

Potentiometric Determination of the Ionization Constant of Nitrous Acid in Aqueous Sodium Perchlorate Solutions at 25°C

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The ionization constant of nitrous acid has been determined potentiometrically in aqueous sodium perchlorate solutions of different ionic strengths. The results could be presented by an equation of the Debye-Hückel type. The negative logarithm of the thermodynamic ionization constant was found to be 3.15 at 25°C.

Previous determinations of the ionization constant of nitrous acid have in all cases except one been based on the addition of a strong mineral acid to a solution of a metal nitrite.

Schümann¹ studied the conductivities of equimolar solutions of sodium nitrite and hydrogen chloride at 25°C. The ionic strengths were about 0.002 and the derived value of the negative logarithm of the ionization constant of nitrous acid 3.35.

The ionization of nitrous acid was studied kinetically by Blanchard.² He compared the catalytic effect of nitric and acetic acid on the rate of decomposition of ammonium nitrite in a solution which was 0.4 M in ammonium nitrate and 0.5 M in sodium nitrite. The concentration of nitric acid varied from 0.025 to 0.258 M and that of acetic acid from 0.2144 to 0.280 M. The volume of nitrogen gas evolved at 25°C in the decomposition of ammonium nitrite was measured and the value of the ionization constant of acetic acid was taken to be 1.8×10^{-5} . The value 3.4 was derived for the negative logarithm of the ionization constant of nitrous acid at an ionic strength of about 0.9.

The ionization constant of nitrous acid was determined analytically by Bauer.³ Carbon dioxide was allowed to bubble through 0.0972–0.129 M solutions of potassium nitrite. When the first ionization constant of carbonic acid was taken to be $10^{-6.52}$, the negative logarithm of ionization constant of nitrous acid was found to be 3.19 at an ionic strength of about 0.1 and 25°C.

Klemenc and Hayek⁴ determined the ionization constant of nitrous acid by measuring the conductivities of mixtures of equimolar solutions of sulphuric

acid and barium nitrite. The ionic strength was about 0.001. They obtained the values $pK = 3.49$ (0°C), 3.34 (12.5°C), and 3.22 (30°C). They also pointed out that no true equilibrium is reached in the experiments of Bauer,³ and that the agreement between the results of Bauer and those of Schümann¹ is fortuitous. The older literature is summarized by Klemenc and Hayek.⁴

Conductivity measurements were performed also by Schmid, Marchgraber and Dunkl⁵ who caused about 0.001 M solutions of sodium nitrite and hydrogen chloride to flow into a conductivity cell where they were mixed. The ionic strength was about 0.002 and the derived values of the negative logarithm of the ionization constant of nitrous acid are 3.46 (0°C), 3.29 (25°C), and 3.15 (50°C).

The latest study of the ionization of nitrous acid seems to be that of Vassian and Eberhardt.⁶ They report having determined the ionization constant of nitrous acid spectrophotometrically at 25°C by measuring the light absorption of about 0.02 M potassium nitrite solutions, the pH of which had been adjusted to 3.25 with perchloric acid. The ionic strengths were adjusted with sodium perchlorate to 1.0 and 0.07. The respective values of pK were 2.80 and 3.29.

Our preliminary experiments showed, however, that already a 0.001 M concentration of a mineral acid and even acetic acid catalyzes the decomposition of a 0.01 M nitrite solution. This means that a part of the acid decomposed in the previous studies of the ionization of nitrous acid and explains why all reported values differ about 0.2–0.4 pK unit from the values we obtained at about the same ionic strengths and at the same temperature.

EXPERIMENTAL

Anhydrous sodium perchlorate (G. F. Smith Chemical Co.) was purified as follows. Some of the salt was dissolved in conductivity water and the resulting solution was adjusted to pH 7 with sodium hydroxide and left to stand overnight, after which it was filtered through a fine glass sinter. The solution was then concentrated by boiling and filtered while still hot (60°C). The precipitated salt was recrystallized from water, dried at 130°C for 5 h, and stored in a desiccator.

The other chemicals used were guaranteed reagents (E. Merck A.G.).

A carbonate-free sodium hydroxide solution was standardized potentiometrically against a weighed amount of potassium biphthalate and found to be 0.09822 N. The acetic acid and perchloric acid solutions were titrated potentiometrically with the sodium hydroxide solution. The stock solutions of acetic and perchloric acids were 0.1742 and 0.02406 M, respectively.

A 0.005 M reference perchloric acid solution ($\text{pH} = -\log [\text{H}^+] = 2.302$ at 25°C) and a 0.1 M solution of acetic acid were prepared by dilution from the stock solutions. A 0.01 M solution of sodium nitrite was prepared by weighing. All these solutions were also made 0.03 M in sodium nitrate and the ionic strengths (I) of the solutions were adjusted with sodium perchlorate to the desired levels. The solutions were prepared in 250- or 100-ml calibrated volumetric flasks.

In preliminary experiments the stabilities of sodium nitrite solutions were studied. A 0.01 M sodium nitrite solution was found to be stable, but all added mineral acids and even acetic acid at a concentration as low as 0.001 M decomposed the nitrite (odour). When the 0.01 M sodium nitrite solution was made 0.03 M in sodium nitrate,⁷ the solution was stable although it was 0.01 M in acetic acid, but mineral acids cause the nitrite to decompose immediately. Sodium perchlorate was not found to promote the decomposition of nitrite in solution.

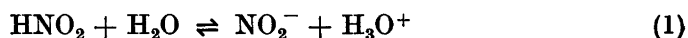
The potentiometric titrations were performed with the solutions in a water thermostat at $25 \pm 0.01^\circ\text{C}$ using a Radiometer PHM 4 Potentiometer and glass electrode-calomel electrode systems for the potential measurements. The glass electrodes were Beckman electrodes no. 41263. The calomel electrodes contained sodium chloride solutions equal in ionic strength to the titrated solutions. The purpose of this was to reduce the liquid junction potentials, which were disregarded in the calculations. Later experiments showed that calomel electrodes containing a solution 0.01 M in sodium chloride and x M in sodium perchlorate function well, and would have been better to use. The titrations were conducted in a nitrogen atmosphere. Magnetic stirrers were used to mix the solutions during the titrations.

The potentials became constant rapidly and reproducibly in the titrations. Calibration measurements were made before and after the titrations. Two glass electrodes were used in the solutions for control. From 4.0 to 10.0 ml of the titrant was added in 0.5-ml portions to 100 ml of the nitrite solution.

The concentrations were corrected for the thermal expansion of the solutions, which was assumed to be the same as that of pure water.

RESULTS

The following two protolytic equilibria were assumed to prevail in the titrated solutions:



The corresponding concentration ionization constants are:

$$K = [\text{H}_3\text{O}^+] [\text{NO}_2^-]/[\text{HNO}_2] \quad (3)$$

$$K_{\text{Ac}} = [\text{H}_3\text{O}^+] [\text{CH}_3\text{COO}^-]/[\text{CH}_3\text{COOH}] \quad (4)$$

and the total concentrations of the acids

$$C = [\text{NO}_2^-] + [\text{HNO}_2] \quad (5)$$

$$C_{\text{Ac}} = [\text{CH}_3\text{COO}^-] + [\text{CH}_3\text{COOH}] \quad (6)$$

From these equations and the electroneutrality principle it follows that

$$K = [\text{H}_3\text{O}^+] (C - A + [\text{H}_3\text{O}^+]) / (A - [\text{H}_3\text{O}^+]) \quad (7)$$

where

$$A = K_{\text{Ac}} C_{\text{Ac}} / (K_{\text{Ac}} + [\text{H}_3\text{O}^+]) \quad (8)$$

The potentiometric measurements gave the pH ($= -\log [\text{H}^+]$) on the assumption that the perchloric acid in the reference solutions was completely ionized.

The values of the ionization constant of acetic acid in aqueous sodium perchlorate solutions at 25°C were calculated from the equation⁸

$$\text{p}K_{\text{Ac}} = 4.757 - 1.018 \sqrt{I} / (1 + 1.597 \sqrt{I}) + 0.2446 I \quad (9)$$

The potentiometric data are given in Table 1.

The values of $\text{p}K$ of nitrous acid calculated from the measured data are presented in Table 2. The values of $\text{p}K$ in column I are mean values from two and those in column II mean values from four titrations, each of which included at least thirteen titration points.

Table 1. Potentiometric titration data for nitrous acid in aqueous sodium perchlorate solutions at 25°C.

Titration added ml	pH										
	4.0	4.070	4.019	4.032	4.012	4.012	4.019	4.017	4.092	4.083	4.320
4.5	4.039	3.987	4.003	3.982	3.979	3.985	3.984	4.058	4.052	4.274	4.269
5.0	4.012	3.961	3.976	3.954	3.950	3.955	3.954	4.024	4.015	4.238	4.230
5.5	3.987	3.936	3.951	3.930	3.925	3.930	3.928	3.998	3.990	4.207	4.197
6.0	3.964	3.913	3.928	3.906	3.902	3.906	3.904	3.969	3.964	4.178	4.165
6.5	3.944	3.894	3.908	3.886	3.883	3.884	3.883	3.949	3.944	4.151	4.141
7.0	3.926	3.875	3.887	3.867	3.863	3.866	3.863	3.928	3.917	4.127	4.117
7.5	3.909	3.856	3.869	3.850	3.843	3.849	3.845	3.909	3.901	4.105	4.096
8.0	3.898	3.839	3.852	3.832	3.827	3.831	3.828	3.889	3.881	4.085	4.074
8.5	3.878	3.823	3.836	3.816	3.810	3.814	3.812	3.872	3.862	4.067	4.055
9.0	3.863	3.808	3.820	3.802	3.796	3.798	3.796	3.857	3.847	4.047	4.037
9.5	3.850	3.796	3.806	3.790	3.782	3.783	3.782	3.845	3.835	4.033	4.022
10.0	3.837	3.784	3.794	3.776	3.768	3.770	3.768	3.830	3.821	4.016	4.004
<i>I</i> ~	0.04	0.09	0.09	0.25	0.25	0.50	0.50	1.00	1.00	2.00	2.00
Column in Table 2	I	I	II	I	II	I	II	I	II	I	II

The results can be presented by the equation

$$pK = pK_0 - 1.023 \sqrt{I}/(1 + \alpha \sqrt{I}) + BI \quad (10)$$

where $pK_0 = 3.148$, $\alpha = 1.622$ and $B = 0.261$ as obtained by the method of least squares on the basis of the mean values of pK in Table 2. The values of pK calculated from eqn. (10) are given in the last column of Table 2.

The values of pK in columns I and II in Table 2 show the general reproducibility of the measurements. It may be mentioned that an inaccuracy of ± 0.1 mV in a potential measurement leads to an error of about ± 0.005 unit in the value of pK .

Table 2. Potentiometrically determined values of the ionization constant of nitrous acid in aqueous sodium perchlorate solutions at 25°C.

<i>I</i>	\sqrt{I}	I <i>pK</i>	II <i>pK</i>	Mean <i>pK</i>	Calc. <i>pK</i>
0.0401	0.200	3.004	—	3.004	3.004
0.0900	0.300	2.941	2.965	2.953	2.965
0.2498	0.500	2.958	2.944	2.951	2.931
0.4996	0.707	2.948	2.942	2.945	2.941
0.9990	1.000	3.017	2.986	3.002	3.019
1.9978	1.414	3.245	3.225	3.236	3.230

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