

Note

ACID DISSOCIATION CONSTANTS OF *m*-TOLUIDINIUM AND *p*-ANISIDINIUM IONS IN FORMAMIDE AT DIFFERENT TEMPERATURES

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In a previous communication [1], we reported the acid dissociation constants of *p*-toluidinium and *p*-hydroxyanilinium ions in formamide at several temperatures as determined from e.m.f. measurements using cells of the type,



where B represents the base. We now report the acid dissociation constants of *m*-toluidinium and *p*-anisidinium ions in formamide at different temperatures following the same procedure. This is a part of our general programme to study various types of ionic equilibria in this interesting solvent which has a dielectric constant higher than that of water and also a much wider liquid range

EXPERIMENTAL

m-Toluidine (Laboratory Reagent) was purified by distillation and *p*-anisidine (Laboratory Reagent) by crystallizing it twice from hot water.

The hydrochlorides of the bases were prepared by the neutralization of the base with HCl (AnalaR grade) and their subsequent purification was carried out as follows. The solution of *p*-anisidinium hydrochloride obtained after neutralization was made free from colouring matter with active charcoal and the salt obtained by evaporating the solution on a water bath. It was purified by crystallization from methanol containing a few drops of conc. HCl. *m*-Toluidine hydrochloride obtained by crystallization from the solution obtained after neutralization of the base was purified by crystallizing it twice from cold water. The purity of *p*-anisidine and the solid hydrochlorides of the bases was checked by m.p. and that of *m*-toluidine was checked by b.p. measurements. The chemicals were stored in a desiccator until required. Formamide was purified as described earlier by Dash and Nayak [2].

Solutions for e.m.f. measurements were prepared by dissolving appropriate (weighed) amounts of the base and its hydrochloride in known weights of formamide. The design of the cell was similar to that recommended by Daniels et al. [3].

The procedure for filling the cell, thermostating of the solutions and measurement of the e.m.f. were similar to those mentioned in our previous communication [1]. All e.m.f. measurements made were reduced to 760 mm pressure.

RESULTS AND DISCUSSION

The dissociation constants were obtained by the usual method as described in our previous paper [1]. The acid dissociation constant, K_a , of the anilinium ion is related to the e.m.f., E , of the cell



through the equation

$$\frac{(E - E^0)}{2.303RT} + \log \frac{m(\text{BH}^+) m(\text{Cl}^-)}{m(\text{B})} = -\log K_a - \log \frac{\nu(\text{BH}^+) \nu(\text{Cl}^-)}{\nu(\text{B})} \quad (1)$$

where m and ν are, respectively, the molalities and the activity coefficients of the species shown in parentheses.

The left-hand side of eqn. (1), which may be represented by $-\log K'_a$, will vary with the ionic strength of the medium and will yield $-\log K_a$ of the anilinium ion when extrapolated to zero ionic strength, the ionic strength of the solution being given by m_2 . The $\text{p}K_a$ values of the anilinium ions, as obtained by this procedure, are given in Tables 1 and 2 together with other relevant data.

As noted earlier, the results are definitely in contradiction with the Born equation [4] which predicts the behaviour of the dissociation constant with

TABLE 1

Determination of $-\log K_a$ of the *m*-toluidinium ion in formamide from the study of the cell
 $\text{Pt, H}_2 | \text{B}(m_1), \text{BHCl}(m_2) | \text{AgCl} - \text{Ag}$

$10^2 m_1$ (mole kg^{-1})	$10^2 m_2 = 10^2 \mu$ (mole kg^{-1})	E (V)	$\frac{F(E - E^0)}{2.303 RT}$	$-\log \frac{m_2^2}{m_1}$	$-\log K'_a$	$-\log K_a$
<i>10°C (283.15 K)</i>						
0.613	0.933	0.6255	7.348	1.848	5.50	5.72 ± 0.12
0.317	1.275	0.5850	6.627	1.290	5.34	
0.867	1.369	0.6025	6.938	1.665	5.27	
0.636	1.420	0.5895	6.707	1.499	5.21	
0.649	1.740	0.5877	6.675	1.331	5.34	
1.029	1.825	0.5851	6.629	1.490	5.14	
<i>15°C (288.15 K)</i>						
0.971	0.752	0.6396	7.555	2.235	5.32	5.38 ± 0.09
1.094	1.417	0.5974	6.816	1.736	5.08	
1.138	2.073	0.5802	6.515	1.423	5.09	
0.540	2.221	0.5637	6.227	1.039	5.19	
0.825	2.306	0.5580	6.127	1.191	4.94	
0.509	2.328	0.5525	6.030	0.973	5.06	

TABLE 1 (continued)

$10^2 m_1$ (mole kg ⁻¹)	$10^2 m_2 = 10^2 \mu$ (mole kg ⁻¹)	E (V)	$\frac{F(E - E^0)}{2.303 RT}$	$-\log \frac{m_2^2}{m_1}^*$	$-\log K'_a$	$-\log K_a$
<i>20°C (293.15 K)</i>						
1.653	0.873	0.6421	7.551	2.336	5.22	5.37 ± 0.08
2.362	1.007	0.6454	7.608	2.367	5.24	
1.809	1.079	0.6324	7.384	2.191	5.19	
2.054	1.473	0.6246	7.250	1.976	5.27	
2.041	1.522	0.6112	7.019	1.945	5.07	
1.831	1.784	0.6010	6.844	1.761	5.08	
<i>25°C (298.15 K)</i>						
1.889	1.029	0.6315	7.324	2.251	5.07	5.19 ± 0.09
1.354	1.088	0.6234	7.187	2.059	5.13	
1.982	1.247	0.6040	6.859	2.105	4.75	
1.839	1.593	0.5980	6.757	1.860	4.90	
1.617	1.598	0.6178	7.092	1.802	5.29	
4.156	4.284	0.5515	5.971	1.355	4.62	
<i>30°C (303.15 K)</i>						
0.826	0.968	0.6333	7.311	1.945	5.37	5.69 ± 0.12
0.904	1.641	0.5794	6.414	1.526	4.89	
1.841	1.991	0.5980	6.724	1.667	5.06	
2.970	2.304	0.5898	6.587	1.748	4.84	
2.829	2.335	0.5827	6.469	1.715	4.75	
3.038	2.417	0.5825	6.466	1.716	4.75	
<i>35°C (308.15 K)</i>						
1.216	0.332	0.6879	8.160	3.043	5.12	5.22 ± 0.03
0.960	0.659	0.6472	7.195	2.345	5.15	
1.968	1.381	0.6214	7.072	2.014	5.06	
2.396	1.663	0.6073	6.842	1.938	4.90	
3.017	1.969	0.6094	6.876	1.891	4.99	
2.980	2.659	0.5805	6.403	1.625	4.78	
<i>40°C (313.15 K)</i>						
1.971	0.568	0.6769	7.926	2.786	5.14	5.23 ± 0.04
0.872	0.591	0.6596	7.648	2.397	5.25	
2.260	0.811	0.6658	7.747	2.536	5.21	
2.271	0.847	0.6589	7.636	2.501	5.14	
1.425	1.093	0.6222	7.045	2.077	4.97	
2.690	2.357	0.6012	6.707	1.685	5.02	
<i>45°C (318.15 K)</i>						
1.245	0.697	0.6647	7.681	2.409	5.27	5.22 ± 0.13
2.363	0.972	0.6512	7.467	2.398	5.07	
2.193	1.137	0.6360	7.226	2.230	5.00	
2.447	1.178	0.6386	7.267	2.246	5.02	
2.512	1.390	0.6505	7.456	2.114	5.34	
2.231	1.997	0.6082	6.785	1.748	5.04	

* In eqn. (1), the term $\log \{[m(\text{BH}^+) m(\text{Cl}^-)]/m(\text{B})\} \approx \log(m_2^2/m_1^2)$.

TABLE 2

Determination of $-\log K_a$ of the *p*-anisidinium ion in formamide from the study of the cell
 Pt, $H_2|B(m_1), BHCl(m_2)|AgCl-Ag$

$10^2 m_1$ (mole kg ⁻¹)	$10^2 m_2 = 10^2 \mu$ (mole kg ⁻¹)	E (V)	$\frac{F(E - E^0)}{2.303 RT}$	$-\log \frac{m_2^2}{m_1}$	$-\log K'_a$	$-\log K_a$
<i>10°C (283.15 K)</i>						
1.592	1.320	0.6627	8.009	1.961	6.05	6.16 ± 0.04
0.733	1.372	0.6491	7.767	1.590	6.18	
1.891	1.481	0.6628	8.011	1.935	6.08	
1.275	1.850	0.6409	7.621	1.571	6.05	
2.046	3.442	0.6249	7.336	1.237	6.10	
1.503	3.926	0.6011	6.913	0.989	5.92	
<i>15°C (288.15 K)</i>						
0.961	1.076	0.6575	7.866	1.919	5.95	5.89 ± 0.10
1.118	1.528	0.6479	7.700	1.680	6.02	
0.669	1.792	0.6441	7.633	1.318	6.32	
0.847	2.038	0.6408	7.575	1.309	6.27	
1.219	2.767	0.6308	7.399	1.202	6.20	
0.649	3.027	0.6157	7.137	0.851	6.29	
<i>20°C (293.15 K)</i>						
0.745	0.545	0.6866	8.314	2.399	5.92	6.06 ± 0.10
0.572	1.509	0.6593	7.847	1.400	6.45	
1.224	2.184	0.6578	7.821	1.409	6.41	
0.634	2.326	0.6340	7.411	1.069	6.34	
0.810	2.467	0.6348	7.425	1.124	6.30	
0.648	3.798	0.6113	7.021	0.653	6.37	
<i>25°C (298.15 K)</i>						
0.509	0.549	0.6757	8.072	2.227	5.85	5.80 ± 0.08
0.908	0.850	0.6651	7.894	2.099	5.79	
1.109	0.982	0.6639	7.874	2.061	5.81	
0.786	1.283	0.6559	7.738	1.679	6.06	
1.229	1.426	0.6515	7.663	1.781	5.88	
0.760	1.741	0.6272	7.251	1.399	5.85	
<i>30°C (303.15 K)</i>						
0.701	0.938	0.6603	7.761	1.901	5.86	6.01 ± 0.08
1.382	1.490	0.6493	7.577	1.794	5.78	
1.127	1.792	0.6372	7.375	1.545	5.83	
3.017	2.136	0.6424	7.463	1.820	5.64	
1.496	2.326	0.6269	7.204	1.452	5.76	
2.647	2.357	0.6309	7.271	1.678	5.59	
<i>35°C (308.15 K)</i>						
0.832	0.609	0.6765	7.975	2.351	5.62	5.61 ± 0.11
0.521	0.888	0.6615	7.729	1.820	5.91	
1.454	0.998	0.6659	7.800	2.165	5.64	
1.809	1.581	0.6466	7.485	1.859	5.63	
1.082	1.786	0.6393	7.365	1.530	5.83	
0.532	1.806	0.6250	7.132	1.213	5.92	

TABLE 2 (continued)

$10^2 m_1$ (mole kg ⁻¹)	$10^2 m_{12} = 10^2 \mu$ (mole kg ⁻¹)	E (V)	$\frac{F(E - E^0)}{2.303 RT}$	$-\log \frac{m_2^2}{m_1}$	$-\log K'_a$	$-\log K_a$
<i>40°C (313.15 K)</i>						
1.069	1.019	0.6755	7.903	2.013	5.89	5.94 ± 0.04
2.605	1.888	0.6662	7.752	1.864	5.89	
1.035	2.451	0.6350	7.251	1.236	6.01	
1.292	2.570	0.6335	7.228	1.292	5.94	
1.875	3.782	0.6174	6.968	1.118	5.85	
1.589	4.216	0.6103	6.853	0.951	5.90	
<i>45°C (318.15 K)</i>						
0.555	0.704	0.6780	7.894	2.049	5.85	5.89 ± 0.04
0.678	1.048	0.6629	7.652	1.790	5.86	
0.681	1.485	0.6548	7.525	1.490	6.04	
0.612	1.807	0.6391	7.276	1.273	6.00	
1.237	3.362	0.6272	7.087	1.039	6.05	
1.212	4.112	0.6099	6.814	0.855	5.96	

the dielectric constant of the medium. The pK_a values are found, as usual, to be higher in formamide than in water, although the former happens to be a solvent with a higher dielectric constant. The results are, however, in agreement with the general behaviour shown by weak acids in this solvent and the reason for the discrepancy stated earlier must be sought in the differing basicities of the two solvents as pointed out earlier by Nayak and Dash [5].

The effect of temperature on pK_a appears to be somewhat irregular, although there is a general trend for it to decrease with the former. The irregularities noticed in the pK_a values are in agreement with our previous studies with *p*-toluidinium and *p*-hydroxyanilinium ions [1] in this solvent and could be due to minute structural changes in the solvent with change of temperature.

TABLE 3

Thermodynamic values for the dissociation process

$BH^+ \rightleftharpoons B + H^+$ in formamide and water at 25°C (298.15 K)

Base (B)	$\Delta G^0 \times 10^{-3}$ (J)		$\Delta H^0 \times 10^{-3}$ (J)		ΔS^0 (J K ⁻¹)	
	Water	Forma- mide	Water	Forma- mide	Water	Forma- mide
<i>m</i> -Toluidine	26.86 **	29.61 *	31.21 **	17.48 *	14.60 **	-40.70 *
<i>p</i> -Anisidine	30.57 ***	33.09 *	34.87 ***	11.49 *	14.38 ***	-72.45 *

* Present work.

** Ref. 6.

*** Ref. 7.

TABLE 4

pK_a values of *m*-toluidinium and *p*-anisidinium ions in different solvents at 25°C (298.15 K)

Ion	Water	Acetonitrile	Nitromethane	Formamide
	($D = 78.54$) (ref. 8)	($D = 36.8$) (ref. 9)	($D = 35.9$) (ref. 10)	($D = 109.5$) (present work)
<i>m</i> -Toluidinium	4.76	10.81	9.70	5.19
<i>p</i> -Anisidinium	5.34	12.05	10.28	5.80

The various thermodynamic properties such as ΔG^0 , ΔH^0 and ΔS^0 which can be computed from the pK_a values and their variation with temperature on the assumption that ΔH^0 does not change very much over the temperature range used are given in Table 3 together with similar data for aqueous medium which are available in literature.

The assumption stated above appears quite reasonable in view of the fact that plots of $\log K_a$ vs. $1/T$ are found to be almost linear for both the anilinium ions.

For the sake of comparison, the pK_a values for these two anilinium ions in various solvents as found in the literature are also shown in Table 4.

Although these values clearly demonstrate the failure of the Born equation, they do indicate the significant role of the dielectric constant of the medium, D , on the dissociation process.

It is further found, in accordance with our previous observation in the cases of *p*-toluidinium and *p*-hydroxyanilinium ions, that the heat of dissociation decreases in formamide while the free energy of dissociation increases. This is due to the lower entropy of dissociation in formamide than in water. In fact, the entropy assumes a significantly negative value in formamide while it has a positive value in water. This supports our previous contention that the dissociation of protonated bases has a net structure-making effect in formamide while it has a net structure-breaking effect in water. It may be due to the greater solvation of the free base (resulting from the dissociation of anilinium ions) in formamide than in water on account of lower hydrophobic interaction in the former as suggested earlier [1].

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