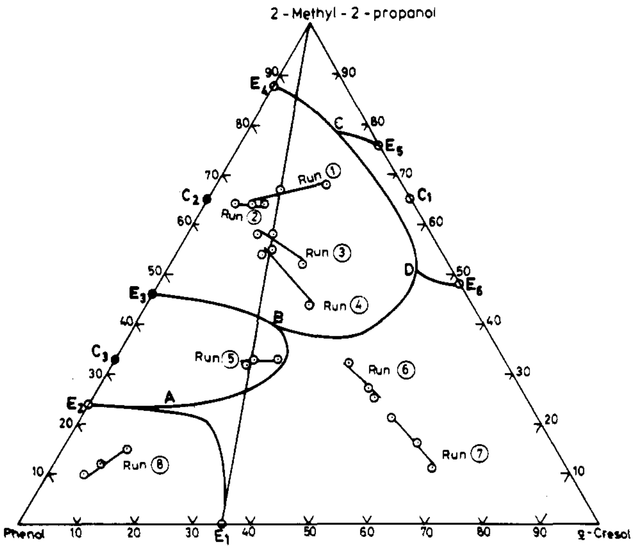

Figure 5. Feasibility runs of the ternary system phenol–*o*-cresol–2-methyl-2-propanol.

solid phase from its eutectic mixture is in the range from 84 to 91 mol % and the purity from 63 to 75 mol %. Recrystallization may yield higher purity. The resulting solid-phase composition from the ternary mixture in run 1 was used in run 2 for the second crystallization at 15.5 °C; the purity of phenol in the solid phase improved from 74.9 to 83.6 mol %. Figure 5 shows that 2-methyl-2-propanol forms two adducts with phenol over the different concentration range. The feasibility runs in a larger region denoted by E_3BDCE_4 yield better results for separation of phenol from eutectic mixtures than those in a smaller region denoted by E_2ABE_3. Runs 6 and 7 performed in the *o*-cresol-rich region yielded low phenol purity in the solid phase (<30 mol %) while the purity of phenol in the solid phase obtained from run 8 in the phenol-rich region was >90 mol %. All the runs were performed over the temperature range from −10 to +20 °C and would require reasonable refrigeration duty.

Conclusions

Enthalpy changes on complex formation were used to calculate the selectivity of a solvent for a given pair of close boiling organic components. 2-Methyl-2-propanol appears to be a suitable solvent for separation of phenol from its mixture with *o*-cresol. A ternary phase diagram for this system was constructed. Using multistage crystallization, a reasonable purity of phenol can be achieved.

Registry No. Phenol, 108-95-2; *o*-cresol, 95-48-7; 2-methyl-2-propanol, 75-65-0.

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Solvent Effects on the Dissociation of Nitrobenzoic Acids in Water + *N*,*N*-Dimethylformamide at 25 °C

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The dissociation constants and molar conductivities at infinite dilution of benzoic and 2-, 3-, and 4-nitrobenzoic acids have been determined in *N*,*N*-dimethylformamide + water mixtures at 25 °C. The experimental data have been analyzed by means of the Lee and Wheaton equation. The results are compared with previous findings for these acids in some other water–cosolvent mixtures.

Introduction

The binary mixtures of *N*,*N*-dimethylformamide (DMF) with water (W) are nonideal and show extrema in various excess thermodynamic functions (*1*–*3*). The present paper is on the study of the dissociation of benzoic and 2-, 3-, and 4-nitrobenzoic acids in binary mixtures of *N*,*N*-dimethylformamide with water ranging in composition from 0% to 50% (wt/wt). The molar conductances of the dilute solutions of the acids have been measured at 25 °C. The conductance–concentration data have been analyzed for the derivation of pK_a and Λ_0 values. The finished results are compared with those previously found for other water–cosolvent mixtures (*4*, *5*). Finally the solvent effect on the ionization of these acids has been discussed in terms of the free energy change on the transfer of the respective carboxylate ion from water to water–cosolvent mixtures.

Experimental Section

The acids were the same as those used in previous studies (*4*, *5*). DMF was from E. Merck and was further purified as detailed earlier (*6*).

Conductance measurements were carried out using an autobalance precision bridge (Wayne Kerr, B641) at 1592 Hz in the same way as described elsewhere (*4*–*6*). Two different cells with cell constants 0.876 and 1.013 ± 0.0015 cm^{-1} were used. The cells were calibrated following the method of Fuoss and co-workers (*7*) using aqueous KCl solutions in the concentration range (2–30) × 10^{-4} mol dm^{-3}. The reproducibility of the conductance measurements was better than ±0.5%. The conductance data are given in Table II. The accuracy of molar conductances is ±0.2%. No solvent corrections were

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Table I. Densities (ρ), Viscosities (η), and Dielectric Constants (D) for DMF + Water at 25 °C

wt % DMF	ρ/(g cm^{-3})	η/(mPa s^{-1})	D
0	0.9971	0.890	78.54
10	0.9964	1.153	76.78
20	0.9963	1.326	74.65
30	0.9971	1.665	72.00
40	0.9968	2.042	68.92
50	0.9961	2.338	64.96
60	0.9934	2.491	60.48
70	0.9913	2.580	55.50

applied. The densities (ρ) and viscosities (η) of DMF–W mixtures were measured in the same way as detailed earlier (*6*), and the values of dielectric constants (ϵ) were taken or interpolated from the literature (*8*, *9*). These values are collected in Table I. Triply distilled water was used as an aqueous medium or for the preparation of water–cosolvent mixtures.

Results and Discussion

The experimental data were treated by the method proposed by Pethybridge and Taba (*10*), which uses the Lee and Wheaton conductance equation in its series form (*11*, *12*). The molar conductances at infinite dilution (Λ_0), standard deviations, (σ_Λ/%), based on the observed and calculated Λ values, and the acid dissociation constants (K_a ($=1/K_A$)), where K_A is the association constant, are listed in Table III, and were deduced from the equations

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

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

$$-(\ln f) = \beta k/2(1 + kR) \qquad \beta = e^2/\epsilon kT \qquad (3)$$

for Λ_0 and K_A values which minimize

$$\sigma_\Lambda = \sum_j [\Lambda_j(\text{calcd}) - \Lambda_j(\text{obsd})]^{1/2}/(n - 2) \qquad (4)$$

by a least-squares analysis. The computer program was kindly supplied by Dr. Gilkerson. $\Delta X/X$ is the relaxation field effect, and Δ_{el} is the electrophoretic countercurrent, $1/k$ is the radius of the ion atmosphere, ϵ is the dielectric constant of the solvent, e is the electron charge, k is Boltzmann's constant, R is the Gurney-sphere diameter, γ is the fraction of solute present as unpaired ion, C is the molarity of the solution, f is the activity coefficient, and β is twice the Bjerrum distance (*13*).

The Gurney-sphere diameter serves as an adjustable parameter chosen to minimize the sum of the square of the residual in the fitting of the conductance function to experimental data. However, for carboxylic acids the variation in σ, the standard deviation, as a function of R is too small to be significant and shows no minimum in the R vs σ_Λ/% plot. On the basis of the recommendation of Fuoss (*14*), the value of R was set at twice the Bjerrum distance. Trial calculations with R set at 10 times this value changed the pK_a value by ±0.01 or less. The values of Λ_0 and K_A are reported in Table III. For an equilibrium of the type

$$\text{HA} \underset{K_a}{\overset{K_A}{\rightleftharpoons}} \text{H}^+ + \text{A}^-$$

the free energy change on dissociation of an acid is given by the expression

$$\Delta G° = -RT \ln K_a \qquad (6)$$

where K_a ($=1/K_A$) is the dissociation constant. Therefore, in the present case the free energy change on transfer of the acid from water to water–cosolvent mixture on dissociation, at 25 °C, was calculated using the equation

$$\Delta G°_{tr}(\text{HA}) = 5.71(\text{p}K_a^{s} - \text{p}K_a^{w}) \quad \text{kJ mol}^{-1} \qquad (6a)$$

Table II. Molar Conductivities (Λ) for Solutions of Acids in DMF–Water at 25 °C

10^4C/ (mol dm^{-3})	Λ/(S cm^2 mol^{-1}) at various wt % DMF					
	10	20	30	40	50	60
			2-Nitrobenzoic Acid			
1.923	263.36	196.30	134.40	89.27	42.26	29.9
3.703	253.80	184.22	123.45	77.48	34.32	24.1
5.355	245.09	175.43	115.60	70.90	31.10	21.2
6.896	238.66	167.78	109.58	66.15	28.77	19.4
8.333	233.10	163.66	104.82	62.76	26.70	18.2
9.677	228.09	158.93	101.21	59.51	25.29	17.2
10.937	224.06	154.99	98.09	57.36	24.09	16.4
12.121	220.41	151.51	95.35	55.42	23.08	15.8
13.235	216.92	147.74	93.35	53.94	22.25	15.1
14.285	214.14	145.27	91.32	52.48	21.55	14.6
15.277	211.22	142.91	89.76	51.27	20.93	14.2
16.216	208.62	140.55	88.03	50.42	20.37	13.8
17.105	206.62	138.86	86.46	49.23	19.79	13.5
17.948	204.522	137.01	85.47	48.47	19.33	13.2
18.750	202.82	135.63	84.31	47.66	18.92	12.8
			3-Nitrobenzoic Acid			
1.923	213.50	146.40	89.28	62.92	32.01	
3.703	174.06	122.32	72.39	51.28	25.31	
5.355	159.73	108.07	64.08	45.02	22.37	
6.896	146.47	99.96	58.34	40.81	20.00	
8.333	137.91	92.99	54.59	37.77	18.18	
9.677	130.16	87.97	51.55	35.71	17.22	
10.937	125.00	84.34	49.25	34.05	16.39	
12.121	120.48	81.35	47.27	32.53	15.62	
13.235	116.07	78.22	45.64	31.38	14.56	
14.288	113.79	76.03	44.24	30.44	14.36	
15.277	109.53	73.73	43.12	29.64	14.21	
16.216	107.26	72.29	42.08	28.93	13.88	
17.105	105.19	70.75	41.08	28.26	13.55	
17.948	103.26	69.68	40.35	27.68	13.33	
18.759	101.72	68.43	39.60	27.13	13.12	
			4-Nitrobenzoic Acid			
0.962	223.22	159.65	104.15	77.04	60.83	
1.852	197.67	138.81	95.56	64.29	49.30	
2.629	180.97	126.58	85.10	57.19	43.51	
3.459	169.45	117.63	78.48	51.87	39.26	
4.167	160.38	111.83	73.98	48.43	36.52	
4.839	152.90	106.45	70.14	45.76	34.42	
5.469	147.07	102.98	67.63	43.65	32.28	
6.061	142.30	98.80	64.99	41.93	31.43	
6.618	138.21	95.83	62.50	40.50	30.32	
7.143	134.58	93.29	60.60	39.32	29.37	
7.639	131.53	91.17	59.17	38.22	28.56	
8.108	128.78	89.32	57.70	37.21	27.87	
8.553	126.58	87.65	56.86	36.42	27.24	
8.975	125.00	86.20	55.55	35.71	26.69	
9.375	123.25	84.69	54.76	35.08	26.20	
			Benzoic Acid			
1.923	99.75	61.84	38.65	24.12	13.81	
3.704	77.87	47.34	29.03	18.05	10.55	
5.357	65.86	40.43	24.58	15.25	9.00	
6.897	59.07	36.20	21.90	13.58	7.96	
8.333	54.38	33.28	20.07	12.42	7.29	
9.677	50.91	31.30	18.72	11.62	6.74	
10.938	48.21	29.46	17.69	10.94	6.47	
12.121	46.04	28.12	16.86	10.41	6.16	
13.230	44.25	27.01	16.17	10.00	5.81	
14.286	42.75	26.09	15.60	9.66	5.59	
15.276	41.48	25.29	15.12	9.35	5.43	
16.216	40.36	24.61	14.70	9.09	5.25	
17.105	39.39	24.01	14.33	8.81	5.12	
17.949	48.53	23.49	14.01	8.63	4.98	
18.750	37.77	23.02	13.72	8.47	4.89	

where pK_a = −(log K_a), and the free energy change on transfer of carboxylate ions, $\Delta G°_{tr}(\text{A}^-)$, was calculated according to the procedure detailed by Wells (*15*, *16*):

$$\Delta G°_{tr}(\text{A}^-) = \Delta G°_{tr}(\text{HA}) - \Delta G°_{tr}(\text{H}^+) + 5.71 \log [(18.01/M_s)(\rho_s/\rho_w)] \qquad (7)$$

Table III. Conductance Parameters for Acids in DMF–W Mixtures at 25 °C

wt % DMF	Λ_0/ (S cm^2 mol^{-1})	K_A/ (dm^3 mol^{-1})	ΔK_A/%	σ_A/%	pK_a
		2-Nitrobenzoic Acid			
0	401.48 ± 0.07	157	0.011	0.035	2.195
10	278.79 ± 0.05	278	0.044	0.041	2.555
20	215.47 ± 0.02	513	0.046	0.042	2.710
30	153.55 ± 0.05	821	0.014	0.003	2.915
40	113.06 ± 0.06	1779	0.010	0.005	3.250
50	70.36 ± 0.03	3507	0.011	0.011	3.545
60	54.17 ± 0.04	7313	0.012	0.015	3.864
		3–Nitrobenzoic Acid			
0	406.06 ± 0.14	2976	0.012	0.008	3.495
10	318.73 ± 0.11	3737	0.034	0.032	3.572
20	217.68 ± 0.10	3830	0.024	0.026	3.583
30	140.89 ± 0.07	4985	0.011	0.014	3.697
40	110.45 ± 0.03	6854	0.014	0.012	3.836
50	63.42 ± 0.05	10210	0.022	0.019	4.009
		4-Nitrobenzoic Acid			
0	369.85 ± 0.24	2857	0.010	0.007	3.455
10	282.18 ± 0.12	2973	0.015	0.011	3.473
20	203.26 ± 0.15	3657	0.027	0.035	3.551
30	162.88 ± 0.05	6480	0.022	0.010	3.800
40	123.37 ± 0.26	9616	0.089	0.045	3.983
50	105.18 ± 0.18	17139	0.008	0.006	4.234
		Benzoic Acid			
0	383.08 ± 0.65	15667	0.011	0.015	4.195
10	261.12 ± 0.36	22259	0.024	0.021	4.347
20	176.05 ± 0.34	27619	0.009	0.006	4.441
30	135.62 ± 0.24	45649	0.007	0.004	4.659
40	103.08 ± 0.88	73542	0.041	0.032	4.866
50	75.06 ± 0.86	84139	0.042	0.031	4.925

Table IV. Values for Standard Molar Free Energy of Transfer $\Delta G^\circ_{tr}(A^-)$ for Anions from Water to Water–Cosolvent at 25 °C

	ΔG°_{tr}/(kJ mol^{-1}) at various wt % cosolvent				
	10	20	30	40	50
			2-Nitrobenzoate		
a	1.5	4.0	6.2	11.0	13.1
b	3.4	7.9	12.8	15.2	16.3
c	6.0	11.0	14.8	16.4	18.7
d	5.3	10.6	13.8	15.4	17.4
e	5.6	9.8	13.8	18.1	22.0
f	6.0	14.05	19.2	22.5	20.4
g	6.9	11.11	14.2	16.7	18.7
			3-Nitrobenzoate		
a	0.8	3.0	5.0	7.8	9.8
b	2.1	6.9	10.7	12.8	14.0
c	3.0	10.1	11.5	12.7	14.7
d	3.2	7.6	9.0	11.8	12.1
e	3.3	7.0	10.3	14.5	17.2
f	4.6	12.0	15.6	17.0	16.6
g	5.4	8.8	11.3	12.8	14.1
			4-Nitrobenzoate		
a	1.0	4.2	6.3	8.8	10.8
b	3.5	6.9	11.2	12.8	13.0
c	2.7	9.9	11.9	12.8	14.0
d	3.0	7.4	9.1	11.7	12.1
e	3.0	5.6	7.9	10.0	11.8
f	4.4	11.2	14.9	16.6	15.8
g	4.9	8.8	12.1	13.7	15.5
			Benzoate		
a	1.3	4.3	7.0	10.1	13.7
b	2.3	6.9	12.5	14.8	15.7
c	3.1	10.9	12.5	14.4	15.8
d	3.3	8.0	10.7	12.0	14.8
e	4.7	9.1	13.6	17.0	21.5
f	5.9	13.2	17.9	19.6	20.7
g	5.7	9.6	13.4	14.5	15.2

[a] MeOH–W. [b] EtOH–W. [c] 1-PrOH–W. [d] ACN–W. [e] Ac–W. [f] THF–W. [g] DMF–W.

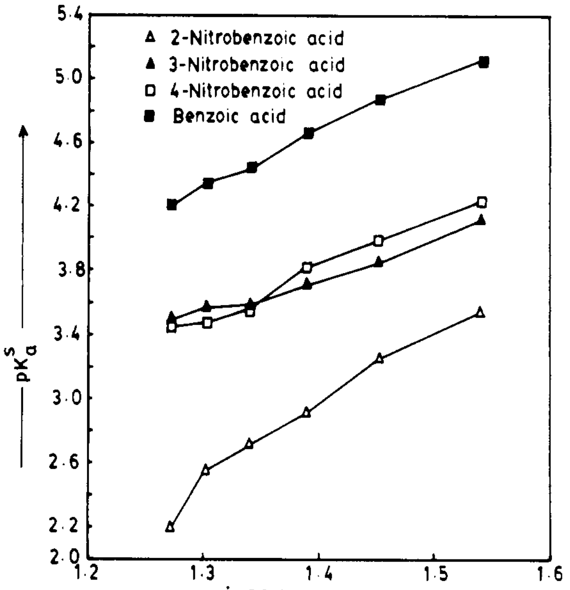

Figure 1. Dependence of pK_a values for acids on the inverse dielectric constant (1/ε) of DMF–water mixtures at 25 °C.

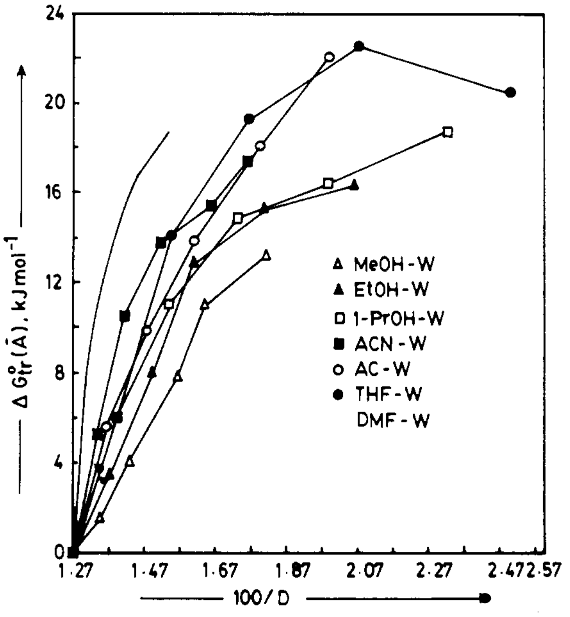

Figure 2. Dependence of values of the free energy change G°_{tr}(Å) on transfer of 2-nitrobenzoate ion from water to water–cosolvent mixtures on the inverse dielectric constant values (1/ε) for these solvent systems at 25 °C.

where s and w refer to water–cosolvent mixture and water, respectively. The other symbols are the same as defined in ref 16. The values of $\Delta G^\circ_{tr}(H^+)$, i.e., free energy change on transfer of a proton from water to these solvent mixtures, were taken from ref 16. The derived values of pK_a are collected in Table III. The $\Delta G^\circ_{tr}(A^-)$ values for each anion in various water–cosolvent mixtures are plotted in Figures 2–5 against the inverse of permitivity (1/ε) of these solvent mixtures, respectively.

Conductance Results. Table III shows that the Λ_0 values for 2-, 3-, and 4-nitrobenzoic and benzoic acids decrease with addition of DMF. This may be attributed to a relative increase in the viscosity value of the DMF–W mixtures (see Table I). No literature values for Λ_0 for these acids in DMF–W mixtures were available; therefore, no comparison could be made.

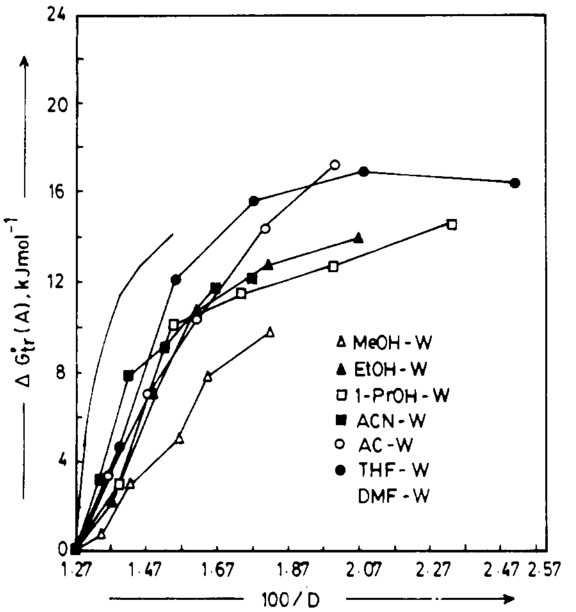

Figure 3. The same as Figure 2 for 3-nitrobenzoate ion.

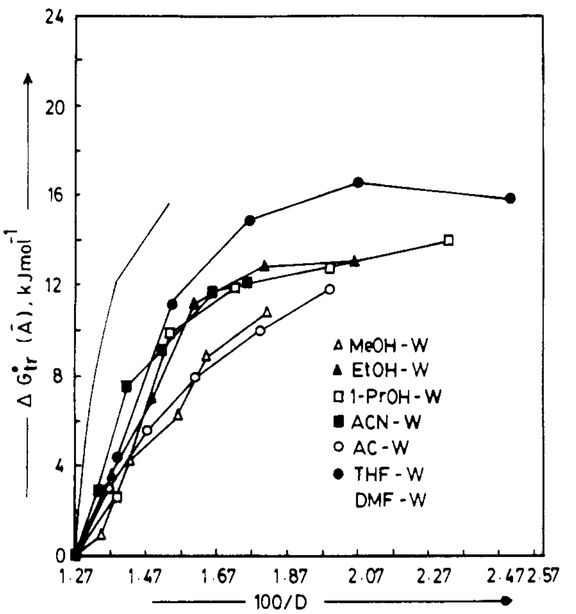

Figure 4. The same as Figure 2 for 4-nitrobenzoate ion.

Dissociation Constant Values. The pK_a values reported in Table III are correct to ±0.01. In Figure 1, the pK_a values for four acids are plotted as a function of the reciprocal dielectric constant ($1/\epsilon$) of the solvent mixtures. The plots are nonlinear. The nonlinear plots are also found if one plots the dependence of $\Delta G°_{tr}(A^-)$ values on the composition of water–cosolvent mixtures (see Figures 2–5). Such a type of dependence may be attributed to specific solute–solvent interactions. The values of $\Delta G°_{tr}(A^-)$ for these acids in different solvent systems were derived from pK_a values taken from previous papers (*4*, *5*, *17*). The pK_a values of benzoic and 2- and 3-nitrobenzoic acids are available in the literature in a few DMF–water mixtures (*18*, *19*). These values have been derived potentiometrically. Present values differ slightly from literature values because of various approximations used in the determination of pH* values in mixed solvent systems.

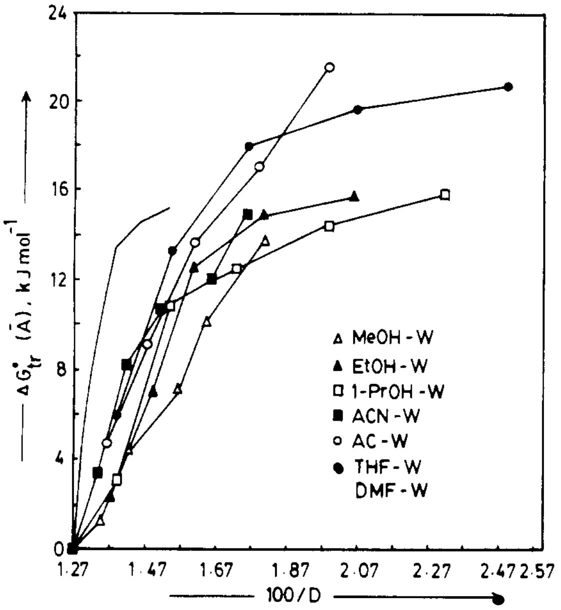

Figure 5. The same as Figure 2 for benzoate ion.

In the present study it has been found that the acids dissociate according to the order 2-nitrobenzoic acid > 3-nitrobenzoic acid > 4-nitrobenzoic acid > benzoic acid.

Registry No. DMF, 68-12-2; benzoic acid, 65-85-0; 2-nitrobenzoic acid, 552-16-9; 3-nitrobenzoic acid, 121-92-6; 4-nitrobenzoic acid, 62-23-7; benzoate, 766-76-7; 2-nitrobenzoate, 771-70-0; 3-nitrobenzoate, 16885-78-2; 4-nitrobenzoate, 2906-29-8.

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