

Dissociation of 5,5'-Diethylbarbituric Acid in 80% Ethanol-Water

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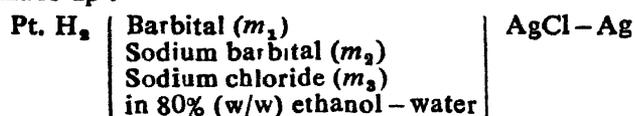
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The ionisation constant of barbital (5,5' diethyl barbituric acid) has been determined by e.m.f. methods at temperatures varying from 15 to 45° in a mixed solvent consisting of 80% (w/w) ethanol + 20% water. The values found for pK are 9.456, 9.510, 9.546, 9.588, 9.623, 9.674 and 9.728, respectively at 15, 20, 25, 30, 35, 40 and 45°. Related thermodynamic functions like the Gibbs free energy, entropy, enthalpy and heat capacity changes have been evaluated. Certain polynomials have been suggested for implementing Gronwall, LaMer and Sandved corrections and a computer has been used for carrying out the iterative calculations involved.

MEASUREMENTS reported here were undertaken on account of biological significance including the sedative effects of the barbiturates and constitutes a part of a more comprehensive project¹. The 5,5'-disubstituted-barbituric acids and their salts have been in use as buffers to cover the pH range 6-9. Krahl² studied the effects of variation in ionic strength and temperature on the apparent dissociation constants of thirty substituted-barbituric acids in aqueous medium. Robinson and Biggs reported³ the measurement of thermodynamic ionisation constants of seven 5,5'-disubstituted-barbituric acids at 25° in aqueous medium by spectrophotometric method.

In the present work the following cell (A) was made up :



and its e.m.f. measured at different temperatures.

Experimental

5,5'-Diethylbarbituric acid and its sodium salt (E. Merck, proanalysis) were used as such. Sodium chloride (AnalaR) was recrystallised from water. Absolute ethanol (Bengal Chemicals) left overnight over CaO, was purified by refluxing with magnesium ethoxide for about 12 h followed by distillation⁴. The cell solutions were prepared by weight methods (with vacuum corrections) using 80% (w/w) ethanol + 20% (w/w) water as solvent. Concentrations are expressed in molality *m* (moles per kilogram of mixed solvent).

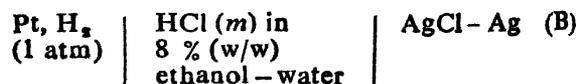
Cells and electrodes : The cells were of Pyrex glass throughout, constructed so as to permit the

use of two silver-silver chloride electrodes and one hydrogen electrode⁵. Any two of the three compartments could be interconnected at a time by a three-way Pyrex glass stop-cock. Gases which entered into the cell through a side tube at the bottom of each compartment escaped through outlets provided near the top. The hydrogen and nitrogen gases were presaturated by bubbling them through solutions identical to that in the cell. The silver-silver chloride electrodes were of the thermal-electrolytic type⁶, allowed to age for a week in 0.05 N KCl solution and were then soaked in the experimental solution for about 48 h before use. Platinum electrodes were replatinised after each use. This procedure helped in obtaining equilibrium potentials within the short time of 2-3 h.

Results and Discussion

The recorded e.m.f. values were corrected to a partial pressure of 1 atm. An interpolation procedure⁷, which utilised the straight line plots of log *p* as function of 1/*T* (where *p* and *T* are the pressure and thermodynamic temperatures respectively) was used where figures were not readily available. Bubbler depth corrections have been neglected.

The standard e.m.f. *E*^o of the cell (B) at temperatures 15 to 45° were measured earlier¹,



and are given in Table 4, along with other measurements. The e.m.f. of cell (A) using ten different solutions of different molalities were measured. Each solution was assigned a number and the details of their molalities are given in Table 1. The

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corrected e.m.f. values at each temperature are given in Table 2.

TABLE 1—MOLALITIES OF SOLUTIONS

Solution no.	m_1 $\times 10^3$ mol kg $^{-1}$	m_2 $\times 10^3$ mol kg $^{-1}$	m^3 $\times 10^3$ mol kg $^{-1}$
1.	1.010 3	2 020 5	5.051 4
2.	1 011 2	2.526 7	4 042 6
3.	1.010 8	3.032 3	3.036 4
4.	1 012 1	4.043 4	1.012 1
5.	7.119 5	1 017 2	1.017 1
6.	6 094 3	1 016 2	2 031 4
7.	5 072 6	1.014 6	3.043 4
8.	4 052 6	1.013 4	4.052 8
9.	3 035 7	1.011 9	5.059 6
10.	2.021 2	1 010 7	6 063 8

electronic charge, D the dielectric constant and a_0 the 'closest distance of approach' parameter. The use of polynomials in order to evaluate $f_3(X)$ and $f_5(X)$ did not contribute significantly to an error in the estimation of γ_{\pm} (since the contribution of the extended terms Ext./ln 10 to the value of $\log \gamma_{\pm}$ is small).

The fifth degree polynomials (equations 5 and 6) were evolved using the desk-top computer (DCM 1121).

$$10^5 \times f_3(x) = 0.03170 - 2.0725x + 1.1986x^2 + 5.9510x^3 - 9.1706x^4 + 3.8341x^5 \quad (5)$$

$$10^5 \times f_5(x) = 0.0470 - 3.4361x + 17.775x^2 - 31.529x^3 + 23.923x^4 - 6.6572x^5 \quad (6)$$

TABLE 2—CORRECTED E.m.f. (V) VALUES AT DIFFERENT TEMPERATURES

Solution no.	15°	20°	25°	30°	35°	40°	45°
1.	0.767 33	0.775 24	0 783 16	0.791 36	0.798 67	0.806 01	0.813 31
2.	0.779 31	0 787 56	0.795 82	0.804 42	0.812 18	0 820 02	0.827 81
3.	0 791 76	0.800 11	0 808 49	0 817 21	0 825 39	0.833 71	0.841 92
4.	0.827 77	0.836 39	0 844 99	0.853 79	0 862 50	0.871 30	0 880 02
5.	0 749 97	0.757 51	0 765 05	0.772 68	0.779 59	0.786 62	0 793 55
6.	0.734 90	0.742 14	0.749 36	0.756 71	0 763 81	0 770 97	0.778 08
7.	0.727 91	0 735 01	0.742 10	0.749 44	0.756 00	0.762 62	0.769 17
8.	0.724 51	0.731 40	0.738 29	0.745 35	0 751 62	0 757 98	0.764 26
9.	0.724 58	0 731 88	0 739 21	0 746 88	0.753 79	0.760 74	0.767 63
10.	0.728 39	0.735 81	0.743 21	0.750 88	0.757 80	0 764 75	0.771 59

The individual ionic molalities were given as $m_{\text{Na}^+} = m_2 + m_3$, $m_{\text{Bar}^-} = m_2 + m_{\text{H}}$, $m_{\text{Cl}^-} = m_3$ and $m_{\text{HBar}} = m_1 - m_{\text{H}}$, where $m_1 = m_{\text{barbital}}$, $m_2 = m_{\text{NaBar}}$, $m_3 = m_{\text{NaCl}}$. The subscripts H, Na, Bar, Cl and Hbar refer to the hydrogen, sodium, barbital, chloride ions and the undissociated acid respectively. The ionic strength is given by

$$I = m_2 + m_3 + m_{\text{H}} \quad (1)$$

The e.m.f. of the cell (B) is given by

$$E = E^0 - (RT/F) \ln m_{\text{H}} m_{\text{Cl}} \gamma_{\text{H}} \gamma_{\text{Cl}} \quad (2)$$

The equation for the mean activity coefficient γ_{\pm} may be written in the extended form,

$$-\log \gamma_{\pm} + \beta I = \frac{AI^{1/2}}{1 + Ba_0 I^{1/2}} - \frac{\text{Ext.}}{\ln 10} + \log(1 + 0.07026I) \quad (3)$$

where A and B are the Debye-Hückel parameters converted to the molality scale. The mean molar mass of the solvent is 0.03513 kg mol $^{-1}$. The contribution of the extended terms to $-\log_{10} \gamma_{\pm}$ for a 1-1 electrolyte can be expressed as

$$(\text{Ext.}) = \left(\frac{e^2}{kDTa_0}\right)^2 f_3(X) + \left(\frac{e^2}{kDTa_0}\right)^5 f_5(X) \quad (4)$$

where $X = Ba_0 I^{1/2}$, k is Boltzmann constant, e the

The equation for the dissociation constant is

$$K' = \frac{m_{\text{H}}(m_2 + m_{\text{H}})}{m_1 - m_{\text{H}}} \gamma_{\pm}^2 \quad (5)$$

and

$$pK' = -\log K' = pK - BI$$

where K represents the thermodynamic dissociation constant and the prime on it denotes the dissociation constant at I (ionic strength) and B is a constant linear in I .

Analysis of data: The values of m_{H} and pK' at each ionic strength were calculated using an iterative procedure similar to that used elsewhere⁹ with the help of a desk-top computer (DCM micro system 1121). The computer had been programmed to take in the values of the e.m.f., the molalities, temperature and the values of the various constants arising in the Debye-Hückel extended equation. A regression analysis was then carried out by the method of least squares using the facilities available in the micro-computer to give the pK at zero ionic strength, the correlation coefficient and other relevant statistical data. The values of the derived quantities m_{H} , I , pK' and $-\log \gamma_{\pm}$ at 25° are given in Table 3. The plots of I vs pK' extrapolated to zero ionic strength were linear at each temperature. The relevant data are given in Table 4-

TABLE 3 - VALUES OF DERIVED QUANTITIES

Solution no.	Temp. -25°, β=0, α=0.56 nm			
	mH × 10 ¹⁰	I × 10 ³	pK'	-log γ ± × 10
1.	9.008 6	7.071 9	9.348 2	3.019 6
2.	6.645 3	6.5 9 3	9.369 0	2.946 2
3.	5 210 5	6 068 7	9.379 7	2.868 4
4.	3.481 9	5.060 5	9.395 0	2.694 4
5.	54 340	2.034 3	9.494 2	1.921 6
6.	58 157	3.047 6	9.462 0	2.243 0
7.	57.793	4.057 9	9.435 4	2.491 5
8.	55.348	5.066 1	9.398 0	2.695 5
9.	46.376	6.071 6	9.384 6	2 8 8 9
10.	35.537	7.074 5	9.354 3	3.020 0

TABLE 4

Temp. °C	a ₀ nm	E _m ⁰ V	pK	Corr. coeff.
15	0.54	0.147 13	9.456	-0.99
20	0.54	0.140 80	9.510	-0.99
25	0.56	0.135 45	9.546	-0.99
30	0.50	0.129 63	9.588	-0.98
35	0.52	0.123 86	9.623	-0.97
40	0.52	0.117 10	9.674	-0.96
45	0.54	0.110 02	9.728	-0.94

The following polynomial for the variation of the standard electrode potential² with temperature was used,

$$E^{\circ} = 0.14074 - 10051.0 \times 10^{-7} (t-20) - 88 757 \times 10^{-7} (t-20)^2 \quad (8)$$

The standard mean deviation of pK at 25° was ± 0.004. An error of ± 0.017 units of pK both at the lowest and the highest ionic strengths was caused by a change of ± 0.1 mV in the measured e.m.f. Similarly, an error of 1% in the concentration of barbital was reflected in a change of ± 0.0044 units in the value of pK' (at both ends of the ionic strength scale) at 25°. The values of pK' were found to remain practically unchanged for changes of β from 0 to 1.0. However, m_H and -log γ_± decreased as β was increased for any particular molality of barbital, as was expected. A rise in pK with temperature was noticed. However, in the regression analysis the correlation coefficient (pK' vs I) decreased slightly with increase of temperature (Table 4) indicating progressively increasing inaccuracy of measurement with rise in temperature. Indeed, it was observed that for stable e.m.f. values it took more time at higher temperatures than at lower ones. The values of pK from 15 to 45° were 'fitted' by conventional methods of regression for polynomials to equation¹⁰ (9),

$$pK = (A/T) + CT + D \quad (9)$$

giving A = 802.7 deg, C = 1.7489 × 10⁻³ deg⁻¹ and D = 1.6366.

Values of ΔG°, ΔS°, ΔH° and ΔC_p° for the dissociation of barbital were calculated from the constants of equation (9) (Table 5). Values of ΔH° obtained with the help of equation (9) were used to form a polynomial in T of the form of equation (10).

$$\Delta H^{\circ} = 17.312 \times 10^3 - 19.275T - 27.121 \times 10^{-3}T^2 - 69 959 \times 10^{-6}T^3 \quad (10)$$

So that

$$-\Delta C_p^{\circ} = 19 275 + 54 241 \times 10^{-3}T + 20 988 \times 10^{-6}T^2 \quad (11)$$

Another polynomial of the form of equation (12)

$$\log K = (A/T) - C + DT - ET^2 \quad (12)$$

evaluated in the hope of a better 'fit' gave

$$\log K = 46219 3/T - 467.575 + 1.52052T - 1.69119 \times 10^{-3}T^2 \quad (13)$$

The effects of such an equation on the standard thermodynamic functions are also given in Table 5. From Table 5 it is obvious that while there is reasonable unanimity between values of ΔG°, ΔS°, and ΔH° from the two polynomial equations (9) and (13), values of ΔC_p° are quite different except at 303.15 K. ΔC_p° is thus sensitive to the degree of the polynomial used. The results for ΔC_p° obtained by equation (9) are perhaps to be preferred on grounds of the type of polynomial used being more conventional.

TABLE 5

Temp °C	ΔG (× 10 ⁻³ J mol ⁻¹)		ΔS° (JK ⁻¹ mol ⁻¹)		ΔH° (10 ⁻³ J mol ⁻¹)		ΔC _p ° (JK ⁻¹ mol ⁻¹)	
	From eqn. (9)	From eqn. (13)	From eqn. (9)	From eqn. (13)	From eqn. (9)	From eqn. (13)	From eqn. (9)	From eqn. (13)
15	52.197	52.162	-224.3	-240.5	-12.434	-17.116	-193.0	646.2
20	53.327	53.373	-227.6	-231.7	-13.407	-14.565	-196.3	372.7
25	54.473	54.486	-231.0	-227.7	-14.397	-13.405	-199.7	89.4
30	55.616	55.648	-234.3	-228.7	-15.403	-13.687	-203.0	-203.5
35	56.816	56.770	-237.7	-234.5	-16.427	-15.457	-206.4	-506.2
40	58.013	57.999	-241.0	-245.1	-17.467	-18.765	-209.7	-818.6
45	59.227	59.251	-244.4	-260.6	-18.524	-23.659	-213.1	-1140.7

It is interesting to note that while a polynomial with a higher power in T as in equation (13) should have been a better fit for the experimental data than one of the type of equation (9), some of the derived thermodynamic quantities differ appreciably. However, variations such as these are fairly well documented. For instance, Harned and Robinson¹¹ have carried out several computation based on the data for formic acid. The variation of $\log K$ with T for formic acid has been fitted to the following equations :

$$\log K = A - B/T - CT - D \log T \quad (a)$$

$$= A - B/T - C \log T \quad (b)$$

$$= -A/T + B - CT \quad (c)$$

$$= -A + BT - CT^2 \quad (d)$$

Thus while the polynomial in equation (a) has four terms on the right-hand-side, the others have only three. The experimental data for the formic acid was found to fit equation (b) best. However, equations (a) - (c) were also nearly as good. (Thus, in the case of formic acid, the deviations from the standard value have been reported to be $\pm 6.5 \times 10^{-4}$, $\pm 6.4 \times 10^{-4}$, $\pm 6.6 \times 10^{-4}$ and $\pm 12 \times 10^{-4}$ by the respective use of equations (a), (b), (c) and (d).

Judging from the trend of similar work published on the temperature dependence of dissociation constants of other acids, an expression of the type included in equation (9) seems preferable. However, there still remains this doubt of the inherent accu-

racy of the thermodynamic quantities so derived from the e.m.f. data.

Since the Gibbs free energy is not particularly affected by structural factors, while enthalpy and entropy are¹², some insight into the structural features is also obtained from changes in enthalpy and entropy. The negative values of ΔH° and ΔS° in a medium of 80% ethanol + 20% water suggest that the presence of a large proportion of ethanol makes the mixed solvent composition less associated than pure water, that is, a structural breakdown is favoured relative to water.

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