diagram. Region IV contains multiplicity of two solutions given by an unstable focus and an unstable solution.

The boundary line with D = 0 is characterized by a pair of real eigenvalues with one being equal to trace and the other a simple zero eigenvalue. So the stability of the solution is determined by the sign of trace. The line characterized by T = 0 with D < 0possesses two pure imaginary complex eigenvalues, and each such steady-state solution represents a center point. These solutions can be called as neutrally stable solutions with nonvanishing finite imaginary parts. The curve having the discriminant $\Delta = 0$ and nonzero trace is a locus of solutions with only eigenvalue equal to half the trace. So it follows that the stability of such solutions is governed by the sign of trace. We may add to our discussion that when the curves T = 0 and D = 0 cross each other, the intersection point is where homoclinic bifurcation can occur.

The stability exchange takes place when the trace and determinant change signs. For T < 0 and D > 0 the solution is termed as stable. As trace changes sign from negative to positive, the system crosses through the Hopf bifurcation point at T = 0 and later goes into the limit cycle region. Another possible bifurcation occurs as trace remains negative and determinant changes sign from positive to negative. The system with T > 0 and D > 0 can also bifurcate to a state where determinant changes sign, with trace remaining positive. The last two states give rise to unstable states, and no further possibility of exchange exists between them. The two types of chemical instabilities⁵ occur when following conditions are met: when a stable steady-state solution identified by the condition T < 0 and D > 0 changes as $T \rightarrow -0$ with determinant sign remaining unchanged, one type of instability sets in, whereas the other type of instability occurs when $D \rightarrow +0$ and trace remains negative. In other words, this also implies that the circle traced out by the eigenvalues in the Im λ -Re λ plane as the bifurcating parameter changes lies entirely to the left half of the imaginary axis. A typical solution diagram $(x_s \text{ versus } Da_1)$ obtained by using the DERPAR routine⁴ is shown in Figure 2. The



Figure 2. Solution diagram showing bistability.

model in its present form has also been tested for the occurrence of isolated families of solutions in the form of isola or mushroom by using the criterion as discussed.⁴ It was observed that no such features are possible for the present model in the realistic ranges of parameter values.

Conclusion

The bifurcation analysis has been carried out for the Encillator model and the conditions for occurrence of instabilities are derived. The analysis shows variety of features like multiplicity, unstable and stable oscillatory solutions, unique stable and unstable states, saddle points, points of homoclinic bifurcation, locus of two types of instabilities, etc. The solution diagram, however, shows that bistability is predominant, in the parameter region where a solution for the condition determinant equal to zero exists.

Ultrasonic Absorption Study of the Complex Formation of Cadmlum(II) Carboxylates in **Aqueous** Solution

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Ultrasonic absorption of aqueous cadmium(II) acetate, propionate, and n-butyrates has been measured with a pulse technique over the frequency range 3-260 MHz. The single relaxations observed in the metal-rich concentration regions are attributed to the complex formation of cadmium(II) carboxylates via the Eigen-Tamm mechanism of stepwise association. The reaction parameters are determined from the concentration dependences of the relaxation frequency and amplitude. The association constant for outer-sphere complexing and the rate constant for ligand substitution lie in the ranges 0.91-1.14 and (4.1-5.4) \times 10⁸ s⁻¹, respectively, both being almost independent of the nature of the carboxylate ions, in contrast to the case of zinc(II) carboxylates previously reported. The volume changes of the outer-sphere complexing and those of the ligand substitution are determined to be 1.7-2.4 and 4.6-6.7 cm³ mol⁻¹, respectively; these values are very different from those of cadmium(II) thiocyanate reported earlier.

Introduction

The ultrasonic absorption method has been used extensively in kinetic studies of fast reactions in solution.¹ Specifically, a large number of ultrasonic relaxation studies in solution have involved metal-complexation phenomena,² and most of the relaxations have been successfully interpreted in terms of the stepwise association picture proposed by Eigen and Wilkins.³

In a recent paper,⁴ we reported the results of the ultrasonic absorption studies on aqueous zinc(II) formate, acetate, and propionate. We noted that the absorption data correlate well with the complexation mechanism of stepwise association wherein some ligand dependences are observed in both the association constant for outer-sphere complexing and the rate constant for ligand substitution. However, a definite conclusion has not been reached

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 Stuchr, J.; Yeager, E. Physical Acoustics; Mason, W. P., Ed.; Aca-

demic Press: New York, 1965; Vol. II, Part A, p 351.

⁽³⁾ Eigen, M.; Wilkins, R. G. Adv. Chem. Ser. 1964, 49, 55. (4) Tamura, K. J. Phys. Chem. 1989, 93, 7358.



Figure 1. Ultrasonic absorption spectra of aqueous cadmium(II) acetate solutions, at 25 °C and I = 2 M. The number in parentheses corresponds to the sample number in Table I. The solid curves are the calculated single-relaxation curves. The arrows indicate the relaxation frequencies.

owing to the experimental uncertainties involved in these reaction parameters. Before pursuing this problem further, it would be worthwhile to carry out similar studies on cadmium(II) carboxylates, which are expected to show rather *normal* kinetic behavior compared with zinc(II) complexes.^{5,6} The present work is concerned with the ultrasonic absorption studies of aqueous cadmium(II) acetate, propionate, and *n*-butyrate. Absorption in aqueous cadmium(II) formate was not large enough to obtain data covering a sufficiently wide concentration range for the kinetic analysis. Another purpose of this work is to compare the result with that of aqueous cadmium(II) thiocyanate reported earlier,⁶ where the volume change of the outer-sphere complexing showed a fairly large negative value.

Experimental Section

All chemicals used were of reagent grade. Sample solutions of cadmium(II) acetate or propionate were prepared by dissolving $Cd(NO_3)_2$ ·4H₂O and the corresponding sodium carboxylate, i.e., $CH_3CO_2Na\cdot 3H_2O$ or $C_2H_5CO_2Na$, in distilled water. Solutions of cadmium(II) *n*-butyrate were made up from $Cd(NO_3)_2$ ·4H₂O and stock solution of sodium *n*-butyrate, which was prepared from *n*-butyric anhydride through hydrolysis and neutralization by the addition of concentrated NaOH solution. The ionic strength, *I*, of the solutions was kept constant at 2 M by the addition of NaNO₃. The pH of the solutions was adjusted with HNO₃ and/or NaOH.

The ultrasonic absorption was measured by the pulse technique over the frequency range 3-260 MHz and the velocity of sound at 3 MHz. The details of the measurements have been described previously.^{4,5} The absorption coefficient at each frequency was determined by the average of at least three measurements; the experimental reproducibility was within $\pm 2\%$.

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

Results and Discussion

The experimental conditions are summarized in Table I, where Σ Cd and ΣX denote the stoichiometric concentrations of cadmium(II) and carboxylate ions, respectively; ρ is the density and c the velocity of sound. Representative sound absorption spectra



Figure 2. Ultrasonic absorption spectra of aqueous cadmium(II) propionate solutions, at 25 °C and I = 2 M. The notations and remarks are the same as in Figure 1.



Figure 3. Ultrasonic absorption spectra of aqueous cadmium(II) *n*butyrate solutions, at 25 °C and I = 2 M. The notations and remarks are the same as in Figure 1.

are shown in Figures 1-3. All the absorption spectra can be expressed by the single-relaxation equation

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

where α is the absorption coefficient and f the frequency of sound; f_r and A are the relaxation frequency and amplitude, respectively; B is the high-frequency value of α/f^2 . The absorption parameters f_r, A, and B were determined by fitting the data to eq 1 with a least-squares routine⁶ and are listed in Table I. Table I as well as Figures 1-3 indicate an apparent trend of the spectra. That is, compared at the same stoichiometric composition and pH, the relaxation amplitude is larger with the higher carboxylate; a similar trend was observed also with aqueous zinc(II) carboxylates.⁴

As shown in Table I, the experiments were carried out in the concentration ranges of $\Sigma Cd = 0.1-0.8$ M and $\Sigma X = 0.1-0.3$ M, where the concentration ratio $\Sigma Cd/\Sigma X$ was selected as high as possible to minimize the formation of higher complexes. The pH range of the measurements was 4-6, with most of the experiments carried out near pH 6. With the above pH range, hydrolysis of cadmium ion⁷ and absorption due to the dissociation equilibrium

⁽⁵⁾ Tamura, K. J. Chem. Phys. 1985, 83, 4539.

⁽⁶⁾ Tamura, K. J. Phys. Chem. 1987, 91, 4596. The error intervals of the reaction parameters shown in Table II of this paper are found to be in error owing to an over-simplified method of calculations. The corrected error intervals (99.7% confidence area) are as follows: $K_{12} = 1.05 \pm 0.41$, $K_{23} = 23.4 \pm 9.6$, $k_{22} = (4.8 \oplus 1.5) \times 10^8$ s⁻¹, $k_{32} = (2.1 \pm 0.2) \times 10^7$ s⁻¹, $\Delta V_{12} = -5.8 \oplus 3.2$ cm³ mol⁻¹, and $\Delta V_{23} = 10.6 \pm 3.0$ cm³ mol⁻¹; the error intervals of the volume changes include the effects of the uncertainties involved in K_{12} and K_{23} .

 ⁽⁷⁾ Matsui, H.; Ohtaki, H. Bull. Chem. Soc. Jpn. 1974, 47, 2603. Barnum,
 D. W. Inorg. Chem. 1983, 22, 2297.

TABLE I: Experimental Conditions and Ultrasonic Absorption Parameters^a for Aqueous Cadmium(II) Carboxylate Solutions at 25 °C and I = 2.0 M

5	sample	ΣCd, M	ΣΧ, Μ	pН	ρ , g cm ⁻³	<i>c</i> , m s ^{−1}	$f_{\rm r}$, MHz	$10^{17}A$, cm ⁻¹ s ²	$10^{17}B$, cm ⁻¹ s ²
					Aceta	te			
	1	0.100	0.100	6.00	1.1111	1578	13.3 ± 0.5	118 ± 5	22.3 • 0.3
	2	0.200	0.100	5.00	1.1142	1565	19.2 ± 0.8	73 ± 2	23.2 ± 0.3
	3	0.200	0.100	5.99	1.1157	1567	17.8 ± 0.8	85 ± 3	23.4 ± 0.4
	4	0.200	0.150	6.00	1.1174	1571	19.4 ± 0.6	127 ± 3	23.4 ± 0.4
	5	0.200	0.200	4.00	1.1145	1569	17.4 ± 0.6	97 ± 3	23.2 ± 0.3
	6	0.300	0.150	6.00	1.1218	1563	22.8 ± 0.8	97 ± 2	24.1 ± 0.4
	7	0 300	0 200	5 99	1 1 2 3 7	1563	22.0 ± 0.0	139 ± 3	256 ± 0.4
	8	0 400	0.200	3.98	1 1219	1550	27.6 ± 1.2	$\frac{100}{63+2}$	23.0 ± 0.4 24.4 ± 0.5
	ğ	0 400	0.200	5 00	1 1268	1553	26.4 ± 1.1	99 + 3	256 ± 0.6
	าด์	0 400	0.200	6.00	1 1278	1553	269 ± 10	104 + 2	25.3 ± 0.5
	11	0.500	0.200	5.98	1 1316	1543	301 ± 0.8	83 ± 1	25.5 ± 0.5 257 + 0.4
	12	0.600	0.200	6.00	1 1 3 4 8	1532	31.7 ± 1.5	72 + 2	25.7 ± 0.4
	13	0.700	0.200	5.91	1 1375	1519	330 ± 15	60 ± 1	20.0 ± 0.0
	140	0.200	0.200	5.80	1 1 5 4 4	1574	39.7 ± 1.4	52 ± 1	27.2 ± 0.0
	150	0.800	0.200	5.80	1 1 5 8 6	1525	36.2 ± 1.7	32 ± 1 97 ± 3	20.8 ± 0.4
	15	0.800	0.300	5.80	1.1500	1525	50.6 ± 1.2	0/ ± 2	29.3 ± 0.7
					Propion	ate			
	16	0.100	0.100	5.99	1.1113	1579	10.9 ± 0.4	192 ± 8	23.1 ± 0.3
	17	0.200	0.100	6.02	1.1174	1571	15.6 ± 0.4	126 ± 3	23.2 ± 0.3
	18	0.200	0.150	6.00	1.1177	1575	14.7 ± 0.4	214 ± 5	24.6 ± 0.3
	19	0.200	0.200	5.00	1.1179	1572	14.5 ± 0.2	261 ± 4	25.6 ± 0.3
	20	0.300	0.150	6.00	1.1219	1563	18.8 ± 0.6	147 ± 4	24.9 ± 0.5
	21	0.300	0.200	6.01	1.1255	1566	18.2 ± 0.5	211 ± 5	26.6 ± 0.5
	22	0.400	0.200	3.99	1.1215	1547	21.9 ± 1.0	$90. \pm 3$	25.3 ± 0.5
	23	0.400	0.200	5.00	1.1250	1552	21.7 ± 0.6	148 ± 3	26.1 ± 0.5
	24	0.400	0.200	6.01	1.1279	1552	23.3 ± 0.8	144 ± 3	265 ± 0.5
	25	0.500	0.200	6.00	1 1317	1547	25.5 ± 0.8	119 + 3	26.2 ± 0.5
	26	0.600	0 200	5.00	1 1 3 3 3	1532	28.7 ± 0.0 28.7 ± 1.2	90 + 2	27.2 ± 0.3
	27	0.600	0.200	6.01	1 1352	1534	27.0 ± 0.9	101 ± 2	27.3 ± 0.7 28.2 ± 0.6
	28	0.700	0.200	6.00	1 1 380	1525	30.2 ± 1.0	84 ± 2	20.2 ± 0.0 27 3 ± 0.5
	290	0.800	0.200	4 99	1 1535	1525	34.0 ± 1.3	69 ± 1	27.3 ± 0.5 27.4 ± 0.5
	30	0.800	0.200	6.01	1 1532	1523	37.0 ± 1.5	73 ± 7	27.4 ± 0.5
	314	0.800	0.200	6.00	1 1575	1523	315 ± 0.8	110 - 2	20.1 ± 0.0
	51	0.000	0.500	0.00	1.1575.	1551	51.5 ± 0.8	119 ± 2	50.0 ± 0.5
					n-Butyr	ate			
	32	0.100	0.100	5.01	1.1115	1579	9.5 ± 0.2	224 ± 6	23.0 ± 0.3
	33	0.200	0.100	5.00	1.1161	1571	13.9 ± 0.5	145 ± 5	23.8 ± 0.3
	34	0.200	0.100	6.00	1.1165	1573	13.5 ± 0.4	169 ± 5	23.7 ± 0.3
	35	0.200	0.200	4.00	1.1152	1574	13.8 ± 0.4	170 ± 5	24.2 ± 0.3
	36	0.300	0.100	6.01	1.1199	1560	16.3 ± 0.7	124 ± 5	24.4 ± 0.4
	37	0.300	0.200	4.00	1.1192	1562	17.5 ± 0.6	141 ± 4	24.7 ± 0.4
	38	0.400	0.100	5.99	1.1231	1548	19.8 ± 0.7	89 ± 2	24.7 ± 0.4
	39	0.400	0.200	4.00	1.1250	1551	20.5 ± 0.7	120 ± 3	25.2 ± 0.4
	40	0.400	0.200	5.00	1.1305	1559	19.7 ± 0.4	120 ± 3 185 ± 3	26.8 ± 0.4
	41	0.400	0.200	6.01	1.1297	1562	20.2 ± 0.7	193 ± 5	26.9 ± 0.6
	42	0.500	0.200	5.00	1.1317	1548	22.4 ± 0.7	149 + 3	27.0 ± 0.5
	43	0.500	0.200	6.01	1.1320	1550	22.4 ± 0.6	157 + 3	268 + 05
	44	0.600	0.200	5 99	1.1348	1536	256 + 00	127 ± 3	20.0 ± 0.0
	45	0.700	0.200	6.01	1 1 3 9 5	1578	27.4 ± 1.0	122 ± 3 107 ± 2	27.0 + 0.6
	460	0.800	0.200	5 99	1 1 5 3 6	1525	282 + 00	107 ± 2 07 ± 7	27.9 ± 0.0 28.8 ± 0.4
	470	0.800	0.200	5.64	1 1612	1525	20.2 ± 0.9	74 ± 2	20.0 ± 0.4 21 0 ± 0.9
		0.000	0.300	5.04	1.1012	1352	20.7 ± 1.0	140 2 3	51.2 ± 0.8

"The error interval denotes the 99.7% confidence area. $^{b}I = 2.3$ M. $^{c}I = 2.2$ M.

TABLE II: Reaction Parameters^a for the Formation of Cadmium(II) Carboxylates at 25 °C and $I = 2 M^b$

ligand	K ₁₂	K ₂₃	$10^{-8}k_{23}$, s ⁻¹	$10^{-7}k_{32}$, s ⁻¹	$\Delta V_{12},$ cm ³ mol ⁻¹	$\Delta V_{23},$ cm ³ mol ⁻¹
CH ₃ CO ₂ -	0.91 ± 0.40	12.2 ± 5.8	5.4 ± 2.0	4.4 ± 0.5	2.3 ± 2.4	4.6 ± 1.9
C ₂ H ₅ CO ₂ -	1.14 ± 0.31	13.9 ± 4.1	4.2 ± 0.9	3.0 ± 0.2	2.4 ± 1.8	5.6 ± 1.3
<i>n</i> -C ₃ H ₇ CO ₂ ⁻	1.01 ± 0.32	14.8 ± 5.1	4.1 ± 1.1	2.7 ± 0.2	1.7 ± 2.8	6.7 ± 2.2

^aThe error intervals denote 99.7% confidence area. ^bThe equilibrium constants used are the following: $pK_H = 4.59$, $^{10}K_1 = 12 \pm 1$, $K_2 = 4.1 \pm 0.5$, and $K_3 = 2.5 \pm 0.4$, ⁹ for the cadmium(II) acetate system; $pK_H = 4.73$, $^{10}K_1 = 17 \pm 1$, $K_2 = 3.7 \pm 0.5$, and $K_3 = 4.6 \pm 0.8$, ⁹ for the cadmium(II) propionate system; $pK_H = 4.69$, $^{10}K_1 = 16 \pm 1$, and $K_2 = 6.8 \pm 0.5$, ⁹ for the cadmium(II) *n*-butyrate system; the error intervals denote the standard errors. The pK_H values are those at 20 °C and I = 1 M.

of carboxylic acids can be ruled out. In fact, blank solutions, consisting of either cadmium nitrate or sodium carboxylates, showed no discernible relaxation effect in the frequency range 15–260 MHz. Under our experimental conditions, the following reaction equilibria can be considered:⁸⁻¹⁰

where H, M, and X denote hydrogen, cadmium, and carboxylate ions, respectively; the charges of the ions are omitted for simplicity.

(8) Perrin, D. D. Stability Constants of Metal-Ion Complexes; Pergamon Press: New York, 1983; Part B.

$$HX \rightleftharpoons H + X \qquad K_{H} \tag{2}$$

$$MX_{n-1} + X \rightleftharpoons MX_n \qquad K_n \ (n = 1-3) \tag{3}$$

(9) Filipovic, I.; Matsusinovic, T.; Mayer, B.; Piljac, I.; Bach-Dragutinovic, B.; Bujak, A. Croat. Chem. Acta 1970, 42, 541.

(10) Portanova, R.; Tomat, G.; Cassol, A.; Magon, L. J. Inorg. Nucl. Chem. 1972, 34, 1685.



Figure 4. Concentration dependence of f_r for aqueous cadmium(II) carboxylate solutions, at 25 °C and I = 2 M: (**①**) acetate; (**O**) propionate; (**①**) *n*-butyrate.

 $K_{\rm H}$ is the dissociation constant of carboxylic acid, and K_n 's (n = 1-3) are the equilibrium constants for the successive complexation equilibria. The values of K_n used are those by Filipovic et al.⁹ obtained from potentiometric studies and are given, together with the $pK_{\rm H}$ values,¹⁰ in the footnote of Table II. The equilibrium concentrations of all species in solution were calculated from the ΣCd , ΣX , and pH values in Table I; the pH value was converted to the hydrogen ion concentration by using the mean activity coefficient (0.86) of 2 M HNO₃ solution.¹¹ The results confirm that the concentrations of only species M, X, and MX are of a reasonable order of magnitude over all concentration ranges studied. Therefore, the relaxation absorptions under study can be ascribed mainly to the complexation equilibria of n = 1 in eq 3.

The complexation reactions via the stepwise association^{2,3} can be written as

$$M + X \stackrel{k_{12}}{\underset{k_{21}}{\leftarrow}} M(OH_2) \cdot X \stackrel{k_{23}}{\underset{k_{32}}{\leftarrow}} MX$$
(4)

where $M(OH_2)$.X is the outer-sphere complex of an ion pair with the metal ion and ligand still separated by one water molecule; MX is the inner-sphere complex. The ion-pair-formation process (the first step) reaches equilibrium much faster than the ligand-substitution process (the second step), so that the relaxation frequency is given by

$$2\pi f_{\rm r} = k_{23} \left\{ \frac{K_{12}([{\rm M}] + [{\rm X}])}{1 + K_{12}([{\rm M}] + [{\rm X}])} + \frac{1}{K_{23}} \right\}$$
(5)

where the square brackets indicate molar concentrations at equilibrium; $K_{12} (=k_{12}/k_{21})$ and $K_{23} (=k_{23}/k_{32})$ are the equilibrium constants of the first and second steps, respectively, of eq 4. If one includes the rapid dissociation equilibrium of carboxylic acids^{12,13} in the complexation mechanism, the metal ion concentration [M] in eq 5 should be divided by $(1 + \gamma)$ with $\gamma =$ [H]/([X] + $K_{\rm H}$).⁴ However, this effect has been ignored in eq 5 since the quantity γ is less than 8×10^{-3} under the experimental conditions studied. The overall complexation constant K_1 is given by $K_1 = K_{12}(1 + K_{23})$, which enables us to eliminate one of the parameters in eq 5. Thus, the observed f_r was fitted to eq 5 by using K_{12} and k_{23} as adjustable parameters. The results for the three reaction systems are shown in Figure 4, with the plots of $2\pi f_r$ vs ([M] + [X]). Each of the solid lines in the figure expresses the calculated f_r , which agrees well with the observed f_r in the entire concentration range studied; the root-mean-square (rms)



Figure 5. $(2RT\beta_{\mu}m/\pi\Gamma)^{1/2}$ vs $\{1 + K_{12}([M] + [X])\}^{-1}$ plot for aqueous cadmium(II) carboxylate solutions, at 25 °C and I = 2 M: (**①**) acetate; (**O**) propionate; (**①**) *n*-butyrate.

percentage deviations between the calculated and observed values of f_r are 4.7, 3.6, and 3.5 for the acetate, propionate, and *n*-butyrate systems, respectively. The reaction parameters determined are shown in Table II.

As shown in Figure 4, the calculated f_r agrees uniformly well with the observed f_r in the pH range 4-6, for all three reaction systems. This result implies that the rate constant k_{23} in eq 5 is, within experimental error, independent of the hydrogen ion concentration. Thus, the major contribution to the relaxations is attributable to the complex formation through the reaction path involving the metal and carboxylate ions (as shown in eq 4), and it does not include the contribution from a pathway via the reaction between the metal ion and the neutral ligand HX.

Table II shows that the values of the association constant K_{12} of the outer-sphere complex and the rate constant k_{23} of the ligand substitution lie in the narrow ranges 0.91–1.14 and $(4.1-5.4) \times$ 10^8 s⁻¹, respectively. These values are close to the corresponding values obtained earlier for aqueous cadmium(II) thiocyanate, i.e., $K_{12} = 1.05$ and $k_{23} = 4.8 \times 10^8 \,\mathrm{s}^{-1}$ (at 25 °C and $I = 3 \,\mathrm{M}$).⁶ The above results indicate the following: In the first place, the independence of K_{12} on the nature of ligand supports the previous argument⁴ that the high ionic strength adopted in these studies does not affect the activity coefficient factors of the systems in different ways for the different carboxylate ions. In the second place, the independence of the rate constant k_{23} on the nature of ligand is very consistent with Eigen and Tamm's concept; the rate of formation of the inner-sphere complex is controlled by the rate of release of a water molecule from the inner coordination sphere of the metal and thus is nearly independent of the nature of the entering ligand. The above results are in contrast to those obtained previously for zinc(II) formate, acetate, and propionate systems, where the reaction parameters are found to vary significantly, i.e., $K_{12} = 1.1 - 1.8$ and $k_{23} = (6.7 - 11.8) \times 10^7 \text{ s}^{-1}$, and indicate a tendency that the association constant is larger while the rate constant smaller with the higher carboxylate. Thus, the kinetic behavior of zinc ion appears to be anomalous in this respect. However, a definite conclusion cannot be reached, as mentioned previously,⁴ owing to the uncertainties involved in these reaction parameters.

For the reaction scheme of eq 4, the maximum excess absorption per wavelength, μ_m (= $cAf_r/2$), is given by⁴

$$\mu_{\rm m} = \frac{\pi\Gamma}{2RT\beta_{\rm s}} \left\{ \frac{\Delta V_{12}}{1 + K_{12}([{\rm M}] + [{\rm X}])} + \Delta V_{23} \right\}^2 \tag{6}$$

with¹⁴

$$\Gamma = K_{12}K_{23}[M][X] \frac{1 + K_{12}([M] + [X])}{1 + K_1([M] + [X])}$$
(7)

where R is the gas constant, T the absolute temperature, and β_s

⁽¹¹⁾ Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed.; Butterworths: London, 1959; p 491.
(12) Sano, T.; Miyazaki, T.; Tatsumoto, N.; Yasunaga, T. Bull. Chem.

 ⁽¹²⁾ Sano, 1.; Miyazaki, 1.; Tatsumoto, N.; Yasunaga, T. Bull. Chem.
 Soc. Jpn. 1973, 46, 43.
 (13) Jackopin, L. G.; Yeager, E. Technical Report No. 35; ONR Contract

⁽¹³⁾ Jackopin, L. G.; Yeager, E. Technical Report No. 55; UNK Contract No. 1439(04), Project No. 384-305, Western Reserve University, 1969.

⁽¹⁴⁾ The expression for Γ is the reduced form of the previous one.⁴

the adiabatic compressibility of the solution; ΔV_{12} and ΔV_{23} are the reaction volume changes of the first and second steps, respectively, in eq 4. The observed μ_m was fitted to eq 6 by using ΔV_{12} and ΔV_{23} as adjustable parameters. The results are shown in Figure 5 with the plots of $(2RT\beta_s\mu_m/\pi\Gamma)^{1/2}$ vs $(1 + K_{12}([M]$ $+ [X])^{-1}$. Each of the straight lines expresses the calculated value, and the slope and intercept of the line correspond to the ΔV_{12} and ΔV_{23} values, respectively. The rms percentage deviations between the calculated and observed values of μ_m are 7.5, 5.7, and 7.3 for the acetate, propionate, and n-butyrate systems, respectively. The values of ΔV_{12} and ΔV_{23} determined in this manner are shown in Table II; the error intervals include the effects of the uncertainties involved in K_{12} and K_{23} .

The ΔV_{12} values in Table II lie in the range 1.7-2.3 cm³ mol⁻¹, which is almost similar to the values, ranging from -0.2 to +2.5cm³ mol⁻¹, obtained previously for zinc(II) carboxylates.⁴ It would be interesting to note that the above values, although involving relatively large uncertainties, are not far from the value 3.2 cm³ mol⁻¹ (at 25 °C and I = 0) estimated by Grant,¹⁵ using the Hemmes equation,¹⁶ for the 2-1 valent ion pairs. The ΔV_{23} values in Table II lie in the narrower range 4.6-6.7 cm³ mol⁻¹ than the values (4.7-10.5 cm³ mol⁻¹) for zinc(II) complexes.⁴ In this respect

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also, the result of the cadmium(II) complexes is more consistent with that expected from the model of simple liberation of a coordinated water molecule upon ligand substitution than that of the zinc(II) complexes. Compared with the common ligands of acetate and propionate, the ΔV_{23} values for the cadmium(II) complexes are less by 3-5 cm³ mol⁻¹ than those for the zinc(II) complexes. The result can be accepted since cadmium ion has a larger ionic radius than zinc ion and thus exerts weaker electrostriction on the coordinated water molecules than does zinc ion. On the other hand, the volume changes found earlier for cadmium(II) thiocyanate,⁶ i.e., $\Delta V_{12} = -5.8$ and $\Delta V_{23} = 10.6$ cm³ mol⁻¹, are very different from the corresponding values in Table II, even taking into account the difference of the ionic strengths adopted. Comparison of these values with those of Table II suggests a peculiarly contracted state of the outer-sphere complex of cadmium(II) thiocyanate.

The result of the present study shows that the complex formation of cadmium(II) carboxylates is normal in any respect from the viewpoint of Eigen and Tamm's concept. It makes the anomalies of the complexation of zinc(II) complexes more outstanding. Thus, we are convinced again of the importance of further studies on the complexation of zinc ion with the other ligands. The results of the studies will be reported succeedingly.

Registry No. Cadmium(II) acetate, 543-90-8; cadmium(II) propionate, 16986-83-7; cadmium(II) butyrate, 19657-13-7.

Effects of Mixing Mode and Stirring Rate on the Bistability of the $BrO_3^{-}/Br^{-}/Ce^{3+}$ System

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We report the effects of stirring and of six different modes of mixing the three reactant feedstreams of the BrO₃⁻/Br⁻/Ce³⁺ system on its bistability hystereses. Stirring and mixing have very different dynamical consequences since the former controls the reactor homogeneity while premixing allows one to explore otherwise inaccessible regions of parameter space by selectively initiating reactions between different pairs of reactants. One mixing mode leads to the development of a second hysteresis with an oscillatory branch.

Introduction

The effects of stirring rate^{1,2} and of the reactant mixing mode^{3,4} on chemical instabilities in continuous stirred flow reactors (CSTR) have shown that the idealized description of nonlinear dynamic systems by homogeneous models may fail to account for important dynamical behavior arising in real systems due to the coupling between chemical and hydrodynamic modes.

In the chlorite/iodide system, enhanced stirring¹ and feedstream premixing³ have similarly stabilizing effects on the bistability hysteresis. The oscillations, previously thought to be the signature

of the homogeneous system, were identified² as heterogeneous noise-induced structures that exist only in a small region of parameter space. Recently we reported⁴ a preliminary study of stirring and mixing (SM) effects on the bistability hysteresis of the minimal $BrO_3^{-}/Br^{-}/Ce^{3+}$ system, with flow rate as the control parameter, where two streams containing $(BrO_3^- + H_2SO_4)$ and $(Br^{-} + Ce^{3+} + H_2SO_4)$, respectively, were fed into the CSTR either through separate ports (non-premixed NPM) or premixed (PM). It was found, among other things, that enhanced stirring and reactant premixing leads to quite opposite and specific dynamical responses, the former shifting the hysteresis to lower flows while the latter moves the hysteresis to higher flow rates. In the present paper we extend the previous study by exploring the effects of six different sequences (modes) of mixing of the three reactant streams on the stirring dependence of the hysteresis. With three reactant streams, any of the three pairs can be combined into "partially premixed" PPM streams, and these binary flows can be further combined in a second premixer located slightly downstream from the first into a "totally premixed" PM single feedstream. Since some binary mixtures are clearly reactive, the choice of the premixed reactant pairs allows one to select one or another reaction sequence from several competing pathways. The

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 In the previous work, ⁴ the "NPM" mode employed (B + C) premixed attempts of the problem of the problem. (Paris)

externally in a bottle and pumped through a single channel, while here (B + C) was premixed in situ for ca. 0.5 s, depending on the flow rate.