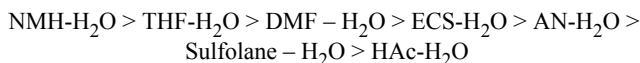


The Dissociation Constant of p-Nitroanilinium Ions in Water-Sulfolane Solvents at 25°C

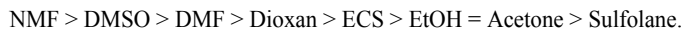
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ABSTRACT. The dissociation constants of p-nitroanilinium ions have been determined in water-sulfolane mixtures at 25°C using spectrophotometric method. The $p(K)_{BH^+}$ is found to decrease with progressive addition of sulfolane which indicates that the basicity of the medium is increased by the addition of sulfolane. The relative basicity of the medium is compared with other water-solvent mixtures and it is found that the basicity decreases in the order of:



The acidity function, H_0 , of HCl in H₂O-sulfolane mixtures is also determined and is found to increase with increase of the organic solvent component for a fixed acid concentration. This is explained due to the salting in effect, which differs with the organic solvent. It showed a decrease in the order of:



KEYWORDS: Dissociation constant, p-nitroaniline, solvent effect, sulfolane, acidity function.

Introduction

The spectrophotometric method for the determination of the dissociation constant of an acid or base is useful and rapid one for organic compounds with absorption spectra dependent on the concentration of hydrogen ion in the solvent. The effect of changing the solvent composition on the pK is a useful means of inferring changes in the pattern of ion-solvent interactions in binary solvent systems such as water-non-aqueous solvent mixtures^[1-4]. The acidity constant and

the proton transfer equilibria were investigated to show the effect of solvent on the activity of an acid or base and the proton transfer process^[5-10].

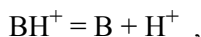
The present paper reports the spectrophotometric determination of the dissociation constant of p-nitroanilinium ions in various water-sulfolane mixtures at 25°C.

Experimental

Spectrograde sulfolane and doubly distilled deionized water were used for preparing the water-sulfolane mixtures. Constant boiling hydrochloric acid solutions were used for preparing the various dilute hydrochloric acid solutions. p-Nitroaniline (BDH grade) was purified by two crystallizations from hot distilled water^[11] and 50% H₂O-EtOH mixture and then dried in vacuo. Stock solutions of this indicator was prepared in 50% H₂O-sulfolane mixture.

Outline of the Present Method

The dissociation constants of p-nitroanilinium ions in water-sulfolane mixtures were determined spectrophotometrically in a manner similar to that previously described. The pK_{BH^+} values in the molal scale for the isoelectric dissociation process of the indicator;



in water-sulfolane mixtures were obtained by extrapolation of the plots of pK_{BH^+} of equation (3) against μ to $\mu = 0$.

$$pK_{\text{BH}^+}^{\text{obs}} = -\log m_{\text{H}^+} - \log \frac{\alpha}{1-\alpha} \quad (1)$$

$$pK_{\text{BH}^+}^{\text{obs}} = pK_{\text{BH}^+} + \log \frac{\gamma_{\text{H}^+} \cdot \gamma_{\text{B}}}{\gamma_{\text{BH}^+}} \quad (2)$$

$$= pK_{\text{BH}^+} + f(\mu) \quad (3)$$

where α and $(1 - \alpha)$ are the fractions of the indicator species present in the neutral form (B) and ionic form (BH⁺), respectively, and $\alpha/(1 - \alpha)$ is determined from the measurements of spectral absorbancies of the solution having the effective molal concentration of H⁺ equals to m_{H^+} and of the solutions containing the completely acid and basic forms of the indicator.

Procedure

A series of solutions was prepared by adding weighed amounts of standard HCl solutions and the solvent to weighed amounts of the indicator (p-nitroaniline) solutions. The spectral absorbance of each solution was measured at $25 \pm 0.05^\circ\text{C}$ on MSE Spectro-plus spectrophotometer at 380-385 nm where

the absorbance showed a maximum for the base form. The absorbance of the protonated form of the indicator was determined by measurement in a solution of 4M HCl while the absorbance of the pure basic form was obtained directly in 0.5M sodium acetate solution.

Results and Discussion

Table 1 gives the experimental results of the pK_{BH^+} values of p-nitroanilinium ions in HCl solutions of different concentrations. The relation between pK'_{BH^+} and molality is a linear-one and obeys the following equation:

$$pK'_{BH^+} = PK_{BH^+} + S m \quad (4)$$

TABLE 1. pK'_{BH^+} values in aqueous HCl solutions of different concentrations (molalities).

m (HCl)	pK'_{BH^+}
0.096	0.980
0.188	0.966
0.390	1.030
0.592	1.127
0.774	1.134
0.963	1.131
1.069	1.273
1.257	1.282
1.450	1.238
1.625	1.433
1.808	1.316

The correlation coefficient (slope) is equal to 0.937 and the intercept gives the dissociation constant of the p-nitroanilinium ions in pure aqueous HCl solution and equal to 0.950. This value is in excellent agreement with that cited in literature^[3,11].

Table 2 presents the values of pK_{BH^+} for the p-nitroanilinium ions in water-sulfolane mixtures of different solvent percentages. As can be seen from the variation of pK_{BH^+} with wt% of solvent, (Fig. 1), that addition of sulfolane causes a decrease in the pK_{BH^+} for the nitroanilinium ion within a concentration range < 66.18% sulfolane. Such concentration range may be described as water-rich region. Also, the ΔpK is linearly related to the reciprocal of the dielectric constant of the medium, $1/\epsilon$, (Fig. 2), with a correlation coefficient of 0.98. A similar trend of decreasing $p(K)_{BH^+}$ with the increase of organic solvent content

has also been observed for all other media that have been studied as presented in Fig. 1. This behaviour may be explained by considering the equilibrium:

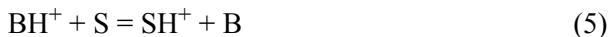


TABLE 2. pK_{BH^+} , $\Delta\text{pK}_{\text{BH}^+}$ [$(\text{pK}_{\text{BH}^+})_{\text{pure water}} - (\text{pK}_{\text{BH}^+})_{\text{solvent mixture}}$] and dielectric constant of the solution mixture.

Wt. % sulfolane	Dielectric constant (ϵ)	pK_{BH^+}	ΔpK
0.0	78.3	0.950	0.000
9.60	74.8	0.793	-0.156
18.62	72.1	0.630	-0.320
27.56	69.6	0.442	-0.508
35.77	67.4	0.352	-0.598
43.62	65.4	0.293	-0.657
51.89	63.1	0.216	-0.734
66.18	60.2	-0.178	-1.128

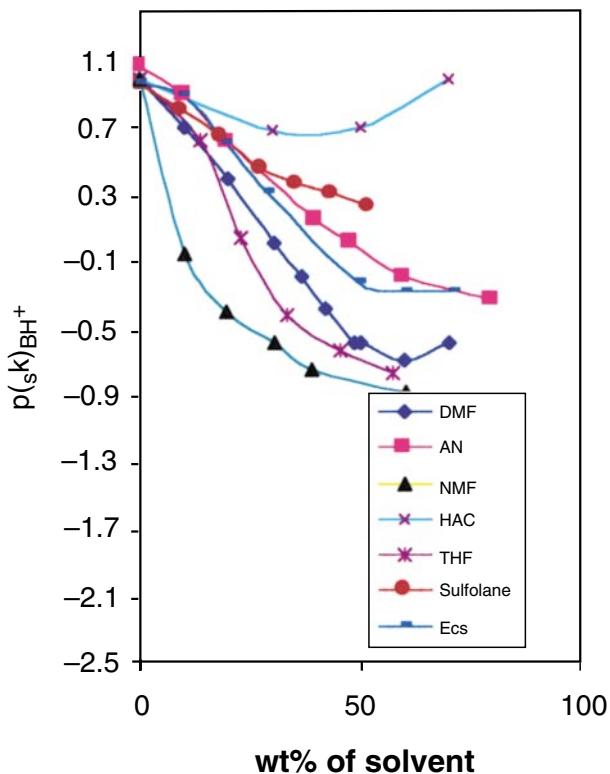


FIG. 1. Variation of $\text{p}(\text{s},\text{k})_{\text{BH}^+}$ of p-nitroaniline with weight percent of different solvent mixtures at 25°C.

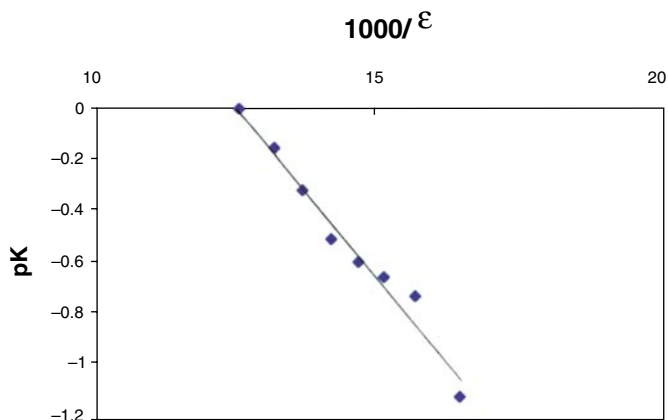
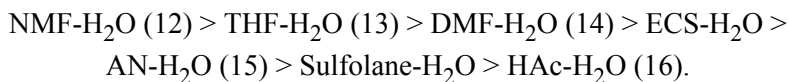


FIG. 2. Variation of medium effects with dielectric constant in sulfolane water mixtures at 25°C for p-nitroaniline indicator.

This reaction indicates the abstraction of a proton from the indicator acid species by an acceptor solvent molecule. Hence, the basicity of the second component of the solvent mixture relative to water is an important variable in studying solvent effects. Thus, $p(K)_{BH^+}$ decreases if the equilibrium is shifted to the right, *i.e.* if the basicity of the solvent increases, and vice versa. Accordingly, the relative basicities of the solvent mixture could be predicted and are found to decrease in the order.



The effect of further addition of the organic solvent to the water solvent on the dissociation constant of the indicator at constant temperature is given in Fig. 1. It is observed that there is a change in the slope at high concentrations of the organic solvent which may be described as the organic solvent-rich region. It could also be concluded that the behaviour in the water-rich region is only slightly dependent on the co-solvent^[12-16], while in the organic solvent rich mixtures, the proton dissociation differ substantially from one co-solvent to the other. This behaviour may be explained qualitatively as being due to the change in the solvation of the ions. So, Fig. 1 shows that p-nitroaniline has the strongest preference for NMF, most poorly solvated by HAc.

The solvent effect on the dissociation of BH^+ ion in the mole fraction scale has been also calculated using the Gibb's free energy equation^[17]:

$$\Delta G_t^0 = 2.303 RT \Delta pK \quad (6)$$

which indicates the change in the free energy of proton transfer from water to water-sulfolane solvent mixture. The results are summarized in Table 3. The

values of ΔG_t^{ON} computed using the respective values of ΔpK expressed in the mole fraction scale, are obtained from the corresponding values of ΔG_t^{O} expressed in the molal scale by the usual relation^[18]. It is observed that values of ΔG_t^{ON} become more negative with the increasing proportion of sulfolane in the medium, which means that the transfer of the proton from water to sulfolane is a spontaneous process.

TABLE 3. Standard Gibbs energy of transfer from water to sulfolane-water mixtures at 25°C.

Mole fraction	1.566	3.262	5.388	7.714	10.39	13.948	22.191
ΔG_t^{O} cal/mol	-214.1	-439.2	-697.3	-820.8	-901.8	-1007.5	-1548.3
ΔG_t^{ON} cal/mol	-264.9	-539.97	-855.98	-1036.5	-1177.4	-1354.84	-2040.7

The Gibb's free energy change, ΔG_t^{O} , accompanying the transfer of one mole of species (i) from the standard state in water to that in the solvent concerned can be expressed by the following equation:

$$\Delta G_t^{\text{O}} = \Delta G_t^{\text{O}}(\text{B}) + [\Delta G_t^{\text{O}}(\text{H}^+) - \Delta G_t^{\text{O}}(\text{BH}^+)] \quad (7)$$

The first term on the right-hand side of this equation indicates the free energy changes associated with the transfer of the neutral molecule (B) from water to the solvent mixture. The second term refers to the difference between free energies of transfer BH^+ and H^+ . The first one explains the stabilization of the base, when additional organic solvent is added to water while the other deals with the selective solvation by either water or sulfolane, of H^+ or BH^+ in the mixed solvent medium.

Acidity Function H_0

Values of H_0 at several HCl concentration in H_2O + sulfolane solvent mixtures are calculated from the relation:

$$H_0 = p(K)_{\text{BH}^+} - \log \left(\frac{m_{\text{BH}^+}}{m_{\text{B}}} \right) \quad (8)$$

The results of changing the acidity function with acid concentration at different percentages of sulfolane are shown in Table 4. The values of H_0 decreased as the acid concentration increased. At the same time, for constant acid molality, H_0 increased with increasing sulfolane content in the solvent mixtures. Similar trend was observed previously for m-nitroaniline indicator in the same solvent^[1]. It indicates that the solvent basicity increases by addition of the organic solvent which may be attributed to the progressive breakdown of the tetrahedral structure of water. Fig. 3 shows the effect of changing composition of some organic solvents on the acidity function, H_0 , for a definite acid concentration in

case of p-nitroaniline. Generally, there is an initial increase in H_0 with increasing organic solvent composition, which may be due to the decrease of the activating coefficient of the molecular indicator base f_B (salting-in effect). As more water is replaced by the solvent, H_0 passes through a maximum and then drops as H_3O^+ ions are converted to the solvated protons. Consequently, one may generally expect that in the case of the p-nitroaniline indicator, the salting-in effect, decreases in the order:

NMF > DMSO > DMF > Dioxan > ECS > EtOH = Acetone > Sulfolane .

TABLE 4. H_0 of HCl solution in sulfolane- H_2O mixtures at 25°C for p-nitroaniline.

m_{HCl}	(v/v)% sulfolane							
	0	10	20	30	40	50	60	70
0.1	0.97	1.23	1.42	1.6	1.64	1.7	1.54	2.5
0.2	0.675	0.89	1.08	1.2	1.34	—	1.52	1.7
0.4	0.305	0.599	0.73	0.92	1.03	1.06	1.24	1.1
0.6	0.042	0.42	0.58	0.73	0.84	0.86	1	0.88
0.8	-0.12	0.37	0.51	0.61	0.71	0.6	0.75	0.73
1	-0.255	0.25	0.38	0.46	0.58	0.53	0.56	0.51
1.2	-0.392	0.23	0.33	0.42	0.52	0.46	0.46	0.39
1.4	-0.575	0.2	0.26	0.39	0.42	0.38	0.29	0.29
1.6	-0.59	0.14	0.25	0.36	0.38	0.24	0.23	0.21

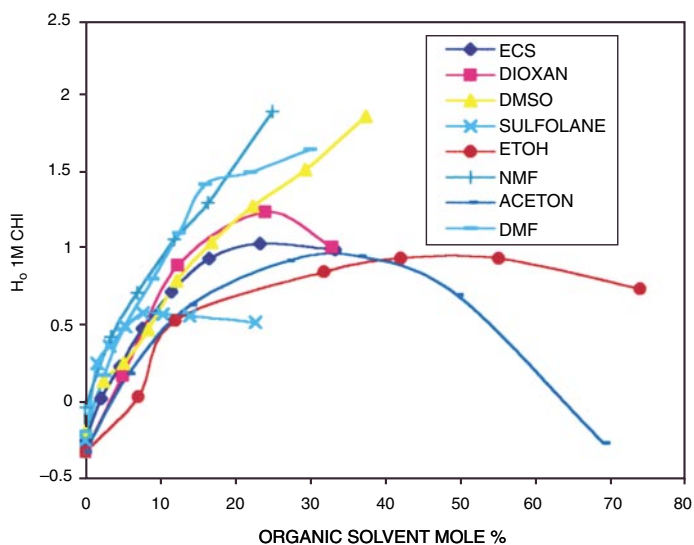


FIG. 3. Variation of H_0 (1M HCl) with solvent composition for p-nitroaniline.

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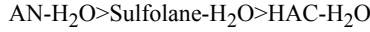
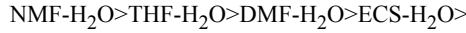
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ثابت التفكك لايون الباربا - نيتروأنيلين في الماء - السيلفولان عند درجة حرارة ٢٥ م°

مشاعل الخالدي

قسم الكيمياء ، كلية العلوم للبنات
الدمام - المملكة العربية السعودية

المستخلص. استخدمت الطريقة الطيفية لتعيين ثابت التفكك للقاعدة الضعيفة p-nitroaniline ذات الشحنة BH^+ في مخاليط من الماء والسلفولين عند درجة حرارة ٢٥ م° ، وأوضحت نتائج البحث أن قيمة PK_{BH^+} تقل مع الإضافة المتزايدة من السلفولين ، مما يوضح أن قاعدية الوسط تزداد بإضافة السلفولين ، كما تم مقارنة قاعدية الوسط مع مخاليط الماء - ، المذيبات العضوية ، حيث أمكن وضع الترتيب تبعاً لنقص القاعدية :



كذلك تضمن البحث تعيين الدالة الحامضية لمحاليل حمض الهيدروكلوريك ووجد أنها تزيد بزيادة كمية المذيب العضوي في نطاق المدى المستخدم ، كما أظهر تغير قيمة الدالة الحمضية في المحاليل المختلفة على أن تغير معامل النشاطية هو العامل الرئيس في ما يطلق عليه التأثير الملحي الداخلي ، وتم دراسة سلوك الدالة الحمضية في المذيبات الأخرى الغنية بالماء ووجد أن النقص في قيمة الدالة الحمضية يتبع الترتيب الآتي :

