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Dissociation Constant and Related Thermodynamic Quantities for 2-Aminopyridinium Ion from 5 to 40 °C

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The dissociation of protonated 2-aminopyridine (2-AMP) has been studied by emf measurements of the cell without transference $Pd;H_2$(g, 1 atm)|2-AMP·HCl,2-AMP|AgCl;Ag over the temperature range 5–40 °C. The pK_a is given by the equation pK_a = 2070.72/T − 5.2546 + 0.885972 ln T, where T is the thermodynamic temperature. The value at T = 298.15 K is 6.739, or intermediate between 9.114 for protonated 4-aminopyridine and ~5.2 for pyridinium ion. The changes of enthalpy, entropy, and heat capacity for the dissociation process were derived from the change of pK_a with temperature.

Introduction

In earlier work, thermodynamic quantities for the dissociation of 4-aminopyridinium ion in water (*1*) and in 50 wt % methanol–water (*2*) were determined. The unprotonated base, 4-aminopyridine, has been proposed as a titrimetric standard for acidimetry (*3*). It is also useful as a component of buffer solutions for pH control in the region 8.5–9.5 (*1*). Slightly weaker bases are, however, more suitable for the regulation of pH in the physiologically important region 7–8, for measurements of the pH of blood (pH ~7.4 at 37 °C), and for the study of acid–base processes in seawater (pH 8.0–8.3 at room temperature). Furthermore, few buffer systems with pH close to 7 are known. The tautomer, 2-aminopyridinium ion, has a pK_a of 6.7 at 25 °C. Thus, substitution of the amino group in the para position produces a base that is 250 times as strong as the related ortho-substituted compound.

The dissociation constant of 2-aminopyridinium ion has been determined from pH measurements with the glass electrode, usually at a single temperature (*4*, *5*). The measurements of Jonassen and Rolland (*6*), however, were made at 25, 35, and 45 °C, while those of Bellobono and Monetti (*7*) covered the range 5–45 °C. Christensen et al. (*8*) determined pK_a and the associated changes in enthalpy and entropy for the dissociation process at 10, 25, and 40 °C by calorimetry, while heats of protonation have been measured by other investigators (*9*, *10*).

The dissociation and related thermodynamic properties of 2-aminopyridinium ion (2-AMP·H^+) are of sufficient practical and theoretical interest as to warrant further investigation by rigorous thermodynamic methods. They have now been studied by measurements of the electromotive force of cells without transference. The cell

$$\mathrm{Pd;H_2(g,\ 1\ atm)|2\text{-}AMP{\cdot}HCl}(m)\mathrm{,2\text{-}AMP}(m)\mathrm{|AgCl;Ag} \qquad (1)$$

was studied at eight temperatures from 5 to 40 °C.

Experimental Section

The cell solutions, consisting of equal molalities (m) of 2-aminopyridine and its hydrochloride salt, were prepared by dilution of a stock solution formed by adding the appropriate amount of the base to a solution of HCl. 2-Aminopyridine was obtained from Eastman Kodak Co. and was recrystallized from benzene and dried under vacuum. An assay of 99.8% was found by acid–base titration. The HCl solution was prepared by dilution of the twice-distilled azeotrope with water; it was standardized gravimetrically by weighing AgCl. Water with a conductivity in the range 7×10^{-7}–9×10^{-7} S cm^{-1} was obtained by distillation in an all-glass still. All solutions were prepared by weight and were purged with hydrogen gas before the cells were filled.

The cell vessels were of all-glass construction and were provided with saturators consisting of three compartments, in order to minimize changes of composition resulting from extended bubbling of the hydrogen gas. Commercial hydrogen gas was purified by passage through two DeOxo purifiers containing platinum catalyst. Although no difficulties were experienced in the studies of 4-AMP buffer solutions (*1*, *2*) with platinum/hydrogen electrodes, the potentials of this type of electrode drifted steadily in solutions of 2-AMP, presumably because of a slow reduction reaction such as occurs in phthalate solutions (*11*). When the platinum foils were plated with palladium black, however, the drift was reduced, in general, to less than 0.1 mV over a period of 24–30 h. Preparation of the palladium chloride plating solution has been described elsewhere (*12*). A palladium wire served as an anode. The silver–silver chloride electrodes were of the thermal–electrolytic type (*12*).

The standard emf ($E°$) of the cell was determined by measurements of the emf of the cell with platinized Pt electrodes and Ag;AgCl electrodes, containing HCl at a molality of 0.01 mol kg^{-1} (*13*). The observed values of the emf were corrected in all instances to a hydrogen partial pressure of 1 atm (101.325 kPa) by reference to the table given elsewhere (*12*). The emf was measured with a digital voltmeter reading to 0.01 mV, and temperatures were determined with a Hewlett-Packard quartz thermometer.

Results and Calculations

The corrected values of the emf for cell 1 from 5 to 40 °C are summarized in Table I, and the standard emf ($E°$) is given at the foot of the table. The equilibrium constant for the process

$$\mathrm{2\text{-}AMP{\cdot}H^+ \rightleftharpoons 2\text{-}AMP + H^+} \qquad (2)$$

is related to the emf (E) and the Nernst slope, $k = (RT \ln 10)/F$, by

$$-\log K_a = \frac{E - E°}{k} + \log \frac{m_{BH}m_{Cl}}{m_B} + \log \frac{\gamma_{BH}\gamma_{Cl}}{\gamma_B} \qquad (3)$$

where B and BH represent the base 2-AMP and its protonated form, respectively. The unknown value of the last term of eq 3 can be estimated by the "extended" form of the Debye–Hückel equation

$$\log \frac{\gamma_{BH}\gamma_{Cl}}{\gamma_B} = \frac{-2AI^{1/2}}{1 + B\mathring{a}I^{1/2}} + \beta I \qquad (4)$$

in which A and B are constants of the Debye–Hückel theory (*12*) and å (the ion-size parameter) and β are adjustable constants.

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Table I. Electromotive Force (V) of Cell 1 Containing Equimolal Mixtures of 2-Aminopyridinium Chloride and 2-Aminopyridine from 5 to 40 °C

m/(mol kg^{-1})	5 °C	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C
0.009 999	0.745 26	0.745 30	0.745 11	0.744 81	0.744 52	0.744 02	0.743 33	0.742 53
0.019 984	0.730 28	0.729 91	0.729 68	0.729 18	0.728 53	0.727 74	0.726 76	0.725 67
0.030 00	0.721 73	0.721 26	0.720 68	0.719 84	0.719 28	0.718 33	0.717 25	0.715 96
0.039 97	0.716 07	0.715 59	0.714 93	0.714 08	0.713 14	0.712 09	0.710 85	0.709 50
0.050 08	0.711 41	0.710 76	0.710 03	0.709 15	0.708 09	0.706 86	0.705 58	0.704 14
0.059 98	0.707 57	0.706 81	0.706 46	0.705 74	0.703 80	0.703 00	0.701 56	0.700 04
0.070 00	0.704 21	0.702 89	0.702 18	0.701 48	0.700 59	0.699 41	0.698 05	0.696 52
0.080 00	0.701 64	0.701 04	0.700 31	0.699 29	0.697 90	0.696 70	0.695 02	0.693 47
0.090 00	0.699 91	0.699 04	0.698 08	0.696 94	0.695 71	0.694 33	0.692 79	0.691 11
0.100 00	0.697 59	0.696 71	0.695 78	0.694 60	0.693 38	0.691 93	0.690 35	0.688 60
$E°$	0.234 25	0.231 59	0.228 73	0.225 71	0.222 51	0.219 22	0.215 77	0.212 20

Table II. pK_a of 2-Aminopyridinium Ion from 5 to 40 °C and Constants of Eq 6

t/°C	pK_a	$10^3 s^a$	t/°C	pK_a	$10^3 s^a$
5	7.177	3.9	25	6.739	2.8
10	7.060	6.2	30	6.640	1.8
15	6.949	5.8	35	6.543	1.8
20	6.841	5.2	40	6.449	1.6

$A = 2070.72$
$B = -5.2456$
$C = 0.885972$

[a] s = standard deviation for regression from the extrapolation line.

The pH of equimolal 2-AMP buffer solutions lies between 6.4 and 7.2, and consequently hydrolysis of BH^+ and B was negligible and the buffer ratio was unity in all of the solutions. Furthermore, the ionic strength (I) is equal to m. Accordingly, eq 3 and 4 were combined to calculate, for each value of m, an "apparent" K_a (designated K_a') which becomes equal to the thermodynamic K_a upon extrapolation to $m = 0$, where the last term of eq 3 goes to zero:

$$-\log K_a' \equiv -\log K_a - \beta m = \frac{E - E^\circ}{k} + \log m - \frac{2Am^{1/2}}{1 + B\mathring{a}m^{1/2}} \qquad (5)$$

The best value of the ion-size parameter å was assumed to be that value which led to the smallest standard deviation of regression in the linear extrapolation. The effect of varying å on pK_a and on the standard deviation s at 25 °C is shown by the following data:

å/Å	pK_a	$10^3 s$
0	6.728	4.1
4	6.732	3.3
6	6.736	2.9
7	6.738	2.83
7.5	6.739	2.82
8	6.740	2.82
8.5	6.741	2.84
9	6.742	2.87

On this basis, å was taken to be 7.5 Å in treating the data at each of the eight temperatures. The results are given in Table II. It will be noted that the standard deviations are larger at the low temperatures (5-20 °C) than at 25 °C and above. The cause appears to be a slow response of the electrodes, noticeable at the lower temperatures. For this reason, platinum electrodes are preferable to palladium electrodes for use in systems where reduction by hydrogen does not present a problem.

The values of pK_a were fitted to eq 6, where T is the thermodynamic temperature (T = °C + 273.15), by the method of Ives and Moseley (*14*). The constants A, B, and C of eq 6 are included in Table II. The pK_a at the eight temperatures from T = 278.15 to 313.15 K is represented by eq 6 with a standard deviation of 0.0009.

$$\mathrm{p}K_a = A/T + B + C \ln T \qquad (6)$$

Table III. Thermodynamic Quantities for the Dissociation of 2-Aminopyridinium Ion and 4-Aminopyridinium Ion at 298.15 K

	2-AMP·H$^+$	4-AMP·H^{+a}
pK_a	6.739	9.114
$\Delta G°$/(cal mol^{-1})	9193 ± 2.0^b	12431
$\Delta H°$/(cal mol^{-1})	8266 ± 40^b	11255
$\Delta S°$/(cal K^{-1} mol^{-1})	−3.11 ± 0.12^b	−3.94
$\Delta C_p°$/(cal K^{-1} mol^{-1})	−4 ± 7^b	−4

[a] Data from ref 3. [b] Uncertainty is one standard deviation.

The standard thermodynamic functions for the dissociation process, eq 2, can be derived readily from the constants A, B, and C of eq 6:

$$\Delta G°/(\mathrm{cal\ mol^{-1}}) = 4.5757(A + BT + CT \ln T) \qquad (7)$$

$$\Delta H°/(\mathrm{cal\ mol^{-1}}) = 4.5757(A - CT) \qquad (8)$$

$$\Delta S°/(\mathrm{cal\ K^{-1}\ mol^{-1}}) = -4.5757(B + C + C \ln T) \qquad (9)$$

$$\Delta C_p°/(\mathrm{cal\ K^{-1}\ mol^{-1}}) = -4.5757C \qquad (10)$$

(1 thermochemical calorie = 4.184 J). The values of these thermodynamic functions for the dissociation of 2-AMP·H$^+$ at T = 298.15 K are compared with similar data for 4-AMP·H$^+$ in Table III. The standard deviations have been calculated from the uncertainties in pK_a by the method of Please (*15*); they are included in Table III.

In general, our results for pK_a are consistent with earlier estimates. At 25 °C, the present value of 6.739 is slightly higher than 6.71 based on measurements with the glass electrode (*6*, *7*). At the other temperatures studied by Bellobono and Monetti (*7*), the comparison is as follows (our results in parentheses): 5 °C, 7.14 (7.177); 15 °C, 6.98 (6.949); 20 °C, 6.82 (6.841); 35 °C, 6.54 (6.543). Their data have assigned uncertainties of 0.02-0.03 unit. At 40 °C, Christensen et al. (*8*) found 6.43 by their calorimetric method, as compared with our value of 6.449, but their value (6.25) at 10 °C is obviously in error; from their $\Delta G°$ at 10 °C, one calculates pK_a = 6.94, to be compared with 7.060 from the emf of cells without transference.

The same authors have given a value of 8.40 kcal mol^{-1} for the enthalpy of dissociation at 25 °C, in close agreement with the calorimetric value of 8.39 kcal mol^{-1} found by Mortimer and Laidler (*10*) earlier. The data of Bellobono and Monetti (*7*) yield $\Delta H°$ values from 8.17 to 8.29 kcal mol^{-1}, depending on the method of data treatment, as compared with 8.27 kcal mol^{-1} from this investigation. Their values for $\Delta S°$ are in the range −3.0 to −3.5 cal K^{-1} mol^{-1}. The present work gives −3.1 cal K^{-1} mol^{-1}, while calorimetry, combined with pK_a, yields −4.1 cal K^{-1} mol^{-1} (*10*) and −2.5 cal K^{-1} mol^{-1} (*8*).

It is generally agreed that it is the ring nitrogen of 4-AMP that has much the greater attraction for the proton (*16*). With pK_b ≈ 8.8, pyridine itself is a very weak base. Substitution of the amine group in the 4 position (para) increases the basicity of the ring nitrogen by 10 000-fold (pK_b = 4.9), probably through resonance stabilization of the cation rather than the free base itself (*17*). Increased density of charge on the ring nitrogen, together with a residual positive charge on the amino nitrogen, allows for the greatly enhanced basicity that is observed. This effect is present in reduced intensity in 2-AMP (pK_b = 7.3), with the result that the basicity of 2-AMP is intermediate between that of 4-AMP and the parent pyridine.

The thermodynamic quantities for the dissociation of 2-aminopyridinium ion and 4-aminopyridinium ion are similar, suggesting that the differences in the dissociation processes are largely matters of degree rather than of kind. In both instances, the entropy changes are small, which is characteristic of isoelectric dissociation processes in general. The differences in basic strength are thus attributable to enthalpy contributions.

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Critical Constants, Vapor Pressure, and Saturated Volumes of Hexafluoroacetylacetone

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The critical temperature, pressure, and volume were determined for hexafluoroacetylacetone. The vapor–ligand equilibrium was determined from the temperature of 422.8 K to the critical temperature. Vapor–pressure equations were suggested to correlate the data. The densities of saturated liquid and saturated vapor were determined in the above temperature range.

Introduction

In recent years, fluoro compounds have found increasing use on an industrial scale. Banks (*1*) gives many examples of the increasing industrial use of fluoro compounds. Accurate vapor–liquid equilibrium data and accurate correlations are very important for the design of the industrial equipment that will handle the liquid and the vapor. Very little research has been done on the vapor–liquid equilibrium of fluoro compounds. The purpose of this study is to find the critical properties and the vapor–liquid equilibrium of hexafluoroacetylacetone. No previous study of the vapor–liquid equilibrium of hexafluoroacetylacetone has been found in the literature. The vapor–liquid equilibrium was studied from 422.8 K to the critical point. Many equations have been suggested in the literature to correlate the vapor–liquid equilibrium as given by Nieto and Thodos (*2*). In this work the data were correlated by two equations of the form

$$\log P = A + B/T \qquad (1)$$

$$\log P = A + B/T + CT \qquad (2)$$

The least-squares method and Gaussian elimination were used to find the constants in eq 1 and 2. The percentage deviation defined as 100 × [(calculated pressure) – (measured pressure)]/(measured pressure) was calculated for the two equations. Also, the specific volumes of the saturated vapor and the saturated liquid were measured.

Experimental Section

The hexafluoroacetylacetone used in this study was supplied by Koch-light Laboratores Ltd., England, with a stated purity of 98%. The hexafluoroacetylacetone was further purified by placing it in contact with activated molecular sieves to absorb traces of moisture and was then degassed.

Liquid samples may contain small amounts of dissolved air. If accurate vapor–liquid equilibrium is to be obtained, the sample must be degassed. Ronc and Ratcliff (*3*) discussed three ways of degassing. The degassing method used in this work is different from their methods. The hexafluoroacetylacetone was degassed by subjecting it to a cycle of freezing, pumping, melting, and freezing. The degassed sample was kept in a flask attached to a high-vacuum train and surrounded by a mixture of dry ice and acetone.

Apparatus and Procedure

The apparatus and the methods for the measurements have been described in previous publications (*4*). The temperature was measured by the platinum resistance type 385. The platinum resistance with its electronic digital indicator, type 2180A, was supplied by Fluke. It can read to 0.01 K and has a maximum error of ±0.02 K.

The pressure was measured by a pressure gauge manufactured by Matheson with an absolute accuracy of ±0.025%. The experimental tube was constructed from precision-bore

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