

The Dissociation Constant of *m*-Nitroanilinium Ion in Water-Tetrahydrofuran Solvents at 25 °C

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The dissociation constant of *m*-nitroanilinium ion has been determined in water and in six water-tetrahydrofuran mixtures. The results are compared with those for water-methanol mixtures.

Key words: Dissociation constant; ionization constant; mixed solvents; *m*-nitroaniline; tetrahydrofuran.

1. Introduction

For the dissociation of a weak acid of the charge type A^+B^0 , $BH^+ \rightleftharpoons H^+ + B$, the Born equation [1]¹ predicts that the influence of solvent on the dissociation constant will be governed by the dielectric constant:

$$pK_s - pK_w = \frac{Ne^2}{2RT \ln 10} \left\{ \frac{1}{\epsilon_s} - \frac{1}{\epsilon_w} \right\} \left\{ \frac{1}{r_{H^+}} - \frac{1}{r_{BH^+}} \right\} \quad (1)$$

where ϵ is the dielectric constant, w designates the solvent as water and s another solvent which may be a mixed solvent such as water-methanol; r is the radius of the ion specified by the subscript and, in the case of the hydrogen ion, it is, presumably, the radius of the hydrated ion, H_3O^+ or $H_9O_4^+$ [2]. There can be no doubt that this equation describes correctly the electrostatic energy changes for a macroscopic system of spheres in a continuous dielectric medium. However, it may require modification for microscopic systems where the influence of dielectric saturation of solvent molecules around an ion is important [3]. Moreover, the equation is not concerned with energy changes accompanying the transfer of the neutral molecule from one solvent to another and it has been shown that this is by no means negligible in the case of the transfer of tris(hydroxymethyl)aminomethane from water to water-methanol solvents [4].

The medium effect on the dissociation constant of *m*-nitroanilinium ion has been determined [5] in water-methanol mixtures as solvent; this paper is concerned

with the dissociation constant of this acid in water-tetrahydrofuran solvents with the object of comparing the medium effect in water-methanol and water-tetrahydrofuran solvents of the same dielectric constant.

2. Method

The dissociation constant of *m*-nitroanilinium ion in a number of water-tetrahydrofuran solvents was determined by the spectrophotometric method described in several previous publications [5–10]; the notation used in this paper is that used before. The validity of Beer's Law for this system was demonstrated by measurements of optical density of alkaline solutions in 62.5 wt percent tetrahydrofuran with the concentration of *m*-nitroaniline varying from 2×10^{-4} to $8 \times 10^{-4} m$.

3. Materials

For the purpose of purification, *m*-nitroaniline was recrystallized from methanol. Tetrahydrofuran was refluxed over anhydrous sodium sulphate for three days and then distilled.

4. Results

The experimental results are given in table 1. In this work, *m*-nitroaniline was dissolved in hydrochloric acid solutions. Some of the *m*-nitroaniline reacted with hydrochloric acid to form the nitroanilinium ion, thereby reducing the hydrogen ion concentration; the fraction of the nitroaniline reacting in this way is given by the spectrophotometric data as $(D_2 - D)/(D_2 - D_1)$. Allowance for this has been made

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¹ Figures in brackets indicate the literature reference at the end of this paper.

TABLE 1. Dissociation constant of *m*-nitroanilinium ion in water-tetrahydrofuran at 25 °C

$10^3 m_{\text{HCl}}$	D	$-\log m_{\text{H}^+}$	$\log \frac{D-D_1}{D_2-D}$	pK
Water. Concentration of <i>m</i> -nitroaniline: $3.6 \times 10^{-4} m$; $D_1 = 0.041$; $D_2 = 0.508$				
3.961	0.262	2.424	-0.047	2.471
3.260	.288	2.510	+0.050	2.460
2.081	.340	2.710	.250	2.460
1.006	.408	3.032	.565	2.467
				Average pK 2.465
12.5 wt percent Tetrahydrofuran. Concentration of <i>m</i> -nitroaniline: $3.6 \times 10^{-4} m$; $D_1 = 0.041$; $D_2 = 0.485$				
9.370	0.238	2.038	-0.098	2.136
7.118	.267	2.159	+0.016	2.143
5.058	.304	2.309	.162	2.147
3.516	.345	2.468	.337	2.131
2.570	.374	2.605	.477	2.128
				Average pK 2.137
25 wt percent Tetrahydrofuran. Concentration of <i>m</i> -nitroaniline: $3.7 \times 10^{-4} m$; $D_1 = 0.041$; $D_2 = 0.475$				
37.92	0.204	1.424	-0.221	1.645
31.08	.227	1.510	-.125	1.635
24.06	.256	1.622	-.008	1.630
16.53	.302	1.786	+0.179	1.607
9.735	.350	2.016	.393	1.623
				Average pK 1.628
37.5 wt percent Tetrahydrofuran. Concentration of <i>m</i> -nitroaniline: $3.7 \times 10^{-4} m$; $D_1 = 0.041$; $D_2 = 0.491$				
76.50	0.264	1.117	-0.008	1.125
62.30	.294	1.207	+0.109	1.098
52.58	.313	1.280	.184	1.096
41.66	.340	1.382	.297	1.085
				Average pK 1.101
50 wt percent Tetrahydrofuran. Concentration of <i>m</i> -nitroaniline: $3.8 \times 10^{-4} m$; $D_1 = 0.042$; $D_2 = 0.510$				
92.86	0.342	1.033	+0.252	0.781
87.77	.348	1.057	.276	.780
83.13	.352	1.081	.293	.788
73.03	.371	1.137	.374	.763
				Average pK 0.778

62.5 wt percent Tetrahydrofuran. Concentration of *m*-nitroaniline:

$3.8 \times 10^{-4} m$; $D_1 = 0.042$; $D_2 = 0.526$				
95.12	0.398	1.022	+0.444	0.578
91.20	.400	1.040	.454	.586
83.36	.416	1.079	.532	.547
75.15	.421	1.125	.557	.568
				Average pK 0.570
75 wt percent Tetrahydrofuran. Concentration of <i>m</i> -nitroaniline: $3.9 \times 10^{-4} m$; $D_1 = 0.042$; $D_2 = 0.542$				
294.3	0.316	0.532	+0.084	0.448
193.2	.363	.714	.254	.460
112.0	.418	.951	.482	.469
				Average pK 0.459

All measurements were made at a wavelength of 380 nm in 1 cm cells. The concentration of *m*-nitroaniline was 3.6 mol liter⁻¹.

in calculating the values of $-\log m_{\text{H}^+}$ given in the third column of table 1.

5. Discussion

The dissociation constant of *m*-nitroanilinium ion is plotted in figure 1 as a function of the reciprocal of the dielectric constant of the medium, using values of the dielectric constant determined by Critchfield, Gibson, and Hall [11]. The figure also contains a plot of the dissociation constant of *m*-nitroanilinium ion as a function of ϵ^{-1} , in water-methanol solvents, using data published previously [5]. This figure emphasizes once again, what has been said several times before in earlier papers from this laboratory, that the Born effect does not give a complete description of solvent effects on acidity, particularly if the *macroscopic* dielectric constant is used. Thus, at $\epsilon = 40$, $\epsilon^{-1} = 0.025$, interpolation in figure 1 gives $pK = 1.39$ for a water-methanol mixture and $pK = 0.78$ for a tetrahydrofuran mixture, each of the same dielectric constant, a significant difference, well beyond the limit of experimental error.

It might be argued that the comparison is invalid because there must be considerable ion-pair formation in hydrochloric acid solutions of such comparatively low dielectric constant. It is true that neglect of such ion-pair formation would result in a pK value of *m*-nitroanilinium ion higher than the true one. Thus, we can make the two curves in figure 1 coincide if we invoke ion-pair formation for water-tetrahydrofuran solvents and assume that it is absent in water-methanol solvents of the same dielectric constant. Or, alternatively, that there is some ion-pair formation in a water-methanol solvent and even more in a water-tetrahydrofuran solvent of the same dielectric constant. This, however, only resolves one difficulty at the expense of another; for most, if not all, theories of ion-pair formation demand that it depends upon the dielectric constant of the medium. Consequently, if we adjust

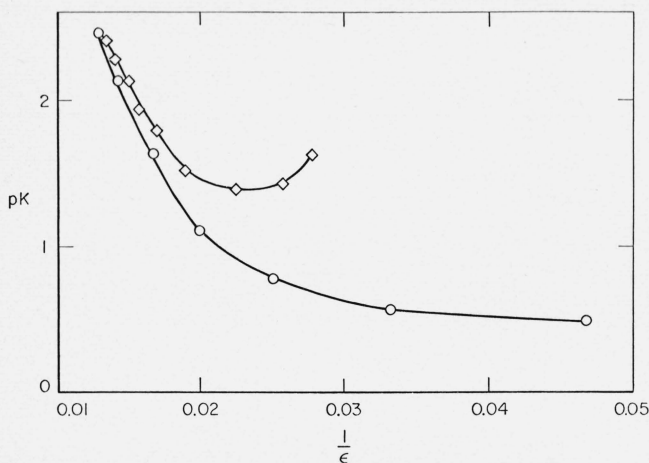


FIGURE 1. Dissociation constant of *m*-nitroanilinium ion as a function of the dielectric constant of the solvent.

□ Water-methanol solvent.
○ Water-tetrahydrofuran solvent.

the extent of ion-pair formation in two solvent mixtures of the same dielectric constant so as to make the dissociation constants of *m*-nitroanilinium ion equal, we negate the theoretical requirement that ion-pair formation between hydrogen and chloride ions should be equal in two solvents of the same dielectric constant.

It is difficult to decide if there is ion-pair formation between H^+ and Cl^- ions in these tetrahydrofuran-rich solvents. The dielectric constant of the 75 percent tetrahydrofuran solvent is $\epsilon = 21.44$ [11], 3.652 times smaller than that of water at the same temperature, 25 °C. The Bjerrum critical distance [12], which is $q = 3.58 \text{ \AA}$ for water as solvent, is, therefore, 13.07 \AA for 75 percent tetrahydrofuran, a distance within which a considerable amount of ion-pairing is possible.

Roy and Sen [13] have measured the emf of the cell Pt; H_2 (g, 1 atm), HCl (*m*) in water-tetrahydrofuran, AgCl; Ag. Their conclusion is that there is no appreciable ion association at 8.98 and 18.21 percent tetrahydrofuran, that, at 27.20 percent, there is barely noticeable evidence of ionic association; interaction appears to be considerable at 73.03 percent and hydrochloric acid is a weak electrolyte in 89 percent tetrahydrofuran. Our interpretation of the lower curve of figure 1 is, therefore, correct up to 50 percent tetrahydrofuran ($\epsilon^{-1} = 0.025$); the highest value to which our comparison of *pK* values of *m*-nitroanilinium ion in water-methanol and water-tetrahydrofuran extends is $\epsilon^{-1} = 0.028$.

However, their contention that there is considerable ionic association of hydrochloric acid in 73.03 percent tetrahydrofuran merits examination. It is consistent with the Bjerrum critical distance, but it does not seem to be consistent with some activity coefficient data they quote (table 1 of ref [13]). The Debye-Hückel equation for the activity coefficient of a 1:1 electrolyte is

$$-\log \gamma = \frac{Ad_0^{1/2} m^{1/2}}{1 + Bad_0^{1/2} m^{1/2}} \quad (2)$$

Using values of the dielectric constant and density of 73.03 percent tetrahydrofuran solution, interpolated from the data of Critchfield et al. [11], and putting $\tilde{a} = 4.3 \text{ \AA}$, the value adopted by Bates and Bower [14] for aqueous solutions, values of the activity coefficient of hydrochloric acid in 73.02 percent tetrahydrofuran have been calculated and compared in table 2 with those observed [13]. The observed activity coefficient is somewhat lower than the calculated values (except at 0.1 *m*) but the difference is small and cannot correspond to any marked amount of ion-pair formation. Whatever may be the final answer to this question about ion-pair formation in tetrahydrofuran-rich solvents, it will not affect the principal conclusion demonstrated by figure 1, that the macroscopic dielectric constant of the solvent is not the only variable upon which the dissociation constant of a weak acid depends.

TABLE 2. Activity coefficient of hydrochloric acid in 73.03 percent tetrahydrofuran at 25 °C

<i>m</i>	γ obs. (ref. [13])	γ calc.
0.0001	0.929	0.932
.001	.798	.808
.005	.626	.644
.01	.535	.560
.05	.341	.354
.1	.296	.279

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