JOURNAL OF RESEARCH of the National Bureau of Standards—A. Physics and Chemistry
Vol. 71A, No. 1, January–February 1967

Dissociation Constant of *m*-Nitrophenol in 50 Wt Percent Methanol-Water Solvent from 25 to 40 °C and Related Medium Effects

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(August 15, 1966)

The dissociation constant of *m*-nitrophenol in 50 wt percent methanol-water as solvent has been determined at 25, 30, 35, and 40 °C. A spectrophotometric method was used, together with acidity functions for buffer solutions in 50 percent methanol derived from previous emf measurements. Values of the enthalpy and entropy changes on dissociation of the phenol have been calculated. A comparison with corresponding values for the dissociation of *m*-nitrophenol in aqueous solution affords a measure of the medium effect. The medium effect for *m*-nitrophenol lies intermediate between that for *o*-nitrophenol and that for *p*-nitrophenol.

Key Words: Dissociation, electrolytes, methanol, *m*-nitrophenol, nonaqueous solvents, phenols, thermodynamics.

1. Introduction

The acidic dissociation of ammonium ion is an acid-base process (protolysis) of charge type A^+B°. Ammonium ion dissociates to give an uncharged product, NH_3:

$$NH_4^+ \rightleftharpoons H^+ + NH_3.$$

The dissociation constant for an A^+B° process (expressed as pK) is invariably reduced if, instead of water as solvent, 50 wt percent methanol is used. This is true for the ammonium ion [1][2] and the protonated forms of tris(hydroxymethyl)aminomethane [2], 4-aminopyridine [3], aniline, and methyl- and dimethylaniline [4]. The contrary behavior is found for dissociation processes of charge type $A^\circ B^-$ such as acetic acid,

$$HAc \rightleftharpoons H^+ + Ac^-$$

whose pK values are higher in 50 percent methanol than in water. This has been shown to be true for acetic acid itself [5] and for a number of other acids [4] of the same charge type. Data are now presented for an acid of the phenolic type, *m*-nitrophenol, and it is shown that its pK values follow the same pattern.

2. Method

The principle of the spectrophotometric method used in this work is as follows. Consider three solutions of *m*-nitrophenol, all of the same stoichiometric concentration. Let acid be added to the first solution to convert the phenol entirely into its molecular form, HN. Let alkali be added to the second solution to convert the phenol entirely into its dissociated form, N^-. Let the third solution contain a buffer mixture. The optical densities of the three solutions, each at the same wavelength, are D_1, D_2, and D, respectively. Then $\alpha = (D - D_1)/(D_2 - D_1)$ is the proportion of phenol present in the anionic form, N^-, and the dissociation constant of the phenol is given by:

$$pK = -\log a_{H^+} - \log (D - D_1)/(D_2 - D) - \log \gamma_{N^-}/\gamma_{HN}. \qquad (1)$$

This can be written as:

$$pK = p(a_H \gamma_{Cl}) - \log (D - D_1)/(D_2 - D) - \log \gamma_{N^-}/(\gamma_{HN}\gamma_{Cl^-}) \qquad (2)$$

where the acidity function $p(a_H\gamma_{Cl})$ designates the quantity $-\log (m_{H^+}\gamma_{H^+}\gamma_{Cl^-})$.

It is advantageous to use a buffer solution whose $p(a_H\gamma_{Cl})$ value is approximately equal to the pK value of the phenol; α is then about 0.5 and the ratio $(D - D_1)/$

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[2] Figures in brackets indicate the literature references at the end of this paper.

D_2-D) can be measured with maximum accuracy. Buffer solutions which are equimolal in tris(hydroxymethyl)aminomethane and its hydrochloride in 50 percent methanol have values of $p(a_H\gamma_{Cl})$ about 8 [6]. *m*-Nitrophenol, however, has a pK value nearly 9 in this solvent medium. Some measurements were made (table 1) of the pK value of *m*-nitrophenol at 25 °C using this equimolal buffer solution, but it was thought desirable to use solutions with a higher value of the buffer ratio m_2/m_1, where m_2 is the molality of tris(hydroxymethyl)aminomethane and m_1 that of its hydrochloride.

The problem is to obtain $p(a_H\gamma_{Cl})$ values for these buffer solutions, and to do so it is necessary to revert to some earlier work. The pK value of tris(hydroxymethyl)aminomethane in its protonated form (designated pK_T in order to distinguish it from the pK value of *m*-nitrophenol) is given by:

$$pK_T = p(a_H\gamma_{Cl}) - \log (m_2/m_1) - \log \gamma_T/(\gamma_{TH^+} \cdot \gamma_{Cl^-}) \qquad (3)$$

where T designates tris(hydroxymethyl)aminomethane and TH^+ the protonated form. It has been shown [2, 7] that the last term can be represented as:

$$-\log \gamma_T/(\gamma_{TH^+} \cdot \gamma_{Cl^-}) = -2AI^{1/2}/(1+BaI^{1/2}) + \beta I. \qquad (4)$$

Here A and B are constants of the Debye-Hückel equation and β is the parameter of the term linear in the ionic strength. For tris(hydroxymethyl)aminomethane in 50 percent methanol, it was found that a satisfactory representation of the data could be obtained with $a=0$. Hence,

$$p(a_H\gamma_{Cl}) = pK_T + \log (m_2/m_1) + 2AI^{1/2} - \beta I. \qquad (5)$$

Using $p(a_H\gamma_{Cl})$ values already tabulated [6], values of $\beta = 1.22$, 1.26, 1.32, and 1.32 kg mol^{-1} at 25, 30, 35, and 40 °C, respectively, are calculated.

These values of β are valid for solutions in which tris(hydroxymethyl)aminomethane and its hydrochloride are present in equimolal amounts. The assumption is now made that these values also hold for solutions in which the buffer ratio is not unity. Some doubt may be held as to the validity of this assumption. In the determination of the dissociation constant of tris(hydroxymethyl)aminomethane in aqueous solution, Bates and Hetzer [8] found eq (4) was satisfactory with $a=0$. They used solutions containing only tris(hydroxymethyl)aminomethane and its hydrochloride. Datta, Grzybowski, and Weston [9], however, added potassium chloride to their solutions and found that $a=3.2$ Å gave a good representation of their results. Nevertheless, the use of β values independent of the buffer ratio seems to be justified by the fact that it leads to concordant pK values (table 1) at 25 °C with buffer ratios of $m_2/m_1 = 1.007$, 4.06, and 5.98.

3. Experimental Procedure

Degrees of dissociation, α, of *m*-nitrophenol were measured spectrophotometrically in the usual manner. A stable single-beam spectrophotometer was used. It had been found in earlier studies to be capable of precise and reproducible measurements of the optical density in the visible and ultraviolet regions of the spectrum.

A thermostated cell block was constructed using the metal cell holder supplied with the spectrophotometer. The holder has provision for four cells, and a heater was placed in each of the outer cell positions (fig. 1). These heaters were formed by winding 7 ft of 26 B and S nichrome wire, insulated with glass spaghetti, on to each of two aluminum blocks. The complete heaters fitted snugly into the cell holder. The heater windings were connected in series.

A thermistor cemented to the cell holder served as a sensor in a temperature-control circuit. A second thermistor, used for temperature measurement, was mounted on a movable metal bracket so that it could be placed in the solution in one of the cells or moved aside when solutions were being changed. Leads from the heaters and thermistors terminate in a six-pin socket mounted on the cell holder; the leads from a corresponding six-pin plug were passed through a hole in the lid of the cell compartment.

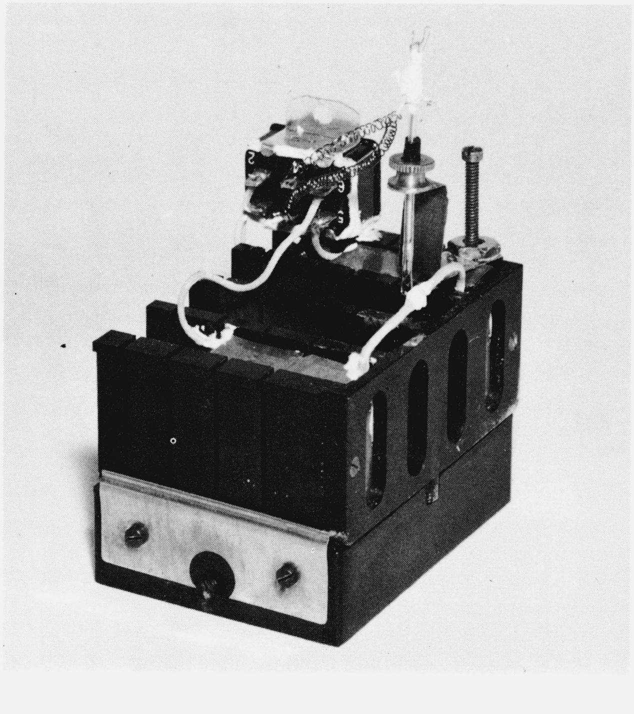

FIGURE 1. *Controlled-temperature cell block for spectrophotometric measurements.*

The resistance of the measuring thermistor was determined using a d-c Wheatstone bridge. The leads from the regulating thermistor were connected to the input of a commercial electronic proportional temperature controller. The heaters constitute the load for this controller. Provision was made for connecting a 100- or 250-Ω ballast load in series with the heaters. Using this apparatus, the temperature of the solutions could be regulated between room temperature and 50 °C with a constancy of 0.01 °C.

The *m*-nitrophenol, of a commercial grade believed to be highly pure, was recrystallized twice from water. Its melting point, found to be 96 °C after crystallization, agreed well with values given in the literature. The buffer solutions were prepared from tris base, standard hydrochloric acid, and purified methanol in the manner described in an earlier publication [2].

TABLE 1. *Dissociation constant of* m-*nitrophenol in 50 wt percent methanol from 25 to 40 °C*

	I	$-2 \log \gamma$	400 mμ		390 mμ	
			D	*pK*	D	*pK*
25 °C	log $m_2/m_1 = 0.003$		$D_1 = 0.051$,	$D_2 = 0.840$	$D_1 = 0.119$,	$D_2 = 0.840$
	0.01988	0.204	0.131	8.977	0.188	8.998
	.03974	.271	.144	8.971	.199	8.995
	.05955	.318	.150	8.989	.205	8.996
	.07921	.354	.157	8.990	.216	8.983
	.09858	.383	.175	8.943	.233	8.930
			Mean *pK*	8.97_4	Mean *pK*	8.98_0
	log $m_2/m_1 = 0.608$		$D_1 = 0.052$,	$D_2 = 0.847$	$D_1 = 0.122$,	$D_2 = 0.840$
	0.00722	0.127	0.264	8.982	0.312	8.987
	.01455	.175	.287	8.973	.333	8.977
	.02178	.209	.297	8.983	.347	8.973
	.02903	.238	.312	8.974	.359	8.968
	.03604	.260	.318	8.983	.365	8.975
			Mean *pK*	8.97_9	Mean *pK*	8.97_6
	log $m_2/m_1 = 0.777$		$D_1 = 0.059$,	$D_2 = 0.930$	$D_1 = 0.135$,	$D_2 = 0.925$
	0.00581	0.115	0.359	8.974	0.405	8.979
	.01159	.159	.387	8.974	.433	8.964
	.01737	.190	.407	8.957	.452	8.954
	.02313	.216	.425	8.947	.467	8.947
	.02880	.237	.441	8.936	.483	8.933
			Mean *pK*	8.95_6	Mean *pK*	8.95_5
30 °C	log $m_2/m_1 = 0.608$		$D_1 = 0.054$,	$D_2 = 0.841$	$D_1 = 0.120$,	$D_2 = 0.831$
	0.00722	0.129	0.235	8.933	0.286	8.924
	.01455	.178	.256	8.924	.300	8.932
	.02178	.213	.266	8.932	.311	8.934
	.02903	.240	.276	8.932	.321	8.930
	.03604	.263	.285	8.932	.327	8.936
			Mean *pK*	8.93_1	Mean *pK*	8.93_1
	log $m_2/m_1 = 0.777$		$D_1 = 0.060$,	$D_2 = 0.919$	$D_1 = 0.131$,	$D_2 = 0.909$
	0.00581	0.117	0.311	8.943	0.361	8.936
	.01159	.160	.338	8.930	.385	8.925
	.01737	.192	.352	8.937	.400	8.922
	.02313	.218	.367	8.927	.411	8.922
	.02880	.240	.373	8.940	.420	8.923
			Mean *pK*	8.93_4	Mean *pK*	8.92_6
35 °C	log $m_2/m_1 = 0.608$		$D_1 = 0.054$,	$D_2 = 0.829$	$D_1 = 0.121$,	$D_2 = 0.819$
	0.00722	0.130	0.207	8.887	0.259	8.886
	.01455	.180	.222	8.896	.273	8.888
	.02178	.215	.236	8.883	.283	8.890
	.02903	.244	.244	8.887	.292	8.888
	.03604	.266	.251	8.889	.297	8.894
			Mean *pK*	8.88_7	Mean *pK*	8.88_9
	log $m_2/m_1 = 0.777$		$D_1 = 0.062$,	$D_2 = 0.909$	$D_1 = 0.131$,	$D_2 = 0.904$
	0.00581	0.118	0.277	8.897	0.331	8.886
	.01159	.163	.301	8.888	.350	8.885
	.01737	.195	.319	8.878	.369	8.869
	.02313	.221	.329	8.882	.376	8.877
	.02880	.245	.341	8.878	.388	8.872
			Mean *pK*	8.88_5	Mean *pK*	8.87_8
40 °C	log $m_2/m_1 = 0.777$		$D_1 = 0.065$,	$D_2 = 0.907$	$D_1 = 0.133$,	$D_2 = 0.894$
	0.00581	0.120	0.250	8.858	0.303	8.848
	.01159	.166	.268	8.859	.320	8.848
	.01737	.198	.284	8.850	.335	8.838
	.02313	.224	.293	8.853	.342	8.845
	.02880	.246	.310	8.833	.359	8.820
			Mean *pK*	8.85_1	Mean *pK*	8.84_0

The concentration of *m*-nitrophenol was 5.83×10^{-4}, 5.80×10^{-4}, and 6.34×10^{-4} *m* in the buffer solutions for which log (m_2/m_1) was 0.003, 0.608, and 0.777, respectively. All optical measurements were made in cells 1 cm in length; m_2 is the molality of tris(hydroxymethyl)aminomethane, $m_1 (= I)$ that of its hydrochloride.

4. Results

Table 1 gives experimental details of the measurements; I, the total ionic strength of the solution, is equal to m_1, the concentration of tris(hydroxymethyl)-aminomethane hydrochloride; 2 log γ is an abbreviation for $\log \gamma_T/(\gamma_{TH^+} \cdot \gamma_{Cl^-})$ and has been calculated using eq (4). Measurements were made at two wavelengths, using 1 cm cells. In calculating values of *pK* a small correction was made for the effect of *m*-nitrophenol on the $p(a_H \gamma_{Cl})$ value of the buffer solution [10].

Mean values of *pK* at 25, 30, 35, and 40 °C are given below, where they are compared with corresponding values for the dissociation process in aqueous solution [11].

	pK		
	In 50 percent methanol	In water	ΔpK
°C			
25	8.97_0	8.35_5	0.61_5
30	8.93_0	8.28_1	$.64_6$
35	8.88_4	8.23_2	$.65_2$
40	8.84_6	8.16_7	$.67_9$

The difference, $\Delta pK = pK$ in 50 percent MeOH $- pK$ in H_2O, is a measure of the medium effect. The value of ΔpK at 25 °C for *m*-nitrophenol in 50 wt percent methanol (0.615) falls between the values for *o*-nitrophenol (0.687) and *p*-nitrophenol (0.536) for the same temperature and solvent [12]. The quantity $\Delta G° = 2.3026 RT \Delta pK$ is the change in Gibbs free energy for the transfer reaction:

$$HN(s) + H^+(w) + N^-(w) = HN(w) + H^+(s) + N^-(s), \qquad (6)$$

where w stands for water and s for 50 percent methanol. $\Delta G°$ for this reaction increases from 0.84 kcal mol^{-1} at 25 °C to 0.97 kcal mol^{-1} at 40 °C (1 cal = 4.1840 J). This is in marked contrast to what has been observed with protonated tris(hydroxymethyl)aminomethane [2], where the medium effect is almost independent of temperature, ΔpK being -0.251 at 25 °C and -0.248 at 40 °C. The Gibbs free energy change corresponding to the medium effect on tris · H$^+$ is thus -0.34 kcal mol^{-1} at 25 °C. The different signs of the medium effects for these two acids are a consequence of the difference in charge type of the two dissociation reactions.

The pK values of *m*-nitrophenol in 50 percent methanol can be represented as a function of temperature (T) in °K by the equation

$$pK = 6.352 + 780.8/T \tag{7}$$

with a maximum error of 0.002 in pK. It follows that the enthalpy change on dissociation in 50 percent methanol is 3.57 kcal mol^{-1} compared with 5.14 kcal mol^{-1} in water, while the entropy change is -29 cal deg^{-1} mol^{-1} compared with -21 cal deg^{-1} mol^{-1} in water. Thus reaction (6), the transfer of hydrogen and phenolate ions from water to 50 percent methanol and of phenol molecules from 50 percent methanol to water is accompanied by an enthalpy change $\Delta H° = -1.57$ kcal mol^{-1} and an entropy change $\Delta S° = -8$ cal deg^{-1} mol^{-1}.

5. References

[1] M. Paabo, R. G. Bates, and R. A. Robinson, J. Phys. Chem. **70,** 247 (1966).
[2] M. Woodhead, M. Paabo, R. A. Robinson, and R. G. Bates, J. Res. NBS **69A** (Phys. and Chem.) No. 3, 263 (1965).
[3] M. Paabo, R. A. Robinson, and R. G. Bates, Anal. Chem. **38,** 1573 (1966).
[4] A. L. Bacarella, E. Grunwald, H. P. Marshall, and E. L. Purlee, J. Org. Chem. **20,** 747 (1955).
[5] T. Shedlovsky and R. L. Kay, J. Phys. Chem. **60,** 151 (1956).
[6] M. Woodhead, M. Paabo, R. A. Robinson, and R. G. Bates, Anal. Chem. **37,** 1291 (1965).
[7] R. G. Bates and G. D. Pinching, J. Res. NBS **42,** 419 (1949).
[8] R. G. Bates and H. B. Hetzer, J. Phys. Chem. **65,** 667 (1961).
[9] S. P. Datta, A. K. Grzybowski, and B. A. Weston, J. Chem. Soc. (London) 792 (1963).
[10] R. A. Robinson and A. K. Kiang, Trans. Faraday Soc. **51,** 1398 (1955).
[11] R. A. Robinson and A. Peiperl, J. Phys. Chem. **67,** 2860 (1963).
[12] R. A. Robinson and R. G. Bates, J. Res. NBS **70A** (Phys. and Chem.) No. 6, 553 (1966).

(Paper 71A1–430)