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Study of the Dissociation Constants of Some Weak Indicator Bases in Ethyl Cellosolve - Water Solvent Mixtures

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Abstract. A spectrophotometric method has been used for the determination of the dissociation constants of some weak indicator bases in various ethyl cellosolve (ECS)-water solvent mixtures at 25ºC. The indicators used are p-nitro, o-nitro and m-nitroaniline. The dissociation constants are found to decrease with increase of ECS for all investigated indicators which indicates that the basicity of the medium is increased by the addition of solvent. The acidity function, H°, of HCl in water-ECS mixtures is also determined and is found to increase with concentration increase of organic solvent for a fixed acid concentration. This is explained owing to the salting-in effect which depends on the used solvent type.

Keywords: Dissociation constant, o-nitroaniline, m-nitroaniline, p-nitroaniline, solvent effect, ethyl cellosolve, acidity function.

Introduction

Determination of the dissociation constant, pK, of an acid or base is useful and rapid one for organic compounds using spectrophotometric method via absorption spectra depended on the concentration of hydrogen ions 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 interaction in the binary solvents systems such as water-non aqueous solvent mixtures[1-5]. 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[6-16].

The present work investigates the spectrophotometric determination of the dissociation of o-nitro, m-nitro and p-nitroaniline in different water-ECS mixtures 25ºC.

Materials and Methods

Materials

Ethyl cellosolve [2-ethoxyethanol or ethylene glycol monoethyl ether] of the BDH grade was purified as described elsewhere[15]. The indicators: o-nitro, p-nitro and m-nitroaniline (Riedel de Haen Company) were purified and their stock solutions were prepared in 50% alcohol-water mixtures. Constant boiling HCl solutions were used for preparing the different acid solutions using doubly distilled water.

Procedure

The solutions were prepared as described earlier[17]. Stock solutions of HCl obtained from the middle fractions of the twice-distilled constant boiling HCl solution, were prepared in the various experimental compositions. The concentration of the acid solution was always checked gravimetrically by precipitation as AgCl. The spectral absorbances of these solutions were determined at 25ºC with a MSE spectro-plus spectrophotometer with 1 cm cell, using bidstilled water or the mixed solvents as a blank. The maximum absorbance for the base form of the indicators used in water were found to occur at 380-385 nm, 415-420 nm, and 355-385 nm for p-nitro, o-nitro and m-nitroaniline respectively[18].

A series of solutions was prepared by adding weighed amounts of standard HCl solutions and the solvents to weighed amounts of the indicator (o-nitro or p-nitro or m-nitroaniline) solutions. The spectral absorbance of each solution was measured.

Results and Discussion

Calculation of Dissociation Constant (p ($_s$k) BH$^+$)

Values of p($_s$k)BH$^+$ for a selected anilinium ion in water-ECS solvent mixtures were calculated from the relation[19].

$$\mathrm{P}({}_{\mathrm{s}}\mathrm{k})_{\mathrm{BH+}} = -\log \mathrm{m}_{\mathrm{H}}^{+} + \log \mathrm{I} - \log\,(\gamma_{\mathrm{H}}^{+}\,\gamma_{\mathrm{B}}/\gamma_{\mathrm{BH}}^{+}) \tag{1}$$

$$\mathrm{p}({}_{\mathrm{s}}\mathrm{k})_{\mathrm{BH+}} = \mathrm{p}({}_{\mathrm{s}}\mathrm{k})_{\mathrm{BH+}}^{-} - \log\,(\gamma_{\mathrm{H}}^{+}\,\gamma_{\mathrm{B}}/\gamma_{\mathrm{BD}}^{+}) \tag{2}$$

$$\mathrm{p}({}_{\mathrm{s}}\mathrm{k})_{\mathrm{BH+}} = \mathrm{p}({}_{\mathrm{s}}\mathrm{k})_{\mathrm{BH+}}^{-} - \mathrm{Sm} \tag{3}$$

Where B represents the free base, I is the ratio of the concentrations of the two forms of the indicator and γ the activity coefficient of the particular species. The indicator ratio I is calculated from the relation:

$$I = \frac{m_{BH^{+}}}{m_{B}} = \frac{I-\alpha}{\alpha} = \frac{D_1 - D}{D - D_2}\ . \tag{4}$$

Where α and (1 – α) are the fraction of the indicator species present in the neutral and ionized forms respectively, and D_1, D_2 and D are the absorbance of the completely base form of the indicator molecule (in 0.5 M sodium acetate), completely acid form (in the presence of 4M HCl), and of solutions of the partially transformed indicator respectively. It must be pointed out that values of the optical density (D) for all indicators studied always show an increase with the enrichment of the solvent with ECS. Values of D_2 are found to be very small in the case of p-nitroaniline solvent mixtures and are neglected, while values of D_2 for o-nitroaniline and m-nitroaniline indicators seem to have significant values and they are considered in the calculation of I.

Considering Eq. (3), the values of $p({}_sk)_{BH+}$ and S were obtained by applying the least-squares method.

Table 1 represents the values of the dissociation constants for p-nitro, o-nitro and m-nitroanilinium ions in ECS-water mixtures. Figure 1 represents the variation of the dissociation constant for each indicator with solvent composition. It is seen that the addition of ECS to water causes an initial decrease in $p(sk)_{BH+}$ for all indicators. However, in the case of m-nitroaniline, a minimum is obtained nearly at 58% (W/W) ECS. So, the order of basicity increase for indicators used is as follows: o-nitro < p-nitro < m-nitroaniline.

Table 1. Variation of $p(K)_{BH+}$ with solvent composition for p-nitro, o-nitro and m-nitroaniline at 25°C.

ECS v/v %	$p(K)_{BH+}$		
	p-nitro	o-nitro	p-nitroanilline
00	0.590	–0.283	2.334
10	0.887	–0.606	2.190
20	0.592	–1.123	1.917
30	0.297	–	–
40	0.109	–1.189	1.687
50	–0.243	–1.208	1.354
60	–0.254	–1.274	1.108
70	–0.288	–	1.421

This trend shows that the position of the nitro group in the ring has a particular effect on the basicity of the amino group. The lower value of $p(sk)_{BH+}$ was obtained for o-nitroaniline may be due to the presence of both inductive and mesomerice effect for nitro group[3].

The change of the dissociation constant of the indicator in water-ECS solvent mixtures with respect to that in aqueous medium (ΔpK) is calculated for the indicators. Figure 2 represents the plot of the (ΔpK) for these indicators as a

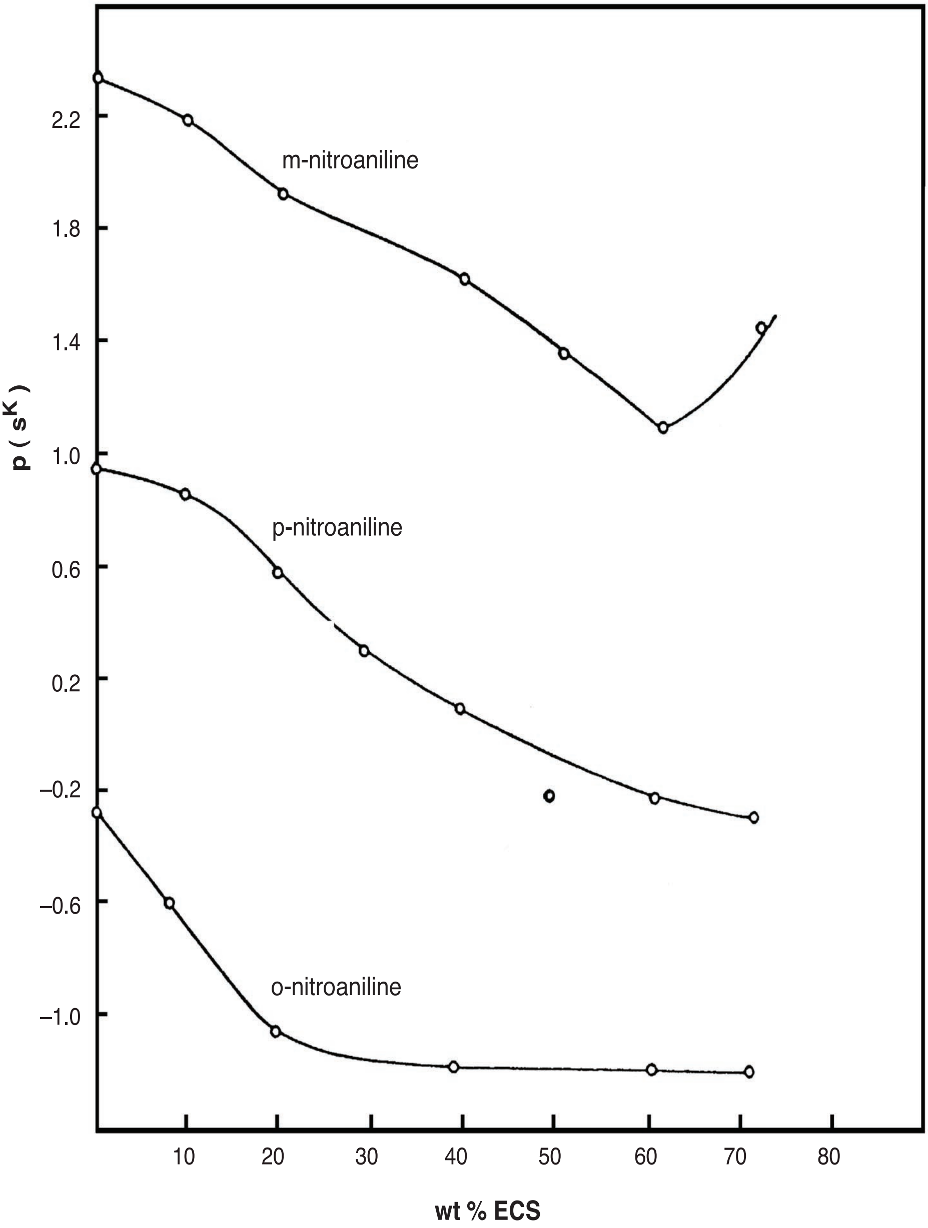

Fig. 1. Variation of pK with weight percent of ECS-water mixture at 25ºC.

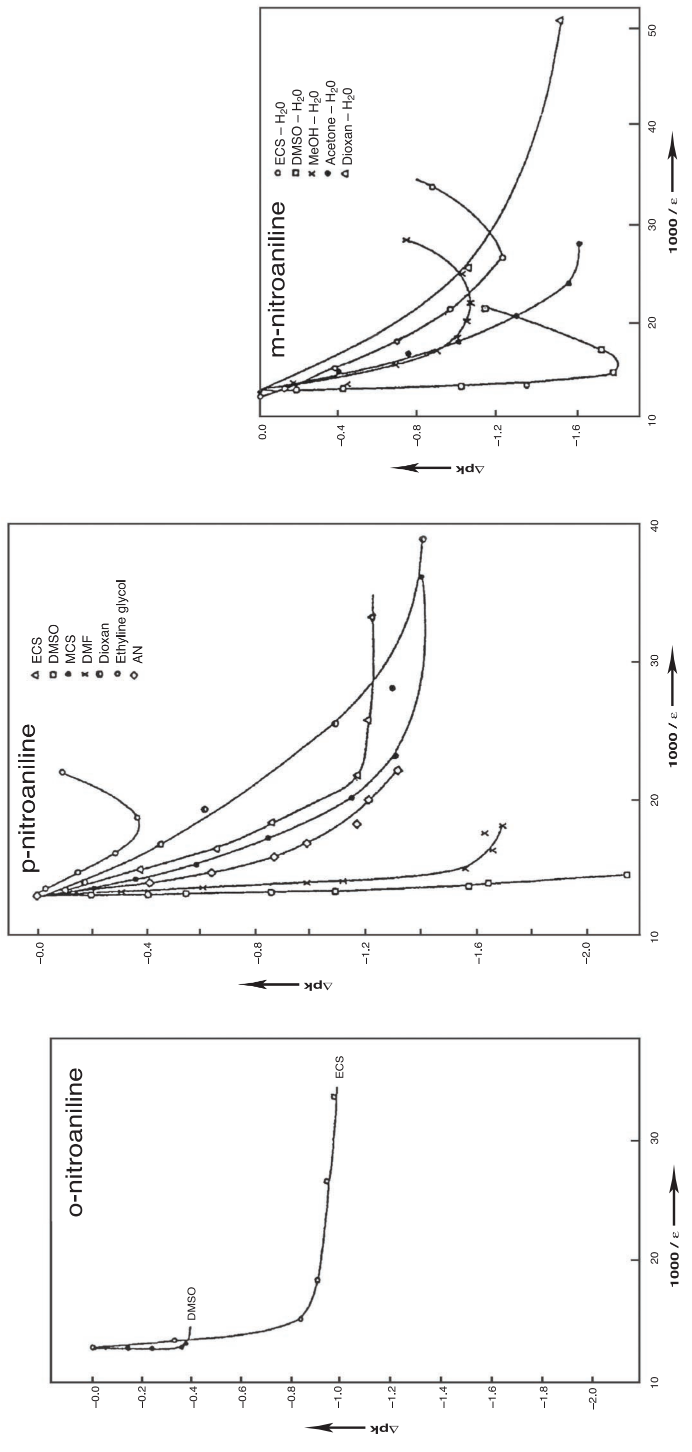

Fig. 2. Variation of Δpk with dielectric constant in ECS-H_2O at 25°C for indicators.

function of reciprocal dielectric constant on the medium. The values of (ΔpK) may be helpful in predicting the order of changing relative basicities for some organic solvents with water. From the figure, it was found that (ΔpK) decrease steeply with increasing of organic solvents and decreasing dielectric constant. This behavior may be explained qualitatively as being due to the change in the salvation of the ions, in which the radius of ions undergoes the corresponding changes. Thus, for the p-nitroaniline indicator, the solvent basicity decreases in the order: DMSO-H_2O > DMF-H_2O > AN-H_2O > MCS-H_2O > ECS-H_2O > Dioxane-H_2O > Ethyleneglycol-H_2O. This shows that p-nitroaniline has the strongest reference for DMSO and is most poorly solvated by ethyleneglycol.

On considering the Gibb's free energy equation[18]:

$$\Delta G_t^0\,(i) = 2.303 \quad RT \quad \Delta pK \tag{5}$$

Values of the free energy ΔG_t^0 change for proton transfer from water to water-ECS solvent mixtures are calculated. As the solvent effect should preferably be expressed in the mole fraction scale, the values of $\Delta G_t^{0^N}$ computed by using the respective values of $p({}_sK)_{BH^+}^N$ in the mole fraction scale, are obtained from the corresponding values of $p({}_sK)_{BH^+}$ in the molal scale by the usual relation[19,20], see Table 2. It is observed that values of $\Delta G_t^{0^N}$ become more negative with the increasing of proportion of ESC in the medium, which indicates that transfer of the proton from water to ESC-H_2O solvent mixture is spontaneous process.

Table 2. Standard Gibb's free energy change of proton-transfer from water to ECS-water mixtures at 25ºC.

(1) o-nitroanilline

mole fraction	0.178	0.474	0.115	0.232	0.327
ΔG_t^0 cal/mol	–440.27	–1141.44	–1229.77	–1256.95	–1346.63
$\Delta G_t^{0^N}$ cal/mol	–480.36	–1161.99	–1452.19	–1644.22	–1839.89

(2) m-nitroanilline

mole fraction	0.212	0.481	0.117	0.169	0.239	0.343
ΔG_t^0 cal/mol	–195.68	–566.65	–960.72	–1330.33	–1665.97	–1240.64
$\Delta G_t^{0^N}$ cal/mol	–243.24	–670.09	–1188.04	–1636.07	–2061.39	–1750.21

(3) p-nitroanilline

mole fraction	2.148	0.468	0.763	0.115	0.165	0.233	0.333
ΔG_t^0 cal/mol	–89.68	–486.47	–887.33	–1142.80	–1621.12	–1636.07	–1683.63
$\Delta G_t^{0^N}$ cal/mol	–137.25	–587.31	–1043.61	–1367.02	–1920.07	–2024.70	–2183.69

Considering the equilibrium represented by the equation:

$$BH^+ \Leftrightarrow B + H^+ \tag{6}$$

Therefore,

$$\Delta G_t^0 = \Delta G_t^0\,(B) - \{\Delta G_t^0\,(BH^+) - \Delta G_t^0\,(H^+)\} \tag{7}$$

The first term on the right-hand side of this equation represents the slandered Gibbs energy of transfer aniline from water to the solvent mixture, while the second term between brackets shows the difference between Gibbs energies of transferee of anilinium BH^+ and H^+ ions. The first part explains the stabilization of the base with increasing organic solvent in the mixture while the other deals with the selective salvation by either water or ESC, of H^+ or BH^+ in the mixed solvent medium.

The variation of ΔGt° for all indicators with mole fraction of ECS is shown in Fig. 3. The solvent effects on the dissociation equilibria of the indicators are more or less similar in aqueous-ECS solvents. So, ΔGt° values for m-nitroaniline pass through a minimum with gradual increasing of ECS. Such trend is not observed for p-nitroaniline since the solvent composition did not extend high enough to locate it. However, it should be mentioned that a similar trend was observed previously in water-methanol[3] and water-2-methoxyethanol[20] for o- and m-nitroanilinium ions was observed at non aqueous solvents. Therefore, it is easy to interpret the decrease of Δpk with increasing ECS content as due to the smaller values of ΔGt° (B) and ΔGt° (H^+) than ΔGt° (BH^+) in the solvent mixture.

Values of H_0 at several HCl in water-ECS solvent mixtures are calculated from the following relation[1,7]:

$$H_0 = P({}_wK)_{BH+} - \log I \tag{8}$$

Figure 4 shows the trend of changing the acidity function with acid concentration at different percentages of organic solvent in case p-nitroaniline indicator. It is observed that H_0 decreases as the acid concentration increases. At same time, H_0 shows an increase with the increase of ECS content in the solvent mixture for a definite acid concentration. This trend indicates that the solvent basicity increases by further addition of the organic solvent, which may be attributed to the progressive breakdown of the tetrahedral structure of water. Thus instead of having the structure $(H_2O)_4\,H^+$, one may have the species $(H_2O)_2\,H^+$ as well. Since the proton affinity in the open structure $(H_2O)_4\,H^+$ is less than that in the compact structure. The latter will be holding the proton more firmly[20-24].

Figure 5 shows the effect of the changing composition of some organic solvents on the acidity function, for a definite acid concentration in case of p-nitroaniline. Generally, there is an initial increase in H_0 with increasing organic

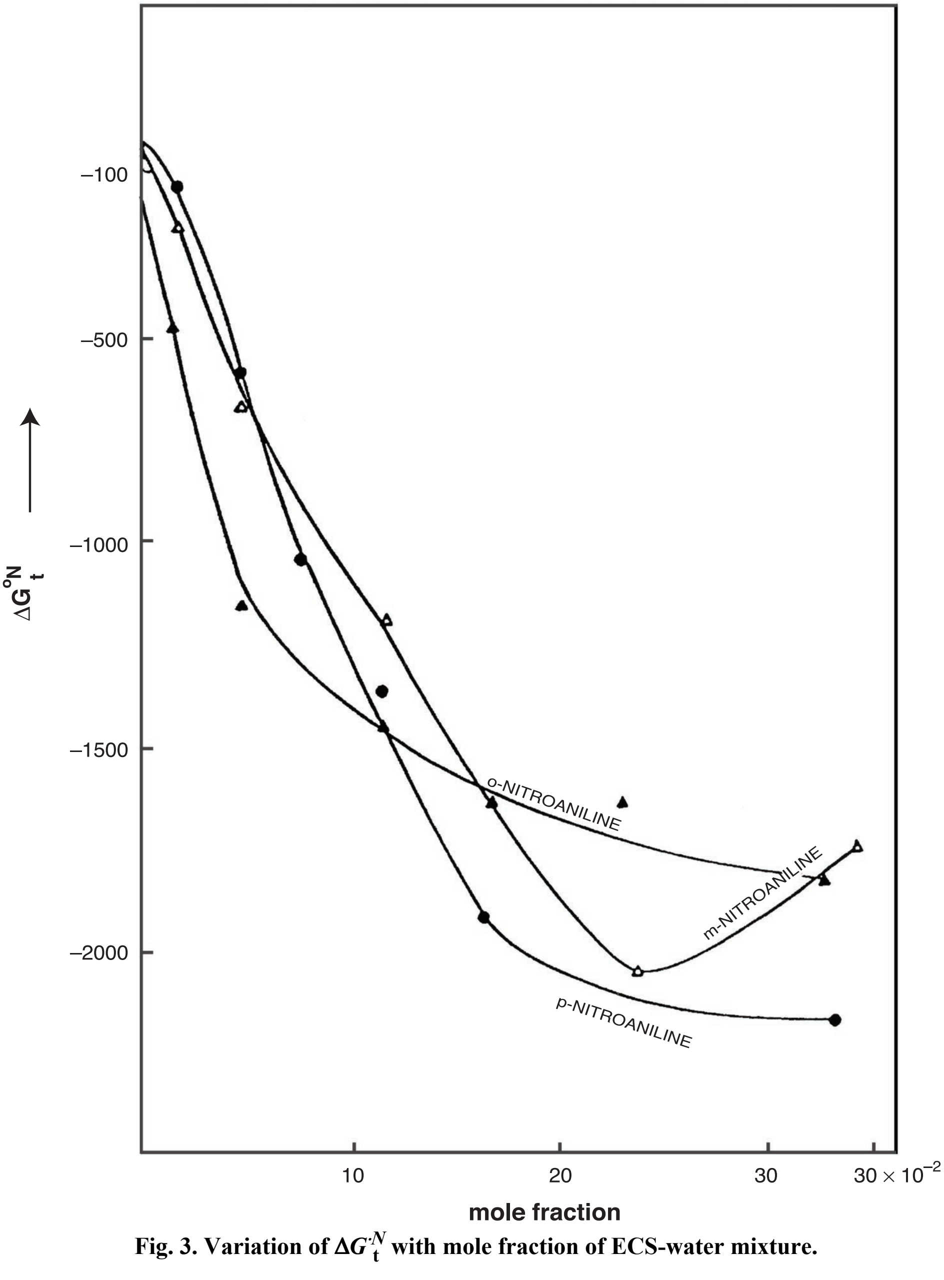

Fig. 3. Variation of $\Delta G_t^{\cdot N}$ with mole fraction of ECS-water mixture.

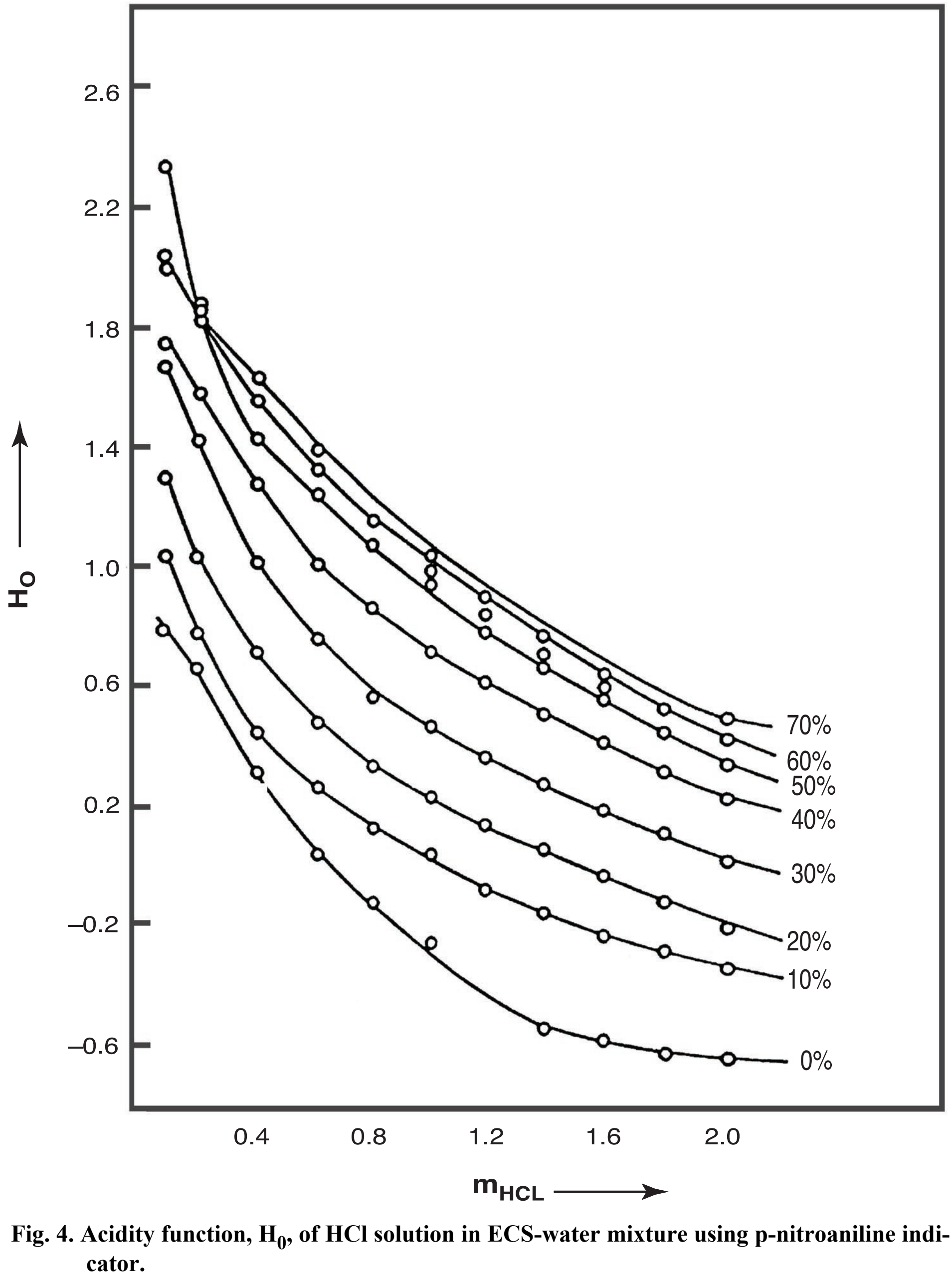

Fig. 4. Acidity function, H_0, of HCl solution in ECS-water mixture using p-nitroaniline indicator.

solvent composition, which may be due to the decrease of the activity 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. If this is the case, one may generally expect that in the case of the p-nitroaniline indicator, the salting-in effect decreases in the order: H_2O-ETOH = H_2O-Acetone < H_2O-MCS = H_2O-ECS < H_2O-Dioxane < H_2O-MF < H_2O-MSO.

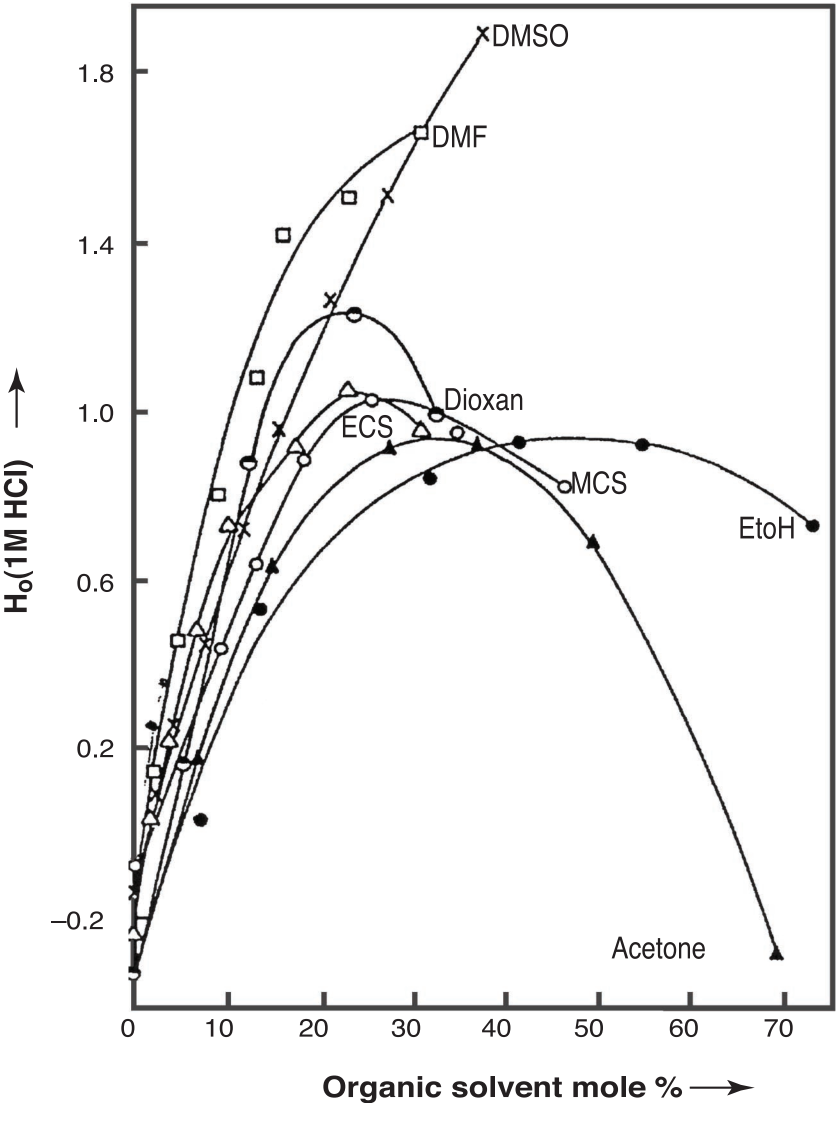

Fig. 5. Variation of H_0 (1 M HCl) with solvent composition for p-nitroaniline.

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دراسة ثوابت التفكك لبعض الكواشف القاعدية الضعيفة في مخاليط الإيثل سيليوسولف – المـاء المذيبة

مشاعل الخالدي و آسيا طه
قسم الكيمياء ، كلية البنات للعلوم
الدمـــام – المملكة العربية السعودية

المستخلص. استخدمت الطريقة السبكتروفوتومترية لتعيين ثوابت التفكك لبعض الكواشف القاعدية الضعيفة، مثل النيترو أنيلين المحتوي على مجموعة نيترو في مواقع مختلفة بالنسبة لمجموعة الأمين (الأورثو – الميتا – البارا) في مخاليط المذيب المختلفة التركيب من الإيثيل سيليوسولف – الماء عند درجة حرارة ٢٥ْم. وقد أوضحت الدراسة أن ثوابت التفكك تقل بزيادة الإيثيل سيليوسولف لكل الكواشف، مما يدل على أن وجوده يزيد من قاعدية الوسط. كما أن الدالة الحمضية لحمض الهيدروكلوريك في مخاليط الماء – الإيثيل سيليوسولف قد عينت، وقد وجد أنها تزيد مع زيادة تركيز المذيب العضوي عند تركيز ثابت من الحمض.