

# Infrared Titration of Aqueous Sulfuric Acid

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This paper presents the infrared (IR) titration of aqueous sulfuric acid solutions (0.50 M) obtained by the attenuated total reflection (ATR) sampling technique. After subtracting the water spectra, the spectra of the ionic species of H<sub>2</sub>SO<sub>4</sub> in the 0–14 pH range were separated by factor analysis (FA) which also gave their abundance. The results were in agreement with the theoretical calculation of the distribution of the species. Three sulfate species were found: HSO<sub>4</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and HSO<sub>4</sub><sup>-</sup>/HCl. The latter stands for the bisulfate–hydronium complex formed by the addition of HCl to obtain measurements in the 0–0.47 pH range. For 0.50 M sulfuric acid, the comparison between the experimentally IR-determined quantities and the theoretical values gave a mean activity coefficient of 0.12 ± 0.04, a value comparable to that from electrochemical measurements. Three types of water were quantitatively determined in the solutions: acidic water, basic water, and neutral water. The latter is always present while the two others are present in the low and high pH range, respectively. Another type of water strongly associated with the sulfates is also present. Moreover, knowledge of the behavior of the different types of water as the titration proceeded permitted us to give the details of the neutralization reactions of aqueous sulfuric acid by sodium hydroxide.

## 1. Introduction

Sulfuric acid is a major industrial chemical and an important component of atmospheric aerosols responsible for smog. Because of this, its thermodynamic properties have been extensively studied. Clegg et al. formalized the data for aqueous sulfuric acid solutions from 0 to 6 mol/kg in a general self-consistent description.<sup>1</sup> To study the vibrational characteristic of sulfuric acid solutions, Raman spectroscopy<sup>2–9</sup> was preferred to IR spectroscopy since the high IR absorptivity of water and the high degree of corrosion of sulfuric acid solutions render the latter method difficult to use.<sup>10</sup> Nevertheless, IR reflection spectroscopy was used to overcome some of these difficulties.<sup>11,12</sup> The vibrational studies indicated that sulfuric acid completely dissociates in water<sup>1,5–7,10,13–14</sup> and that the species HSO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> are not simultaneously present with the nonionic form. The dissociation mechanism of bisulfate has been reported to be related to the solvation of the ions and their association with hydronium ion (H<sub>3</sub>O<sup>+</sup>).<sup>6–7,14</sup>

With IR reflection spectroscopy of aqueous solutions, the accuracy of the measurements is low.<sup>11,12</sup> For measurements made by transmission, the difficulties reside in making films only a few micrometers thick with precision and with a known path length.<sup>15</sup> In contrast, ATR measurements are easy to make and the film thickness, which depends only on the optical properties of the substrate and films, is fixed and thus gives highly reproducible spectra.<sup>16–24</sup>

The spectrum of water is strongly modified when a binary salt, a strong acid, or a strong base is added to the solution.<sup>10–12,18–19,25</sup> We have recently shown that when a binary salt is dissolved in water, the ATR spectrum's modification is proportional to that of the imaginary part of the refractive index

$k(\nu)$ . Therefore, the ATR spectrum's changes directly reflect the chemical modifications of water due to its strong interaction with the ions.<sup>20</sup> The NaCl,<sup>19</sup> KCl,<sup>22</sup> HCl,<sup>18</sup> and NaOH<sup>18</sup> binary systems showed that, depending on the ions present, the interactions with water were different. Furthermore, (1) the change in the spectrum of water is proportional to the concentration of the pair of ions; (2) four different types of species of water are identified: neutral water, salt-solvated water, HCl- and NaOH-solvated waters; (3) one type of water is unchanged by the presence of another type except when there is a chemical reaction such as when a solution of HCl is added to a solution of NaOH. Based on these premises, a simple method of subtracting the water spectra from the spectra of different aqueous solutions was developed.<sup>18,19,21</sup>

IR-ATR titration of aqueous solutions has been reported for glycine,<sup>16</sup> BOPA (a glycinate surfactant),<sup>17</sup> and NaOH.<sup>21</sup> After subtracting the water spectra, factor analysis (FA) performed on the whole spectrum of all the solutions was used to separate the species and determine their abundance as a function of pH.<sup>16,17</sup> The titration of sulfuric acid by NaOH and HCl using Raman spectroscopy made almost three decades ago was based on the integrated intensities of the 981 and 1050 cm<sup>-1</sup> bands for SO<sub>4</sub><sup>2-</sup> and HSO<sub>4</sub><sup>-</sup> ions,<sup>6</sup> respectively. We therefore decided to look at the titration of sulfuric acid with the new IR techniques available.

The purpose of the present paper is to report (1) the IR-ATR titration of aqueous sulfuric acid using pertinent equations; (2) the IR spectra of ionic species of aqueous sulfuric acid with the relative ionic quantities in the 0–14 pH range; (3) the quantitative determination by IR of the different types of water present throughout the titration; and (4) details on the neutralization reactions that go on in the aqueous solutions.

## 2. Theoretical Considerations

**2.1. Factor Analysis.** The basic principles of factor analysis (FA) applied to chemical analysis can be found in Malinowski

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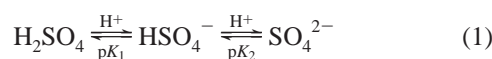
and Howery's book.<sup>26</sup> The mathematical formulation developed therein leads to abstract factors. By applying constraint conditions to the procedure, the method directly provides the *real* spectra and *real* multiplication factors (MFs).<sup>27–29</sup> By applying a normalization procedure, the MFs supply the concentration of the species. The IR titration of glycine was successfully performed using this procedure.<sup>16</sup> It was also used in a first step analysis of the IR titration of an amphoteric surfactant.<sup>17</sup>

In the case of systems for which a set of experimental spectra have been obtained, some spectra may represent pure or almost pure species. For example, the species of malic acid and disodium malate, at pH far from  $pK_a$ , are pure<sup>18</sup> and the two spectra obtained once the water spectra have been removed are the principal spectra for FA. With these spectra, FA can be achieved directly using a personal computer. The principal spectra for each solution are taken, multiplied by their MFs, and the results are added. The sums are subtracted from their corresponding experimental spectra to give the residue spectra which are minimized by an iterative procedure.<sup>27</sup>

**2.2. Sample Composition from MFs.** For the dilute sulfuric acid and potassium sulfate aqueous solutions studied by Querry et al., the authors assumed that the extinction coefficient  $k$  was a linear combination of the molecular extinction coefficients of the different species directly proportional to their concentrations.<sup>11</sup> This supposition will be verified with FA by obtaining the MFs. In previous studies on aqueous solutions of sulfuric acid by Raman spectroscopy, a band of sulfate ion was used to determine the composition of the solutions.<sup>6,7</sup> In the present study, the entire IR spectrum was used to perform the analysis. This procedure reduced the error in the determination of the ionic composition and water content of the solutions. Water content is determined by using water's reference spectra and obtaining their MFs. After subtracting the water spectra from the spectra of the solutions, the spectra of the ionic species are chosen to represent the spectra of the purest ionic species. These are used to determine the MFs of the different solutions.

**2.3. Theoretical Volumetric Titration Curves.** For a glycinate amphoteric surfactant, we developed the equations for the titration based on the equations of dissociation, conservation of the species, electroneutrality,<sup>16–17</sup> and with the activity coefficients constant and equal to unity. For the titration of  $H_2SO_4$ , the activity coefficients are not constant<sup>1,5,8,23</sup> and therefore the equations developed for the glycinate cannot be directly used. The problem must be reworked from the beginning.

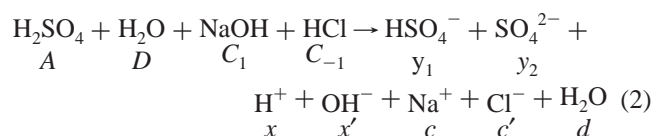
**2.3.1. Definition of the Problem.** For titration by an acid or a base, the problem is written as if both titrants were added simultaneously in order to simplify the mathematics. At the end, the two cases are separated. The following species are present in the solutions: (1) aqueous  $H_2SO_4$ , the titrate; (2) aqueous HCl, a strong acid; (3) aqueous NaOH, a strong base; and (4)  $Na^+$  and  $Cl^-$ , the counterions. The titrants (a strong base or a strong acid) dissociate completely in water. For sulfuric acid we have



The first dissociation constant,  $pK_1 = -3$ , indicates that  $H_2SO_4$  is completely dissociated in water above  $pH = 0$ .<sup>30,31</sup> Raman spectroscopy has also shown that in the 0–14 pH range  $HSO_4^-$  and  $SO_4^{2-}$  ions are present and not  $H_2SO_4$ .<sup>5–7</sup>

The chemical state reached by the mixture is given in eq 2 where the left member represents the starting point and the right

one, the equilibrium state of the mixture:



The second line in (2) represents the quantities (in mol) involved during the titration measurements. Quantities  $A$ ,  $C_1$ ,  $C_{-1}$ , and  $D$  are known. The equations necessary for the theoretical calculations of the titration curves are the dissociation equilibrium equations, the equations of conservation of the species, and the equation of electroneutrality.<sup>32–33</sup>

**2.3.1.1. Equilibrium Relations.** The dissociation equilibrium equations between  $HSO_4^-$  and  $SO_4^{2-}$  are

$$\frac{[SO_4^{2-}][H^+]}{[HSO_4^-]} \frac{\gamma_{SO_4^{2-}}\gamma_{H^+}}{\gamma_{HSO_4^-}} = K_2 \quad (3)$$

$$\frac{[H^+][OH^-]}{[H_2O]} \frac{\gamma_{H^+}\gamma_{OH^-}}{\gamma_{H_2O}} = K_0 \quad (4)$$

where  $\gamma_i$  are the activity coefficients of the species present in the solutions and  $[H^+]$  stands for  $[H_3O^+]$  or  $[H_5O_2^+]$  as the case may be (we will not settle the dispute here). The dissociation constants are the thermodynamic constants. To simplify, we define

$$\frac{\gamma_{HSO_4^-}}{\gamma_{SO_4^{2-}}} = \Gamma_2 \quad (5)$$

$$\frac{\gamma_{H_2O}}{\gamma_{OH^-}} = \Gamma_0 \quad (6)$$

The total volume of the solution is  $V$  and, eqs 3 and 4 may be written as follows:

$$y_2 = y_1 K_2 \Gamma_2 \frac{V}{\gamma_{H^+x}} \quad (7)$$

$$x' = d K_0 \Gamma_0 \frac{V}{\gamma_{H^+x}} \quad (8)$$

**2.3.1.2. Conservation of Species.** The relations for the conservation of species lead to

$$C_1 = c \quad \text{and} \quad C_{-1} = c' \quad (9)$$

$$A = y_1 + y_2 \quad (10)$$

$$D + 2A + C_{-1} = d + x + y_1 \quad (11)$$

$$D + C_1 = d + x' \quad (12)$$

**2.3.1.3. The Electroneutrality Relation.** Since the solutions are electrically neutral at all times, this condition is applied to the equilibrium state which gives us the remaining equation necessary to solve the problem:

$$y_1 + 2y_2 + c' + x' = c + x \quad (13)$$

2.3.2. Resolution of the Problem. 2.3.2.1. Amount of Species as a Function of pH. We define variable  $X$  as follows:

$$X = \frac{V}{\gamma_{H^+X}} = \frac{1}{\gamma_{H^+}[H^+]} \quad (14)$$

$X$  is related to the value obtained from the pH-meter; that is  $X = 10^{\text{pH}}$ .<sup>34</sup>

Combining eqs 7, 10, and 14 gives

$$y_1 = \frac{A}{1 + K_2\Gamma_2X} \quad (15)$$

$$y_2 = \frac{A}{\frac{1}{K_2\Gamma_2X} + 1} \quad (16)$$

The relative distribution of HSO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> as a function of pH is obtained by dividing eqs 15 and 16 by  $A$  and replacing  $X$  by  $10^{\text{pH}}$ .

Combining eqs 8, 10, and 14–16 with eq 13 gives

$$A \frac{1 + 2K_2\Gamma_2X}{1 + K_2\Gamma_2X} + dK_0\Gamma_0X + C_{-1} - C_1 - \frac{V}{\gamma_{H^+X}} = 0 \quad (17)$$

2.3.2.2. Evaluating the Quantity of Matter (in mol) from the Mass of the Products. The quantities (in mol) of base NaOH ( $C_1$ ) and acid HCl ( $C_{-1}$ ) are

$$C_1 = m_1 \frac{\epsilon_1}{M_1}; \quad C_{-1} = m_{-1} \frac{\epsilon_{-1}}{M_{-1}} \quad (18)$$

where the  $m$ 's are the masses of titrant solution in the sample,  $M$ 's their molar masses, and  $\epsilon$ 's the concentrations of the titrant solutions in terms of relative masses. The subscripts 1 and -1 are for the base and acid, respectively. We use the index  $\delta$  to designate the titrant:  $\delta = 1$  and  $-1$  for the base and acid solutions, respectively. Experimentally, the two titrants are never present together, each one being used alone. Therefore, for a given sample,  $\delta$  will have a single value. The relative mass of the initial aqueous solution of H<sub>2</sub>SO<sub>4</sub> is noted  $\epsilon_2$ . The molar mass of H<sub>2</sub>SO<sub>4</sub> is  $M_2$ . We therefore have the relation

$$A = m_2 \frac{\epsilon_2}{M_2} = (m - m_\delta) \frac{\epsilon_2}{M_2} \quad (19)$$

where  $m$  is the total mass of the sample.

The original quantity of water,  $D$ , is calculated from the amount of water in the mixture

$$D = m_\delta \frac{1 - \epsilon_\delta}{M_{H_2O}} + m_2 \frac{1 - \epsilon_2}{M_{H_2O}} = m_\delta \frac{1 - \epsilon_\delta}{M_{H_2O}} + (m - m_\delta) \frac{1 - \epsilon_2}{M_{H_2O}} \quad (20)$$

2.3.2.3. Experimental Parameters. The experiments were performed by measuring the volumes and masses involved in the titration. Using the same total volume for each sample, the mass of titrant,  $m_\delta$ , can be isolated.<sup>16,17</sup> The total volume  $V$  is kept constant while mass  $m_2$  is a simple function of total mass  $m$  and  $m_\delta$ . It is necessary to express values  $A$ ,  $C$ , and  $D$  as functions of  $m_\delta$  and  $X$ . Then  $m_\delta$  is isolated as a function of  $X$ , which in turn is a solution of the problem.

2.3.2.4 Mass of Titrant. Performing the titration, we measured mass  $m_\delta$  of the titrant and total mass  $m$  of the resulting mixture when volume  $V$  was completed. We therefore have  $m_2 = m -$

$m_\delta$ . Note that the total mass  $m$  is not constant, indicating that the density of the mixture depends on the quantity of titrant. Density measurements of the mixtures show that it is possible to approximate mass  $m$  as a linear function of titrant mass,  $m_\delta$ :

$$m = \rho V = \rho_0 V + \Delta\rho V = \rho_0 V + \rho_\delta m_\delta \quad (21)$$

where  $\rho_\delta$  is a nondimensional parameter ( $\rho_\delta = \Delta\rho V/m_\delta$ ). By combining eqs 19 and 21,  $A$  becomes

$$A = \frac{\epsilon_2}{M_2} [\rho_0 V - (1 - \rho_\delta) m_\delta] \quad (22)$$

Note that the value of  $A$  depends only on variable  $m_\delta$  ( $\rho_\delta$  is a constant parameter deduced from the measurements of  $m$  and  $m_\delta$  taken together).

2.3.2.5. Evaluating the Quantity of Water (in mol). Combining eqs 8, 14, 18, and 20 with eq 12 gives the quantity of water ( $d$ ) in the sample at equilibrium

$$d = \left\{ \rho_0 V \frac{1 - \epsilon_2}{M_{H_2O}} + m_\delta \left[ \frac{1 - \epsilon_\delta}{M_{H_2O}} + \frac{1 + \delta}{2} \frac{\epsilon_\delta}{M_\delta} + (\rho_\delta - 1) \frac{1 - \epsilon_2}{M_{H_2O}} \right] \right\} / \{1 + K_0\Gamma_0X\} \quad (23)$$

2.3.2.6. Result. Combining eqs 18, 22, and 23 with eq 17 and isolating  $m_\delta$  gives

$$m_\delta = \left\{ \rho_0 V \left[ \frac{\epsilon_2}{M_2} \frac{1 + 2K_2\Gamma_2X}{1 + K_2\Gamma_2X} + \frac{1 - \epsilon_2}{M_{H_2O}} \frac{K_0\Gamma_0X}{1 + K_0\Gamma_0X} \right] - \frac{V}{\gamma_{H^+X}} \right\} / \left\{ \frac{\epsilon_\delta}{M_\delta} \frac{\delta + \frac{(\delta - 1)}{2} K_0\Gamma_0X}{1 + K_0\Gamma_0X} + (1 - \rho_\delta) \frac{\epsilon_2}{M_2} \frac{1 + 2K_2\Gamma_2X}{1 + K_2\Gamma_2X} - \frac{(1 - \epsilon_\delta) - (1 - \rho_\delta)(1 - \epsilon_2)}{M_{H_2O}} \frac{K_0\Gamma_0X}{1 + K_0\Gamma_0X} \right\} \quad (24)$$

Replacing  $X$  by  $10^{\text{pH}}$  in eq 24 gives

$$m_\delta = \left\{ \rho_0 V \left[ \frac{\epsilon_2}{M_2} \frac{1 + 2K_2\Gamma_2 10^{\text{pH}}}{1 + K_2\Gamma_2 10^{\text{pH}}} + \frac{1 - \epsilon_2}{M_{H_2O}} \frac{K_0\Gamma_0 10^{\text{pH}}}{1 + K_0\Gamma_0 10^{\text{pH}}} \right] - \frac{V}{\gamma_{H^+} 10^{\text{pH}}} \right\} / \left\{ \frac{\epsilon_\delta}{M_\delta} \frac{\delta + \frac{\delta - 1}{2} K_0\Gamma_0 10^{\text{pH}}}{1 + K_0\Gamma_0 10^{\text{pH}}} + (1 - \rho_\delta) \frac{\epsilon_2}{M_2} \frac{1 + 2K_2\Gamma_2 10^{\text{pH}}}{1 + K_2\Gamma_2 10^{\text{pH}}} - \frac{(1 - \epsilon_\delta) - (1 - \rho_\delta)(1 - \epsilon_2)}{M_{H_2O}} \frac{K_0\Gamma_0 10^{\text{pH}}}{1 + K_0\Gamma_0 10^{\text{pH}}} \right\} \quad (25)$$

Equations 24 and 25 provide the value for the mass of titrant  $m_\delta$  as a function of  $[H^+]$  and pH, respectively. Equations 15 and 16 give the amount of the two species of sulfuric acid present in the samples.

### 3. Experimental Section

3.1. Chemicals and Solutions. Sulfuric acid (Aldrich Chemical Co., purity 98%) was used without further purification. The basic titrant was sodium hydroxide (Fisher Scientific, purity

**TABLE 1: Input and Results for the IR Titration of H<sub>2</sub>SO<sub>4</sub> at 26.5 °C**

region	input			pH	IR results		
	mass of				MFs of water <sup>a</sup>		
	12.06 mol/L HCl (g)	19.1 mol/L NaOH (g)	10 mL sample (g)		basic water ±0.003	acidic water ±0.003	pure water ±0.003
I	1.0030		10.3642	0.16	0.000	1.073	-0.163
	0.5181		10.3205	0.28	0.000	0.785	0.151
	0.2499		10.3194	0.38	0.000	0.629	0.323
I/II			10.2330	0.48	0.000	0.479	0.466
		0.0423	10.3010	0.51	0.000	0.451	0.495
		0.0842	10.3049	0.53	0.000	0.423	0.530
II		0.1209	10.2911	0.58	0.000	0.397	0.552
		0.1622	10.2995	0.61	0.000	0.372	0.581
		0.2041	10.2694	0.72	0.000	0.341	0.612
		0.2499	10.3325	0.75	0.000	0.302	0.649
		0.2853	10.2906	0.80	0.000	0.280	0.678
		0.3728	10.3515	0.89	0.000	0.225	0.738
		0.4551	10.3117	1.02	0.000	0.164	0.803
		0.5406	10.3695	1.22	0.000	0.120	0.855
III		0.5797	10.4273	1.24	0.000	0.094	0.879
		0.6178	10.3856	1.36	0.000	0.079	0.902
		0.6611	10.3736	1.53	0.000	0.055	0.930
		0.7030	10.4353	1.70	0.000	0.040	0.948
		0.7469	10.4484	1.98	0.000	0.021	0.978
		0.7833	10.4755	2.58	0.000	0.006	0.995
		0.8204	10.5093	12.38	0.007	0.000	0.999
IV		0.8619	10.5302	12.82	0.035	0.000	0.968
		0.9086	10.5429	13.00	0.059	0.000	0.946
		0.9582	10.5311	13.15	0.087	0.000	0.915
		0.9851	10.5800	13.16	0.103	0.000	0.898
		1.0251	10.5946	13.20	0.126	0.000	0.874

<sup>a</sup> Multiplying factors (MFs) obtained from IR measurements (see text).

97%) in a solution of  $485 \pm 7$  g/L (12.13 M) and the acid titrant was concentrated hydrochloric acid (Fisher Scientific,  $370 \pm 10$  g/L (density 1.19 g/mL, 12.06 M)). Deionized water was used to prepare the aqueous solutions. High concentrations of titrant were used to obtain samples with approximately the same sulfuric acid concentration.

A stock solution of  $0.50 \pm 0.01$  M H<sub>2</sub>SO<sub>4</sub> was prepared by weighing  $25.0 \pm 0.1$  g of concentrated sulfuric acid in an empty 500 mL volumetric flask and adding water to complete the volume. The solution weighed  $511.5 \pm 0.1$  g and its pH was 0.48. Each sample was prepared by first weighing titrant NaOH or HCl in an empty 10 mL volumetric flask, then completing the volume with the H<sub>2</sub>SO<sub>4</sub> stock solution, and weighing it again. HCl solution was used as a titrant to obtain the three solutions at the lowest pH because 0.50 M H<sub>2</sub>SO<sub>4</sub> gives a pH of 0.48. Solutions whose pH is between 0 and 0.48 are necessary for the comprehension of the system. A series of 26 samples in the 0–14 pH range were prepared, the composition of which is given in Table 1. Each sample was divided into two parts: one part for the IR measurements and one part for the pH measurements.

Neutral water, 1.54 M HCl, and 2.23 M NaOH were used to obtain the reference spectra (or principal spectra) of neutral water, acidic water, and basic water that were used to subtract the water spectra from the spectra of the sulfuric acid solutions.

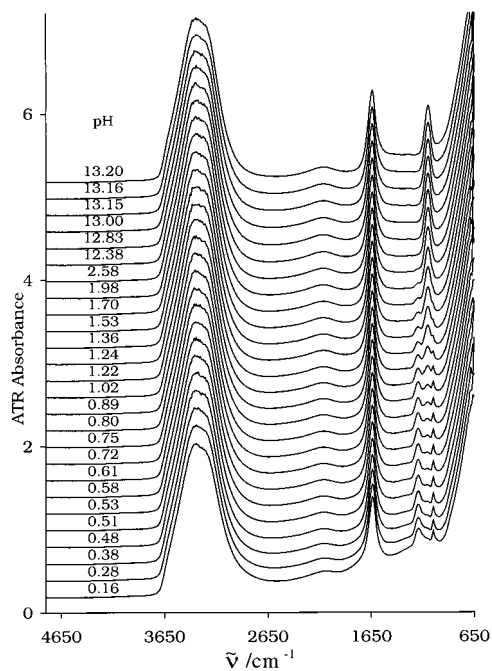
**3.2. pH Measurements.** The pH was measured at room temperature ( $26.5 \pm 0.3$  °C) with a pH meter (Omega model PHH-253) equipped with a combination electrode (Analytical Sensors, Inc., model PH10107B-03-B). Prior to any series of measurements a two-point calibration was made at pH = 2.00 and 7.00, or 7.00 and 10.00.

**3.3. IR Measurements.** The IR measurements were obtained using a model 510P Nicolet FT-IR spectrometer with a TGS detector. Two KBr windows isolate the measurement chamber

from the outside. The samples were contained in a Circle cell (SpectraTech, Inc.) equipped with a ZnSe crystal rod in an ATR configuration (making 11 internal reflections, the incident beam is at an angle of 45° with respect to the rod's axis). The spectral range of the ZnSe rod in the spectrophotometer is situated between 4800 and 650 cm<sup>-1</sup>. For the sake of comparison, the spectrum of pure H<sub>2</sub>SO<sub>4</sub> (98%) was taken by transmission between KBr windows protected by a thin film of paraffin. All spectra were taken under a nitrogen flow to ensure low CO<sub>2</sub> and water vapor residues in the spectrometer. For each spectrum taken at  $26.5 \pm 0.3$  °C, an accumulation of 200 scans with a resolution of 4 cm<sup>-1</sup> was obtained. The cell was carefully washed and dried before each measurement. Model 510P is a single-beam spectrometer, and a background was taken with the empty cell before the measurement of each sample.

Because of the variation of the penetration depth with wavelength, the use of an ATR configuration causes some variations in the spectra compared to the transmission configuration. However, it has been shown that the modifications of the ATR spectrum of water in aqueous solutions are directly proportional to the modifications of its  $k(\nu)$  spectrum.<sup>20</sup> Therefore, accurate quantitative analysis can be directly made using the ATR spectra of the solutions.

The IR measurements consisted of obtaining the ATR background intensity  $R_0$  and the ATR sample intensity  $R$ . The ratio  $R/R_0$  produced intensity  $I$  for the spectral range being studied. Next, the 2152 data points  $\{I(\tilde{\nu}) \text{ vs } \tilde{\nu} \text{ (in cm}^{-1}\text{)}\}$  of each spectrum were transferred to a Microsoft Excel spreadsheet program on a personal computer where the numerical treatments were performed. Intensities  $I$  were then transformed in absorbance,  $\log(1/I)$ . No baseline correction was made other than a small shift (less than 0.02 au) in the intensity scale in order to



**Figure 1.** IR-ATR spectra of 26 mixtures of 0.50 M H<sub>2</sub>SO<sub>4</sub> at increasing pH. Except for the bottom one situated at 0.2 au, each spectrum is shifted by 0.2 au from the preceding one.

obtain null absorption in the 4600–4450 cm<sup>-1</sup> region, based on reported values for the extinction coefficient of neutral water.<sup>24</sup>

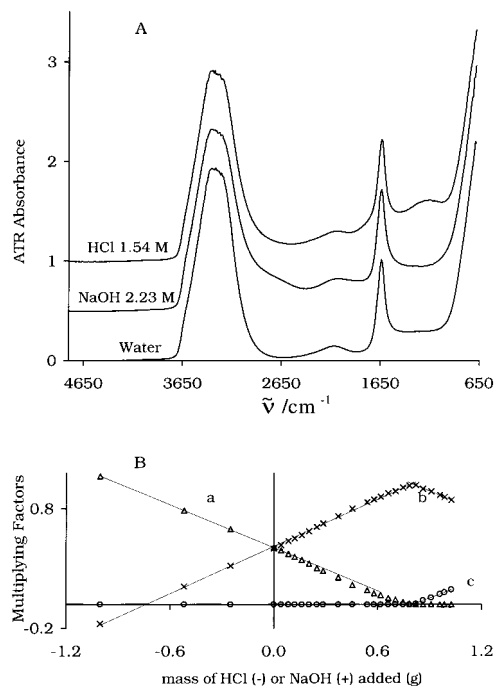
**3.4. Factor Analysis.** Factor analysis was divided into two steps: first, the subtraction of the water spectra and, second, the separation of the ionic species of sulfuric acid.

**3.4.1. Subtraction of the Water Spectra.** The subtraction of the water spectra was performed using three reference spectra: neutral water and NaOH- and HCl-solvated waters.<sup>18–19,21</sup> This was done by subtracting from the spectrum of each sample the reference spectra multiplied by the proper MF and, in an iterative procedure, increasing the MFs to their respective maximum value with the limitation that the resulting spectrum must have no negative bands. Reference spectra cannot be obtained by a linear combination of the others, although they are not orthogonal spectra. The NaOH and HCl aqueous solutions used to define the basic and acidic waters contain some water organized as in neutral water.<sup>22</sup>

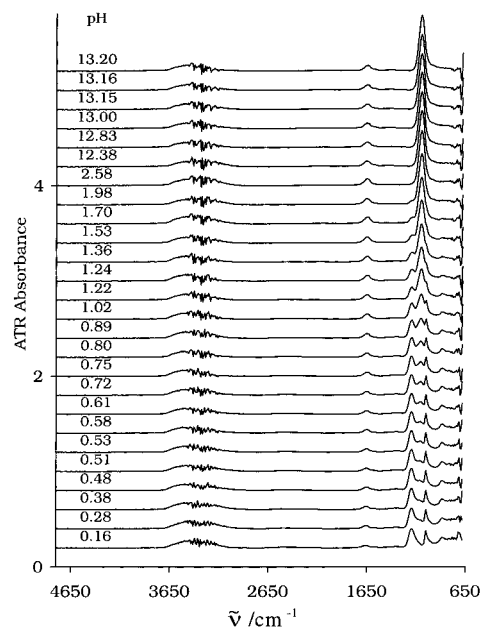
**3.4.2. Ionic Species of Sulfuric Acid.** The reference spectra for the ionic species used in FA for the 26 spectra of aqueous H<sub>2</sub>SO<sub>4</sub> were determined from the experimental spectra by choosing the ones that represent the pure or almost pure species. Each reference spectrum was multiplied by its MF which was varied in an iterative procedure to obtain the best fit by minimizing the difference between experimental and calculated spectra. The latter were obtained by adding the products of the reference spectra with their MFs. Because the absorption of water in the 3400 cm<sup>-1</sup> region and below 750 cm<sup>-1</sup> was near saturation, resulting in a noisy signal in these frequency ranges, we eliminated these regions in the minimization procedure.

## 4. Results and Discussion

**4.1. Spectra of the Mixtures of Aqueous H<sub>2</sub>SO<sub>4</sub> and NaOH or HCl.** The 26 experimental spectra of 0.50 M H<sub>2</sub>SO<sub>4</sub> in the 0.16–13.20 pH range are given in Figure 1. Important spectral changes are observed in the 1300–800 cm<sup>-1</sup> range, changes which are related to the varying ionic composition of sulfuric acid as the pH is modified. In parallel, the spectrum of water is



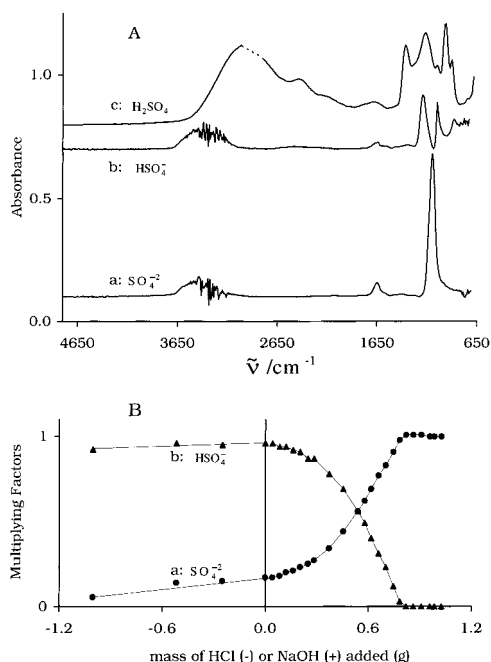
**Figure 2.** (A) IR-ATR reference spectra of water: neutral water; basic water (2.23 M NaOH); and acidic water (1.54 M HCl). The two top spectra are shifted. (B) Multiplying factors (MFs) for the types of water as a function of titrant: (a) acidic water (Δ); (b) neutral water (×); (c) basic water (○) (negative quantities are for HCl; positive ones for NaOH).



**Figure 3.** Spectra of Figure 1 after subtraction of the water spectra. Same order as in Figure 1.

modified as it changes from an acidic to a basic situation. The changes in the water spectra are similar to those observed in aqueous NaOH and aqueous HCl.<sup>11,12,18,21,25</sup>

**4.2. Water Content.** **4.2.1. Subtraction of the Water Spectra.** The reference spectra of acidic, basic, and neutral water used for the subtraction are given in Figure 2A. The absorption in the 2100 cm<sup>-1</sup> region is used to monitor the subtraction process. The MFs obtained by the subtraction of the water spectra from the series of spectra in Figure 1 are given in Figure 2B. The resulting spectrum for each sample is displayed in Figure 3. After subtraction, the resulting spectra have a flat baseline

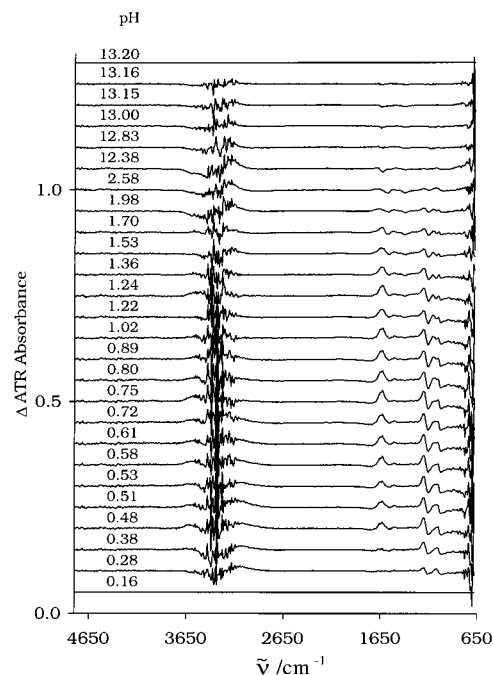


**Figure 4.** Results of FA on the IR-ATR spectra of aqueous sulfuric acid when two ionic species are retrieved. (A) IR spectra of (a)  $\text{SO}_4^{2-}$ ; (b)  $\text{HSO}_4^-$ ; and (c) IR-transmission spectrum of pure  $\text{H}_2\text{SO}_4$  (98%). In the latter, the dashed line (---) is the region of the CH vibrations of the paraffin film used to protect the IR windows. (B) Corresponding MFs: (a)  $\text{SO}_4^{2-}$  (●); (b)  $\text{HSO}_4^-$  (▲).

situated at the zero intensity level. Some absorption remains in the 3300 and 1650  $\text{cm}^{-1}$  regions which we attribute to water being in strong interaction with the sulfate ions. The MFs obtained by the subtraction of the water spectra are given in Table 1. In this table, the sample with the lowest pH has a small negative value because the reference spectra are not orthogonal. When water is added to sulfuric acid,  $\text{HSO}_4^-$  and  $\text{H}_3\text{O}^+$  ions are formed. To evaluate the quantities of the latter, we used the reference spectrum of aqueous HCl since it forms the desired cation while the anion does not absorb. The replacement of  $\text{Cl}^-$  by another anion only slightly modifies the position of the cation bands but, as we see later, its absorptivity varies.<sup>35</sup>

**4.3. Results Obtained by Factor Analysis.** **4.3.1. Factor Analysis with Two Principal Factors.** **4.3.1.1. IR Spectra.** The spectral changes observed in Figure 3 indicate that at least two principal species of sulfuric acid are present in the aqueous solutions. From eq 1 these are  $\text{HSO}_4^-$  and  $\text{SO}_4^{2-}$ . Since the spectra for the solutions with the highest pH remain unchanged, we chose the spectrum of the sample at  $\text{pH} = 13.20$  for the spectrum of species  $\text{SO}_4^{2-}$ , which we designate as the first principal factor. At the lowest pH ( $\text{pH} 0.16$ ), the solution contains mainly  $\text{HSO}_4^-$  and a certain amount of  $\text{SO}_4^{2-}$ . Since the spectrum of the latter is known, it was quantitatively subtracted to give a pure spectrum of  $\text{HSO}_4^-$ , which we designate as the second principal factor. This subtraction procedure was previously used on the reflectance spectra of an aqueous sulfuric acid system by Querry et al.<sup>11</sup> The spectrum of the principal factors normalized to 0.48 M are given in Figure 4A: a,  $\text{SO}_4^{2-}$  and b,  $\text{HSO}_4^-$ . Figure 4Ac shows the spectrum of pure  $\text{H}_2\text{SO}_4$ , given for comparison purposes. The most intense bands of the latter are not present in the ionic spectra (a and b), confirming that the 26 samples do not contain any molecular form of sulfuric acid.<sup>5-7,11</sup>

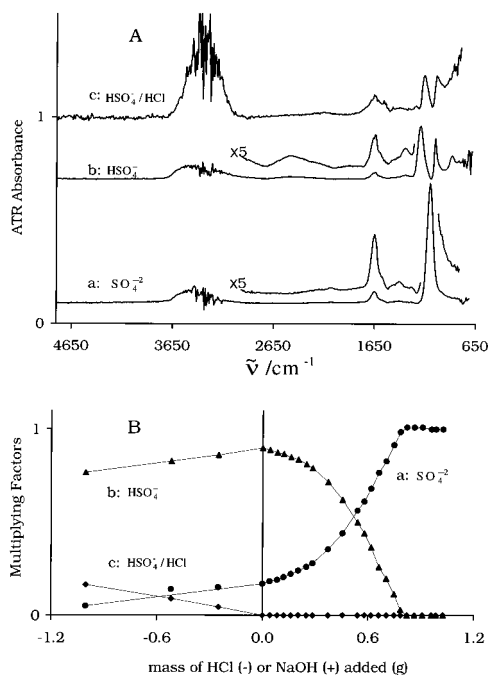
**4.3.1.2. Distribution of the Species.** With the principal spectrum of  $\text{SO}_4^{2-}$  and of  $\text{HSO}_4^-$ , the MFs of each sample, giving the proportion of each species as a function of titrant,



**Figure 5.** Differences between experimental (Figure 3) and the sum of the calculated spectra taking the two principal spectra of Figure 4A and multiplying them by their MFs from Figure 4B. Same order as in Figure 1. Except for the bottom one situated at 0.05 au, each spectrum is shifted by 0.05 au from the preceding one.

were determined. These are found in Figure 4B. To verify that the spectra retrieved and the distribution of the species are correct, we multiplied the MFs of each solution by their proper spectra (Figure 4A) and added the results. The spectra resulting from this operation are subtracted from the experimental spectra of Figure 3 to give the difference spectra shown in Figure 5. This figure reveals a small residual spectrum starting at  $\text{pH} 0.28$ , increasing to  $\text{pH} 0.9$  and decreasing to  $\text{pH} 2.6$ . The choice of any other two different principal spectra did not improve the situation. This result indicates that there is another species in the system, a minor one.

**4.3.2. Factor Analysis with Three Principal Factors.** **4.3.2.1. IR Spectra.** In addition to the two species mentioned in the previous section, we chose as third species the one at  $\text{pH} 0.48$ , because no titrant was added to the solution. The two lower pH species contain small amount of the other species. Following proper subtraction of the minority species and normalization of the spectra to 0.48 M sulfuric acid we obtained the spectra observed in Figure 6A. Lines a, b, and c are the spectra of  $\text{SO}_4^{2-}$ ,  $\text{HSO}_4^-$ , and  $\text{HSO}_4^-/\text{HCl}$ , respectively. Compared to the spectra of the other species, the signal-to-noise ratio of the third is lower because its concentration is less than the others. The assignment of the bands are given in Table 3. Although spectrum c resembles spectrum b, they differ in the position and shape of the bands. This indicates that the new species  $\text{HSO}_4^-/\text{HCl}$  is genuine. A similar species has been observed by Raman and identified as  $\text{HSO}_4^-$  ion pair.<sup>38</sup> Compared to the pure species, the Raman bands of the ion pair are shifted by about 20  $\text{cm}^{-1}$ . These shifts are similar to what we observed between pure  $\text{HSO}_4^-$  and  $\text{HSO}_4^-/\text{HCl}$  species. In Table 3, several weak bands that were not previously observed because of the high absorptivity of water have been identified. These bands are assigned to combination and harmonic of the ionic species and to water complexed to the ionic species. The water of the latter is different from neutral, basic, and acidic waters because the spectra of these species have been subtracted. Therefore, the



**Figure 6.** Results of FA on the IR-ATR spectra of the ionic species of aqueous sulfuric acid when three ionic species are retrieved by FA. (A) IR spectra of (a) SO<sub>4</sub><sup>2-</sup>; (b) HSO<sub>4</sub><sup>-</sup>; (c) HSO<sub>4</sub><sup>-</sup>/HCl (spectra are shifted upward; left limits are at 0 au). (B) Corresponding MFs: HSO<sub>4</sub><sup>-</sup> (▲); SO<sub>4</sub><sup>2-</sup> (●); HSO<sub>4</sub><sup>-</sup>/HCl (◆).

remaining water bands identified in Table 3 come from water strongly bonded to the ionic species, in other words, complexed to them.  $\nu_1$  of SO<sub>4</sub><sup>2-</sup> appears as a weak shoulder at 982 cm<sup>-1</sup>, a value comparable to that of Raman.<sup>38</sup> Because of  $T_d$  symmetry of SO<sub>4</sub><sup>2-</sup>,  $\nu_1$  should not be active in IR. The three water molecules (see below), associated with SO<sub>4</sub><sup>2-</sup> species perturb the symmetry and render  $\nu_1$  slightly active. The intensity of  $\nu_1$  and of the bands of water associated with the SO<sub>4</sub><sup>2-</sup> species are constant throughout the presence of this species in the pH range 14–0. This indicates that the complex formed (SO<sub>4</sub><sup>2-</sup>·3H<sub>2</sub>O) is stable throughout this pH range. The water band associated with HSO<sub>4</sub><sup>-</sup>/HCl is stronger than the one associated with the pure species and indicates that more water molecules are bonded to HSO<sub>4</sub><sup>-</sup>/HCl than to the pure HSO<sub>4</sub><sup>-</sup> species. This matter will be discussed below.

**4.3.2.2. Distribution the Species.** The MFs obtained with three species are displayed in Figure 6B. The differences between the experimental spectra (Figure 3) and those calculated by multiplying the principal spectra by their MFs and adding the products are given in Figure 7. These results are much better than those obtained using only two principal factors (Figure 5), although some very small residuals remain in the region between pH 0.6 and 2.6. Efforts to decrease these residuals by choosing another set of principal spectra or by adding another principal spectrum were unsuccessful. This can be explained by the low intensity of these residuals and by the possibility that more than one species may exist in this pH region. Nevertheless, the amount of these species, if they exist, is negligible and hardly affects the rest of our analysis, which will be made with the three ionic species identified as SO<sub>4</sub><sup>2-</sup>, HSO<sub>4</sub><sup>-</sup>, and HSO<sub>4</sub><sup>-</sup>/HCl.

**4.4. Determining of the Activity Coefficients.** The volumetric titration of aqueous sulfuric acid by aqueous NaOH and the normal distribution of the ionic species are given in Figure 8A and B, respectively. In Figure 8A, the experimental quantities (in grams, O) of HCl and NaOH as a function of pH

(Table 1) are compared to the theoretical ones (dashed line, - - -) calculated with eq 25 where the mean activity coefficients,  $\Gamma_0$ ,  $\Gamma_2$ , and  $\gamma_{H^+}$ , were made equal to unity. The quantities used in the calculations are listed in Table 2. At pH lower than 3, the theoretical curve does not agree with the experimental data. To correct the situation, one must take the real mean activity coefficient which, for aqueous sulfuric acid, is known to be far below unity.<sup>1,4–5,8,23,34</sup>

**4.4.1. Determining  $\Gamma_2$  ( $\equiv \gamma_{HSO_4^-} / \gamma_{SO_4^{2-}}$ ).** Applying eqs 3 and 5 at the equivalence of the two principal ionic species of aqueous sulfuric acid leads to  $\Gamma_2$ , the ratio of the activity coefficient of HSO<sub>4</sub><sup>-</sup> to that of SO<sub>4</sub><sup>2-</sup> (eq 5):

$$\Gamma_2 = 10^{(pK_2 - pH_{\text{equipartition}})} \quad (26)$$

The equivalence of the aqueous sulfuric acid ionic forms is situated near the intercept of the distribution curves obtained by IR (Figure 6B and Table 1 gives for pH<sub>equipartition</sub> a value of approximately 1.22). Taken from several sources, the value of  $K_2$  at 25 °C is 0.0120,<sup>30,31</sup> 0.011,<sup>36</sup> 0.0105<sup>1</sup> and 0.0101.<sup>37</sup> The mean value of  $K_2$  put into eq 26 gives for 0.50 M H<sub>2</sub>SO<sub>4</sub> the value of  $5.5 \pm 0.5$  for  $\Gamma_2$ .

**4.4.2. Determining  $\Gamma_0$  ( $\equiv \gamma_{H_2O} / \gamma_{OH^-}$ ).** At high pH (16 > pH > 13) where  $K_0\Gamma_0 \cdot 10^{pH} \ll 1 \ll K_2\Gamma_2 \cdot 10^{pH}$ , eq 25 can be approximated by

$$m_\delta \approx \rho_0 V \frac{2 \frac{\epsilon_2}{M_2} + \frac{1 - \epsilon_2}{M_{H_2O}} K_0 \Gamma_0 10^{pH}}{\frac{\epsilon_\delta}{M_\delta} + 2(1 - \rho_\delta) \frac{\epsilon_2}{M_2}} \approx G + \rho_0 V \frac{\frac{1 - \epsilon_2}{M_{H_2O}} K_0 \Gamma_0 10^{pH}}{\frac{\epsilon_\delta}{M_\delta} + 2(1 - \rho_\delta) \frac{\epsilon_2}{M_2}} \quad (27)$$

where  $G$  is a constant corresponding to a titrant equivalent of 2 for the complete neutralization of sulfuric acid. Equation 27 indicates that the shape of the volumetric titration curve at high pH depends only on  $\Gamma_0$ , the activity coefficient of water over that of OH<sup>-</sup> (eq 6). Adjusting the theoretical curve to the experimental one gives the mean activity coefficient of water  $\Gamma_0 = 1.5 \pm 0.3$ .

**4.4.3. Determining  $\gamma_{H^+}$  (Activity Coefficient of H<sub>3</sub>O<sup>+</sup> (indicated by H<sup>+</sup>)).** At low pH (0.5 > pH) where  $K_0\Gamma_0 \cdot 10^{pH} \ll 1$  and  $K_2\Gamma_2 \cdot 10^{pH} \ll 1$ , eq 25 is approximated by

$$m_\delta \approx \frac{\rho_0 V \frac{\epsilon_2}{M_2} - \frac{V}{\gamma_{H^+} 10^{pH}}}{-\frac{\epsilon_\delta}{M_\delta} + (1 - \rho_\delta) \frac{\epsilon_2}{M_2}} \approx -H + \frac{\frac{V}{\gamma_{H^+} 10^{pH}}}{\frac{\epsilon_\delta}{M_\delta} - (1 - \rho_\delta) \frac{\epsilon_2}{M_2}} \quad (28)$$

where  $H$  is a constant corresponding to the first ionization of sulfuric acid in water. Equation 28 indicates that at low pH, the volumetric titration curve depends only on the activity coefficient of the protons. In fact, it depends on the mean activity coefficient of aqueous HCl,  $\gamma_{H^+}$ . Fitting the theoretical curve to the experimental one gives  $\gamma_{H^+} = 0.64 \pm 0.09$ .

The volumetric titration curve of sulfuric acid was calculated assuming the three mean activity coefficients to be constant in

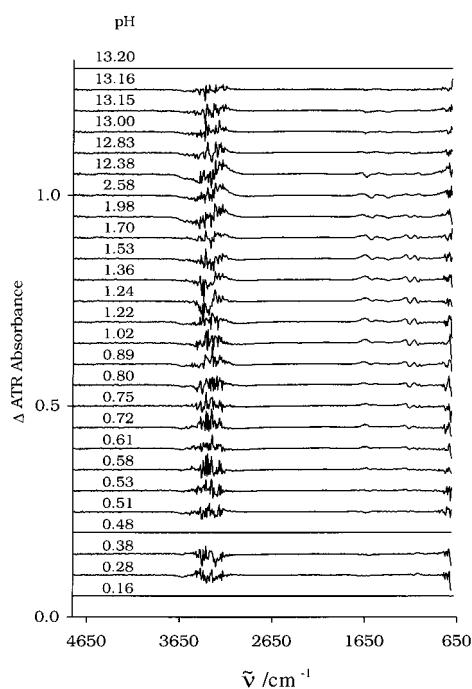
**TABLE 2: Numerical Values Used for the Calculation of Volumetric Titration Curves<sup>a</sup>**

$M_1$ (g)	$M_{-1}$ (g)	$M_2$ (g)	$M_{\text{H}_2\text{O}}$ (g)	$\epsilon_1$ (g/g)	$\epsilon_{-1}$ (g/g)	$\epsilon_2$ (g/g)	$\rho_1$	$\rho_{-1}$	$\rho_0$ (g/L)	$V$ (L)	$K_2$	$K_0$
40.00	36.46	98.06	18.02	0.485	0.37	0.049	0.313	0.131	1023	0.01	0.012	$1.8 \times 10^{-16}$

<sup>a</sup> See list of symbols.**TABLE 3: Positions (in  $\text{cm}^{-1}$ ) of the Ionic Species of 0.50 M Sulfuric Acid:  $\text{SO}_4^{2-}$  and  $\text{HSO}_4^-$  (See Figure 6)**

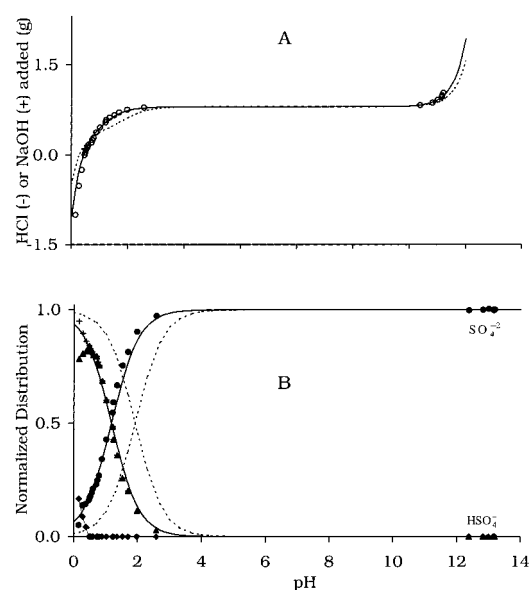
$\text{SO}_4^{2-}$					$\text{HSO}_4^-$ <sup>b</sup>					$\text{HSO}_4^-$ ion pair <sup>b</sup>	$\text{HSO}_4^-/\text{HCl}$ <sup>b</sup>
$d$	Raman		IR	assignment <sup>a</sup>	Raman		IR	IR	assignment <sup>a</sup>	Raman	IR
	$e$	$f$	$g$		$e$	$f$	$h$			$g$	$f$
			3435 <sub>w,b</sub>	O–H st.(H <sub>2</sub> O)			3400	3430 <sub>w,vb</sub>	O–H st (H <sub>2</sub> O), O–H st (HOSO <sub>3</sub> <sup>-</sup> ) <sup>c</sup>		3357 <sub>m,b</sub>
			2180	$2\nu_3$				2489 <sub>vw,vb</sub> 2240 <sub>vw,vb</sub>	comb (1198 + 1051)		2478 <sub>vw,b</sub> 2226 <sub>vw,b</sub>
			2080 <sub>w,b</sub>	$\nu_1 + \nu_3,$ $\nu_2 + \nu_L$ (H <sub>2</sub> O)							
			1648 <sub>w</sub> 1572 <sub>sh</sub>	O–H def (H <sub>2</sub> O) $\nu_2 + \nu_3$			1655	1895 <sub>vw,vb</sub> 1648 <sub>w</sub> 1602 <sub>w,sh</sub>	def H <sub>2</sub> O comb (1198 + 445)		1672 <sub>w</sub> 1551 <sub>w</sub>
			1403 <sub>w,b</sub> 1279 <sub>w,b</sub>	$\nu_1 + \nu_2$ $2\nu_4, \nu_1 + \nu_4$				1349 <sub>vw</sub>	comb (887+445)		
1104	1102	1130 <sub>w</sub>	1099 <sub>s</sub>	$\nu_3$ : a-st	1200	1200 <sub>w</sub>	1205	1198 <sub>m</sub> 1149 <sub>sh</sub>	SO <sub>3</sub> d-st har (2 × 584)	1220 <sub>w</sub>	1156 <sub>m</sub> 1128 <sub>sh</sub>
981	986	980 <sub>mm</sub>	982 <sub>w,sh</sub>	$\nu_1$ : s-st	1050	1057 <sub>s</sub>	1052	1051 <sub>m</sub>	SO <sub>3</sub> s-st	1030 <sub>s</sub> 950 <sub>m</sub>	1039 <sub>m</sub> 985 <sub>sh</sub>
					875	905 <sub>m</sub>	890	887 <sub>m</sub>	S–OH st	885 <sub>m</sub>	868 <sub>m</sub>
613	598	545 <sub>sh</sub>		$\nu_4$ : a-def	595	600 <sub>s</sub>	584		SO <sub>3</sub> d-def	600 <sub>s</sub>	
451	443	400 <sub>sh</sub>		$\nu_2$ : s-def	417	450 <sub>m</sub>	445		SO <sub>3</sub> rock	430 <sub>s</sub>	

<sup>a</sup> The bands related to complexed water are indicated by (H<sub>2</sub>O). Symbols: st, stretch; def, deformation; a-, asymmetric; s-, symmetric; d, degenerate; comb, combination; har, harmonic. Intensities: s, strong; m, medium; w, weak; b, broad; sh, shoulder; v, very. <sup>b</sup>  $\text{HSO}_4^-$  is  $\text{HOSO}_3^-$ . <sup>c</sup> The OH stretch band of  $\text{HOSO}_3^-$  is weaker than that of H<sub>2</sub>O. <sup>d</sup> Reference 39. <sup>e</sup> Reference 5. <sup>f</sup> Reference 38 (obtained using FA). <sup>g</sup> This work. <sup>h</sup> Reference 10.



**Figure 7.** Differences between experimental (Figure 3) and the sum of the calculated spectra taking the three principal spectra of Figure 6A and multiplying them by their MFs from Figure 6B. Same presentation as in Figure 5.

the 0–14 pH range. This assumption was justified by the fact that the sulfuric acid concentration is approximately the same in all samples: 0.48–0.50 M. The results of the calculations



**Figure 8.** Titration curves as a function of pH of 10 mL of 0.50 M sulfuric acid. (A) Volumetric titration curve: calculated values with a mean activity coefficient of one (---) and with a mean activity coefficient of  $\Gamma_2 = 5.5$ ,  $\gamma_{\text{H}^+} = 0.64$ ,  $\Gamma_0 = 2.0$  (—, see text); experimental values (○). (B) IR titration curves giving the relative distribution of  $\text{HSO}_4^-$  (▲);  $\text{SO}_4^{2-}$  (●);  $\text{HSO}_4^-/\text{HCl}$  (◆); sum of  $\text{HSO}_4^-$  and  $\text{HSO}_4^-/\text{HCl}$  (+). The lines are as in (A).

are represented by the full lines in Figure 8A for the titration curve and in Figure 8B for the normalized distribution curves as a function of pH. The calculated values coincide with the experimental ones. Only a small discrepancy between experi-



mental and calculated values is observed after the equivalence point, which is most probably due to some small extra intermediate species in this pH range. Despite this minor discrepancy, the comparison between calculated and experimental values indicates that the results are satisfactory. This in turn indicates that the calculation procedure is correct and that the above approximations are also satisfactory. For 0.50 M sulfuric acid, the mean activity coefficient  $\gamma_{\text{H}^+}/\Gamma_2$  obtained from the calculated curves and the ones derived from IR measurements is  $0.12 \pm 0.03$ . This value, which corresponds to the literature values obtained from electrochemical measurements ( $0.155$ ,<sup>34</sup>  $0.146 \pm 0.04$ ,<sup>8</sup> and  $0.142$ ),<sup>1</sup> indicates that the procedure given here is a direct way of obtaining the mean activity coefficients.

**4.5. Normalized Distribution of the Ionic Species of Sulfuric Acid.** Figure 6B gives the MFs of the ionic species retrieved from the IR spectra as a function of the mass of titrant. The intensity scale in this figure depends on the choice of the reference spectra. Also, the amount of sulfuric acid varies for all samples (see section 2.3.2.4). To adequately interpret Figure 6B, one must convert the scales into molar equivalent titrant.

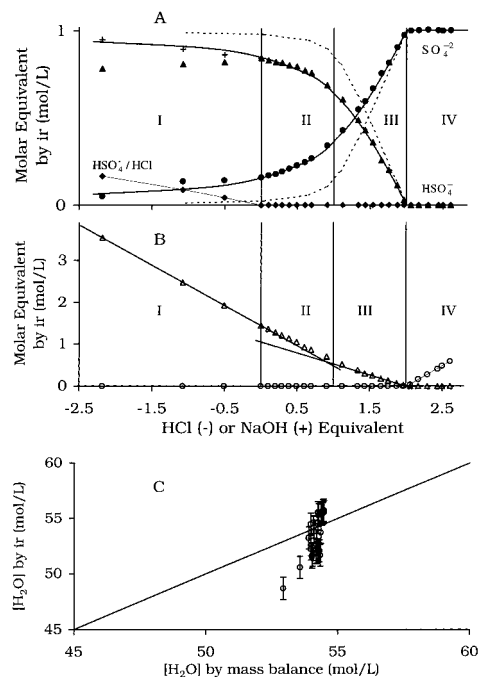
**4.5.1. Normalization.** The normalization of the MFs' molar equivalent titrant is obtained by dividing the MFs by the amount of sulfuric acid in the sample and multiplying the results by the maximum amount of sulfuric acid in the series of samples (the sample without titrant, i.e.,  $m_\delta = 0$ ). The mass of sulfuric acid corresponding to the sample without titrant is noted  $m_0$ . The normalized distribution of the three principal ionic species of aqueous sulfuric acid is  $Q_i$  given by

$$Q_i = \frac{\text{MF}_i}{\frac{m - m_\delta}{m_0}} \quad (29)$$

where indices  $i = 1, 2,$  and  $3$  represent each of the three species. The mass of titrant ( $m_\delta$ ) and the total mass ( $m$ ) of the 10 mL volume of the solution were measured. The difference between these two quantities represents mass  $m_2$  of stock solution of sulfuric acid in the mixture. The equivalent titrant,  $P$  (the abscissa in Figure 9A,B) is given by

$$P = \delta \frac{\frac{m_\delta \epsilon_\delta}{M_\delta}}{\frac{(m - m_\delta) \epsilon_2}{M_2}} \quad (30)$$

**4.5.2. Normalized Distribution.** The normalized distributions of the sulfuric acid ionic species as a function of equivalent titrant are plotted in Figure 9A. The experimental values obtained by IR are indicated as follows: ( $\blacktriangle$ ), HSO<sub>4</sub><sup>-</sup>; ( $\bullet$ ), SO<sub>4</sub><sup>2-</sup>; ( $\blacklozenge$ ), HSO<sub>4</sub><sup>-</sup>/HCl; (+), sum of HSO<sub>4</sub><sup>-</sup> and HSO<sub>4</sub><sup>-</sup>/HCl. Using eqs 14–16, 22, and 25, the theoretical values are calculated with the activity coefficients of one ( $\gamma_{\text{H}^+} = \Gamma_2 = \Gamma_0 = 1$ ) and are represented by the dashed lines (---). These theoretical values are far from the experimental results. When the previously obtained values of the activity coefficients ( $\gamma_{\text{H}^+} = 0.64$ ,  $\Gamma_2 = 5.5$ , and  $\Gamma_0 = 1.5$ ) are used, we obtain the results indicated by the full lines (—). Except in the region of HCl equivalent (region I), the normalized distribution of the species determined by IR matches the theoretical values. The equations to obtain the latter were developed for two of the species. Since, using IR, we detected two bisulfate species in region I: HSO<sub>4</sub><sup>-</sup> ( $\blacktriangle$ ) and HSO<sub>4</sub><sup>-</sup>/HCl ( $\blacklozenge$ ) (Figure 9A), we added these two sets



**Figure 9.** (A) Normalized distribution of the ionic species of aqueous sulfuric acid (0.50 M): HSO<sub>4</sub><sup>-</sup> ( $\blacktriangle$ ); SO<sub>4</sub><sup>2-</sup> ( $\bullet$ ); HSO<sub>4</sub><sup>-</sup>/HCl ( $\blacklozenge$ ); sum of HSO<sub>4</sub><sup>-</sup> and HSO<sub>4</sub><sup>-</sup>/HCl (+). The dashed lines (---) are for the calculated distribution when the mean activity coefficients are one and the full line (—) when they are  $\Gamma_2 = 5.5$ ,  $\gamma_{\text{H}^+} = 0.64$ ,  $\Gamma_0 = 1.5$  (see text). (B) Amount of water in the 26 mixtures: basic water ( $\circ$ ) and acidic water ( $\Delta$ ) in molar equivalent from the IR spectra as a function of equivalent titrant. (C) Comparison of the total amount of water obtained from IR with that obtained from mass balance. The straight line is for the ideal situation.

of values to give the values indicated by (+). These new values in region I fall on the theoretical curves and serve to validate the IR and theoretical results. The equipartition of SO<sub>4</sub><sup>2-</sup> and HSO<sub>4</sub><sup>-</sup> falls near 1.22 NaOH equivalent which is a value comparable to a value derived from the Raman work of Chen and Irish.<sup>6</sup> These results indicate that the IR titration of aqueous sulfuric acid was successfully performed.

**4.6. Quantitative Analysis of the Water Subtraction.** **4.6.1. Quantities of Waters.** The MFs of the different types of water are given in Figure 2B. The data from this figure (Table 1) were transformed from mass into molar HCl and NaOH equivalent in order to compare the values retrieved by IR with those from mass balance. This is illustrated in Figure 9B. Starting from the left side (lowest pH), the amount of NaOH retrieved by IR ( $\circ$ ) is zero until the second neutralization is achieved. Increasing the amount of NaOH produces some free aqueous NaOH in the solution as indicated by a slope of  $1.00 \pm 0.02$  in region IV (Figure 9B). When HCl was added to the stock solution (region I), the slope of the amount of acidic water ( $\Delta$ ) was  $0.96 \pm 0.02$ . These results indicate that the subtraction of the IR water spectra is consistent with the expected composition of the samples in these two regions (I and IV, Figure 9B) and that the subtraction procedure is adequate. The lower value obtained for the slope of the acidic water when HCl is added confirms that HCl-solvated water is part of the new entity formed that we named HSO<sub>4</sub><sup>-</sup>/HCl. In regions II and III, as expected, no alkaline water was retrieved. In both regions, the amount of acidic water ( $\Delta$ ) varied linearly with slopes of  $1.00 \pm 0.05$  and  $0.50 \pm 0.05$ , respectively.

The comparison between the total amount of water retrieved by IR and that calculated from the mass balance is recorded in Figure 9C. Except for the three lowest pH values, where some

**TABLE 4: Parameters of the Five Ionic Complexes in Aqueous Sulfuric Acid**

species	HCl		H <sub>3</sub> O <sup>+</sup> mol equiv	Na <sup>+</sup> mol equiv	name
	mol equiv	found			
H <sub>3</sub> O <sup>+</sup> /HSO <sub>4</sub> <sup>-</sup>	a	1.25	1	0	y <sub>11</sub>
Na <sup>+</sup> /HSO <sub>4</sub> <sup>-</sup>	0		0	1	y <sub>12</sub>
2H <sub>3</sub> O <sup>+</sup> /SO <sub>4</sub> <sup>2-</sup>	b	2.47	2	0	y <sub>21</sub>
H <sub>3</sub> O <sup>+</sup> /Na <sup>+</sup> /SO <sub>4</sub> <sup>2-</sup>	c	1.67	1	1	y <sub>22</sub>
2Na <sup>+</sup> /SO <sub>4</sub> <sup>2-</sup>	0		0	2	y <sub>23</sub>

HCl was added to the solution (which will be discussed below), the values obtained by IR and from the mass balance are the same within experimental error ( $54 \pm 1$  M). This comparison shows that the water subtraction operation was successful and that the amount of water determined by IR is reliable. Therefore, quantitative analysis of the amount of acidic water retrieved by IR in regions II and III can further be discussed.

**4.6.2. Water in Strong Interaction with Ionic Species.** Previous results on the IR study of aqueous ionic solutions indicated that the water spectrum is modified due to strong interactions between the ions and water and that these modifications depended on the type of ion pairs.<sup>18–22</sup> However, in the present study, acidic water proved to be in strong interaction with H<sub>3</sub>O<sup>+</sup>/SO<sub>4</sub><sup>2-</sup>/Na<sup>+</sup>, 2H<sub>3</sub>O<sup>+</sup>/SO<sub>4</sub><sup>2-</sup>, and H<sub>3</sub>O<sup>+</sup>/HSO<sub>4</sub><sup>-</sup> species. This water was satisfactorily subtracted as HCl-solvated water and its amount determined by FA. Using IR and Raman spectroscopy, Irish et al. have previously postulated some ion pairing between HSO<sub>4</sub><sup>-</sup> and H<sub>3</sub>O<sup>+</sup> ions in water,<sup>6,7</sup> which depended on the hydration of H<sub>3</sub>O<sup>+</sup>.<sup>11</sup> The line broadening observed in Raman was attributed to the hydration number and to ultrafast proton transfer. We observed by IR some pairing between these two ions but no line broadening. Therefore, the observed modifications of the HSO<sub>4</sub><sup>-</sup> spectrum when HCl is added are principally due to ion pairing and clustering with water.

Acidic water is obviously related to the amount of hydronium ion in the solution. The amount of acidic water retrieved by IR in the 0.50 mol/L sulfuric acid solution was 1.44<sub>4</sub> molar equivalent of HCl-solvated water. From Figure 9A we obtained the relative ionic concentrations of H<sub>3</sub>O<sup>+</sup>/HSO<sub>4</sub><sup>-</sup> and 2 H<sub>3</sub>O<sup>+</sup>/SO<sub>4</sub><sup>2-</sup> which are 0.84<sub>1</sub> and 0.15<sub>9</sub>, respectively. On the basis of the evaluation of the hydronium ion concentration made by the spectrum of aqueous HCl, the H<sub>3</sub>O<sup>+</sup> was evaluated at 1.44<sub>4</sub> HCl molar equivalent (Figure 9B). The latter is composed of H<sub>3</sub>O<sup>+</sup>/Cl<sup>-</sup> pair which forms clusters with water.<sup>18,21</sup> Since the initial solution was electrically neutral and Cl<sup>-</sup> does not absorb in IR, we expected a value of  $0.84_1 + 2 \times 0.15_9 = 1.15_9$  HCl molar equivalent since both ionic forms of sulfuric acid are associated with H<sub>3</sub>O<sup>+</sup> (Table 5). The difference between the expected value of 1.15<sub>9</sub> and the observed value of 1.44<sub>4</sub> HCl molar equivalent is above the experimental error and can be interpreted in two

ways. On the basis of the broadening of  $\nu_1$  band of SO<sub>4</sub><sup>2-</sup> situated at 981 cm<sup>-1</sup>, Irish and Chen proposed that the proton of HSO<sub>4</sub><sup>-</sup> is partly dissociated and partly associated with water.<sup>7</sup> Throughout the pH range, however, the  $\nu_3$  band of SO<sub>4</sub><sup>2-</sup> situated at 1098 cm<sup>-1</sup> shows no broadening (Figures 3 and 5). In this respect,  $\nu_3$  should not differ from  $\nu_1$ . Consequently, the interpretation of Irish and Chen is not valid. The interpretation that we propose is based on the strong interaction of some water molecules with the ions pairs. We know from previous results that the spectrum of water is greatly influenced by the presence of pair of ions.<sup>18–22</sup> Therefore, the absorptivity due to the aqueous hydronium ion pair H<sub>3</sub>O<sup>+</sup>/HSO<sub>4</sub><sup>-</sup> (with  $n$  molecules of water) is different than that of pair H<sub>3</sub>O<sup>+</sup>/Cl<sup>-</sup>.

In the following, we evaluated the amount of acidic water (in terms of equivalent HCl-solvated water, the IR standard used here for acidic water) associated with each of the ionic species of sulfuric acid. Let  $a$  and  $b$  be the amount of acidic water associated with each species, respectively. From IR analysis, the relation between the two quantities is

$$b = \frac{1.44_4 - 0.84_1 a}{0.15_9} = 9.08 - 5.29a \quad (31)$$

Since  $a$  is related to one and  $b$  to two hydronium ions,  $b$  should be approximately twice the value of  $a$ . It follows that  $a = 1.25 \pm 0.05$  and  $b = 2.47 \pm 0.27$ .

From the situation at the frontier of regions III and IV (Figure 9, A and B), the molar equivalent HCl-solvated water associated with H<sub>3</sub>O<sup>+</sup>/SO<sub>4</sub><sup>2-</sup>/Na<sup>+</sup>,  $c$ , can be determined as follows. In region III, the addition of NaOH transforms both species H<sub>3</sub>O<sup>+</sup>/SO<sub>4</sub><sup>2-</sup>/Na<sup>+</sup> and Na<sup>+</sup>/HSO<sub>4</sub><sup>-</sup> into 2Na<sup>+</sup>/SO<sub>4</sub><sup>2-</sup>. The former does not change the amount of SO<sub>4</sub><sup>2-</sup>. Therefore, the variation of species SO<sub>4</sub><sup>2-</sup> gives the amount of species Na<sup>+</sup>/HSO<sub>4</sub><sup>-</sup> being transformed into species 2Na<sup>+</sup>/SO<sub>4</sub><sup>2-</sup> (Figure 9A). Moreover, the decrease of HCl-solvated water reflects the transformation of H<sub>3</sub>O<sup>+</sup>/SO<sub>4</sub><sup>2-</sup>/Na<sup>+</sup> into 2Na<sup>+</sup>/SO<sub>4</sub><sup>2-</sup> (Figure 9B). These variations are  $0.70 \pm 0.05$  and  $0.50 \pm 0.05$ , respectively. From the above results we obtained

$$c = \frac{0.50}{1 - 0.7} = 1.67 \pm 0.5 \quad (32)$$

These results indicate that the strength of an acid in aqueous solution can be determined by IR. The values of  $a$ ,  $b$ , and  $c$  are tabulated in Table 4 where they are compared to the H<sub>3</sub>O<sup>+</sup> molar equivalents. In each case, the values of the latter are lower than those of the former and confirm that sulfuric acid is stronger than hydrochloric acid.<sup>31</sup> The values obtained above for  $a$ ,  $b$ , and  $c$  are confirmed in the two following sections by further analysis of the details of the titration of sulfuric acid by NaOH.

**TABLE 5: Species Present in the Different Regions of the Titration of H<sub>2</sub>SO<sub>4</sub> by NaOH and HCl<sup>a</sup>**

region	I	I/II	II	III	IV
pH	0.00–0.47	0.48	0.49–0.95	0.96–3.00	3.01–13.40
descripn	HCl added	H <sub>2</sub> SO <sub>4</sub> in water	NaOH added up to first neutralizn	NaOH added up to second neutralizn	NaOH added after second neutralizn
name/symbols <sup>b</sup>	H <sub>2</sub> O H <sub>3</sub> O <sup>+</sup> /Cl <sup>-</sup> H <sub>3</sub> O <sup>+</sup> /HSO <sub>4</sub> <sup>-</sup>	H <sub>2</sub> O H <sub>3</sub> O <sup>+</sup> /HSO <sub>4</sub> <sup>-</sup>	H <sub>2</sub> O H <sub>3</sub> O <sup>+</sup> /HSO <sub>4</sub> <sup>-</sup> Na <sup>+</sup> /HSO <sub>4</sub> <sup>-</sup> 2H <sub>3</sub> O <sup>+</sup> /SO <sub>4</sub> <sup>2-</sup>	H <sub>2</sub> O Na <sup>+</sup> /HSO <sub>4</sub> <sup>-</sup> H <sub>3</sub> O <sup>+</sup> /SO <sub>4</sub> <sup>2-</sup> /Na <sup>+</sup>	H <sub>2</sub> O 2Na <sup>+</sup> /SO <sub>4</sub> <sup>2-</sup> Na <sup>+</sup> /OH <sup>-</sup>
y <sub>11</sub> (Δ)					
y <sub>12</sub> (▲)					
y <sub>21</sub> (○)					
y <sub>22</sub> (⊗)					
y <sub>23</sub> (●)					

<sup>a</sup> H<sub>2</sub>O: neutral water; The slash (/) indicates that the ionic species are together. <sup>b</sup> The symbols are those of Figure 10.

#### 4.7. Details of the Titration of Sulfuric Acid by NaOH.

**4.7.1. Species Involved in the Titration.** The titration is divided in four regions (Figure 9, A and B): the initial 0.50 M sulfuric acid solution is situated at the frontier of regions I and II; region I is where HCl was added; region II is where up to one NaOH equivalent was added; region III is where between one and two NaOH equivalents were added; region IV is where more than two NaOH equivalents were added. Table 5 gives the different species present in the regions and below we provide some details of the ionic interactions starting with the regions which are the easiest to interpret.

**Region IV** (pH  $\geq$  12.38) is the region where NaOH is added to the solution after the second neutralization. The IR intensity of the SO<sub>4</sub><sup>2-</sup> species is constant (Figure 9A) but that of basic water is directly proportional to the NaOH equivalent added above the second neutralization (Figure 9B). The residues between the calculated and experimental spectra (Figure 7) contain only noise, indicating that no other species are present. These results were expected and indicate that FA procedure is adequate to retrieve the species and determine their concentration. Two types of water were subtracted from the original spectra: neutral water and basic water. On the principal spectrum of SO<sub>4</sub><sup>2-</sup>, we observe some absorption in the 3400 and 1650 cm<sup>-1</sup> regions (Figure 6Aa) that we assigned to water complexed (strongly associated) to 2Na<sup>+</sup>/SO<sub>4</sub><sup>2-</sup> pair. Comparing the amount of water retrieved by IR with that calculated from the mass balance, we arrived at a value of 54  $\pm$  1 M. The uncertainty level of 1 M of water indicates that fewer than 2–3 water molecules are complexed to the pair 2Na<sup>+</sup>/SO<sub>4</sub><sup>2-</sup>. We also compared the integrated intensity of the 3400 cm<sup>-1</sup> band of 2Na<sup>+</sup>/SO<sub>4</sub><sup>2-</sup> (Figure 6Aa) with that of neutral water (Figure 2A) and found that there are 2.8  $\pm$  0.8 molecules of water per 2Na<sup>+</sup>/SO<sub>4</sub><sup>2-</sup> ion pair. Both methods gave a plausible value of 2 molecules of water complexed to the pair Na<sup>+</sup>/SO<sub>4</sub><sup>2-</sup>.

**Frontier between Regions I and II.** The original solution situated at this frontier is composed of 84% HSO<sub>4</sub><sup>-</sup> and 16% SO<sub>4</sub><sup>2-</sup> (Figure 9A) with H<sub>3</sub>O<sup>+</sup> as counterion. By Raman spectroscopy, Irish and Chen obtained similar values: 82.5% and 17.5% for the two sulfate ions, respectively.<sup>7</sup>

**Region I.** As HCl is added to the solution, the amount of SO<sub>4</sub><sup>2-</sup> (16%) decreased to the benefit of a new entity that we named HSO<sub>4</sub><sup>-</sup>/HCl (Figures 6 and 9A and Table 5). In reality this new entity is H<sub>3</sub>O<sup>+</sup>/HSO<sub>4</sub><sup>-</sup>/H<sub>3</sub>O<sup>+</sup>/Cl<sup>-</sup>·nH<sub>2</sub>O or HSO<sub>4</sub><sup>-</sup>/2H<sub>3</sub>O<sup>+</sup>/Cl<sup>-</sup>·nH<sub>2</sub>O. Besides the added HCl, the only change occurring in this region is a slow transformation of SO<sub>4</sub><sup>2-</sup> into HSO<sub>4</sub><sup>-</sup> (eq 1). The IR measurements of acidic water are approximately 4% less than the added HCl solution (Figure 9B). Since the acidic water spectrum has been subtracted from the spectrum of Figure 6Ac, we are left with HSO<sub>4</sub><sup>-</sup>·nH<sub>2</sub>O on the spectrum. Since OH of HSO<sub>4</sub><sup>-</sup> should absorb but very little in the 3500 cm<sup>-1</sup> region, the band situated in this region is assigned to water, complexed to the ionic cluster. By comparing the integrated intensity of the latter with that of the  $\nu_{OH}$  of water, we estimated that *n* is approximately equal to 11. This value is partly confirmed by the IR results (Figure 9C): in the three samples containing HCl, the total amount of water retrieved by IR is below the value obtained by the mass balance and the difference is outside the experimental error. Therefore, some water was not taken into account. This water was different from neutral and acidic (HCl-solvated) water and consequently was not subtracted from the IR spectra of these samples. Furthermore, the difference between the values obtained by IR and those obtained from the mass balance increased with the HCl added, that is with the amount of species HSO<sub>4</sub><sup>-</sup>/HCl. Because

of the error involved in its determination, the value of 11 obtained here is a rough approximation. It is nevertheless a reasonable value.

**Region II.** Here again, starting from the solution at the frontier of regions I and II, composed of H<sub>3</sub>O<sup>+</sup>, 84% HSO<sub>4</sub><sup>-</sup>, and 16% SO<sub>4</sub><sup>2-</sup>, NaOH is added to the solution. The NaOH is involved in three neutralization reactions: (1) H<sub>3</sub>O<sup>+</sup>/HSO<sub>4</sub><sup>-</sup> pair is transformed into Na<sup>+</sup>/HSO<sub>4</sub><sup>-</sup> pair; (2) 2H<sub>3</sub>O<sup>+</sup>/SO<sub>4</sub><sup>2-</sup> pair is transformed into H<sub>3</sub>O<sup>+</sup>/SO<sub>4</sub><sup>2-</sup>/Na<sup>+</sup>, and (3) H<sub>3</sub>O<sup>+</sup>/HSO<sub>4</sub><sup>-</sup> pair into H<sub>3</sub>O<sup>+</sup>/SO<sub>4</sub><sup>2-</sup>/Na<sup>+</sup>. The first two reactions lead to a decrease in the concentration of H<sub>3</sub>O<sup>+</sup> (Figure 9B), while the concentrations of HSO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> remain unchanged. The third reaction leaves the concentration of H<sub>3</sub>O<sup>+</sup> unchanged while the transformation of HSO<sub>4</sub><sup>-</sup> into SO<sub>4</sub><sup>2-</sup> is in the proportion of one to one (Figure 9A). The solutions in region II contained the following species (Table 5): H<sub>3</sub>O<sup>+</sup>/HSO<sub>4</sub><sup>-</sup>; 2H<sub>3</sub>O<sup>+</sup>/SO<sub>4</sub><sup>2-</sup>; Na<sup>+</sup>/HSO<sub>4</sub><sup>-</sup>; and H<sub>3</sub>O<sup>+</sup>/SO<sub>4</sub><sup>2-</sup>/Na<sup>+</sup>.

**Region III.** The NaOH added to the solution in this region produces the following neutralization reactions: (1) reduction of Na<sup>+</sup>/HSO<sub>4</sub><sup>-</sup> pair into 2 Na<sup>+</sup>/SO<sub>4</sub><sup>2-</sup> and (2) at the same time transformation of H<sub>3</sub>O<sup>+</sup>/SO<sub>4</sub><sup>2-</sup>/Na<sup>+</sup> into 2Na<sup>+</sup>/SO<sub>4</sub><sup>2-</sup>. The slope of acidic water is about -0.5 and the absolute slopes of the variation of HSO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> are below unity (Figure 9, A and B). In this region the samples contained the following species: H<sub>3</sub>O<sup>+</sup>/HSO<sub>4</sub><sup>-</sup>; Na<sup>+</sup>/HSO<sub>4</sub><sup>-</sup>; H<sub>3</sub>O<sup>+</sup>/SO<sub>4</sub><sup>2-</sup>/Na<sup>+</sup>; 2Na<sup>+</sup>/SO<sub>4</sub><sup>2-</sup>; and very little 2H<sub>3</sub>O<sup>+</sup>/SO<sub>4</sub><sup>2-</sup>.

**4.7.2. Amount of the Different Pairs of Ions in the Solution.** From the IR measurements of the sulfuric acid solutions, we obtained the amounts of neutral water, acidic water, HSO<sub>4</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>. In the preceding section we determined the amount of acidic water from HCl-solvated water obtained by IR. This amount is not exactly equal to the amount of hydronium ion in the sample. Furthermore, using experimental results we determined the amount of acidic water associated with the different sulfate ion pairs. We will now determine the amount of the different ion pairs in the samples.

The different ionic species of sulfuric acid solvated in water retrieved by IR are listed in Table 4 together with the associated acidic water (expressed as HCl molar equivalent), H<sub>3</sub>O<sup>+</sup>, and Na<sup>+</sup> counterions. The corresponding labels given to them are  $y_C$ ,  $y_H$ , and  $y_N$ , respectively. The amounts of HSO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in the solutions were determined by FA on the IR spectra and are given the labels  $y_1$  and  $y_2$ , respectively. The amount of Na<sup>+</sup> ( $y_N$ ) was obtained from the mass balance. The distribution equations for each ionic group in the neutralization of aqueous sulfuric acid are as follows (see Table 4):

$$y_1 = y_{11} + y_{12} \quad (33)$$

$$y_2 = y_{21} + y_{22} + y_{23} \quad (34)$$

$$y_C = ay_{11} + by_{21} + cy_{22} \quad (35)$$

$$y_H = y_{11} + 2y_{21} + y_{22} \quad (36)$$

$$y_N = y_{12} + y_{22} + 2y_{23} \quad (37)$$

These equations are valid only for the neutralization of the acid by the base, that is for  $0 \leq y_N \leq 2$ . The concentration of H<sub>3</sub>O<sup>+</sup> ( $y_H$ ) was obtained from  $y_1$  and  $y_2$  using eq 3:

$$[H_3O^+] = K_2 \frac{\Gamma_2 y_1}{\gamma_{H+y_2}} \quad (38)$$

which when divided by the concentration of sulfuric acid in the sample ( $M$ ) gives the  $H_3O^+$  molar equivalent  $y_H$ :

$$y_H = K_2 \frac{\Gamma_2 y_1}{\gamma_{H^+} y_2 M} \quad (39)$$

Equations 33, 34, 36, and 37 together give

$$y_N + y_H = y_1 + 2y_2 \quad (40)$$

The conservation of sulfuric acid implies that  $y_2 + y_1 = 1$ . In eqs 39 and 40,  $y_2$  is replaced by  $1 - y_1$  and subsequently by using eq 39,  $y_H$  is replaced by its function of  $M$  so that eq 40 becomes

$$y_1^2 + y_1 \left( y_N - \frac{K_2 \Gamma_2}{\gamma_{H^+} M} - 3 \right) + 2 - y_N = 0 \quad (41)$$

The solution of eq 41 for  $0 \leq y_N \leq 2$  is

$$y_1 = - \left\{ \left( y_N - \frac{K_2 \Gamma_2}{\gamma_{H^+} M} - 3 \right) + \sqrt{\left( y_N - \frac{K_2 \Gamma_2}{\gamma_{H^+} M} - 3 \right)^2 - 4(2 - y_N)} \right\} / 2 \quad (42)$$

The quantities of  $HSO_4^-$  ( $y_1$ ) obtained by eq 42 were very close to the values obtained from IR measurements (Figure 9A), indicating that the mathematical treatment is self-consistent. Equation 42 is equivalent to eq 15 in which variable  $X$  was replaced by its function of titrant equivalent  $y_N$ .

Resolving eqs 33 to 37 gives

$$y_{21} = \frac{y_C + c y_N - 2c y_2 - c y_1 + (c - a) y_{11}}{b - 2c} \quad (43)$$

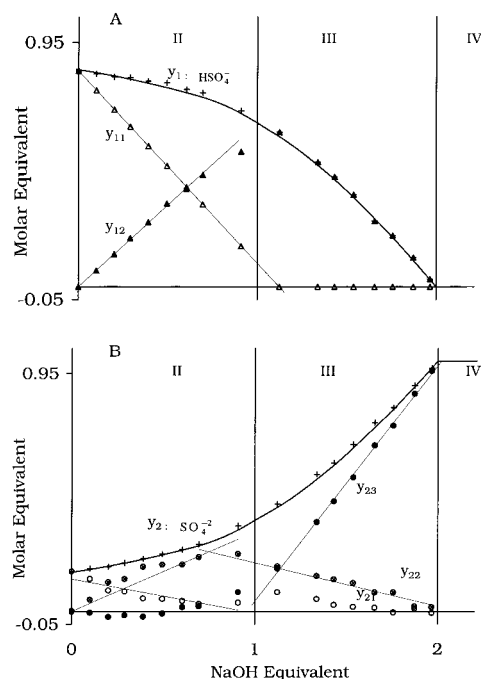
$$y_{22} = \frac{b y_1 + 2b y_2 - b y_N - 2y_C + (2a - b) y_{11}}{b - 2c} \quad (44)$$

$$y_{23} = \frac{-b y_2 - (b - c) y_1 + (b - c) y_N + y_C - (a + c - b) y_{11}}{b - 2c} \quad (45)$$

$$y_{12} = y_1 - y_{11} \quad (46)$$

Equation 40 indicates that eqs 33–37 are not linearly independent. Therefore, only four among the five unknowns ( $y_{11}$ ,  $y_{12}$ ,  $y_{21}$ ,  $y_{22}$ , and  $y_{23}$ ) can be retrieved. To overcome the impasse, chemical evidence must be found so that the quantities of the five species can be determined. As a first approximation, we considered the situation of the aqueous sulfuric acid without titrant which in Figure 9A is situated at the intercept of regions I and II, where the relative amount of  $H_3O^+/HSO_4^-$  in the solution is 0.84. The NaOH added to the solution (region II) neutralizes  $H_3O^+/HSO_4^-$  to form both  $Na^+/HSO_4^-$  and  $H_3O^+/SO_4^{2-}/Na^+$  in a 9:1 proportion. This ratio was obtained using an iterative procedure whereby the values above and below this ratio gave unacceptable results such as negative quantities for one of the species.

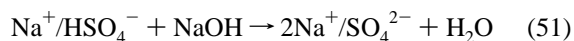
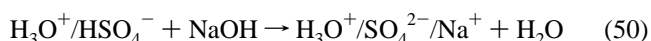
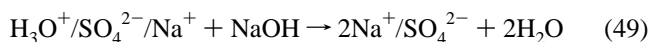
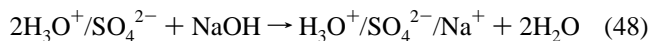
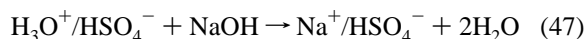
By determining the quantities of  $HSO_4^-$  ( $y_{11}$ ) the impasse was resolved and the other values could be determined by applying eqs 43–46. The results are given in Figure 10: frame A for the  $HSO_4^-$  species ( $y_1$ ) consisting of groupings  $H_3O^+/HSO_4^-$  ( $y_{11}$ ) and  $Na^+/HSO_4^-$  ( $y_{12}$ ) and frame B for the  $SO_4^{2-}$  species ( $y_2$ ) consisting of groupings  $2H_3O^+/SO_4^{2-}$  ( $y_{21}$ );  $H_3O^+/$



**Figure 10.** Normalized distribution of the five complexes of aqueous sulfuric acid. (A)  $HSO_4^-$  complexes where  $y_{11}$  is for  $H_3O^+/HSO_4^-$  ( $\Delta$ );  $y_{12}$ , for  $HSO_4^-/Na^+$  ( $\blacktriangle$ );  $y_1$  for total  $HSO_4^-$ , experimental (+) and calculated (-). (B)  $SO_4^{2-}$  complexes where  $y_{21}$  is for  $2H_3O^+/SO_4^{2-}$  ( $\circ$ );  $y_{22}$  is for  $H_3O^+/SO_4^{2-}/Na^+$  ( $\otimes$ );  $y_{23}$  is for  $2Na^+/SO_4^{2-}$  ( $\bullet$ );  $y_2$ , total  $SO_4^{2-}$ , experimental (+) and calculated (-).

$SO_4^{2-}/Na^+$  ( $y_{22}$ ); and  $2Na^+/SO_4^{2-}$  ( $y_{23}$ ). From these results, it is seen that grouping  $H_3O^+/SO_4^{2-}/Na^+$  remains below 25% and that grouping  $2Na^+/SO_4^{2-}$  does not exist before the first neutralization is completed.

**4.8. Relative Partial Reactions Involved in the Neutralization Reaction.** The neutralization reactions involved in the titration of aqueous sulfuric acid by aqueous sodium hydroxide are the following (Figure 11):



The variations of NaOH equivalent involved in reactions 47–51 are noted  $r$ ,  $s$ ,  $t$ ,  $u$ , and  $w$ , respectively. Table 6 summarizes the variation of the amounts of the different ion groups in the solution during the titration. From the data in Table 6, we have the following relations:

$$s = - \frac{dy_{21}}{dy_N} \quad (52)$$

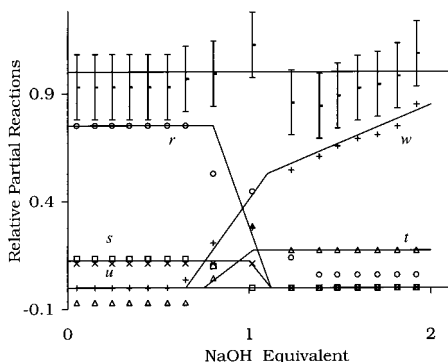
$$w = -u - \frac{dy_1}{dy_N} \quad (53)$$

$$t = u - \frac{dy_{22}}{dy_N} - \frac{dy_{21}}{dy_N} = u - \frac{dy_2}{dy_N} + \frac{dy_{23}}{dy_N} \quad (54)$$

**TABLE 6: Variation of Different Ionic Species in the Neutralization of Aqueous Sulfuric Acid by Aqueous NaOH from Eqs 47–51<sup>a</sup>**

	$dy_1/dy_N$	$dy_{11}/dy_N$	$dy_{21}/dy_N$	$dy_{22}/dy_N$	$dy_H/dy_N$	$dy_C/dy_N$
reaction 47	0	-r	0	0	-r	-ar
reaction 48	0	0	-s	+s	-s	-s(b-c)
reaction 49	0	0	0	-t	-t	-ct
reaction 50	-u	-u	0	+u	0	-u(a-c)
reaction 51	-w	0	0	0	0	0
total	-u-w	-r-u	-s	s+u-t	-r-s-t	-ar-s(b-c)-ct-u(a-c)

<sup>a</sup>  $y_1 \equiv \text{HSO}_4^-$ ;  $y_N \equiv \text{Na}^+$ ;  $y_{11} \equiv \text{H}_3\text{O}^+/\text{HSO}_4^-$ ;  $y_{21} \equiv 2\text{H}_3\text{O}^+/\text{SO}_4^{2-}$ ;  $y_{22} \equiv \text{H}_3\text{O}^+/\text{SO}_4^{2-}/\text{Na}^+$ ;  $y_H \equiv \text{H}_3\text{O}^+$ ;  $y_C \equiv$  acidic water (as aqueous HCl molar equivalent).



**Figure 11.** Relative partial reactions involved in the neutralization of H<sub>2</sub>SO<sub>4</sub> by NaOH: *r*, for reaction 47 (○); *s*, for reaction 48 (□); *t*, for reaction 49 (△); *u*, for reaction 50 (×); and *w* for reaction 51 (+). Top is the sum of the five reactions. The straight line at the 1.0 level is for the theoretical values.  $\text{H}_3\text{O}^+/\text{HSO}_4^- + \text{NaOH} \rightarrow \text{Na}^+/\text{HSO}_4^- + 2\text{H}_2\text{O}$  (eq 47, ○);  $2\text{H}_3\text{O}^+/\text{SO}_4^{2-} + \text{NaOH} \rightarrow \text{H}_3\text{O}^+/\text{SO}_4^{2-}/\text{Na}^+ + 2\text{H}_2\text{O}$  (eq 48, □);  $\text{H}_3\text{O}^+/\text{SO}_4^{2-}/\text{Na}^+ + \text{NaOH} \rightarrow 2\text{Na}^+/\text{SO}_4^{2-} + 2\text{H}_2\text{O}$  (eq 49, △);  $\text{H}_3\text{O}^+/\text{HSO}_4^- + \text{NaOH} \rightarrow \text{H}_3\text{O}^+/\text{SO}_4^{2-}/\text{Na}^+ + \text{H}_2\text{O}$  (eq 50, ×);  $\text{Na}^+/\text{HSO}_4^- + \text{NaOH} \rightarrow 2\text{Na}^+/\text{SO}_4^{2-} + \text{H}_2\text{O}$  (eq 51, +).

**TABLE 7: Linear Approximations of the Variation of the Amount of the Five Complexes of Aqueous Sulfuric Acid Neutralized by Aqueous NaOH (Figure 10)<sup>a</sup>**

	first slope	ordinate at origin	second slope	ordinate at origin
$y_{11}$	-0.911	0.838		
$y_{12}$	0.805	0.002		
$y_{21}$	-0.066	0.156		
$y_{22}$	0.263	-0.010	-0.156	0.421
$y_{23}$			0.933	-0.941

<sup>a</sup> For symbols, see Table 6.

$$r = \frac{dy_1}{dy_N} + 2 \frac{dy_{21}}{dy_N} + \frac{dy_{22}}{dy_N} + 1 - u = 1 - u + \frac{dy_{21}}{dy_N} - \frac{dy_{23}}{dy_N} \quad (55)$$

To resolve eqs 52–55 it is necessary to obtain the variation of the amounts of the five different ion groups in relation to the titrant added ( $y_N$ ). Except for the decrease of  $\text{Na}^+/\text{HSO}_4^-$  ( $y_{12}$ ) which is not linear (Figure 10A) the derivatives in eqs 52–55 are represented by the slopes in Figure 10. To solve these equations we need to have one of the five unknowns *r*, *s*, *t*, *u*, and *w*. At the intercept of regions I and II, there is no species  $\text{Na}^+/\text{HSO}_4^-$  ( $y_{12}$ ), so that  $w = 0$  and therefore eq 53 reduces to

$$u = -\frac{dy_1}{dy_N} \quad (56)$$

From Figure 9A or 10A, a value of  $u = 0.113$  is obtained at the intercept of regions I and II. We assumed that this value remained constant until all  $\text{H}_3\text{O}^+/\text{HSO}_4^-$  ( $y_{11}$ ) disappeared, a reasonable assumption considering that other values produced erratic results for the curves in Figure 11. Using this value, eqs

52–55 are resolved to obtain the values of *r*, *s*, *t*, and *w* which are plotted in Figure 11. From the latter, we determined that 75% of the first NaOH equivalent neutralizes  $\text{H}_3\text{O}^+/\text{HSO}_4^-$  to give  $(0.9 \times 75\%) = 67.5\%$   $\text{Na}^+/\text{HSO}_4^-$  and  $(0.1 \times 75\%) = 7.5\%$   $\text{H}_3\text{O}^+/\text{SO}_4^{2-}/\text{Na}^+$ . The remaining 25% neutralizes one  $\text{H}_3\text{O}^+$  associated with  $2\text{H}_3\text{O}^+/\text{SO}_4^{2-}$ . The second NaOH equivalent transforms 70% of  $\text{Na}^+/\text{HSO}_4^-$  and 30% of  $\text{H}_3\text{O}^+/\text{SO}_4^{2-}/\text{Na}^+$  into  $2\text{Na}^+/\text{SO}_4^{2-}$ .

The sums of the relative partial reactions involved throughout the neutralization reaction of sulfuric acid solutions by NaOH solutions (Figure 11) are situated at the theoretical level of  $1.0 \pm 0.1$ . This result shows that the analysis is self-consistent.

## 5. Conclusion

The present work shows that, using IR spectroscopy, it is possible to observe the titration of aqueous sulfuric acid by aqueous sodium hydroxide. Some new interesting results have been obtained. The analysis based on the complete IR spectrum of aqueous solutions of sulfuric acid solutions is a perceptible improvement compared to preceding work by Raman spectroscopy and band fitting analysis. The appraisal of the quantities of water that was done using IR shows that it corresponds within experimental limits to the mass balance.

The IR spectra of aqueous sulfuric acid at different pH level show that some water molecules are complexed with the ionic species. The species  $\text{HSO}_4^-$  and  $\text{SO}_4^{2-}$  in aqueous solutions do not influence each other when both species are present. Such a situation was observed in the spectra of mixtures of aqueous solutions of HCl and NaCl.<sup>21</sup>

The complete sequence of reactions involved in the neutralization of aqueous sulfuric acid by aqueous sodium hydroxide was determined by IR spectroscopy. Starting from the low pH side, the following five groupings are involved in the neutralization:  $\text{H}_3\text{O}^+/\text{HSO}_4^-$ ,  $\text{Na}^+/\text{HSO}_4^-$ ,  $2\text{H}_3\text{O}^+/\text{SO}_4^{2-}$ ,  $\text{H}_3\text{O}^+/\text{SO}_4^{2-}/\text{Na}^+$ , and  $2\text{Na}^+/\text{SO}_4^{2-}$ . The ionic species in these groupings are strongly linked together, indicating that the anions are not separated from their cations, except when involved in the neutralization. The concept of hydration shells for ions in water which would involve the separation of the ions cannot be used to explain the present results. Rather, anions and cations (ions and counterions) must be taken together. Some water molecules strongly interact with each grouping to form complexes. The IR spectra indicate that the water molecules involved in one type of complex is different than that in another. This is in full accord with previous results reported for HCl, NaOH and NaCl. The clusters formed by the ionic complexes of sulfuric acid and water molecules can now be more precisely studied.

Direct evaluation of the ratio of the activity coefficients of bisulfate to sulfate ion in water was rendered possible by IR spectroscopy:  $\Gamma_2 = \gamma_{\text{HSO}_4^-}/\gamma_{\text{SO}_4^{2-}} = 5.5 \pm 0.5$  for 0.50 M sulfuric acid. Furthermore, for that solution, the mean activity coefficient of  $0.12 \pm 0.03$  observed in the present study is in

agreement with published values obtained from electrochemical measurements.

### Glossary

$V$	total volume of the sample (in L)
$A$	total amount (in mol) of sulfuric acid in the sample
$D$	total amount (in mol) of water initially in the sample
$C_1$	amount (in mol) of NaOH added to the sample
$C_{-1}$	amount (in mol) of HCl added to the sample
$y_1$	amount (in mol) of $\text{HSO}_4^-$ present in the sample at equilibrium
$y_2$	amount (in mol) of $\text{SO}_4^{2-}$ present in the sample at equilibrium
$x$	amount (in mol) of $\text{H}^+$ present in the sample at equilibrium
$x'$	amount (in mol) of $\text{OH}^-$ present in the sample at equilibrium
$c$	amount (in mol) of $\text{Na}^+$ ions present in the sample at equilibrium
$c'$	amount (in mol) of $\text{Cl}^-$ ions present in the sample at equilibrium
$d$	amount (in mol) of water present in the sample at equilibrium
$K_2$	second dissociation constant of sulfuric acid in water
$K_0$	dissociation constant of water: $1.805 \times 10^{-16}$ at 25.0 °C
$\gamma_{\text{SO}_4^{2-}}$	activity coefficient of aqueous $\text{SO}_4^{2-}$
$\gamma_{\text{HSO}_4^-}$	activity coefficient of aqueous $\text{HSO}_4^-$
$\gamma_{\text{H}^+}$	activity coefficient of aqueous $\text{H}_3\text{O}^+$
$\gamma_{\text{OH}^-}$	activity coefficient of aqueous $\text{OH}^-$
$\gamma_{\text{H}_2\text{O}}$	activity coefficient of water
$\Gamma_2$	$\gamma_{\text{HSO}_4^-}/\gamma_{\text{SO}_4^{2-}}$ : ratio of the activity coefficient of $\text{HSO}_4^-$ to that of $\text{SO}_4^{2-}$
$\Gamma_0$	$\gamma_{\text{H}_2\text{O}}/\gamma_{\text{OH}^-}$ : ratio of the activity coefficient of $\text{H}_2\text{O}$ to that of $\text{OH}^-$
$X$	linear variable for pH: $X = 10^{\text{pH}}$
$M_{\text{H}_2\text{O}}$	molar mass of water: 18.0152 g/mol
$M_1$	molar mass of the strong base: 40.00 g/mol
$M_{-1}$	molar mass of the strong acid: 36.46 g/mol
$M_2$	molar mass of sulfuric acid: 98.06 g/mol
$\delta$	$\delta$ selects the titrant used: base, $\delta = +1$ ; acid, $\delta = -1$
$\epsilon_\delta$	relative concentration of the titrant solution (w/w)
$\epsilon_2$	relative concentration of the sulfuric acid stock solution (w/w)
$m$	total mass of the sample (in g)
$m_\delta$	mass of the titrant added to the sample (in g)
$m_2$	mass of the stock solution of sulfuric acid added to the sample (in g)
$m_0$	mass of the stock solution of sulfuric acid in the sample without titrant (in g)
$\rho_0$	density of the stock solution of sulfuric acid (in g/L)
$\rho$	density of the sample (in g/L)
$\rho_\delta$	variation of the total density of the sample divided by the inverse of the partial density of the titrant: $\rho_\delta = (\rho - \rho_0)V/m_\delta$ (nondimensional)
$P$	equivalent titrant
$Q_i$	normalized distribution of species $i$

$a$	HCl-solvated water molar equivalent of aqueous $\text{H}_3\text{O}^+/\text{HSO}_4^-$
$b$	HCl-solvated water molar equivalent of aqueous $2\text{H}_3\text{O}^+/\text{SO}_4^{2-}$
$c$	HCl-solvated water molar equivalent of aqueous $\text{H}_3\text{O}^+/\text{SO}_4^{2-}/\text{Na}^+$

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