February, 1990] © *1990 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *63, 581—585 (1990)*

The Ionization Constants of Nitrobenzoic and Benzoic Acids in Water-Ethanol Mixture at 25 °C from Conductance Measurements[†]

M. S. K. Niazi,* M. Zafar Iqbal Khan, J. Ali, and M. Ahmad
Department of Chemsitry, Quaid-i-Azam University, Islamabad, Pakistan
(Received February 20, 1989)

Molar conductances of dilute solutions of 2-, 3-, 4-nitrobenzoic and benzoic acids are reported at 25 °C in ethanol-water (EtOH-H_2O) mixtures over composition range from 0 to 70 wt% of ethanol. The ionization constants and limiting molar conductances of these acids have been computed from the data using Fuoss 1978 conductance equation. Solvent effect on the ionization of acids in EtOH-H_2O mixtures has been discussed in terms of free energy of transfer of respective anions of the acids from H_2O to EtOH-H_2O mixtures. It is found that the order of ionization of these acids in EtOH-H_2O system is 2-nitrobenzoic acid>3-nitrobenzoic acid ≃4-nitrobenzoic acid>benzoic acid.

Previous reports from this laboratory presented the study of thermodynamic dissociation constants of aminobenzoic, pyridinecarboxylic, and some amino acids in ethanol-water (EtOH-H_2O) mixtures;[1] and the solvent effect on the ionization of 2-, 3-, and 4-nitrobenzoic acids in methanol-water (MeOH-H_2O) mixtures[2] at 25 °C respectively. In both reports benzoic acid was taken as a model compound since it has been widely studied in alcohol-water mixed solvent system.

Ethanol-water constitute nonideal binary solvent system,[3] in which solvent-solvent interactions play a considerable part and properties of the mixtures cannot always be interpreted on the basis of continuous miscibility of the components in all mixtures. Solvent effect of such system as in Ref. 1 was differentiating on the ionization of neutral acids and on those which exist as zwitterions (dipolar in nature). Present paper reports molar conductances of dilute solutions of 2-, 3-, 4-nitrobenzoic and benzoic acids in EtOH-H_2O mixtures ranging in composition from 0 to 70 wt% ethanol, at 25 °C. The limiting molar conductance (Λ_0) and the ionization constants (K_d) of the four acids were computed from conductance-concentration data using Fuoss 1978 conductance equation with some modifications.[4] From the $pK_a(=-\log K_d)$ values of these acids in EtOH-H_2O mixtures values of free energy of transfer of carboxylate ions ($\Delta G^\circ_{tr}(A^-)$) from H_2O to EtOH-H_2O mixtures have been calculated. The results are discussed in terms of solvent effect on the ionization of nitrobenzoic acids and solute-solvent interactions.

Experimental

The acids were of ultrahigh purity product of E. Merck. These were recrystallized and dried in a way already described elsewhere.[2] Acids and KCl were stored in a desiccator over P_2O_5.

Ethanol (Absolute-Merck) was purified according to procedure described by Shedlovsky et al.[5] After refluxing with magnesium ethoxide, ethanol was distilled under nitrogen gas and middle fraction was collected in nitrogen filled flask. Further, it was immediately used after distillations. Deionized water was twice distilled for preparation of solvent mixtures and as aqueous medium. It was also stored in a flask filled with nitrogen gas. The specific conductances of EtOH and H_2O were between $2—5\times10^{-8}$ and $2—4\times10^{-7}$ S cm^{-1} respectively. The EtOH-H_2O mixture were prepared in w/w composition.

The viscosities and densities of EtOH-H_2O mixture were measured in the same way as described earlier[6] and are in a good agreement with those cited in literature.[5,7] The dielectric constants of mixtures were taken from literature.[5,7]

Conductance measurements were carried out using an autobalance precision bridge (Wayne Kerr, B641) at 1592 Hz in the same way as described elsewhere.[7,8] Two different cells with cell constants 0.5498 and 1.0532 cm^{-1} were used. The temperature of water bath was controlled at 25+0.02 °C. The cells were calibrated following the known procedures[9] using KCl solutions in the concentration range $(2—30)\times10^{-4}$ mol dm^{-3}. Duplicate measurements of each mixture were made. The results varied within ±0.1% only.

Calculations and Results

Physical properties of EtOH-H_2O mixtures are listed in Table 1. The molar concentrations and corresponding values of the molar conductances are given in Table 2 for all the four acids in solvent

Table 1. Physical Properties of EtOH-H_2O Mixtures at 25 °C

% EtOH (w/w)	d g·cm^{-3}	η cP[a)]	D
0	0.9971	0.890	78.54
10	0.9811	1.325	72.80
20	0.9662	1.810	66.99
30	0.9530	2.409	62.10
40	0.9318	2.375	55.02
50	0.9074	2.361	48.50
60	0.8866	2.234	43.40
70	0.8637	2.013	36.70

d=density; η=viscosity; D=dielectric constant.
a) 1 P=0.1 Pa s.

[†] Financial support from University Research Fund is acknowleged gratefully.

Table 2. Molar Conductivities, Λ (S cm^2 mol^{-1}) and Molar Concentrations, C (mol dm^{-3}) of Acids in Ethanol-Water Mixtures at 25 °C

Wt% EtOH	0	10	20	30	40	50	60	70	
10^4C	Λ	Λ	Λ	Λ	Λ	Λ	Λ	10^4C	Λ
				2-Nitrobenzoic acid					
1.923	387.36	284.44	169.61	143.61	96.62	53.42	32.01	0.961	17.13
5.357	368.57	262.83	147.83	114.63	72.78	38.36	22.45	2.678	12.23
8.333	354.40	247.82	134.82	100.38	62.31	32.27	18.74	4.167	10.27
10.938	344.02	237.42	126.54	92.10	56.49	28.99	16.77	5.498	9.22
13.235	335.82	229.52	120.57	86.44	52.61	26.85	15.49	6.618	8.53
15.227	329.18	223.29	116.03	82.29	49.80	25.32	14.58	7.639	8.04
17.105	323.64	218.18	112.44	79.07	47.66	24.16	13.90	8.553	7.66
18.750	318.96	213.96	109.52	76.52	45.98	23.25	13.36	9.375	7.37
20.238	314.95	210.39	107.10	74.44	44.61	22.53	12.93	10.119	7.14
21.591	311.47	207.33	105.05	72.69	43.47	21.92	12.56	10.796	6.94

Wt% EtOH	10	20	30	40	50	60	70		0
10^4C	Λ	Λ	Λ	Λ	Λ	Λ	10^4C	Λ	Λ
				3-Nitrobenzoic acid					
8.333	134.76	77.05	44.42	27.43	19.01	10.16	4.167	9.04	176.06
10.938	121.92	68.86	39.49	24.29	16.78	8.93	5.498	7.95	159.33
13.235	113.38	63.55	36.32	22.28	15.36	8.16	6.618	7.25	148.24
15.277	107.24	59.77	34.09	20.89	14.38	7.62	7.639	6.77	140.22
17.105	102.56	56.93	32.41	19.88	13.64	7.23	8.533	6.42	134.13
18.750	98.86	54.70	31.09	19.01	13.06	6.92	9.375	6.14	129.30
20.238	95.87	52.71	30.05	18.35	12.60	6.67	10.119	5.92	125.38
21.591	93.38	51.43	29.19	17.81	12.23	6.46	10.796	5.87	122.15
1.923	211.39	132.61	79.711	50.83	36.24	19.90	0.961	17.86	274.88
5.357	157.01	91.87	53.49	33.28	23.22	12.49	2.678	11.23	206.10

Wt% EtOH	0	10	30	70	20		40	50	60
10^4C	Λ	Λ	Λ	Λ	10^4C	Λ	Λ	Λ	Λ
				4-Nitrobenzoic acid					
2.678	245.87	180.51	85.43	12.55	5.357	102.02	43.15	25.28	14.59
4.167	218.38	155.93	71.31	10.54	8.333	85.73	35.64	20.81	11.94
5.498	201.15	141.41	62.96	8.92	10.973	76.72	31.61	18.40	10.53
6.618	189.36	131.80	58.93	8.15	13.275	70.85	29.03	16.88	9.64
7.639	181.03	125.15	55.45	7.62	15.222	66.67	27.21	15.86	9.02
8.553	174.02	119.66	52.84	7.22	17.105	63.53	25.85	15.03	8.56
9.375	168.61	115.45	50.79	6.91	18.750	61.07	24.80	14.41	8.20
10.119	164.15	112.00	49.14	6.66	20.238	59.08	23.95	13.91	7.91
10.796	160.43	109.18	47.77	6.42	21.590	57.44	23.25	13.50	7.67
0.962	301.99	238.22	121.41	19.78	1.923	146.25	65.35	38.73	22.82

Wt%	0	10	20	30	40	50	60	70	
10^4C	Λ	Λ	Λ	Λ	Λ	Λ	Λ	10^4C	Λ
				Benzoic acid					
5.357	115.63	57.19	40.56	24.17	11.97	8.38	6.57	2.678	6.48
8.333	95.96	50.02	33.04	19.72	9.52	6.72	5.26	4.167	5.25
10.973	85.29	42.57	29.09	17.37	8.23	5.86	4.60	5.498	4.50
13.275	78.423	39.21	26.59	15.89	7.49	5.33	4.18	6.618	4.09
15.222	73.58	37.76	24.84	14.85	7.04	4.96	3.89	7.639	3.80
17.105	69.95	36.36	23.56	13.90	6.54	4.69	3.67	8.533	3.59
18.250	67.12	33.91	22.54	13.04	6.19	4.48	3.51	9.375	3.43
20.238	64.85	32.75	21.73	12.42	5.93	4.31	3.38	10.119	3.31
21.590	62.97	31.42	21.07	12.00	5.76	4.17	3.27	10.796	3.20
1.923	172.28	95.22	64.19	38.09	19.23	13.98	10.96	0.962	10.78

mixtures of different compositions listed therein. The experimental data were analyzed with Fuoss 1978 conductance equation[4] with some modifications. The limiting molar conductances (Λ_0) and ionization constants ($K_d=1/K_A$ where K_A is association constants for the process $H^+ + A^- \underset{K_d}{\overset{K_A}{\rightleftarrows}} H^+A^-$) were deduced from the set of equations;

$$\Lambda=p[\Lambda_0(1+\Delta X/X)+\Delta\Lambda_e] \quad (1)$$

$$=p[\Lambda_0-S(t)C_i^{1/2}+E(t)C_i\ln C_i+J_1(t,\beta/R)C_i+J_2(t,\beta/R)C_i^{3/2} \quad (2)$$

$$K_A=C^2f^2\gamma^2/(1-\gamma) \quad (3)$$

and

$$-\ln f = e^2\gamma/2D\kappa T(1+kR) \qquad (4)$$

where $\beta(=e^2/D\kappa T)$ is twice the Bjerrum distance, p is the fraction of acid contributing to the conductance current $\Delta X/X$ is the relaxation field effect, $\Delta\Lambda_e$ is the electrophoretic countercurrent, $1/k$ is the radius of the ion atomsphere, D=dielectric constant of the solvent, e is the electron charge, κ is Boltzmann constant, R is the Gurney-sphere diameter, γ is the fraction of solute present as unpaired ions, C is the molarity of the solution, $C_i=C\gamma$. The activity coefficients were calcualted from the Debye-Hückel equation (Eq. 4).

The Gurney-sphere diameter serves as an adjustable parameter chosen to minimize the sum of the square of the residuals in the fitting of the conductance function to experimental data. However, for weak acids the variation in σ, the standard deviation, as a function of R is too small to be significant in comparison to the experimental scatter of the data. Based on the recommendation of Fuoss,4) the value of R was set at twice the Bjerrum distance ($R=e^2/DkT$). Trial calculations with R set at ten times this values lowered pK_a by only ±0.01.

Table 3 lists Λ_0 values and K_d values of each acid in ethanol-water mixture. Values of σ_Λ(%) are standard deviation expressed as a percentage of Λ_0. Figure 1 is a plot of pK_a for the four acids versus composition of solvent mixtures.

The solvent effect on the ionization of nitrobenzoic acids was calculated using relationship

$$\delta(\Delta G^\circ_{tr}(HA)) = RT \ln(K_a^w/K_a^s) \qquad (5)$$

$$= 5.71(pK_a^s - pK_a^w) \text{ (in kJ mol}^{-1}\text{)} \qquad (6)$$

where s and w refer to mixed solvent and H$_2$O respectively, and pK_a are respective values of $-\log K_d$ in these media. The free energy of transfer of carboxylate ions of each acid was calculated using Wells procedure10)

$$\Delta G^\circ_{tr}(A^-) = RT \ln(K_a^w/K_a^s) - \Delta G^\circ_{tr}(H^+) \qquad (7)$$

or

$$\Delta G^\circ_{tr}(A^-) = 5.71\,(pK_a^s - pK_a^w) - \Delta G^\circ_{tr}(H^+) + 5.71 \log\left(\frac{18.01\, d_s}{M_s \cdot d_w}\right) \qquad (8)$$

where $M_s=100/(w/46.07)+((100-w)/18.015)$, w is the weight% of ethanol in mixture, d_w and d_s are densities of pure water and mixtures at 25 °C. The values of $\Delta G^\circ_{tr}(H^+)$ were taken from literature.11) The dependence of values of $G^\circ_{tr}(A^-)$ of each nitrobenzoate and benzoate ions on composition of mixture (EtOH-H$_2$O) is shown in Fig. 2.

In case of benzoic acid in 60 and 70% EtOH-H$_2$O water system, association of (H$^+$A$^-$) was so high that extrapolation to zero concentration was impossible. For these systems, a plot of $\log\Lambda$ against $\log C$ was linear, with slope equal to −0.5. The conductance parameters were derived using Aprano et al. procedure.17) They have suggested that in such cases Arrhenius approximation $\gamma=\Lambda/\Lambda_0$ (i.e. neglecting the effect of long-range electrostatic forces) should be used, so that the mass action equation reduces to

$$C\Lambda^2 = \Lambda_0^2/K_A \qquad (9)$$

which predicts a slope of −0.5 for the log-log plots and calls for constancy of the $C\Lambda^2$ product. By a short extrapolation of plots of Walden product $\Lambda_0\eta$ against mole fraction of ethanol, values of Λ_0 could be estimated for these systems, and then from the average

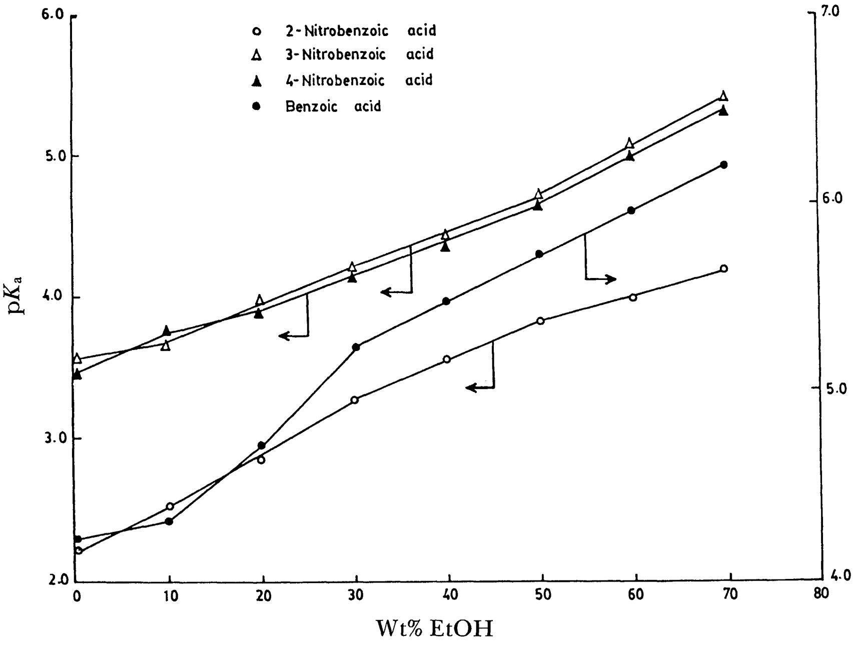

Fig. 1. Dependence of pK_a values of acids on composition of ethanol-water mixtures at 25 °C.

Table 3. Conductance Parameters of Acids in ($EtOH-H_2O$) Mixtures at 25 °C

%EtOH w/w	Λ_0 S cm^2 mol^{-1}	σ_Λ %	K_d
	2-Nitrobenzoic acid		
0	401.56	0.005	6.412×10^{-3}
10	304.97	0.010	2.993×10^{-3}
20	190.97	0.008	1.385×10^{-3}
30	184.31	0.015	5.236×10^{-4}
40	141.87	0.020	2.748×10^{-4}
50	92.17	0.023	1.503×10^{-4}
60	62.34	0.017	1.054×10^{-4}
70	30.24	0.024	5.636×10^{-5}
	3-Nitrobenzoic acid		
0	406.65	0.045	3.125×10^{-4}
10	315.26	0.070	2.052×10^{-4}
20	257.05	0.057	1.037×10^{-4}
30	186.34	0.031	6.022×10^{-5}
40	145.24	0.008	3.543×10^{-5}
50	132.49	0.015	1.935×10^{-5}
60	103.75	0.020	8.548×10^{-6}
70	107.72	0.033	3.111×10^{-6}
	4-Nitrobenzoic acid		
0	370.35	0.013	3.471×10^{-4}
10	337.08	0.020	1.626×10^{-4}
20	275.02	0.041	1.142×10^{-4}
30	227.00	0.022	5.846×10^{-5}
40	174.28	0.008	4.235×10^{-5}
50	115.32	0.017	2.070×10^{-5}
60	86.78	0.046	1.111×10^{-5}
70	97.64	0.044	4.808×10^{-6}
	Benzoic acid		
0	394.33±8.93	0.041	6.237×10^{-5}
10	292.24±6.55	0.038	4.735×10^{-5}
20	264.22±5.33	0.035	2.070×10^{-5}
30	204.13±1.78	0.018	6.123×10^{-6}
40	131.27±2.24	0.045	3.265×10^{-6}
50	105.35±4.37	0.045	1.963×10^{-6}
60	(125.22)[a]	—	(1.109×10^{-6})[a]
70	(130.48)[a]	—	(6.607×10^{-7})[a]

a) Values estimated using Eq. 9 i.e. approximate values.

of $C\Lambda^2$ for a given system, the corresponding association constant was calculated. A summary of the derived constants is given in Table 3.

Discussion

The pK_a values of benzoic and 2-, 3-, and 4-nitrobenzoic acids in H_2O are in good agreement with those quoted in literature mainly derived by potentiometric methods. The ionization constants of these acids in a few mixtures of $EtOH-H_2O$ are also available in literature[12] which are in accord with values reported in this paper. Lahiri et al.[3] have studied 4-nitrobenzoic acid in $EtOH-H_2O$ system by solubility and potentiometric methods. The pK_a values derived by them are less than those derived in this study. This may be due to their procedural digression from the normal potentiometric method for determination of pK_a values of carboxylic acids in mixed solvent

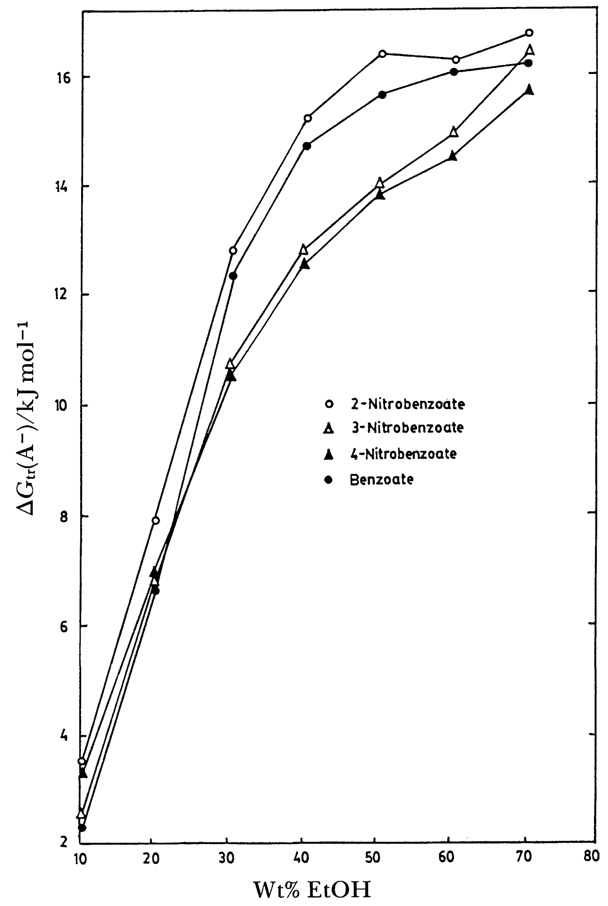

Fig. 2. Dependence of transfer free energy values of carboxylate anions on the composition of ethanol-water mixtures at 25 °C.

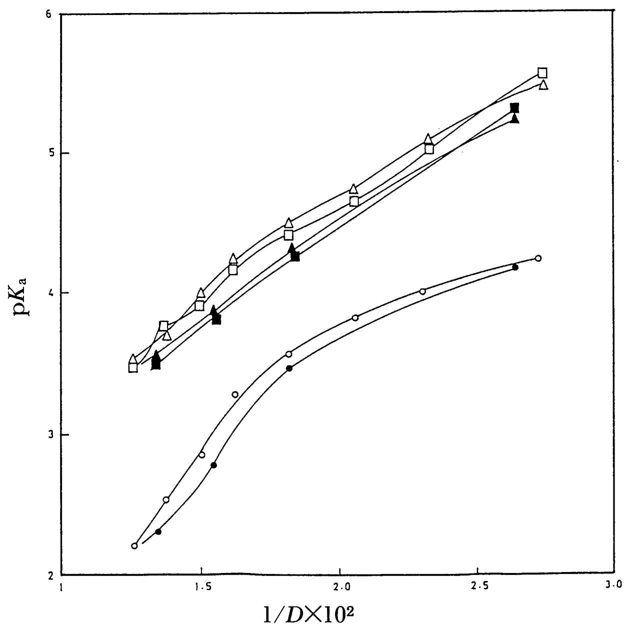

Fig. 3. Dependence of pK_a values of 2-nitrobenzoic (○, ●), 3-nitrobenzoic (△, ▲), and 4-nitrobenzoic acids (□, ■) on inverse of dielectric constant of $EtOH-H_2O$ and $MeOH-H_2O$ systems at 25 °C. Filled symbols for $MeOH-H_2O$ system.

system.[1,14] They measured pH values of saturated solution of 4-nitrobenzoic acid and calculated the respective pK_a values.

It has been found that these acids easily dissociate in MeOH-H_2O mixtures as compared in EtOH-H_2O mixtures. This would be attributed to lower values of relative viscosities and higher values of dielectric constants of MeOH-H_2O media as compared with EtOH-H_2O mixed solvent system (see Fig. 3).

Figure 1 shows that the plots of the respective pK_a values of nitrobenzoic and benzoic acids versus % composition of EtOH-H_2O mixtures are nonlinear in mixtures with contents of EtOH more than 50%. Similarly in Fig. 2, plots of free energy of transfer of nitrobenzoate ions ($\Delta G_{tr}(A^-)$) in kJ mol^{-1} versus solvent composition are nonlinear. These values of $\Delta G_{tr}(A^-)$ become more positive as acids get transferred from aqueous to EtOH-H_2O mixtures with higher contents of EtOH. It means that all these acids show remarkable deviation from pK_a' calculated by using Born's equation:

$$\Delta G_{tr}(el)=pK'_a=122\ (1/D-0.0128)[(1/r_{H^+}+1/r_{A^-})] \qquad (10)$$

where r_{H^+}, r_{A^-} are respective ionic radii of proton and anion of an acid.

These deviations suggest that the effect of EtOH-H_2O mixtures on the acidity of nitrobenzoic acids does not depend solely on electrostatic features, as predicted by Born.[15] It may also be caused by ignoring the variation in dielectric constant of the solvent molecules in the vicinity of an ion.[1] Further, it is found that on division of ΔG_{tr}(diss) into ΔG_{tr}(el)(electrostatic free energy) and ΔG_{tr}(chem)(the non-electrostatic chemical free energy) parts, the contribution of chemical free energy increases as the EtOH concentration is raised. It means that specific chemical interactions are taking place between solvent molecules and the ions of respective acid. Similar conclusion can be drawn from calculations of ΔP_a (the change in proton affinity of conjugate base (A^-) of an acid) values detailed by Wells:[18]

$$\Delta P_a=5.707(\Delta pK_a)+\Delta G_{tr}(H^+)-C \qquad (11)$$

where C is the last term in Eq. 8.

The ionization or dissociation order in respect of the acids studied in (EtOH-H_2O) mixtures turns out to be: 2-nitrobenzoic acid$>$3-nitrobenzoic acid$\simeq$4-nitrobenzoic acid$>$benzoic acid. It means that proton is easily released from 2-nitro substituted acid as compared with 3- and 4-nitro substituted acids. It can be attributed to difference of intramolecular hydrogen bonding, inductive and resonance effects of the substituent and its respective position on the benzene ring with respect to carboxyl group.[12a] Further, 2-nitrobenzoate anions are more solvated than 3- and 4 nitrobenzoate anions with solvent molecules.

Finally the normalized Walden products ($\eta^s\Lambda^s/\eta^w\Lambda^w$) against percentage of EtOH in EtOH-H_2O system, decreases as the solvent mixture is riched in ethanol. The changes in the Walden product are not only due to viscosity or dielectric constant variations but also to an altering proton transfer mechanism.[16]

References

1) M. S. K. Niazi and J. Mollin, *Bull. Chem. Soc. Jpn.*, **60**, 2605 (1987).

2) M. S. K. Niazi, *Bull. Chem. Soc. Jpn.*, **62**, 1253 (1989).

3) a) F. Franks and D. J. Ives, *Q. Rev. Chem. Soc.*, **20**, 1 (1966). b) F. Franks and D. J. Reid, "Water a Comprehensive Treatise," ed by F. Franks, Plenum Press, New York, N. Y. (1973), Vol. 2, p. 323.

4) R. M. Fuoss, *J. Phys. Chem.*, **82**, 2424 (1978).

5) H. O. Spivey and T. Shedlovsky, *J. Phys. Chem.*, **71**, 791 (1967).

6) O. Fischer, M. S. K. Niazi, and E. Fischerova, *Electrochim. Acta*, **27**, 791 (1982).

7) J. J. Lee and M. D. Lee, *Korean J. Chem. Eng.*, **5**, 5 (1988).

8) M. S. K. Niazi, O. Fischer, and E. Fischerova, *J. Solution Chem.*, **15**, 957 (1968).

9) J. E. Lind, J. J. Zwolenik, and R. M. Fuoss, *J. Am. Chem. Soc.*, **81**, 1557 (1959).

10) C. F. Wells, *Thermochim. Acta*, **130**, 127 (1988).

11) C. F. Wells, *J. Chem. Soc., Faraday Trans. 1*, **80**, 2445 (1984).

12) a) E. J. King, "Acid Base Equilibria," Pergamon Press, Oxford (1965), p. 174. b) R. Thuaire, *J. Chim. Phys.*, **67**, 1076 (1976).

13) B. P. Dey, S. C. Dutta, and S. C. Lahiri, *Indian J. Chem., Sect. A*, **25**, 1105 (1986).

14) R. G. Bates and Z. Pawlak, *J. Solution Chem.*, **5**, 213 (1976).

15) M. Born, *Z. Phys.*, **1**, 45 (1920).

16) G. Poulias, N. Papadopoulos, and D. Jannakoudakis, *Electrochim. Acta*, **30**, 431 (1985).

17) A. D.' Aprano and R. M. Fuoss, *J. Phys. Chem.*, **73**, 401 (1969).

18) C. F. Wells, *J. Chem. Soc., Faraday Trans. 1*, **74**, 636 (1978).