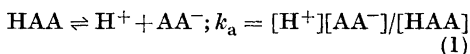


The Dissociation Constant for Acetylacetone in 1 M Sodium Perchlorate Solution at 15–45°C

J. O. LILJENZIN

Department of Nuclear Chemistry, Chalmers University of Technology, Fach, S-402 20 Göteborg 5, Sweden

The recently developed AKUFVE¹ apparatus makes it easy to carry out solvent extraction experiments at different temperatures.² Determination of stability constants and thermodynamic functions for metal acetylacetonates^{3,4} requires a knowledge of the value of the dissociation constant (k_a) for acetylacetone (HAA) in the same ionic medium as the aqueous phase used, and at the appropriate temperature. The dissociation constant here is defined as



Undissociated acetylacetone has an absorption maximum at 273 nm with a molar extinction coefficient⁵ of 1490 M⁻¹ cm⁻¹, whereas the acetylacetonate anion (AA⁻) has its maximum at 292 nm with a molar extinction coefficient of 23 600 M⁻¹ cm⁻¹. Separate experiments in buffer solutions (containing sodium perchlorate) at pH 11 showed no evidence of decomposition of the acetylacetonate ion at 25°C, but slow decomposition (10 % in one hour) did occur at 50°C.

In view of these facts it was decided to determine the relative amounts of HAA and AA⁻ spectrophotometrically as a function of $-\log[\text{H}^+]$ during an acid-base titration. This method is more compatible with the AKUFVE experiments than a method using buffer solutions of known pH.⁵ Knowledge of the ratio $[\text{HAA}]/[\text{AA}^-]$ for different values of $-\log[\text{H}^+]$ makes possible an easy and precise calculation of k_a .

Experimental. Chemicals. Acetylacetone was purified in the manner described by Rydberg.⁶ The sodium perchlorate solution was made by neutralization of concentrated HClO₄ (Merck *p.a.*) with 10 M NaOH (pH-Tamm). 0.1 M sodium hydroxide was made from Titrisol (Merck *p.a.*) and NaClO₄ added to make it

1.0 M in ClO₄⁻. Before use this solution was standardized against potassium biphthalate by potentiometric titration. 0.1 M perchloric acid in 0.9 M NaClO₄ was prepared from concentrated HClO₄ and standardized by potentiometric titration with the 0.1 M sodium hydroxide solution.

Procedure. Known amounts of 1 M NaClO₄, 0.1 M HClO₄ solution, and acetylacetone were mixed in a titration vessel equipped with a small centrifugal pump made from plexiglas, and were then immersed in a thermostat. The liquid in the titration vessel was circulated by the pump through a 1 mm cell placed in a double beam spectrophotometer (Perkin-Elmer 350). The hydrogen ion concentration was measured with a glass electrode calibrated at each temperature used in the manner described by Andersson *et al.*² The emf was measured with a precision of ± 0.1 mV, which is equivalent to about ± 0.002 units in $\log[\text{H}^+]$.

The perchloric acid and the acetylacetone were titrated with the 0.1 M sodium hydroxide solution. After each addition of base, the emf of the glass electrode was measured and the absorption spectrum was recorded between 240 and 400 nm. The additions of base were continued until no further increase in absorbance at 292 nm was observed. The final part of the titration was carried out as fast as possible to minimize the destruction of HAA at the highest hydroxyl ion concentrations. The total time for a complete titration was less than 1 h with only 5 to 10 min at $-\log[\text{H}^+]$ above 10.

The experiments were carried out at 15, 25, 35, and 45°C.

Calculations. The partial overlap of the absorption bands for HAA and AA⁻ must be taken into account in a precise calculation of the ratio $[\text{AA}^-]/[\text{HAA}]$.

If we denote the molar extinction coefficients at 292 nm by ϵ_{HAA} for HAA, and by ϵ_{AA} for AA⁻, and if Beer's law is valid, the total absorbance (a) at 292 nm is given by

$$a = \epsilon_{\text{HAA}}l[\text{HAA}] + \epsilon_{\text{AA}}l[\text{AA}^-] \quad (2)$$

where l is the cell thickness.

From eqn. 2 and a material balance the following equation is obtained

$$[\text{HAA}]/[\text{AA}^-] = \epsilon_r/(a_r v_r - 1) - 1 \quad (3)$$

where

$$\epsilon_r = (\epsilon_{\text{AA}} - \epsilon_{\text{HAA}})/\epsilon_{\text{HAA}}; a_r = a/a_0;$$

$$v_r = (v_0 + v_b)/v_0$$

Here a_0 is the absorbancy (292 nm) and v_0 is the volume of solution at the start of the experiment, when practically no AA^- is present in the acid solution. v_b is the volume of base added. To increase the precision a_0 is calculated from ϵ_{HAA} , v_0 , and the amount of acetylacetone added.

The pK_a for acetylacetone was determined by plotting $\log [HAA]/[AA^-]$ against $-\log[H^+]$. This gives a straight line with $pK_a = -\log[H^+]$ at $\log[HAA]/[AA^-] = 0$ (eqn. 1).

Results and discussion. Beer's law was found to be valid for both HAA and AA^- in the concentration range used (0.1 to 1 mM). The ϵ_r values were redetermined from the pK_a values obtained with the original ϵ_r , the highest and lowest absorbancies recorded, corresponding values of $-\log[H^+]$, and the amount of HAA added. The calculation was repeated using the new ϵ_r thus obtained. After two to three iterations consistent values were obtained. The change in pK_a due to the adjustment of ϵ_r was about ± 0.01 . This procedure eliminates the uncertainty in the separately measured ϵ_{AA^-} , and thus increases the accuracy.

The results from a typical experiment are shown in Fig. 1. Fig. 2 shows the pK_a determined as a function of temperature. As can be seen the values fall on a straight line. The equation for this line is

$$pK_a = (9.3027 \pm 0.0003) - (0.01228 \pm 0.00028)T \quad (4)$$

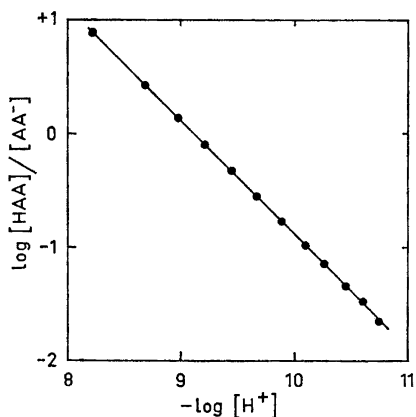


Fig. 1. Results from a titration experiment at 15°C.

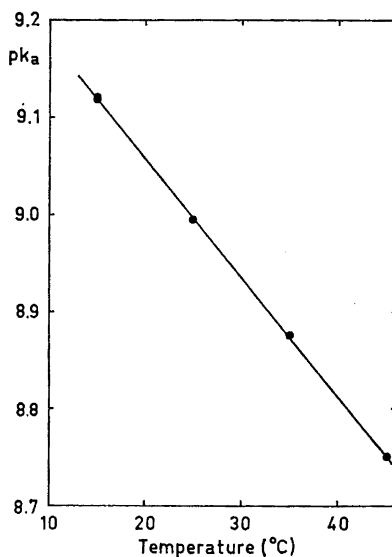


Fig. 2. The variation of pK_a with temperature for acetylacetone in 1 M $NaClO_4$. The straight line corresponds to eqn. 4.

where T denotes the temperature in degrees centigrade. The constants in eqn. 4 were determined by a least squares method. The errors given are the 95% confidence intervals. Eqn. 4 can be used to calculate pK_a for acetylacetone in the temperature range 10 to 50°C, which is used in the AKUFVE experiments. The small extrapolations (5°C) at both ends of the investigated interval seem to be justified in view of the good linearity within the measured range. pK_a values calculated from eqn. 4 should be correct to at least two places of decimals.

In Table 1 a comparison is made between the pK_a values calculated from eqn. 4, and values from Ref. 7 and from Laloi *et al.*⁵ at low ionic strength. As can be seen from Table 1 the agreement is remarkably good. It is, however, important to notice the different definitions of k_a used. In our experiments k_a is defined according to eqn. 1, with brackets denoting concentrations, whereas in Refs. 5 and 7 the following definition is employed

$$k_a' = (H^+)(AA^-)/(HAA) \quad (5)$$

where parentheses denote activities.

Table 1. The pK_a values for acetylacetone at different temperatures and different ionic strengths (μ). The values within parenthesis are computed from eqn. 4. pK_a and pK_a' are defined by eqns. 1 and 5, respectively.

Temperature (°C)	pK_a' ($\mu=0$) Ref. 7	pK_a' ($\mu\sim 0$) Ref. 5	pK_a ($\mu=1$) This work
10	9.10	9.11 ± 0.02	(9.180)
15			9.118
20	9.02	9.00 ± 0.02	9.119
25			(9.057)
30	8.95		8.994
35			(8.934)
38		8.92 ± 0.02	8.876
40	8.86		(8.836)
45			(8.812)
			8.750

The activity coefficients for the ions H^+ and AA^- in 1 M $NaClO_4$ can both be estimated to be 0.63.⁸ At 25°C we have found the same pK_a -value in 1 M $NaClO_4$ as that given for zero ionic strength (pK_a').⁷ This information can be used to estimate the activity factor of HAA in 1 M $NaClO_4$. The value obtained (0.4) is small, due partly to a shift in the keto-enol equilibrium towards the keto-form caused by the sodium perchlorate. The evidence for this shift is:

a. The distribution ratio of HAA between xylene and sodium perchlorate solutions decreases by a factor of 0.81 when $[NaClO_4]$ increases from 0.01 to 1 M.⁹ The enol form has a higher distribution ratio than the keto form.⁶

b. When the sodium perchlorate concentration increases from 0.002 to 1 M,

the gross molar extinction coefficient (274 nm, pH 2.7) of HAA decreases by a factor 0.82. The enol form has a higher extinction coefficient than the keto form.⁵ c. NMR measurements show a decrease in the percentage of enol form when the concentration of sodium perchlorate increases.¹⁰

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