A J_- Acidity Function for Solutions of Sodium Hydroxide in Water–Ethanol and Water–Dimethyl Sulfoxide Mixtures

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The addition of hydroxyl ions to substituted benzaldehydes according to the reaction $ArCHO + OH^- \rightleftarrows ArCH(OH)O^-$ is used to establish J_- acidity scales in water–ethanol and water–Me$_2$SO mixtures containing sodium hydroxide as a base. Both in water–ethanol and in water–Me$_2$SO mixtures the pK values of the addition reaction are linearly correlated with the Hammett substituent constants. The reaction constant ρ is independent of the solvent composition, confirming that substituted benzaldehydes form a suitable set of J_- indicators for hydroxide solutions in water–ethanol and water–Me$_2$SO mixtures of different composition. J_- scales, representing J_- as a function of the sodium hydroxide concentration, are only slightly affected by the presence of ethanol up to 90 vol %. Similarly the J_- value of 0.01 or 0.1 M sodium hydroxide shows only a very small increase on increasing the ethanol content from 90 to 98 vol %. The effect of Me$_2$SO is much more pronounced especially at concentrations higher than 80 vol %, but this effect is very much smaller than that of the Me$_2$SO percentage on H_- values based on proton abstraction from anilines.

Basicity scales for strongly alkaline aqueous solutions of alkali metal and quaternary ammonium hydroxides seem to be reasonably well established both for reactions involving dissociation of protons[2] (H_-) and for reactions which result in addition of hydroxyl ions[3] (J_-).

In organic solvents, the acidity function H_-, based on hydrogen ion abstraction from neutral indicator acids, in solutions of alkali metal alkoxides in various alcohols,[2] and the acidity J_- function (denoted as H_R^-), based on additions of methoxides and ethoxides to neutral indicator acids, in dimethyl sulfoxide–methanol and ethanol mixtures[4] have been reported. These scales involve arbitrary choice of water as the solvent for determination of the dissociation constant of the anchoring acid.

For mixtures of organic solvents with water, the available information[2] is derived only from reactions involving dissociation of hydrogen ion, leading to acidity function H_-. Measurements for solutions containing a constant concentration of a base and a varying ratio of water and the organic solvent were carried out using sodium alkoxides as bases in mixtures of water and alcohols[5] as well as tetramethylammonium hydroxide as the base in mixtures of water with pyridine,[6] tetramethylenesulfone,[6] and dimethyl sulfoxide.[6,7] When 0.005 M sodium ethoxide was used, a relatively modest increase of the value of H_- (from 11.74 to 13.35) was observed[5] on increasing the ethanol concentration from 0 to 100 mol %. In solutions containing 0.011 M tetramethylammonium hydroxide and increasing dimethyl sulfoxide (Me$_2$SO) concentration, the increase in the value of H_- was found to be much more dramatic, from 12.0 in water to 26 in 99.5 mol % Me$_2$SO. The increase in the value of H_- with Me$_2$SO concentration was smaller at concentrations below 85 mol %, but very steep at higher Me$_2$SO concentrations.[7]

Substituted benzaldehydes have been proved to be a useful series of acid–base indicators for reactions involving addition of hydroxide ions in strongly alkaline aqueous media,[3] and it seemed logical to extend their use to solutions of sodium hydroxide in water–ethanol and water–Me$_2$SO mixtures. In the first case, it was of interest whether the competition between addition of hydroxide and ethoxide ions will be reflected in the dependence of the J_- function on ethanol concentration. In the case of water–Me$_2$SO mixtures, it was considered of importance to investigate whether the radical change at higher Me$_2$SO concentrations, observed for H_- values and attributed to changes in solvation of the hydroxide ion, will be observed for the addition reaction as well.

In addition to determination of the J_- function at constant sodium hydroxide concentration (0.01 M) and varying ethanol

or Me$_2$SO content, measurements were carried out which made possible the definition of acidity function J_- in solutions containing fixed percentages of the organic solvent component and varying concentrations of sodium hydroxide. Such scales provide the possibility of preparing solutions of known J_- in mixtures containing a given concentration of the organic component and thus seem to be of practical importance (e.g., for electroanalytical measurements). They have rarely been reported, even for the H_- function.

Furthermore, equilibrium constants K_2 for the formation of the adduct corresponding to the reaction

$$ArCHO + OH^- \rightleftharpoons ArCH(OH)O^- \qquad (1)$$
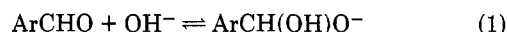
were determined by the overlap procedure in solutions containing fixed concentrations of the organic component and the effect of solvent composition on the Hammett reaction constant ρ was followed.

Experimental Section

Most of the benzaldehydes employed were obtained from Aldrich Chemical Co., Milwaukee, Wis. Purity was checked chromatographically and by measurement of boiling or melting points. The few benzaldehydes the purity of which proved to be unsatisfactory were recrystallized from ether or ethanol solutions.

Two sets of 0.01 M stock solutions of the benzaldehydes were prepared, one in absolute ethanol and one in Me$_2$SO, to be used for the experiments in water–ethanol and water–Me$_2$SO mixtures, respectively. Both Me$_2$SO (Baker Chemical Co.) and ethanol were used without purification.

Sodium hydroxide stock solutions were prepared of three different concentrations, viz., 0.1, 1.0, and 10 M. The 0.1 and 1.0 M solutions were obtained by diluting Baker reagent grade Dilut-it standardized solutions. The 10 M solution was prepared by dilution of 50% "Baker Analyzed" sodium hydroxide (18.86 M). Carbonate-free water was used for all dilutions and the solutions were protected from contact with air.

Uv spectra were recorded with a Unicam-SP-800-A (Pye Unicam, Cambridge, England) recording spectrophotometer, using matched quartz cells (10 mm optical path).

All solutions used for the measurement of spectra were prepared by mixing adequate volumes of the hydroxide and benzaldehyde stock solutions together with an appropriate amount of water and ethanol or Me$_2$SO. All these solutions were made up to a total volume of 10 ml.

In the majority of cases, the absorbance at 250–280 nm was measured in solutions containing 1×10^{-4} M of the benzaldehyde studied. In solutions containing higher concentrations of Me$_2$SO, these benzenoid absorption bands were overlapped by a cutoff due to solvent absorption. In those cases, the absorbance corresponding to n–π^* transition of the carbonyl group at 290–310 nm was measured. Because of the lower extinction coefficient of this absorption band, measurements were then carried out in 5×10^{-4} M benzaldehyde solutions.

Table I. pK_2 Values for Substituted Benzaldehydes in Water–Ethanol Mixtures

Registry no.	Benzaldehyde	$\sigma_x{}^a$	1% EtOH pK_2	10% EtOH pK_2	Δ^b	50% EtOH pK_2	Δ^b	90% EtOH pK_2	Δ^b
555-16-8	p-NO$_2{}^c$	+0.78	−1.05	−1.26	0.21	−1.28	0.23	−1.84	0.79
10203-08-4	3,5-diCl^c	+0.74	−0.91	−0.97	0.06				
99-61-6	m-NO$_2{}^c$	+0.71	−0.81	−1.11	0.30	−1.06	0.25	−1.11	0.30
24964-64-5	m-CN^c	+0.68	−0.64	−0.79	0.15	−0.85	0.21	−0.95	0.31
105-07-7	p-CN^c	+0.66	−0.84	−1.01	0.17			−1.25	0.41
6287-38-3	3,4-diCl	+0.60	−0.19						
455-19-6	p-CF$_3$	+0.55	−0.32	−0.46	0.14	−0.68	0.36	−0.88	0.56
454-89-7	m-CF$_3$	+0.41	−0.07						
587-04-2	m-Cl	+0.37	+0.12	−0.26	0.38	−0.05	0.17	−0.46	0.58
456-48-4	m-F	+0.34	+0.22	−0.03	0.25	0.00	0.22	−0.41	0.63
104-88-1	p-Cl	+0.23	+0.54	+0.27	0.27	+0.27	0.27	−0.11	0.65
58325-13-6	p-COO$^-$	+0.13	+0.38						
591-31-1	m-OCH$_3$	+0.11	+0.76	+0.55	0.21				
459-57-4	p-F	+0.06	+0.09					+0.43	0.56
100-52-7	H	0.00	+1.05					+0.48	0.57
620-23-5	m-CH$_3$	−0.07	+1.18						
104-87-0	p-CH$_3$	−0.17	+1.48						
123-11-5	p-OCH$_3$	−0.27	+2.04						
38144-52-4	m-O$^-$	−0.71	+2.12						

^{a} Hammett substituent constants.[18] ^{b} $\Delta = pK_2$ (H$_2$O) $- pK_2$ (solvent mixture). ^{c} pK_2 values of these compounds were obtained by extrapolation of a [log ($C_{\text{ArCH(OH)O}}$-$/C_{\text{ArCHO}}$) $-$ log C_{NaOH}] vs C_{NaOH} plot to $C_{\text{NaOH}} = 0$.

Table II. pK_2 Values for Substituted Benzaldehydes in Water–Me$_2$SO Mixtures

Benzaldehyde	10% Me$_2$SO pK_2	Δ^a	50% Me$_2$SO pK_2	Δ^a	80% Me$_2$SO pK_2	Δ^a	90% Me$_2$SO pK_2	Δ^a
p-NO$_2{}^b$	−1.14	0.0.9	−1.29	0.24	−2.03	0.98	−2.35	1.30
m-NO$_2{}^b$	−0.94	0.13						
m-CN^b	−0.90	0.26						
p-CN^b	−0.92	0.08	−1.10	0.26	−1.67	0.83	−2.18	1.34
p-CF$_3$	−0.43	0.11	−0.67	0.35	−1.27^c	0.95	−1.64^c	1.32
m-Cl	0.00	0.12	−0.21	0.33	−1.21^c	(1.33)		
m-F			−0.09	0.32				
p-Cl	+0.49	0.06	+0.28	0.26				
m-OCH$_3$	+0.64	0.12						
H	+0.86	0.19						
m-CH$_3$	+1.20	(−0.02)						

^{a} $\Delta = pK_2$ (H$_2$O) $- pK_2$ (mixed solvent). ^{b} For these compounds, pK_2 was found by extrapolation of the [log ($C_{\text{ArCH(OH)O}}$-$/C_{\text{ArCHO}}$) $-$ log C_{NaOH}] plot. ^{c} Determined in 5 × 10^{-4} M benzaldehyde solutions.

The ionization ratios $C_{\text{ArCH(OH)O}}$-$/C_{\text{ArCHO}}$ needed were calculated from experimentally accessible absorbancies, using expression 2

$$C_{\text{ArCH(OH)O}}\text{-}/C_{\text{ArCHO}} = (A_0 - A)/(A - A_R) \qquad (2)$$

where A_0 is the absorbance of the benzaldehyde solution at such a hydroxyl ion concentration or in a buffer of such a pH that no addition of OH$^-$ to benzaldehyde occurs and A_R is the residual absorbance in a solution where all of the benzaldehyde is present as the anion Ar-CH(OH)O$^-$. A is the absorbance at the given OH$^-$ concentration. Unless otherwise stated, the values of A, A_0, and A_R were measured at the wavelength of maximum benzenoid absorption (250–280 nm). The value of A_R was usually obtained by an extrapolation procedure.

Values of $C_{\text{ArCH(OH)O}}$-$/C_{\text{ArCHO}}$ for each benzaldehyde derivative were measured at 10–15 different sodium hydroxide concentrations in solutions containing fixed ethanol or Me$_2$SO concentrations ranging from 1 to 90 vol %. Since spectra obtained in the presence of 1% ethanol were indistinguishable from spectra recorded in purely aqueous solutions, it was possible to use absorbancies obtained in 1% ethanolic solutions for the calculation of pK_2 (H$_2$O) values. Ionization ratios were also determined in benzaldehyde solutions containing a constant concentration of sodium hydroxide (0.01 M) and an ethanol or Me$_2$SO content which was varied between 1 and 98 vol %.

The addition of ethanol appears to have an appreciable influence on the absorptivity of substituted benzaldehydes. Generally the molar absorptivity decreases by about 40% when increasing the ethanol content of the solution from 1 to 90 vol %. Moreover, there is a slight shift of both the benzenoid and the carbonyl band to shorter wavelengths. These changes must be taken into consideration when ab-

sorbancies in solutions containing varying concentrations of ethanol are compared. No such effects were observed in the study of solutions containing varying amounts of Me$_2$SO.

Unless otherwise stated spectra were time independent over the 3–5 min needed for recording the spectra.

Results

pK_2 Values. Attention has been paid first to the values of equilibrium constant K_2 of substituted benzaldehydes in individual mixed solvents with reference to a standard state in those particular solvents. For this purpose, ratios of $C_{\text{ArCH(OH)O}}$-$/C_{\text{ArCHO}}$ were determined in each solvent mixture as a function of hydroxide concentration. For benzaldehydes with electronegative substituents, the value of the equilibrium constant K_2 defined as

$$K_2 = (C_{\text{ArCH(OH)O}}\text{-}/C_{\text{ArCHO}}C_{\text{OH}}\text{-})$$
$$\times (f_{\text{ArCH(OH)O}}\text{-}/f_{\text{ArCHO}}f_{\text{OH}}\text{-}) \qquad (3)$$

can be obtained by extrapolation of the plot of [log ($C_{\text{ArCH(OH)O}}$-$/C_{\text{ArCHO}}$) $-$ log C_{NaOH}] against concentration of sodium hydroxide to $C_{\text{NaOH}} = 0$ (i.e., $\mu = 0$).

For benzaldehydes with higher pK_2 values, the overlap procedure[8] can be used. Values obtained by both procedures in the individual solvent mixtures are summarized in Tables I and II.

Table III. J_- of Solutions of NaOH in H$_2$O–EtOH

$J_- \equiv 14 + \mathrm{p}K_2$ (as determined in water) $+ \log C_{\mathrm{ROH}^-}/C_{\mathrm{R}}$

C_{NaOH}	J_- (1% EtOH)	J_- (10% EtOH)	J_- (50% EtOH)	J_- (90% EtOH)
0.01	11.91			
0.05	12.74			
0.1	13.07	13.20	13.57	13.41
0.2	13.45	13.66	13.73	13.92
0.3	13.68	13.80	13.86	14.14
0.4	13.89	13.94	14.00	14.27
0.5	13.97	14.04	14.14	14.41
0.6	14.04	14.12	14.22	14.53
0.7	14.10	14.20	14.28	14.60
0.8	14.18	14.22	14.34	14.67
0.9	14.24	14.30	14.40	14.73
1.0	14.28	14.34	14.48	14.77
1.32				14.95
1.5	14.52	14.56	14.70	
1.89				15.15
2.0	14.69	14.72	14.80	
2.5	14.85	14.92	14.96	
3.0	14.95	15.06	15.16	
3.5	15.08	15.22		
4.0	15.20	15.38		
4.5	15.32	15.50		
5.0	15.47	15.62		
6.0	15.69			
7.0	15.69			
8.0	16.16			
9.0	16.34			
10.0	16.54			
11.0	17.20			
12.0	17.45			

In every solvent system studied, $\mathrm{p}K_2$ values above a certain limit (dependent on the solvent system) could not be measured owing to either limited solubility of sodium hydroxide or changes of the spectra with time indicating competitive processes at high organic solvent concentrations.

Variations in the differences, Δ, between $\mathrm{p}K_2$ (H$_2$O) and $\mathrm{p}K_2$ (mixed solvent) for each individual solvent composition are relatively small (Tables I and II), indicating that reaction 1 for different substituted benzaldehydes is almost equally influenced by the change in solvent composition. This fact, together with the existing evidence[3] that for aqueous hydroxide solutions substituted benzaldehydes form a suitable set of J_- indicators, proves that it is indeed justified to use substituted benzaldehydes also for the establishment of J_- scales in water–ethanol and water–Me$_2$SO mixtures.

J_- for Hydroxide Solutions in Aqueous Ethanol. From the $\mathrm{p}K_2$ (H$_2$O) values and values of $\log C_{\mathrm{ArCH(OH)O}^-}/C_{\mathrm{ArCHO}}$ at a given C_{OH^-} in a given solvent mixture, it is possible to calculate J_- values for the solvent mixture under consideration using the definition

$$J_- \equiv \mathrm{p}K_\mathrm{w} + \mathrm{p}K_2 \,(\mathrm{H_2O}) + \log \frac{C_{\mathrm{ArCH(OH)O}^-}}{C_{\mathrm{ArCHO}}} \qquad (4)$$

where $\mathrm{p}K_\mathrm{w}$ is the autoprotolytic constant of water. This definition expresses J_- values with reference to a standard state in pure water and therefore basicities of sodium hydroxide solutions in mixed solvents can be compared to basicities of sodium hydroxide solutions in water by J_- values.

Calculated values (Table III) of J_- in ethanol–water mixtures show a dependence on sodium hydroxide concentration (Figure 1) resembling that in water.

To investigate the influence of ethanol concentrations higher than 90 vol % on the values of the J_- function, two series of measurements were carried out in which the sodium hydroxide concentration was kept constant at 0.01 and 0.1 M,
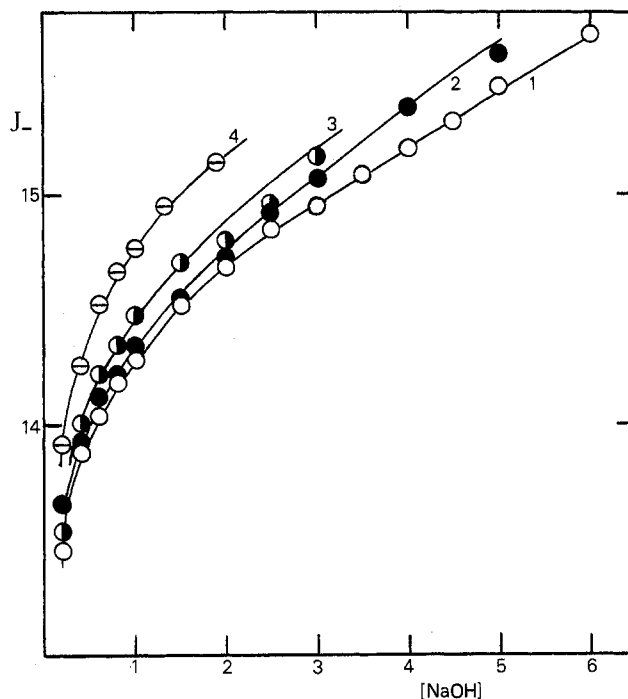

Figure 1. Dependence of the J_- acidity function on sodium hydroxide concentration in water–ethanol mixtures of different composition: curve 1 (O), 1 vol % EtOH; curve 2 (●), 10 vol % EtOH; curve 3 (◑), 50 vol % EtOH; curve 4 (⊖), 90 vol % EtOH.
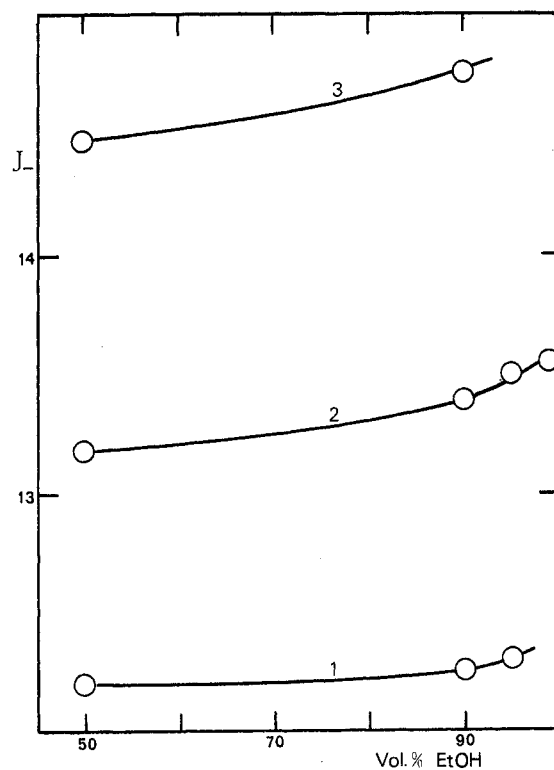

Figure 2. Influence of ethanol on the J_- value of 0.01 M (curve 1) and 0.1 M (curve 2) sodium hydroxide. The two points of curve 3 are taken from Figure 1 for 1 M sodium hydroxide.

respectively, and the concentration of ethanol changed, using p-nitrobenzaldehyde (for the 0.01 M NaOH solutions) and m-trifluoromethyl- and m-chlorobenzaldehyde (for the 0.1 M NaOH solutions) as indicators. After correction for medium effects caused by ethanol, the slight decrease in benzenoid absorption observed resulted in a small increase in J_- with increasing ethanol concentration (Figure 2), paralleling the
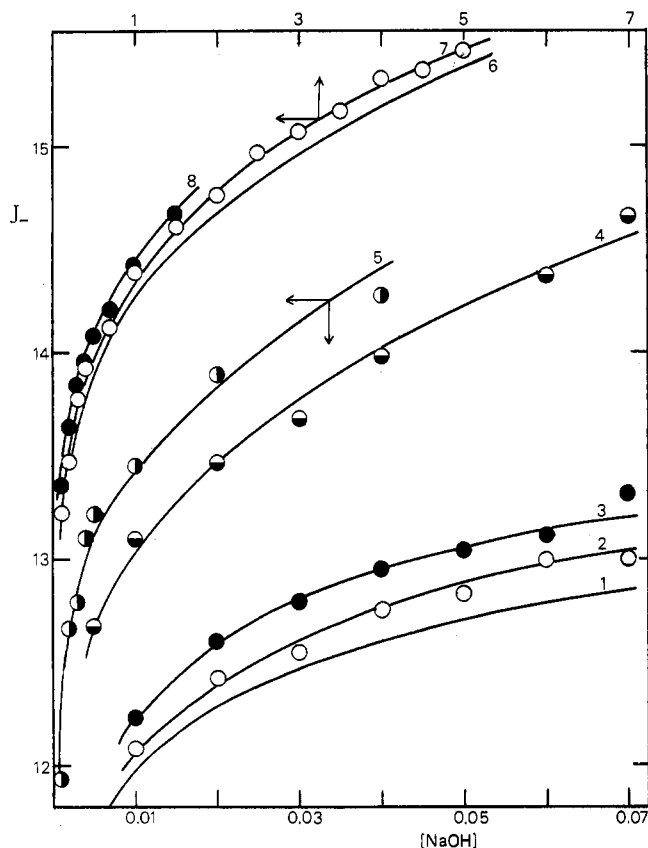
Figure 3. Dependence of the J_- acidity function on sodium hydroxide concentration in water–Me₂SO mixtures of different composition. Curves 1 and 6: aqueous solutions. Curves 2 and 7 (O): 10 vol % Me₂SO. Curves 3 and 8 (●): 50 vol % Me₂SO. Curve 4 (◒): 80 vol % Me₂SO. Curve 5 (◐): 90 vol % Me₂SO. The [NaOH] scale on top of the figure refers to curves 6, 7, and 8, the one on the bottom to curves 1, 2, 3, 4, and 5.

Table IV. J_- **of Solutions of NaOH in Water–Me₂SO Mixtures**

C_{NaOH}	J_- (10% Me₂SO)	J_- (50% Me₂SO)	C_{NaOH}	J_- (80% Me₂SO)	J_- (90% Me₂SO)
0.01	12.08	12.23	0.001		11.93
0.02	12.43	12.60	0.002		12.66
0.03	12.54	12.79	0.003		12.79
0.04	12.75	12.94	0.004		13.10
0.05	12.82	13.04	0.005	12.67	13.22
0.06	12.89	13.11	0.006		13.20
0.07	12.98	13.31	0.007		13.24
0.1	13.22	13.35	0.008		13.24
0.2	13.47	13.63	0.01	13.09	13.45
0.3	13.78	13.84	0.02	13.46	13.89
0.4	13.92	13.95	0.03	13.68	
0.5	13.99	14.07	0.04	13.98	14.27
0.6	14.01	14.19	0.06	14.37	
0.7	14.12	14.21	0.07	14.65	
0.8	14.17	14.25			
0.9	14.24	14.35			
1.0	14.38	14.40			
1.5	14.61	14.67			
2.5	14.76				
2.0	14.97				
3.0	15.07				
3.5	15.17				
4.0	15.33				
4.5	15.37				
5.0	15.46				

Table V. J_- **in Water–Me₂SO Mixtures Containing 0.01 M NaOH**

% Me₂SO (v/v)	J_-	n^a	Average deviation	Indicators used
50	12.26	2	0.04	p-NO₂, p-CN
80	12.97	2	0.09	p-NO₂, p-CN
90	13.48	6	0.13	p-NO₂, p-CN, p-CF₃,[b] m-Cl,[b] m-F,[b] p-Cl
91	13.58	3	0.11	m-Cl,[b] m-F,[b] p-Cl
92	13.77	4	0.16	P-CF₃,[b] m-Cl,[b] m-F,[b] p-Cl
93	13.84	3	0.12	m-Cl,[b] m-F,[b] p-Cl
94	13.98	4	0.09	m-Cl,[b] m-F,[b] p-Cl, m-OCH₃[b]
95	14.08	4	0.14	p-CN, m-Cl,[b] m-F,[b] p-Cl
96	14.28	4	0.11	m-Cl,[b] m-F,[b] p-Cl, m-OCH₃[b]
97	14.62	4	0.18	m-Cl,[b] m-F,[b] p-Cl, m-OCH₃[b]
98	15.07	3	0.06	m-F,[b] p-Cl, m-OCH₃[b]

[a] Number of measurements. [b] Measurements with these compounds were carried out in 5×10^{-4} M benzaldehyde solution.

trend calculated for 1 M sodium hydroxide solutions from Figure 1.

J_- for Hydroxide Solutions in Aqueous Me₂SO. J_- values for solutions containing fixed amounts of Me₂SO and varying sodium hydroxide concentrations were determined (Table IV) using eq 4 and show a similar trend for all Me₂SO concentrations investigated (Figure 3).

The effect of Me₂SO contents above 90 vol % was studied in mixtures where the sodium hydroxide concentration was kept constant at 0.01 M and the Me₂SO content varied. p-Nitro-, p-cyano-, p-trifluoromethyl-, m-chloro-, m-fluoro-, p-chlorobenzaldehydes and m-anisaldehyde were used as indicators. At Me₂SO concentrations higher than 90 vol %, some of the spectra (particularly those of m-Cl, m-F, p-Cl, and m-OCH₃ benzaldehyde) became time dependent and extrapolation of absorbance measurements to zero time became necessary. Hence, the calculated J_- values displayed a larger average deviation (Table V) at these higher Me₂SO concentrations. Below 80 vol % Me₂SO the average deviation was hardly ever higher than 0.05. The dependence of J_- on Me₂SO concentration was compared with that of H_- (Figure 4).

Discussion

Structural Effects and Solvent. The effect of solvent on the equilibrium of reaction 1 can be first discussed in terms of effects on the susceptibility to substituent effects. The values of pK_2, characterizing this equilibrium, are a satisfactorily linear function of the Hammett constants σ_x as shown by the values of the correlation coefficient r (Table VI). The values of reaction constant ρ are practically independent of

the ethanol concentration (Table VI), as was already indicated by the almost constant value of the differences Δ between pK_2 (H₂O) and pK_2 (mixed solvent) for a given composition of the mixed solvent (Table I). The same situation is indicated for Me₂SO mixtures (Table II) by the small variations in Δ for any given solvent composition. The number of accessible pK_2 values was in this case too small to allow a meaningful determination of reaction constants ρ. The structural dependence for various water–ethanol mixtures is thus represented by a set of parallel lines. The shifts between these lines are given by the difference between the pK_2^H values (pK of reaction 1 for the unsubstituted benzaldehyde) in the different solvent mixtures.

Provided that the influence of the water–ethanol composition on the reaction involving addition of hydroxyl ions to benzaldehydes can be characterized by any parameter Y_i (the
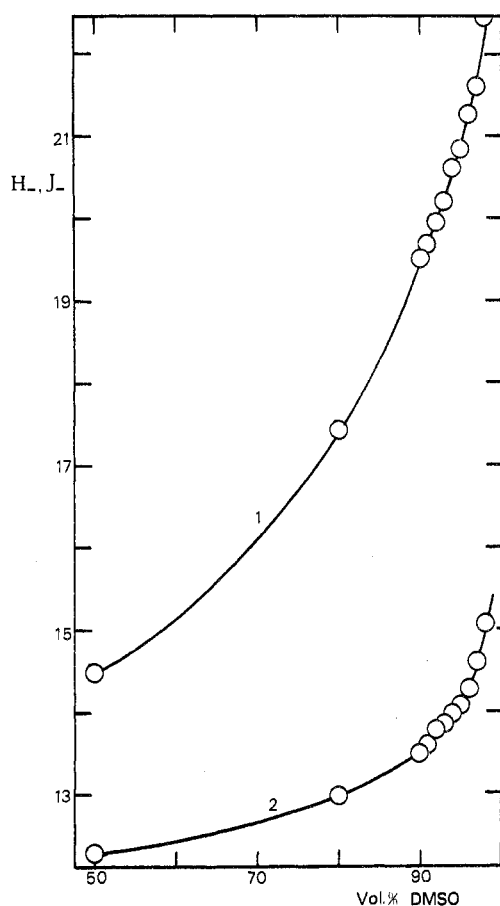
Figure 4. Acidity functions H_- (curve 1) and J_- (curve 2) for water–Me_2SO mixtures containing 0.01 M base (tetramethylammonium hydroxide in case of H_- and sodium hydroxide in case of J_-).

Table VI. Influence of Ethanol Percentage on the Free Energy Relationship $pK_2 = -\rho\sigma_x + pK_2^H$

% EtOH (v/v)	ρ^a	Std dev in ρ	pK_2^{Hb}	Std dev in pK_2^H	n^c	r^d
1	2.65	0.09	1.08	0.05	18	−0.987
10	2.58	0.17	0.82	0.10	10	−0.984
50	2.84	0.18	0.97	0.11	7	−0.991
90	2.58	0.20	0.52	0.11	10	−0.973

^{a} Reaction constant. ^{b} pK_2 for the unsubstituted benzaldehyde. ^{c} Number of measurements. ^{d} Linear correlation coefficient.

application of Y_- used for benzoic acid dissociations in ethanol–water mixtures[9] might be doubtful), application of the relation $\rho_{Y_i} - \rho_{Y_0} = C(Y_i - Y_0)$ would indicate that the value of C (0.638 for benzoic acids[9] and −0.573 for anilines[10]) is close to zero for the benzaldehyde reaction (1).

The Validity of the J_- Function. For aqueous sodium hydroxide solutions the validity of the J_- function, describing the basicity of a solution by its ability to add hydroxyl ions to a carbonyl group to form an anion of the geminal diol, has been proved earlier.[3] For all substituted benzaldehydes studied both in water–ethanol and water–dimethyl sulfoxide (Me_2SO), the value of log ($C_{ArCH(OH)O}$-/C_{ArCHO}) determined from absorbance measurements was found to be a linear function of the J_- function with a slope varying between 0.95 and 1.05 in the region of J_- values where measurements were possible. The Cannizzaro reaction or other consecutive processes did not affect the measurements at 25 °C except in solutions containing the highest concentrations of Me_2SO. Careful measurements with derivatives bearing electronegative substituents did not indicate any evidence for formation of dianions of the geminal diol [$ArCH(O^-)_2$]. Hence it can be concluded that benzaldehydes are simpler indicators than cyanostilbenes,[4] where competition of carbanion formation, even if evidently not predominant, cannot be completely excluded. The behavior of the benzaldehydes is also simpler than that of nitroaromatic compounds where measurements of equilibria leading to the formation of Meisenheimer complexes were complicated by consecutive reactions,[11] by uptake of a second hydroxyl ion,[12a] or by complicated changes in the absorption spectra.[12]

Comparison of Aqueous and Water–Ethanol Solutions. The effect of the presence of ethanol in aqueous solutions of

sodium hydroxide is generally speaking, small. This is shown by the similar shape of the dependence of J_- on sodium hydroxide concentration (Figure 1) and by the small differences in J_- values obtained at the different constant ethanol concentrations up to 90 vol % (Table III). Even when the concentration of sodium hydroxide was kept constant (e.g., 0.1 M), the difference between J_- values in 90 vol % ethanol and 98 vol % ethanol was only 0.16 J_- units (Figure 2). In this range of ethanol concentrations, it is necessary to consider the competitive influence of ethoxide ions, the addition of which would result in a decrease of the C_6H_5CO absorbance indistinguishable from the decrease due to hydroxyl ion addition. In 90 vol % ethanol, the ratio of hydroxide and ethoxide concentrations is about 1:1, while in 98 vol % ethanol, it is possible to extrapolate[13] that about 90% of the base will be present as the ethoxide ion.

The relatively modest increase in the value of the J_- function when increasing the ethanol content of a sodium hydroxide solution from 90 to 98 vol % indicates that either the nucleophilic reactivity of the ethoxide ion under these conditions does not differ substantially from that of the hydroxide ion while solvation of the hydroxide ion and the geminal diol anion is similar to solvation of the ethoxide ion and the hemiacetal anion, or that compensation of effects takes place.

The procedure by which Yagil and Anbar calculated theoretical H_- values[14b] can be applied to the J_- function as well and leads to

$$J_- = 14 + \log C_{OH^-} - n \log C_{H_2O} \qquad (5)$$

where C_{H_2O} is the free water concentration and n can be considered[14a] either as the hydration number of the hydroxide ion or as the difference in hydration numbers between ($ArCHO + OH^-$) and $ArCH(OH)O^-$. Calculations of J_- with $n = 3$ and $n = 4$ were made for aqueous sodium hydroxide solutions, using for C_{H_2O} the expression $C_{H_2O} = d - 0.001$ ($18n + 40$)C_{OH^-} in which d is the density of the solution (Table VII). Comparison of the calculated values with the experimental J_- values for aqueous sodium hydroxide solutions seems to indicate a change in n with the concentration of sodium hydroxide. In solutions which are 2 M in sodium hydroxide or less, the best agreement between calculated and experimental J_- values if obtained for n larger than 4, between 3 and 5 M for $n = 4$, and between 6 and 8 M for $3 > n > 4$. Although the results for aqueous sodium hydroxide solutions with concentrations between 9 and 11 M also suggest a value of n between 3 and 4, it is more likely that in this concentration range a further dehydration takes place causing an increase in the activity of the OH^- ion. Under those circumstances, it is no longer appropriate to calculate J_- values by formula 5, which only takes into account the mass action effect of the decrease in free water concentration.

An attempt to apply eq 5 to the calculation of J_- values in ethanol–water mixtures containing base, using the expression

Table VII. Theoretical and Experimental Values of J_- for Aqueous NaOH Solutions

C_{NaOH}	J_- (exp)	J_- (theor)$_{n=3}$[a]	J_- (theor)$_{n=4}$[a]
1	14.28	14.08	14.12
2	14.69	14.46	14.58
3	14.95	14.73	14.90
4	15.20	14.95	15.20
5	15.47	15.16	15.51
6	15.69	15.35	15.82
7	15.96	15.56	16.17
8	16.16	15.78	16.58
9	16.34	16.01	17.09
10	16.64	16.27	17.71
11	17.20	16.50	18.61
12	17.45		

[a] J_- (theor) $= 14 + \log C_{OH^-} - n \log C_{H_2O}$ where $C_{H_2O} = d - 0.001 (18n + 40) C_{OH^-}$ (d is density of the solution).

$C_{H_2O} = d - 0.001 C_{OH} - (18n + 40) - 0.0079x$ (x is the volume percentage of ethanol present), failed especially for the higher ethanol percentages where it led to J_- values considerably higher than actually found. This again indicates that the decrease in free water concentration which takes place on adding increasing amounts of ethanol is largely compensated for by the fact that the ethanol in many respects displays a behavior similar to the water it replaces.

Comparison of Aqueous and Water-Me₂SO Solutions. The increase in J_- with increasing Me₂SO concentration cannot be ascribed to a change in one single physical or chemical property. It is necessary to consider the change in dielectric constant, the effect of hydrogen bonding between Me₂SO and water (particularly at high Me₂SO concentrations), the change in water activity, dispersion interactions, and the effect of Me₂SO on the structure of water and on the hydration of the hydroxide ion. These aspects of the increase in the basicity of solutions containing a constant amount of base with increasing Me₂SO content have been adequately discussed by Dolman and Stewart.[7]

The question which needs some further discussion is why the effect of Me₂SO concentration on the J_- acidity function describing hydroxide ion addition to benzaldehydes is considerably smaller (Figure 4) than the effect on the H_- function obtained from measurements involving proton abstraction from anilines and diphenylamines.

Some idea about the origin of this difference might be obtained by comparing the expression for H_-[14a]

$$H_- = 14 + \log C_{OH^-} - (n + 1) \log a_{H_2O} + \log \frac{f_{HA} f_{OH^-}}{f_{A^-}} \quad (6)$$

with a similar expression which can be derived for the J_- function:

$$J_- = 14 + \log c_{OH^-} - n \log a_{H_2O} + \log \frac{f_{ArCHO} f_{OH^-}}{f_{ArCH(OH)O^-}} \quad (7)$$

From 6 and 7, the difference between H_- and J_- is found to be

$$H_- - J_- = -\log a_{H_2O} + \log \frac{f_{HA}}{f_{A^-}} - \log \frac{f_{ArCHO}}{f_{ArCH(OH)O^-}}$$

Using available information on activity of water in water–Me₂SO mixture,[15] the value $H_- - J_- + \log a_{H_2O}$ is larger than zero, which indicates that the ratio f_{HA}/f_{A^-}, for the H_- indicator acids, is considerably larger than the ratio of $f_{ArCHO}/f_{ArCH(OH)O^-}$ for the benzaldehydes used as J_- indicators. Probably this difference in activity coefficient ratios is due to a larger extent of charge delocalization in the A^- anion compared to the geminal diol anion, which causes an extra stabilization of A^- (manifested by a decrease in f_{A^-}) by dispersion interaction with Me₂SO.

The acidity function J_- (denoted as J_M) for addition of methoxide ions to benzaldehydes[16] increases also much less steeply with base concentration than acidity function obtained for additions of methoxide ion to polynitrobenzenes[17] or α-cyanostilbenes.[4]

The foregoing considerations confirmed that the acidity function approach to the properties of strongly acidic or strongly alkaline media leads to acidity scales which not only depend on the investigated solvent system but also on the nature of the indicators used.

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