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Dissociation Constants of α-D-Isosaccharinic Acid: "Composite" and "Intrinsic" Values

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The transformation of α-D-isosaccharinic acid into α-D-isosaccharino-1,4-lactone proceeds relatively slowly. Consequently, the transformation constant, K_L, has been determined kinetically in 1.0 $mol \cdot dm^{-3}$ $NaClO_4$ and at 23 °C. A previous determination in 0.1 $mol \cdot dm^{-3}$ $NaClO_4$ and at 23 °C has been reinterpreted. The values obtained have been coupled with other data in the literature to demonstrate that the magnitude of the transformation constant is independent of ionic strength, and its value was determined to be $\log K_L^\circ = 0.80 \pm 0.02$. Data from the literature for the dissociation of α-D-isosaccharinic acid have been re-evaluated to determine both the "intrinsic" and "composite" dissociation constants at zero ionic strength, namely, $\log K_a^\circ = -4.04 \pm 0.06$ and $\log K_c^\circ = -4.90 \pm 0.07$, respectively. The present data permit a much more thorough understanding of the aqueous chemistry of α-D-isosaccharinic acid to be ascertained than has previously been possible.

Introduction

Low- and intermediate-level nuclear wastes are frequently stored in concrete-lined repositories. A proportion of the wastes in the repositories are in the form of cellulose-containing materials. The long-term degradation of concrete in contact with groundwater will result in solutions of high pH which, in turn, will degrade the cellulose to produce organic byproducts such as α-D-isosaccharinic acid.

A number of studies[1−4] have shown that α-D-isosaccharinic acid can form strong complexes with actinides and other metals that might be present in the repositories, thereby enhancing the solubility of these actinides/metals. As a consequence, knowledge of the behavior of α-D-isosaccharinic acid is crucial for understanding the potential mobility of radionuclides in the environment of the nuclear waste repositories.

It is well-known[5−8] that α-D-isosaccharinic acid undergoes a lactonization reaction. The two forms of the acid are illustrated in Figure 1. The reaction between the two forms is described by reaction 1.

$$\mathrm{HISA} \leftrightarrow \mathrm{ISA_L} + \mathrm{H_2O} \qquad (1)$$

where HISA is the protonated carboxylic acid (α-D-isosaccharinic acid); ISA_L is the lactone form (α-D-isosaccharino-1,4-lactone); and the stability of the reaction is described by the lactonization or transformation constant. Ekberg et al.[5] have shown that the conversion between the carboxylic acid form and the lactone occurs relatively slowly, a process that can be monitored kinetically although this fact has not been adequately understood. This behavior has also been shown for other similar hydroxycarboxylic acids.[9,10] The transformation reaction complicates the proton dissociation of the acid to form the α-D-isosaccharinate ion, and two dissociation constants, an "intrinsic" and a "composite" constant, have been proposed. The intrinsic constant is a measure of only the proton dissociation of α-D-isosaccharinic acid to the α-D-isosaccharinate ion, whereas the composite constant is a measure of the sum of the proton dissociations of both the carboxylic acid and the lactone to give the α-D-isosaccharinate ion. The composite constant is similar to that defined for the dissociation of carbonic acid (H_2CO_3), where a composite constant is given for all dissolved CO_2, where the total analytical dissolved CO_2 concentration, [H_2CO_3*], is equated to the sum of the concentrations of [$H_2CO_3(aq)$] and [$CO_2(aq)$].[11] Thus, a similar concentration can be defined for the total HISA concentration, [HISA*], which is equal to the sum of the concentrations of [HISA] and [ISA_L], and the composite constant is related to the concentration of [HISA*].

The complexity in the aqueous chemistry of α-D-isosaccharinic acid has led to considerable uncertainty with respect to the magnitude of the dissociation constant.[8] This is exacerbated by the fact that the transformation reaction occurs slowly.[5] Additional uncertainties associated with whether studies have measured the intrinsic or composite constant have led to a very uncertain dissociation constant being selected for α-D-isosaccharinic acid in a recent review of its thermochemistry.[8]

As a consequence of the uncertainty in the aqueous chemistry of α-D-isosaccharinic acid, there is a need to re-evaluate the

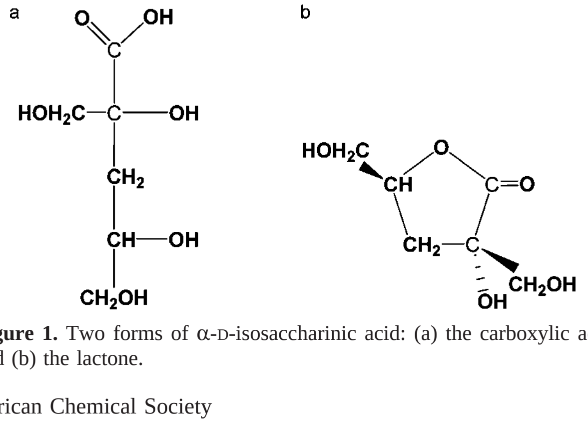

Figure 1. Two forms of α-D-isosaccharinic acid: (a) the carboxylic acid and (b) the lactone.

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dissociation and transformation reactions and their associated constants. In this study, the transformation constant in 1 $\text{mol}\cdot\text{dm}^{-3}$ $NaClO_4$ and at 23 °C has been measured from kinetic data. The constant has been combined with other data available in the literature to determine the transformation constant at zero ionic strength as well as both the intrinsic and composite dissociation constants also at zero ionic strength.

Experimental Section

Chemicals. Solutions of α-D-isosaccharinic acid were prepared from calcium α-D-isosaccharinate ($Ca(ISA)_2$: 98 % purity, Alfa-Aesar). To prepare the acid, a Sigma Dowex-50W (8 % cross-linkage, 76689-17-3) ion-exchange resin was employed to remove the calcium. Solutions of (0.1 and 1.0) $\text{mol}\cdot\text{dm}^{-3}$ $NaClO_4$ were prepared from sodium perchlorate monohydrate (Merck, pro analysi). Solutions of 0.1 $\text{mol}\cdot\text{dm}^{-3}$ NaOH, 1.0 $\text{mol}\cdot\text{dm}^{-3}$ NaOH, 0.1 $\text{mol}\cdot\text{dm}^{-3}$ $HClO_4$, and 1.0 $\text{mol}\cdot\text{dm}^{-3}$ $HClO_4$ were prepared with Riedel-de Haën Titrisol ampules. Standard pH buffers were used in the calibration of the pH electrode and were from Radiometer Analytical (7.000, 10.012 and 12.45) and Mettler-Toledo (4.01).

Method. The transformation constant, K_L, in 1 $\text{mol}\cdot\text{dm}^{-3}$ $NaClO_4$ and at (23.0 ± 0.3) °C has been determined from the rate of conversion of HISA to ISA_L. An approximately 10 $\text{mmol}\cdot\text{dm}^{-3}$ solution of HISA, at a pH of approximately 1, was prepared from a stock solution of alkaline ISA using 1 $\text{mol}\cdot\text{dm}^{-3}$ $HClO_4$. Analysis by ion chromatography was commenced immediately after the addition of the $HClO_4$, with one measurement being taken every 10 to 15 min up to a total of about 500 min reaction time. The transformation behavior followed typical first-order reaction kinetics, and the appropriate equations were used to determine both the rate and transformation constants. The ion chromatography analyses were performed with a Dionex DX-100 ion chromatograph using conductivity detection. Organic compounds were detected using an IonPac ICE-AS6 column, HFBA eluent, and AMMS-ICE II suppressor/TBAOH regenerant. The performance of this column, which uses a Donnan exclusion mechanism for retention and separation of weakly ionized acids based on differences in pK_a, was found to be superior to an anionic column. Although the detector only measures ISA^-, any HISA present in a sample being analyzed will be converted to ISA^- during its passage through the suppresor, and consequently, the measurement gives $[ISA^-]$ + [HISA].

Determination of Transformation Constant from Transformation Kinetics. At low pH, where the concentration of the deprotonated form of ISA is negligible, there is interaction between HISA and ISA_L as described by eq 1. The stability constant for this reaction (K_L) can be described by eq 2, where k_1 is the forward and k_{-1} the backward rate constant, and the subscript eq denotes that the concentrations are at equilibrium. The mass balance between these latter two forms can be described by eq 3.

$$K_L = k_1/k_{-1} = [ISA_L]_{eq}/[HISA]_{eq} = [ISA_L]_{eq}/([ISA]_{total} - [ISA_L]_{eq}) \quad (2)$$

$$[ISA]_{total} = [HISA] + [ISA_L] = [HISA]_{eq} + [ISA_L]_{eq} \quad (3)$$

The interaction between the protonated (HISA) and lactone (ISA_L) form of ISA is a relatively slow process that can be followed kinetically. The rate of transformation of HISA to ISA_L can be described by eq 4.

$$d[ISA_L]/dt = k_1[HISA] - k_{-1}[ISA_L] \quad (4)$$

The rate of change of reaction 1 can be followed by initially preparing a solution of ISA^- at high pH (where the concentrations of both HISA and ISA_L are negligible) and then quickly adding acid to convert the ISA^- to HISA and determining the concentration of ISA_L (calculated by subtracting the measured HISA concentration from the total ISA concentration) at various times using ion chromatography. Thus, eq 4 needs to be converted into an equation that only contains terms relating to the concentration of ISA_L. This can be achieved by substituting the equilibrium and mass balance equations (eqs 2 and 3) into eq 4, which upon rearrangement leads to eq 5.

$$d[ISA_L]/dt = (k_1 + k_{-1})([ISA_L]_{eq} - [ISA_L]) \quad (5)$$

Further rearrangement and integration gives eq 6.

$$\ln(([ISA_L]_{eq} - [ISA_L])/[ISA_L]_{eq}) = -(k_1 + k_{-1})t \quad (6)$$

Equation 6 can also be rearranged to give eq 7.

$$\ln([ISA_L]_{eq} - [ISA_L]_t) = \ln([ISA_L]_{eq}) - (k_1 + k_{-1})t \quad (7)$$

Thus, it is apparent that a plot of $\ln([ISA_L]_{eq} - [ISA_L]_t)$ against time should be linear with an intercept equal to $\ln([ISA_L]_{eq})$ and a slope equal to $-(k_1 + k_{-1})$. The value of K_L can then be obtained from the determined value of $[ISA_L]_{eq}$ and the total concentration of ISA, i.e., $K_L = [ISA_L]_{eq}/([ISA]_{total} - [ISA_L]_{eq})$. Further, given that K_L is also equal to k_1/k_{-1}, the individual values of k_1 and k_{-1} can be determined from this equality and the slope of the linear fit.

The measured kinetic data for an ionic strength of (0.1 and 1.0) $\text{mol}\cdot\text{dm}^{-3}$ $NaClO_4$ are listed in Table 1 and displayed in Figure 2, in which the linear relationship between $\ln([ISA_L]_{eq} - [ISA_L]_t)$ and time is illustrated. The data in Table 1 for 0.1 $\text{mol}\cdot\text{dm}^{-3}$ are from Ekberg et al.[5] but have been re-evaluated in the present work. There is, however, a problem in determining the data given in Table 1 and illustrated in Figure 2. That is, it is difficult to determine the actual value of $[ISA_L]_{eq}$. An attempt was made, in this study, to determine this value by allowing the reaction to proceed for long times, but there were always uncertainties as to whether true equilibrium had been attained at these long times. Consequently, the value was determined iteratively in the linear regression since the value for $[ISAL]_{eq}$ in the expression $\ln([ISA_L]_{eq} - [ISA_L]_t)$ must be equal to the value determined from the intercept (i.e., $\ln[ISA_L]_{eq}$) in the regression. It was found that the final value determined for $[ISA_L]_{eq}$ by the regression analysis in this iterative approach was marginally higher than the measured concentration, at long reaction times, indicating that equilibrium in the solution had not been fully reached. Table 2 contains the values of K_L, k_1, and k_{-1} determined from the regression analysis for the data from the two ionic strengths.

The value in 0.1 $\text{mol}\cdot\text{dm}^{-3}$ $NaClO_4$ has been previously determined by Ekberg et al.[5] However, the methodology used in this earlier work relied on a value for $[ISA_L]_{eq}$ that was

Table 1. Kinetic Data Acquired for the Determination of the Transformation Constant, K_L, in (0.1 and 1.0) mol·dm^{-3} NaClO$_4$ and at 23 °C

0.1 mol·dm^{-3} NaClO$_4$			1.0 mol·dm^{-3} NaClO$_4$		
t	$[ISA_L]_t$		t	$[ISA_L]_t$	
min	mmol·dm^{-3}	$\ln([ISA_L]_{eq} - [ISA_L]_t)$[a]	min	mmol·dm^{-3}	$\ln([ISA_L]_{eq} - [ISA_L]_t)$[a]
13.5	0.36	1.38	15.3	0.92	2.09
24.5	0.67	1.30	27.2	1.40	2.03
35.0	0.88	1.24	38.9	1.82	1.97
45.5	1.06	1.19	50.4	2.16	1.93
56.5	1.28	1.12	62.0	2.64	1.85
67.0	1.41	1.08	73.5	2.91	1.81
77.5	1.60	1.01	85.0	3.45	1.72
88.5	1.70	0.97	96.8	3.97	1.62
99.0	1.87	0.90	108.9	4.37	1.54
109.5	1.99	0.85	120.9	4.71	1.46
120.0	2.13	0.79	132.9	5.18	1.35
130.5	2.28	0.72	145.0	5.18	1.34
141.5	2.41	0.66	157.0	5.46	1.27
152.0	2.53	0.60	169.0	5.82	1.16
162.5	2.62	0.54	181.0	6.00	1.10
173.5	2.71	0.49	193.1	6.39	0.96
184.0	2.79	0.44	205.1	6.63	0.87
194.5	2.92	0.36	217.1	6.88	0.76
205.5	3.00	0.30	229.1	6.99	0.71
216.0	3.09	0.23	241.2	7.07	0.66
226.5	3.16	0.17	253.2	7.12	0.64
237.0	3.23	0.11	265.2	7.33	0.52
247.5	3.33	0.02	277.3	7.51	0.41
269.0	3.36	−0.01	289.3	7.58	0.36
295.5	3.56	−0.24	301.3	7.70	0.27
316.5	3.61	−0.31	313.4	7.74	0.25
337.0	3.72	−0.46	325.4	7.86	0.15
357.5	3.80	−0.61	337.4	7.82	0.18
378.5	3.85	−0.70	349.4	7.94	0.07
399.0	3.90	−0.80	361.4	8.06	−0.04
419.5	3.95	−0.93	373.5	8.12	−0.11
440.5	4.02	−1.11	385.5	8.16	−0.16
			397.5	8.24	−0.26
			409.5	8.22	−0.23
			421.6	8.34	−0.39
			433.6	8.39	−0.47
			445.6	8.43	−0.53
			457.7	8.52	−0.70
			469.7	8.50	−0.67
			481.8	8.57	−0.80
			493.9	8.55	−0.78

[a] The value for $[ISA_L]_{eq}$ was determined by iterative regression analysis (see Table 2) such that the value used in the term ($\ln([ISA_L]_{eq} - [ISA_L]_t)$) was equal to the value determined from the intercept of the regression equation.

determined by measurement of the ISA$_L$ concentration after a long period of time (ca. 1300 min). It is clear from subsequent analysis of the data that has been performed in the present work that equilibrium had not been established in the experiment performed by Ekberg et al.[5] Thus, the value of $[ISA_L]_{eq}$ determined experimentally by Ekberg et al.[5] was slightly smaller than, but outside the uncertainty bounds of, the value that they determined numerically (i.e., from regression analysis). Consequently, the data from Ekberg et al.[5] were reevaluated in this study using the iterative procedure outlined above.

The value determined for log K_L was the same (Table 2), within the uncertainty bounds, in both (0.1 and 1.0) mol·dm^{-3} NaClO$_4$, i.e., 0.80 ± 0.02 and 0.81 ± 0.04, respectively. This is to be expected since both the reactant, HISA, and the product, ISA$_L$, are uncharged, and consequently the dependence of the reaction on ionic strength should be minimal.

It is also possible to determine the value of the transformation constant from the data given in the study of Cho et al.[7] They studied the acidity and structure of ISA using solutions of NaISA and Ca(ISA)$_2$. From the data presented by Cho et al.,[7] values of 6.52 and 5.25, respectively, can be calculated for K_L from the two solutions. These values were determined in solutions close to zero ionic strength. It has been assumed in this study that the transformation constant for the conditions studied by Cho et al.[7] is the average of the above two values and that the uncertainty spans the range of the two values, leading to a value for log K_L of 0.77 ± 0.05. This value is in excellent agreement with the values determined in this study at higher ionic strengths and again indicates that the magnitude of the transformation reaction is independent of ionic strength.

The value for the transformation constant at zero ionic strength is taken as the average of the above three independent values, i.e., log $K_L^o = 0.79 \pm 0.04$. This value is within the uncertainty estimates of all three of the measured values.

Dissociation Constants. The association reaction of α-D-isosaccharinate and its concomitant constant, K_1, are given in eqs 8 and 9.

$$ISA^- + H^+ \leftrightarrow HISA \tag{8}$$

$$K_1 = [HISA]/[H^+][ISA^-] \tag{9}$$

Similarly, the association reaction of α-D-isosaccharino-1,4-lactone and its constant, K_2, is given by eqs 10 and 11.

$$ISA^- + H^+ \leftrightarrow ISA_L \tag{10}$$

$$K_2 = [ISA_L]/[H^+][ISA^-] \tag{11}$$

The composite association constant, K_3, is written in terms of the total analytical concentration of HISA, i.e., $[HISA^*] = [HISA] + [ISA_L]$, in a similar manner to that of carbonic acid, $[H_2CO_3^*] = [H_2CO_3] + [CO_2(aq)]$.[11] Thus

$$K_3 = [HISA^*]/[H^+][ISA^-] = ([HISA] + [ISA_L])/[H^+][ISA^-] \tag{12}$$

The transformation constant was defined in eq 2, from which the concentration of the lactone can be defined by

$$[ISA_L] = K_L[HISA] \tag{13}$$

Substituting this equation into eq 12 gives

$$K_3 = ([HISA](1 + K_L))/[H^+][ISA^-] = K_1(1 + K_L) \tag{14}$$

Inversion of eq 14 leads to the relationship between the composite dissociation constant, K_c, and the intrinsic dissociation constant, K_a

$$K_c = K_a/(1 + K_L) \tag{15}$$

where $K_c = 1/K_3$ and $K_a = 1/K_1$.

It is apparent from eq 15 that the intrinsic dissociation constant of α-D-isosaccharinic acid is larger than the composite dissociation constant. Furthermore, it is also evident from the above discussion that the intrinsic dissociation constant is larger than the dissociation constant of α-D-isosaccharino-1,4-lactone by a factor of K_L.

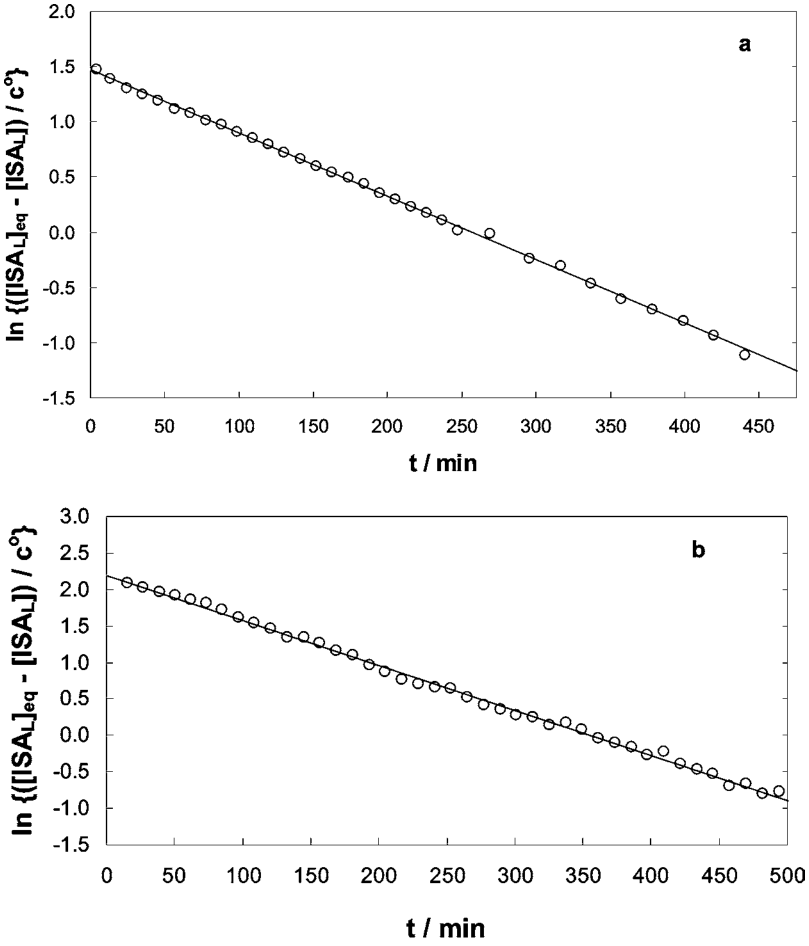

Figure 2. Plot of ln($[ISA_L]_{eq} - [ISA_L]$) versus time in (a) 0.1 mol·dm^{-3} $NaClO_4$ and (b) 1.0 mol·dm^{-3} $NaClO_4$ at 23 °C. The $[ISA_L]_{eq}$ and $[ISA_L]$ concentrations are in mmol·dm^{-3}, and c^o is equal to 1 mmol·dm^{-3}.

Table 2. Equilibrium and Kinetic Data at 23 °C Determined from the Transformation Kinetic Experiment[a]

$[ISA]_{total}$ mmol·dm^{-3}	$[ISA]_{eq}$[b] mmol·dm^{-3}	$(k_1 + k_{-1})$[c] min^{-1}	K_L[d]	log K_L	k_1 min^{-1}	k_{-1} min^{-1}
		0.1 mol·dm^{-3} $NaClO_4$				
5.04	4.35	0.00574	6.27	0.80	0.00495	0.00079
	0.03	0.00003	0.29	0.02	0.00004	0.00003
		1.0 mol·dm^{-3} $NaClO_4$				
10.40	9.01	0.00618	6.51	0.81	0.00536	0.00082
	0.13	0.00005	0.63	0.04	0.00009	0.00007

[a] The uncertainty is given below each value and is at the 95 % confidence level. [b] Value determined from intercept of iterative linear regression (see Figure 2). [c] Value determined from slope of iterative linear regression (see Figure 2). [d] Value determined from $[ISA]_{eq}$ and $[ISA]_{total}$ through eq 2.

Table 3. Reported Dissociation Constants of α-D-Isosaccharinic Acid at Various Ionic Strengths and ca. 25 °C

I/mol·dm^{-3}	log K_a	reference
0.0015	−4.02 ± 0.05[a]	Motellier et al.[10]
0.002	−4.05 ± 0.05[a]	Motellier and Charles[11]
0.01	−3.83 ± 0.1[a]	Hagberg[12]
0.1	−3.75 ± 0.1[a]	Hagberg[12]
0.1	−3.77 ± 0.1[a]	Hagberg et al.[13]
1.0	−3.78 ± 0.05	Ekberg et al.[9]
1.0	−3.65 ± 0.05	Rao et al.[14]

[a] Uncertainties assigned by this study.

Ekberg et al.[12] measured the intrinsic dissociation constant by performing a rapid potentiometric titration that minimized the formation of the lactone. The constant obtained is in good agreement with other literature data[13−17] at variable ionic strength, as is shown in Table 3. Given the good agreement, it is clear that these other studies have also measured the intrinsic constant. If the studies had measured the composite dissociation constant, they would differ by a factor of 7.17 (= 1 + 6.17, from eq 15; where 6.17 is equal to $10^{0.79}$, the value for the transformation constant given above). The composite dissociation constant, therefore, would be approximately 0.86 log units more negative than the intrinsic dissociation constant. This difference is much greater than can be explained from variations in the constant with changes in ionic strength over the range listed in Table 3 (about (0 to 1) mol·dm^{-3}).

The specific ion interaction theory (SIT) has been used to determine the intrinsic dissociation constant of α-D-isosaccharinic acid at zero ionic strength using the data listed in Table 3. For α-D-isosaccharinic acid, the SIT can be expressed (for K_a, the inverse of eq 9) by the following equation

$$\log K_a - 2D = \log K_a{}^\circ - \Delta\varepsilon I \tag{16}$$

where D is equal to $0.509I^{1/2}/(1 + 1.5I^{1/2})$; I is the ionic strength (in mol·kg^{-1}); the value of 2 comes from Δz^2, the difference in the sum of the square of the charge of the products minus the sum of the square of the charge of the reactants; and $\Delta\varepsilon$ (= $\varepsilon(ISA^-, Na^+) + \varepsilon(H^+, ClO_4^-)$) is the specific ion interaction coefficient.[8] A plot of log $K_a - 2D$ against I should be linear with an intercept of log $K_a{}^\circ$ and a slope of $-\Delta\varepsilon$ as shown in

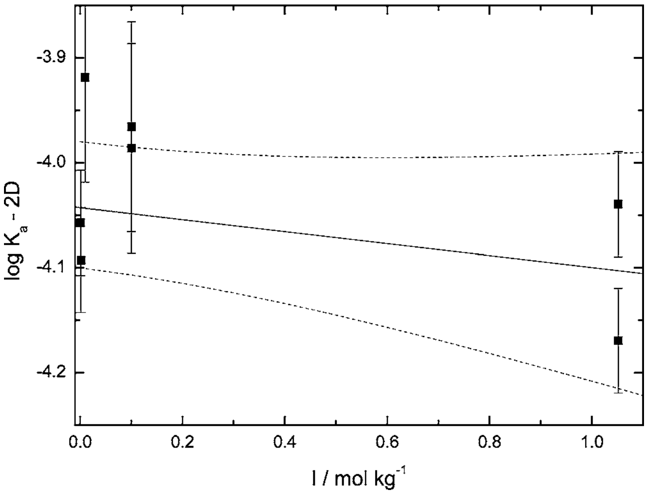

Figure 3. Variation of the dissociation constant at ca. 25 °C with respect to ionic strength, *I*, using the specific ion interaction theory. The solid line is the best fit of the weighted linear regression, and the dotted lines are the 95 % confidence limits.

Figure 3. The value of log $K_a°$ determined from the weighted (using the uncertainty in each value. Table 3) linear regression is -4.04 ± 0.06, where the uncertainty is the 95 % confidence value. Also, the value of $\Delta\varepsilon$ was found to be (0.06 ± 0.09) kg·mol^{-1}; from this value, the magnitude of the interaction between ISA$^-$ and Na$^+$, $\varepsilon(\text{ISA}^-, \text{Na}^+)$, was found to be $-(0.08 \pm 0.09)$ kg·mol^{-1} [the value for $\varepsilon(\text{H}^+, \text{ClO}_4^-)$ was taken from Hummel et al.[8]]. This latter value assumes that the interaction coefficient between the uncharged HISA molecule and charged ions (Na$^+$ or ClO$_4^-$) is equal to zero. It is within the range found for other monovalent anions with sodium.[8] Although some of the data used in the regression performed using eq 16 were not obtained from measurements undertaken in NaClO$_4$, these measurements were at the lower ionic strengths where differences between different media are relatively small. Nevertheless, the assigned uncertainties, as listed in Table 3, were increased for these data.

Using the values calculated at zero ionic strength for the intrinsic dissociation constant, log $K_a°$, and the transformation constant, log K_L, the dissociation constant for the lactone, log$(K_a)_L$ $(= -\log K_2)$, at zero ionic strength is obtained from the summation of the two values, i.e., -4.83 ± 0.07. In addition, the composite constant, log $K_c°$, is determined by using eq 15, i.e., -4.90 ± 0.07.

A value of -4.46 was obtained for log $K_a°$ by Rai et al.[18] while determining the solubility of Ca(ISA)$_2$. There is no indication given in this work that the transformation reaction had been taken into account, and thus, it is possible that the composite dissociation constant was determined. However, the dissociation constant obtained by Rai et al.[18] is between what is derived in this work for the intrinsic and composite dissociation constants. In addition, the solubility data were interpreted in terms of formation of the aqueous complex Ca(ISA)$_2$. Subsequently, Rai et al.[19] reanalyzed their earlier work where the formation of the Ca(ISA)$_2$(aq) complex was excluded. Instead, dissolution of Ca(ISA)$_2$(s) to Ca^{2+} and ISA$^-$ was proposed, with the reinterpreted solubility constant being consistent with other data in the literature.[20,21] As a consequence, the validity of the ISA dissociation constant obtained in the earlier work is questionable. This conclusion was also reached by Hummel et al.[8] in their review of ISA complexation.

The dissociation of α-D-isosaccharinic acid was also studied by Cho et al.[7] The values determined for log $K_a°$ in the study were -3.27 in NaISA solutions and -3.36 in Ca(ISA)$_2$ solutions. These are considerably different from the value determined in this study, but the difference is approximately equal to log K_L. Because of this difference, Hummel et al.[8] suggested that Cho et al.[7] had actually measured the intrinsic dissociation constant. Certainly, this is not inconsistent with the difference between the intrinsic and composite dissociation constants, i.e., 0.86 log units. If the value measured by Cho et al.[7] is the intrinsic constant, this would suggest that the data listed in Table 3 are for the composite dissociation constant. However, the dissociation constants determined by Cho et al.[7] were obtained from D$_2$O solutions from which a solution pH was estimated from the solution pD. The pH was then used to determine the log K_a. The estimation of a dissociation constant relevant to an H$_2$O solvent from measurements taken in D$_2$O is clearly problematic. Further, as argued above, the data listed in Table 3 relate to the intrinsic rather than the composite dissociation constant. As such, the log $K_a°$ value determined by Cho et al.[7] is inconsistent with other data most likely because of the difficulties in conversion of the data from D$_2$O to H$_2$O.

More recently, Rao et al.[17] have studied the protonation of α-D-isosaccharinic acid at 25 °C and in 1.0 mol·dm^{-3} NaClO$_4$. The value they determined for the dissociation constant was -3.64 ± 0.05 in good agreement with the earlier value of Ekberg et al.[12] in the same medium. Rao et al.[17] concluded that they had measured the composite dissociation constant since it was lower than the dissociation constant determined earlier by Cho et al.[7] that they believed was the intrinsic dissociation constant. From the difference in the two values, they determined that the value for log K_L was 0.37 at $I = 0$. However, this value is 0.4 log units lower than can be determined from the data provided by Cho et al.[7] for log K_L (see above). Rao et al.[17] performed titrations from pH values above and below the log K_a. Thus, the conversion of HISA to ISA$_L$ in these titrations, particularly in the titration from pH values above the log K_a, would have been minimal since initially there would have been a low HISA concentration and that subsequently would only be slowly converted to ISA$_L$. Given the similarity of the log K_a measured by Rao et al.[17] with that measured by Ekberg et al.,[12] the latter who designed their experiment to measure the intrinsic dissociation constant, it is suggested that the former also measured the intrinsic constant.

The thermochemistry of α-D-isosaccharinic acid complexation has recently been reviewed by Hummel et al.[8] Because of the inconsistencies in the literature associated with identification of the composite and intrinsic dissociation constants, Hummel et al. chose a value of -4.0 ± 0.5 for the composite dissociation constant of α-D-isosaccharinic acid at zero ionic strength. It is apparent from the information presented in the present study that the value selected by Hummel et al.[8] is for the intrinsic dissociation constant, and the composite dissociation constant is some 0.9 log units lower.

Speciation of α-D-Isosaccharinic Acid. The speciation of α-D-isosaccharinic acid is illustrated in Figure 4 as a function of $-\log[\text{H}^+]$ for 0.1 mol·dm^{-3} NaClO$_4$. The relevant constants for this ionic strength are -3.70 for log K_a, 0.79 for log K_L, and -4.56 for log K_c.

Ekberg et al.[5] studied the speciation of α-D-isosaccharinic acid in 0.1 mol·dm^{-3} NaClO$_4$ by preparing a number of solutions containing the acid at different pH values and allowing them to reach equilibrium. The concentration of ISA$^-$ plus HISA was measured using ion chromatography. The data are also plotted in Figure 4. It is clear that the solid thick line shown on the figure, representing [ISA$^-$] + [HISA], obtained from the

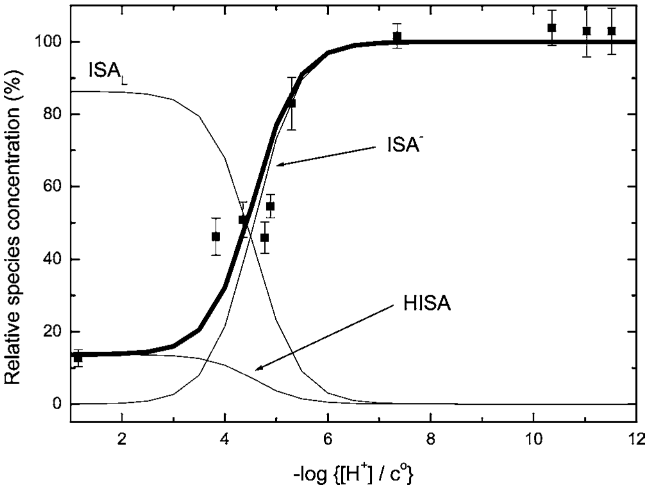

Figure 4. Relative concentrations of α-D-isosaccharinic acid in 0.1 mol·dm^{-3} $NaClO_4$ and at 23 °C. The solid thick line represents the percentage of ISA$_{total}$ given by the concentration of HISA and ISA$^-$. The points and their respective uncertainties are the measured values for this same sum of concentrations from Ekberg et al.[5] The proton concentration is in mol·dm^{-3}, and $c°$ is equal to 1 mol·dm^{-3}.

constants listed above, is in reasonable accordance with the equilibrium concentrations determined by Ekberg et al.[5] This confirms the speciation of α-D-isosaccharinic acid and its associated acid and transformation (lactonization) constants that have been derived in this study.

Enthalpy of Dissociation. The enthalpy of dissociation of α-D-isosaccharinic acid has been studied by both Ekberg et al.[5] and Rao et al.[17] The enthalpy in the former study[5] was determined from the variation of the dissociation constant over a small temperature range [(23 to 44) °C], and the enthalpy was found to be $-(21.5 \pm 1.5)$ kJ·mol^{-1}, although this value was later re-evaluated using a statistical approach where an enthalpy of $-(21.2 \pm 0.5)$ kJ·mol^{-1} was derived.[6] Rao et al.[17] determined the enthalpy using an isoperibol calorimetric titration and obtained a value of $-(7.94 \pm 0.03)$ kJ·mol^{-1}; this latter value is significantly different from that determined by Ekberg et al.[5,6]

As indicated earlier, the measurement of the dissociation constant using potentiometry by Ekberg et al.[5] gave the intrinsic constant, and thus, the enthalpy they determined also relates to that for the intrinsic dissociation represented in eq 8. On the contrary, the calorimetric measurement of the enthalpy of dissociation requires a thermal equilibration period which is likely sufficient to enable formation of the lactone. Thus, it is probable that the enthalpy determined by Rao et al.[17] relates to that represented by eq 10. On this basis, therefore, and taking both enthalpies into account, the enthalpy of the lactonization reaction (eq 1) is endothermic and equal to $(-7.94 \pm 0.03 + 21.2 \pm 0.5) = (13.3 \pm 0.3)$ kJ·mol^{-1}. These data relate to the enthalpy at 25 °C.

Conclusions

Results from studies of the transformation of α-D-isosaccharinic acid to α-D-isosaccharino-1,4-lactone, obtained from both the present study and previous studies available in the literature, demonstrate that, as expected, the magnitude of the reaction is independent of ionic strength. This independence allowed the value at zero ionic strength to be determined from the average of the various values available and was found to be $\log K_L° = 0.79 \pm 0.04$. The magnitude of this constant indicates that, at equilibrium, the lactone dominates over the carboxylic acid form.

Data available in the literature for the dissociation of α-D-isosaccharinic acid are relatively consistent when differences in ionic strength are considered. This enabled the dissociation constant at zero ionic strength to be determined. Given that the transformation reaction proceeds slowly, the available data in the literature are for the intrinsic dissociation constant which, at zero ionic strength, was found to be -4.04 ± 0.06 ($\log K_a°$). From the intrinsic dissociation constant and the transformation constant, the composite dissociation constant, $\log K_c°$, was found to be -4.90 ± 0.07.

The enthalpy of reaction of the dissociation to give the α-D-isosaccharinate ion was found earlier[5] to be $-(21.2 \pm 0.5)$ kJ·mol^{-1}, whereas it is suggested that the calorimetric determination,[17] giving a value of $-(7.94 \pm 0.03)$ kJ·mol^{-1}, is for the formation of α-D-isosaccharino-1,4-lactone. Taking these two values together, the enthalpy of the lactonization reaction was calculated to be (13.3 ± 0.3) kJ·mol^{-1}. The data relate to the enthalpy at 25 °C.

All of these data are required to fully understand the aqueous behavior of α-D-isosaccharinic acid. These data will be of essential value in understanding the complexation capacity of the acid in nuclear waste repositories.

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