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An ultrasonic absorption study of the complex formation of zinc(II) thiocyanate in aqueous solution

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A new method of analysis for the ultrasonic absorption of systems involving multiple coupled equilibria is described. The method consists of calculating the relaxation frequencies and amplitudes under a postulated reaction mechanism using trial values of the rate constants and volume changes and of comparing the computed absorption α/f^2 (absorption coefficient over frequency squared) directly with the experimental one. Application of this method to the ultrasonic absorption study of aqueous zinc(II)-thiocyanate solutions reveals that the relaxation absorption is ascribed to the successive complex formation equilibria

$$\operatorname{Zn}(\operatorname{SCN})_{n-1}^{3-n} + \operatorname{SCN}^{-} \underset{k_{-n}}{\overset{\kappa_{n}}{\rightleftharpoons}} \operatorname{Zn}(\operatorname{SCN})_{n}^{2-n}, \quad n = 1-4.$$

The rate constants and volume changes of the above reactions are determined. The method proves to be especially effective when the absorption spectra are associated with multiple coupled equilibria and accordingly too broad to be separated to discrete relaxation processes by the usual method of analysis.

I. INTRODUCTION

Ultrasonic absorption method has been used extensively in kinetic studies of fast reactions in solution.¹ The main advantage of this method is that, in common with other stationary relaxation techniques, the primary absorption data, which represent the spectrum of relaxation times and amplitudes, are independent of the magnitude of the perturbation. Thus, the complete interpretation of the relaxation data in terms of the reaction kinetics can be performed through the precise analysis of both the relaxation times and amplitudes.

In general, the sound absorption spectra involving several relaxation processes are expressed by

$$\frac{\alpha}{f^2} = \sum_{i} \frac{A_i}{1 + (f/f_{ri})^2} + B,$$
(1)

where α is the sound absorption coefficient and f the frequency of sound; f_{ri} and A_i are the relaxation frequency and amplitude, respectively, for the *i*th relaxation process; B is the high frequency value of α/f^2 . The relaxation frequency f_{ri} is related to the relaxation time τ_i as $\tau_i^{-1} = 2\pi f_{ri}$. The absorption parameters f_{ri} , A_i , and B are usually obtained by fitting the absorption data to Eq. (1). In the studies of systems involving multiple coupled equilibria, however, one is often faced with the problem that the absorption spectra cannot be readily analyzed in terms of relaxation processes because of a distribution of the relaxation times. The first problem in practice is to specify the number of relaxation processes, for it is always possible to obtain slightly better fit to the data by increasing the number of computed relaxation processes. On the other hand, to fit the data to the minimum possible number of relaxation times might eliminate a very real, but lowamplitude, relaxation process.² According to Rassing and Lassen's simulation analysis,³ it is hardly possible to detect the presence of two relaxation effects unless $f_{r1}/f_{r2} > 4$ and $0.25 < A_1/A_2 < 4$. The second problem is that one must determine, in general, (2m + 1) unknown parameters (m relaxation frequencies, m relaxation amplitudes, and B) for the analysis of an experimental absorption curve. As the number of unknown parameters increases with the number of coupled equilibria, the reliability of the values determined decreases rapidly. Therefore, an independent method of determination of the relaxation amplitudes considerably facilitates the relaxation analysis.

In the previous paper,⁴ we derived a general expression of the ultrasonic relaxation amplitudes for coupled chemical equilibria and proposed a method of simulation analysis which consists of calculating the expected relaxation frequencies and amplitudes of a given or postulated reaction mechanism using estimated or trial values of the rate constants and volume changes and of comparing the computed absorption α/f^2 directly with the experimental one. In the present work, we shall examine the validity of the method by applying it to the analysis of ultrasonic absorption in aqueous zinc(II)-thiocyanate solutions. The system was chosen because it gives large ultrasonic absorption over fairly wide concentration range and the complexation equilibria in the system have been comparatively well known.^{5,6} The main purpose of this work is to demonstrate the use of the new method of analysis through the kinetic treatment of the absorption data.

II. EXPERIMENTAL

All chemicals used were of reagent grade. Sample solutions were prepared by dissolving $Zn(NO_3)_2 \cdot 6H_2O$ and NaSCN into distilled water and by adjusting the pH with HNO₃. The ionic strength *I* of the solutions was kept at 3 by the addition of NaNO₃.

The send-receive pulse technique was used for all ultrasonic absorption measurements. A Matec 6600 pulse modulator and receiver with different plug-in units, 1204B master synchronizer, and 666B rf pulse comparator furnished the basic electronics. The plug-in unit used were models 755 (1–

TABLE I. Experimental conditions⁴ and ultrasonic absorption parameters calculated from the reaction parameters in Table II.

Sample	ΣZn	ΣSCN		ρ	c	f_{r1}	f_{n}	f_{r3}	ſ.,4	A ₁	<i>A</i> ₂	A ₃	A ₄	В	
No.	(M	I)	рН	(g cm ⁻³)	(m s ⁻¹)		(N	(Hz)	<u></u>		<u></u>	$(10^{-17} \text{cm}^{-1})$	s ²)		rms %°
1	0.100	0.100	4.6	1.1567	1622	79	32.8	12.4	1.85	0.3	0.5	93.8	488	21.5	3.3
2	0.200	0.100	4.5	1.1563	1614	75	33.2	12.8	2.28	0.4	0.5	105	352	23.2	1.3
3	0.200	0.200	2.5	1.1568	1612	87	32.9	13.7	2.35	1.6	4.2	336	607	21.9	2.4
4	0.200	0.200	3.5	1.1571	1611	87	32.9	13.7	2.35	1.6	4.2	336	607	21.9	1.9
5	0.200	0.200	4.6	1.1574	1615	87	32.9	13.7	2.35	1.6	4.2	336	608	21.0	2.0
6	0.200	0.400	4.4	1.1591	1618	107	36.2	15.3	2.56	4.4	27.6	850	1038	21.5	2.2
7	0.200	0.600	4.2	1.1605	1609	124	41.4	16.6	2.85	5.6	59.7	1197	1447	21.5	2.0
8	0.200	0.800	3.9	1.1598	1607	141	47.3	17.7	3.19	5.4	83.5	1355	1765	21.7	2.4
9	0.0500	1.00	4.5	1.1447	1626	203	67.3	20.7	4.71	0.5	20.3	303	487	23.3	1.7
10	0.100	1.00	4.3	1.1493	1621	185	61.3	19.4	4.18	1.4	44.0	702	1159	25.3	1.9
11	0.200	1.00	4.1	1.1578	1608	158	53.7	18.9	3.60	4.4	94.2	1346	1863	23.4	2.6
12	0.200	1.50	3.9	1.1459	1608	207	72.7	23.3	5.07	1.7	81.1	861	1124	22.0	2.4
13	0.200	2.00	4.3	1.1319	1611	263	97.0	30.7	7.21	0.5	54.0	385	381	22.7	2.1
14	0.200	2.50	4.2	1.1186	1611	322	125	40.3	9.74	0.1	34.1	163	119	22.6	2.9
15	0.400	0.100	4.6	1.1547	1601	71	33.9	13.3	3.16	0.3	0.3	93.7	155	23.5	2.0
16	0.400	0.200	4.6	1.1577	1602	79	33.0	14.7	3.02	1.5	3.1	286	213	22.9	1.8
17	0.400	0.400	4.3	1.1624	1607	94	34.6	17.0	2.92	5.6	29.6	709	270	22.7	1.9
18	0.400	0.800	3.7	1.1796	1608	119	42.9	19.8	3.10	11.8	139	1287	587	25.0	2.2
19	0.600	0.150	4.4	1.1555	1587	72	33.7	14.5	3.85	0.6	0.7	151	78.7	24.3	2.8
20	0.600	0.300	4.3	1.1604	1590	82	33.3	16.8	3.50	3.1	9.3	399	59.8	24.8	1.4
21	0.600	0.600	4.0	1.1690	1591	98	37.0	20.0	3.22	10.8	86.4	804	40.3	22.9	1.5
22	0.600	0.800	3.6	1.1850	1606	108	41.1	21.3	3.21	15.7	163	1002	69.1	24.2	2.2
23	0.800	0.200	4.4	1.1565	1574	73	33.7	15.9	4.37	1.0	1.5	190	25.6	25.3	2.7
24	0.800	0.400	4.2	1.1634	1581	83	33.9	19.0	3.82	5.0	21.3	444	1.3	25.2	2.0
25	0.800	0.800	3.8	1.1751	1583	101	40.2	22.4	3.40	17.0	164	760	6.0	22.5	2.4

* 25 °C and I = 3.

^b The rms % deviation between the computed and observed values of α/f^2 .

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FIG. 1. Ultrasonic absorption spectra of zinc(II)-thiocyanate solutions; $\Sigma Zn = 0.4$ and 0.8 M and $\Sigma Zn/\Sigma SCN = 1.0-4.0$, at 25 °C and I = 3. The number in brackets corresponds to the sample number in Table I. The solid curve expresses the α/f^2 value calculated from the absorption parameters in Table I.

20 MHz), 760 (10–90 MHz), and 765 (90–300 MHz). The design of ultrasonic cells, equipped with 20 mm diameter xcut quartz crystals as transducers, was similar to those described previously.⁷ The experimental frequency ranged from 3 to 260 MHz by using the odd harmonics of the quartz crystals of the fundamentals of 1, 5, and 20 MHz. The technique consists of displaying the received pulse train on an oscilloscope together with the standard pulse; the amplitude of the latter can be adjusted by means of the pulse comparator in decibels. Thus, with increasing the path length, the attenuation of the received pulse was measured by comparing the pulse amplitude with that of the standard pulse.

The calibration of the apparatus was carried out over



FIG. 2. Ultrasonic absorption spectra of zinc(II)-thiocyanate solutions; $\Sigma Zn = 0.2$ M and $\Sigma SCN = 0.1-0.8$ M, at 25 °C and I = 3. The number in brackets corresponds to the sample number in Table I. The solid curve expresses the α/f^2 value calculated from the absorption parameters in Table I.



FIG. 3. Ultrasonic absorption spectra of zinc(II)-thiocyanate solutions; $\Sigma Zn = 0.2$ M and $\Sigma SCN = 1.0-2.5$ M, at 25 °C and I = 3. The number in brackets corresponds to the sample number in Table I. The solid curve expresses the α/f^2 value calculated from the absorption parameters in Table I.

the entire frequency range by determining the absorption of various liquids—water, *n*-butyl alcohol, benzene, and carbon disulfide. The values of α/f^2 were constant within $\pm 5\%$ independent of *f*. The average values were 21.9×10^{-17} (35–260 MHz), 81.0×10^{-17} (7–140 MHz), 955×10^{-17} (3–19 MHz), and 5820×10^{-17} cm⁻¹ s² (3–19 MHz), for water, *n*-butyl alcohol, benzene, and carbon disulfide, respectively, at 25 °C. These values compare well with the corresponding literature values 22.0×10^{-17} , 81.3×10^{-17} , 940×10^{-17} , 10^{-17} cm⁻¹ s² (1–8 MHz).¹¹

The velocity of sound was measured at 3 MHz. The method consisted of giving a definite time delay ($\sim 10 \,\mu$ s) to the echo pattern on the oscilloscope by means of the delay function of 1204B and measuring the decrease of the path length which was required to return the leading edge of the first echo signal again at the same horizontal position as before the displacement. The calibration was carried out by the same experiments on water. The errors of the measurements were ± 3 m/s. The density of the solutions was determined by a Gay-Lussac pycnometer.

All the measurements were carried out at 25.00 ± 0.05 °C.

III. RESULTS AND DISCUSSION

Table I shows the experimental conditions together with the density ρ and the velocity of sound c. Here, ΣZn and ΣSCN denote the stoichiometric concentrations of zinc(II) and thiocyanate ions, respectively. As shown in Table I, the experiments were carried out over fairly wide concentration range of $\Sigma Zn = 0.05-0.8$ M and $\Sigma SCN = 0.1-2.5$ M, covering ligand-rich as well as metal-rich regions i.e., $\Sigma Zn/\Sigma SCN = 0.05-4$. All these solutions showed marked relaxation absorption. Representative sound absorption spectra are shown in Figs. 1-3.

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The relaxation absorption was observed in all the solutions containing zinc and thiocyanate ions, while blank solutions of either $Zn(NO_3)_2$ or NaSCN showed no discernible relaxation effect in the same frequency range. Variation of *pH* from 2.5 to 4.6 proved to have no observable effect on the absorption (see Table I). The above result indicates that the relaxation absorption under study is ascribed to the formation reactions of zinc(II) thiocyanate complexes, but neither to hydrolysis reaction of Zn^{2+} nor to protonation reaction of SCN⁻. According to the equilibrium studies,^{5,6} the following complex formation equilibria exist in solution under the present experimental conditions

$$\operatorname{Zn}(\operatorname{SCN})_{n-1}^{3-n} + \operatorname{SCN}^{-} \underset{k_{-n}}{\stackrel{\sim}{\Longrightarrow}} \operatorname{Zn}(\operatorname{SCN})_{n}^{2-n} K_{n}, \quad n = 1-4,$$
(2)

where K_n 's denote the equilibrium constants for the corresponding equilibria. There is no spectroscopic evidence for bridging through thiocyanate ions.¹² Therefore, the observed sound absorption may be associated with some or all of these complexation equilibria.

By including the four successive complexation equilibria in Eq. (2) and adopting the usual relaxation treatment, the reciprocal relaxation times $\lambda_i (= 1/\tau_i)$ are found to be the solutions of the secular equation

$$D(\lambda) = \begin{vmatrix} a_{11} - \lambda & a_{12} & a_{13} & a_{14} \\ a_{21} & a_{22} - \lambda & a_{23} & a_{24} \\ a_{31} & a_{32} & a_{33} - \lambda & a_{34} \\ a_{41} & a_{42} & a_{43} & a_{44} - \lambda \end{vmatrix} = 0.$$
(3)

By employing the equilibrium relations $K_n = k_n/k_{-n}$ (n = 1-4), the determinant elements a_{ii} 's are given by⁴

$$\begin{aligned} a_{11} &= k_1([Zn] + [SCN] + 1/K_1), \quad a_{12} &= k_1([Zn] - 1/K_1), \quad a_{13} = a_{14} = k_1[Zn], \quad a_{21} = k_2([ZnSCN] - [SCN]), \\ a_{22} &= k_2([ZnSCN] + [SCN] + 1/K_2), \quad a_{23} = k_2([ZnSCN] - 1/K_2), \quad a_{24} = k_2[ZnSCN], \quad a_{31} = k_3[Zn(SCN)_2], \\ (4) \\ a_{32} &= k_3\{[Zn(SCN)_2] - [SCN]\}, \quad a_{33} = k_3\{[Zn(SCN)_2] + [SCN] + 1/K_3\}, \quad a_{34} = k_3\{[Zn(SCN)_2] - 1/K_3\}, \\ a_{41} &= a_{42} = k_4[Zn(SCN)_3], \quad a_{43} = k_4\{[Zn(SCN)_3] - [SCN]\}, \quad a_{44} = k_4\{[Zn(SCN)_3] + [SCN] + 1/K_4\}, \end{aligned}$$

where the square brackets indicate the molar concentration at equilibrium, and where the charges of the ions are omitted for the sake of simplicity. Solving Eq. (3) and noting that $\lambda_i = 2\pi f_{ri}$, we may obtain four relaxation frequencies. Let them be f_{r1}, f_{r2}, f_{r3} , and f_{r4} ($f_{r1} > f_{r2} > f_{r3} > f_{r4}$).

The maximum excess absorptions per wavelength, $\mu_{\max,i}$, corresponding to f_{i} are expressed by⁴

$$\mu_{\max,i} = \frac{\pi}{2RT\beta_s \lambda_i} \frac{\left\{ \sum_{n=1}^{4} (-1)^n r_n |M_{n1}(\lambda_i)| \Delta V_n \right\}^2}{\sum_{n=1}^{4} r_n |M_{n1}(\lambda_i)|^2}, \quad (5)$$

where R is the gas constant, T the absolute temperature, and β_s the adiabatic compressibility of the solution; ΔV_n is the adiabatic volume change of the *n*th step of Eq. (2); $|M_{n1}(\lambda_i)|$ is the minor of the determinant $D(\lambda_i)$ with respect to the *n*,1 element. Here, r_n is the exchange rate of the *n*th reaction

$$k_n = k_n [\text{Zn}(\text{SCN})_{n-1}] [SCN], \quad n = 1-4.$$
 (6)

The relaxation amplitude A_i of the *i*th relaxation process is given by

$$A_i = 2\mu_{\max,i}/(f_{ri}c). \tag{7}$$

Therefore, using trial values of the rate constants k_n 's and the volume changes ΔV_n 's, we can calculate the relaxation frequencies f_n 's and the relaxation amplitudes A_i 's through Eqs. (3)-(7), and then α/f^2 by Eq. (1) (with appropriately determined values of B). Thus, we may compare the computed values of α/f^2 with the experimentally obtained values at all the frequencies and over all the solutions studied. The equilibrium constants used are given in the footnote of Table II. The simulation analysis was carried out on computer by iterating the eight adjustable parameters k_n and ΔV_n (n = 1-4). The adjustable parameters were optimized by minimizing the rms percentage deviation between the computed and observed values of α/f^2 . Here, the B values in Eq. (1) were determined so as to give the best fit of the absorption data of the individual spectra to Eq. (1). The actual fitting procedure was as follows. First, the absorption data in the metal-rich concentration region $(\Sigma Zn/\Sigma CN \ge 1)$ were taken and fitted to the double-relaxation equation based on the first two successive complexation equilibria [i.e., n = 1and 2 in Eq. (2)]. Thus, the approximate values of the parameters $k_1, k_2, \Delta V_1$, and ΔV_2 were determined. Second, with the parameters thus obtained and by adjusting the rest of the parameters (i.e., k_3 , k_4 , ΔV_3 , and ΔV_4), all the absorption data were fitted to the quadruple-relaxation equation associated with the four successive complexation equilibria. Finally, all the eight parameters were readjusted around the approximate values so as to give the best fittings. Simultaneously, the values of the four equilibrium constants K_1, K_2 , K_3 , and K_4 were also adjusted within the reported error intervals.

As shown in Figs. 1-3, the calculated α/f^2 values agree well with the experimental values in the whole frequency

TABLE II. Rate constants and volume changes for the formation of zinc(II) thiocyanate complexes at 25 °C and I = 3.^a

n ^b	$k_n(\mathbf{M}^{-1}\mathbf{s}^{-1})$	$k_{-n}(s^{-1})$	$\Delta V_n (\text{cm}^3 \text{ mol}^{-1})$
1	$(3.6 \pm 0.3) \times 10^7$	$(7.0 \pm 0.6) \times 10^{6}$	4.0 + 0.2
2	$(1.49 \pm 0.03) \times 10^{8}$	$(7.3 \pm 0.2) \times 10^7$	11.5 + 0.2
3	$(5.4 \pm 1.1) \times 10^{8}$	$(3.8 \pm 0.8) \times 10^8$	10.8 + 0.5
4	$(6.4 \pm 1.8) \times 10^8$	$(2.3 \pm 0.7) \times 10^8$	4.6 ± 0.5

^a The equilibrium constants used (Ref. 6): $K_1 = 5.10 \pm 0.03$, $K_2 = 2.16 \pm 0.12$, $K_3 = 1.36 \pm 0.33$, and $K_4 = 2.13 \pm 0.61$, at 25 °C and I = 1.

^bThe number indicates the reaction step in Eq. (2).

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range studied; the rms % deviation for all the 498 data points is 2.2. Table I shows the values of the absorption parameters f_{ri} , A_i , and B thus determined, together with the rms % deviation for the individual spectra. The values of the rate constants and volume changes obtained are shown in Table II. The contribution to the relaxation absorption of the individual complexation equilibria can be realized from the uncertainty intervals (99.7% confidence areas) of the pertinent reaction parameters.

Alternative mechanisms, which consist of less number of the equilibria in Eq. (2), were also tested, unsuccessfully. The double-relaxation equation based on the first two successive complexation equilibria cannot express even the absorption data in the metal-rich concentration region (the rms % deviation = 4.3). The triple-relaxation equation associated with the first three successive complexation equilibria, although explaining the absorption data in the metalrich concentration region fairly well, cannot express all the absorption data studied (the rms % deviation = 5.5). Thus, the mechanism adopted in this study, consisting of the four coupled complexation equilibria, proved to be the simplest reaction mechanism for interpreting the absorption data.

For comparison, the absorption data were analyzed as usual by fitting the data to Eq. (1), with f_{ri} , A_i , and B as adjustable parameters. Here, a nonlinear least squares routine, in which the rms % deviation between the computed and observed values of α/f^2 is minimized, was employed. The absorption spectra of the solutions in the metal-rich concentration region can be fitted to the single-relaxation equation, while the spectra of the other solutions need the double-relaxation equation for fitting. In the latter case, however, the obtained relaxation parameters involve rather large uncertainties. Therefore, an analysis with further increase in number of the computed relaxation processes is practically not feasible. The values of the relaxation frequencies thus obtained increase as a whole with an increase of either the metal or ligand concentration, analogous to the f_{ri} values in Table I. Those values lie between the f_{r_2} and f_{r_4} values in Table I and may represent, in a sense, some mean relaxation frequencies.¹³

The k_1 value in Table II is quite reasonable when compared with the rate constant $(2.8-15) \times 10^7 \,\mathrm{M^{-1} \, s^{-1}}$ (at 20-25 °C and I = 0.1 - 0.2) of the reactions of Zn^{2+} with univalent anionic ligands such as glycinate^{14,15} and murexide.¹⁶ Unfortunately, the lack of the similar studies in this field¹⁷ prevents the comparison of the other k_n values in Table II with the values from different sources. However, the increasing association rate of thiocyanate ion with the higher complexes is likely to be in line with the similar tendency¹⁸ indicated by the formation of the cadmium(II) cyanide complexes Cd(CN)⁺ and Cd(CN)₃⁻. As expressed by Eqs. (5) and (7), the relaxation amplitude A_i is proportional to the squares of the linear combination of ΔV_n 's, the signs of which, therefore, cannot be determined by absorption measurement alone. The ΔV_n values in Table II were obtained by assigning a positive value to ΔV_1 . These values in Table II are reasonable compared with the ΔV 's found for the association of bivalent metal ions with anionic ligands.¹⁵

The present work shows that the relaxation absorption in zinc(II)-thiocyanate solutions can be explained by a reaction mechanism consisting of the four coupled complexation equilibria. Through this investigation, we consider that the validity of the present method of analysis is well confirmed. The method will provide an effective means for the analysis of the ultrasonic absorption spectra which are associated with multiple coupled equilibria and accordingly too broad to be separated to discrete processes by the usual method of analysis.

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