fe}=4.02\times10^{-3}$ mol dm^{-3}, $C_{HL}=4.87\times10^{-3}$ mol dm^{-3}, pH=2.12, and the data used are pK_a=9.17 and log K_1=10.5. f) $C_{Al}=9.96\times10^{-4}$ mol dm^{-3}, $C_{HL}=2.14\times10^{-3}$ mol dm^{-3}, pH=3.58, and the data used are pK_a=9.17 and log K_1=9.7.

It is informative to follow the change in concentration of such species as M^{n+}, ML^{n-1}, and $ML_2{}^{n-2}$ as a function of aeration time. As aeration proceeds, $[ML_2{}^{n-2}]$ decreases with an accompanying increase in $[M^{n+}]$ (and also in $[ML^{n-1}]$ when C_{HL} is sufficiently large compared to C_M). In the case of Fe(III) given in Table 3, there was observed a steady state with respect to the ML^{n-1} species, which may result from C_{HL} being nearly equal to C_M. It appears that the K_2 value thus derived for each metal falls gradually as aeration proceeds. This is quite unreasonable and is probably caused by the assumption made in the second step, that is, the Q_{HL}/V vs. t plot follows a parabolic curve. In reality, the log(Q_{HL}/V) vs. log t plots show a slight deviation from the linearity and this trend is pronounced with prolonging aeration time. Therefore, the differential treatment of experimental results employed here to estimate K_2 led to erroneous evaluation of 1:2 association constants.

If it is convenient to follow the rate of decrease in the concentration of the associated species instead of measuring the releasing rate of the volatile solute expelled from the aqueous into the gaseous phase, the rate equation can be expressed as

$$-d[A\cdot B]/dt = kK^{-1}[A\cdot B][B]^{-1}$$
$$= kK^{-1}[A\cdot B](C_M - [A\cdot B])^{-1},$$

which becomes, on integration and with $[A\cdot B]=[A\cdot B]_o$, the initial (t=0) concentration

$$C_B \ln[A\cdot B] - [A\cdot B] = -kK^{-1}t + C_B \ln[A\cdot B]_o - [A\cdot B]_o,$$

where A, B, and A·B denote the volatile, nonvolatile, and associated species, respectively, K is an association constant, and k is a rate constant of the expulsion of A from the aqueous phase in the absence of B. This is essentially the same form as that previously used to determine the disproportionation constant of mercury(I).[1)] Implicit in this rate equation and also in Eq. 4 (and Eq. 7) is the assumption that the transfer of volatile solute from the aqueous into the gaseous phase is the rate-determining step. If, on the other hand, an association equilibrium is the rate-determining step. the association constant cannot be estimated. This is a limitation on the applicability of the present method.

In general, it is somewhat difficult to measure association constants between nonvolatile and highly volatile solutes, because it is hard to maintain constant the concentration of the latter in the aqueous medium. The present method is applicable only to very volatile solutes, and in this respect seems complementary. The present technique need not maintain the volatile solute concentration constant, and its total concentration in the aqueous medium can easily be determined by aerating the medium with an inert gas for a prolonged period and by trapping the released solute during the aeration

An important application of the method proposed here will be encountered when hydrophobic interaction is to be studied in the aqueous environment between nonvolatile and volatile solutes.

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