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Kinetic and Equilibrium Studies of the Complex Formation of Mercury(II) Acetate in Aqueous Solutions

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An ultrasonic absorption study has been carried out on aqueous acidic solutions of mercury(II) acetate. The absorption data shows a single-relaxation phenomenon in the frequency range of 15—95 MHz. On the other hand, the results of the pH measurement indicate that the only mecury(II) acetate complexes conceivable in solution are of the HgL^+ and HgL_2 forms (L^- denotes the acetate ion); the succesive formation constants of these complexes, together with the mercury(II) hydrolysis constants, are also determined. The equilibrium constants reported are: 2.1×10^3 for K_1, 4.9×10^3 for K_2, 6×10^{-4} for K_{h1}, and 1.0×10^{-3} for K_{h2}, at 30 °C and $I=1$. On the basis of the above results, the ultrasonic relaxation absorption is ascribed to the complex formation reaction: $HgL^+ + L^- \rightleftharpoons HgL_2$. The rate constants and the volume change of this reaction are determined to be: $k_f^\circ=7.8\times10^9\ M^{-1}\ s^{-1}$, $k_b^\circ=1.6\times10^6\ s^{-1}$, and $\Delta V=18\ cm^3\ mol^{-1}$, at 30 °C.

It is well known[1)] that the rate of a metal-complex formation reaction in an aqueous solution is controlled by the water release from the metal and that the rate constant of this step depends strongly on the nature of the metal ion, *e.g.*, on the charge, the electronic configuration, the ionic radius, and the coordination number. Although many studies[2)] have provided us with much information about the complexation kinetics for most "labile" metals, few kinetic studies about mercury(II) complexes[2,3)] have been made up to the present. This is because some experimental difficulties exist in the studies; *e.g.*, mercury(II) exhibits a considerable hydrolysis-tendency, and it is one of the most labile of metals.

The purpose of the present study is to obtain kinetic information on mercury(II) acetate complexes through an elucidation of ultrasonic absorption in aqueous mercury(II) acetate solutions. The kinetic analysis of the absorption data requires an exact knowledge about the nature of complexes in solution and about the formation constants. The literature[4—6)] gives little information on these constants, and so the present study included a determination of them by means of a pH measurement method.

Experimental

Equilibrium Measurements. The formation constants of the mercury(II) acetate complexes were obtained from the pH measurements. A Hitachi-Horiba Expandomatic pH meter, Model F-7SS, with general-purpose glass and calomel electrodes was used and calibrated with standard buffer solutions. The pH values were determined to an accuracy of ±0.005 unit. Sample solutions were prepared from mercury(II) acetate and stock solutions of nitric acid and/or acetic acid; the ionic strength was kept constant at $I=1$ by the addition of $NaNO_3$. The concentrations of the acid solutions were determined by titrating with standard NaOH.

The experiments were carried out for three kinds of systems. The first contains 0.001—0.4 M mercury(II) acetate and 0.01—0.4 M nitric acid; pH=1.0—3.1. The second contains 0.15—0.5 M mercury(II) acetate, 0.02—0.1 M nitric acid, and 0.25 M acetic acid; pH=2.0—2.6. The third contains 0.005—0.4 M mercury(II) acetate and 0.07—0.25 M acetic acid; pH=2.7—3.3. The dissociation constant of acetic acid was also obtained from the pH measurement of solutions containing 0.025—0.9 M acetic acid and 0.01—0.2 M sodium acetate ($I=1$ with $NaNO_3$); the pH value lay in the 3.3—4.5 range.

The concentrations of hydrogen ions in the solutions were calculated from the measured pH values by using an apparent activity coefficient, γ_H, which was determined by the pH measurement of solutions containing nitric acid at various concentrations and sufficient amounts of $NaNO_3$ to maintain the ionic strength at unity. All the pH measurements were carried out at 30.0±0.5 °C.

Kinetic Measurement. Sample solutions were prepared from mercury(II) acetate and sodium acetate. The pH values of the solutions were adjusted by the addition of perchloric acid; no supporting electrolytes were added. The ultrasonic absorption was measured in the frequency range of 5—95 MHz by the pulse technique[7)] at 30.00±0.05 °C.

The relaxation absorption spectra were represented by the single-relaxation equation:

$$\frac{\alpha}{f^2}=\frac{A}{1+(f/f_r)^2}+B, \tag{1}$$

or:

$$(\alpha'\lambda)=\left(\frac{\alpha}{f^2}-B\right)cf=\frac{2\mu_m(f/f_r)}{1+(f/f_r)^2}, \tag{2}$$

where α is the ultrasonic absorption coefficient; f, the frequency of the sound; f_r and A, the relaxation frequency and amplitude, respectively; B, the high-frequency value of α/f^2; $(\alpha'\lambda)$, the excess absorption per wavelength; c, the velocity of sound, and μ_m $(=cAf_r/2)$, the maximum excess absorption per wavelength.

The values of f_r, A, and B were determined by fitting the data to Eq. 1. A least-squares fit was obtained by using a routine in which the root-mean-square percentage deviation between the experimental and calculated α/f^2 values was minimized.

Results and Discussion

The Formation Constants of Mercury(II) Acetate Complexes. In the mercury(II) acetate systems studied, the following equilibria may exist:

$$HL \overset{K_H}{\rightleftharpoons} H^+ + L^-, \tag{3}$$

$$Hg(OH)_{m-1}^{3-m} \overset{K_{hm}}{\rightleftharpoons} Hg(OH)_m^{2-m} + H^+, \qquad m=1, 2, \tag{4}$$

$$HgL_{n-1}^{3-n} + L^- \overset{K_n}{\rightleftharpoons} HgL_n^{2-n}, \qquad n=1, 2, \cdots N, \tag{5}$$

where L^- denotes the acetate ion and where K_H is the dissociation constant of acetic acid; the $K_{\mathrm{h}m}$'s are the mercury(II) hydrolysis constants, and the K_n's, the formation constants of the complexes. Then, the average number, $\bar{n}$, of acetate ions bound to the central metal may be defined by[8]

$$\bar{n} = \frac{\sum_{n} n\beta_n[\mathrm{L}^-]^n}{1+\sum_{n}\beta_n[\mathrm{L}^-]^n}, \qquad \beta_n = K_1K_2\cdots K_n, \tag{6}$$

where the brackets indicate the molar concentration at equilibrium and where the summation is to be carried out for all the whole values of n from 1 to N.

In the first place, the data analysis was tried by ignoring the hydrolysis Reactions 4 from the above equilibria. Then, we could evaluate $[\mathrm{L}^-]$ and $\bar{n}$ by means of the following relations:[6]

$$[\mathrm{L}^-] = K_\mathrm{H}(\textstyle\sum\mathrm{acid} - [\mathrm{H}^+])/[\mathrm{H}^+], \tag{7}$$

$$\bar{n} = \{\textstyle\sum\mathrm{L} - (1+[\mathrm{H}^+]/K_\mathrm{H})[\mathrm{L}^-]\}/\textstyle\sum\mathrm{Hg}, \tag{8}$$

where $\sum\mathrm{Hg}$ and $\sum\mathrm{L}$ are the total stoichiometric concentrations of mercury(II) and acetate ions, respectively, and where $\sum\mathrm{acid}$ is the sum of those of nitric and acetic acids. The dissociation constant, K_H, was determined from the measured hydrogen-ion concentrations of the acetic acid–sodium acetate system by means of the relation: $\mathrm{p}K_\mathrm{H} = \mathrm{p}[\mathrm{H}^+] + \log\{(C_1 - [\mathrm{H}^+])/(C_2 + [\mathrm{H}^+])\}$, were C_1 and C_2 are the stoichiometric concentrations of acetic acid and sodium acetate, respectively. The K_H value obtained is shown in Table 1; it was used for the evaluation of $[\mathrm{L}^-]$ and $\bar{n}$ (Eqs. 7 and 8).

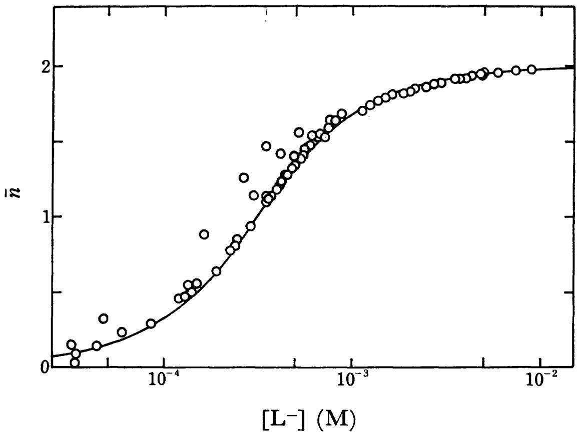

Fig. 1. Graph of $\bar{n}$ *vs.* $[\mathrm{L}^-]$ for the mercury(II) acetate system at 30 °C and $I=1$. Open circle refers to the $\bar{n}$ and $[\mathrm{L}^-]$ values determined approximately by Eqs. 7 and 8. The solid curve expresses the $\bar{n}$ value calculated by Eq. 6 using the K_1 and K_2 values in Table 1.

As is shown in Fig. 1, a graph of the $\bar{n}$ *vs.* $[\mathrm{L}^-]$ plot thus obtained forms almost a single curve except for some data in the low $[\mathrm{L}^-]$ region which exhibit somewhat large deviations from the curve. Probably these deviations reflect the fact that the effect of the hydrolysis reactions cannot be ruled out in this region. Furthermore, the fact that the $\bar{n}$ value increases as a whole with an increase in $[\mathrm{L}^-]$ and tends to an asymptotic value of 2 in the high $[\mathrm{L}^-]$ region indicates that the only mercury(II) acetate complexes conceivable in solution are of the HgL^+ and HgL_2 forms.

Since graphical methods for determining equilibrium constants[9] may not be simply applied to the present systems, the data analysis was carried out as follows. From the equilibria (3—5) with $m=1$, 2 and $n=1$, 2, we obtain the following conservation relations:

$$\textstyle\sum\mathrm{Hg} = [\mathrm{Hg}^{2+}]\left(1+\frac{K_{\mathrm{h}1}}{[\mathrm{H}^+]}+\frac{K_{\mathrm{h}1}K_{\mathrm{h}2}}{[\mathrm{H}^+]^2}+K_1[\mathrm{L}^-]+K_1K_2[\mathrm{L}^-]^2\right), \tag{9}$$

$$\textstyle\sum\mathrm{L} = [\mathrm{L}^-]\left(1+\frac{[\mathrm{H}^+]}{K_\mathrm{H}}\right)+[\mathrm{Hg}^{2+}](K_1[\mathrm{L}^-]+2K_1K_2[\mathrm{L}^-]^2), \tag{10}$$

$$\textstyle\sum\mathrm{acid} = [\mathrm{H}^+]\left(1+\frac{[\mathrm{L}^-]}{K_H}\right)-[\mathrm{Hg}^{2+}]\left(\frac{K_{\mathrm{h}1}}{[\mathrm{H}^+]}+\frac{2K_{\mathrm{h}1}K_{\mathrm{h}2}}{[\mathrm{H}^+]^2}\right). \tag{11}$$

If a set of values is given to the four parameters, $K_{\mathrm{h}1}$, $K_{\mathrm{h}2}$, K_1, and K_2, the values of $[\mathrm{Hg}^{2+}]$ and $[\mathrm{L}^-]$ may be evaluated from the known values of $\sum\mathrm{Hg}$, $\sum\mathrm{L}$, and $[\mathrm{H}^+]$ by using Eqs. 9 and 10. Then, Eq. 11 enables us to calculate $\sum\mathrm{acid}$. Therefore, the values of the equilibrium constants were determined by repeating a number of similar calculations, in which the values of the parameters were varied independently, and finally by obtaining a set of values which minimize the root-mean-square percentage deviation between the experimental and calculated $\sum\mathrm{acid}$ values. The calculations were carried out by using a computer program. The values of the equilibrium constants obtained are shown in Table 1. The calculated $\sum\mathrm{acid}$ values agree with the experimental values within ±3%. The $\bar{n}$ value was recalculated by means of Eq. 6 using the K_1 and K_2 values in Table 1; it is shown by a solid line in Fig. 1. The calculated curve is consistent with the $\bar{n}$ *vs.* $[\mathrm{L}^-]$ plot which was obtained approximately by means of Eqs. 7 and 8.

TABLE 1. EQUILIBRIUM CONSTANTS FOR THE AQUEOUS MERCURY(II) ACETATE SYSTEM AT 30 °C AND $I=1$

Dissociation constant of acetic acid	$K_\mathrm{H} = (3.19 \pm 0.07)\times 10^{-5}$
Mercury(II) hydrolysis constants	$K_{\mathrm{h}1} = (6 \pm 2)\times 10^{-4}$ $K_{\mathrm{h}2} = (1.0 \pm 0.4)\times 10^{-3}$
Formation constants of mercury(II) acetate complexes	$K_1 = (2.1 \pm 0.1)\times 10^{3}$ $K_2 = (4.9 \pm 0.3)\times 10^{3}$

The $K_{\mathrm{h}1}$ and $K_{\mathrm{h}2}$ values in Table 1 are within the ranges of those reported by the earlier workers.[4] On the other hand, the results obtained for mercury(II) acetate complexes are very different from those reported by Banerjea and Singh.[6] They reported the presence of four kinds of complexes (*i.e.*, $n=1$—4) in solution and obtained these values: 3.59×10^5, 5.54×10^3, 9.6×10^3, and 6.1×10^3 for K_1, K_2, K_3, and K_4, respectively, at 30 °C and $I=1$. Their K_1 value is larger by almost two orders of magnitude than the corresponding one in Table 1, though their K_2 value is close to that obtained here. For comparison, the $\bar{n}$ value was calculated by means of Eq. 6 using their four equilibrium constants; it ranges from 1.1 to 4 in the $[\mathrm{L}^-]$ range in Fig. 1,

TABLE 2. EXPERIMENTAL CONDITIONS AND ULTRASONIC RELAXATION PARAMETERS FOR THE AQUEOUS MERCURY(II) ACETATE SYSTEM[a)] AT 30 °C

Sample No.	$\sum$L (M)	pH	Equilibrium concentrations of species (10^{-2} M)[b)] HL	L^-	Hg^{2+}	$HgOH^+$	$Hg(OH)_2$	HgL^+	HgL_2	f_r (MHz)	A (10^{-17} cm^{-1} s^2)	B (10^{-17} cm^{-1} s^2)
1	1.08	2.28	23.5	0.17	4.4	0.25	0.04	6.8	38.5	54±13	21±2	22±2
2	1.10	2.51	20.1	0.25	2.3	0.22	0.06	5.2	42.2	38±5	30±2	24±1
3	1.13	2.83	17.2	0.46	0.8	0.15	0.09	3.1	45.8	35±3	48±2	23±1
4	1.15	3.28	15.7	1.17	0.1	0.07	0.11	1.3	48.4	21±2	113±9	24±2
5	1.18	3.56	16.2	2.30	—	0.03	0.10	0.7	49.2	19±1	146±7	23±1
6	1.10	2.46	21.0	0.24	2.6	0.22	0.05	5.5	41.6	43±12	45±4	21±5
7	1.30	2.46	35.2	0.39	0.9	0.08	0.02	3.5	45.4	37±8	71±7	19±4
8	1.50	2.46	52.6	0.56	0.4	0.04	0.01	2.3	47.2	33±3	95±5	18±2
9	1.70	2.46	71.3	0.72	0.2	0.02	0.01	1.7	48.1	27±2	114±8	22±2
10	2.00	2.46	100	0.91	0.1	0.01	—	1.1	48.8	27±5	109±14	22±3
11	2.25	2.46	125	1.03	—	0.01	—	0.8	49.2	27±7	93±18	22±4

a) Each solution contains 0.500 M $\sum$Hg. b) I=0.2—1.3.

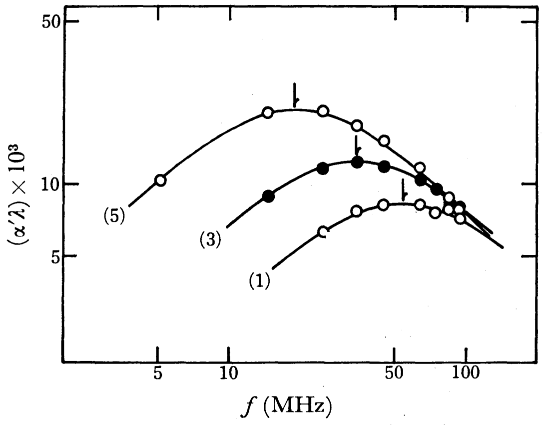

Fig. 2. Graph of $(\alpha'\lambda)$ *vs.* f for the mercury(II) acetate system containing $HClO_4$ in a definite concentration (*ca.* 0.2 M), at 30 °C. The arrow indicates the relaxation frequency. The number in parentheses refers to the sample number in Table 2.

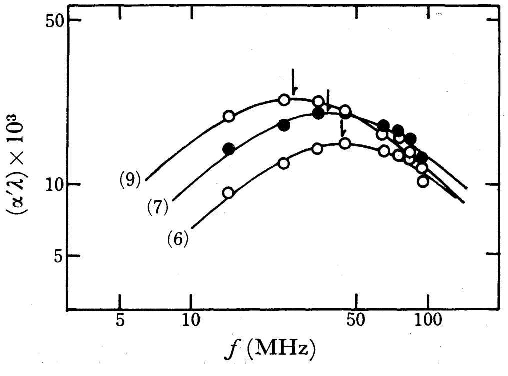

Fig. 3. Graph of $(\alpha'\lambda)$ *vs.* f for the mercury(II) acetate system in a definite pH (2.46), at 30 °C. The arrow indicates the relaxation frequency. The number in parentheses refers to the sample number in Table 2.

being too large to be consistent with the present results.

Ultrasonic Absorption of Mercury(II) Acetate Solutions. The experimental conditions and the adsorption parameters obtained are summarized in Table 2. The data consist of those from two kinds of systems. One contains $HClO_4$ in a definite concentration of *ca.* 0.2 M (sample No. 1—5), while the other has been adjusted to a definite pH of 2.46 (sample No. 6—11). Representative absorption curves for these systems are shown in Figs. 2 and 3, where the excess absorption per wavelength $(\alpha'\lambda)$ is plotted against f.

The equilibrium concentrations of species in solution were evaluated from the $\sum$Hg, $\sum$L, and pH values in Table 2, together with the values of the equilibrium constants which were calculated from those in Table 1 by using Meites' equation[10)] for the activity coefficients of ions. Calculations by a recurrence method resulted in self-consistent values for the equilibrium concentrations, the ionic strength, the activity coefficients, and the corrected equilibrium constants. The results are also shown in Table 2.

The kinetic analysis of the absorption data was carried out by associating the relaxation process with one of the equilibria (3—5). An examination of the concentration dependence of the observed relaxation frequency showed that only the following reaction is consistent with the experimental data (furthermore, all the species in this reaction are considered to be of a reasonable order of magnitude over the whole concentration range studied):

$$HgL^+ + L^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} HgL_2. \qquad (12)$$

The relaxation frequency associated with this reaction is expressed by

$$2\pi f_r = k_f^\circ\{\gamma_\pm^2([HgL^+]+[L^-])+1/K_2^\circ\}, \qquad (13)$$

where $\gamma_\pm$ is the mean activity coefficient of HgL^+ and L^-, and where the superscript (o) indicates the quantities at I=0. In the above expression, the equilibrium relation of $K_2^\circ = k_f^\circ/k_b^\circ$ is employed. As is shown in Fig. 4, a graph of the f_r *vs.* $\{\gamma_\pm^2([HgL^+]+[L^-])+1/K_2^\circ\}$ plot gives a straight line passing through the point of origin, and the rate constant, k_f°, was obtained from the slope of this line. The values of k_f° and k_b° $(=k_f^\circ/K_2^\circ)$ are shown in Table 3. The maximum excess absorption per wavelength corresponding to Eq. 13 is given by

$$\mu_m = \frac{(\pi\Delta V)^2}{2RT\beta_s}\left\{\frac{1}{[HgL^+]}+\frac{1}{[L^-]}+\frac{1}{[HgL_2]}\right\}^{-1}, \qquad (14)$$

where R is the gas constant; T, the absolute temperature

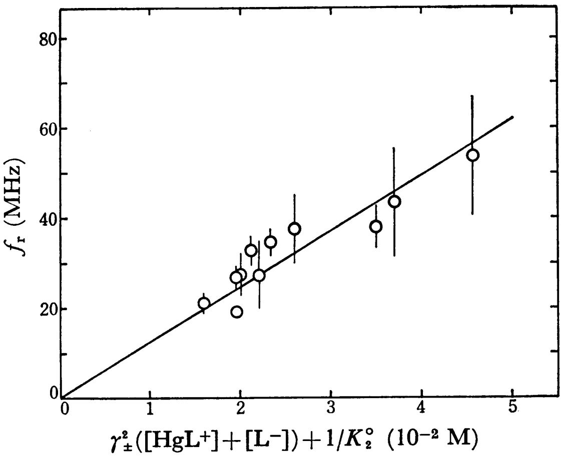

Fig. 4. Graph of f_r *vs.* $\{\gamma_\pm^2([\mathrm{HgL}^+]+[\mathrm{L}^-])+1/K_2^\circ\}$ for the mercury(II) acetate system at 30 °C. The vertical lines indicates the uncertainty intervals given in Table 2.

Table 3. Kinetic results for the formation of $Hg(CH_3CO_2)_2$ at 30 °C

Rate constants	$k_f^\circ=(7.8\pm0.9)\times10^9\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ $k_b^\circ=(1.6\pm0.2)\times10^6\ \mathrm{s}^{-1}$
Volume change	$\Delta V=18\pm2\ \mathrm{cm}^3\ \mathrm{mol}^{-1}$ a)

a) Effective value in the I range of 0.2—1.3.

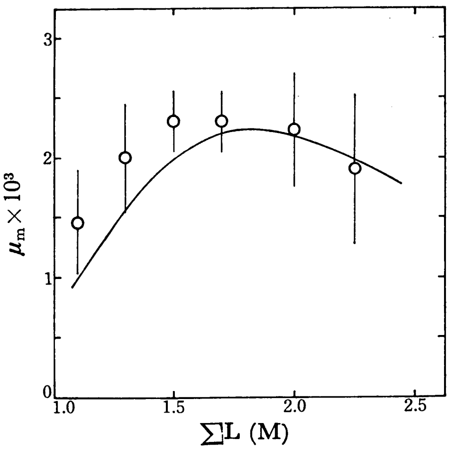

Fig. 5. Graph of μ_m *vs.* $\sum$L for the mercury(II) acetate system under the conditions of $\sum$Hg=0.500 M, pH=2.46, and 30 °C. The vertical lines indicate the uncertainty intervals obtained from the data in Table 2. The solid curve expresses the μ_m value calculated by Eq. 14 using the ΔV value in Table 3.

and β_s, the adiabatic compressibility of the solution; ΔV is the volume change of the complex formation reaction 12. The ΔV value was determined by Eq. 14; it is also shown in Table 3. Figure 5 shows the observed μ_m values plotted against $\sum$L for the solutions of $\sum$Hg =0.5 M and pH=2.46, while the calculated μ_m value is also shown by the solid line. The calculated curve expresses fairly well the concentration dependence of the observed μ_m value. These results indicate that the observed relaxation absorption is associated with Reaction 12.

By an electric-field-dispersion method, Eigen and Eyring[3] obtained the rate constant, (5—10)×10^9 M^{-1} s^{-1} (at 24—25 °C and $I\approx0$), for the $HgCl_2$ formation reaction. The similarity of the k_f° value in Table 3 to the above value indicates that the formation reactions of the mercury(II) complexes proceed *via* the Eigen mechanism,[11,12] which involves the loss of a water molecule in the rate-determining step. By assuming that the outer-sphere association process reaches equilibrium much faster than the ligand substitution, the complex formation rate constant, k_f, may be expressed in terms of the association constant, K_o, of the outersphere complex and the rate constant, k_o, of ligand substitution; *i.e.*, $k_f=K_ok_o$. For Reaction 12, the K_o value was estimated to be 1.3 (at I=0) by means of the Fuoss equation,[13] in which the center-to-center distance between the reaction partners was assumed to be 5 Å. Then, the k_f° value in Table 3 gives $k_o=6\times10^9$ s^{-1}, which is in line with the corresponding values reported for the d^{10} cations:[1] *i.e.*, (2.5—3)×10^7 s^{-1} for Zn^{2+}, (2.5—4)×10^8 s^{-1} for Cd^{2+}, and 2×10^9 s^{-1} for Hg^{2+}, at 20 °C.

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