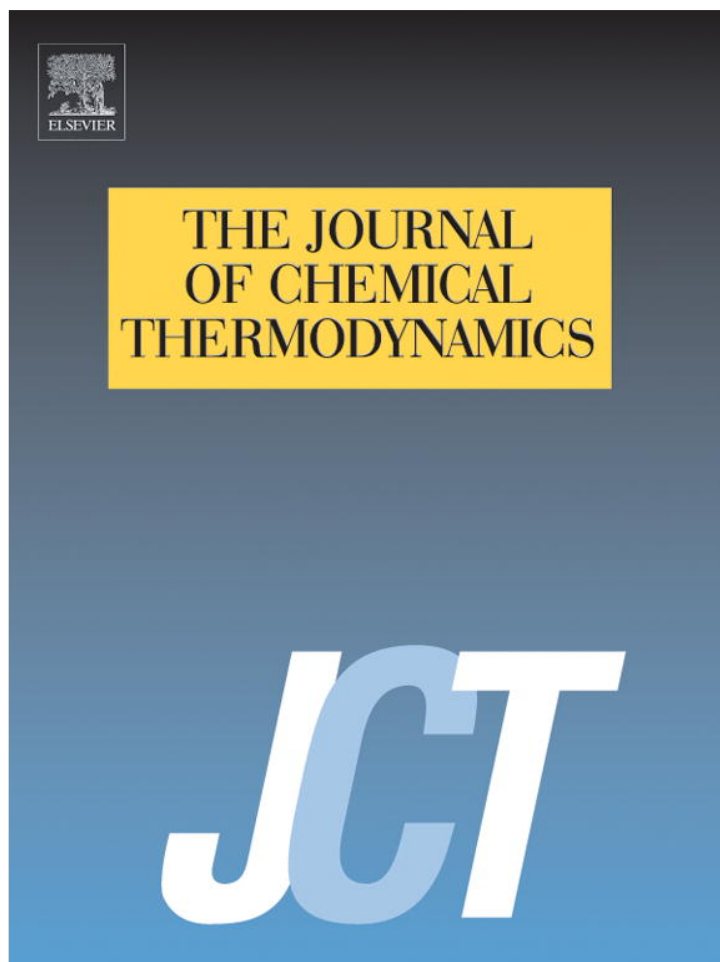


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Standard molar volumes and heat capacities of aqueous solutions of sodium trifluoromethanesulfonate at temperatures up to 573 K and pressures to 28 MPa

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ABSTRACT

Densities and heat capacities of aqueous solutions of sodium trifluoromethanesulfonate (sodium triflate) of concentrations from 0.025 to 0.3 mol · kg⁻¹ were measured with high temperature, high pressure custom-made instruments at temperatures up to 573 K and at pressures up to 28 MPa. Standard molar volumes and standard molar heat capacities were obtained via extrapolation of the apparent molar properties to infinite dilution. The results for volumetric properties are consistent with earlier literature data, but no previous measurements exist for heat capacities of sodium triflate at superambient conditions. The new data were used for calculating the standard molar volumes and heat capacities for the triflate anion and compared with the results for triflic acid that should be essentially identical within the expected error margins. At temperatures above 473 K an effort was made to refine the processing of literature data for HCl(aq), taking into account its partial association, and subsequently to modify the value for Na⁺ ion calculated from the standard thermodynamic values of NaCl(aq) where its ion pairing was already considered. This approach yields reasonable agreement at high temperatures between the values for triflate ion calculated from its salt and those for triflic acid.

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1. Introduction

The knowledge of thermodynamic data of large and weakly charged anions as a function of temperature is of direct interest for obtaining the standard thermodynamic properties¹ for higher valence aqueous cations. They tend to ion pair strongly with most anions at intermediate and high temperatures due to the much lower values of the dielectric constant of water, making interpretation of experimental results complicated and of uncertain value. Since the time scale of thermal decomposition of trifluoromethane sulfonic (triflic) anion at high temperatures is low [1] (relative to the length of flow experiments) and this anion does not tend to associate with cations it is an ideal match in combination with cations of higher va-

lence. In addition, trifluoromethanesulfonates (triflates) replace progressively perchlorates, used in earlier studies, that are less stable in hydrothermal solutions [2]. It is therefore important to have reliable data for the triflic ion over a wide range of temperatures and pressures. Triflates are namely convenient for investigation of lanthanide trivalent ions that are of high interest for geologists, and also as products of nuclear fission and convenient analogues of actinides, not requiring antiradiation equipments for their study.

According to a generally accepted convention, assigning zero to the standard thermodynamic properties of the hydrogen cation, the standard data obtained for triflic acid are equal to those for the triflic anion. Yet it is of interest to verify this assumption by new measurements with sodium triflate. In combination with the recommended data for hydrochloric acid and sodium chloride this is an alternative way for calculating the standard thermodynamic data of the triflate anion. An attention has to be, however, paid to partial association of both HCl and NaCl at high temperatures and this effect has to be taken into account.

The volumetric and heat capacity data are of special interest as a gateway for obtaining by integration the Gibbs free energies, necessary for calculating phase or chemical equilibria at hydrothermal

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¹ In the context of this article the standard thermodynamic property of an ionic solute is its corresponding partial molar property at infinite dilution.

conditions. We have published recently the standard molar volumes and standard molar heat capacities of triflic acid up to 573 K and 30 MPa based on direct densimetric and calorimetric measurements [3]. The aim of this paper is to obtain the alternative values for the triflate anion over an extended range of parameters via the experimental data for sodium triflate up to 575 K and 28 MPa.

Some data for aqueous sodium triflate are already available in the literature, yet the only truly high temperature measurements are those for densities published by Xiao and Tremaine [4] in a concentration range between 0.05 and 1.7 mol · kg⁻¹, at temperatures from 283 to 600 K and pressures up to 10 MPa. They used a vibrating tube flow densimeter SODEV O3D [5] at temperatures up to 328 K and pressure of 0.1 MPa, and a customized platinum vibrating tube densitometer at temperatures from 323 K and at higher pressures. Xiao *et al.* [6] measured heat capacities for aqueous solutions of sodium triflate using a Sodev CP-C flow microcalorimeter at 283, 298, 313 and 328 K, at 0.1 MPa, for molalities from 0.05 to 1.6 mol · kg⁻¹. Erickson *et al.* [7] have published recently new data for densities and heat capacities at near ambient temperatures (288, 298, 313, and 328 K) and pressure of 0.1 MPa using a Sodev O2D densitometer and Picker flow microcalorimeter, respectively. In all three papers the experimental data were extrapolated to infinite dilution for obtaining the standard molar volumes and heat capacities of sodium triflate and for calculating the properties of the triflate anion at near ambient conditions that were compared with the data for triflic acid. No data on ionic properties exist, however, at temperatures above 328 K. It is apparent from this short overview that the standard molar heat capacities of sodium triflate are available only at near ambient conditions. New experiments are therefore of interest for accessing the properties of the triflate ion by an approach alternative to that presented in our preceding paper [3] and for comparing the consistency of the resulting data. The experimental equipments used, conditions of measurements and treatment of the data were analogous to those reported earlier for triflic acid.

2. Experimental

2.1. Preparation of solutions and conditions of measurements

The aqueous solutions of sodium trifluoromethanesulfonate (sodium triflate) were obtained by neutralizing a one molal aqueous solution of trifluoromethanesulfonic acid (triflic acid) by a solution of sodium hydroxide of the same molality. A small amount of aqueous solution of triflic acid was then added in excess in order to keep the solution at acid condition with a pH of 6 slightly lower than that at the point of equivalence. Dilute solutions were then prepared by mass from a stock solution using deionised water, which was freshly degassed under reduced pressure before use. The target concentrations were of 0.3, 0.15, 0.05, and 0.025 mol · kg⁻¹. It was found in test experiments that the effect of excess acid in solutions had negligible effect on the measured properties.

All experiments were performed at target temperatures 298, 323, 373, 473, 523, and 573 K and at two pressures; the lower one was changing being somewhat above the saturation pressure of water while the higher was approximately constant and close to 28 MPa. The reference fluid was water that was systematically freshly deionised and degassed.

2.2. Densities

The relative densities of the solutions compared to water were determined by using a vibrating tube flow densitometer constructed in the laboratory and described in detail by Hynek *et al.*

[8]. The instrument is equipped with a Pt/Rh20 vibrating tube and a Pt/Rh10 transporting tube allowing experiments with highly corrosive media. The temperature of the vibrating tube was maintained stable within 0.01 K during one sample run and is believed to be determined with an accuracy to 0.05 K with the exception of the two highest temperatures where the error can be up to 0.1 K due to possible temperature gradients. The pressure in the densitometer was kept stable within 0.05 MPa by a back-pressure regulator and measured with an accuracy to 0.03 MPa.

Density differences $\Delta\rho$ between solution and water (denoted by subscripts s and w) at the same temperature and pressure conditions, were calculated as:

$$\Delta\rho = \rho_s - \rho_w = K \cdot (\tau_s^2 - \tau_w^2). \quad (1)$$

The measured periods corresponding to solution and water τ_s and τ_w were typically constant to 10⁻⁵ ms. The calibration constant K that is temperature and pressure dependent was determined at each experimental condition by measurements with 3 mol · kg⁻¹ NaCl solution up to 423 K and pure nitrogen at higher temperatures. The error in the calibration constant is estimated to 0.3%. The density of water was calculated with the equation of Hill [9], the density of NaCl solution was obtained from the recommendation of Archer [10] and the density of N₂ is that reported in a handbook by Perry and Chilton [11].

Unlike for triflic acid where the densities at 298.15 K were reported at 0.1 and 31 MPa, the volumetric measurements with sodium triflate at the lowest temperature were performed at high pressure only. Values of the apparent molar volumes V_ϕ were calculated from the relationship:

$$V_\phi = M/\rho_s - \Delta\rho/m\rho_s\rho_w, \quad (2)$$

where M is the molar mass (kg · mol⁻¹) of the sodium triflate acid and m is molality.

2.3. Heat capacities

The heat capacity density product ratio of each solution relative to water was determined using a high-temperature/high-pressure Picker-type differential flow calorimeter, whose detailed description as well as measuring procedure can be found in the publication by Hnedkovsky *et al.* [12]. Experiments were performed starting with the temperature of 323 K. The error in the temperature determination of the calorimeter block was estimated to 0.1 K. A high-pressure pump working at a constant volumetric flow rate was used to supply the base flow (3.0 · 10⁻² cm³ · s⁻¹) to the calorimeter. The pressure in the system was measured with a Bourdon-type pressure gauge with an accuracy of 0.1 MPa and maintained constant within 0.05 MPa by a back-pressure regulator placed at the end of the outlet stream from the calorimeter.

The ratio of specific (per unit mass) heat capacities of solution and water, $c_{p,s}/c_{p,w}$ is related to the heating powers in the measuring cell of the calorimeter by the relation:

$$c_{p,s}/c_{p,w} = (\rho_w/\rho_s)_{SL} \{1 + f \cdot (P_s - P_w)/P_w\}, \quad (3)$$

where $(\rho_w/\rho_s)_{SL}$ is the water-solution density ratio in the sample loop maintained at a constant temperature of 298 K and pressure of experiment and f is the correction factor for heat losses. P_s and P_w are the heating powers supplied to maintain the temperature rise constant ($\Delta T \cong 2$ K) when running the solution of interest or water through the experimental cell, respectively. Thus differential arrangement is used to compensate for fluctuations in temperature and flow rate only. The heat loss factor f (ranging typically between 1 and 1.1) was determined by changing the water base flow rate in the sample cell in order to mimic a change in heat capacity; the uncertainties in f do not exceed 2.5%. The heat capacities are

reported at a temperature $T = T_{\text{block}} + 0.5\Delta T$. At each temperature the function of the calorimeter was verified by measuring the heat capacity of 0.5, 1, and 3 mol · kg⁻¹ NaCl solutions, the results were in good agreement with literature values [10,12].

The apparent molar heat capacities $C_{p,\phi}$ can then be obtained as

$$C_{p,\phi} = M \cdot c_{p,s} + \Delta c_p / m = c_{p,w} \{ (M + 1/m) \cdot c_{p,s} / c_{p,w} - 1/m \}, \quad (4)$$

where Δc_p is the difference between the specific heat capacity of solution and water.

3. Results

3.1. Volumes

All experimental values of density differences and calculated apparent molar volumes are given in Appendix A, along with their uncertainties $\sigma\Delta\rho$ and σV_ϕ considering the propagation of errors in the individual measured quantities (periods τ_s and τ_w , calibration constant K and molality). The uncertainty in V_ϕ is particularly high for the lowest concentration due to the analytical form of equation (2) where error in $\Delta\rho$ is largely amplified with decreasing molality. Figures 1 and 2 illustrate the variation of the apparent molar volumes as a function of the square root of ionic strength at different temperatures and at pressures close to water saturation pressure line and 28 MPa, respectively. For comparison the literature values [4] are also included at temperatures close to our experimental ones. The full lines correspond to the weighted fit by the simplified Pitzer equation (see below) while the dotted lines connecting literature data points are just to lead the eye. These graphic presentations show well the initial gradual increase of the apparent molar volumes with temperature and a strong drop at the two highest temperatures, where also the concentration dependence is the most pronounced due to the increase of the Debye–Hückel limiting slopes. Literature data are in a reasonable agreement with our results considering that they were not measured at identical pressures (tables A1 and A2).

For determining the standard molar volumes an extrapolation to infinite dilution of the apparent molar volumes was performed

at each temperature and pressure using an equation based on the Pitzer ion-interaction model. For 1:1 electrolytes it holds:

$$V_\phi = V^\circ + 2 \frac{A_V}{b} \ln(1 + bl^{1/2}) + 2RTB_V m + C_V m^2 \quad \text{with} \\ B_V = \beta_V^0 + 2\beta_V^1 f(I), \quad (5)$$

where $b = 1.2 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ and I is the ionic strength. A_V is the Debye–Hückel law limiting slope reflecting the volumetric and dielectric properties of water, for which the recommendations by Archer and Wang [13] were used. The adjustable parameters are the standard molar volume, V° , expressing interaction between solute and solvent, and the second and third virial coefficients β_V^0 , β_V^1 and C_V reflecting interactions between ions in the solution. Since the new experimental data were available only in a limited concentration range (below 0.3 mol · kg⁻¹) a simplified two parameter version

$$V_\phi - \frac{A_V}{b} \ln(1 + bl^{1/2}) = V^\circ + Zm \quad \text{with } Z = 2RTB_V = 2RT\beta_V^0. \quad (6)$$

was sufficient for fitting the data at all temperatures and pressures, therefore in this approximation $\beta_V^1 = C_V = 0$. Table 1 lists the standard molar volumes V° together with the β_V^0 parameters obtained by the least-squares weighted regression of the data in appendix A1. The listed uncertainties in V° are statistical estimates obtained from the correlation procedure that reflect mainly the scatter of experimental V_ϕ values while the possible systematic errors are not taken explicitly into account. Therefore they do not express the overall uncertainty in the standard molar volume that we estimate to 1 and 5 cm³ · mol⁻¹ at the lower and upper temperature limits, respectively. Our results are compared with the standard molar volumes from Xiao and Tremaine [4] where an empirical expression was reported expressing their standard molar volume of sodium triflate as a function of temperature and water compressibility κ_w .

$$V^\circ(\text{NaCF}_3\text{SO}_3) = a_1 + \frac{a_2}{T - 228} + a_3 T + a_4 \kappa_w + a_5 T \kappa_w, \quad (7)$$

which allows to make calculations exactly at conditions of our experiments. It is apparent that the agreement can be considered

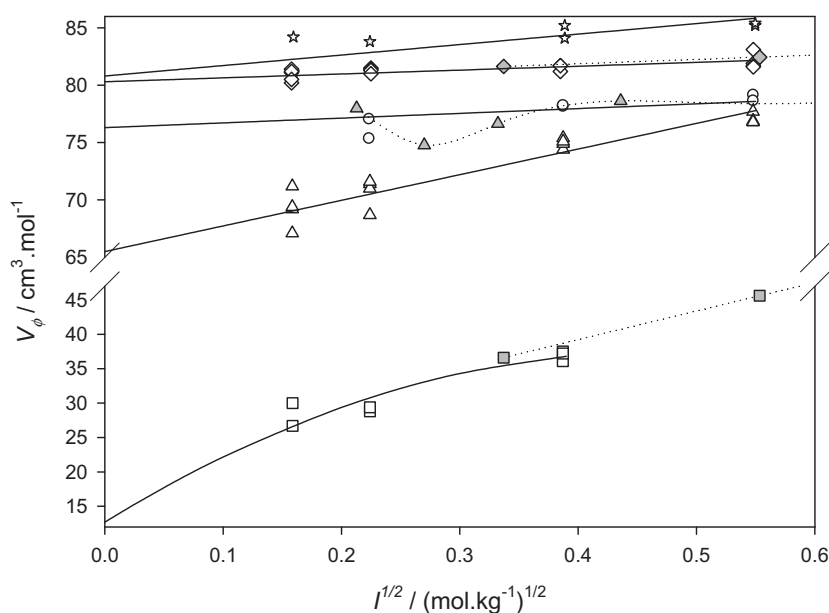


FIGURE 1. Apparent molar volumes of sodium triflate as a function of square root of ionic strength near saturation pressure of water and comparison with literature [4]. (○) 323.15 K, 0.14 MPa, (☆) 473.38 K, 2.64 MPa, (◇) 373.17 K, 1.12 MPa, (△) 523.15 K, 10.46 MPa, (□) 573.16 K, 10.57 MPa, (◆) 373.12 K, 0.50 MPa (lit), (▲) 523.55 K, 10.15 MPa (lit), (■) 573.39 K, 10.13 MPa (lit). The dotted lines are for help of eye.

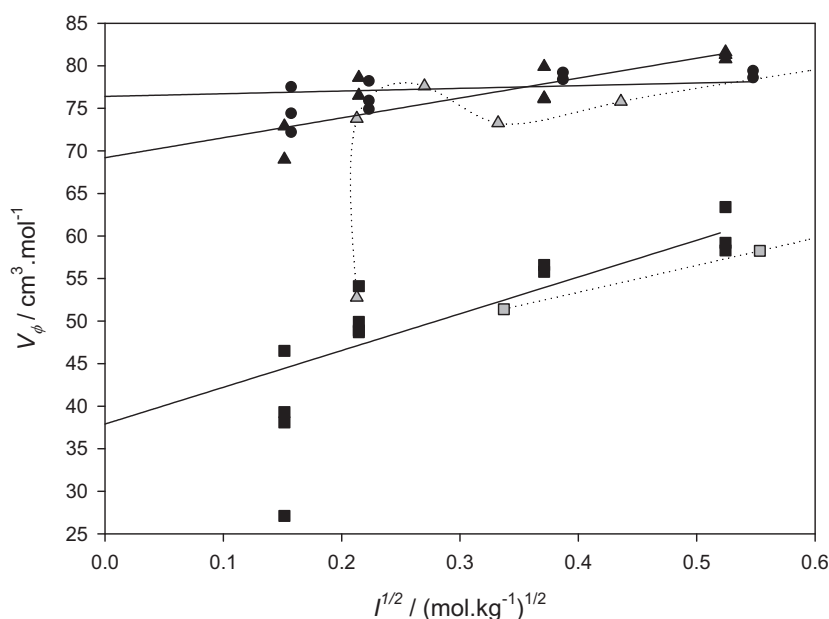


FIGURE 2. Apparent molar volumes of sodium triflate as a function of square root of ionic strength at high target pressure and comparison with literature [4]. (●) 323.15 K, 27.45 MPa, (▲) 523.00 K, 28.04 MPa, (■) 573.85 K, 27.67 MPa, (▲) 523.57 K, 20.40 MPa (lit), (■) 573.32 K, 19.87 MPa (lit) The dotted lines are for help of eye.

as quite reasonable, within the claimed uncertainty of our values. The low temperature data at atmospheric pressure published recently by Erickson *et al.* [7] should be also mentioned. Their values of standard molar volumes are 74.1, 76.3, and 77.6 cm³ · mol⁻¹ at 298.15, 313.15, and 328.15 K, respectively, yet the comparison with our data can be only semiquantitative since they were not obtained at quite identical temperature and /or pressure.

Figure 3 illustrates the evolution of the standard molar volumes of sodium triflate as a function of temperature near saturation pressure and at 28 MPa, including an insert with a detailed picture of near ambient conditions. The behavior of V^0 is a typical one of a strong electrolyte in water with a flat maximum near 473 K and an important drop at higher temperatures scaling with increase in the compressibility of water [14,15]. Similarly as for the triflic acid [3] the high pressure data at near and not far removed from ambient temperatures are slightly lower compared to those measured close to the saturation pressure of water, yet this difference is within the uncertainty of their determination.

3.2. Heat capacities

Differences between heat capacities of solution and water ΔC_p obtained from the measured $c_{p,s}/c_{p,w}$ ratios and the calculated apparent molar heat capacities $C_{p,\phi}$ are given in Appendix 2, along with their estimated uncertainties $\sigma\Delta C_p$ and $\sigma C_{p,\phi}$. They were obtained as an estimate considering the propagation of errors in individual measured quantities (density of solution, heat loss factor, heating powers and molality of solutions), more detailed description of the uncertainties estimation can be found in literature [12,16]. A similar observation like for apparent molar volume holds for the increase of uncertainty in $C_{p,\phi}$ with decreasing molality of solute. Figure 4 shows for illustration the apparent molar heat capacities as a function of square root of ionic strength at four different temperatures from 322 to 573 K at a target pressure of 28 MPa and also at 10 MPa for the highest temperature only. The lines correspond to the weighted fit by the simplified Pitzer equation (see below). Generally, the trend in $C_{p,\phi}$ is analogous to that in V_ϕ , however, since the heat capacity is the second order derivative property the changes with concentration as well as with temperature and pressure are more pronounced.

The standard molar heat capacities were obtained by an extrapolation to infinite dilution of the apparent molar heat capacities using an equation based on the Pitzer ion-interaction model. It holds for a 1:1 electrolyte:

$$C_{p,\phi} = C_p^0 + \frac{A_C}{b} \ln(1 + bl^{1/2}) - 2RT^2 B_C m + C_C m^2 \quad \text{and} \\ B_C = \beta_C^0 + 2\beta_C^1 f(I), \quad (8)$$

where A_C is the Debye–Hückel law limiting slope for heat capacities that was obtained from literature [13]. The standard molar heat capacity

C_p^0 and the second and third virial coefficients β_C^0 , β_C^1 and C_C are adjustable parameters. Similarly as for the apparent molar volumes only two parameters are significant and a simplified relationship was used

$$C_{p,\phi} - \frac{A_C}{b} \ln(1 + bl^{1/2}) = C_p^0 + Z_C m \quad \text{with } Z_C = -2RT^2 B_C \\ = -2RT^2 \beta_C^0, \quad (9)$$

thus setting $\beta_C^1 = C_C = 0$. The values of C_p^0 and β_C^0 obtained by the weighted least-squares regression of the data in Appendix 2 are reported in table 2 and illustrated in figure 5. Again the error margins for the standard molar heat capacities are statistical values resulting from the correlation procedure that reflects mainly the data scatter. The systematic errors that might occur especially near the upper temperature limit due to possible temperature gradients in the calorimeter block are not considered. Considering this uncertainty we expect that our data at infinite dilution are reliable to better than 5 per cent at the two highest temperatures and certainly more accurate at lower temperatures. The trend shown in figure 5 is analogous to that in figure 3 for the standard molar volumes. Yet it is not possible to distinguish for the standard molar heat capacities any pressure dependence at temperatures up to 473 K as the differences between the values at high and low pressures are smaller than the sum of their statistical uncertainties. Similarly like for the standard molar volumes the pressure dependence of heat capacities below 473 K looks negligible compared to experimental errors of measured quantities. Only for the two highest temperatures the usual picture for a strong electrolyte is observed with

TABLE A1

Density differences $\Delta\rho = \rho_s - \rho_w$ and apparent molar volumes V_ϕ of sodium triflate solutions at different temperatures and pressures.

$m/\text{mol} \cdot \text{kg}^{-1}$	$\Delta\rho/\text{kg} \cdot \text{m}^{-3}$	$\sigma\Delta\rho/\text{kg} \cdot \text{m}^{-3}$	$V_\phi/\text{cm}^3 \cdot \text{mol}^{-1}$	$\sigma V_\phi/\text{cm}^3 \cdot \text{mol}^{-1}$
<i>298.1 K, 31.03 MPa</i>				
0.0235	2.33	0.05	73.1	2.0
0.0235	2.36	0.05	71.7	2.0
0.0235	2.38	0.05	70.9	2.0
0.0507	4.92	0.07	74.9	1.3
0.0507	4.93	0.07	74.7	1.3
0.0507	4.95	0.07	74.2	1.3
0.1487	14.35	0.15	74.7	1.0
0.1487	14.38	0.15	74.5	1.0
0.1487	14.32	0.15	74.9	1.0
0.2882	27.29	0.26	75.5	0.9
0.2882	27.36	0.26	75.3	0.9
0.2882	27.26	0.26	75.6	0.9
<i>323.1 K, 0.14 MPa</i>				
0.0501	4.82	0.16	75.3	3.2
0.0501	4.73	0.16	77.0	3.2
0.1503	13.93	0.20	78.1	1.4
0.1503	13.91	0.20	78.2	1.4
0.3007	27.26	0.30	79.1	1.0
0.3007	27.39	0.30	78.6	1.0
<i>323.1 K, 27.45 MPa</i>				
0.0250	2.36	0.15	77.4	5.8
0.0250	2.49	0.15	72.1	5.8
0.0250	2.44	0.15	74.3	5.8
0.0501	4.80	0.15	75.8	3.0
0.0501	4.85	0.15	74.8	3.0
0.0501	4.69	0.15	78.1	3.0
0.1503	13.81	0.20	79.1	1.3
0.1503	13.92	0.20	78.3	1.3
0.3007	27.24	0.29	79.3	1.0
0.3007	27.49	0.29	78.5	1.0
<i>373.2 K, 1.12 MPa</i>				
0.0249	2.25	0.07	81.1	3.0
0.0249	2.24	0.07	81.4	3.0
0.0249	2.24	0.07	81.2	3.0
0.0249	2.27	0.07	80.2	3.0
0.0249	2.26	0.07	80.5	3.0
0.0506	4.54	0.08	81.5	1.7
0.0506	4.54	0.08	81.4	1.7
0.0506	4.55	0.08	81.3	1.7
0.0506	4.56	0.08	81.0	1.7
0.1482	13.17	0.15	81.7	1.1
0.1482	13.24	0.15	81.2	1.1
0.1482	13.16	0.15	81.7	1.1
0.3003	26.32	0.26	81.9	1.0
0.3003	26.38	0.26	81.7	1.0
0.3003	25.98	0.26	83.1	1.0
0.3003	26.38	0.26	81.6	1.0
<i>373.2 K, 27.46 MPa</i>				
0.0250	2.33	0.09	78.2	3.9
0.0250	2.27	0.09	80.7	3.9
0.0250	2.30	0.09	79.6	3.9
0.0250	2.28	0.09	80.2	3.9
0.0253	2.30	0.09	80.5	3.8
0.0253	2.30	0.09	80.6	3.8
0.0253	2.28	0.09	81.3	3.8
0.0253	2.32	0.09	79.6	3.8
0.0496	4.46	0.10	81.3	2.1
0.0496	4.53	0.10	79.9	2.1
0.0496	4.56	0.10	79.4	2.1
0.0496	4.49	0.10	80.8	2.1
0.0500	4.52	0.10	80.9	2.1
0.0500	4.53	0.10	80.7	2.1
0.0500	4.53	0.10	80.7	2.1
0.0500	4.51	0.10	81.2	2.1
0.1494	13.31	0.16	81.6	1.1
0.1494	13.41	0.16	80.9	1.1
0.1494	13.32	0.16	81.5	1.1
0.1494	13.43	0.16	80.7	1.1
0.1500	13.43	0.16	81.1	1.1
0.1500	13.46	0.16	80.9	1.1
0.1500	13.43	0.16	81.1	1.1

TABLE A1 (continued)

$m/\text{mol} \cdot \text{kg}^{-1}$	$\Delta\rho/\text{kg} \cdot \text{m}^{-3}$	$\sigma\Delta\rho/\text{kg} \cdot \text{m}^{-3}$	$V_\phi/\text{cm}^3 \cdot \text{mol}^{-1}$	$\sigma V_\phi/\text{cm}^3 \cdot \text{mol}^{-1}$
0.1500	13.39	0.16	81.4	1.1
0.2934	25.89	0.27	81.4	1.0
0.2934	25.97	0.27	81.1	1.0
0.2934	25.94	0.27	81.2	1.0
0.2934	25.95	0.27	81.2	1.0
0.3004	26.48	0.27	81.5	1.0
0.3004	26.52	0.27	81.3	1.0
0.3004	26.50	0.27	81.4	1.0
0.3004	26.51	0.27	81.4	1.0
473.4 K, 2.64 MPa				
0.0254	2.18	0.18	84.2	9.2
0.0254	2.23	0.18	81.1	9.2
0.0502	4.31	0.18	83.8	4.8
0.1510	12.83	0.22	84.1	1.9
0.1510	12.71	0.22	85.2	1.9
0.3020	25.13	0.30	85.2	1.3
0.3020	25.08	0.30	85.4	1.3
473.5 K, 28.52 MPa				
0.0250	2.26	1.86	79.0	95.1
0.0250	2.35	1.86	74.2	95.1
0.0501	4.63	1.86	75.9	47.4
0.0501	4.34	1.86	83.4	47.5
0.0501	4.40	1.86	81.9	47.4
0.1503	12.62	1.87	86.0	15.8
0.1503	13.48	1.87	78.7	15.8
0.3007	25.48	1.88	83.8	7.9
0.3007	25.59	1.88	83.3	7.9
523.2 K, 10.46 MPa				
0.0251	2.35	0.18	69.2	10.9
0.0251	2.35	0.18	69.4	10.9
0.0251	2.38	0.18	67.1	10.9
0.0251	2.32	0.18	71.2	10.9
0.0502	4.71	0.18	68.7	5.6
0.0502	4.62	0.18	71.4	5.6
0.0502	4.63	0.18	71.0	5.6
0.0502	4.61	0.18	71.6	5.6
0.1500	13.33	0.22	75.4	2.2
0.1500	13.44	0.22	74.4	2.2
0.1500	13.39	0.22	74.9	2.2
0.1500	13.36	0.22	75.1	2.2
0.3000	25.98	0.30	77.7	1.5
0.3000	26.14	0.30	76.9	1.5
0.3000	26.15	0.30	76.8	1.5
0.3000	26.15	0.30	76.8	1.5
523.0 K, 28.04 MPa				
0.0230	2.12	0.54	72.9	34.4
0.0230	2.18	0.54	69.0	34.4
0.0460	4.05	0.54	78.6	17.2
0.0460	4.12	0.54	76.5	17.2
0.1377	11.95	0.55	79.9	5.9
0.1377	12.29	0.55	76.2	5.8
0.1377	12.30	0.55	76.1	5.8
0.2750	23.32	0.58	81.6	3.1
0.2750	23.38	0.58	81.3	3.1
0.2750	23.47	0.58	80.8	3.1
573.2 K, 10.57 MPa				
0.0252	2.76	0.14	26.7	10.6
0.0252	2.72	0.14	30.0	10.6
0.0502	5.44	0.14	28.8	5.6
0.0502	5.43	0.14	29.4	5.6
0.1498	15.52	0.20	37.5	2.5
0.1498	15.64	0.20	36.1	2.5
0.1498	15.55	0.20	37.2	2.5
573.9 K, 27.67 MPa				
0.0230	2.61	0.44	27.1	34.5
0.0230	2.47	0.44	38.1	34.5
0.0230	2.45	0.44	39.3	34.5
0.0230	2.36	0.44	46.5	34.5
0.0460	4.51	0.45	54.1	17.3
0.0460	4.64	0.45	48.9	17.3
0.0460	4.62	0.45	49.9	17.3
0.0460	4.65	0.45	48.7	17.3

(continued on next page)

TABLE A1 (continued)

$m/\text{mol} \cdot \text{kg}^{-1}$	$\Delta\rho/\text{kg} \cdot \text{m}^{-3}$	$\sigma\Delta\rho/\text{kg} \cdot \text{m}^{-3}$	$V_\phi/\text{cm}^3 \cdot \text{mol}^{-1}$	$\sigma V_\phi/\text{cm}^3 \cdot \text{mol}^{-1}$
0.1377	13.26	0.46	56.6	5.9
0.1377	13.32	0.46	55.8	5.9
0.2750	26.06	0.50	58.3	3.2
0.2750	25.92	0.50	59.2	3.2
0.2750	25.26	0.50	63.4	3.2

a C_p^0 values diving strongly with increasing temperature, the effect being attenuated by increase of pressure. As a property being a derivative of enthalpy that exhibits itself divergence at the critical point of water scaling with the solvent expansivity, C_p^0 has a complex “s” like variation when passing through the critical region of water. For a nonvolatile solute it exhibits always a negative and positive divergence when the critical temperature of water is approached from below and from above, respectively [14,15]. The comparison with literature is possible only at near ambient temperature, where the data of Xiao *et al.* [6] are plotted in figure 5. They are somewhat lower compared to our measurements: 193.6, 206.3 and 202.1 J · K⁻¹ · mol⁻¹ at 298, 313 and 328 K, respectively. Quite recently Erickson *et al.* [7] reported for C_p^0 at the same conditions the values 194.7, 203.6 and 212.0 J · K⁻¹ · mol⁻¹.

4. Standard molar volumes and heat capacities of triflate anion CF_3SO_3^- (aq)

Standard molar properties of triflate ion can be determined in two ways. The first one applies the usual hydrogen convention, assigning zero value to the standard thermodynamic properties of the hydrogen cation. Assuming in addition complete dissociation of triflic acid in aqueous solutions at all experimental conditions, the standard molar properties reported earlier [3] are equal to those of the triflate anion. The other way is to calculate standard molar properties of triflate ion from the combination of measured properties of sodium triflate NaCF_3SO_3 and the same properties of sodium cation Na^+ . In this case we need to assume negligible association of Na^+ and CF_3SO_3^- ions and reliable knowledge of the properties of Na^+ from literature sources. Comparison of obtained results for triflate ion allows the check of compatibility of the presented data with those measured by us earlier in the same conditions [3] as well as the verification of the above stated assumptions.

The assumption of complete dissociation of both triflic acid and its sodium salt cannot be scrutinized *a priori* because of the lack of relevant data. In case of Na^+ ion, several approaches are available for calculating its standard molar properties, e.g. the HKF model [17] and SOCW model [18]. While predictions of these models for Na^+ at temperatures below 500 K are in good mutual agreement, the differences increase at elevated conditions. At the extreme of our experimental conditions (573.9 K and 10.5 MPa) the two above models give reasonably similar values for V^0 (−14.9 and −10.7 cm³ · mol⁻¹, respectively) but the discrepancy is large for C_p^0 (−80 and −337 J · K⁻¹ · mol⁻¹, respectively). There may be several reasons for such difference: insufficient model flexibility in a wide range of conditions, the fact that the literature data used for model adjustment prevail at near ambient conditions thus high temperature values were underrated in correlations, and inaccuracy of data used for model adjustment. This possible inaccuracy follows not only from experimental uncertainties, but also from the fact that the measured properties of aqueous electrolytes at finite concentrations must be extrapolated to infinite dilution and assigned to individual ions. In case of HCl(aq) and NaCl(aq) that are instrumental for evaluation of Na^+ ion data, this extrapolation is generally based on the assumption of complete dissociation.

However, both HCl and NaCl are not completely dissociated namely at higher concentrations and at temperatures above ~500 K [19,20]. This fact substantially compromises the predictions of models that are based on correlation of standard molar properties stemming from extrapolations of experimental data not corrected for ion association.

Reliable evaluation of Na^+ ion standard molar properties at high temperatures thus requires data or models for HCl(aq) and NaCl(aq) taking into account the effect of partial association. Sedlbauer and Wood [21] published the SOCW model parameters for NaCl(aq), resulting from comprehensive data treatment at near-critical conditions and including association. No such model is available for HCl(aq), but volumetric data for this system at emperatures above 523 were reported by Sharygin and Wood [22] and Trevani *et al.* [23] and a few heat capacities also by Sharygin and Wood [22].

4.1. Volumes

The values of $V^0(\text{Tr}^-)$ at temperatures below 500 K were determined by three different approaches. The HKF revised model [17] and the SOCW model [18] were used for calculating the properties of $V^0(\text{Na}^+)$ directly. In addition, the recommended data for $V^0(\text{NaCl})$ were obtained from the correlation of Archer² [10] and the properties of sodium ion were evaluated with the help of experimental data for HCl(aq) reported at the same or similar conditions by Sharygin and Wood [22]: $V^0(\text{Na}_{\text{Archer-SW}}^+) = V^0(\text{NaCl}_{\text{Archer}}) - V^0(\text{HCl}_{\text{SW}})$. As a result we have three types of volumetric data for sodium cation, $V^0(\text{Na}_{\text{HKF}}^+)$, $V^0(\text{Na}_{\text{SOCW}}^+)$ and $V^0(\text{Na}_{\text{Archer-SW}}^+)$ that we have combined with our measurements of $V^0(\text{NaCF}_3\text{SO}_3)$ to obtain the contribution of triflate anion, see table 3. The agreement among various approaches is good, the only difference larger than experimental uncertainty (7 cm³ · mol⁻¹) appears for the recommendations of Archer [10] combined with data by Sharygin and Wood [22] at 473 K and 28 MPa.

For temperatures above 500 K the literature apparent molar volumes of HCl [22,23] were corrected for ion association and extrapolated to infinite dilution in the same way as described by Trevani *et al.* [23]. The extrapolation equation based on the Pitzer model was

$$V_\phi = V_{\text{ions}}^0 + \alpha \cdot \Delta V_I^0 + (1 - \alpha) \left(\frac{A_\nu}{b} \ln(1 + bI^{1/2}) + 2RTI(B_\nu + C_\nu I) \right), \quad (10)$$

where α is the degree of association, I is the ionic strength ($I = (1 - \alpha)m$), and ΔV_I^0 is the difference between the standard molar volumes of HCl's ion pair and HCl in ionized form, $\Delta V_I^0 = V_{\text{ions}}^0$. The degree of association was calculated from the thermodynamic association constant and activity coefficient model reported by Simonson *et al.* [24]. Dimensionality of the fitting equation (10) can be decreased by applying thermodynamic relationship

$$\Delta V_T^0 = -RT(\partial \ln K_{\text{as}}/\partial p)_T = -RT\kappa_w(\partial \ln K_{\text{as}}/\partial \ln \rho_w)_T. \quad (11)$$

² No correction for association was considered by Archer when establishing his recommended thermodynamic data for NaCl(aq) covering temperature range between 250 and 600 K.

TABLE A2

Specific heat capacity differences $\Delta c_p = c_{p,s} - c_{p,w}$ and apparent molar heat capacities $C_{p,\phi}$ of sodium triflate solutions at different temperatures and pressures.

$m/\text{mol} \cdot \text{kg}^{-1}$	$\Delta C_p/J \cdot \text{K}^{-1} \cdot \text{kg}^{-1}$	$\sigma \Delta C_p/J \cdot \text{K}^{-1} \cdot \text{kg}^{-1}$	$C_{p,\phi}/J \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$\sigma C_{p,\phi}/J \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
322.7 K, 2.00 MPa				
0.0501	-23.20	0.95	251.4	19.1
0.1503	-69.87	1.15	241.6	7.9
0.1503	-69.60	1.15	243.4	7.8
0.3007	-137.08	1.64	238.8	5.8
322.8 K, 27.98 MPa				
0.0250	-11.18	0.53	259.7	21.4
0.0501	-22.60	0.57	253.8	11.4
0.0501	-22.69	0.57	252.1	11.4
0.1503	-67.88	0.85	245.6	5.8
0.1503	-67.33	0.85	249.3	5.8
0.3007	-131.91	1.41	247.5	4.9
0.3007	-131.98	1.41	247.3	4.9
374.1 K, 1.35 MPa				
0.0249	-12.36	0.45	226.8	18.3
0.0499	-24.62	0.50	227.6	10.2
0.0499	-24.51	0.50	229.9	10.2
0.0499	-24.58	0.50	228.4	10.2
0.1497	-72.07	0.86	231.4	5.9
0.1497	-73.73	0.86	220.1	5.9
0.1497	-72.87	0.86	226.0	5.9
0.2988	-146.08	1.52	211.3	5.4
0.2988	-142.86	1.51	222.6	5.3
0.2988	-143.19	1.51	221.5	5.3
374.2 K, 28.38 MPa				
0.0250	-12.45	1.70	215.2	68.1
0.0501	-24.09	1.70	230.5	34.3
0.0501	-23.59	1.70	240.5	34.3
0.0501	-24.01	1.70	232.1	34.3
0.1503	-70.03	1.82	237.4	12.4
0.1503	-70.38	1.82	235.1	12.4
0.3007	-138.75	2.13	230.1	7.4
0.3007	-138.75	2.13	230.1	7.4
424.0 K, 10.56 MPa				
0.0251	-14.49	2.52	156.2	101.0
0.0251	-14.54	2.52	154.0	100.9
0.0501	-28.72	2.53	157.9	51.0
0.1503	-80.48	2.63	186.7	17.9
0.1503	-80.45	2.63	186.9	17.9
0.1503	-82.27	2.63	174.5	17.9
0.1503	-83.03	2.63	169.3	17.9
0.3007	-159.10	2.89	179.5	10.1
0.3007	-159.59	2.89	177.8	10.1
424.0 K, 28.47 MPa				
0.0250	-13.58	0.85	181.6	34.2
0.0501	-26.75	0.88	188.8	17.8
0.1503	-78.19	1.16	193.7	7.9
0.1503	-78.90	1.16	188.8	7.9
0.3007	-153.10	1.73	191.9	6.0
0.3007	-152.73	1.72	193.2	6.0
473.2 K, 2.90 MPa				
0.0251	-17.46	0.52	73.1	20.7
0.0501	-34.15	0.61	84.1	12.3
0.0501	-34.20	0.61	83.1	12.3
0.0501	-34.21	0.61	82.8	12.3
0.1503	-99.31	1.19	93.7	8.1
0.1503	-99.22	1.19	94.3	8.1
0.1503	-98.83	1.19	96.9	8.1
0.3005	-191.79	2.06	100.3	7.2
0.3005	-191.91	2.06	99.9	7.2
0.3005	-192.01	2.06	99.5	7.2
473.2 K, 28.38 MPa				
0.0460	-31.58	0.59	58.7	13.0
0.0460	-31.69	0.59	56.4	13.0
0.1377	-87.16	1.06	102.8	7.9
0.1377	-87.61	1.06	99.4	7.9
0.1377	-87.63	1.06	99.2	7.9
0.1377	-87.24	1.06	102.2	7.9
0.2750	-167.94	1.72	111.1	6.6
0.2750	-166.90	1.71	115.1	6.5
0.2750	-167.15	1.72	114.1	6.5

(continued on next page)

TABLE A2 (continued)

$m/\text{mol} \cdot \text{kg}^{-1}$	$\Delta C_p/J \cdot \text{K}^{-1} \cdot \text{kg}^{-1}$	$\sigma \Delta C_p/J \cdot \text{K}^{-1} \cdot \text{kg}^{-1}$	$C_{p,\phi}/J \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$\sigma C_{p,\phi}/J \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
524.2 K, 10.48 MPa				
0.0249	-23.53	0.57	-124.3	23.0
0.0506	-46.94	0.76	-111.0	15.1
0.0506	-47.14	0.76	-114.9	15.2
0.0506	-46.94	0.76	-110.8	15.1
0.1482	-130.40	1.62	-77.5	11.2
0.1482	-130.01	1.62	-74.8	11.2
0.3003	-248.60	2.76	-45.8	9.7
0.3003	-249.01	2.76	-47.2	9.7
524.0 K, 28.26 MPa				
0.0230	-20.16	0.62	-85.7	27.1
0.0460	-38.54	0.74	-50.1	16.2
0.0460	-38.86	0.74	-57.3	16.2
0.0460	-39.08	0.74	-62.1	16.2
0.0460	-38.61	0.74	-51.6	16.2
0.1482	-117.39	1.47	-18.1	10.2
0.1482	-117.42	1.47	-18.2	10.2
0.2962	-220.84	2.38	10.7	8.4
0.2962	-221.22	2.38	9.3	8.5
573.9 K, 10.54 MPa				
0.0249	-47.41	0.90	-935.1	36.4
0.0249	-47.20	0.90	-926.8	36.3
0.0504	-91.76	1.44	-859.5	28.8
0.0504	-91.51	1.43	-854.4	28.7
0.0504	-91.63	1.44	-856.8	28.7
0.1482	-244.41	3.37	-714.3	23.3
0.1482	-244.53	3.37	-715.1	23.3
0.1482	-244.70	3.37	-716.2	23.3
0.2962	-447.07	5.46	-609.3	19.4
0.2962	-447.33	5.46	-610.2	19.4
0.2962	-447.14	5.46	-609.5	19.4
573.9 K, 27.70 MPa				
0.0230	-29.61	0.67	-408.2	29.3
0.0460	-58.19	0.95	-391.0	20.7
0.0460	-58.15	0.95	-390.1	20.7
0.0990	-120.10	1.66	-349.7	17.1
0.0990	-120.26	1.66	-351.4	17.1
0.0990	-120.20	1.66	-350.8	17.1
0.1482	-172.12	2.27	-306.9	15.7
0.1482	-172.40	2.27	-308.9	15.7
0.2962	-320.51	3.79	-253.2	13.5
0.2962	-321.59	3.80	-257.0	13.5
0.2962	-321.20	3.80	-255.6	13.5
0.2962	-321.79	3.81	-257.7	13.5
0.2962	-321.80	3.81	-257.7	13.5
0.2962	-322.00	3.81	-258.4	13.5
0.2962	-322.77	3.82	-261.2	13.5

TABLE 1

Standard molar volumes V° , Debye–Hückel law limiting slopes A_V [13], the Pitzer correlation parameters β_V° for sodium triflate at different temperatures and pressures; comparison with the literature values.

T/K	p/MPa	$V^\circ/\text{cm}^3 \cdot \text{mol}^{-1}$	$A_V/\text{cm}^3 \cdot \text{mol}^{-1/2}$	$10^5 \cdot \beta_V^\circ/\text{kg} \cdot \text{mol}^{-1} \cdot \text{MPa}^{-1}$	$V^\circ(^*)/\text{cm}^3 \cdot \text{mol}^{-1}$
323.13	0.14	76.3 ± 1.6	2.359	101.7	76.8
373.17	1.12	80.3 ± 0.6	4.098	-1.301	80.9
473.38	2.64	80.8 ± 1.4	14.96	-75.13	80.0
523.15	10.5	65.5 ± 0.9	31.27	-61.57	68.3
573.16	10.6	12.7 ± 3.6	99.60	-521.4	15.4
298.08	31.0	73.3 ± 0.9	1.736	104.6	72.0
323.15	27.5	76.4 ± 1.9	2.198	106.3	75.7
373.21	27.5	80.0 ± 0.3	3.675	-8.867	79.9
473.50	28.5	78.1 ± 5.7	11.98	18.72	80.1
523.00	28.0	69.2 ± 3.2	24.60	82.14	71.2
573.85	27.7	37.9 ± 5.9	63.02	-121.5	38.7

(*) Values calculated from equation (6) reported by Xiao and Tremaine [4].

allowing to calculate this difference from the model for association constant as a function of temperature and pressure or water density. The association constant K_{as} was provided for HCl(aq) as a

function of temperature and water density ρ_w [24]. The three remaining adjustable parameters of the correlation equation (V_{ions}°, B_V, C_V) were found in all cases statistically significant. The

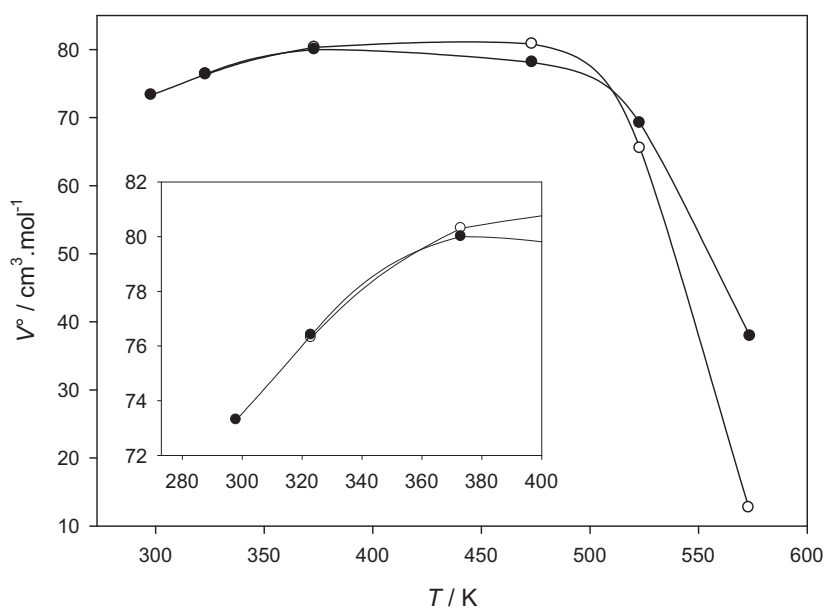


FIGURE 3. Standard molar volumes of sodium triflate as a function of temperature. (○) near saturation pressure of water, (●) near 28 MPa.

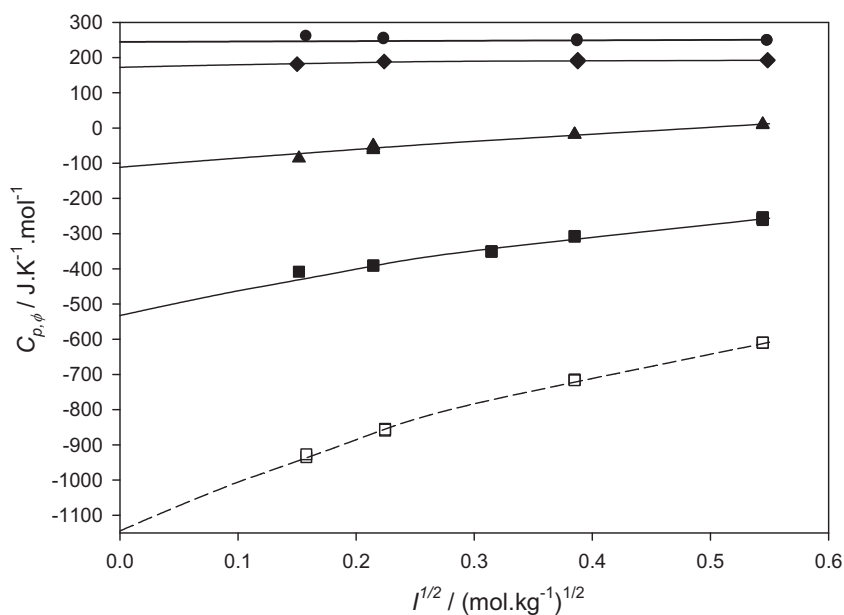


FIGURE 4. Apparent molar heat capacities of sodium triflate as a function of square root of ionic strength, at different temperatures and pressures. (●) 322.84 K, 27.98 MPa, (◆) 423.99 K, 28.47 MPa, (▲) 523.97 K, 28.26 MPa, (■) 573.86 K, 27.70 MPa, (□) 573.86 K, 10.54 MPa.

TABLE 2

Standard molar heat capacities C_p° , Debye–Hückel law limiting slopes A_c [13], the Pitzer correlation parameters β_c^0 for sodium triflate at different temperatures and pressures.

T/K	p/MPa	$C_p^\circ/J \cdot K^{-1} \cdot mol^{-1}$	$A_c/J \cdot K^{-1} \cdot mol^{-1}$	$10^5 \cdot \beta_c^0/kg \cdot mol^{-1} \cdot K^{-2}$
322.67	2.00	240 ± 14	39.69	3.4927
374.08	1.35	221 ± 9	60.57	4.0103
423.98	10.56	157 ± 15	94.20	1.9775
473.23	2.90	50.7 ± 2	185.48	2.5984
524.20	10.48	-187 ± 4	396.92	2.0083
573.86	10.54	-1145 ± 3	1533.32	6.6545
322.84	27.98	244 ± 7	37.27	2.5798
374.22	28.38	228 ± 6	54.94	3.0276
423.99	28.47	172 ± 7	85.23	1.7546
474.20	28.38	45.2 ± 15	146.78	-1.0186
523.97	28.26	-112 ± 6	291.88	0.027615
573.86	27.70	-533 ± 7	769.14	2.8859

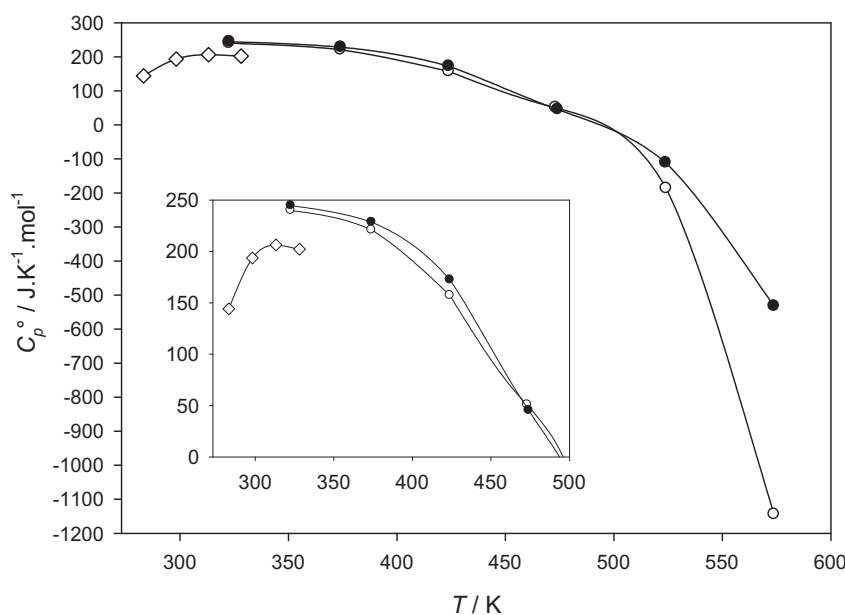


FIGURE 5. Standard molar heat capacities of sodium triflate as a function of temperature and pressure and comparison with literature [6]. (○) near saturation pressure of water, (●) near 28 MPa, (◇) literature data at atmospheric pressure.

TABLE 3

Standard molar volumes of sodium and triflate ions at temperatures below 500 K.

T/K	p/MPa	$V^{\circ}/\text{cm}^3 \cdot \text{mol}^{-1}$							
		HCl ⁽¹⁾	Na ⁺ (2)	Na ⁺ (3)	Na ⁺ (4)	Tr ⁻ (5)	Tr ⁻ (6)	Tr ⁻ (7)	HTr ⁽⁸⁾
298.15	0.1	17.81	-1.3	-1.2	-1.2				75.4
323.13	0.1	17.91	-0.3	-0.2	0.0	76.6	76.5	76.3	77.8
373.17	1.1	15.42	1.2	0.4	1.6	79.1	79.9	78.7	79.5
473.38	2.6	-3.78	1.7	-1.7	3.6	79.1	82.5	77.2	77.8
298.08	31.0	18.11	-0.1	-0.1	-0.1	73.4	73.4	73.4	74.6
323.15	27.5	18.18	0.6	0.7	0.8	75.8	75.7	75.6	76.8
373.21	27.5	15.94	1.8	1.2	2.4	78.2	78.8	77.6	79.2
473.50	28.5	0.22	1.9	-0.5	4.8	76.2	78.6	73.3	80.4

(1) Experimental data from Sharygin and Wood [22].

(2) Calculated from the SOCW model, Sedlbauer *et al.*, [18].

(3) Calculated from the HKF model, Tanger and Helgeson [17].

(4) Obtained from a combination of NaCl(aq) (Archer [10]) and HCl(aq) (Sharygin and Wood [22]) data.

(5) Combination of results from table 1 with (2).

(6) Combination of results from table 1 with (3).

(7) Combination of results from table 1 with (4).

(8) Data for HTr(aq) from Pourtier *et al.* [3].

results in table 4 correspond to the values of V_{ions}° and also included are the values of V° for HCl(aq) obtained from correlation with equation (5) ($\beta_{\text{V}}^{-1} = 0$), without any correction for association. While at temperature of 523 K the association does not seem to affect much the volumetric values, the differences are sizable at 573 K, increasing from 10 to 18 $\text{cm}^3 \cdot \text{mol}^{-1}$ with decreasing pressure.

Standard molar volumes for HCl(aq) in table 4 are available at similar conditions as our measurements with NaTr solutions, so they can be applied for evaluation of ionic volumes for triflate ion. Recalculation to our exact conditions was performed by simple interpolation or extrapolation of the results from table 4. The standard molar volumes of triflate ion are finally obtained from combination of the data in table 1, with those for NaCl(aq) calculated from the SOCW model [21] in combination with the values for HCl(aq), see table 5.

Figure 6 illustrates the evolution of the standard molar volumes of triflate anion CF_3SO_3^- calculated from the measurements with NaTr(aq) as a function of temperature, near saturation pressure and at 28 MPa in comparison with the data for HTr(aq) [3]. The plots use the data from table 3 (based on SOCW values for Na⁺

TABLE 4

Standard molar volumes of HCl(aq) in ionized form from extrapolation of data at temperatures above 500 K.

T/K	p/MPa	$V^{\circ}/\text{cm}^3 \cdot \text{mol}^{-1}$	$V^{(3)}/\text{cm}^3 \cdot \text{mol}^{-1}$
523.20	10	$-27.3^{(1)} \pm 1$	-26.1
573.26	10	$-108.4^{(1)} \pm 1$	-90.2
523.62	14	$-25.9^{(2)} \pm 1$	-26.2
573.11	14	$-96.7^{(2)} \pm 3$	-83.9
523.21	28	$-18.4^{(1)} \pm 1$	-17.8
573.31	28	$-64.5^{(1)} \pm 1$	-54.8

(1) Sharygin and Wood [22] data corrected for association.

(2) Trevani *et al.* [23] data corrected for association.

(3) Extrapolations without correction for association.

ion) and from table 5. The agreement between the two alternative ways for obtaining the ionic data is good, generally within the combined uncertainties of data and models used for their evaluation.

TABLE 5

Standard molar volumes of triflate ion at temperatures above 500 K.

T/K	p/MPa	$V^\circ(\text{NaTr})/\text{cm}^3 \cdot \text{mol}^{-1}$	$V^{\circ(1)}(\text{NaCl})/\text{cm}^3 \cdot \text{mol}^{-1}$	$V^{\circ(2)}(\text{HCl})/\text{cm}^3 \cdot \text{mol}^{-1}$	$V^{\circ(3)}(\text{Na}^+)/\text{cm}^3 \cdot \text{mol}^{-1}$	$V^\circ(\text{Tr}^-)/\text{cm}^3 \cdot \text{mol}^{-1}$	$V^{\circ(4)}(\text{HTr})/\text{cm}^3 \cdot \text{mol}^{-1}$
523.15	10.5	65.5 ± 0.9	-24.7	-27.1	2.4	63.1	62.0
573.16	10.6	12.7 ± 3.6	-108.3	-106.6	-1.7	14.4	7.4
523.00	28.0	69.2 ± 3.2	-15.2	-18.4	3.2	66	68.4
573.85	27.7	37.9 ± 5.9	-65.0	-64.5	-0.5	38.4	34.2

(1) Data for NaCl(aq) calculated from the SOCW model, Sedlbauer and Wood [21].

(2) Data for HCl(aq) by interpolation of the results from table 4.

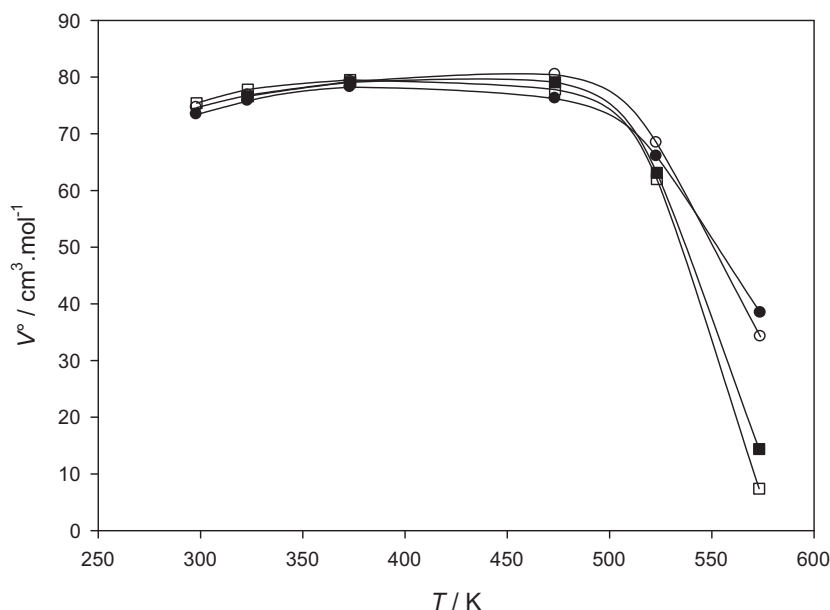
(3) Data for Na⁺(aq) are from linear combination of NaCl(aq) and HCl(aq) values.(4) Data for HTr(aq) from Pourtier *et al.* [3], calculated from experimental data without considering possible association of HTr

FIGURE 6. Standard molar volumes of triflate anion (CF_3SO_3^-) at different temperatures, and pressures (tables 3 and 5). (■) data obtained from NaTr – $\text{Na}^+_{(\text{SOCW})}$ near saturation pressure of water, (●) data obtained from NaTr – $\text{Na}^+_{(\text{SOCW})}$ near 28 MPa, (□) HTr near saturation pressure of water [3], (○) HTr, near 28 MPa [3].

TABLE 6

Standard molar heat capacity of sodium and triflate ions at temperatures below 500 K.

T/K	p/MPa	$C_p^\circ/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$								
		HCl	$\text{Na}^+ (3)$	$\text{Na}^+ (4)$	$\text{Na}^+ (5)$	$\text{Tr}^- (6)$	$\text{Tr}^- (7)$	$\text{Tr}^- (8)$	HTr ⁽⁹⁾	
322.67	2.0	-112 ⁽¹⁾	44	49	54	196	191	186	183	
374.08	1.4	-126 ⁽¹⁾	46	51	50	175	170	171	162	
423.98	10.6		32	46		125	111		113	
473.23	2.9		-15	29		65	22		4	
322.84	28.0	-103 ⁽²⁾	46	55	60	198	189	184	192	
374.22	28.4	-115 ⁽²⁾	48	54	54	180	174	174	169	
423.99	28.5	-162 ⁽²⁾	35	48	52	137	124	120	132	
474.20	28.4	-243 ⁽²⁾	-7	38	51	52	7	-6	26	

(1) Experimental data from Tremaine *et al.* [25].

(2) Experimental data from Sharygin and Wood [22].

(3) Calculated from the SOCW model, Sedlbauer *et al.* [18].

(4) Calculated from the HKF model, Tanger and Helgeson [17].

(5) Obtained from a combination of NaCl(aq) (Archer [10]) and HCl(aq) (Tremaine *et al.* [25] or Sharygin and Wood [22]) data.

(6) Combination of results from table 2 with (3).

(7) Combination of results from table 2 with (4).

(8) Combination of results from table 2 with (5).

(9) Data for HTr(aq) from Pourtier *et al.* [3].

4.2. Heat capacities

In analogous way to the standard molar volume calculations, the values of $C_p^\circ(\text{Na}^+)$ were determined below 500 K by three different ways: from the HKF model [17], from the SOCW model [18], and combining the recommended data for NaCl(aq) [8] with those

for HCl(aq) by Tremaine *et al.* [25] or Sharygin and Wood [22]. The contribution of triflate anion to standard molar heat capacity at lower temperatures is listed in table 6. The agreement among various approaches is not satisfactory unlike for the standard molar volume, namely at temperature 473 K for both pressures the differences are significant. This is probably due to a particular shape of

TABLE 7

Standard molar heat capacities of HCl(aq) in ionized form from extrapolation of data at temperatures above 500 K.

T/K	p/MPa	$C_p^{\circ(1)}/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$C_p^{\circ(2)}/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
523.92	28	-393 ± 5	-359
574.17	28	-966 ± 32	-508

(1) Sharygin and Wood [22] data corrected for association.

(2) Extrapolations without correction for association.

the heat capacity function that changes only slightly in temperature interval from about 320 K to 470 K but undergoes steep changes at lower and mainly at higher temperatures. It is difficult for any model to describe accurately such behavior and it is known that equations such as HKF and SOCW have problems at temperatures around 470 K and above [26].

At temperatures above 500 K the measured apparent molar heat capacities of HCl(aq) by Sharygin and Wood [19] were corrected for ion association and extrapolated to infinite dilution using analogous procedure as in case of apparent molar volumes. The extrapolation equation based on the Pitzer model was

$$C_{p,\phi} = C_{p,\text{ions}}^{\circ} + \alpha \cdot \Delta C_{p,x}^{\circ} + (1 - \alpha) \left(\frac{A_c}{b} \ln(1 + bI^{1/2}) - 2RT^2I(B_C + C_C I) \right) + \Delta H_r(\partial\alpha/\partial T)_p, \quad (12)$$

where α is again the degree of association and $\Delta C_{p,r}^{\circ}$ is the difference between standard molar heat capacity of HCl ion pair and HCl in ionized form, $\Delta C_{p,r}^{\circ} = C_{p,\text{ip}}^{\circ} - C_{p,\text{ions}}^{\circ}$ and ΔH_r corresponds to the en-

thalpy change during the association. The last term on the right-hand side is the so-called relaxation term [27], accounting for the thermal shift associated with the change in equilibrium composition during the measurement of the solution heat capacity. The degree of association was calculated again from the thermodynamic association constant and activity coefficient models reported by Simonson *et al.* [24] and term $(\partial\alpha/\partial T)_p$ was evaluated numerically. The ΔH_r term was approximated simply by the extended Debye-Hückel equation $\Delta H_r = \Delta H_r^{\circ} + \frac{A_{\text{H}}}{b} \ln(1 + bI^{1/2})$ supposing that the use of the Pitzer virial expansion would not substantially change the value of ΔH_r while considerably increasing the complexity of calculations. Similarly as in case of ΔV_r° , the difference between standard molar properties for ion pair and ions can be estimated for enthalpy and heat capacity from thermodynamic relations

$$\Delta H_r^{\circ} = RT^2(\partial \ln K_{\text{as}}/\partial T)_p, \quad \Delta C_{p,r}^{\circ} = (\partial \Delta H_r^{\circ}/\partial T)_p. \quad (13)$$

allowing to calculate these differences from the above model [24] for the association constant. The three remaining adjustable parameters of the correlation equation ($C_{p,\text{ions}}^{\circ}$, B_C , C_C) were found in all cases statistically significant. The results in table 7 correspond to the values of $C_{p,\text{ions}}^{\circ}$; also included in the table are values of C_p° for HCl(aq) obtained from correlation with equation (8), without the correction for association. The difference is almost 100% at 573 K, suggesting large contribution of ion association to heat capacity at elevated temperatures.

Unfortunately due to the lack of experimental data above temperature of 500 K at pressures close to the saturation pressure of water the standard molar heat capacities for HCl(aq) are available

TABLE 8

Standard molar heat capacities of triflate ion at temperatures above 500 K.

T/K	p/MPa	$C_p^{\circ}(\text{NaTr})/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$C_p^{\circ(1)}(\text{NaCl})/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$C_p^{\circ(2)}(\text{HCl})/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$C_p^{\circ(3)}(\text{Na}^+)/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$C_p^{\circ(0)}(\text{Tr}^-)/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$C_p^{\circ(4)}(\text{HTr})/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
523.97	28.3	-112 ± 6	-392	-393	1	-113	-193
573.86	27.7	-533 ± 7	-850	-966	116	-657	-594

(1) Data for NaCl(aq) calculated from the SOCW model, Sedlbauer and Wood [21].

(2) Data for HCl(aq) from table 7.

(3) Data for Na⁺(aq) are from linear combination of NaCl(aq) and HCl(aq) values.

(4) Data for HTr(aq) from Pourtier *et al.* [3], calculated from experimental data without considering possible association of HTr.

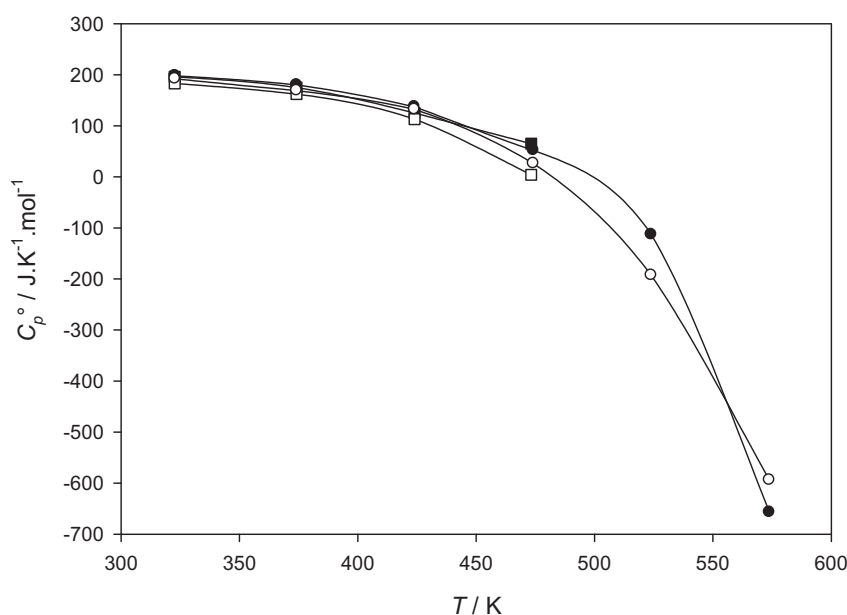


FIGURE 7. Standard molar heat capacities of triflate anion (CF₃SO₃⁻) at different temperatures, and pressures (tables 6 and 8). (■) data obtained from NaTr – Na⁺(SOCW) near saturation pressure of water, (●) data obtained from NaTr – Na⁺(SOCW) near 28 MPa, (□) HTr near saturation pressure of water [3], (○) HTr near 28 MPa [3].

only at pressure of 28 MPa and can be therefore applied for evaluation of the late ion at this isobar only. The standard molar heat capacities of the triflate ion at the two highest temperatures are then obtained similarly like for volumes from combination of the data in table 2 with those for NaCl(aq) calculated from the SOCW model [18] in combination with the values for HCl(aq), see table 8.

Figure 7 illustrates the evolution of the standard molar heat capacities of the triflate anion CF_3SO_3^- calculated from the measurements with NaTr(aq) as a function of temperature, near saturation pressure and at 28 MPa in comparison with the data for HTr(aq) [3]. The plots use the data from table 6 (based on SOCW values for Na^+ ion) and from table 8. The agreement between the two alternative ways for obtaining the ionic data is less satisfactory than in the case of the volumetric data and agreement can be considered as semi quantitative. The comparison was not made for lower pressures above 473 K because of the missing experimental data for heat capacities of HCl(aq). We did not consider useful to perform calculations using existing models that do not take into account strong association of HCl(aq) at elevated temperatures.

5. Conclusion

It is apparent from above that some inconsistency still exists between the standard molar volumes and heat capacities of HTr on one side and of Tr^- ion (calculated from the NaTr, HCl and NaCl data) on the other side. This might be to a certain extent also due to the partial association of HTr at the two highest temperatures. Some additional high temperature measurements for HCl(aq) close to saturated vapour pressure of water are also needed. Yet the values reported in this and in the earlier studies present a considerable progress in the knowledge of thermodynamic behavior of aqueous triflate ion up to at least 573 K. At this moment it is probably the most accurately described aqueous ion at temperatures above 473 K, within the framework of hydrogen convention, suitable for high temperature study of higher valence cations. As such, it can be namely used for refinement of geochemical models and, as a consequence, for better understanding of reaction and phase properties of highly charged species in hydrothermal solutions.

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