

The Dissociation Constant of 3-Nitrobenzoic Acid in H₂O and D₂O and in their DMSO Mixtures

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The dissociation constant of 3-nitrobenzoic acid was determined in H₂O-DMSO and D₂O-DMSO mixtures up to the DMSO mol fraction of 0.18 by potentiostatic titration. The Debye-Hückel treatment was used to correct the observed dissociation constants to zero ionic strength. Also a direct treatment characteristic of potentiostatic titration was applied in the extrapolation of thermodynamic constants and a good fit with the values obtained by the Debye-Hückel treatment was obtained.

The plot of *pK* versus the mol fraction of DMSO was observed to be linear both in H₂O and D₂O. By the aid of these linear relationships the *pK* values in pure H₂O and D₂O could be extrapolated.

The method of potentiostatic titration in determining dissociation constants is useful, especially when the measurements are carried out in different solvents as all empirical corrections due to the transfer of electrodes from one medium to another can be avoided. By this method it is possible to determine concentration dissociation constants by which thermodynamic constant of sufficient accuracy can be obtained.¹

The solubility of 3-nitrobenzoic acid in water is relatively low so that the acid solution needed for the titrations had to be prepared in a properly chosen organic solvent. Since the *pK* values in light and heavy water were determined the solvent had to be such that it did not contain any exchangeable hydrogen. Dimethyl sulfoxide proved to be an excellent solvent in both respects. The *pK* value of 3-nitrobenzoic acid (approx. 3.5) is appropriate when the best possible applicability of the titration method is concerned.

One aim has been to determine the difference $pK_{D_2O} - pK_{H_2O}$ ($= \Delta pK$) for 3-nitrobenzoic acid as accurately as possible. The dependence of the *pK* value on the mol fraction of DMSO is also expected to be of interest although the measurements cover only the mol fractions of DMSO up to 0.18. An important aspect is the search for such mixtures H₂O-DMSO and D₂O-DMSO, where the *pK* values compared with those in H₂O and D₂O, respectively, have changed with the value of ΔpK .

EXPERIMENTAL

Reagents. The light water employed was distilled water. The heavy water was purchased from Norsk Hydro. Its deuterium mol fraction was 0.998. Both light and heavy water were degassed under reduced pressure. The 3-nitrobenzoic acid was a purissimum product of Koch-Light Laboratories Ltd. It was recrystallized from water and dried at 373 K for 6 h. The observed melting point was 415.7–416.2 K (lit. value² 415.25). The acid used in the titrations was in a DMSO solution having a concentration of 0.500 mol/dm³. The potassium hydroxide solution was prepared in light water from Merck's ampoule. Its concentration was 0.1997 mol/dm³. The potassium hydroxide solution in D₂O was prepared by dissolving potassium hydroxide pellets (Merck *p.a.*) in D₂O. The pellets were rinsed with D₂O before dissolving. The concentration of the prepared KOD was 0.2149 mol/dm³ and its deuterium mol fraction 0.994. The other chemicals were of analytical grade and used as received.

Titration procedure. The zero instrument was a Metrohm Compensator E 388 equipped with a combined glass silver-silver chloride electrode. The titration procedure B described by Kankare was employed.³ The volumes of acid and base were added to the solution using an Agla micrometer syringe. The titrations were car-

ried out in a thermostated jacketed vessel under nitrogen atmosphere. A Lauda thermostat was used to control the temperature within ± 0.05 K. The titration mixtures were prepared by weighing proper amounts of water and DMSO. The initial volume, V_0 , of the titration mixture was 20×10^{-3} dm³ in all experiments. The added volumes of the acid were of constant magnitudes in all experiments ($a_1 = 1.00 \times 10^{-5}$ mol and $a_1 = 1.00 \times 10^{-4}$ mol).

Evaluation of dissociation constants. The concentration dissociation constants of 3-nitrobenzoic acid were calculated from eqn. (1) where Z is the degree of deprotonation

$$K' = Z[H^+]/(1 - Z) \quad (1)$$

and $[H^+]$ the hydrogen-ion concentration. Both of these can be evaluated from the slope and intercept of the titration curve in the usual manner. The ionic strength at the end of the titration was calculated to be aZ/V , where a is the total amount of the added acid and V is the total volume of the titration mixture. In addition to this the ionic strength was increased by known amounts of potassium chloride so that the constants were usually determined at five different ionic strengths in each water-DMSO mixture.

The thermodynamic dissociation constants were evaluated by the aid of the Debye-Hückel

$$pK = pK' - 2 \log y_{\pm} = pK' + \frac{2Az^2 I^{1/2}}{1 + Ba I^{1/2}} \quad (2)$$

extrapolation (2). In the above equation y_{\pm} denotes the mean molar activity coefficient, I the ionic strength, and z the ionic charge. The ionic size parameter Ba was chosen as 2.5.⁴ The parameter A was calculated separately for each titration mixture of a certain mol fraction of DMSO. The value of A at 298.15 K is known to be $354.42/D^{3/2}$, where D is the macroscopic dielectric constant of the solvent.⁵ This constant was evaluated by the aid of the values measured in several H₂O-DMSO mixtures by Lindberg and Kenttämää.⁶

The obtained equations of least squares were then modified for H₂O and D₂O with the values determined by Vidulich *et al.*⁷ to give formulas (3) and (4).

$$D_{H_2O} = 78.39 - 8.711 x_{DMSO} - 47.46 x_{DMSO}^2 \quad (3)$$

$$D_{D_2O} = 78.06 - 8.711 x_{DMSO} - 47.46 x_{DMSO}^2 \quad (4)$$

In these equations x_{DMSO} denotes the mol fraction of DMSO in the solvent. The assumption made here that the dielectric constant of D₂O-DMSO mixtures varies in a similar way as that in H₂O-DMSO mixtures is justified, because the measurements were carried out at a moderately low DMSO content.

For the sake of comparison the thermodynamic constants were also determined in the following direct way. The measured Z values and $[H^+]$ values (as pH) were plotted against the square root of the ionic strength by the aid of the method of least squares. The thermodynamic constant, K , can then be calculated from eqn. (1) with the aid of the values of Z and $[H^+]$ at zero ionic strength.

RESULTS AND DISCUSSION

The necessary data and the determined constants in H₂O have been tabulated in Table 1 as an example. From these values the thermodynamic constant can be obtained by extrapolation. This is shown in Table 2.

If pK is evaluated from the values in Table 1 by the direct method, the values of (0.5427 ± 0.0035) and $(2.721 \pm 0.003) \times 10^{-4}$ are obtained for Z and $[H^+]$ at zero ionic strength. From these values, eqn. (1) gives the value of 3.491 for pK .

The plots of pK_{H_2O} and pK_{D_2O} versus x_{DMSO} are given in Fig. 1. Linear regression analysis can be applied to determine pK_{H_2O} and pK_{D_2O} values

Table 1. The values of the concentration dissociation constants of 3-nitrobenzoic acid in H₂O ($x_{DMSO} = 0.00279$ at the end of the titration).

c_{KCl} /mol dm ⁻³	b_1^a /10 ⁻⁶ mol	$[H^+]^a$ /10 ⁻⁴ mol dm ⁻³	Z^a	I	pK'^a
0.0500	6.181	3.095	0.6197	0.05337	3.297 ± 0.006
0.0250	5.918	2.963	0.5933	0.02823	3.364 ± 0.006
0.0100	5.809	2.909	0.5823	0.01317	3.392 ± 0.010
0.0075	5.785	2.902	0.5799	0.01066	3.397 ± 0.005
0.0050	5.685	2.847	0.5699	0.00810	3.423 ± 0.004
0.0025	5.649	2.828	0.5662	0.00558	3.433 ± 0.003

^a Mean values from at least three determinations.

Table 2. The thermodynamic dissociation constant of 3-nitrobenzoic acid in H₂O ($x_{\text{DMSO}} = 0.00279$; $A = 0.5109$).

$I^{1/2}$	$-2 \log \gamma_{\pm}$	pK'	pK
0.2310	0.1503	3.297	3.447
0.1680	0.1213	3.364	3.485
0.1148	0.0913	3.392	3.483
0.1032	0.0840	3.397	3.481
0.0900	0.0752	3.423	3.498
0.0747	0.0644	3.433	3.497

in respective pure waters. The results obtained are tabulated in Table 3, from which the ΔpK values, i.e. the values of $pK_{\text{D}_2\text{O}} - pK_{\text{H}_2\text{O}}$, can be calculated. These are within the experimental error of equal magnitude viz. (0.412 ± 0.010) and (0.401 ± 0.017) as calculated by means of the Debye-Hückel approximation and the direct method, respectively. The ΔpK value has been determined earlier by McDougall and Long.⁸ The value 0.50 obtained by them is somewhat higher than ours. However, their $pK_{\text{H}_2\text{O}}$ value is also higher (3.62) and seems to be the only one of this magnitude among the reported ones. Dippy and Lewis⁹ report 3.493, Briegleb and Bieber¹⁰ 3.450, and Peltier and Pichevin¹¹ 3.53. The agreement between these values and ours is satisfactory.

The agreement between the pK values obtained by the Debye-Hückel method and by the direct method is excellent especially in H₂O. This means that the direct method can be applied as a purely empirical method, at least in this case, when thermodynamic constants are evaluated.

As for the values in Table 3 it is observed that there exists a linear correlation between the pK values and the mol fraction of DMSO.

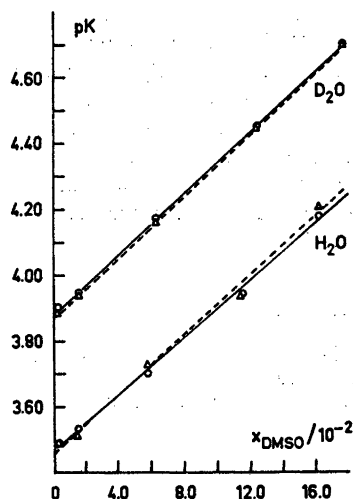


Fig. 1. The plot of pK of 3-nitrobenzoic acid versus x_{DMSO} in H₂O and D₂O. (The circles denote the points obtained by the Debye-Hückel treatment and the triangles those obtained by the direct method. Solid lines refer to the circles and dotted lines to the triangles.)

A roughly similar behavior is observed with benzoic acid, although the measurements are extended up to $x_{\text{DMSO}} = 0.8$ in this case.¹² There are insufficient data to test the variation of the pK value with the inverse of the dielectric constant as predicted by the Born equation. However, it seems that these plots are curved, but the amount of data does not give justification for any conclusions. It thus seems that this acid falls into the same category as those studied by Bell in dioxane-water mixtures.¹³

As can be seen from Fig. 1, the mol fraction of DMSO in the H₂O-DMSO mixture which corresponds to pure D₂O with respect to the dissociation of 3-nitrobenzoic acid is approx-

Table 3. The slopes and intercepts of the linear plots of pK versus x_{DMSO} (Fig. 1). (The intercepts refer to pK values in pure H₂O or D₂O.)

	Method	Slope	Intercept	Coeff. of correlation
H ₂ O	D-H	4.311 ± 0.077	3.465 ± 0.007	0.9995
D ₂ O	D-H	4.594 ± 0.071	3.877 ± 0.007	0.9996
H ₂ O	"Direct"	4.468 ± 0.182	3.462 ± 0.017	0.9975
D ₂ O	"Direct"	4.707 ± 0.001	3.863 ± 0.001	0.999993

imately 0.096. The mol fraction of DMSO in the D_2O -DMSO mixture which causes an increase of magnitude of ΔpK in pK is approximately 0.090. Low mol fractions of DMSO bring about an increase in the structural order of the system.¹⁴ The above mol fractions thus indicate the well-known fact that there is more order in the structure of D_2O than in that of H_2O .

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Received September 10, 1975.