Bull. Chem. Soc. Jpn., 63, 3619—3624 (1990)

Solvent Effect on the Dissociation of Benzoic and Nitrobenzoic Acids in Acetonitrile-Water Mixtures at 298 K

M. S. K. Niazi* and J. Ali
Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan
(Received December 27, 1989)

The thermodynamic dissociation constants and the limiting molar conductivities of 2-, 3-, and 4-nitrobenzoic and benzoic acids have been determined in water-acetonitrile mixtures at 298 K. It is found that the acids dissociate in the dereasing order as 2-nitrobenzoic acid>3-nitrobenzoic acid≈4-nitrobenzoic acid>benzoic acid. The conductance-concentration data were analyzed with the Lee and Wheaton equation. The present results are compared with the previous ones for these acids in alcohol-water system, and are interpretted in terms of solute-solvent interactions, intramolecular hydrogen bondings, resonance and inductive effects along with the substituent position.

The acid/base equilibria in alcohol-water mixtures are well known.[1-5] Further, acidity constants of acids in bare dipolar aprotic solvents and their binary mixtures with water have been reported in literature.[6-9] There are a few studies of solvent effect on the ionization/dissociation of carboxylic acids/bases in acetonitrile-water (ACN-W) mixtures.[10,11] ACN-W system has been investigated by many workers,[12-15] and it has been found to be nonideal binary solvent system consisting of three distinct regions: x=0 to 0.2, x=0.2 to 0.8, and x>0.8. And these solvent mixtures show the sharp maxima of viscosity excess functions and dielectric properties.[13] Acetonitrile does not appear to be strong breaker of water structure. It is weaker both an acid and a base than water. This insight has tempted us to investigate the dissociation of nitrobenzoic acids in ACN-W system.

Present paper reports molar conductances of dilute solutions of 2-,3-, 4-nitrobenzoic and benzoic acids in ACN-W mixtures ranging in composition from 0—50 wt% of ACN at 298 K. The conductance-concentration data have been analyzed with the Lee-Wheaton equation,[16] for the derivation of the limiting molar conductance (Λ°) and the association constant of the process ($H^+ + A^- \underset{K_D}{\overset{K_A}{\rightleftarrows}} H^+A^-$). From the K_A values, respective pK_a ($-\log K_A$) values for these acids have been determined. Solvent effect on the dissociation of nitrobenzoic acids has been computed in terms of standard free energy change (ΔG_{tr}) on transfer of these acids from water to ACN-W mixtures. Finished results are compared with those previously reported in alcohol-water mixtures.[1-3]

Experimental

Nitrobenzoic acids (Merck) were recrystallized from ethanol-water mixture, and were used after drying under vacuum over P_2O_5.

Acetonitril (Merck Puriss P.A.) was passed through 3 Å molecular sieves, distilled in a column and the middle fraction was collected. Its specific conductance was better than 5×10^{-8} cm Ω^{-1}.

Details of the experimental procedure have been published previously.[2,3,17] No solvent corrections were applied.

Calculation and Results

The physical properties of ACN-W mixtures are given in Table 1. These values are in complete agreement with the values cited in the literature.[10,12,13]

Values of the molar conductances at different concentrations are given in Table 2, for all four acids in solvent mixture of different composition. The experimental data were analyzed with the Lee and Wheaton conductance equation in its series fom.[16] The selection of this equation was tentative, for it is based on the model which takes into account the dissociation process and short range interactions. The Λ° and K_A values were deduced from the equation:

$$\Lambda = \gamma[\Lambda_0(1+\Delta X/X) - \Delta\Lambda_{el}], \qquad (1)$$

$$K_A = (1-\gamma)/\gamma^2 f^2 c, \qquad (2)$$

$$-\ln f = bk/2(1+kR),\ b = e^2/D\kappa T, \qquad (3)$$

for Λ° and K_A values which minimize

$$\sigma_\Lambda = \sum_j [\Lambda_j(\text{calcd}) - \Lambda_j(\text{obsd})]^2/(n-2). \qquad (4)$$

All the symbol have their usual meanings.

In the case of carboxylic acids no minimum is observed in an $R-\sigma_\Lambda$(%) plot.[23] The R values were varied from 3 Å to 10 Å. The conductance parameters

Table 1. Physical Properties of ACN-W Mixtures at 298 K

ACN wt%	d g cm^{-3}	η cP$^{a)}$	D
0	0.9971	0.893	78.54
10	0.9878	0.980	74.66
20	0.9587	0.971	70.48
30	0.9388	0.912	65.78
40	0.9137	0.844	60.20
50	0.8916	0.749	55.70
60	0.8666	0.655	50.77
70	0.8445	0.573	46.52

a) 1 cP=10^{-3} Pa s.

of the acids in ACN-W mixture are reported in Table 3.

The solvent effect on the dissociation of nitrobenzoic acids was calculated according to the procedure detailed by Wells, i.e.[19]

$$\Delta G^{\circ}_{\mathrm{tr}}\,(\mathrm{HA}) = 5.71\,(\mathrm{p}K_{\mathrm{a}}^{\mathrm{s}} - \mathrm{p}K_{\mathrm{a}}^{\mathrm{w}}) \text{ in kJ mol}^{-1}, \tag{5}$$

and the free energy of transfer of carboxylate ions,

Table 2. Molar Conductances of Acids in ACN-W Mixtures at 298 K

wt% ACN	10	20	30	40	50	60
10^4C	Λ	Λ	Λ	Λ	Λ	Λ
			2-Nitrobenzoic acid			
3.846	279.08	183.67	127.48	74.62	45.96	24.22
7.407	254.35	156.99	103.62	58.82	35.04	18.33
10.710	237.40	141.36	91.01	51.30	29.89	15.58
13.793	224.77	130.73	82.86	46.48	26.74	13.91
16.666	214.92	122.93	77.08	43.03	24.57	12.76
19.354	206.97	116.89	72.71	40.44	22.89	11.92
21.875	200.37	112.05	69.27	38.46	21.74	11.27
24.242	194.80	108.06	66.47	36.78	20.74	10.75
26.470	190.02	104.71	64.15	35.43	19.92	10.32
28.571	185.87	101.84	62.17	34.28	19.24	9.96
30.555	182.22	99.36	60.48	33.30	18.66	9.65
32.432	179.00	97.19	59.01	32.44	18.15	9.39
34.210	176.09	95.27	57.71	31.71	17.71	9.15
35.897	173.49	93.56	56.56	31.05	17.32	8.95
37.500	171.13	92.03	55.53	30.46	16.98	8.77
			3-Nitrobenzoic acid			
3.846	158.79	82.54	63.03	32.74	23.65	
7.407	127.92	64.08	48.978	24.71	17.69	
10.710	111.84	55.11	42.09	20.97	14.96	
13.793	101.54	49.54	37.84	18.71	13.32	
16.666	94.26	45.67	34.89	17.16	12.19	
19.354	88.73	42.81	32.70	16.02	11.37	
21.875	84.46	40.57	30.99	15.14	10.74	
24.242	80.94	38.78	29.63	14.44	10.23	
26.470	78.08	37.29	28.49	13.86	9.82	
28.571	75.66	36.05	27.54	13.37	9.47	
30.555	73.46	34.98	26.73	12.96	9.17	
32.432	71.64	34.06	26.02	12.61	8.92	
34.210	70.05	33.25	25.41	12.29	8.69	
35.897	68.61	32.54	24.87	12.02	8.50	
37.500	67.35	31.90	24.38	11.78	8.32	

Table 2. (Continued)

wt% ACN 10		20			30	40	50
10^4C	Λ	10^4C	Λ	10^4C	Λ	Λ	Λ
			4-Nitrobenzoic acid				
0.961	224.98	1.923	111.39	3.846	67.55	31.82	26.29
1.851	201.68	3.703	90.36	7.407	52.52	23.89	19.71
2.629	186.34	5.355	79.24	10.710	45.19	20.24	16.68
3.458	175.24	6.896	72.09	13.793	40.63	18.03	14.85
4.167	166.73	8.333	67.02	16.666	37.47	16.54	13.61
4.839	159.94	9.677	63.18	19.354	35.12	15.41	12.69
5.469	154.38	10.937	60.16	21.875	33.29	14.56	11.99
6.0606	149.71	12.121	57.71	24.242	31.83	13.88	11.42
6.6178	145.73	13.235	55.68	26.470	30.61	13.32	10.96
7.1430	142.30	14.285	53.94	28.571	29.59	12.85	10.57
7.6390	139.29	15.277	52.46	30.555	28.72	12.45	10.24
8.1080	136.63	16.216	51.16	32.432	27.96	12.11	9.96
8.5530	133.24	17.105	50.03	34.210	27.30	11.81	9.71
8.9750	132.15	17.948	49.03	35.897	26.71	11.54	9.49

wt% ACN	10	20	30		40	50
10^4C	Λ	Λ	Λ	10^4C	Λ	Λ
			Benzoic acid			
3.846	76.92	34.76	23.51	1.961	14.78	10.71
7.407	58.31	25.88	17.76	3.846	9.88	6.24
10.711	49.59	21.84	14.59	5.660	7.95	4.92
13.793	44.29	19.41	12.94	7.407	6.75	4.11
16.666	40.66	17.76	11.83	9.091	6.06	3.63
19.354	37.98	16.55	11.01	10.714	5.60	3.26
21.875	35.91	15.62	10.38	12.281	5.17	3.02
24.242	34.25	14.87	9.88	13.793	4.89	2.83
26.470	32.89	14.26	9.47	15.254	4.68	2.68
28.571	31.75	13.75	9.13	16.666	4.47	2.58
30.555	30.77	13.32	8.84	18.032	4.27	2.44
32.432	29.93	12.95	8.59	19.355	4.13	2.34
34.210	29.19	12.62	8.37	20.635	4.02	2.18
35.897	28.55	12.33	8.18	21.875	3.91	2.12
37.500	27.97	12.08	8.01	23.077	3.77	

Table 3. Conductance Parameters for Acids in ACN-W Mixtures at 298 K

ACN wt%	Λ_0 S cm^2 mol^{-1}	K_A dm^3 mol^{-1}	σ_Λ %	σ_K %	p$K_\mathrm{A}(c)$
		2-Nitrobenzoic acid			
0	401.48±0.23	165	0.043	0.089	2.195
10	322.14±0.28	455	0.013	0.123	2.658
20	251.25±0.16	1317	0.043	0.174	3.119
30	217.65±0.16	3185	0.028	0.206	3.503
40	149.65±0.15	5316	0.031	0.441	3.725
50	118.21±0.22	11050	0.022	0.542	4.0400
60	82.64±0.13	21489	0.011	0.333	4.355
		3-Nitrobenzoic acid			
0	406.06±0.14	2976	0.008	0.124	3.495
10	286.95±0.75	3845	0.065	0.165	3.584
20	199.62±0.17	7903	0.020	0.240	3.899
30	152.50±0.15	24059	0.011	0.176	3.956
40	118.61±0.24	24990	0.055	0.312	4.397
50	102.62±0.21	38046	0.004	0.302	4.580
		4-Nitrobenzoic acid			
0	369.85±0.24	2857	0.033	0.077	3.455
10	268.59±0.11	3239	0.030	0.089	3.510
20	191.85±0.18	6523	0.023	0.107	3.814
30	161.78±0.12	8806	0.018	0.170	3.944
40	127.39±0.22	21656	0.020	0.322	4.335
50	109.51±0.14	34648	0.011	0.267	4.539
		Benzoic acid			
0	383.08±0.88	15667	0.020	0.060	4.195
10	252.44±0.37	19777	0.017	0.069	4.296
20	163.83±0.67	46304	0.022	0.112	4.665
30	122.87±0.28	90942	0.004	0.156	4.958
40	79.14±0.23	154654	0.011	0.214	5.189
50	65.23[a]	337137[a]	—	—	5.527[a]

a) Values derived from extrapolation using the method given in Refs. 3 and 4.

$\Delta G^{\circ}_{\mathrm{tr}}$ (A^-), was calculated according to the procedure detailed by Wells, i.e.[19]

$$\Delta G_{\mathrm{tr}}(\mathrm{A}^-) = 5.71\ (\mathrm{p}K^{\mathrm{s}}_{\mathrm{a}} - \mathrm{p}K^{\mathrm{w}}_{\mathrm{a}}) - \Delta G_{\mathrm{tr}}(\mathrm{H}^+) + 5.71\ \log[(18.01/M_{\mathrm{s}})\cdot(d_{\mathrm{s}}/d_{\mathrm{w}})]\ \text{in kJ mol}^{-1} \qquad (6)$$

where s and w referred to ACN-W mixture and water respectively. The other symbols are the same as defined in Ref. 19. The values of $\Delta G_{\mathrm{tr}}(\mathrm{H}^+)$ i.e. free energy change on transfer of proton from W to ACN-W mixtures were taken from literature.[20] The derived values of $\mathrm{p}K^{\mathrm{s}}_{\mathrm{a}}$ are collected in Table 3.

Discussion

Limiting Molar Conductances. Table 2 shows that the Λ_0 values for 2-,3-, and 4-nitrobenzoic and benzoic acids decrease with addition of ACN in water. Similarly, it is shown in Fig. 3, that the plots of the normalized Walden products ($\Lambda^{\mathrm{s}}\eta^{\mathrm{s}}/\Lambda^{\mathrm{w}}\eta^{\mathrm{w}}$) decrease with the increase of acetonitrile contents in ACN-W mixtures. Comparring these results with those previously found for these acids in alcohol-water mixtures (see Fig. 3 and Table 4a), it is observed that no maximum is seen in these plots. While in alcohol-water mixtures, the normalized Walden products show maximum value at about 20 to 30 wt% composition. These findings may be attributed to appreciable relative increase for the viscosities of alcohol-water mixtures than those of ACN-W mixtures. Figure 5 further, explains the dependence of the values of viscosities on composition for water-cosolvent mixtures. As explained by other workers,[15] the ACN-W mixtures constitute a solvent system that differs in structure from the systems constituted by alcohols with

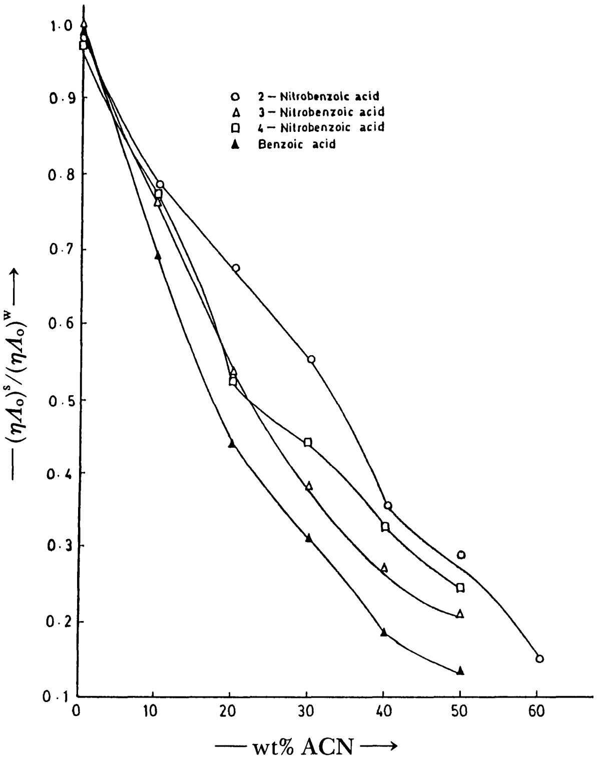

Fig. 3. The dependence of the normalized Walden products for the acids on the composition of ACN-W mixtures at 298 K.

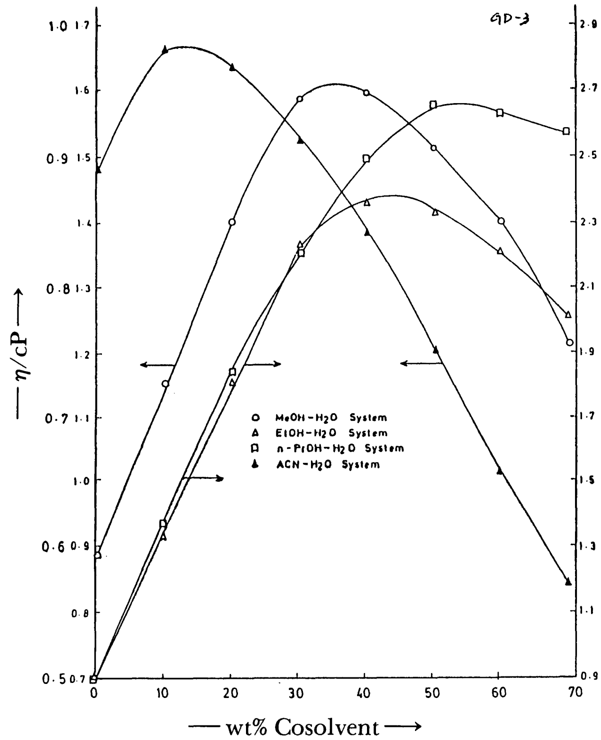

Fig. 5. The dependence of the viscosities of water-cosolvent mixtures on the composition of these mixtures at 298 K.

Table 4a. The Normalized Walden Products, $(\Lambda_0\eta)^{\mathrm{s}}/(\Lambda_0\eta)^{\mathrm{w}}$, Values for Acids in Water-Cosolvent Mixtures at 298 K

	Cosolvent							Cosolvent					
wt%	0	10	20	30	40	50	wt%	0	10	20	30	40	50
		2-Nitrobenzoic acid							4-Nitrobenzoic acid				
a	1.000	1.119	0.966	1.086	0.940	0.605	a	1.000	1.355	1.507	1.448	1.249	0.820
b	1.000	1.177	0.131	1.126	0.979	0.948	b	1.000	1.061	1.375	1.237	1.013	0.912
c	1.000	0.884	0.682	0.561	0.353	0.217	c	1.000	0.800	0.566	0.448	0.326	0.218
		3-Nitrobenzoic acid							Benzoic acid				
a	1.000	1.155	1.288	1.086	0.950	0.860	a	1.000	1.158	1.455	1.243	0.923	0.743
b	1.000	1.100	1.159	0.893	0.761	0.759	b	1.000	1.046	1.097	0.990	0.695	0.704
c	1.000	0.778	0.536	0.385	0.277	0.186	c	1.000	0.693	0.445	0.383	0.187	0.135

a: EtOH-W, b: *n*-PrOH-W, c: ACN-W. The Values for a and b were taken from the Refs. 2 and 3.

Table 4b. The Λ^0 (S cm^2 mol^{-1}), Values for Acids in Water-Cosolvent Mixtures at 298 K

wt% Cosolvent	0	10	20	30	40	50	60
			2-Nitrobenzoic acid				
a	401.48	301.88	190.74	184.10	141.45	91.65	60.91
b	401.48	315.21	224.65	180.70	141.69	127.62	104.26
c	401.48	322.14	251.25	217.65	149.65	118.21	82.64
			3-Nitrobenzoic acid				
a	406.06	315.45	257.42	186.18	144.61	131.74	102.46
b	406.06	272.68	227.03	145.03	111.37	103.39	—
c	406.06	286.95	199.62	152.50	118.61	102.62	—
			4-Nitrobenzoic acid				
a	369.85	336.93	274.30	226.06	173.15	114.38	85.53
b	369.85	261.08	245.35	182.90	135.14	116.08	—
c	369.85	268.59	191.85	161.78	127.39	109.51	—
			Benzoic acid				
a	383.08	298.24	274.32	201.11	133.45	107.35	125.22
b	383.08	229.85	202.72	151.64	123.20	90.44	—
c	383.08	252.44	163.83	122.87	79.14	65.22	—

a: EtOH-W, b: *n*-PrOH-W, c: ACN-W mixtures.

Table 5. The pK_a Values for Acids in Water-Cosolvent Mixtures at 298 K

Cosolvent wt%	p$K_a(c)$						
	0	10	20	30	40	50	60
			2-Nitrobenzoic acid				
a	2.195	2.33	—	2.79	—	3.45	—
b	2.195	2.499	2.853	3.277	3.544	3.814	3.960
c	2.195	2.817	2.905	3.429	3.70	4.200	4.623
d	2.195	2.658	3.119	3.503	3.725	4.040	4.333
			3-Nitorbenzoic acid				
a	3.495	3.51	—	3.88	—	4.17	—
b	3.495	3.587	3.984	4.217	4.440	4.711	—
c	3.495	3.596	4.040	4.141	4.349	4.790	—
d	3.495	3.584	3.897	3.956	4.394	4.580	—
			4-Nitrobenzoic acid				
a	3.450	3.50	—	3.86	—	4.30	—
b	3.450	3.788	3.938	4.227	4.365	4.486	—
c	3.450	3.498	3.967	4.187	4.322	4.634	—
d	3.450	3.510	3.814	3.944	4.335	4.539	—
			Benzoic acid				
a	4.195	4.31	—	4.94	—	5.56	—
b	4.195	4.321	4.683	5.217	5.484	5.712	—
c	4.195	4.288	4.882	5.083	5.393	5.629	—
d	4.195	4.296	4.665	4.958	5.189	5.527	—

a: MeOH-W; b: EtOH-W; c: 1-PrOH-W; d: ACN-W. Values of a, b, c taken from Refs. 2 and 3, respectively.

water. In aqueous region with $x<0.2$, it can be written for a monobasic co-solvent

$$(H_2O)_{bulk} + CH_3CN = CH_3CN\cdots HOH + (LP)_{free} \quad (7)$$

This lone-pair molecule of water seems to be of prime importance in its interactions with the acids. And this is depicted in relatively more decrease of the Λ^0 values of these acids in ACN-W mixtures than those found in alcohol-water mixtures.[2,3]

Dissociation Constant. The pK_a values of benzoic and nitrobenzoic acids increase with the increase of acetonitrile contents in water (see Tables 3 and 5). This may be attributed to relative decrease of dielectric constants of ACN-W mixtures. It is shown in Fig. 1 that the dependence of pK_a values for nitrobenzoic acids on inverse of dielectric constants of ACN-W mixtures is nonlinear. The same is observed for the dependence of ΔG_{tr} (A^-) values on the composition of ACN-W mixtures (see Fig. 2). These plots are also nonlinear. Such type of dependence may be attributed to specific solute-solvent interactions. In addition to eletrostatic interactions as detailed by Born,[22]

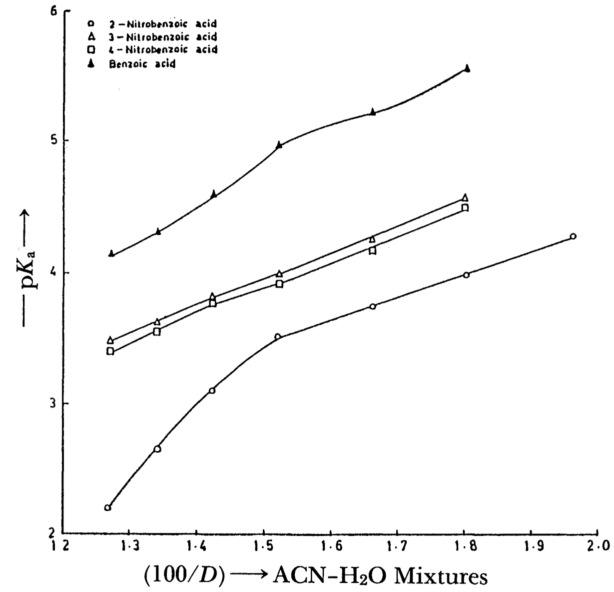

Fig. 1. The dependence of pK_a values of acids on the inverse of dielectric constants of ACN-W mixtures at 298 K.

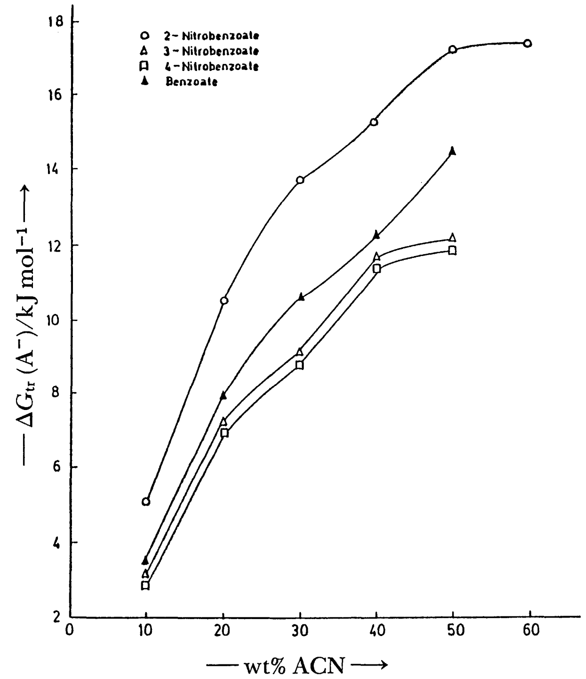

Fig. 2. The dependence of free enegy change on transfer of the anions from water to acetonitrile-water mixture at 298 K.

there are specific chemical interactions taking place between the ions and the solvent molecules. The origin of these interactions is from the contribution of non-electrostatic part of the standard free energy of transfer as the acids or their carboxylate ions get transfer from water to ACN-W mixtures.

It has been found that pK_a values for nitrobenzoic acids for ACN-W mixtures are less than those previously found for alcohol-water mixtures[1-3] (see Table 5). It is found that the ACN-W mixtures are less basic than those constituted by alcohols with water. Further, it is shown in Fig. 4, that the order for the dielectric constants for water-cosolvent mixtures of the same composition is $D_{\text{ACN-W}} \approx D_{\text{MeOH-W}} > D_{\text{EtOH-W}} > D_{\text{1-PrOH-W}}$. The bulk dielectric constant of water-cosolvent mixtures is not only the sole parame-

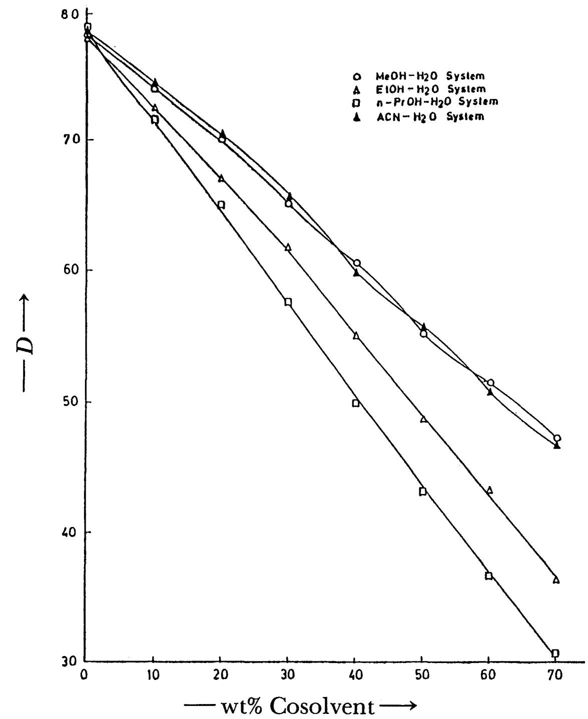

Fig. 4. The dependence of the dielectric constants of water-cosolvent mixtures on the composition of these mixtures at 298 K.

Table 6. The Values for Standard Molar Free Energy of Transfer, ΔG°_{tr}(A$^-$) kJ mol^{-1}, for Anions, from Water to Water-Cosolvent Mixtures at 298 K

Cosolvent wt%	10	20	30	40	50	60
			2-Nitrobenzoate			
a	3.35	7.86	12.76	15.20	16.31	16.16
b	5.98	11.00	14.83	16.40	18.74	20.06
c	5.32	10.58	13.82	15.39	17.37	17.59
			3-Nitrobenzoate			
a	2.13	6.89	10.71	12.83	14.00	15.02
b	3.03	10.06	11.47	12.68	14.68	—
c	3.19	7.62	8.98	11.82	12.08	—
			4-Nitrobenzoate			
a	3.54	6.88	11.02	12.76	12.98	13.44
b	2.71	9.90	11.99	12.78	14.05	—
c	2.98	7.36	9.14	11.67	12.06	—
			Benzoate			
a	2.33	6.88	12.47	14.80	15.73	—
b	3.11	10.87	12.46	14.42	15.81	—
c	3.26	7.99	10.70	12.03	14.78	—

a: EtOH-W, b: *n*-PrOH-W, c: ACN-W. Values for a and b were taken from Refs. 2 and 3, respectively.

ter determining the dissociation order of the acids.

As seen in Table 5, the dissociation order for the acids is specific for each solvent system. There are differences in solute-solvent interactions in each system. The alcohols mixed with water all show extrema in the variation of properties such as the relative partial molal volumes, $\overline{V}_2-V_2^{\circ}$, the viscosity η (Fig. 5), and they all show minimum in the excess entropy of mixing ΔS^{E}, at $x_2<0.5$.[21] But the physical properties of ACN-W mixtures, differ from the properties of alcohol-water mixtures, having a minimum in ΔS^{E} at $x_2=0.2$, and a maximum in the ultrasonic absorption at $x_2=0.4$, small maximum in η at low x_2 and no minimum in $\overline{V}_2-V_2^{\circ}$. Consequently, the variation of values for $\mathrm{p}K_\mathrm{a}$ and $\Delta G^{\circ}_{\mathrm{tr}}$ (A^-) with composition of acetonitrile-water mixtures and with that for alcohol-water has been found differently (see Tables 5 and 6).

Finally it has been found that the dissociation order in respect of the acids studied in ACN-W mixtures turns out to be; 2-nitrobenzoic>3-nitrobenzoic≈4-nitrobenzoic>benzoic. This observed difference of acidities among the same isomers of nitrobenzoic acid could be due to difference of intramolecular hydrogen bondings, inductive and resonance effect of nitro-group ($-\mathrm{NO_2}$) for its position with respect to carboxyl group on the benzene ring and hence, more solvation of 2-nitrobenzoate ion than 3-nitrobenzoate and 4-nitrobenzoate ions.

Financial support from the University Reseach Fund is acknowledged greatfully.

References

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

2) a) M. S. K. Niazi, *Bull. Chem. Soc. Jpn.*, **62**, 1253 (1989); b) M. S. K. Niazi, M. Zafar Iqbal Khan, J. Ali, and M. Ahmad, *Bull. Chem. Soc. Jpn.*, **63**, 581 (1990).

3) M. S. K. Niazi, S. S. Shah, J. Ali, and M. Z. I. Khan, *J. Solution Chem.*, **19**, 681 (1990).

4) J.-P. Morel, *J. Chim. Phys.*, **67**, 895 (1970).

5) A. Pal and S. C. Lahiri, *Z. Phys. Chem. (Leipzig)*, **268**, 378 (1987).

6) S. M. Petrov, Yu. I. Umanskii, I. F. Mullin, and A. N. Tertichny, *Russ. J. Phys. Chem.*, **47**, 363 (1973).

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

8) Z. Pawlak and R. G. Bates, *J. Solution Chem.*, **4**, 817 (1975).

9) S. N. Petrov, Yu. I. Umannskii, N. D. Golikova, L. A. Sannlina, and F. S. Chasibova, *Z. Fiz. Khim.*, **43**, 2964 (1969).

10) A. D' Aprano and R. M. Fuoss, *J. Phys. Chem.*, **73**, 400 (1969).

11) Z. Pawlak, *J. Chem. Thermodyn.*, **19**, 443 (1987).

12) Y. P. Handa and G. C. Benson, *J. Solution Chem.*, **10**, 291 (1981).

13) C. Moreau and G. Douheret, a) *J. Chem. Thermodyn.* **8**, 403, (1976); b) *Thermochimica Acta*, **13**, 3859 (1975).

14) V. Zelano and P. Mirti, *Z. Phys. Chem. (N. F.)*, **138**, 31 (1983).

15) M. C. R. Symons, *Acc. Chem. Res.*, **19**, 179 (1981).

16) a) W. H. Lee and R. J. Wheaton, *J. Chem. Soc., Faraday Trans. 2*, **74**, 743, 1456 (1978); b) A. D. Pethybridge and S. S. Taba, *J. Chem. Soc., Faraday Trans. 1*, **76**, 368 (1980).

17) M. S. K. Niazi, O. Fischer, and E. Fischerova, *J. Solution Chem.*, **15**, 957 (1986).

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

19) C. F. Wells, *Aust. J. Chem.*, **36**, 1739 (1983).

20) G. S. Groves and C. F. Wells, *J. Chem. Soc., Faraday Trans. 1*, **81**, 1985 (1985).

21) D. A. Armitage, M. J. B. Blandamer, M. J. Foster, N. J. Hidden, and K. W. Morcom, *Trans. Faraday Soc.*, **64**, 1193 (1968).

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

23) R. M. Fuoss, *J. Phys. Chem.*, **82**, 2427 (1978).