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ORIGINAL PAPER

Volumetric properties of aqueous solutions of quinic acid and its sodium salt

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Abstract The apparent molar volume of quinic acid and its sodium salt were determined from the density data of aqueous solutions up to molality of 0.4 mol kg^{-1} and in the temperature range from 293.15 to 328.15 K. The apparent molar volume of sodium quinate comprises the ionic and the associated ion-pair contributions. From the apparent molar volumes of quinic acid and the quinate ion, the molecular contributions to that of quinic acid are derived. At 298.15 K, the limiting apparent molar volume of quinic acid is 119.8 ± 0.5 cm^3 mol^{-1}, and that of the quinic ion is 111.6 ± 0.3 cm^3 mol^{-1}. Similarly, at 298.15 K, the limiting apparent molar expansibility of sodium quinate is 0.198 ± 0.003 cm^3 mol^{-1} K^{-1}, and that of quinic acid is 0.142 ± 0.003 cm^3 mol^{-1} K^{-1}. From these limiting ionic and molecular apparent molar volumes, the limiting volume change caused by ionization of quinic acid was calculated as -8.2 cm^3 mol^{-1} at 298.15 K. The coefficients of thermal expansion of these solutions were calculated from the density data, and from these the apparent molar expansibilities of quinic acid and its sodium salt were derived.

Keywords Density data · Expansibility · Quinic acid · Sodium quinate · Natural products · Carboxylic acids

Introduction

D-(−)-Quinic acid [(1*R*,3*R*,4*R*,5*R*)-(−)-1,3,4,5-tetrahydroxycyclohexane-1-carboxylic acid] (Fig. 1) is a weak electrolyte that is of considerable biological interest. It is found free and in the form of various esters, which primarily include caffeic, ferulic, sinapic and gallic acids [1]. Quinic acid occupies a predominant position among the metabolites of D-glucose, and it is also a biogenic precursor of shikimic acid, which is involved in the biosynthesis of many natural products that contain an aromatic ring, including essential amino acids and folic acid [1]. Quinic acid has four chiral centres, and it is commercially available in a form of very high enantiomeric purity. It thus represents an attractive starting material for asymmetric multistep syntheses of naturally occurring substances and related compounds [2, 3]. Quinic acid is a polyfunctional molecule, with five functional groups that can coordinate to metallic ions [4–6], and it can interact with proteins in a variety of ways [7] (Fig. 1).

The volumetric properties of an electrolyte in solution can provide useful information for insights into interactions that occur in aqueous solution between the ions, the associated electrolyte and the solvent. From a theoretical point of view, the most useful quantities are the limiting values of the apparent molar volume and the apparent molar expansibility, since these only depend on the intrinsic size of the ion and on ion–solvent interactions [8, 9]. The densities of solutions of quinic acid are not published in the literature. Thus, we used here the measured densities of quinic acid and sodium quinate in the temperature range from 293.15 to 328.15 K to determine the apparent molar volumes, V_ϕ, and expansibilities, ϕ_E, of their aqueous solutions. The temperature dependence of the volume changes caused by the ionization of quinic acid was determined.

Results and discussion

The density data for aqueous solutions of sodium quinate and quinic acid as a function of solute molality and

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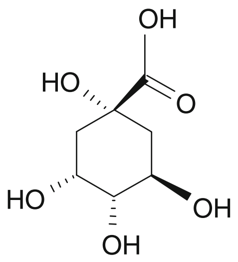

Fig. 1 Structure of D-(−)-quinic acid: (1*R*,3*R*,4*R*,5*R*)-(−)-1,3,4,5-tetrahydroxycyclohexane-1-carboxylic acid

temperature are given in Table 1. The density data for sodium quinate and quinic acid were converted to apparent molar volumes, V_ϕ (cm^3 mol^{-1}), using

$$V_\phi = \frac{(d_0 - d)}{cd_0} + \frac{M_2}{d_0}, \tag{1}$$

where c is the molar concentration (mol dm^{-3}), d_0 is the density of pure water (g cm^{-3}) and M_2 is the molar mass of the solute (g mol^{-1}). The density data for pure water were taken from [10]. The data for apparent molar volume are given in Table 2. The uncertainty of the apparent molar volume determination, ΔV_ϕ, is calculated from

$$(\Delta V_\phi)^2 = \left(-\frac{\Delta d}{cd_0}\right)^2, \tag{2}$$

since ΔV_ϕ is not seriously influenced by uncertainties in molality and the density of water. ΔV_ϕ ranges from 0.43 cm^3 mol^{-1} at the lowest molality to 0.04 cm^3 mol^{-1} at the highest molality.

In analysing the partial molar volumes of sodium quinate, an ionic association process was assumed, i.e. an equilibrium between free ions and the associated ion pairs ($\mathrm{Na^+Qu^-}$), as

$$\mathrm{Qu^-} + \mathrm{Na^+} \rightleftarrows \mathrm{Na^+Qu^-}. \tag{3}$$

The equilibrium association constant for reaction 3 is given by

$$K_\mathrm{A} = \frac{a_{\mathrm{Na^+Qu^-}}}{a_{\mathrm{Na^+}} a_{\mathrm{Qu^-}}}, \tag{4}$$

where a are the activities of the relevant species. Equation 4 can be given as

$$K_\mathrm{A} = \frac{(1-\gamma)}{\gamma^2 c} \frac{f_{\mathrm{Na^+Qu^-}}}{f_i^2}, \tag{5}$$

where γ is the fraction of free, unassociated ions in the solution, and f_i is the activity coefficient of the corresponding ions ($i = \mathrm{Na^+}, \mathrm{Qu^-}$) $(f_i)^2 = f_{\mathrm{Na^+}} f_{\mathrm{Qu^-}}$. In Eq. 5, some simplification can be introduced by assuming $f_{\mathrm{Na^+Qu^-}} \cong 1$.

Table 1 The density, *d*, of aqueous solutions of sodium quinate (NaQu) and quinic acid (HQu) in the temperature range from 293.15 to 328.15 K

m (mol kg^{-1})	*d* (g cm^{-3}) at *T* (K)[a]					
	293.15	298.15	303.15	308.15	318.15	328.15
NaQu						
0.03095	1.001438	1.000243	0.998817	0.997171	0.993306	0.988756
0.06220	1.004670	1.003442	1.001988	1.000319	0.996411	0.991828
0.07680	1.006158	1.004916	1.003447	1.001768	0.997842	0.993239
0.12696	1.011235	1.009940	1.008426	1.006707	1.002714	0.998061
0.16923	1.015466	1.014127	1.012574	1.010823	1.006775	1.002078
0.19430	1.017970	1.016609	1.015035	1.013631	1.009183	1.00446
0.21744	1.020232	1.018848	1.017255	1.015467	1.011359	1.006612
0.29381	1.027658	1.026207	1.024553	1.022710	1.018510	1.013691
0.36328	1.034226	1.032710	1.031001	1.029109	1.024827	1.019945
0.41018	1.038587	1.037029	1.035282	1.033357	1.029021	1.024097
HQu						
0.040329	1.001187	0.999998	0.998577	0.996939	0.993080	0.988524
0.075086	1.003678	1.002472	1.001032	0.999377	0.995486	0.990904
0.118418	1.006778	1.005540	1.004074	1.002395	0.998463	0.993844
0.173238	1.010670	1.009390	1.007885	1.006173	1.002186	0.997527
0.20500	1.012897	1.011600	1.010079	1.008349	1.004335	0.999653
0.26392	1.016961	1.015623	1.014068	1.012305	1.008236	1.003507
0.281944	1.018213	1.016862	1.015294	1.013523	1.009433	1.004691
0.351561	1.022889	1.021495	1.019888	1.018082	1.013932	1.009139
0.398355	1.026032	1.024610	1.022977	1.021149	1.016959	1.012126

[a] The uncertainty of the density measurements was ±1 × 10^{-5} g cm^{-3}

Table 2 The apparent molar volume, V_{ϕ}, of sodium quinate (NaQu) and quinic acid (HQu) for aqueous solutions in the temperature range from 293.15 to 328.15 K

m (mol kg^{-1})	V_{ϕ} (cm^{3} mol^{-1}) at T (K)^{a}					
	293.15	298.15	303.15	308.15	318.15	328.15
NaQu						
0.03095	109.38	110.55	111.52	112.49	114.05	115.17
0.06220	109.52	110.64	111.59	112.47	113.96	115.08
0.07680	109.75	110.84	111.80	112.65	114.11	115.31
0.12696	110.11	111.19	112.14	112.98	114.42	115.58
0.16923	110.27	111.35	112.29	113.12	114.55	115.71
0.19430	110.27	111.33	112.26	113.09	114.51	115.67
0.21744	110.44	111.49	112.41	113.24	114.65	115.80
0.29381	110.67	111.68	112.58	113.39	114.77	115.90
0.36328	111.02	112.03	112.92	113.71	115.08	116.19
0.41018	111.23	112.23	113.12	113.91	115.26	116.37
HQu						
0.040329	117.92	118.77	119.44	120.09	121.27	122.45
0.075086	118.69	119.41	120.05	120.66	121.82	122.93
0.118418	118.82	119.58	120.23	120.85	122.02	123.13
0.173238	118.81	119.58	120.29	120.93	122.12	123.20
0.20500	118.83	119.58	120.26	120.91	122.08	123.14
0.26392	118.95	119.70	120.38	121.03	122.20	123.27
0.281944	118.91	119.67	120.35	120.99	122.18	123.25
0.351561	119.10	119.85	120.53	121.16	122.34	123.40
0.398355	119.08	119.83	120.50	121.13	122.30	123.36

[a] The uncertainty of the apparent molar volume determination is from 0.4 cm^{3} mol^{-1} at the lowest molality to 0.04 cm^{3} mol^{-1} at the highest

The activity coefficients of the ions, f_i, can be calculated using the Debye–Hückel equation for 1:1 electrolytes, in the following form:

$$\ln f_i = -\frac{\kappa^{*}\beta(\gamma c)^{1/2}}{2\left(1+\kappa^{*}R(\gamma c)^{1/2}\right)}, \tag{6}$$

where $\kappa^{*} = (8\pi N_{\mathrm{A}}e^{2}/DkT)^{1/2}$, $\beta = e^{2}/DkT$, e is the elementary charge, D is the dielectric constant of water, and k and N_{A} are the Boltzmann and Avogadro constants, respectively. In the calculation of f_i, the distance between the ions (the distance parameter), R, was chosen as 0.5 nm for sodium quinate, i.e. $R = 1/2[R(\mathrm{Na}^{+}) + R(\mathrm{Qu}^{-})]$, where $R(\mathrm{Qu}^{-}) = 0.5$ nm [11] and $R(\mathrm{Na}^{+}) = 0.5$ nm [12]. Similar distance parameters were used in the calculation of the association constants [13]. In this calculation, the values of the general physical constants and the constants that depend on the properties of water and temperature were taken from the literature [14, 15]. The fraction of free, unassociated ions, γ, was estimated by a series of successive approximations using Eqs. 5 and 6 and the association constants [13], until a constant value of γ was obtained.

Sodium quinate is partially associated in aqueous solution [13], so the ions and ion pairs of the salt contribute to the apparent molar volume. For such systems, relative to the degree of association, the apparent molar volume can be expressed as the sum of the apparent molar volumes of the associated ion pair V_{a}, and the sum of the apparent molar volumes of the corresponding ions, $\sum V_i$ [9]:

$$V_{\phi} = (1-\gamma)V_{\mathrm{a}} + \gamma\sum V_i. \tag{7}$$

The apparent molar volume of the associated ion pair was calculated from

$$V_{\mathrm{a}} = V_{\mathrm{a}}^{0} + b_{\mathrm{a}}(1-\gamma)c, \tag{8}$$

where V_{a}^{0} is the limiting apparent molar volume of the associated ion pair, and b_{a} is an empirical constant.

For 1:1 electrolytes, the sum of the apparent molar volumes of the ions in solution, $\sum V_i$, can be approximated according to the Redlich–Mayer equation [16]

$$\sum V_i = \sum V_i^{0} + A_{\mathrm{v}}(\gamma c)^{1/2}, \tag{9}$$

where A_{v} is the Debye-Hückel limiting slope [14], which is converted to a molar concentration scale by dividing it by the square root of the density of pure water. $\sum V_i^{0}$ is the sum of the limiting apparent molar volumes of the corresponding ions, whereby

$$\sum V_i^{0} = V_{\mathrm{Na}^{+}}^{0} + V_{\mathrm{Qu}^{-}}^{0}. \tag{10}$$

$V_{\mathrm{Na}^{+}}^{0}$ values at particular temperatures were calculated from the review of Millero [17], as the conventional partial molar volumes of the ions.

Following the suggestion of Schwitzgebel [18], by combining Eqs. 1 and 5–9, the following equation was subtracted and used for the least-squares treatment of the experimental d and γc data:

$$\begin{aligned} d = {} & d_0 + \left[M_2 - d_0\sum V_i^{0}\right]\gamma c - d_0 A_{\mathrm{v}}(\gamma c)^{3/2} \\ & + \left[M_2 - d_0 V_{\mathrm{a}}^{0}\right]K_{\mathrm{A}}(\gamma c)^{2}\mathrm{e}^{\left(-\frac{\kappa^{*}\beta(\gamma c)^{1/2}}{1+\kappa^{*}R(\gamma c)^{1/2}}\right)} \\ & - b_{\mathrm{a}}d_0K_{\mathrm{A}}^{2}(\gamma c)^{4}\mathrm{e}^{\left(-\frac{2\kappa^{*}\beta(\gamma c)^{1/2}}{1+\kappa^{*}R(\gamma c)^{1/2}}\right)}. \end{aligned} \tag{11}$$

From the fitting procedure for sodium quinate solutions, estimates were made for the limiting apparent molar volume of the associated sodium quinate, V_{a}^{0}, the empirical constant b_{a}, and the limiting apparent molar volume of the quinate ion, $V_{\mathrm{Qu}^{-}}^{0}$. The fraction of ionization, γ, is between 50% in concentrated solutions and 90% in dilute solutions. From the data given in Table 3, it can be seen that, with increasing temperature, V_{a}^{0} and $V_{\mathrm{Qu}^{-}}^{0}$ increase and b_{a} decreases. The uncertainties of the limiting apparent molar volume of the quinate anion are less than 0.4%, with those of the sodium quinate ion pairs at around 6% (due to

Table 3 The limiting apparent molar volume of the associated compound, V_a^0, the empirical constant, b_a, the limiting apparent molar volume of the quinate ion, $V_{Qu^-}^0$ and the limiting volume change for the dissociation of quinic acid in water, as a function of temperature

Species	NaQu		Qu^-	HQu		
T (K)	V_a^0 (cm^3 mol^{-1})	$b_a \times 10^3$ (dm^6 mol^{-2})	$V_{Qu^-}^0$ (cm^3 mol^{-1})	V_a^0 (cm^3 mol^{-1})	$b_a \times 10^3$ (dm^6 mol^{-2})	$-\Delta V_v^0$ (cm^3 mol^{-1})
293.15	110.7 (±5.8)	11.5 (±2.2)	110.59 (±0.25)	119.06 (±0.48)	0.80 (±0.26)	8.5 (±0.7)
298.15	111.7 (±6.1)	11.6 (±2.4)	111.57 (±0.28)	119.79 (±0.45)	0.79 (±0.23)	8.2 (±0.7)
303.15	112.2 (±5.7)	11.0 (±2.5)	112.15 (±0.31)	120.48 (±0.45)	0.77 (±0.23)	8.3 (±0.8)
308.15	112.8 (±5.9)	10.9 (±2.5)	112.84 (±0.30)	121.13 (±0.58)	0.74 (±0.22)	8.3 (±0.9)
318.15	113.5 (±6.2)	10.4 (±2.6)	114.09 (±0.31)	122.31 (±0.49)	0.70 (±0.23)	8.2 (±0.8)
328.15	115.0 (±7.0)	10.1 (±2.7)	115.13 (±0.32)	123.42 (±0.51)	0.56 (±0.21)	8.3 (±0.8)

the uncertainties of the association constant determination [13]), with the uncertainties of the empirical constant b_a from 20% to 30%. The calculated densities via Eq. 11 are accurate within the experimental errors of the density determinations, i.e. 2×10^{-5} g cm^{-3}. The assumption that the limiting molar volume of the associated ion pair is independent of concentration (i.e. omitting b_a) provides poor representation of the experimental densities.

In analysing the partial molar volumes of quinic acid, which is also partially dissociated according to the equilibrium between the undissociated quinic acid and the free ions, the following was assumed:

$$\mathrm{HQu(aq)} \underset{K_A}{\overset{K_a}{\rightleftarrows}} \mathrm{H^+(aq)} + \mathrm{Qu^-(aq)}. \tag{12}$$

This results in the disappearance of undissociated quinic acid and the formation of hydrogen and quinate ions. The dissociation constant, K_a, and its reciprocal value, i.e. the association constant, K_A, for this reaction are given by

$$K_a = \frac{a_{H^+} a_{Qu^-}}{a_{HQu}} \quad \text{and} \quad K_A = \frac{a_{HQu}}{a_{H^+} a_{Qu^-}}. \tag{13}$$

For the analysis of the partial molar volumes of quinic acid, the same form of the equations and the assumptions were used as for sodium quinate. In Eqs. 4–11, the subscripts representing the sodium ion Na^+ are thus changed to H^+, and Na^+Qu^- to HQu. In the calculation of f_i and γ, the distance between the ions (the distance parameter), R, for quinic acid was chosen as 0.7 nm, which was determined in the same way as that for sodium quinate, and $R(H^+) = 0.9$ nm [19]. For the association constant, the reciprocal of the dissociation constant from [13] was taken. Equation 11 was used for the least-squares treatment of the experimental data for d and c collected in Table 1. The fitting procedure for aqueous solutions of quinic acid was used to estimate the limiting apparent molar volume of the associated quinic acid, V_a^0, and the empirical constant b_a. The fraction of ionization is from 3% in concentrated solutions to 10% in dilute solutions. In this procedure, $\sum V_i^0$ was calculated using Eq. 10, as adapted to quinic acid, i.e. $\sum V_i^0 = V_{H^+}^0 + V_{Qu^-}^0$. In calculations, the limiting partial molar volume of the quinate ion, $V_{Qu^-}^0$, was taken from Table 3, and the limiting partial molar volume of the hydrogen ion, $V_{H^+}^0$, was zero, according to the adopted convention proposed by Millero [17]. From the data in Table 3, it is apparent that, with increasing temperature, V_a^0 increases and b_a decreases slightly. The uncertainty of V_a^0 is 0.4%, and for the empirical constant b_a, 30%. The densities calculated via Eq. 11 are accurate within the experimental errors of the density determinations, i.e. 2×10^{-5} g cm^{-3}. As before, the assumption that the limiting molar volume of the associated ion pair is independent of concentration (omitting b_a) provides poor representation of the experimental densities.

Figure 2 shows the dependence of $\sum V_i$ and V_a on the square root of the molar concentration at 293 K for both compounds. From the left side of Fig. 2, it is evident that, for aqueous salt solutions, the sodium and quinate ions contribute predominantly to the apparent molar volume (especially in dilute solutions), while with increasing concentrations, the apparent molar volume of the associated ion pairs gradually becomes more important. The calculated V_a varies (at 293 K) from 111.0 cm^3 mol^{-1} at infinite dilution up to 113.0 cm^3 mol^{-1} at the highest concentration, and the calculated $\sum V_i$ from 108.8 cm^3 mol^{-1} at infinite dilution up to 109.6 cm^3 mol^{-1} at the highest concentration. From the right side of Fig. 1, it is seen that the undissociated acid predominantly contributes to the apparent molar volume of quinic acid in aqueous solutions. The calculated V_a varies (at 293 K) from 119.1 cm^3 mol^{-1} at infinite dilution up to 119.4 cm^3 mol^{-1} at the highest concentration, and the calculated $\sum V_i$ from 110.6 cm^3 mol^{-1} at infinite dilution up to 111.7 cm^3 mol^{-1} at the highest concentration.

The limiting volume change for ionisation [20] of sodium quinate and quinic acid, ΔV_v^0, at specific temperatures was calculated as

$$\Delta V_v^0 = \sum V_i^0 - V_a^0. \tag{14}$$

ΔV_v^0 for sodium quinate is very small, and due to the large experimental error of the limiting apparent molar

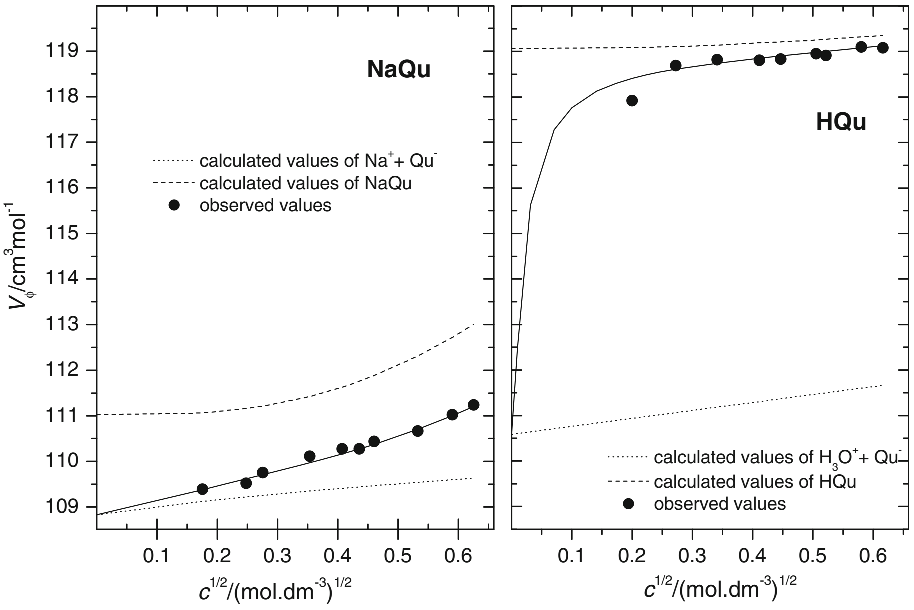

Fig. 2 Apparent molar volume of sodium quinate (NaQu) and quinic acid (HQu) versus the square root of the molar concentration, in aqueous solutions at 293 K. Experimental data (*circles*), fitted curve according to Eq. 11 (*continuous lines*) and calculated values for $\sum V_i^0$ (*dotted lines*) and V_a^0 (*dashed lines*)

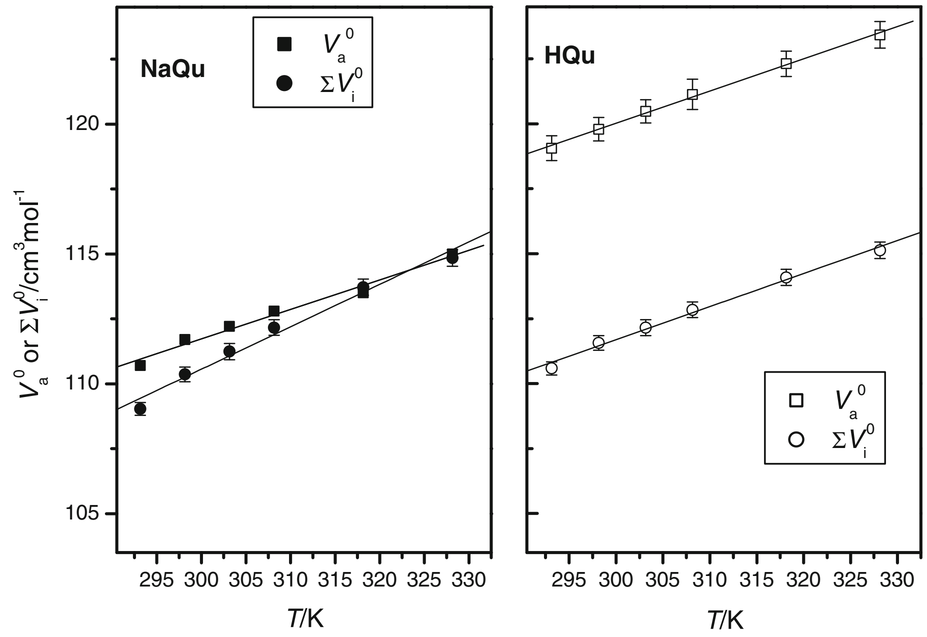

Fig. 3 Dependence of V_a^0 and $\sum V_i^0$ of sodium quinate and quinic acid in aqueous solutions on temperature

volumes of the associated ion pairs, ΔV_v^0 is assumed to be zero at all temperatures. The ΔV_v^0 obtained for quinic acid and given in Table 3 is negative, and within the experimental error, it is independent of temperature.

The limiting apparent molar expansibility of the species investigated was calculated from the linear dependence of V_a^0 and $\sum V_i^0$ on temperature (Fig. 3). The limiting apparent molar expansibility of undissociated quinic acid ($\partial V_a^0/\partial T$) is 0.124 ± 0.003 cm^3 mol^{-1} K^{-1}, and that for the quinate anion, $\left(\partial V_{\mathrm{Qu}^-}^0 \big/ \partial T\right)$, is 0.127 ± 0.006 cm^3 mol^{-1} K^{-1}. These values can be considered as equal, within the experimental error. This is in agreement with the adopted convention of partial molar ionic volumes and expansibilities [17], where the partial molar expansibility of the hydrogen ion is zero. The limiting apparent molar expansibility for the ionisation process of quinic acid ($\partial \Delta V_v^0/\partial T$) is small, 0.003 cm^3 mol^{-1} K^{-1}.

The expansion coefficient, α^* (in K^{-1} units), is defined as

$$\alpha^* = \frac{\left(\partial V_\phi^0 \big/ \partial T\right)_P}{V_\phi^0}, \tag{15}$$

where $V_\phi^0 = V_{\mathrm{Qu}^-}^0$. The expansion coefficient for the quinate ion was calculated to be (1.14 ± 0.05) × 10^{-3} K^{-1} at 298 K. α^* for the quinate ion was calculated for all temperatures, and it is positive and decreases slightly with increasing temperature.

For the interpretation of the temperature dependence of the density data, we followed the suggestion of Klofutar and Tasič [21]. From the density data given in Table 1, the coefficient of thermal expansion of a mixture of dissociated and undissociated compound, α (K^{-1}), was evaluated as defined:

$$\alpha = -\frac{1}{d}\left(\frac{\partial d}{\partial T}\right)_{P,m}. \tag{16}$$

Table 4 The A_1 and A_2 parameters of Eq. 17, and the $(\partial A_1/\partial T)_P$ derivative for temperature of parameter A_1, for quinic acids and sodium quinate in aqueous solutions at temperatures from 293.15 to 328.15 K

T (K)	A_1 [g cm^{-3} (mol kg)$^{-1}$]	$-A_2 \times 10^3$ [g cm^{-3} (mol kg)$^{-2}$]	$-(\partial A_1/\partial T)_P \times 10^4$ [g cm^{-3} (mol kg)$^{-1}$ K^{-1}]
NaQu			
293.15	0.10457	14.92	2.115
298.15	0.10347	14.60	1.948
303.15	0.10254	14.40	1.781
308.15	0.10174	14.25	1.614
318.15	0.10033	13.88	1.281
328.15	0.09914	13.44	0.947
HQu			
293.15	0.07359	9.450	1.381
298.15	0.07289	9.368	1.287
303.15	0.07228	9.322	1.192
308.15	0.07171	9.247	1.098
318.15	0.07073	9.139	0.909
328.15	0.06989	8.980	0.720

The density data at a given temperature were fitted according to the following equation:

$$d = d_0 + A_1 m + A_2 m^2, \tag{17}$$

where A_1 and A_2 are coefficients that depend on solute, solvent and temperature. The least-squares values of the coefficients are given in Table 4. The coefficient of thermal expansion of the solution was obtained by differentiating the expression for the density shown in Eq. 17 with respect to the temperature at constant pressure and molality, and by dividing the derivative obtained by d (g cm^{-3}). This gave the following relationship:

$$\alpha = \alpha_0 + B_1 m + B_2 m^2, \tag{18}$$

where α_0 is the thermal expansion coefficient of pure water [22], and the B_1 and B_2 regression coefficients are given by

$$B_1 = -\frac{1}{d_0}\left[A_1\alpha_0 + \left(\frac{\partial A_1}{\partial T}\right)_P\right], \tag{19}$$

$$B_2 = \frac{1}{d_0}\left[\frac{A_1}{d_0}\left(A_1\alpha_0 + \left(\frac{\partial A_1}{\partial T}\right)_P\right) - \left(A_2\alpha_0 + \left(\frac{\partial A_2}{\partial T}\right)_P\right)\right]. \tag{20}$$

The coefficient A_1 of Eq. 17 depends on temperature, as a second-order polynomial fit; the derivative $(\partial A_1/\partial T)_P$ is given in Table 4. The coefficient A_2 of Eq. 17 depends linearly on temperature; the derivative $(\partial A_2/\partial T)_P$ is (4.07 ± 0.58) × 10^{-5} g cm^{-3} (mol kg)$^{-2}$ K^{-1} for sodium quinate, and (1.30 ± 0.04) × 10^{-5} g cm^{-3} (mol kg)$^{-2}$ K^{-1} for quinic acid. Figure 4 shows the dependence of the thermal expansion coefficient on the molality at fixed temperatures,

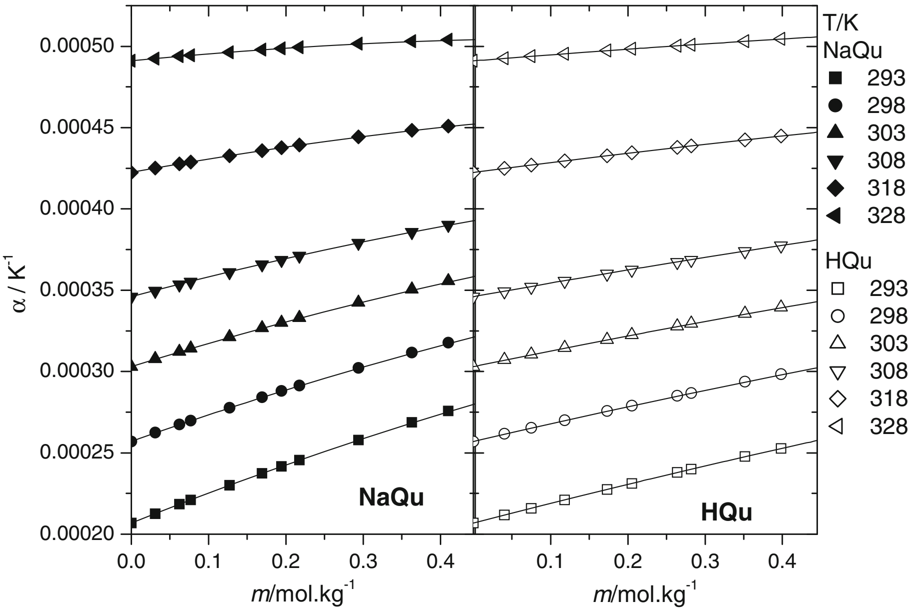

Fig. 4 Dependence of the thermal expansion coefficient on molality of aqueous solutions of sodium quinate and quinic acid at temperatures from 293.15 to 328.15 K

where it can be seen that the thermal expansion coefficients of these solutions are grater than that of water [22], and that they increase with increasing molality of solution and with temperature. At lower temperatures, the difference between the thermal expansion coefficient of quinic acid and its salt is significant, while at higher temperatures the difference decreases.

Table 5 Dependence of the coefficients B_1 and B_2 of Eq. 18 and the limiting molar expansibility of quinic acid and its sodium salt in aqueous solution on temperature

T (K)	$B_1 \times 10^4$ (kg mol^{-1} K^{-1})	$-B_2 \times 10^5$ (kg^2 mol^{-2} K^{-1})	ϕ_E^0 (cm^3 mol^{-1} K^{-1})[a]
HQu			
293.15	1.231	2.02	0.148
298.15	1.102	1.87	0.142
303.15	0.977	1.73	0.135
308.15	0.855	1.60	0.128
318.15	0.616	1.36	0.114
328.15	0.382	1.14	0.100
NaQu			
293.15	1.902	5.72	0.213
298.15	1.687	5.42	0.198
303.15	1.477	5.13	0.182
308.15	1.270	4.86	0.166
318.15	0.865	4.36	0.135
328.15	0.467	3.89	0.104

[a] The uncertainty of the limiting molar expansibility determination is ±0.003 cm^3 mol^{-1} K^{-1}

In the evaluation of the coefficients B_1 and B_2, the values of α_0 and d_0 given by Kell [22] were used. The coefficients of Eqs. 19 and 20 are listed in Table 5, where it can be seen that coefficient B_1 is positive and decreases with increasing temperature, while B_2 is negative and its absolute value decreases with increasing temperature. The values of B_1 and B_2 are more pronounced for the salt than for the acid.

The apparent molar expansibility coefficient of the solute, ϕ_E (cm^3 mol^{-1} K^{-1}), is defined as in [9]:

$$\phi_E = \frac{(\alpha - \alpha_0)}{md_0} + \alpha V_\phi. \tag{21}$$

Taking into account Eq. 18, we obtain

$$\phi_E = \frac{(B_1 + B_2 m)}{d_0} + \left(\alpha_0 + B_1 m + B_2 m^2\right) V_\phi. \tag{22}$$

The limiting apparent molar expansibility of quinic acid and for its salt, ϕ_E^0 (cm^3 mol^{-1} K^{-1}), can now be given by

$$\phi_E^0 = \frac{B_1}{d_0} + \alpha_0 V_\phi^0. \tag{23}$$

The calculated values of ϕ_E^0 decrease with increasing temperature (Table 5; Fig. 5). Figure 5 shows the dependence of the apparent molar expansibility of the solute, calculated according to Eq. 22, on the molality at temperatures studied, for sodium quinate and quinic acid. The apparent molar expansibilities of sodium quinate and quinic acid in aqueous solution decrease with increasing molality and increase with increasing temperature. The influence of temperature and molality on the apparent molar expansibility of sodium quinate is greater than for quinic acid.

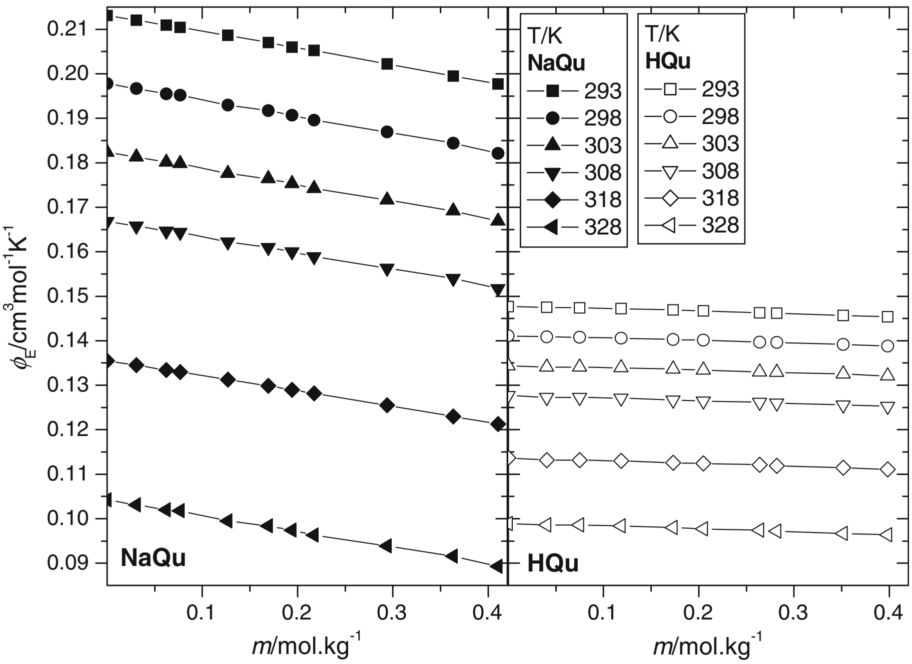

Fig. 5 Dependence of the apparent molar expansibility coefficient of solute on molality for aqueous solutions of sodium quinate and quinic acid at temperatures from 293.15 to 328.15 K

Experimental

Materials

D-(−)-Quinic acid (CAS 77-95-2) from Sigma (mass fraction >0.99) was re-crystallized three times from water–ethanol. Sodium quinate monohydrate was prepared by careful neutralization of aqueous solution of D-(−)-quinic acid with sodium hydroxide, evaporation of the water, and recrystallization from methanol–diethyl ether solution. Purity was checked by analyses of the elements C and H (Perkin Elmer, 2400 Series II CHNS/O Analyzer) and by acid–base titration. For titration of sodium quinate, the sodium ions were exchanged for hydrogen ions (Dowex, Type 50 WX8). Purities of 99.9% for the acid and 99.6% for the salt were determined. The crystallization of sodium quinate as the monohydrate was also confirmed by heating the salt to 380 K, with loss of the corresponding quantity of water. Both of the compounds were kept in a vacuum desiccator over P_2O_5. Water (Millipore, Milli-Q Ultrapure Water Purification Systems, Gradient) with specific conductivity of 0.06 μS cm^{-1} at 298.15 K was used for preparation of the solutions. The solutions investigated were prepared on a molal concentration scale (mol kg^{-1}) by precise weighing, using a digital balance (Mettler Toledo, AT201, Switzerland) accurate to $\pm 1 \times 10^{-5}$ g.

Density measurements

The densities, d (g cm^{-3}), of the aqueous solutions of quinic acid and its sodium salt were measured using an oscillating tube density meter (Anton Paar, model DMA 5000), equipped with two platinum (Pt 100) thermometers for temperature control. This was calibrated with Milli-Q water and air, with corrections for humidity at temperatures of 273.15, 313.15 and 333.15 K and at atmospheric pressure. The temperature in the measuring cell was regulated to better than ±0.01 K. The repeatability of the density measurements was 1×10^{-6} g cm^{-3}, and the uncertainty was $\pm 1 \times 10^{-5}$ g cm^{-3}.

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