Solubility of Silver Tungstate in Aqueous Sodium Nitrate Solutions with Different pH Values at 25 °C. Evaluation of a Solubility *vs.* Ionic Strength Relation Valid for Ionic Strength up to 1.0 mol dm⁻³
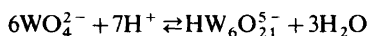
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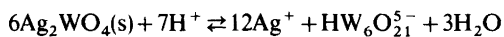Fysisk-Kemisk Institut, DTH 206, DK-2800 Lyngby, Denmark

The solubility of stable silver tungstate has been measured in aqueous sodium nitrate solutions at I = 0.1 and I = 0.5 mol dm⁻³ and $4 < \text{pH} < 10$. The pH-dependence of the solubility is used to test a previously outlined theory. The ionic strength dependence of the solubility is used to outline the relation:

$$\ln s = \ln s_0 + 1.941 I^{\frac{1}{2}} (1 + I^{\frac{1}{2}})^{-1}$$

valid for $0 \leq I \leq 1.0$. Equilibrium constants for the following two equilibria

$$6\text{WO}_4^{2-} + 7\text{H}^+ \rightleftharpoons \text{HW}_6\text{O}_{21}^{5-} + 3\text{H}_2\text{O}$$

and

$$6\text{Ag}_2\text{WO}_4(\text{s}) + 7\text{H}^+ \rightleftharpoons 12\text{Ag}^+ + \text{HW}_6\text{O}_{21}^{5-} + 3\text{H}_2\text{O}$$

are found at different ionic strengths covering the interval $0 \leq I \leq 1.0$. The ionic strength dependences on these equilibria are found to be in accordance with theories outlined by Debye-Hückel and Brønsted.

Regarding the solubility of silver tungstate, much confusion and great discrepancies are found among the reported values.[1−5] At this institute the solubility of silver tungstate has been investigated in aqueous sodium nitrate solutions at various ionic strengths, pH and temperatures. Results representing measurements on dilute electrolyte solutions (c_{NaNO_3} below approximate 3×10^{-2} mol dm⁻³) and measurements on 1.0 mol dm⁻³ sodium nitrate solutions have previously been reported in this journal.[6]

In the present paper results from solubility measurements on 0.1 mol dm⁻³ and 0.5 mol dm⁻³ will be presented. The presentation is initiated for two main reasons:

(1) The results give support to the theories outlined earlier,

(2) the new results together with those reported earlier create the basis of establishing a relationship between the solubility of silver tungstate and the concentration of sodium nitrate in aqueous solutions up to $c_{\text{NaNO}_3} = 1.0$ mol dm⁻³.

In addition, some protolytic constants are calculated at different ionic strengths and the ionic strength dependences are discussed.

EXPERIMENTAL

The descriptions of chemicals, of preparing saturated solutions of thermodynamic stable silver tungstate, and of solubility determinations are reported earlier.[6] Only a few additional remarks shall be given to the procedure of preparing thermodynamic stable silver tungstate.

Freshly precipitated silver tungstate prepared by adding excess of aqueous sodium tungstate to well-stirred aqueous solution of silver nitrate is not stable, but undergoes chemical reactions, in which also protons are involved.[6] Therefore, the silver tungstate precipitate was allowed to equilibrate at least one year with the aqueous solution, (further equilibration was found to be unnecessary, shorter equilibration time has not been tried), whereupon it was rinsed in distilled and de-ionized water until the specific conductivity of a saturated solution in this water at 25 °C was below 20×10^{-6} ohm⁻¹ cm⁻¹. Due to scattering in the reported values of molar conductivity of the tungstate ion it is impossible to

give an exact value of the specific conductance of a saturated aqueous solution of silver tungstate at 25 °C. Two examples shall illustrate this: Landolt-Börnstein [7] gives the value 138.8 ohm^{-1} cm^2 mol^{-1} for the molar conductance of WO_4^{2-} at 25 °C. This, together with the value 62.2 ohm^{-1} cm^2 mol^{-1} for the molar conductance of Ag^+ gives the specific conductivity for a saturated solution of silver tungstate to 15.0×10^{-6} ohm^{-1} cm^{-1} when the value 5.7×10^{-5} mol dm^{-3} is used for the solubility.[6] From the data of Watkins and Jones [8] the molar conductivity of WO_4^{2-}-ion can be calculated to 223 ohm^{-1} cm^2 mol^{-1} at 25 °C. This gives a specific conductivity of a saturated Ag_2WO_4-solu-

tion of 19.8×10^{-6} ohm^{-1} cm^{-1}.

Therefore, we decided that the ultimate test of the cleanness of our silver tungstate product should be that the specific conductance of a saturated aqueous solution was below 20×10^{-6} ohm^{-1} cm^{-1}.

The saturated solution was then filtered after which the silver tungstate was dried at 50 °C and used to prepare saturated aqueous sodium nitrate solutions as described earlier.[6]

RESULTS AND DISCUSSION

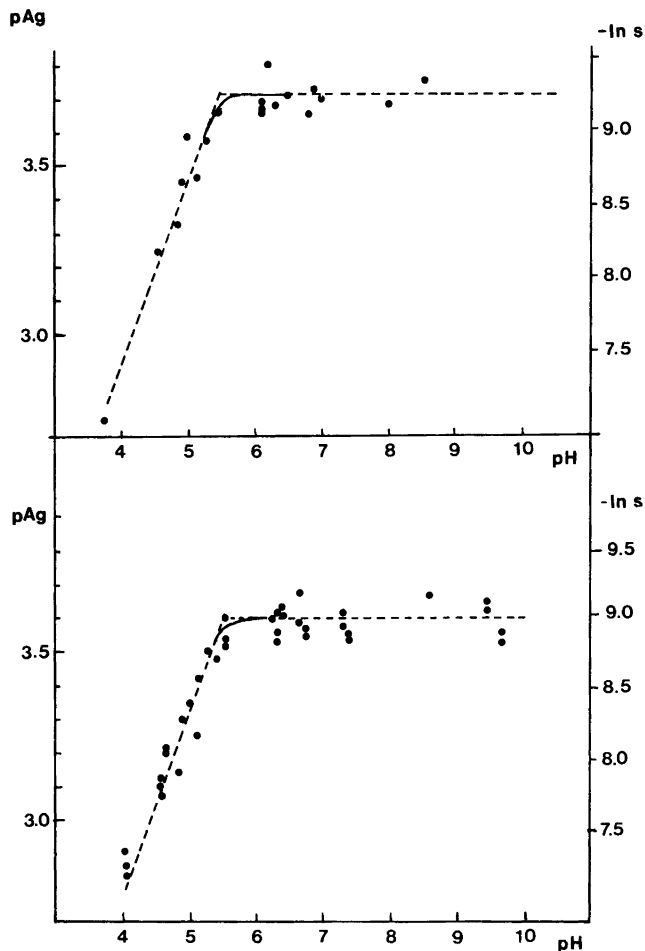The pH-dependence of the solubility of stable silver tungstate has been investigated at two

Fig. 1. Solubility of stable silver tungstate in aqueous sodium nitrate solutions as a function of pH. Upper curve: $C_{NaNO_3} = 0.1$ mol dm^{-3}. Lower curve: $C_{NaNO_3} = 0.5$ mol dm^{-3}. The two horizontal dotted lines are drawn through the mean value of experimental data corresponding to pH > 6.0. The two other dotted straight lines are drawn with a slope 7/13 through the intercept with the horizontal lines. The intercepts are calculated by means of eqn. (6).

different ionic strengths, i.e. $I = 0.1$ and 0.5, respectively. The ionic strength was kept constant by means of sodium nitrate and the investigation was performed by titrimetric determination of silver ions in saturated aqueous solutions at 25 °C. The results are shown in Fig. 1.

Great similarities are observed between these results and the results previously reported for the solubility of stable silver tungstate in 1.0 mol dm^{-3} aqueous sodium nitrate solutions.[6] As an example: By regarding Fig. 1 it seems most likely that, also in the present case, some protolytic reactions are involved in the solubility process in weak acidic medium, whereas pAg obviously can be regarded as constant for pH > 6. Due to the uniformity − at first glance almost identity − among previously reported values and those reported in Fig. 1, we found it permissible to assume that the solubility of silver tungstate in both cases is governed by the same reactions. This means that the present results (Fig. 1) can be used as an independent test in order to support − or reject − the theories outlined earlier. The main features on the theories shall shortly be mentioned: According to Arnek and Sasaki[9] the first step in the acidification of WO_4^{2-}-ion can be expressed by eqn. (1), with the equilibrium constant

$$6WO_4^{2-} + 7H^+ \rightleftarrows HW_6O_{21}^{5-} + 3H_2O \tag{1}$$
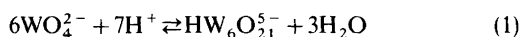
β_1. This equation, together with the saturation equilibrium, gives eqn. (2). Eqn. (2) together with the expression for the solubility product, eqn. (3), and eqn. (1) gives eqn. (4), where $\beta_1' = \beta_1/(C_{H_2O})^3$. Eqn. (4)

$$C_{Ag^+} = 2(C_{WO_4^{2-}} + 6C_{HW_6O_{21}^{5-}}) \tag{2}$$

$$(C_{Ag^+})^2 C_{WO_4^{2-}} = K_c \tag{3}$$

$$(C_{Ag^+})^{13} - 2K_c(C_{Ag^+})^{10} - 12\beta_1' K_c^6 (C_{H^+})^7 = 0 \tag{4}$$

expresses the concentration of silver-ions in saturated solutions of silver tungstate as a function of pH. This dependence can be calculated from knowledge of the two constants, K_c and β_1'. On the other hand, if the pH-dependence of the solubility is determined experimentally, the two constants can be calculated as has been done in 1.0 mol dm^{-3} sodium nitrate solutions. For pH > 6.5 it was assumed that the term $12\beta_1' K_c^6 (H_{H^+})^7$ vanishes so that eqn. (4) was reduced to $C_{Ag^+} = (2K_c)^{1/3}$ and K_c determined from the mean C_{Ag^+}-value to 1.63

$\times 10^{-11}$ mol^3 dm^{-9}, corresponding to a solubility of 1.6×10^{-4} mol dm^{-3}. For pH-values below 5.5 it was assumed that the term $2K_c(C_{Ag^+})^{10}$ vanishes and eqn. (4) was then reduced to eqn. (5), i.e. a straight

$$pAg = \frac{7}{13} pH - \frac{1}{13} \log(12\beta_1' K_c^6) \tag{5}$$

line with the slope 7/13 from which log β_1' can be calculated to be 57.34.

If eqns. (1)−(5) can be assumed to have general validity in aqueous sodium nitrate solution, the pH-dependence of the solubility can be determined by means of two straight lines:

(1) One horizontal line, valid in neutral media. The position of the line is determined from the mean C_{Ag^+}-value from saturated solutions in these media. From this line the solubility product can be calculated.

(2) One line with a slope 7/13 valid in slightly acidic media. The position of this line is governed by the point of intercept between this line and the horizontal one. This point can be calculated from eqn. (6) if β_1' and K_c are known.

$$pH = \frac{1}{7} \log(12\beta_1' K_c^6) - \frac{13}{21} \log(2K_c) \tag{6}$$

By applying eqn. (4), the intervening part of the curve between the two straight lines can now be calculated.

In Fig. 1 the two horizontal dotted lines represent the two mean values of C_{Ag^+}, calculated from experimental data of C_{Ag^+} in media with pH > 6. Following values were obtained:

(a) For $I = 0.1$; pAg = 3.715 ± 0.015, corresponding to a solubility $s = (9.65 \pm 0.35) \times 10^{-5}$ mol dm^{-3} and a solubility product $K_c = (3.6 \pm 0.4) \times 10^{-12}$ mol^3 dm^{-9}.

(b) For $I = 0.5$; pAg = 3.592 ± 0.009, corresponding to $s = (1.28 \pm 0.04) \times 10^{-4}$ and a solubility product $K_c = (8.4 \pm 0.4) \times 10^{-12}$ mol^3 dm^{-9}.

Previously reported values[6] for $I = 1.0$; pAg = 3.496 ± 0.007 corresponding to $s = (1.60 \pm 0.03) \times 10^{-4}$ mol dm^{-3} and solubility product $K_c = (1.63 \pm 0.08) \times 10^{-11}$ mol^3 dm^{-9}.

Furthermore in Ref. 6 it is shown that the ionic strength dependence of the solubility of silver tungstate in dilute sodium nitrate solutions ($I \leq 0.03$) can be expressed by the Güntelberg equation, eqn. (7), and ln s_0 was determined to be −9.77 ± 0.04.
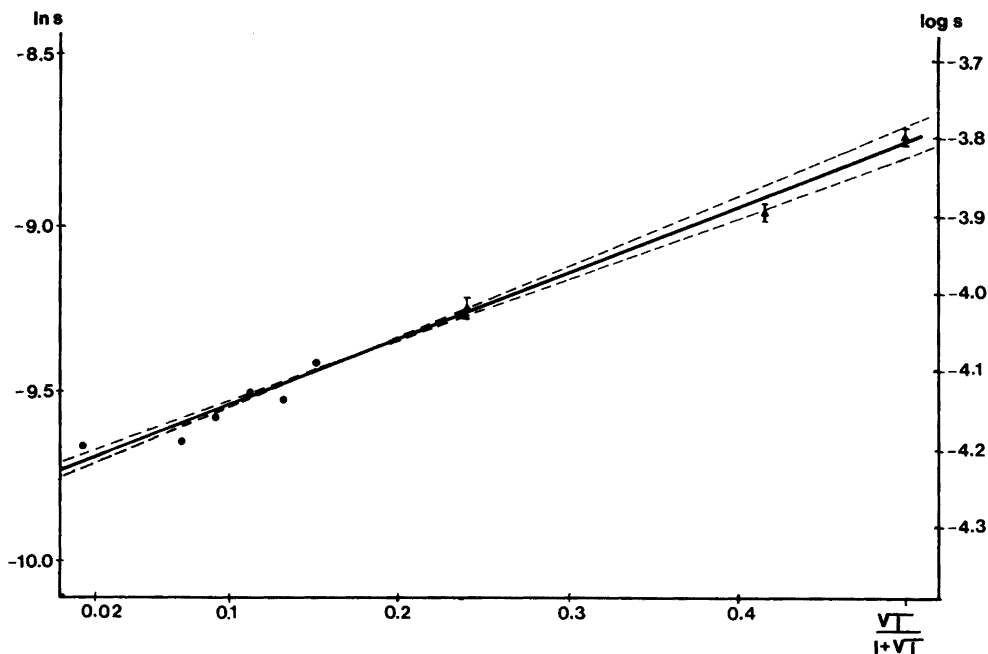
Fig. 2. Güntelberg plot [eqn. (13)] for experimental data of solubility of stable silver tungstate. Data marked as ● are previously reported. The fully drawn line indicates the best straight line through the data. The two dotted lines indicate the 67% uncertainty limit for the straight line.

$$\ln s = \ln s_o + kI^{\frac{1}{2}}(1+I^{\frac{1}{2}})^{-1} \tag{7}$$

The validity of eqn. (7) in more concentrated solutions can be tested by applying the solubility data from dilute ionic media together with those reported above and carrying out a Güntelberg plot. This is done in Fig. 2.

A straight line is fitted through the points with a correlation coefficient $=0.987$. The slope is calculated to be 1.94 ± 0.08 and $\ln s_o$ is determined to be -9.74 ± 0.02, i.e. very close to the value obtained, when only dilute solutions were used in the plot.*

Clearly the Güntelberg equation very nicely describes the ionic strength dependence of ionic equilibria in sodium nitrate solutions up to $C_{NaNO_3} = 1.0 \ mol \ dm^{-3}$, provided(1) that the concentration of the ionic species in the equilibrium can be neglected, compared with the concentrations of sodium and nitrate ions and

(2) that the constant k is determined and valid for any arbitrary ionic species taking part in the

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*This linearity strongly indicates that no possible complex formation between the present ions is substantial enough to be drawn into the calculations.

equilibrium. This can be done by regarding the solubility product of silver tungstate. The relation (8) holds, where K_o is the solubility product at zero ionic strength, a is the activity, and y the activity coefficient of the ions. Since $C_{Ag^+} = 2s = 2C_{WO_4^{2-}}$, eqn. (8) can be written as eqn. (9), where s_o is the

$$K_o = (a_{Ag^+})^2 a_{WO_4^{2-}} = (C_{Ag^+} + y_{Ag^+})^2 C_{WO_4^{2-}} y_{WO_4^{2-}} \tag{8}$$

$$4s_o^3 = 4s^3 y_\pm^3 \tag{9}$$

solubility at zero ionic strength and $y_\pm$ is the mean activity coefficient defined from the equation

$$y_\pm^3 = y_{Ag^+}^2 y_{WO_4^{2-}}.$$

From the Güntelberg modified Debye-Hückel theory we have eqns. (10)−(12), where A is the

$$-\ln y_{Ag^+} = AI^{\frac{1}{2}}(1+I^{\frac{1}{2}})^{-1} \tag{10}$$

$$-\ln y_{WO_4^{2-}} = 4AI^{\frac{1}{2}}(1+I^{\frac{1}{2}})^{-1} \tag{11}$$

$$-\ln y_\pm = 2AI^{\frac{1}{2}}(1+I^{\frac{1}{2}})^{-1} \tag{12}$$

Debye-Hückel constant and I is the ionic strength. Substituting (12) in (9) we have eqn. (13). Comparing (13) with (7), the Debye-Hückel constant is found for aqueous sodium bitrate solutions at 25 °C; eqn. (14),

$$\ln s = \ln s_o + 2AI^{\frac{1}{2}}(1+I^{\frac{1}{2}})^{-1} \qquad (13)$$

$$A = k/2 = 0.97 \qquad (14)$$

compared with the theoretical value [10] 1.17. However, the theoretical value is calculated for an arbitrary ionic species in aqueous solution without taking into account special ion individualities, and is therefore supposed to be valid only in dilute ionic solutions. For further calculations, the value 0.97 will be used.

According to eqn. (4), β'_1 must be known in order to give a full description of the pH-dependence of solubility of stable silver tungstate. That means that in order to completely test the results shown in Fig. 1, the value of β'_1 must be known in 0.1 and 0.5 mol dm^{-3} sodium nitrate solutions. The expression for β'_1 at a given ionic strength is given by eqn. (15).

$$\beta'_1 = \frac{C_{HW_6O_{21}^{5-}}}{(C_{H^+})^7 \cdot (C_{WO_4^{2-}})^6} \qquad (15)$$

The value of β'_1 at ionic strength $=0$ can be expressed as eqn. (16) or eqn. (17).

$$\beta'_1(I=0) = \frac{a_{HW_6O_{21}^{5-}}}{(a_{H^+})^7(a_{WO_4^{2-}})^6} =$$

$$\frac{C_{HW_6O_{21}^{5-}}}{(C_{H^+})^7(a_{WO_4^{2-}})^6} \cdot \frac{y_{HW_6O_{21}^{5-}}}{(y_{H^+})^7(y_{WO_4^{2-}})^6} \qquad (16)$$

$$\ln \beta'_1(I=0) = \ln \beta'_1(I=I) + \ln \frac{y_{HW_6O_{21}^{5-}}}{(y_{H^+})^7(y_{WO_4^{2-}})^6} \qquad (17)$$

Due to the fact that all the concentrations in (15) are very small, the treatment outlined in eqns. (10)$-$(13) can be applied on the last term in eqn. (17) with eqn. (18) as a result. Eqn. (18) is substituted into eqn. (17) which then gives ($A=0.97$) eqn. (19). Utilizing the

$$\ln \frac{y_{HW_6O_{21}^{5-}}}{(y_{H^+})^7(y_{WO_4^{2-}})^6} = 6A \frac{I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} \qquad (18)$$

value $\log \beta'_1(I=1.0) = 57.34$ in eqn. (19) we get eqn. (20) and β'_1 can be calculated at $I=0.5$ and $I=0.1$ to $\log \beta'_1(I=0.5) = 57.56$ and $\log \beta'_1(I=0.1) = 58.00$.

$$\ln \beta'_1(I=0) = \ln \beta'_1(I=I) + 5.82 \cdot \frac{I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} \qquad (19)$$

$$\log \beta'_1(I=I) = 58.60 - 2.53 \frac{I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} \qquad (20)$$

By means of eqn. (6) pH can now be calculated at the point of intercept between the two straight lines in order to establish the position of the second straight line with the slope 7/13. The following pH-values were obtained: At $I=0.5$: pH (intercept) $=5.56$; $I=0.1$: pH (intercept)$=5.53$. Extrapolated values to zero ionic strength are: $\log \beta'_1(I=0)$ $=58.60$, corresponding to pH intercept $=5.45$. Through the two pH intercept-values two straight lines with the slope 7/13 are drawn (shown as dotted lines on Fig. 1). As can be seen, these lines fit the experimental data so nicely that we, on the basis of this fine agreement, feel it justified to make the following three conclusions:

(1) The results shown in Fig. 1 highly support the previously developed theory of the pH-dependence of stable silver tungstate. The theory is shortly outlined in eqns. (1)$-$(5).

(2) The nice fit in Fig. 1 seems to establish the validity of eqn. (20).

(3) By means of experimental data presented here and a theory previously outlined, it is possible to calculate the solubility of stable silver tungstate in aqueous sodium nitrate solutions with ionic strengths <1.0 and at any pH-value in the interval $4<$ pH <10. Fig. 3 shows four calculated curves corresponding to four different ionic strength values.

Now regarding the equilibrium (21) with the equilibrium constant (22). This equilibrium constant can also be written as eqn. (23). The ionic strength

$$6Ag_2WO_4(s) + 7H^+(aq) \rightleftarrows 12Ag^+(aq) +$$
$$HW_6O_{21}^{5-}(aq) + 3H_2O \qquad (21)$$
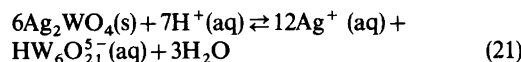
$$\beta_{21} = \frac{(C_{Ag^+})^{12}C_{HW_6O_{21}^{5-}}(C_{H_2O})^3}{(C_{H^+})^7} \qquad (22)$$

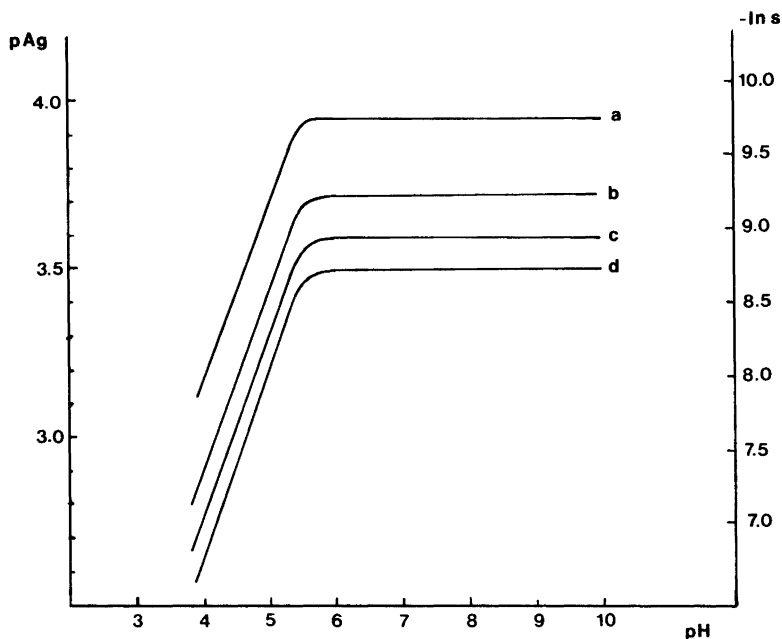$$\beta_{21} = K_c^6\beta_1 = K^6\beta'_1(C_{H_2O})^3 \qquad (23)$$

Fig. 3. Calculated solubilities of stable silver tungstate in different aqueous sodium nitrate solutions as a function of pH. Curve a: $I = 0$; curve b: $I = 0.1$; curve c: $I = 0.5$; curve d: $I = 1.0$. (Units for I: mol dm^{-3}.)

dependence of K_c and β'_1 in aqueous sodium nitrate solutions is evaluated in eqns. (13) and (20), and the proper value of the water concentrations at different ionic strengths can easily be found.[11] So, by means of eqn. (23), the constant β_{21} can be calculated. The values are collected in Table 1, together with the corresponding values of β_1.

Besides illustrating a general ionic strength dependence of ionic equilibria, the results in Table 1 agree with the theories in two decisive ways:

(1) The ionic strength dependence is much more pronounced in β_{21} than in β_1, which is in accordance with the Debye-Hückel theory.

(2) It is noticed that β_1 decreases and β_{21} increases with increasing ionic strength. This is in accordance

with the theory of Brønsted[12-15] which predicts a negative secondary salt effect on (1) and a positive secondary salt effect on (21).

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Table 1. Calculated values of β_1 [equilibrium (1)] and β_{21} [equilibrium (21)] at different ionic strengths in aqueous sodium nitrate solutions.

	$I=0$	$I=0.1$	$I=0.5$	$I=1.0$
β_1	6.8×10^{63}	1.7×10^{63}	5.9×10^{62}	3.4×10^{62}
β_{21}	1.8×10^{-9}	3.7×10^{-6}	2.1×10^{-4}	6.4×10^{-3}

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