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Dissociation Constants of Some Amino Acid and Pyridinecarboxylic Acids in Ethanol-H_2O Mixtures

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The dissociation constants of nicotinic, picolinic, benzoic, and *o*-, *m*-, and *p*-aminobenzoic acids and those of glycine, *dl*-alanine, *β*-alanine, aniline, and pyridine were determined potentiometrically and spectrophotometrically in 0, 10, 30, 50, and 72% (w/w) ethanol-water mixtures at 25 °C at various ionic strengths (0.01—0.5 mol dm^{-3}). The p*K*'s of benzoic, *o*-, *m*-, and *p*-aminobenzoic acids increased with increase of EtOH contents while those of nicotinic acid, picolinic acid, glycine, *dl*-alanine, and *β*-alanine passed through minimum (upto 30% w/w EtOH contents). The p*K*'s of aniline and pyridine were almost the same as those found in literature. The variation in p*K*'s with the solvent composition is discussed in terms of the free energy of transfer from H_2O to EtOH-H_2O mixtures. The zwitterion to neutral molecule ratio of these acids is also discussed in terms of variation of composition of mixtures.

There has been increasing interest during past few years in properties of mixed solvent systems such as water+organic solvent or mixtures of organic solvent themselves.[1] While there have been many physicochemical studies in these mixed solvents, relatively few data are available on the effect of these mixed solvent systems on the dissociation of weak acids or bases.[2–10,20]

Acid-base equilibria of pyridine monocarboxylic acid monoaminobenzoic acids and simple aliphatic amino acids like glycine, *dl*-alanine, *β*-alanine are well known in aqueous medium[11–13,15,21] as in the following;

$$\begin{tikzcd}
N^+H_3CHRCO_2^- \arrow[r, shift left, "H^+"] \arrow[d, shift right, "-H^+"'] \arrow[dr, shift left] & N^+H_3CHRCO_2H \arrow[l, shift left, "-H^+"] \arrow[d, shift right, "-H^+"'] \\
NH_2CHRCO_2^- \arrow[u, shift right, "H^+"'] \arrow[r, shift left, "H^+"] & NH_2CHRCO_2H \arrow[l, shift left, "-H^+"] \arrow[u, shift right, "H^+"'] \arrow[ul, shift left]
\end{tikzcd} \qquad (1)$$

Mostly these substances exist as dipolar zwitterions with varying percentage in aqueous medium. These acids while titrated with strong base and acid dissociate according to Eqs. 2 and 3.

$$K_1 = \frac{[H^+][(N^+H_3CHRCO_2^- + (NH_2CHRCO_2H)]}{[N^+H_3CHRCO_2H]} \qquad (2)$$

and

$$K_2 = \frac{[H^+][(NH_2CHRCO_2^-)]}{[(NH_3^+CHRO_2^-) + (NH_2CHRCO_2H)]} \qquad (3)$$

Generally, these dissociation constants (K_1 and K_2) have been determined potentiometrically and spectrophotometrically in the UV region.[21]

Protonation of aniline and pyridine and dissociation of acetic and benzoic acids are also known in aqueous medium as well as in some mixed solvents.[6,7] Some measurement on dissociation, thermodynamic properties and viscosities of glycine, *dl*-alanine and *β*-alanine are also available in literature.[9,17] We have chosen ethanol (EtOH)-water mixtures of composition 0, 10, 30, 50, and 71.98% weight (w/w) of EtOH. We have determined dissociation constants of pyridine monocarboxylic, benzoic, and acetic acids, aniline, and pyridine in these mixtures titrimetrically and by emf measurements of cells (I) and (II) and spectrophotometrically using the known procedures.[2,14,15,19]

$$\text{Pt, } H_2(1\ \text{atm})/HA(m_1),\ NaA(m_2),\ NaCl(m_3)/AgCl\text{-}Ag \qquad (I)$$

$$\text{Pt, } H_2(1\ \text{atm})/B^+H(m_1),\ B(m_2),\ NaCl(m_3)/AgCl\text{-}Ag \qquad (II)$$

From these p*K* values, the free energy of transfer $-\Delta G_{tr}(\text{dis})$ of these substances have been calculated and are discussed in terms of the effect of composition of solvent mixtures. Some attempts have been made for evaluation of the ratio of (dipolar) zwitterionic form to neutral molecular form of these amino acids in these EtOH-H_2O mixtures.

Experimental

All the substances under study were reagent grade product from Lachema BRNO. Ethanol was of a spectral grade purity from Lachema BRNO and was used without further purification. Doubly distilled conductivity water was used as aqueous medium as well as for preparation of EtOH-H_2O mixtures in a weight by weight composition.

For the determination of p*K*'s, ethanolic and aqueous solutions of the substances under investigation were prepared. The ionic strengths (μ=0.1, 0.2, 0.3, and 0.5 mol dm^{-3}) were maintained with sodium perchlorate (reagent grade, Lachema, BRNO). Titrations were performed with 0.1 M†† sodium hydroxide or perchloric acid (both reagent grade, from Lachema BRNO and Jenapharm respectively) in the same solvent. The pH's were measured using a glass electrode with calomel electrode in aqueous medium and with 0.1 M silver-silver chloride electrode in EtOH-H_2O mixtures at 25 °C. A titration vessel was kept in a thermostat at 25±0.01 °C. The electrode assembly was

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†† 1 M=1 mol dm^{-3}.

calibrated with buffer solutions prepared according to literature.[2,7,19] The UV spectra for 10^{-4}—5×10^{-5} mol dm^{-3} solutions in water or mixtures were obtained with a Pye Unicam SP 1800 spectrophotometer. For spectrophotometric determination of p*K*'s, solutions of the substances were mixed with solutions of perchloric acid of various concentrations or with mixtures of 0.1 M perchloric acid and 0.1 M KH_2PO_4 (reagent grade Lachema, BRNO) in water or ethanolic mixtures. During these experiments pH was measured with a hydrogen electrode against references as mentioned above. The emf's of cells (I) and (II) were also measured with the same pH meter. Solutions of the substances were half neutralized with 0.1 NaOH or 0.1 M $HClO_4$ before putting in cell (I) and cell (II).

Calculations and Results

The p*K*'s of weak acid (HA) and a base (BH^+) with the dissociation processes $HA \overset{K_1}{\rightleftharpoons} H^+ + A^-$ and $BH^+ \overset{K_2}{\rightleftharpoons} B + H^+$ were evaluated from the following equations:

$$pK_1 = pH - \log\frac{[A^-]}{[HA]} - \log\gamma_{A^-} = pK_1' - \log\gamma_{A^-} \qquad (4)$$

$$pK_2 = pH - \log\frac{[B]}{[BH^+]} + \log\gamma_{BH^+} = pK_2' + \log\gamma_{BH^+} \qquad (5)$$

Here, $\log\gamma_{A^-}$ and $\log\gamma_{BH^+}$ were calculated from the Debye-Hückel limiting law (DHLL).[14,15] The values of densities and dielectric constants of water and EtOH-H_2O mixtures at 25 °C were taken from literature.[2,7,19] The values of the radii of these substances used in DHLL were from 3—10 Å. The p*K*'s measured at different μ were plotted against $\mu^{1/2}$ and extrapolated to $\mu=0$, the values being listed in Table 1.

For the evaluation of p*K*'s by the emf method, Eqs. 6 and 7 were used.[2,19,22]

$$E = E^\circ_{Ag\text{-}AgCl} + \frac{2.303}{F}RT\log[(m_{H^+}\cdot\gamma_{H^+})\cdot(m_{Cl^-}\cdot\gamma_{Cl^-})] \qquad (6)$$

$$pK = p\overset{*}{a}_H = -\log m_{H^*}\cdot\gamma_{H^*} = \frac{E - E^\circ_{Ag\text{-}AgCl}}{0.0591} + \log\gamma_{Cl^-} + \log m_{Cl^-} \qquad (7)$$

where values of $E^\circ_{Ag\text{-}AgCl}$ in these mixtures and water were taken from literature.[2,19] These p*K*'a calculated by Eq. 7 were plotted against $\mu^{1/2}$ and extrapolated to $\mu=0$ and are given in Table 1. It was found that these p*K*'s are in accord within ±0.02 p*K* units with those determined by the potentiometric titration method.

The spectrophotometric data were used in Eq. 8 for calculations of p*K*'s.

$$pK = pH + \log\frac{(A - A_2)}{(A_1 - A)} \qquad (8)$$

where A_1 and A_2 are absorbances of substance in acidic and basic media while A is absorbance at some other

Table 1. Thermodynamic Dissociation Constants, pK_1, pK_2, or p*K* of Amino Carboxylic Acids in EtOH-H_2O Mixtures at 298 °K and Zero Ionic Strength ($\mu=0$)

Acids %EtOH	Benzoic p$K\pm\delta$	Nicotinic		Picolinic		*o*-Aminobenzoic		*m*-Aminobenzoic		*p*-Aminobenzoic	
		p$K_2\pm\delta$	p$K_1\pm\delta$	p$K_2\pm\delta$	p$K_1\pm\delta$	p$K_2\pm\delta$	p$K_1\pm\delta$	p$K_2\pm\delta$	p$K_1\pm\delta$	p$K_2\pm\delta$	p$K_1\pm\delta$
0	4.18±0.02	4.83±0.02	2.09±0.04	5.47±0.02	1.82±0.04	4.92±0.02	2.14±0.04	4.78±0.02	3.11±0.04	4.91±0.02	2.39±0.04
10	4.29±0.02	4.58±0.02	1.98±0.04	5.30±0.02	1.74±0.04	5.03±0.02	2.05±0.02	4.88±0.02	3.02±0.04	5.08±0.02	2.21±0.04
30	5.24±0.02	4.37±0.02	1.89±0.04	5.06±0.02	1.63±0.04	5.43±0.02	1.82±0.04	5.14±0.02	2.85±0.04	5.64±0.02	2.05±0.04
50	5.67±0.02	4.60±0.02	1.77±0.04	5.24±0.02	1.54±0.04	6.15±0.02	1.43±0.04	5.51±0.02	2.72±0.04	6.47±0.02	1.80±0.04
72[a]	6.24±0.02	5.03±0.02	1.70±0.04	5.42±0.02	1.61±0.04	6.75±0.02	1.37±0.04	6.18±0.02	2.54±0.04	7.04±0.02	1.71±0.04

Substance %EtOH	Glycine		*dl*-Alanine		*β*-Alanine		Pyridine p$K\pm\delta$	Aniline p$K\pm\delta$	Ethyl nicotinate p$K\pm\delta$	Trigonelline p$K\pm\delta$
	p$K_1\pm\delta$	p$K_2\pm\delta$	p$K_1\pm\delta$	p$K_2\pm\delta$	p$K_1\pm\delta$	p$K_2\pm\delta$				
0	9.78±0.02	2.38±0.02	9.85±0.02	2.39±0.02	10.23±0.02	3.57±0.02	5.13±0.02	4.59±0.03	3.18±0.06	2.92±0.07
10	9.64±0.02	2.47±0.02	9.72±0.02	2.48±0.02	10.03±0.02	3.65±0.02	4.89±0.02	4.42±0.03	2.92±0.06	2.97±0.07
30	9.37±0.02	2.68±0.02	9.55±0.02	2.77±0.02	9.84±0.02	3.88±0.02	4.36±0.02	4.19±0.03	2.64±0.06	3.00±0.07
50	9.41±0.02	3.03±0.02	9.62±0.02	3.13±0.02	9.80±0.02	4.12±0.02	3.92±0.02	3.86±0.03	1.78±0.06	2.99±0.07
72[a]	9.58±0.02	3.21±0.02	9.78±0.02	3.47±0.02	9.99±0.02	4.51±0.02	3.54±0.02	3.73±0.03	1.68±0.06	3.00±0.07

[a] 71.98=72.

Table 2. The $\Delta pK_a = pK_a^s(HA) - pK_a^w(HA)$ and $\Delta G_{tr}(dis)$ (kJ mol^{-1}) Values for Aminocarboxylic Acids in EtOH-H_2O Mixtures at 298 K

Acids %EtOH	Benzoic		Nicotinic		Picolinic		*o*-Aminobenzoic		*m*-Aminobenzoic	
	ΔpK	$\Delta G_{tr}(dis)$	ΔpK	$\Delta G_{tr}(dis)$	ΔpK	$\Delta G_{tr}(dis)$	ΔpK	$\Delta G_{tr}(dis)$	ΔpK	$\Delta G_{tr}(dis)$
10	0.11	0.627	−0.25	−1.425	−0.17	−0.969	0.11	0.627	0.10	0.570
30	1.06	6.042	−0.46	−2.622	−0.41	−2.337	0.51	2.907	0.36	2.052
50	1.49	8.493	−0.23	−1.311	−0.23	−1.311	1.23	7.011	0.73	4.161
72	2.06	11.742	+0.20	−1.14	−0.05	−0.285	1.83	10.431	1.40	7.98

	p-Aminobenzoic		Glycine		*dl*-Alanine		*β*-Alanine		Aniline	
	ΔpK	$\Delta G_{tr}(dis)$	ΔpK	$\Delta G_{tr}(dis)$	ΔpK	$\Delta G_{tr}(dis)$	ΔpK	$\Delta G_{tr}(dis)$	ΔpK	$\Delta G_{tr}(dis)$
10	0.17	0.969	−0.14	−0.798	−0.13	−0.741	−0.20	−1.14	−0.17	−0.969
30	0.73	4.161	−0.41	−2.337	−0.30	−1.71	−0.39	−2.223	−0.40	−2.28
50	1.56	8.892	−0.37	−2.109	−0.13	−0.741	−0.43	−2.451	−0.73	−4.161
72	2.13	12.141	−0.20	−1.14	−0.07	−0.399	−0.24	−1.368	−0.86	−4.902

%EtOH	10		30		50		72	
	ΔpK	$\Delta G_{tr}(dis)$	ΔpK	$\Delta G_{tr}(dis)$	ΔpK	$\Delta G_{tr}(dis)$	ΔpK	$\Delta G_{tr}(dis)$
Pyridine	−0.24	−1.368	−0.77	−4.389	−1.21	−6.897	−1.59	−9.063

pH of medium.[14,15,21] The p*K*'s found by this method agree within ±0.03 units of p*K* with those obtained by the emf method. Therefore, Table 1 gives the average values of p*K*'s of these substances obtained by three methods.

The free energy change in the transfer of these substances from $H_2O(w)$ to EtOH-$H_2O(s)$ mixtures was evaluated from Eq. 9 at 25 °C and are given in Table 2.

$$\left.\begin{aligned}\Delta G_{tr}(dis) &= 2.303\,RT(pK_a^s - pK_a^w)\\ &= 5.70(\Delta pK_a)\end{aligned}\right\} \qquad (9)$$

Where pK_a^s and pK_a^w are dissociation constants in EtOH-H_2O mixtures and in H_2O respectively. The change in proton affinity ΔP_a of conjugate base ($\bar{A}$) of these acids on transfer from H_2O to H_2O+cosolvent were calculated by Eq. 10 at 25 °C and are given in Table 3.

$$\Delta P_a = 5.70\ (\Delta pK_a) + \Delta G_{tr}(H^+) - C \qquad (10)$$

Here constant $C = 5.70 \log(18.01\ d_s/M_s \cdot d_w)$ in molar scale. The average mass M_s of EtOH-H_2O mixtures were calculated from Eq. 11.

$$M_s = 100/(\text{wt\% EtOH}/46.00) + (\text{wt\% } H_2O/18.016) \qquad (11)$$

and $\Delta G^\circ_{tr}(H+)$ are free energies of transfer of proton from H_2O to EtOH-H_2O mixtures and were taken from literature.[23]

Discussion

The reproducibility of the measurements was ±0.01 both in the titrimetric as well as in the emf measurements and was ±0.03 in the spectrophotometric measurements. The p*K* values of all substances determined are in good agreement with earlier reported values in some EtOH-H_2O mixture.[2,7,9,19,24]

In Fig. 1, p*K*'s of nicotinic and picolinic acids, glycine, *dl*-alanine, and *β*-alanine have been plotted against the reciprocal of dielectric constants (ε^{-1}) of EtOH-H_2O mixtures. These p*K*'s decrease as the concentration of EtOH increases upto 30% (w/w) in the EtOH-H_2O mixtures and increase again in mixtures of higher EtOH contents. On the other hand p*K*'s of *o*-, *m*-, and *p*-aminobenzoic acids (Table 1) and those of acetic acid[6] increase with increase in

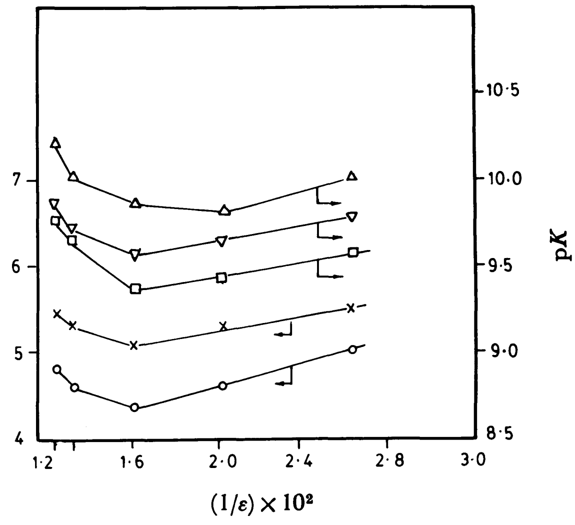

Fig. 1. Dependence of p*K* of Glycine (□) *dl*-alanine (▽), *β*-alanine (△), nicotinic acid (○), and picolinic acid (×) on inverse of permitivities (ε^{-1}) of EtOH-H_2O mixtures.

Table 3. Change in Proton Affinity ΔP_a (kJ mol^{-1}) in Transfer $H_2O \rightarrow EtOH\text{-}H_2O$ System: Values of $-\Delta P_a$ at 25 °C

%EtOH	$\bar{A}$=Conjugate base/Benzoate	Nicotinate	Picolinate	*o*-Amino-benzoate	*m*-Amino-benzoate	*p*-Amino-benzoate	Glycinate	*dl*-Alaninate	*β*-Alaninate	Aniline	Pyridine
10	2.635	0.578	1.038	2.6384	2.578	2.978	2.517	2.517	2.464	1.038	0.638
30	13.623	4.971	5.251	10.491	9.631	11.741	9.291	9.747	9.348	5.301	3.191
50	17.819	8.016	8.016	16.336	13.486	18.216	13.03	13.544	12.351	5.166	2.446
72	20.387	7.505	8.365	19.075	16.625	20.785	13.375	14.801	14.003	3.745	−0.415

%EtOH	$\Delta pK_2=(pK^s-pK^w)$			$RT \ln(\Delta pK_2)=5.7(\Delta pK_2)$		
	Glycinium	*dl*-Alaninium	*β*-Alaninium	Glycinium	*dl*-Alaninium	*β*-Alaninium
10	0.09	0.09	0.08	0.513	0.513	0.456
30	0.30	0.38	0.31	1.71	2.166	1.767
50	0.65	0.74	0.55	3.705	4.218	3.025
72	0.83	1.08	0.94	4.731	6.156	5.358

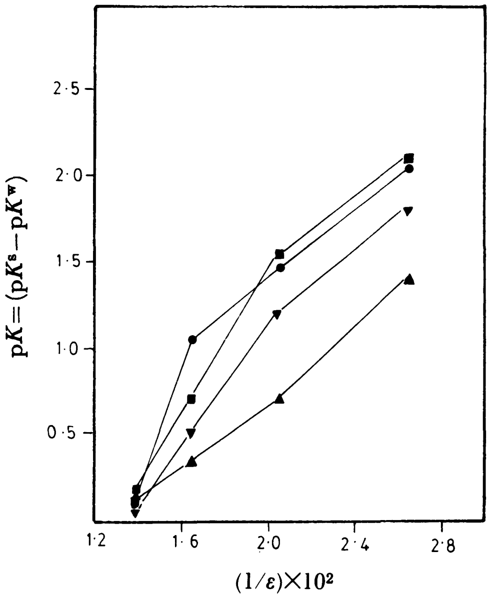

Fig. 2. Dependence of ΔpK of benzoic (●), *o*-(▲), *m*-(▼), and *p*-aminobenzoic acid (■) on inverse of permitivities (ε^{-1}) of $EtOH\text{-}H_2O$ mixtures.

EtOH contents in $EtOH\text{-}H_2O$ mixtures in a similar way as observed in case of benzoic acid (Fig. 2). It means that these aminobenzoic acids exist with stable structure as benzoic acid in $EtOH\text{-}H_2O$ mixtures when ethanol contents are more than 10% (w/w). Further pK_1's of three aminobenzoic acids go on decreasing with increase of EtOH percentage in the same way as observed in case of aniline (Table 1). Therefore, one can postulate that *o*-, *m*-, and *p*-aminobenzoic acids exist as neutral molecules in $EtOH\text{-}H_2O$ mixture rather than zwitterions as found in aqueous medium.

The anomalous dependence of pK_2's of glycine, *dl*-alanine, *β*-alanine, nicotinic, and picolinic acids on composition of $EtOH\text{-}H_2O$ mixtures (Fig. 1) can be attributed to changes in structures of these acids when they transfer from H_2O to $EtOH\text{-}H_2O$ media. Chattopadhyay et al.[9] have determined pK's of glycine, *dl*-alanine, *β*-alanine in some $EtOH\text{-}H_2O$ mixtures and have evaluated K_Z (ratio of zwitterions to neutral molecules) of these acids with conclusion that this ratio (K_Z) decreases with increase of EtOH contents inferring preferential solvation of zwitterions with water and neutral molecules with alcohol. Wada et al.[20] have also determined the K_Z values of glycine in various water+organic solvent mixtures and have concluded that the K_Z value of glycine decreases with increase in the mole fraction of organic solvent. Khan et al.[3] have also postulated these results for nicotinic acid using ^1H NMR spectroscopy in $DMSO\text{-}H_2O$ media and have pointed out that nicotinic acid exists in a neutral from in 80:20% $DMSO\text{-}H_2O$ mixture.

In the present work, we have also chosen not only nicotinic acid but its ethyl ester and trigonelline as model compounds. Table 1 shows that pK''s of trigonelline almost did not change with change in composition of EtOH–H_2O mixtures. However, pK''s of ethyl nicotinate and nicotinic acid decreased with increase of EtOH and become almost equal in 50 and 72% EtOH–H_2O mixtures. This decrease in pK values of nicotinic acid and its ethyl ester follows from the same course of decreasing as observed in case of pyridine with increase in EtOH (Table 1). As it has been assumed in literature[9,11,13] $K_Z=(K_I-K_E)/K_E$, one can verify that from the present values of K_I and K_E of nicotinic acid and its ethyl ester, K_Z is equal to zero in 50% EtOH–H_2O mixtures. This procedure was also followed by Chattopadhyay et al.[9] in case of glycine and *dl*-alanine, etc.

Figure 3 (I—IV) are UV absorption curves of nicotinic acid, its ethyl ester and trigonelline at isoelectric points in 10, 30, 50, and 72% EtOH–H_2O mixtures at 25 °C. The UV spectra of these compounds show that nicotinic acid and its ethyl ester have similar absorption curves in 50 and 72% EtOH–H_2O mixtures but differ in H_2O and 10% EtOH–H_2O mixture. These spectra further assist in concluding that nicotinic acid exists as in a neutral form in EtOH–H_2O mixtures rather than zwitterions as found in aqueous medium.

Table 2 gives the values of free energy change ($-\Delta G_{tr}$(dis)) of dissociation on transfer of these acids from H_2O to EtOH–H_2O mixture. As shown in Fig. 2, the pK''s of aminobenzoic acids and benzoic acid are not linear with variation of composition of EtOH–H_2O mixtures. Almost all compounds studied in the present work show remarkable deviation from ΔpK_a' calculated by using Born's equation.

$$\mathrm{p}K_a = 122\left(\frac{1}{\varepsilon_r}-0.0128\right)[(1/r_{H^+}+1/r_{A^-})]$$

These deviations suggest that the effect of the EtOH–H_2O mixtures on the acidity of these amino

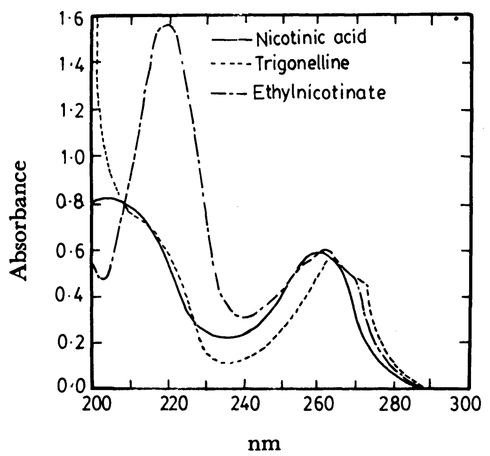

Fig. 3(I). UV spectra of nicotinic acid and its ethylester and trigonelline in 10% EtOH–H_2O mixture, at 25 °C, pH 3.43.

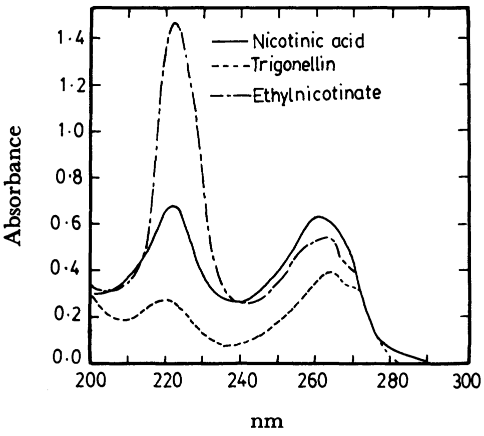

Fig. 3(II). UV spectra of nicotinic acid and its ethylester and trigonelline in 30% EtOH–H_2O mixture, of pH 3.22, at 25 °C.

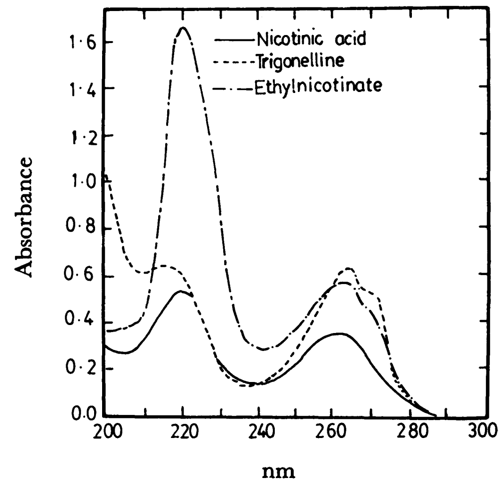

Fig. 3(III). UV spectra of nicotinic acid and its ethylester and trigonelline in 50% EtOH–H_2O mixture, 25 °C, pH 3.04.

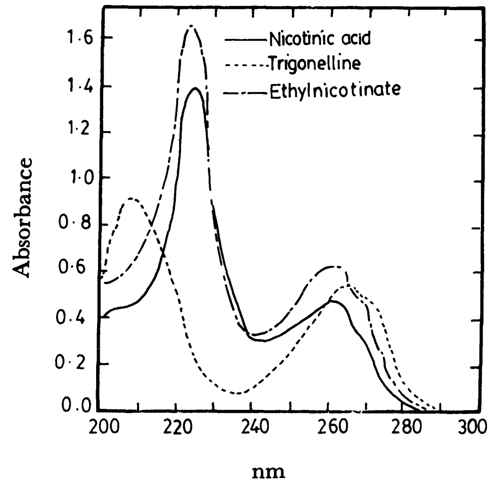

Fig. 3(IV). Same as above in 70% EtOH–H_2O mixture of pH 3.25, at 25 °C.

acids does not depend solely on electrostatic features, as predicated by Born's theory. It may also be caused by ignoring the variation in dielectric constant of the solvent molecules in the vicinity of an ion[25] and of specific change in $RH^{\mp} \rightleftharpoons RH$ i.e. from zwitterions to to neutral molecular form of these acid. If one divides G_{tr}(dis) into ΔG_{tr}(el) - electrostatic free energy and ΔG_{tr}(chem) - the non-electrostatic chemical free energy parts, of all these compounds, it is found that the contribution of the chemical free energy increases as the EtOH concentration is raised in case of aminobenzoic and benzoic acids but it passes through minimum in case of glycine, *dl*-alanine, *β*-alanine, and pyridine monocarboxylic acids. Again previous conclusion can be drawn.

The calculations of proton affinities ($-\Delta P_a$) of the corresponding conjugate bases of these amino acids are given in Table 3 in kJ mol^{-1}. These values show that again glycine, *dl*-alanine, *β*-alanine, and pyridinecarboxylic acids are grouped together giving similar trend in variation of ΔP_a with composition of EtOH–H_2O mixtures. While aminobenzoic acids are grouped together. Therefore, the present study fully supports the conclusion that these amino acids exist as in neutral molecular form in low polarity organic solvent mixtures with water rather than zwitterions as observed in aqueous medium.

Similar results are being found in some methanol–water mixtures and free enthalpy and entropy changes on dissociation of these amino acids are being measured in EtOH–H_2O mixture. These results will be published elsewhere in a near future.

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