J. Indian Chem. Soc.,
Vol. LVII, October 1980, pp. 995-998

Thermochromic Behavior of Buffered Indicator Solutions I. Determination of the Heat of Proton Ionization of Phenolphthalein

F. H. JUMEAN*, M. I. KHAMIS and G. N. SALAITA

Department of Chemistry, University of Jordan, Amman, Jordan

Manuscript received 25 March 1980, accepted 27 July 1980

The apparent heat of proton ionization, $\triangle H'$, for phenolphthalein in aqueous solutions containing 6 per cent ethanol by weight was determined by two methods, (a) the conventional spectrophotometric method in which apparent dissociation constants are obtained as a function of temperature and (b) the novel thermochromic method. The reasonably good agreement between the results of the two methods establishes the latter as a powerful and unique tool for obtaining $\triangle H'$ values of weak acids.

IN an earlier publication[1], one of us (F. H. Jumean) reported on a system whose absorbance was a highly sensitive function of temperature. The system consisted of an aqueous 0 1 *M* glycine solution to which was added a small amount of ethanolic phenolphthalein solution and sufficient 0.1 *M* NaOH to bring the *p*H up to the second acidic pK of the aminoacid. It was then employed, however, as a 'chemical thermometer' for the purpose of measuring temperatures during the course of investigating the thermal behavior of myoglobin solutions, and no attempt was made to examine its thermodynamic properties. In a later presentation[2], however, some of the thermodynamic properties of buffered indicator solutions were described. In this paper, we report on the first of a series of current experimental investigations of the thermodynamic properties of such solutions.

In a system consisting of a buffer HB and an indicator HIn the principal equilibria are

$$HB = B + H^+ \quad \ldots (1)$$

$$HIn = In^- + H^+ \quad \ldots (2)$$

For the case in which the change in the heat capacity, $\triangle C_p$, for both buffer and indicator is assumed to be zero, application of the familiar Van't Hoff expression

$$\log K = \frac{\triangle H}{2.303\ RT} + \text{constant} \quad \ldots (3)$$

readily yields the following expression

$$\log \frac{a_{In^-} \cdot a_{HB}}{a_{HIn} \cdot a_{B^-}} = \frac{-(\triangle H_B - \triangle H_I)}{2.303\ RT} + \text{constant} \quad \ldots (4)$$

in which the symbol a denotes activity and $\triangle H_B$ and $\triangle H_I$ are the heats of proton ionization of buffer and indicator, respectively.

If the mixed system is investigated at a *p*H equal, or close to, the *p*K of the buffer then the ratio a_{HB}/a_{B^-} should remain essentially constant upon varying the temperature despite the accompanying *p*H changes, provided that the buffer concentration is sufficiently high to ensure good buffering capacity. Furthermore, since indicator concentrations are typically very small (in this study *ca.* 3×10^{-5} *M*), activities of indicator species may be replaced by concentrations and equation (4) becomes

$$\log \frac{[In^-]}{[HIn]} = \frac{b}{T} + at \quad \ldots (5)$$

where $b = -(\triangle H_I - \triangle H_B)/2.303\ R$ and the term a is constant. The left handside of equation (5) is accessible from spectrophotometric measurements and a plot of this quantity against 1/T should have a slope equivalent to the term b. Thus, if either one of the $\triangle H$ values is known from independent mesurements, the other may be obtained by employing the thermochromic method. In this paper we report on our attempt to investigate the usefulness and applicability of this method with respect to the common indicator phenolphthalein. Three buffers whose pK values lie within the transformation range of this indicator (*p*H 8-10) were selected *viz.* glycine, isoleucine, and phenol.

Experimental

All chemicals were of reagent grade and were used without further purification. Distilled deionized water

was used for the preparation of all solutions. *p*H measurements were conducted on an Orion research microprocessor Ionalyzer model 901 equipped with calomel and glass electrodes. The instrument was calibrated using two standard boric acid-NaOH buffer solutions. The calibration was repeated every time the temperature was altered, making use of the reported value[8] of -0.0082 for the temperature coefficient (dpH/dT)' of the standard buffer. The reliability of the measurement was better than 0.01 *p*H unit. Spectrophotometric measurements were conducted on a Pye-Unicam SP 8000 spectrophotometer equipped with a thermostatted cell compartment. The temperature inside the cell was continuously monitored to within 0.2° by means of a thermocouple.

Due to the extremely low solubility of phenolphthalein in water, all measurements were carried out on aqueous solutions containing 6 percent ethanol by weight. This condition necessitated the determination of the heats of ionization of three buffers in this medium, since changes in the dielectric constant of the medium have been known to affect values of apparent dissociation constants as well as heats of proton ionization of weak acids[4].

Results and Discussion

Apparent macroscopic dissociation constants, *p*K′ values, for glycine, isoleucine, and phenol were determined in aqueous solutions containing 6 per cent ethanol by weight at an ionic strength of 0.100*M*. The standard procedure of titrating 0.1*M* solutions of the weak acid in a thermostatted cell against standard 0.1*M* sodium hydroxide solution was employed. The experimental *p*K′ values are plotted in Fig. 1 against the reciprocal of the absolute temperature. The plots for glycine (a) and isoleucine (b) are fairly linear, yielding apparent heats of ionization, $\triangle H'$, values, of 10.58 and 11.50 Kcal/mole, respectively. The literature values in purely aqueous solutions of the same ionic strength are 10.75 Kcal/mole for glycine[5] and 11.15 Kcal/mole for isoleucine (estimated from data in ref. 6). Furthermore, the good linearity of plots a and b of Fig. 1 is in accord with the reported small $\triangle C_p$ value[5] of -12 cal/deg. mole for glycine and the likewise small value of -15 cal/deg. mole for isoleucine (also estimated from data in ref. 6). The close agreement between our $\triangle H'$ values for the two aminoacids in the present medium and the literature values for purely aqueous solutions may be readily attributed to the well-known existence of these acids in the predominant zwitterionic form. The proton ionization of a zwitterionic aminoacid is not accompanied by any net change in the total charge, and hence the medium effect upon the energy of this process ought to be very small.

Fig. 1(c) is a similar plot for the temperature dependence of *p*K′ for phenol. The somewhat concave appearance of this plot indicates that $\triangle C'_p$ for phenol, unlike that for the two aminoacids, is significant. Analysis of p the plotted results yields the following expression for the temperature dependence of $\triangle H'$ for phenol :

$$\triangle H' = 5130 - 60\ (T\text{-}25) \qquad \ldots\ (6)$$

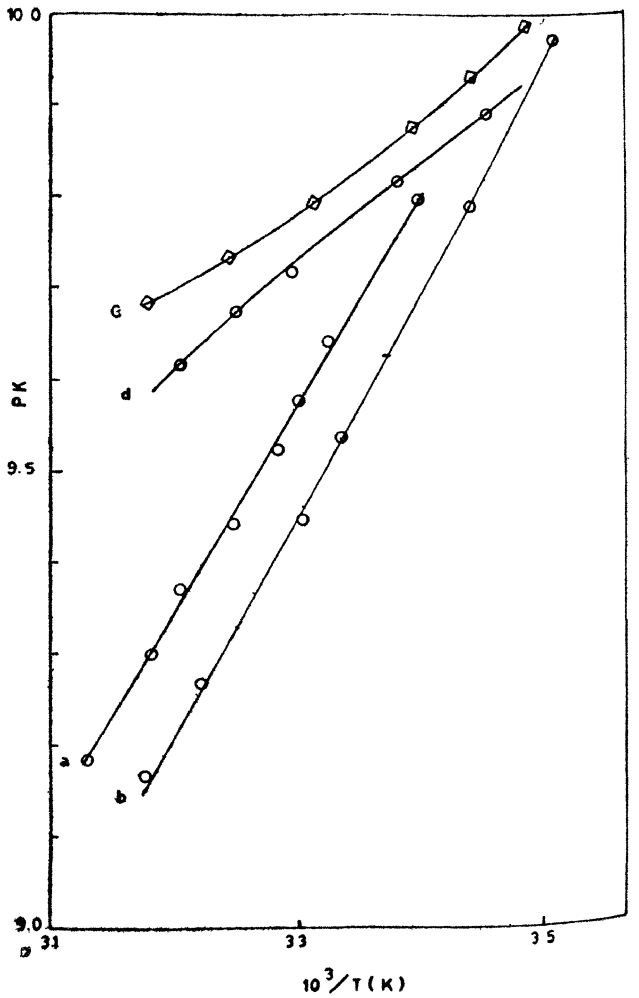

Fig. 1. Plot of *p*K′ *vs.* 1/T for a) glycine, b) isoleucine, c) phenol and d) phenolphthalein.

in which $\triangle H'_{25^\circ} = 5130$ cal/mole and $\triangle C'_p = -60$ cal/deg. mole. Two observations seem pertinent at this point. Firstly, our $\triangle H'_{25^\circ}$ value for phenol is significantly lower than the literature value of 6.1 Kcal/mole[7] in aqueous solution at the same ionic strength. This observation must be solely attributed to the change in medium (see reference 4, for example, for a discussion of medium effects). Secondly, our $\triangle C'_p$, value is more negative than the value of -43 cal/deg. mole in aqueous medium[6], an obeservation which is consonant with the general trend of decreasing $\triangle C_p$ with decreasing dielectric constant of the medium[4]. A detailed discussion of the medium effect is, however, outside the scope of this work, since the primary aim is to obtain reliable values of $\triangle H'$ from a conventional method for comparison with other values obtained from the thermochromic method.

pK' values for for phenolphthalein were obtained over a 30° temperature range by employing the conventional spectrophotometric method in which the optical densities of solutions equimolar in the indicator concentration were measured as a function of pH in the vicinity of the indicator's pK. The following equation was applied :

$$pK' = pH - \log \frac{D - D_a}{D_b - D} \quad \ldots (7)$$

where D is the optical density of the solution at the pH of interest and D_a and D_b are the optical densities of the same solution in very acidic and very basic media, respectively. All measurements were carried out on solutions buffered with boric acid-NaOH buffer containing equimolar concentrations (3.50×10^{-5} M) of the indicator and 6 per cent ethanol by weight. Changes in optical density were monitored at 550 nm, the wavelength maximum of the basic form (In^-) band, at which D_a was equal to zero, It may be noted that log terms of equations (5) and (7) are identical. Fig. 1(d) shows the temperature dependence of pK' for phenolphthalein. The slight convexity of the plot indicates that $\triangle C_p'$ for the indicator is small and positive, but the limited accuracy of the data does not justify an expression analogous to equation (6). The slope of this plot yields a value of 3.92± 0.1 Kcal/mole for $\triangle H'$ of the indicator.

In Table 1 the various $\triangle H'$ values in the present medium are listed alongside the literature values in aqueous solution.

TABLE 1

$\triangle H'$, Kcal/mole

Compound	This work[a]	Literature[b]	Reference
Glycine	10.58	10.75	5
Isoleucine	11.50	11.15	5[c]
Phenol	5.13	6.1	6
Phenolphthalein	3.92	—	—

a. aq. sol'n containing 6 per cent ethanol by weight, I = 0.00M $\triangle H'$ values accurate to within ±0.05 Kcal/mole

b. aq. sol'n, I = 0.100 M

c. estimated value

Thermochromic Results : Fig. 2 shows the temperature dependence of the optical density at 550 nm for solutions containing equimolar ($2.36 \times 10^{-5} M$) concentrations of phenolphthalein and each of the three weak acids under the same conditions of the previous experiments. The pH values for these solutions were somewhat different because of differences in the pK' values between the three weak acids. Inspection of Fig. 2 reveals that the magnitude of the change in optical density for glycine (a) and isoleucine (b) is considerable, whereas that for phenol (c) is slight and accompanied with the appearance of a minimum. This observation

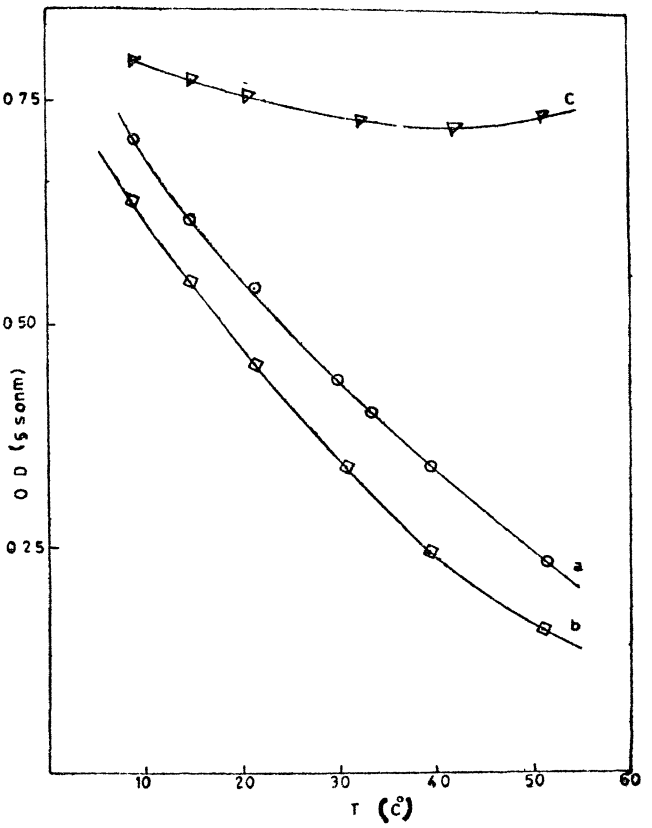

Fig. 2. Typical plots of the dependence of optical density on temperature for indicator solutions containing a) glycine, b) isoleucine and c) phenol.

is in line with the finding (Table 1) that $\triangle H'_B - \triangle H'_I$ values for indicator solutions of the two aminoacids are considerably greater than the corresponding value for phenol. The appearance of a minimum in curve (c) at *ca.* 43° is interesting. At this temperature, $\triangle H'_{43^\circ}$ for phenol is only 4.05 Kcal/mole (from equation 6) and considering that $\triangle H'$ for phenolphthalein was found to have an average value of 3.92 Kcal/mole in the temperature range investigated, this confirms the finding, *vide supra*, that $\triangle C'_p$ for phenolphthalein is small and positive, since at the temperature of minimum optical density the value of the term b is clearly zero (see equation 5).

Fig. 3 is a plot of equation (5) for indicator solutions containing glycine (a), isoleucine (b) and phenol (c). Plots (a) and (b) show good linearity and yield respectively, values of 6.86 and 7.67 Kcal/mole for the quantity $\triangle H'_B - \triangle H'_I$. Since $\triangle H'_B$ values have already been independently determined for the two aminoacids in the same medium (Table 1), two separate values for $\triangle H'_I$ may now be calculated : 3.72 Kcal/mole from the glycine solutions and 3.87 Kcal/mole

from the isoleucine solution. These values are in reasonably good agreement with the value of 3.92 Kcal/mole obtained from the conventional spectrophotometric method.

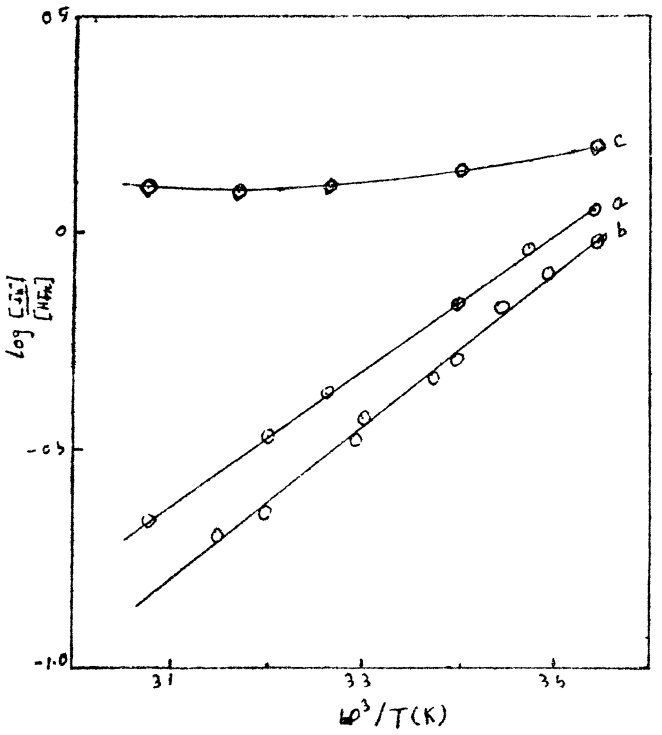

Fig. 3. Plot of equation (5) for indicator solutions with a) glycine, b) isoleucine and c) phenol.

The plot of equation (5) for the phenol-phenolphthalein system, however, is somewhat concave. This behavior indicates that the b value decreases with increasing temperature and ought to be expected from the thermal behavior of this system (Fig. 2, c). At 25°, the slope of this plot yields the value of 1.29 Kcal/mole for the quantity $\triangle H'_B - \triangle H'_I$. Since $\triangle H'_B$ for phenol has already been independently determined with a value of 5.13 Kcal/mole (Table 1), the calculated value for $\triangle H'_I$ would be 3.84 Kcal/mole, again in good agreement with experimental results already presented.

Table 2 summarizes the various $\triangle H'_I$ values obtained in this work.

In conclusion, it may be stated that the application of the thermochromic method to the determination of the heats of proton ionization of weak acids has been shown to yield good and consistent results. The advantages of this method lie in its speed, since no prior pK determination is required, as well as in its reasonable accuracy. The existence of a wide variety of indicators with transition intervals spanning the entire pH range ensure the wide applicability of this method. In a following report we shall deal with systems of large $\triangle C_p$ values and modify equation (5) to make it applicable to such systems.

TABLE 2

System	$\triangle H'_{In} \pm 0.1$, Kcal/mole	Method
Glycine-In	3.72	Thermochromic
Isoleucine-In	3.87	Thermochromic
Phenol-In	3.84	Thermochromic
Boric acid-NaOH-In	3.92	Conventional spectrophotometric

In=Phenolphthalein, I=0.100 *M*. All solutions contain 6 per cent ethanol by weight.

Acknowledgement

The authors wish to thank the University of Jordan for financial support and Dr. E. S. Awad, for reviewing the manuscript.

References

1. F. JUMEAN, M. S. thesis, American University of Beirut, 1966.
2. E. S. AWAD, N. K. ABED and F. H. JUMEAN, Abstracts, Second Science Meeting, Lebanese Association for the Advancement of Science, Beirut, Nov. 1970, p. 65.
3. R. G. BATES, Determination of pH, John Wiley & Sons, Inc , New York, 1964, p. 115.
4. R. G. BATES and R. A. ROBINSON in "Chemical Physics of Ionic Solutions", (Ed.) B. E. CONWAY and R. G. BARRADAS. Johns Wiley & Sons, Inc., New York, 1966, p. 211.
5. E. KING, *J. Amer. Chem. Soc.*, 1951, 73, 155.
6. G. D. FASMAN, (Ed.), "Handbook of Biochemistry and Molecular Biology", vol. 1, Physical and Chemical Data, 3rd edition, CRC Press Inc., Cleveland, Ohio, 1976, p. 228.
7. G. D. FASMAN, (Ed.), "Handbook of Biochemistry and Molecular Biology", vol. 1, Physical and Chemical Data, 3rd edition, CRC Press Inc., Cleveland, Ohio, 1976, p. 230.