Stability Constants of Some Metal Chelates in Mixed Solvent Systems

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The stability constants of Ni(II) acetylacetonates in methanol-, ethanol-, 1-propanol-, 2-propanol-, and dioxane-water and those for Co(II) acetylacetonates in methanol- and 1-propanol–water have been measured at 25° C. Linear relationships were shown when log K_1 or log K_2 was plotted vs. $1/D$. Also, the data have been discussed in terms of the effect of solvent on dissociation and chelation.

DISSOCIATION constants of acetylacetone have been determined in mixed solvent systems (9). The purpose of this work is to investigate in a similar manner the solvent effect on the stepwise formation of Ni(II) and Co(II) acetylacetonates in mixed solvent systems at 25° C. Acetylacetone was selected as the ligand because the resultant metal chelates are stable and readily soluble in the dielectric constant range 80 to 25.

MATERIALS

1-Propanol, 2-propanol, methanol, dioxane (Fisher Certified reagents), and ethanol (Commercial Solvents absolute) were used without further purification. Refractive indices at 25° C., n_D^{25}, agreed closely with reported values (15), corrected (temperature corrections were based on the empirical relation $dn_D/dt = -0.0004$ deg.) to the same temperature (3): 1-propanol, 1.3837 (1.3834); 2-propanol, 1.3756 (1.3756); methanol, 1.3267 (1.3268); dioxane, 1.4200 (1.4197); and ethanol, 1.3592 (1.3590).

Acetylacetone (2,4-pentanedione) and tetramethylammonium hydroxide (10% aqueous solution) were used without further purification. The boiling point range and the refractive index of acetylacetone were 135.5–6.5° C. and 1.4520, respectively. Stock solutions of tetramethylammonium hydroxide were prepared from the Kodak reagent by diluting distilled water and standardized with HCl solution. The nickel and cobalt perchlorate hexahydrates (analytical reagent grade) were obtained from the G. Frederick Smith Co. Stock solutions of these perchlorates were prepared from the above reagents as received, and then the exact concentrations of the metal ions were determined by standardizing them with EDTA solution (Fisher Certified) using murexide as an indicator (18).

The sodium perchlorate (G. Frederick Smith Co.) assay was accomplished by using an ion exchange technique. Sodium ion was exchanged for hydrogen ion on a purified Dowex resin column, and the eluted solution was titrated against sodium hydroxide (Fisher Certified), which had been previously standardized against potassium acid phthalate. Doubly distilled, lead-free perchloric acid (G. Frederick Smith Co.) was used without further purification. Distilled water was used throughout for preparation of aqueous solutions. Standard buffers (pH 2.0, 4.0, 7.0, and 10.0) were obtained from Beckman Scientific Co.

Although the reagents used were previously shown (9–11) to be of sufficient purity for titration studies, an additional precaution was taken. The two-titration method by Calvin and Wilson (5), and modified by Calvin and Melchior (6), was used to eliminate possible errors due to contamination of the reagents used. A possible trace impurity would cause a displacement of both reference and chelate curve and hence cancel out.

Apparatus. The hydrogen ion concentration was determined at 25° ± 0.1° C. with a Beckman Model G pH meter equipped with a glass-saturated calomel electrode system. The glass electrode was the Beckman, Type E-2, No. 40495 which covers the pH range 0 to 14, and the temperature range 15° to 80° C. The reference electrode was the Beckman fiber type saturated calomel No. 39170 with temperature range −5° to 90° C.

The temperature of the constant temperature water bath was checked with a thermometer calibrated by the National Bureau of Standards.

Calibration of Electrodes. The term pH has significance only in aqueous medium. Retaining the terminology of Van Uitert (17), all pH readings taken in mixed solvents will hereafter be called B values. To determine hydrogen ion concentration in mixed solvent systems, it was necessary to calibrate the electrodes and pH meter for the various solvent mixtures with solutions of known hydrogen ion concentration and constant ionic strength.

Into each of seven 50-ml. volumetric flasks were placed 8.62 ml. of 0.05M HCl and 2.00 ml. of 0.22M NaCl. Organic solvent was added to the respective flasks in the order; 0.00, 10.00, 20.00, 25.00, 30.00, 35.00, and 40.00 ml. Each solution was then diluted to the mark at the equilibrium temperature by a measured volume of water delivered at room temperature. The ionic strength, u, in each flask was then 0.0172.

The solution was transferred to a reaction flask and allowed to attain constant temperature and ionic equilibrium before taking B values from the meter. This procedure was followed for each of the five different organic solvents used in these determinations.

Determination of Dissociation Constant of Acetylacetone. Into each of seven 50-ml. volumetric flasks were transferred 5.00 ml. of 0.34M acetylacetone and 3.90 ml. of 0.22M tetramethylammonium hydroxide. Organic solvent was added to the respective flasks in the order: 0.00, 10.00, 20.00, 25.00, 30.00, 35.00, and 40.00 ml. Each solution was diluted to the mark at constant temperature by a measured volume of water delivered at room temperature. These solutions were freshly prepared before use, because they were not stable over long periods of time.

A B value for each solution was determined after equilibrium was reached in the reaction flask.

Determination of Stability Constant. The experimental procedure used in the present work for the determination of dissociation constant of acetylacetone has been described (9).

The method developed by Calvin and Wilson (5), then modified by Calvin and Melchior (6), was used for determining the successive stability constants. Two potentiometric titration curves were required for determining the stability constants for metal acetylacetonates at each solvent composition: titration of perchloric acid and acetylacetone with base in the absence of metal ions, and titration of perchloric acid and acetylacetone with base in the presence of metal ions.

The following amounts of stock solutions were added to each of seven 100-ml. volumetric flasks: without metal

ions, 2.50 ml. of $0.40M$ HClO$_4$; 3.70 ml. of $0.20M$ NaClO$_4$; 10.00 ml. of $0.85M$ acetylacetone; with metal ions, 2.50 ml. of $0.40M$ HClO$_4$; 7.09 ml. of $0.03M$ metal perchlorate; 10.00 ml. of $0.85M$ acetylacetone.

Organic solvent was added to the flasks in both groups in the order: 0.00, 20.00, 40.00, 50.00, 60.00, 70.00, and 80.00 ml. All additions were made at room temperature. Each solution was diluted to the mark with water when the solutions attained constant temperature. The ionic strength in each flask was then 0.0172. The solutions were then titrated with $0.99M$ NaOH.

DISCUSSION

The equilibria involved in the determination of stability constants of metal acetylacetones are

$$HA \rightleftharpoons H^+ + A^- \qquad (1)$$

and

$$M^{2+} + 2A^- \rightleftharpoons MA_2 \qquad (2)$$

where HA is acetylacetone, M^{2+} is either Ni(II) or Co(II) ion, and A^- is the acetylacetonate ion. Equation 2 represents the over-all reaction equilibrium which can be considered to involve two stepwise reactions:

$$M^{2+} + A^- \rightleftharpoons MA^+ \qquad (3)$$

and

$$MA^+ + A^- \rightleftharpoons MA_2 \qquad (4)$$

The concentration equilibrium constants for these reactions can be expressed as follows:

$$K'_D = \frac{[H^+][A^-]}{[HA]} \qquad (5)$$

$$\beta' = \frac{[MA_2]}{[M^{2+}][A^-]^2} \qquad (6)$$

$$K'_1 = \frac{[MA^+]}{[M^{2+}][A^-]} \qquad (7)$$

$$K'_2 = \frac{[MA_2]}{[MA^+][A^-]} \qquad (8)$$

where [ ] designates the molar concentration. K'_D is the concentration dissociation (ionization) constant for acetylacetone. The terms K'_1, K'_2, and β' are the first, second, and over-all concentration stability constants, respectively. The same symbols without the prime correspond to the thermodynamic stability constants.

Although the dissociation constants of acetylacetone in different solvents have already been reported (9), it was felt that to preserve internal consistency, pK_D values (for stability constant determination) should be obtained under the present experimental conditions.

These data are given in Table I. The dielectric constants listed were obtained from the data of Akerlöf (1, 2). Although the values obtained in 1-propanol- and ethanol-water systems are in fair agreement with those reported previously, nevertheless significant differences were found for the methanol-water system at low dielectric constant (below 50). These differences are understandable since more suitable electrodes were used with more accurate mean activity coefficient data (11) and a more direct method for calculating the pK_D's.

Stability constant data were determined for Ni(II) and Co(II) acetylacetonates in mixed solvent systems at 25° C. (Table II).

If the assumption of equivalence of ions of the same charge type is valid, one may use any experimental mean activity coefficient, provided the coefficient for the appropriate solvent composition and total ionic concentration is selected. The mean activity coefficients used were

Table I. Dissociation Constants of Acetylacetone in Methanol-, Ethanol-, 1-Propanol–Water Systems at 25° C.

X_2 Mole Fraction of Organic Solvent	$1/D$	pK'_D	pK_D
METHANOL-WATER			
0.000	0.0127	8.87	8.98
0.099	0.0142	9.01	9.14
0.222	0.0160	9.18	9.32
0.295	0.0172	9.30	9.45
0.383	0.0186	9.42	9.59
0.485	0.0205	9.58	9.77
0.610	0.0230	9.81	10.03
ETHANOL-WATER			
0.070	0.0144	8.99	9.12
0.163	0.0169	9.19	9.35
0.223	0.0187	9.34	9.53
0.270	0.0209	9.46	9.68
0.393	0.0238	9.67	9.94
0.517	0.0276	9.98	10.31
1-PROPANOL-WATER			
0.056	0.0149	9.02	9.16
0.134	0.0183	9.23	9.43
0.188	0.0213	9.40	9.64
0.256	0.0247	9.62	9.91
0.346	0.0294	9.88	10.26
0.473	0.0352	10.16	10.66

obtained by interpolation of the data of Harned and Owen (12) and Gentile, Eberle, and Cefola (11) for hydrochloric acid at an ionic strength of 0.0172 in mixed solvents at 25° C.

The experimental values of pK_D ($pK_D = -\log K_D$) and $\log K$ ($K = K_1$ or K_2) are reliable to ± 0.03 and ± 0.1 log unit, respectively. The pK_D values in water agree with those of Laloi and Rumpf (14), Izatt et al. (13), Eidinoff (8), and Cartledge (7), within the limits of experimental error. Log K_1 and log K_2 values in water at 25° C. for Ni(II) and Co(II) acetylacetonate agree very well with those reported by Maley and Mellor (16) and Izatt et al. (13). The stability constant data for Ni(II) acetylacetonate in 50 weight % dioxane-water at 25° C. are in good agreement with the values of Bryant and Fernelius (4).

SOLVENT EFFECT ON CHELATION

Gentile, Cefola, and Celiano (10) studied the effect of solvent on the dissociation of acetylacetone in the methanol-, ethanol-, 1-propanol-, 2-propanol-, and dioxane-water systems. They found that a plot of pK_D vs. $1/D$, at a given temperature, resolved all the data to a single linear relationship for values of D between 80 and 30.

The pK_D of acetylacetone (present work) when plotted as a function of $1/D$ in methanol-, ethanol-, and 1-propanol-water systems at 25° C. shows that it is not possible to resolve pK_D of a single ligand in different mixed solvents as a function of $1/D$ to a single linear relationship. This leads to a conclusion that the solvent effect on the ligand dissociation is pronounced.

Log K_2 for Ni(II) acetylacetonate is plotted against the reciprocal of the dielectric constant in different solvent systems in Figure 1. In methanol- and ethanol-water systems, the log K_2 data give a linear relationship with respect to $1/D$, whereas the log K_2 data in 1-propanol-, 2-propanol-, and dioxane-water systems show a second linear relationship with a different slope. This observation reveals that methanol and ethanol may be placed in one group, whereas 1-propanol, 2-propanol, and dioxane are in another group with respect to their solvent effect on metal chelation.

Table II. Stability Constants of Ni(II) and Co(II) Acetylacetonates in Mixed Solvent Systems at 25° C.

| $1/D$	$\log K_1'$	$\log K_2'$	$\log \beta'$	$\log K_1$	$\log K_2$	$\log \beta$
		Ni(II) Acetylacetonate				
		METHANOL-WATER				
0.0127	5.94	4.50	10.44	6.05	4.61	10.66
0.0142	6.24	4.72	10.96	6.37	4.85	11.22
0.0160	6.50	4.92	11.42	6.64	5.06	11.70
0.0172	6.70	5.06	11.76	6.85	5.21	12.06
0.0186	6.90	5.13	12.03	7.07	5.30	12.37
0.0205	7.19	5.31	12.50	7.38	5.50	12.88
0.0230	7.70	5.56	13.26	7.92	5.78	13.70
		ETHANOL-WATER				
0.0144	6.31	4.75	11.06	6.44	4.88	11.32
0.0169	6.57	4.98	11.55	6.73	5.14	11.87
0.0187	6.84	5.28	12.12	7.03	5.47	12.50
0.0209	7.12	5.50	12.62	7.34	5.72	13.06
0.0238	7.55	5.85	13.40	7.82	6.12	13.94
0.0276	7.97	6.22	14.19	8.30	6.55	14.85
		1-PROPANOL-WATER				
0.0149	6.05	4.61	10.66	6.19	4.75	10.94
0.0183	6.32	4.80	11.12	6.52	5.00	11.52
0.0213	6.65	5.05	11.70	6.89	5.29	12.18
0.0247	7.03	5.41	12.44	7.32	5.70	13.02
0.0294	7.41	5.71	13.12	7.79	6.09	13.88
0.0352	7.90	6.22	14.12	8.40	6.72	15.12
		2-PROPANOL-WATER				
0.0149	6.09	4.71	10.80	6.23	4.85	11.08
0.0184	6.28	4.90	11.18	6.48	5.10	11.58
0.0208	6.50	5.01	11.51	6.74	5.25	11.99
0.0245	6.87	5.29	12.16	7.16	5.58	12.74
0.0300	7.27	5.63	12.90	7.65	6.01	13.66
		DIOXANE-WATER				
0.0168	6.32	4.82	11.14	6.48	4.98	11.46
0.0236	6.75	5.14	11.89	7.01	5.40	12.41
0.0292	7.10	5.40	12.50	7.47	5.77	13.24
0.0380	7.67	5.73	13.40	8.20	6.26	14.46
0.0520	8.10	6.30	14.40	8.88	7.08	15.96
0.0915	8.91	7.05	15.96	10.56	8.70	19.26
		Co(II) Acetylacetonate				
		METHANOL-WATER				
0.0127	5.40	4.12	9.52	5.51	4.23	9.74
0.0142	5.61	4.32	9.93	5.74	4.45	10.19
0.0160	5.90	4.46	10.36	6.04	4.60	10.64
0.0172	6.14	4.57	10.71	6.29	4.72	11.01
0.0186	6.41	4.83	11.24	6.58	5.00	11.58
0.0205	6.65	5.01	11.66	6.84	5.20	12.04
0.0230	7.05	5.20	12.25	7.27	5.42	12.69
		1-PROPANOL-WATER				
0.0127	5.40	4.12	9.52	5.51	4.23	9.74
0.0149	5.62	4.29	9.91	5.76	4.43	10.19
0.0183	5.95	4.52	10.47	6.15	4.72	10.87
0.0213	6.15	4.71	10.86	6.39	4.95	11.34
0.0247	6.55	5.03	11.58	6.84	5.32	12.16
0.0294	6.95	5.37	12.32	7.33	5.75	13.08
0.0352	7.35	5.72	13.07	7.85	6.22	14.07
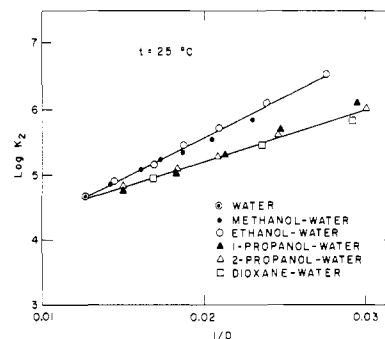
Figure 1. Log K_2 of Ni(II) acetylacetonates vs. $1/D$

One may give a plausible explanation for the above behavior on the basis of the bulk and local dielectric constants of the media. At a given bulk dielectric constant—i.e., 50—for the methanol- and 1-propanol-water systems, the ratio of the number of moles of methanol to 1-propanol is about 3 to 1. Hence, one expects a lower molecular dipole orientation (local dielectric constant) for the methanol-water system as compared with the 1-propanol-water system at the same bulk dielectric constant. Therefore, the lower the local dielectric constant, the higher will be the log K_2 (Figure 1), and this was found experimentally.

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