Acid Dissociation Constant of the Ammonium Ion in Aqueous Ammonium Perchlorate, Sodium Bromide Solutions of Unit Ionic Strength

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Values for the acid dissociation constant of the ammonium ion based on concentration standards in a series of aqueous ammonium bromide, sodium perchlorate solutions, all of unit ionic strength, have been determined. The results seem to indicate that solutions of these two electrolytes in combination might prove useful in investigations of weak bromide complex formation or ion-pairing at a fixed ionic strength.

The results of measurements in seven different media at 25.0 °C are presented in Table 1 as

$$pK_a = -\log[NH_3][H^+]/[NH_4^+]$$

Table 2 gives pK_a values in four of these media at four temperatures, together with $\Delta H°$ and $\Delta S°$ calculated from these results for the reaction:

$$NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$$
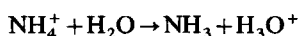
These thermodynamic quantities have not previously been determined in these media, but results from related media agree well with the values reported here.[1]

Harned's rule quantitatively[2] describes the change in activity coefficients of an electrolyte in solutions of constant total molality in which one electrolyte is exchanged for another: the logarithm of the activity coefficient is proportional to the molality of the other component. A similar linear relationship has been found for the pK_a value of acetic acid in salt solutions of constant ionic strength.[3] Such relationships are of the form

$$pK_a = pK_a° + \Delta C_L$$

and describe the change in the $pK_a°$ (valid in a solution of one electrolyte) when one ion is partially substituted for another (corresponding to a concentration change of C_L).

The data for 25.0 °C presented in Table 1 can be accommodated by two such linear relations. When

Table 1. pK_a values for the ammonium ion at 25.0 °C in 1.00 M $(NH_4,Na)(ClO_4,Br)$ aqueous solution.[a]

$[NH_4^+]$ (M)		1.00	0.90	0.50	0.10
$[Na^+]$ (M)			0.10	0.50	0.90
$[ClO_4^-]$ (M)	$[Br^-]$ (M)				
1.00		9.432(9.430)			9.463(9.467)
0.90	0.10		9.428(9.430)		
0.50	0.50	9.414(9.410)		9.435(9.431)	
	1.00	9.384(9.391)		9.414(9.411)	

[a] Numbers in parenthesis are calculated from the formula $pK_a = 9.430 + 0.041[Na^+] - 0.039[Br^-]$; see text.

Table 2. Temperature dependence of the pK_a of the ammonium ion in 1.00 M $(NH_4,Na)(ClO_4,Br)$ aqueous solution and $\Delta H°$ and $\Delta S°$ for the dissociation of the ammonium ion.

$t/°C$	1.000 M NH_4ClO_4	0.900 M NH_4ClO_4 0.100 M NaBr	0.500 M NH_4ClO_4 0.500 M NaBr	1.000 M NH_4Br
18.0		9.659	9.667	9.614
25.0	9.432	9.428	9.435	9.384
30.0	9.278	9.275	9.279	9.219
40.0	8.993	8.988	8.991	8.942
$\Delta H°/kJ\ mol^{-1}$	52.1 ± 0.5	53.0 ± 0.5	53.5 ± 0.6	53.3 ± 1.1
$\Delta S°/J\ mol^{-1}\ K^{-1}$	-6 ± 2	-3 ± 2	-1 ± 2	-1 ± 4

they are combined they yield (calculated by a general linear regression procedure):

$$pK_a = 9.430 + 0.041[Na^+] - 0.039[Br^-]$$

This two-dimensional interpolation formula indicates that when sodium ions are substituted for ammonium ions in ammonium perchlorate solutions (horizontal in Table 1), a change in the pK_a of the ammonium ion is observed. When bromide is substituted for perchlorate (vertical in Table 1) a change is also observed. However, when these substitutions are simultaneous, the effects of the two substitutions balance each other quantitatively.

Equilibrium constants for labile complexes or for ion pairs are often determined using series of solutions of constant ionic strength. The assumption of constant activity coefficients in such series of solutions is only valid, however, if the concentration of the added inert salt is large compared to the concentration of the reacting species. In the case of weak complex formation the reaction medium cannot be kept constant.[4] For example, an investigation of weak bromide complex formation would involve substitution of a significant fraction of the anion of the inert electrolyte with bromide. Ammonium perchlorate and sodium bromide provide an example of a pair of salts which can profitably be used in such investigations, since the changes in ion-activities are minor on substitution of one salt for the other.

Experimental. Analytical grade chemicals and doubly distilled water were employed throughout. Stock solutions of ammonium perchlorate and ammonium bromide were prepared by neutralization of standardized ammonia solutions with standardized perchloric acid and hydrobromic acid solutions, respectively. The degree of neutralization was checked by the very accurate method described by Bjerrum.[5] Each figure in the two tables was obtained by the following procedure: For the temperature and for the salt medium in question four solutions of different ammonia concentration ($0.005 < C_{NH_3} < 0.2$) were prepared, together with a strongly acid solution ($\approx 10^{-2}$ M in the medium in question). Hydrogen ion concentrations were measured with a Radiometer G 202 C glass electrode and a 1.0 M sodium chloride calomel electrode in conjunction with a Radiometer PHM 52 meter. Potential differences between the ammonia solutions showed the potential/pH slope for the electrode to be $100.1 \pm 0.15\%$ of the theoretical calue (from measurements in 72 solutions). From potential differences between the strongly acid solutions and the ammonia solutions, $[H^+]$ in each ammonia

solution was calculated. pK_a based on concentration standards at the temperature and in the salt medium in question was calculated from:

$$pK_a = pH + \log \frac{C_{NH_3} + [H^+] - [OH^-]}{C_{NH_4^+} - [H^+] + [OH^-]}$$

Thus, each value reported is the mean value of measurements in four solutions. Standard deviations on these mean values ranged between 0.001 and 0.004. Standard errors of estimate on the parameters in the two dimensional interpolation formula were 0.003 on the intercept and 0.005 on the coefficients.

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