[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE COLLEGE]

Studies on Coordination Compounds. VI. Measurements of Chelation in Ethanol Solution[1]

BY LEGRAND G. VAN UITERT, W. CONARD FERNELIUS AND BODIE E. DOUGLAS

RECEIVED JANUARY 31, 1953

Potentiometric studies of the chelation of divalent nickel by acetylacetone, malonates and β-keto esters in essentially absolute ethanol have been made. The value of log U_H (correction to be applied to pH meter reading)[2] for a mean stoichiometric electrolyte molarity of 4×10^{-3} is 1.85 ± 0.15. The pK_D value for acetylacetone is about one log unit higher in absolute alcohol than in a water–dioxane mixture which has the same gross dielectric constant as ethanol.[3] The log of the ratio of the first chelate compound formation constant to the second (log K_{f_1}/K_{f_2}) is about 5.0 for nickel chelate compounds in absolute ethanol. The β-keto esters form dichelate compounds with nickel while the malonates form only the monochelate compounds. The ion OEt^- combines with $NiOEt^+$ at a B-value (pH meter reading) that is 3 log units lower than that at which it combines with $NiCh^+$.

Introduction

The considerable tendency for divalent metal ions to associate with water has a marked effect upon the "measured" formation constants of chelate compounds that are determined in its presence. To demonstrate the order of the effect of hydration upon the value of log K_{f_1}/K_{f_2}, measurements were made in ethanol. The observed value was markedly different from that estimated statistically by Calvin and Wilson.[4] In the absence of water, chelation reactions with the malonates and β-keto esters occur much more readily and hence do not necessitate the presence of large concentrations of chelating agent. Data for acetylacetone, malonates and β-keto esters with nickel are reported in this paper.

Experimental

Commercial absolute ethanol was refluxed with a small amount of sodium and then distilled. Part of the distilled ethanol was then treated with sodium to obtain a 0.100 N solution of sodium ethylate. A standard nickel(II) perchlorate solution containing 1×10^{-4} mole of $Ni(ClO_4)_2 \cdot 6H_2O$ per 5 ml. of ethanol was used as the source of the metal ion for each series of measurements. Hence, although some water was present in solution, the same amount was present in every case.

The organic compounds used in this investigation were obtained from the Eastman Kodak Company (acetylacetone, ethyl acetoacetate, ethyl benzoacetate, ethyl α-chloroacetoacetate, ethyl malonate, methyl malonate and ethyl bromomalonate).

The following typical solution was titrated at 30° with the 0.100 N sodium ethoxide solution for each chelation titration: 50 ml. of absolute ethanol; 1×10^{-3} mole of chelating agent; and 1×10^{-4} mole of $Ni(ClO_4)_2 \cdot 6H_2O$. The ethanol mole fraction in solution was $n_2 = 0.999$.

Discussion

pH Meter Measurements in Ethanol, $n_2 = 0.999$.—Accuracy in chelation titrations in absolute alcohol is considerably more difficult to achieve than for the comparable measurements in water–dioxane mixtures. A small change in the dielectric constant of the alcohol solution can have marked effects upon the pH meter readings. Harned[5] has shown that a small change in the dielectric constant from that of absolute alcohol can result in a marked change in the value of E_0^*, the standard potential for the cell Pt: H_2, HCl, AgCl: Ag. The effect is much greater than that for the water–dioxane mixtures. A shift in the value of E_0^* or log γ_0 (the primary medium function)[2] must be accounted for in the log U_H functions or pH meter corrections employed in the calculations. The measured values of log U_H for various concentrations of perchloric acid alone, in the presence of 2×10^{-3} M $Ba(ClO_4)_2 \cdot 3H_2O$, and in the presence of 4×10^{-3} M $NaClO_4 \cdot H_2O$ fall within the limits log $U_H = 1.85 \pm 0.15$. The hydrogen ion activity coefficient (γ) is 0.76 ± 0.01 for these ethanol solutions,[6] hence log U°_H would be approximately equal to $1.85 + \log 1/\gamma \doteq 1.95 \pm 0.16$.

E_0^* for the cell Pt: H_2, HCl, AgCl: Ag is 0.2224 v. in water at 25° and −0.0740 v. in ethanol at 25° ($\Delta E^{\circ *} = 0.2964$ v.). This potential difference is equivalent to 2.48 log units as the value of log γ_0.

$$\log \gamma_0 - \log U^\circ_H = 2.48 - 1.95 = 0.53 \pm 0.16.$$

This difference, as in the case of the water–dioxane solutions, should include the value of the liquid junction potential of the calomel electrode. Any correction needed for the small concentration of water present should also be included. If this latter factor is negligible, the "measured" liquid-junction correction for this solvent, 0.53 ± 0.16, is about the same as that for the water–dioxane solution of the same dielectric constant.[7]

Chelate Compound Formation Curves.—The titration of nickel in the presence of acetylacetone with NaOEt is shown in Fig. 1, curve (4). The chelation of the first group was complete at the beginning of the titration. The acid released by this chelation is titrated over the first equivalent per equivalent of nickel. The second equivalent titrates at a much higher B-value. At the midpoint of this second equivalent $C_2 = B_2 + \log U_H + \log HCh$ or $C_2 = 4.32 + 1.85 - 1.74 = 4.43$. pK_D calculated from the B-value at Δ ml. = 2.5 is equal to 11.9. Hence log K_{f_2} equals 7.5. The value of log K_{f_2} is approximately one unit larger than the comparable value at the same dielectric constant in the water–dioxane system. The difference between the two values is about equal to the difference in the pK_D values for acetylacetone

---

(1) A portion of a dissertation presented by L. G. Van Uitert in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1952.

(2) For definitions of terms, *cf.* L. G. Van Uitert and C. G. Haas, THIS JOURNAL, **75**, 451 (1953).

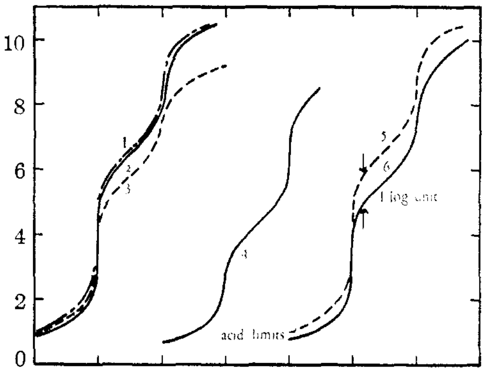
(3) The comparable water–dioxane mixture has a dioxane mole fraction of $n_2 = 0.240$, *cf.* L. G. Van Uitert, W. C. Fernelius and B. E. Douglas, THIS JOURNAL, **75**, 457 (1953).

(4) M. Calvin and K. W. Wilson, *ibid.*, **67**, 2003 (1945).

(5) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 399.

(6) *Ibid.*, p. 550.

(7) Compare log γ_0 − log U°_H, ref. 4.



Ml. of 0.100 N NaOAt.

Fig. 1.—Nickel chelation curves: 1 and 5, ethyl acetoacetate; 2, ethyl benzoacetate; 3, ethyl α-chloroacetoacetate; 4, acetylacetone; 6, ethyl acetoacetate at 5 times the concentration.

in the two solutions. The higher pK_D value in ethanol as compared to the value in a water–dioxane solution of the same dielectric constant can be attributed to the change in protolytic equilibrium from

$$H_2O + H^+ \rightleftharpoons H_3O^+ \text{ to } EtOH + H^+ \rightleftharpoons EtOH_2^+$$

Ethanol is less basic than water, hence the acetylacetone is less dissociated.

β-Keto Esters.—Since the chelation of nickel with acetylacetonate ion is complete at the beginning of the titration, a measure of log (K_{f1}/k_{f2}) cannot be obtained. To determine such a ratio, a compound having a lesser tendency to chelate must be used. The β-keto esters are satisfactory for this purpose.

Titrations were carried out for ethyl acetoacetate, ethyl benzoacetate and ethyl α-chloroacetoacetate. The resulting curves are plotted in Fig. 1. Ethyl acetoacetate was titrated at two concentrations of chelating agent, one five times larger than the other, to ascertain that chelation was occurring for both steps (curves 5 and 6 of Fig. 1).

Curve (6) should be expected to lie 0.70 log unit below this curve. However, a difference of a full log unit is observed. Apparently the introduction of the relatively large concentration of chelating agent has increased the value of log U_H by 0.30 log unit. This phenomenon is associated with the steepness of the E_0* *vs.* $1/D$ curve for ethanol mixtures.[5] The fact that the 0.3 log unit deviation is a medium effect is adequately demonstrated with the malonates.

It should be noted that log $K_{f_1}/K_{f_2} \geq 5.0$ or the ratio of the first chelation constant to the second is of the order of 100,000. This value may be even larger in completely anhydrous alcohol.

The following values have been calculated from these curves in the same manner as for acetylacetone:

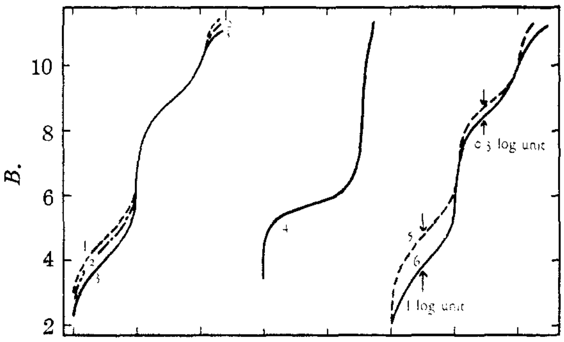
HCh	pK_D	log K_{f_1}	log K_{f_2}
Acetylacetone	11.9	..	7.5
Ethyl acetoacetate	13.9	12.3	7.2
Ethyl benzoacetate	13.7	12.3	7.1
Ethyl α-chloroacetoacetate	12.2	10.6	6.2

The log K_{f_1} values are approximate "minimum" values.

Malonic Esters.—The malonates (ethyl malonate, methyl malonate and ethyl bromomalonate) do not form dichelate compounds with nickel under the conditions employed in these titrations. The end products have the composition Ni(OEt)Ch.

The glass electrode ceases to function properly above the B-value of 11.4 in ethanol; the pK_D values for the malonates could not be obtained as they titrate above this value. The chelate compound formation constants for these malonates with nickel are of the order of log $K_f \geq 8.0$.

The chelation titration curves for these compounds are shown on Fig. 2, curves (1, 2 and 3). Nickel was also titrated with 5 times the concentration of ethyl malonate as in the case of ethyl acetoacetate. The two curves for this chelating agent are shown as curves 5 and 6 of Fig. 2. Note that, as in the case of ethyl acetoacetate, the B-value for the chelation constant of the 5× curve is 1.0 log unit below the other. The B-values are again 0.3 log unit lower than can be accounted for on a mass-action basis. Over the second equivalent of added base, the B-values are 0.30 log unit lower for the 5× curve than for the other. Since OEt^- is combining with the nickel monochelate over this part of the curve, the difference of 0.30 log unit is due to a change in log U_H of this amount as a consequence of the increase in concentration of the chelating agent.



Ml. of 0.100 N NaOEt.

Fig. 2.—Nickel chelation curves: 1 and 5, ethyl malonate; 2, methyl malonate; 3, ethyl bromomalonate; 4, $Ni(ClO_4)_2$; 6, ethyl malonate at 5 times the concentration.

These second equivalent parts of the curves lie about 3 log units above the value at which OEt^- will add to $NiOEt^+$. The titration of $Ni(Cl_4)_2$ alone is shown in curve (4) of Fig. 2. A nickel compound having the stoichiometric ratio 2Ni: 3OEt is first formed. One having the ratio 4Ni: 7OEt is precipitated toward the end of the titration. The first forms at a B-value of 6 while OEt^- adds to the monochelated nickel compound at a B-value of 9.0.

Acknowledgment.—The authors gratefully acknowledge financial support furnished for this work by the United States Atomic Energy Commission through Contract AT(30-1)-907.

State College, Pa.