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Isopiestic Determination of the Osmotic and Activity Coefficients of Aqueous Sodium Trifluoromethanesulfonate at 298.15 K and 323.15 K, and Representation with an Extended Ion-Interaction (Pitzer) Model

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Isopiestic vapor-pressure measurements were made for aqueous sodium trifluoromethanesulfonate, $NaCF_3SO_3(aq)$, using NaCl(aq) as the reference standard. The measurements for $NaCF_3SO_3(aq)$ cover the molality range from 0.13643 mol·kg^{-1} to 5.3735 mol·kg^{-1} at 298.15 K and from 0.14504 mol·kg^{-1} to 4.3070 mol·kg^{-1} at 323.15 K. Values of the four parameters of an extended version of Pitzer's model for osmotic and activity coefficients, with an ionic-strength dependent third virial coefficient, were evaluated for $NaCF_3SO_3(aq)$ at both temperatures, as were those of the usual three-parameter Pitzer model.

Introduction

A considerable number of industrial, environmental, and biochemical fluids are aqueous electrolytes, and the thermodynamic and transport properties of these solutions are strongly influenced by the occurrence of association equilibria. These association equilibria include hydrolytic equilibria, which may directly affect the variation of solubility with changes in pH, and the association of other anions or neutral ligands with metal cations to form complexes. The determination of hydrolysis constants of metal cations was reviewed by Baes and Mesmer.[1]

The determinations of stability constants for complexes are usually made at constant total ionic strength, to reduce the variation of ionic activity coefficients with the solution composition, and usually with the measurements being made at several different total ionic strengths to permit the results to be extrapolated to infinite dilution. It is desirable to use an inert or “indifferent” electrolyte to control the ionic strength during these measurements. That is, neither the anion nor cation of the electrolyte used to control the ionic strength should significantly complex with the anion or cation whose association equilibrium or equilibria are being investigated nor should they cause other chemical reactions to occur such as oxidation or reduction of the investigated ions. Moreover, this “supporting” electrolyte must also be thermally stable during the course of the measurements.

Among the most commonly used electrolytes for controlling the ionic strength during stability constant determinations are NaCl, KCl, other alkali metal chlorides and bromides, $NaNO_3$, and $NaClO_4$.[1] However, many different metal ions form complexes with chloride, bromide, and nitrate ions, and a few metal perchlorates are not soluble enough for stability constant determinations to be made in their solutions. Scott and Taube[2] also noted that the ClO_4^- ion is a sufficiently strong oxidizing agent at room temperature, that it will oxidize Ti(III), V(II), and Eu(II) rapidly, and that its use may produce hazardous compounds, especially when organic compounds are present. Rard[3] similarly noted that most Ru(II) and Ru(III) complexes and compounds are readily oxidized by ClO_4^-, which usually results in the formation of Ru(IV) complexes or compounds.

Methanesulfonic acid, $HCH_3SO_3(aq)$, is a fairly strong and soluble acid that dissociates to yield the $CH_3SO_3^-$ ion. This ion shows little tendency to form complexes or ion pairs with metal ions. Mean molal activity coefficients $\gamma_\pm$ derived from isopiestic measurements have been reported by Gregor et al.[4] at 298.15 K for $HCH_3SO_3(aq)$, along with its Li^+, K^+, Na^+, and NH_4^+ salts, and for three of its tetraalkylammonium salts. Gregor et al. did not report the measured isopiestic molalities or the resulting osmotic coefficients ϕ, but just listed derived values of $\gamma_\pm$ at selected rounded molalities. Subsequently, Covington et al.[5] reported the detailed results from isopiestic measurements for $HCH_3SO_3(aq)$ at 298.15 K for the extensive molality range of 0.1372 mol·kg^{-1} to 40.429 mol·kg^{-1}. Covington et al. obtained the unpublished experimental ϕ values from Gregor et al.[4] and compared them to their new results graphically. Although there was approximate agreement, the earlier results of Gregor et al. were much more scattered, with some values of ϕ from the Gregor et al.

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study deviating by $\Delta\phi \approx 0.02-0.03$ from a smoothed curve drawn through the combined results. Bonner[6] later reported smoothed values of ϕ and $\gamma_\pm$ derived for $LiCH_3SO_3(aq)$, $NaCH_3SO_3(aq)$, and $KCH_3SO_3(aq)$, from isopiestic measurements at 298.15 K, that were generally in agreement with the earlier smoothed isopiestic results of Gregor et al.[4]

Another soluble strong acid whose anion shows little tendency to complex with metal ions is the fluorinated derivative of HCH_3SO_3, trifluoromethanesulfonic acid, HCF_3SO_3, which forms soluble salts with most cations. Anhydrous trifluoromethanesulfonic acid is liquid at room temperature and is completely miscible with water. A crystal structure determination[7] indicates the solid phase consists of a hydrogen bonded infinite chain, and its structure should more properly be written as $\{CF_3SO_2(OH)\}_n$. The trifluoromethanesulfonate anion, $CF_3SO_3^-$, is a weak complexing agent for most metal cations, and as noted by Scott and Taube,[2] it has weak nucleophilic properties and is resistant to reduction by most easily oxidized metal cations. The $CF_3SO_3^-$ ion is kinetically very stable in water, with no observed decomposition at temperatures below 550 K in acidic solution or below 600 K in neutral and alkaline solutions. At higher temperatures, trifluoromethanesulfonic acid decomposes at observable rates, and the kinetics and mechanism of this decomposition reaction have been studied by Fabes and Swaddle.[8] However, because no decomposition is observed near room temperature, thermodynamic measurements may be made for aqueous trifluoromethanesulfonic acid and its salts without encountering any complications arising from sample decomposition.

On the basis of infrared absorption measurements for highly concentrated aqueous solutions, Leuchs and Zundel[9,10] concluded that the acidic hydrogen of $HCF_3SO_3(aq)$ is completely dissociated when the molar ratio of H_2O to HCF_3SO_3 exceeds 1.6. In contrast, on the basis of Raman spectroscopic measurements, Sampoli et al.[11] concluded that $HCF_3SO_3(aq)$ is a weaker acid than $HClO_4(aq)$, comparable in strength to $H_2SO_4(aq)$, but is a stronger acid than $HCH_3SO_3(aq)$. Using similar Raman spectroscopic measurements for 1.8 $mol\cdot dm^{-3}$ to 11.1 $mol\cdot dm^{-3}$ $HCF_3SO_3(aq)$ solutions at (298.0 ± 0.5) K, Edwards[12] derived an approximate dissociation constant of 280 $mol\cdot dm^{-3}$.

Okan and Champeney[13] measured the electrical conductivities of dilute solutions of $NaCF_3SO_3(aq)$, $KCF_3SO_3(aq)$, and $Ni(CF_3SO_3)_2(aq)$ at ($298.1_5 \pm 0.1$) K. Because the molar conductances of all three of these electrolytes approach the Onsager limiting law at low concentrations, the authors of this study concluded that all three were strong electrolytes. Ho and Palmer[14] also performed electrical conductivity measurements for $NaCF_3SO_3(aq)$ at low concentrations but over a wide range of temperatures and pressures, and from these measurements they derived association constants for the neutral ion pair. Their apparent association constant (on the molality concentration scale) at 298.15 K and saturation vapor pressure, $K_m \approx 0.6\ mol^{-1}\cdot kg$, is uncertain because of the small amounts of association at this temperature, but its value does imply that $NaCF_3SO_3(aq)$ is slightly associated even at room temperature. This large uncertainty results because derived values of K_m are very sensitive to the conductivity model used when the amount of ionic association is small.

We searched for articles reporting thermodynamic properties of $NaCF_3SO_3(aq)$, $HCF_3SO_3(aq)$, and other aqueous trifluoromethanesulfonate salts, but very few relevant thermodynamic studies were located. Hedwig and Parker[15] reported the enthalpies of solution of $KCF_3SO_3(s)$, $Ba(CF_3SO_3)_2(s)$, $Cd(CF_3SO_3)_2(s)$, and $Zn(CF_3SO_3)_2(s)$ in water at (298.15 ± 0.05) K, and similar measurements were made for $HCF_3SO_3(s)$ by Benoit and Figeys.[16] Xiao and Tremaine[17] reported densities and apparent molar volumes of $HCF_3SO_3(aq)$ and $NaCF_3SO_3(aq)$ from 283.15 K to 328.15 K at a pressure of 0.1 MPa and of $NaCF_3SO_3(s)$ from 323.05 K to 600.48 K at elevated pressures. Bonner[6] reported smoothed values of ϕ and $\gamma_\pm$ for $HCF_3SO_3(aq)$, $LiCF_3SO_3(aq)$, $NaCF_3SO_3(aq)$, and $KCF_3SO_3(aq)$ derived from isopiestic measurements at 298.15 K. However, Bonner only listed smoothed values of these properties, and the experimental isopiestic molalities were not reported.

Because of the current and potential use of $HCF_3SO_3(aq)$ and $NaCF_3SO_3(aq)$ as "indifferent electrolytes" for controlling ionic strengths during stability constant measurements, accurate experimental values of their osmotic and activity coefficients are needed. The published thermodynamic properties of both $NaCF_3SO_3(aq)$ and $HCF_3SO_3(aq)$ are clearly very limited, even at 298.15 K, and new measurements are needed to supplement these studies. In the present report, isopiestic results are presented for the sodium salt $NaCF_3SO_3(aq)$ at both 298.15 K and 323.15 K. The parameters of an Archer-type[18] modified Pitzer ion-interaction model[19] are evaluated for $NaCF_3SO_3(aq)$ at both temperatures. We also compare the limited amount of published isopiestic results[6] for $NaCF_3SO_3(aq)$ to our new results.

Experimental Section

The experiments were performed at Oak Ridge National Laboratory (ORNL), at both ($298.15 \pm 0.00_3$) K and ($323.15 \pm 0.00_3$) K, using a slightly modified version of a previously described isopiestic apparatus.[20] The experimental conditions and techniques are essentially identical with those described previously.[21−23] Rard and Platford[24] give a detailed description of the isopiestic method with emphasis on experimental aspects.

Eight different stock solutions of NaCl(aq) were used as the isopiestic reference standards. All of these NaCl(aq) reference standard solutions were also used for some of the alkali metal sulfate experiments,[22,23,25] and the preparation of these NaCl(aq) solutions and their molality analyses were described in two of these reports.[22,23] Table 1 summarizes the molalities of the individual NaCl(aq) and $NaCF_3SO_3(aq)$ stock solutions used in the present study. Assumed molar masses for molality calculations are 58.4428 $g\cdot mol^{-1}$ for NaCl, 172.079 $g\cdot mol^{-1}$ for $NaCF_3SO_3$, and 18.0153 $g\cdot mol^{-1}$ for H_2O. All apparent masses were converted to masses using buoyancy corrections.

Prior to the synthesis of the $NaCF_3SO_3(s)$ needed for our isopiestic measurements, several samples of $NaCF_3SO_3(s)$ were prepared by the method described in the following paragraph, and solutions of these samples were examined for anionic impurities using high performance liquid chromatography (HPLC). Several anionic impurities were detected. However, two recrystallizations of the "crude" $NaCF_3SO_3(s)$ from methanol reduced these impurity concentrations to below their HPLC detection limits.

Samples of several different lots of $HCF_3SO_3(l)$ were obtained from Aldrich and Kodak. These $HCF_3SO_3(l)$ samples were then purified by fractional distillation under reduced pressure at temperatures ranging from 333 K to 373 K, with the distillation temperature used in any particular case depending on the level of vacuum applied. Scott and Taube[2] pointed out that distillation is effective for removal of sulfate ions found in some commercial

Table 1. Molalities of NaCl(aq) and $NaCF_3SO_3$(aq) Stock Solutions

series	m(NaCl)[a] mol·kg^{-1}	m(NaCl)[a] mol·kg^{-1}	m($NaCF_3SO_3$)[b] mol·kg^{-1}	m($NaCF_3SO_3$)[b] mol·kg^{-1}
3	0.9852		1.2142	
4	1.0922		1.1909	
5	0.9868[c]	1.1228[d]	1.1197[e]	
6	0.9868[c]		1.1197[e]	1.1964[f]
7	1.1228[d]		1.1964[f]	
8, 11, 12	0.19580		0.19549	
9, 9A,10	0.9869[c]		1.1197[e]	
19, 20	5.5073		1.0035	
21−23	0.9987		1.0035[g]	
24, 25	1.0030		1.0193	

[a] Accepted molalities of these NaCl(aq) isopiestic reference standard stock solutions. See Table 1 of Rard et al.[22] and Table 1 of Palmer et al.[23] for a description of the molality analyses. The numbering of the various series of experiments indicates the chronological order in which the various series of experiments were performed and is identical to that used by Palmer et al.[23] but differs from the numbering system used by Rard et al.[22] [b] Molality obtained by cation-exchange chromatography followed by mass titration of the eluted H^+ with NaOH(aq). [c] These NaCl(aq) stock solutions with $m = 0.9868$ mol·kg^{-1} and with $m = 0.9869$ mol·kg^{-1} are identical. The first value of $m = 0.9869$ mol·kg^{-1} was calculated from the masses of NaCl(s) and of H_2O(l) used, whereas $m = 0.9868$ mol·kg^{-1} was obtained by analysis as described in footnote b. The very slight difference of $\Delta m = 1{\cdot}10^{-4}$ mol·kg^{-1} is insignificant. [d] These two stock solutions are identical. [e] These three stock solutions are identical. [f] These two stock solutions are identical. [g] This stock solution and the one immediately above it are identical.

samples of HCF_3SO_3(l). Several of these HCF_3SO_3(l) samples were converted to $NaCF_3SO_3$(s) by dropwise addition of the acid to a chilled, concentrated methanol solution of Analytical Reagent grade NaOH. A slight excess of HCF_3SO_3 was added to each sample to produce a slightly acidic solution, to eliminate any Na_2CO_3 or $NaHCO_3$ that might have been present in the NaOH solution. The $NaCF_3SO_3$ + methanol solutions were subsequently evaporated to dryness, and the resulting $NaCF_3SO_3$(s) were purified twice by recrystallization from boiling anhydrous methanol (which should remove the small amount of excess acid), and then dried under vacuum over P_2O_5(s) to remove the residual solvent, as described by Palmer and Drummond.[26] The measured pH's of the $NaCF_3SO_3$(aq) stock solutions prepared from these samples of recrystallized $NaCF_3SO_3$(s) fall in the range $6 \leq \mathrm{pH} \leq 8$.

Molalities of the seven $NaCF_3SO_3$(aq) stock solutions were determined by cation exchange followed by potentiometric−pH mass titration of the eluted H^+ with standardized NaOH(aq) as described previously.[22] Because the molalities of all of the $NaCF_3SO_3$(aq) stock solutions and all but one of the NaCl(aq) stock solutions were determined this way, if any systematic errors are present, these errors will partially cancel when osmotic coefficients are calculated. Stock solution molality determinations by both methods were made in duplicate and are reproducible to ≤0.1%.

Table 1 contains a summary of the stock solution molalities obtained from these analyses and identifies which stock solution or solutions were used for each series of experiments. A total of 18 different series of isopiestic experiments were performed. The resulting ϕ values from the various series of experiments for $NaCF_3SO_3$(aq) are generally quite consistent. However, all of the experiments from a few series and a few individual experiments from other series are significantly discrepant. These discrepancies are discussed in the next section.

These isopiestic experiments for $NaCF_3SO_3$(aq) were performed between 1986 and 1988 and during 1992 and 1993. Tables 2 and 3 list the results for the experiments at 298.15 K and 323.15 K, respectively. The average equilibrium molalities for duplicate samples are reported, along with the deviations of individual molalities from their corresponding averages. Each series represents sequential equilibrations of the same pair of duplicate samples of NaCl(aq) and of $NaCF_3SO_3$(aq), where NaCl(aq) serves as the reference standard. For most experiments, the uncertainties of the reported results are limited by the uncertainties in the stock solution molality analyses rather than by the agreement between the molalities of the replicate samples. However, to preserve the internal consistency of each series of experiments, the isopiestic molalities are reported to one or two more figures than are warranted by the absolute accuracy of their determination.

The isopiestic results do not extend to the solubility limit for $NaCF_3SO_3$(s) at either temperature, but they were measured over the molality ranges where $NaCF_3SO_3$(aq) is likely to be used as an "indifferent electrolyte" for controlling ionic strength during stability constant measurements.

The isopiestic equilibrium molality ratios of NaCl(aq) to $NaCF_3SO_3$(aq) for all of the experiments are not very different from unity. Because NaCl(aq) is generally considered to be a nearly completely dissociated electrolyte at these temperatures, the near equality of the molalities implies that $NaCF_3SO_3$(aq) is likewise almost completely dissociated.

For the series 5 experiments at 298.15 K, duplicate samples of each of two different NaCl(aq) stock solutions were used, and for each experiment, the reported averages of the equilibrium molalities of each pair of these solutions differ by only 0.017% to 0.050%. Similarly, duplicate samples of each of two different stock solutions of $NaCF_3SO_3$(aq) were included in the series 6 equilibrations, and the averages of each pair of equilibrium molalities also agree very well, differing by only 0.016% to 0.045%, except for the lowest molality experiment where one of the four $NaCF_3SO_3$(aq) molalities is discrepant. The equilibrium molalities in Tables 2 and 3 for each series are listed from the highest to the lowest molality rather than the actual order of their determination. A total of 5 of the 18 series involved measurements at both temperatures.

Samples of Na_2SO_4(aq), K_2SO_4(aq), Rb_2SO_4(aq), and/or Cs_2SO_4(aq) solutions were also present during some of these isopiestic equilibrations, and those results were published previously.[22,23,25]

Analysis of Thermodynamic Data for $NaCF_3SO_3$(aq)

In addition to the isopiestic results given in Tables 2 and 3, there is one previous isopiestic study for $NaCF_3SO_3$(aq) at 298.15 K.[6] There are no previous isopiestic measurements for this system at 323.15 K.

Molality-based or "practical" osmotic coefficients ϕ were calculated from the fundamental equation for isopiestic equilibrium

$$\phi = \nu^* m^* \phi^* / \nu m \tag{1}$$

where m denotes the molality of $NaCF_3SO_3$(aq), $\nu = 2$ its stoichiometric ionization number, and where $\nu^* = 2$, m^*, and ϕ^* denote the corresponding quantities for the isopiestic reference standard NaCl(aq). Values of ϕ reported in Tables 2 and 3 were computed with eq 1 using the listed

Table 2. Isopiestic Molalities of NaCl(aq) and $NaCF_3SO_3$(aq) and the Osmotic Coefficients of $NaCF_3SO_3$(aq) at 298.15 K[a]

m(NaCl)/mol·kg^{-1}	m($NaCF_3SO_3$)/mol·kg^{-1}	ϕ($NaCF_3SO_3$)	m(NaCl)/mol·kg^{-1}	m($NaCF_3SO_3$)/mol·kg^{-1}	ϕ($NaCF_3SO_3$)
Series 3					
3.3794 ± 0.0010	3.20509 ± 0.00271	1.1326 ($w = 0$)	1.5937 ± 0.0019*	1.47663 ± 0.00127	1.0412 ($w = 0$)
3.2480 ± 0.0001	3.06843 ± 0.00353*	1.1276 ($w = 0$)	1.2454 ± 0.0004	1.15824 ± 0.00003	1.0190 ($w = 0$)
2.4919 ± 0.0003	2.31812 ± 0.00126	1.0924 ($w = 0$)	1.2080 ± 0.0010	1.12450 ± 0.00026	1.0162$_5$ ($w = 0$)
1.9843 ± 0.0005	1.83722 ± 0.00174	1.0649 ($w = 0$)	1.0843 ± 0.0001	1.01206 ± 0.00005	1.0077 ($w = 0$)
1.6418 ± 0.0009	1.52109 ± 0.00012	1.0439$_5$ ($w = 0$)			
Series 4					
1.3439 ± 0.0056**	1.25392 ± 0.00320**	1.0206 ($w = 0.5$)	1.3167 ± 0.0001	1.23107 ± 0.00010	1.0171$_5$ ($w = 0.5$)
Series 5					
2.4151 ± 0.0001^{b}	2.26466 ± 0.00017	1.0784	1.1943 ± 0.0004^{b}	1.11950 ± 0.00096	1.0083
2.4143 ± 0.0003			1.1937 ± 0.0009		
1.7736 ± 0.0002^{b}	1.65543 ± 0.00002	1.0436	1.1854 ± 0.0005^{b}	1.11308 ± 0.00030	1.0065
1.7729 ± 0.0002			1.1856 ± 0.0001		
Series 6					
3.7110 ± 0.0003	3.59047 ± 0.00096^{c}	1.1340$_5$ ($w = 0.5$)	2.7324 ± 0.0012	2.57484 ± 0.00004^{c}	1.0944 ($w = 0.5$)
	3.59105 ± 0.00046	1.1339 ($w = 0.5$)		2.57575 ± 0.00061	1.0940 ($w = 0.5$)
3.6820 ± 0.0024	3.55786 ± 0.00024^{c}	1.1334 ($w = 0.5$)	2.0315 ± 0.0009	1.89671 ± 0.00005^{c}	1.0590 ($w = 0.5$)
	3.55864 ± 0.00090	1.1331 ($w = 0.5$)		1.89727 ± 0.00032	1.0586$_5$ ($w = 0.5$)
3.5271 ± 0.0025	3.39147 ± 0.00015^{c}	1.1277 ($w = 0.5$)	1.4164 ± 0.0004	1.32346 ± 0.00002^{c}	1.0229 ($w = 0.5$)
	3.39241 ± 0.00111	1.1274 ($w = 0.5$)		1.32390 ± 0.00021	1.0226 ($w = 0.5$)
3.1782 ± 0.0023	3.02534 ± 0.00008^{c}	1.1142 ($w = 0.5$)	1.0872 ± 0.0004	1.02091 ± 0.00013^{c}	1.0019 ($w = 0.5$)
	3.02644 ± 0.00105	1.1138 ($w = 0.5$)		1.02137 ± 0.00006	1.0014 ($w = 0.5$)
2.9130 ± 0.0003	2.75591 ± 0.00038^{c}	1.1024$_5$ ($w = 0.5$)	0.8836 ± 0.0002	0.83855 ± 0.00461^{c,**}	(0.9882)^{d}($w = 0.5$)
	2.75640 ± 0.00049	1.1023 ($w = 0.5$)		0.83412 ± 0.00020	0.9880 ($w = 0.5$)
Series 7					
1.2399 ± 0.0010	1.16122 ± 0.00074	1.0117	0.3048 ± 0.0005	0.29561 ± 0.00001	0.9494
0.8279 ± 0.0003	0.78274 ± 0.00038	0.9844	0.2931 ± 0.0004	0.28405 ± 0.00030	0.9502
0.7054 ± 0.0001	0.66976 ± 0.00012	0.9761	0.2876 ± 0.0005	0.27813 ± 0.00071*	0.9523
0.6407 ± 0.0002	0.60989 ± 0.00022	0.9716	0.2561 ± 0.0001	0.24924 ± 0.00019	0.9469
0.5176 ± 0.0002	0.49523 ± 0.00011	0.9637$_5$	0.2520 ± 0.0004	0.24545 ± 0.00002	0.9462
0.4231 ± 0.0007	0.40695 ± 0.00001	0.9573	0.2101 ± 0.0004	0.20548 ± 0.00003	0.9438
0.4177 ± 0.0001	0.40177 ± 0.00009	0.9573	0.2004 ± 0.0004	0.19608 ± 0.00003	0.9438
Series 8					
0.2959 ± 0.0005	0.28619 ± 0.00025	0.9520	0.2021 ± 0.0003	0.19738 ± 0.00024	0.9455
0.2500 ± 0.0004	0.24290 ± 0.00019	0.9486	0.1395 ± 0.0001	0.13678 ± 0.00071**	0.9459
0.2300 ± 0.0003	0.22389 ± 0.00008	0.9475	0.1394 ± 0.0002	0.13643 ± 0.00015	0.9477
Series 10					
0.5046 ± 0.0001	0.48298 ± 0.00017	0.9632	0.4945 ± 0.0004	0.47081 ± 0.00069	0.9681 ($w = 0$)
Series 19					
3.0707 ± 0.0003	2.92490 ± 0.00028	1.1059 ($w = 0.5$)	1.7418 ± 0.0001	1.63101 ± 0.00014	1.0386 ($w = 0.5$)
2.9138 ± 0.0002	2.76396 ± 0.00027	1.0996 ($w = 0.5$)	1.5540 ± 0.0001	1.45581 ± 0.00014	1.0276 ($w = 0.5$)
1.7658 ± 0.0001	1.65368 ± 0.00012	1.0398 ($w = 0.5$)			
Series 20					
5.6914 ± 0.0018^{e}	6.04149 ± 0.00097^{e}	1.1730 ($w = 0$)	4.5972 ± 0.0005	4.61585 ± 0.00069	1.1568
5.4965 ± 0.0001^{e}	5.78730 ± 0.00249^{e}	1.1681$_5$ ($w = 0$)	4.5249 ± 0.0013^{e}	4.60566 ± 0.00032^{e}	1.1358 ($w = 0$)
5.2081 ± 0.0013	5.37349 ± 0.00127	1.1705	4.0910 ± 0.0002^{e}	4.10688 ± 0.00062^{e}	1.1200 ($w = 0$)
5.1748 ± 0.0011	5.33111 ± 0.00052	1.1698	3.7132 ± 0.0007	3.60429 ± 0.00088	1.1305
5.1667 ± 0.0016^{e}	5.38018 ± 0.00005^{e}	1.1567 ($w = 0$)	3.6732 ± 0.0006	3.56000 ± 0.00033	1.1294
5.0307 ± 0.0008	5.14703 ± 0.00121	1.1671	3.5452 ± 0.0004	3.42208 ± 0.00076	1.1247
4.8398 ± 0.0021^{e}	4.98508 ± 0.00092^{e}	1.1453 ($w = 0$)	3.5148 ± 0.0003	3.38654 ± 0.00030	1.1245
Series 21					
0.4939 ± 0.0001	0.47391 ± 0.00018	0.9606 ($w = 0.5$)	0.2541 ± 0.0022**	0.24830 ± 0.00146**	0.9431 ($w = 0.5$)
0.4086 ± 0.0004	0.39358 ± 0.00003	0.9558 ($w = 0.5$)	0.2439 ± 0.0002	0.23759 ± 0.00031	0.9464 ($w = 0.5$)
0.3433 ± 0.0000	0.33237 ± 0.00001	0.9508 ($w = 0.5$)			
Series 22					
3.5651 ± 0.0005	3.43684 ± 0.00064	1.1276	1.2021 ± 0.0001	1.12823 ± 0.00001	1.0077
1.5579 ± 0.0010	1.46544 ± 0.00141	1.0236 ($w = 0$)	1.0530 ± 0.0000	0.99123 ± 0.00008	0.9978
1.3053 ± 0.0001	1.22333 ± 0.00021	1.0142	0.9930 ± 0.0001	0.93591 ± 0.00016	0.9940$_5$
Series 23					
1.0801 ± 0.0001	1.01766 ± 0.00032	0.9982	0.6321 ± 0.0002	0.60312 ± 0.00018	0.9691
0.9248 ± 0.0002	0.87397 ± 0.00030	0.9886	0.6052 ± 0.0004	0.57761 ± 0.00015	0.9682
0.7672 ± 0.0001	0.72837 ± 0.00009	0.9782	0.5680 ± 0.0001	0.54288 ± 0.00023	0.9659
0.7360 ± 0.0002	0.69939 ± 0.00014	0.9762$_5$	0.5345 ± 0.0002	0.51204 ± 0.00013	0.9629
0.6915 ± 0.0006	0.65649 ± 0.00034	0.9757$_5$	0.4457 ± 0.0014*	0.42788 ± 0.00043	0.9594
0.6686 ± 0.0001	0.63664 ± 0.00025	0.9722			

[a] Osmotic coefficients of the reference standard NaCl(aq) were calculated with Archer's equation and parameters.[18] Equilibrium molalities without asterisks have uncertainties of ≤0.1% for $m > 0.5$ mol·kg^{-1} and ≤0.2% for $m < 0.5$ mol·kg^{-1}. Equilibrium molalities are followed by a single asterisk if the scatter of the isopiestic molalities slightly exceeds these values by up to a factor of 2 and by two asterisks for those experiments with even larger scatter. Osmotic coefficients denoted with "($w = 0$)" were given zero weight in our modeling calculations, and those denoted with "($w = 0.5$)" were given a reduced relative weight of 0.5. [b] Duplicate samples of two different NaCl(aq) reference standard stock solutions were used in these experiments. This average molality is for one of these pairs of solutions, and the average molality of the second pair is given immediately below. [c] Duplicate samples of two different $NaCF_3SO_3$(aq) stock solutions were used in these experiments. This average molality is for one of these pairs of solutions, and the average molality of the second pair is given immediately below. [d] This value of ϕ was calculated using the single molality of $NaCF_3SO_3$(aq) that is consistent with the other molality pair rather than the listed average molality. [e] These molalities are from six consecutive experiments that were sandwiched between other experiments at 323.15 K. Although the recorded temperature for these six experiments is 298.15 K, their isopiestic molality ratios are inconsistent with those for our other experiments at this temperature but do agree with the molality ratios obtained at 323.15 K, which suggests the wrong temperature may have been recorded. Not being absolutely certain of this, however, we took the conservative approach and did not include these six ϕ values when evaluating the parameters of eq 2.

Table 3. Isopiestic Molalities of NaCl(aq) and $NaCF_3SO_3$(aq), and the Osmotic Coefficients of $NaCF_3SO_3$(aq) at 323.15 K[a]

m(NaCl) / mol·kg^{-1}	$m(NaCF_3SO_3)$ / mol·kg^{-1}	$\phi(NaCF_3SO_3)$	m(NaCl) / mol·kg^{-1}	$m(NaCF_3SO_3)$ / mol·kg^{-1}	$\phi(NaCF_3SO_3)$
Series 4					
1.2809 ± 0.0009	1.21904 ± 0.00049	1.0058	1.1079 ± 0.0006	1.05584 ± 0.00016	0.9951
1.2019 ± 0.0007	1.14443 ± 0.00054	1.0009	0.5222 ± 0.0003	0.50006 ± 0.00029	0.9649 ($w = 0$)
1.1080 ± 0.0006	1.05587 ± 0.00008	0.9951	0.5186 ± 0.0014*	0.49831 ± 0.00119*	0.9615
Series 8					
0.1981 ± 0.0005	0.19389 ± 0.00065*	0.9422	0.1477 ± 0.0003	0.14504 ± 0.00015	0.9420
Series 9					
4.2751 ± 0.0069*	4.30696 ± 0.00630*	1.1379	3.1708 ± 0.0021	3.09002 ± 0.00227	1.1002
4.0487 ± 0.0026	4.04578 ± 0.00314	1.1318	2.3692 ± 0.0016	2.27170 ± 0.00137	1.0644
3.8504± 0.0018	3.82610 ± 0.00332	1.1246	2.3161 ± 0.0036*	2.21819 ± 0.00368*	1.0622
3.6919 ± 0.0021	3.65018 ± 0.00261	1.1195	1.4687 ± 0.0005	1.39764 ± 0.00039	1.0165
3.6771 ± 0.0013	3.63528 ± 0.00343	1.1186	1.4467 ± 0.0031**	1.37517 ± 0.00216*	1.0163
3.4603 ± 0.0043*	3.39941 ± 0.00378*	1.1109	1.4075 ± 0.0023*	1.33939 ± 0.00162*	1.0130
3.1761 ± 0.0013	3.09594 ± 0.00176	1.1003	1.3760 ± 0.0020*	1.31036 ± 0.00220*	1.0140
Series 9A					
3.1578 ± 0.0015	3.07587 ± 0.00145	1.0998	1.7695 ± 0.0006	1.68467 ± 0.00081	1.0339
2.9852 ± 0.0023	2.89677 ± 0.00198	1.0923	1.6461 ± 0.0004	1.56623 ± 0.00082	1.0271
2.7751 ± 0.0024	2.67989 ± 0.00199	1.0836	1.4902 ± 0.0000	1.41737 ± 0.00004	1.0183
2.4414 ± 0.0010	2.34272 ± 0.00139	1.0683	1.3349 ± 0.0000	1.26939 ± 0.00027	1.0095
2.3322 ± 0.0049**	2.23084 ± 0.00178	1.0646	1.1763 ± 0.0005	1.11968 ± 0.00017	0.9999
2.2597 ± 0.0008	2.16218 ± 0.00126	1.0595	1.0740 ± 0.0003	1.02317 ± 0.00021	0.9937
1.9897 ± 0.0009	1.89774 ± 0.00109	1.0456	1.0532 ± 0.0016*	1.00326 ± 0.00473**	0.9927
Series 10					
1.1036 ± 0.0004	1.05183 ± 0.00019	0.9948	0.5896 ± 0.0003	0.56738 ± 0.00030	0.9624
0.9033 ± 0.0003	0.86323 ± 0.00039	0.9822	0.4751 ± 0.0006	0.45918 ± 0.00011	0.9548
0.7190 ± 0.0002	0.68975 ± 0.00003	0.9703			
Series 11					
0.9010 ± 0.0018	0.85986 ± 0.00148*	0.9834	0.3691 ± 0.0004	0.35759 ± 0.00038	0.9504
0.6667 ± 0.0011	0.63949 ± 0.00072*	0.9683	0.2775 ± 0.0002	0.26926 ± 0.00084*	0.9487
0.4959 ± 0.0005	0.47800 ± 0.00057	0.9579	0.2653 ± 0.0001	0.25809 ± 0.00010	0.9463
Series 12					
0.4486 ± 0.0002	0.43284 ± 0.00029	0.9557	0.4218 ± 0.0001	0.40742 ± 0.00028	0.9541
Series 19					
2.6961 ± 0.0000 [b]	2.54720 ± 0.00008[b]	1.1021 ($w = 0$)	1.8568 ± 0.0001[b]	1.73822 ± 0.00023[b]	1.0569 ($w = 0$)
2.1514 ± 0.0002[b]	2.01634 ± 0.00003[b]	1.0746 ($w = 0$)			
Series 20					
4.1170 ± 0.0004	4.13525 ± 0.00041	1.1306 ($w = 0.5$)	2.5396 ± 0.0008	2.44880 ± 0.00016	1.0695 ($w = 0.5$)
3.4729 ± 0.0032	3.42357 ± 0.00447*	1.1079 ($w = 0.5$)	2.2916 ± 0.0001	2.20173 ± 0.00014	1.0572 ($w = 0.5$)
3.3542 ± 0.0054*	3.28096 ± 0.00082	1.1085 ($w = 0.5$)	2.0164 ± 0.0001	1.93095 ± 0.00005	1.0431 ($w = 0.5$)
3.2683 ± 0.0004	3.20735 ± 0.00173	1.0991 ($w = 0.5$)	1.6892 ± 0.0009	1.61193 ± 0.00002	1.0267 ($w = 0.5$)
3.1566 ± 0.0004	3.08396 ± 0.00002	1.0964 ($w = 0.5$)	1.4471 ± 0.0003	1.38126 ± 0.00010	1.0121_5 ($w = 0.5$)
2.8608 ± 0.0001	2.77751 ± 0.00051	1.0834 ($w = 0.5$)			
Series 24					
1.1793 ± 0.0005	1.12421 ± 0.00045	0.9985	0.7423 ± 0.0006	0.71128 ± 0.00353**	0.9723
1.1463 ± 0.0003	1.09329 ± 0.00051	0.9963	0.6388 ± 0.0001	0.61422 ± 0.00011	0.9649
1.0629 ± 0.0003	0.99943 ± 0.00031	1.0062 ($w = 0$)	0.5799 ± 0.0001	0.55864 ± 0.00002	0.9610
0.9325 ± 0.0003	0.89134 ± 0.00011	0.9833	0.5041 ± 0.0001	0.48674 ± 0.00004	0.9564
0.8608 ± 0.0001	0.82368 ± 0.00012	0.9789	0.4359 ± 0.0001	0.42206 ± 0.00012	0.9521
Series 25					
0.3346 ± 0.0000	0.32507 ± 0.00021	0.9475	0.1644 ± 0.0001	0.16202 ± 0.00050*	0.9375
0.1703 ± 0.0006*	0.16634 ± 0.00093**	0.9455	0.1584 ± 0.0000	0.15553 ± 0.00005	0.9414

[a] Osmotic coefficients of the reference standard NaCl(aq) were calculated with Archer's equation and parameters.[18] Equilibrium molalities without asterisks have uncertainties of ≤0.1% for $m > 0.5$ mol·kg^{-1} and ≤0.2% for $m < 0.5$ mol·kg^{-1}. Equilibrium molalities are followed by a single asterisk if the scatter of the isopiestic molalities slightly exceeds these values by up to a factor of 2 and by two asterisks for those experiments with even larger scatter. Osmotic coefficients denoted with "($w = 0$)" were given zero weight in our modeling calculations, and those denoted with "($w = 0.5$)" were given a reduced relative weight of 0.5. [b] These molalities are from three consecutive experiments that were sandwiched between other experiments at 298.15 K. Although the recorded temperature for these three experiments is 323.15 K, their isopiestic molality ratios are inconsistent with those for our other experiments at this temperature, but do agree with the molality ratios obtained at 298.15 K, which suggests that the wrong temperature may have been recorded. Not being absolutely certain of this, however, we took the conservative approach and did not include these three ϕ values when evaluating the parameters of eq 2.

equilibrium molalities and values of ϕ^* calculated from the extended Pitzer model of Archer for NaCl(aq).[18]

A preliminary graphical comparison of ϕ values for $NaCF_3SO_3$(aq) from the various series of experiments at 298.15 K showed that the derived results from the experiments of series 5−8, 20, 22, and 23 are consistent, except for a very few outlying values. Values of ϕ derived from the experiments of series 21 are also generally in agreement with the seven consistent series, but because these ϕ values are significantly more scattered, they were given lower weight when used for evaluation of model parameters as described below. Lower weights were also given to the two ϕ values from series 4, which are slightly higher and slightly more scattered that those from the seven concordant series, and to the ϕ values from series 19 which are slightly lower.

In contrast, values of ϕ of $NaCF_3SO_3$(aq) at 298.15 K derived from the experiments of series 3 of Table 2 are not consistent with the eight concordant series of experiments at this temperature and were rejected. The ϕ values of series 3 vary from $\Delta\phi \approx 0.008$ to 0.012 higher than those from the other series. We note that the series 3 experiments also involved samples of Na_2SO_4(aq), Cs_2SO_4(aq), and Rb_2SO_4(aq), and those results were reported previously.[22,23] All but one ϕ value for Na_2SO_4(aq) and all of the ϕ values for Cs_2SO_4(aq) corresponding to series 3 were assigned zero weights in the evaluation of ion-interaction model (Pitzer) parameters for those systems, owing to skewing of the molality dependences of their ϕ values. This implies that some type of systematic experimental error was present for those experiments. In contrast, Rb_2SO_4(aq) samples that were included in five of these equilibrations[23] gave ϕ values that are reliable and consistent with values obtained in their other series of isopiestic experiments.

The good results for values of ϕ for Rb_2SO_4(aq) imply that the series 3 experiments were properly equilibrated and that the NaCl(aq) reference standard molalities are reliable. There is only one obvious possible problem that could simultaneously cause the ϕ values for Na_2SO_4(aq), Cs_2SO_4(aq), and $NaCF_3SO_3$(aq) to be systematically in error, but not those of Rb_2SO_4(aq). This possibility is that there was a mix up between these three electrolytes when the mass aliquots were recorded for the various stock solutions of series 3, and thus, all of the calculated equilibrium molalities for these three electrolytes are based on use of inappropriate stock solution molalities.

A similar graphical comparison of our results for $NaCF_3SO_3$(aq) at 323.15 K, which are listed in Table 3, indicates that the values of ϕ for series 4, 8, 9, 9A, 10−12, 24, and 25 are consistent with each other. However, values of ϕ from the series 19 experiments are significantly higher by $\Delta\phi \approx 0.02$ and those of series 20 are slightly lower by $\Delta\phi \approx 0.004$.

As discussed in footnote e of Table 2 and footnote b of Table 3, there is the possibility that the temperature was incorrectly recorded for six of the experiments of series 20 and for three of the experiments of series 19.

Published isopiestic values of ϕ are available for $NaCF_3SO_3$(aq) at 298.15 K. A graphical comparison of our values of ϕ for $NaCF_3SO_3$(aq) at 298.15 K to the smoothed values of Bonner[6] shows that his value of ϕ at 0.1 $mol \cdot kg^{-1}$ is slightly higher than our results, but at higher molalities, his ϕ values are substantially lower than ours, with the differences typically being $\Delta\phi \approx 0.015$−0.025. It is not possible to account for the discrepancies between Bonner's values of ϕ and our values, because he did not report the experimental isopiestic molalities, and thus, the number of his measurements and their precision is unknown. However, we are confident in the accuracy of our experimental results for $NaCF_3SO_3$(aq), except for a few experiments as described in the five preceding paragraphs, because of the generally good consistency between values of ϕ from our numerous series of experiments involving many separately prepared and analyzed stock solutions.

Relative Weights and Least-Squares Fitting

Unit relative weights were assigned to the higher quality experimental ϕ values and zero weights to inaccurate or discrepant values. A few less precise sets of isopiestic experiments from Tables 2 and 3 were assigned reduced weights of $w = 0.5$.

Duplicate samples of two separate $NaCF_3SO_3$(aq) stock solutions were included in the equilibrations of series 6. Two values of ϕ of $NaCF_3SO_3$(aq) were thus calculated for each of these experiments, and each of these duplicate ϕ values was assigned a weight of $w = 0.5$ in the least-squares evaluation of the model parameters.

All of the results for series 3 at 298.15 K for $NaCF_3SO_3$(aq) deviate significantly from those of other series, and their ϕ values were consequently assigned $w = 0$. Values of ϕ for series 4, 19, and 21 at 298.15 K were given lower weights of $w = 0.5$. Similarly, the ϕ results of series 19 for $NaCF_3SO_3$(aq) at 323.15 K were assigned $w = 0$, and those for series 20 were assigned $w = 0.5$.

Analysis Using an Extended Ion-Interaction (Pitzer) Model

We represent the available thermodynamic information for $NaCF_3SO_3$(aq) using Pitzer's model,[19] as extended by Archer[18] to include an ionic-strength dependent third virial coefficient. The relevant equations are given in the modified notation introduced by Clegg et al.,[27] which differs, in a few minor respects, from that used by Archer.

Archer's extension of Pitzer's model may be written in the following form for the osmotic coefficient of $NaCF_3SO_3$(aq) and other 1:1 electrolytes:

$$\phi - 1 = -A_\phi I^{1/2}/(1 + bI^{1/2}) + mB^{\phi}_{\mathrm{M,X}} + 2m^2C^{\mathrm{T}\phi}_{\mathrm{M,X}} \quad (2)$$

where M denotes Na^+, X denotes $CF_3SO_3^-$, m is the stoichiometric molality, $b = 1.2\ kg^{1/2} \cdot mol^{-1/2}$, A_ϕ is the Debye−Hückel limiting law slope for ϕ, and $I = m$ is the molality-based stoichiometric ionic strength. The quantities $B^{\phi}_{\mathrm{M,X}}$ and $C^{\mathrm{T}\phi}_{\mathrm{M,X}}$ are defined to have the following dependences on ionic strength:

$$B^{\phi}_{\mathrm{M,X}} = \beta^{(0)}_{\mathrm{M,X}} + \beta^{(1)}_{\mathrm{M,X}} \exp(-\alpha_{\mathrm{M,X}} I^{1/2}) \quad (3)$$

and

$$C^{\mathrm{T}\phi}_{\mathrm{M,X}} = C^{(0)}_{\mathrm{M,X}} + C^{(1)}_{\mathrm{M,X}} \exp(-\omega_{\mathrm{M,X}} I^{1/2}) \quad (4)$$

where $\alpha_{\mathrm{M,X}}$ is usually assigned a value of 2.0 $kg^{1/2} \cdot mol^{-1/2}$ except for the divalent metal sulfates.[19] Mean activity coefficients $\gamma_\pm$ of $NaCF_3SO_3$(aq) are given by

$$\ln \gamma_\pm = -A_\phi\{I^{1/2}/(1 + bI^{1/2}) + (2/b)\ln(1 + bI^{1/2})\} + m[2\beta^{(0)}_{\mathrm{M,X}} + 2(\beta^{(1)}_{\mathrm{M,X}}/\alpha_{\mathrm{M,X}}{}^2 I)\{1 - (1 + \alpha_{\mathrm{M,X}} I^{1/2} - \alpha_{\mathrm{M,X}}{}^2 I/2) \times \exp(-\alpha_{\mathrm{M,X}} I^{1/2})\}] + m^2[3C^{(0)}_{\mathrm{M,X}} + 4(C^{(1)}_{\mathrm{M,X}}/\omega_{\mathrm{M,X}}{}^4 I^2)\{6 - (6 + 6\omega_{\mathrm{M,X}} I^{1/2} + 3\omega_{\mathrm{M,X}}{}^2 I + \omega_{\mathrm{M,X}}{}^3 I^{3/2} - \omega_{\mathrm{M,X}}{}^4 I^2/2) \times \exp(-\omega_{\mathrm{M,X}} I^{1/2})\}] \quad (5)$$

The usual three-parameter form of Pitzer's ion-interaction model[19] may be obtained from eqs 2 through 5 by setting $C^{(1)}_{\mathrm{M,X}}$ equal to zero, although the numerical multipliers of the "*C*" terms differ in the two formalisms.[18,19]

Values of the Debye−Hückel limiting law slope A_ϕ were taken from the critical evaluation of the relative permittivity (dielectric constant) of water by Archer and Wang,[28] together with Hill's equation of state for water.[29] The least-squares evaluation of the parameters for eqs 2−5 was made using the JMP statistical software package obtained from the SAS Institute.

Table 4 lists the evaluated parameter values for eqs 2−5 for $NaCF_3SO_3$(aq) at 298.15 K and 323.15 K, along with related information. No attempt was made to construct a temperature-dependent thermodynamic model, because enthalpies of dilution and heat capacities are not available nor are osmotic coefficients at other temperatures.

We set $\omega_{\mathrm{M,X}} = 2.5\ kg^{1/2} \cdot mol^{-1/2}$ for these fits, which is the value used in our previous models for Na_2SO_4(aq) and $CaCl_2$(aq) at 298.15 K,[22,30] for H_2SO_4(aq) at 273.15 K to

Table 4. Parameters and Standard Errors for an Extended Pitzer Model Applied to $NaCF_3SO_3(aq)$ and Debye–Hückel Limiting Law Slopes at 298.15 K and 323.15 K, where $m° = 1\ mol·kg^{-1}$

parameter	$T = 298.15$ K parameter value[a]	$T = 323.15$ K parameter value[a]
$\alpha_{M,X}(m°)^{1/2}$	2.0	2.0
$\omega_{M,X}(m°)^{1/2}$	2.5	2.5
$A_\phi(m°)^{1/2}$	0.391 475	0.410 277
	Four Parameter Model Parameters	
$\beta^{(0)}_{M,X}(m°)$	0.120 684 (0.0153)	0.120 445 (0.0293)
$\beta^{(1)}_{M,X}(m°)$	0.406 647 (0.0119)	0.450 368 (0.0118)
$C^{(0)}_{M,X}(m°)^2$	−0.004 727 (0.0312)	−0.004 770 (0.0678)
$C^{(1)}_{M,X}(m°)^2$	0.068 986 (0.1864)	0.039 194 (0.5065)
$\sigma(\phi)$	0.0017_6	0.0016_1
	Three Parameter Model Parameters	
$\beta^{(0)}_{M,X}(m°)$	0.130 191 (0.0048)	0.127 224 (0.0065)
$\beta^{(1)}_{M,X}(m°)$	0.423 173 (0.0103)	0.454 198 (0.0112)
$C^{(0)}_{M,X}(m°)^2$	−0.005 452[b] (0.0127)	−0.005 375[b] (0.0196)
$\sigma(\phi)$	0.0020_5	0.0016_4

[a] The number in parentheses following a coefficient value is the standard error of that coefficient divided by the value of that coefficient. The value of $\sigma(\phi)$ is the weighted standard deviation. The maximum molality to which these parameters for ϕ apply at 298.15 K is 5.3735 $mol·kg^{-1}$ and at 323.15 K is 4.3070 $mol·kg^{-1}$. [b] These values of $C^{(0)}_{M,X}$ may be converted to the C^ϕ parameter of Pitzer's standard model[19] using the relation $C^\phi = 2C^{(0)}_{M,X}$.

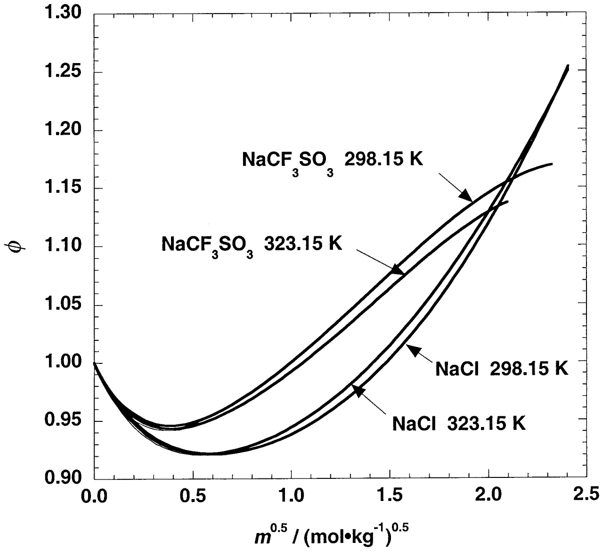

Figure 1. Smoothed values of the osmotic coefficients of $NaCF_3SO_3(aq)$ plotted against the square root of molality at 298.15 K and 323.15 K. For comparison, the ϕ values for NaCl(aq) are shown at the same two temperatures.[18]

328.15 K,[27] for $Rb_2SO_4(aq)$ and $Cs_2SO_4(aq)$ at 298.15 K and 323.15 K,[23] and by Archer[18] for NaCl(aq) at all temperatures. At 298.15 K, the extended Pitzer model with an ionic-strength dependent third virial coefficient gives an excellent representation of the experimental ϕ values for $NaCF_3SO_3(aq)$ and resulted in a significant improvement over the fit with a constant third virial coefficient. However, at 323.15 K, including the $C^{(1)}_{M,X}$ parameter for $NaCF_3SO_3(aq)$ not only resulted in no improvement in the model representation, but including it significantly increased the standard errors of the other parameter values compared to those obtained with the three-parameter fit. Thus, we accepted the four-parameter model at 298.15 K and the three-parameter model at 323.15 K.

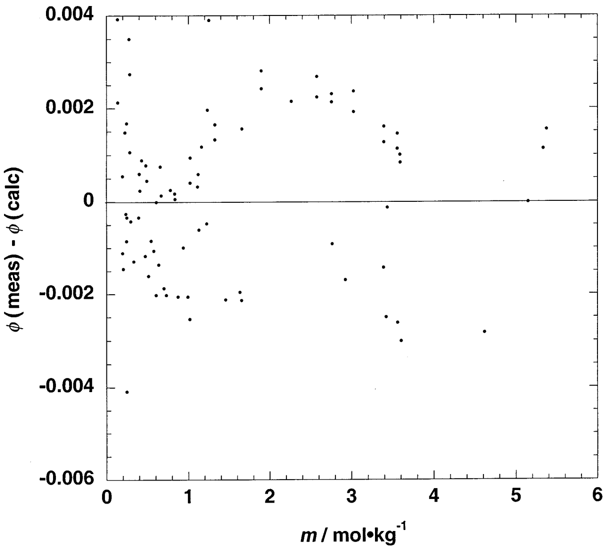

Figure 2. Deviations of the critically assessed experimental osmotic coefficients at 298.15 K for $NaCF_3SO_3(aq)$, as a function of the molality, from the four-parameter extended Pitzer model, using the parameters in Table 4. ●, experimental value.

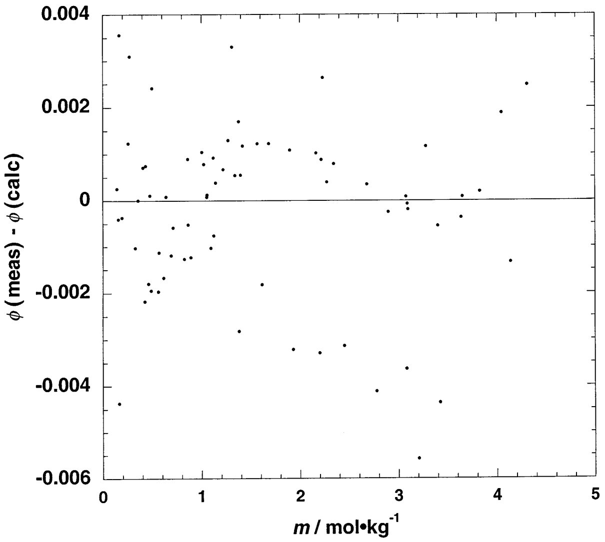

Figure 3. Deviations of the critically assessed experimental osmotic coefficients at 323.15 K for $NaCF_3SO_3(aq)$, as a function of the molality, from the three-parameter standard Pitzer model, using the parameters in Table 4. ●, experimental value.

Figure 1 compares the osmotic coefficients of $NaCF_3SO_3(aq)$ to those of NaCl(aq),[18] both at 298.15 K and 323.15 K. The values of ϕ of $NaCF_3SO_3(aq)$ and NaCl(aq) are qualitatively similar in their magnitudes, and the ϕ of $NaCF_3SO_3(aq)$ are generally higher than those of NaCl(aq), although at high molalities there are crossovers where the ϕ values of NaCl(aq) become larger than those of $NaCF_3SO_3(aq)$. The observed quantitative differences are consistent with $NaCF_3SO_3(aq)$ being slightly more associated and slightly more hydrated than NaCl(aq) at any fixed molality below the crossover molalities, with the maximum differences between their osmotic coefficients being $<0.07\phi$.

Figures 2 and 3 illustrate the residuals between the experimental values of ϕ and those calculated from the least-squares fits with the four-parameter form of eq 2 for $NaCF_3SO_3(aq)$ at 298.15 K and the three-parameter form at 323.15 K, respectively. The patterns of these residuals are essentially random, which indicates that eq 2 represents the experimental results nearly to experimental

Table 5. Smoothed Values of the Osmotic Coefficient ϕ, Water Activity a_w, and Mean Molal Activity Coefficient $\gamma_\pm$ for $NaCF_3SO_3$(aq) at Selected Molalities and at Temperatures of 298.15 K and 323.15 K, Using the Parameters of Table 4 for the Four-Parameter Extended Pitzer Model (298.15 K) or Three-Parameter Pitzer Model (323.15 K)

m/(mol·kg^{-1})	ϕ	a_w	$\gamma_\pm$
	$NaCF_3SO_3$(aq) at 298.15 K		
0.01	0.9696	0.999 651	0.9053
0.02	0.9612_5	0.999 308	0.8766
0.05	0.9502	0.998 290	0.8324
0.1	0.9445	0.996 603	0.7979
0.2	0.9449	0.993 214	0.7680
0.3	0.9499	0.989 785	0.7555
0.4	0.9565	0.986 310	0.7502
0.5	0.9635_5	0.982 791	0.7488
0.6	0.9708	0.979 23	0.7498
0.7	0.9782	0.975 63	0.7523
0.8	0.9854	$0.971\ 99_5$	0.7559
0.9	0.9926	$0.968\ 32_5$	0.7603
1.0	0.9996	0.964 62	0.7653
1.2	1.0133	0.957 13	0.7766
1.4	1.0265	0.949 54	0.7892
1.5	1.0328	0.945 71	0.7958
1.6	1.0390	0.941 86	0.8026
1.8	1.0510	0.934 11	0.8165
2.0	1.0624	0.926 30	0.8307
2.5	1.0886	0.906 60	0.8670
3.0	1.1112	0.8868	0.9031
3.5	1.1304	0.8671	0.9377
4.0	1.1459	0.8478	0.9701
4.5	1.1576	0.8289	0.9993
5.0	1.1655	0.8106	1.0246
5.3735	1.1689	0.7975	1.0406
	$NaCF_3SO_3$(aq) at 323.15 K		
0.01	0.9684	0.999 651	0.9013
0.02	0.9598	0.999 309	0.8717
0.05	0.9485	0.998 293	0.8264
0.1	0.9427	0.996 609	0.7910
0.2	0.9428	0.993 229	0.7599
0.3	0.9472	0.989 814	0.7463
0.4	0.9529	0.986 360	0.7399
0.5	0.9592	0.982 868	0.7372
0.6	0.9656	0.979 34	0.7369
0.7	0.9722	0.975 78	0.7382
0.8	0.9786	$0.972\ 18_5$	0.7405
0.9	0.9851	0.968 56	0.7437
1.0	0.9915	0.964 91	0.7476
1.2	1.0040	0.957 52	0.7566
1.4	1.0161	0.950 04	0.7670
1.5	1.0220	0.946 26	0.7726
1.6	1.0278	0.942 47	0.7784
1.8	1.0391	0.934 83	0.7903
2.0	1.0500	0.927 13	0.8027
2.5	1.0750	$0.907\ 70_5$	0.8346
3.0	1.0967	0.8882	0.8663
3.5	1.1148	0.8688_5	0.8966
4.0	1.1288	0.8498_5	0.9242
4.3070	1.1354	0.8384_5	0.9395

accuracy. The smoothed ϕ and $\gamma_\pm$ values in Table 5 were calculated using the corresponding parameters as reported in Table 4.

Clearly, there is a need for additional thermodynamic characterization of $NaCF_3SO_3$(aq). The available experiments are limited to isopiestic measurements at 298.15 K and 323.15 K, and volumetric measurements to high temperatures.[17]

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