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Infrared Spectroscopy of Aqueous Carboxylic Acids: Comparison between Different Acids and Their Salts

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The attenuated total reflection−infrared (ATR−IR) spectra in the 4800−700 cm^{-1} range of nine carboxylic acids and their sodium salts in aqueous solutions are obtained and analyzed. Overall, 22 species are studied. Six IR titrations are made with five different acids: acetic acid, malic acid, betaine, glycine, and *N*,*N*-((butyloxy)propyl) amino diacetic acid (BOPA). From the spectra of these titrations, the spectra of four types of water (acidic, basic, saline, and pure water) are subtracted, giving spectra with flat baselines without any artificial adjustment. Factor analysis (FA) made on the water-subtracted spectra yield the spectra of the principal species, and their abundances. Titration curves obtained from these precisely fit the theoretical curves and the pK_a values in the literature. The remaining water bands that are not subtracted are assigned to water solute close-bound situations. The hydration number varied from 5 to 1, with an average of almost 2 per carboxyl carbonyl group. The IR CO band positions (±16 cm^{-1}) are assigned to the different species: 1723 and 1257 cm^{-1} for the un-ionized acid double and single bonds; 1579 cm^{-1} for CO_2^- asymmetric stretch; 1406 cm^{-1} for CO_2^- symmetric stretch; and 1094 cm^{-1} for noncarboxylic ethoxy groups. The OH absorption covers the full region, from 3700 to 1700 cm^{-1}, in four bands that are ∼220 cm^{-1} wide. The near-3400 cm^{-1} band is assigned to solvated water, alcoholic OH, and NH groups, because these are hydrogen-bonded groups. The 3000 and 2600 cm^{-1} bands are assigned to the carboxyl OH groups that are hydrogen-bonded to other carboxyl groups in the pure acrylic species or to water in the aqueous solutions cases. The 2100 cm^{-1} band is assigned to a combination band that involves the far-IR absorption. The absorption from 3700 to 1700 cm^{-1}, which is sometimes called the "continuous absorption", cannot be attributed to the hydronium ion (H_3O^+), because the acids are not ionized; rather, it results from the strong hydrogen bonds between water and the carboxylic acids.

1. Introduction

Organic acids constitute an important class of organic molecules that contains carboxylic acids, amino acids, and surfactants. These have vital roles in biological molecules and many chemical processes. The hydroxyl (OH) and carbonyl (CO) groups that form the carboxyl groups (−C═OOH) of these molecules have distinct infrared (IR) spectral signatures. In aqueous solutions, the IR spectra are dominated by the strong absorptivity of water, with principal bands situated in the hydroxyl and carbonyl regions. This renders the task of subtracting the solvent to obtain the solute spectrum difficult. Furthermore, these acids react with bases to form organic salts whose functional groups, modified by the reaction, displace the characteristic bands. As the pH of the solution is increased from pH = 0, for example, the acid is progressively modified into intermediate species. Water is not an inert solvent but reacts with the solute, causing the displacement of the water IR bands. For all these reasons, IR spectroscopy has not been a popular technique for the analysis of aqueous organic acids. However, this technique can be used fruitfully with the use of an attenuated total reflection (ATR) accessory.[1−13] Moreover, principal factor analysis (FA)—which is a numerical method that separates the species spectra[14]—can be used to follow the evolution of an aqueous system quantitatively, under various perturbations such as changes of concentration, pH, and temperature.[3,5−8,10,15,16]

The assignment of the carboxylic acid bands of aqueous organic acids is still a matter of confusion, because of the strong water absorption and the numerous species present. Many, if not all, aqueous carboxylic acids show low-intensity absorption in the 3000−1800 cm^{-1} range that many authors call a "continuum of absorption".[1,17−26] Several authors who have studied different acids proposed an evaluation of this continuum, each time using different spectral reference positions: 1200,[23] 1300,[24] 1800,[23,24] 1900,[25] 1950,[26] 2000,[19,22] and 2200 cm^{-1}.[1,20]

Groups led by Maiorov and Librovitch, who studied inorganic acids in water, reported that the continuum of absorption is proportional to "free" hydronium ions (H_3O^+).[19,20] Hence, the continuum in acidic solutions has been attributed to $(H_2O\cdots H\cdots OH_2)^+$ groupings (aqueous hydronium) in which a strong quasi symmetrical hydrogen bond was observed.[17−26] However, a continuum of absorption was also observed in aqueous solutions when the carboxylic groups are not ionized.[17,26,27] In these solutions, the continuum of absorption cannot be related to free hydronium ions.

The relationship between the pK_a value and the continuum of absorption was evaluated by Leuchs and Zundel with 26 aqueous acids.[25,26] These authors used single wavenumber measurements (1900 cm^{-1} (from ref 25) and 1950 cm^{-1} (from

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ref 26)), along with the degree of dissociation of the acids evaluated from the spectra to establish the relationship. These authors concluded that two different types of acids are observed in relation with the intensity of the continuum, as a function of pK_a. The first type of acid has only one OH acid group and are uncharged when undissociated. The second type of acid has either more than one OH acid group or the acid is charged—i.e., the acid has strong hydrogen-bond acceptor groupings.[26] At the same pK_a, values, the second type of acids yielded greater intensities for the continuum than that of the first type. Leuchs and Zundel assigned the continuum of absorption to hydrogen bonds with great polarizability.[26] These authors suggested that a partial dissociation of the acid occurs when both ions are in close contact with water molecules, because of hydrogen bonding between the molecules. The aforementioned results suggest that the observed continuum of absorption is due to strong interactions with water. However, some pure liquid acids (acetic acid) have exhibited very weak continuums that were explained by the formation of acid dimers via two hydrogen bonds in which both hydrogen-bonded protons tunnel simultaneously.[26,28] A continuum is observed in some other cases where water is not present, such as in pure liquid phosphoric acid.[26]

The study of malic acid, which is a carboxylic acid that is soluble in water in the pH range of 0−14, partly settled the problem.[27] The precision of the evaluation of the continuum of absorption was increased in that study when compared to previous studies, using the complete 3000−1800 cm^{-1} range. Furthermore, a single experimental reference was used to obtain the evaluation of the continuum: the spectra of 1.54 M HCl and 2.23 M NaOH for all acidic and alkaline solutions, respectively. Yielding genuine results, these studies showed that we could analyze organic aqueous acids solutions by ATR−IR and FA. In that article, solid malic, aqueous malic solutions (1.80 M), and aqueous malate solutions were analyzed.[27] After subtracting the water spectrum, the intensity of the continuum of absorption is as follows: aqueous malic acid showed strong intensity; aqueous disodium malate showed no intensity; aqueous monosodium malate showed approximately half the acid intensity; and solid malic acid showed very weak intensity. Because malic acid (1.80 M) is not ionized in water, no "free" hydronium ions (H_3O^+) are present to account for the intensity of the continuum. In the 3700−1800 cm^{-1} range, its spectrum is dominated by four broad peaks that are situated at 3500, 2930, 2580, and 1995 cm^{-1} that were assigned, respectively, to malic-acid-solvated water and alcoholic OH; hydrogen-bonded carboxylic OH; hydrogen-bonded water OH; and a water combination band. Because the intensity of the continuum (in the 3000−1800 cm^{-1} region) is much stronger in aqueous solutions than in pure malic acid, water has a role in the absorptivity through hydrogen bonding between solute and solvated water.

In the present paper, we want to extend the study made on malic acid to eight other carboxylic acids. Together with their sodium salts, these acids form 22 carboxyl containing species. A few of the previously studied organic acids are on the list, but their spectra were reworked, using the more-rigorous data treatment methods that have been developed since their publication. This great number of species was studied to obtain reliable average values of the CO groups in aqueous solutions that can be used for their identification and to compare the species continuum intensities, to identify their origins.

The objective of this study is to analyze the complete MIR spectra of nine aqueous carboxylic acids and their salts. From these spectra, we want to determine the following: (i) the number of species present in the mixtures; (ii) the composition of the species, as a function of pH; (iii) their molar spectra; (iv) their abundances; (v) their hydration numbers; and (vi) the CO single and double bonds positions and molar absorptions. We also want to evaluate the continuum of absorption in the 2500 cm^{-1} region, as a function of the ionic composition. For this purpose, we (a) will obtain the IR spectra of the nine aqueous carboxylic acids and their salts; (b) will make the IR titration in the pH range of 0−14 of six acids; (c) illustrate the IR titration procedure with glycine; (d) subtract the different water types (pure, acidic, basic and saline) from the solution spectra; (e) use FA to obtain the principal factors (spectra and abundances); (f) obtain the residues from the difference between the experimental and calculated spectra; (g) obtain the molar spectra of all the acids and their salts; (h) make the assignment of the CO, CH, and OH bands; and (i) evaluate the continuum of absorption of the different species and determine its origin.

2. Theoretical Considerations

2.1. Factor Analysis. Factor analysis (FA) is performed in a two-step procedure. The fist step is the subtraction of the water spectrum from that of the solutions, using four water principal spectra: pure liquid water, acidic water (1.54 M HCl), alkaline water (2.23 M NaOH), and salt-solvated (5.13 M NaCl) water.[5] Although these spectra are not those of orthogonal factors—they all contain pure (i.e., unperturbed) water—FA can still be performed.[2,4,5,11,27] The subtraction criteria are (i) no negative bands, with special care given to the region near 3660 cm^{-1}, and (ii) the lowest intensity in the 2620−2580 and 1850−1800 cm^{-1} ranges. An absorption increase in these regions is due principally to the so-called continuum of absorption in both acidic and alkaline water. In these regions, the absorptivity of these species is small; thus, care is taken not to go below the limits imposed by them.

The FA second step is the analysis of the spectra that remain after the water subtraction, to obtain the solute principal species. These contain the total amount of solutes and water close-bound to them. For the solutes involved in the titration, mixtures of ionic species are present in the middle pH range (pH 2−11); however, at pH >13, only the most anionic solute species are present and, hence, are retrieved. Similarly, the spectra of the most-cationic principal species are obtained at pH < 1. By definition, the principal spectra do not change in the pH range of 0−14; only their abundances, which are expressed as multiplying factors (MFs), vary progressively. Hence, the other principal species spectra are obtained by systematically subtracting the extreme principal species spectra from those obtained at the other pH, doing so progressively from the extreme pH toward the middle pH values. Each principal spectrum (S_P^j) is multiplied by its MFs (MF_i^j) and added to the others. The resulting spectrum is subtracted from the experimental one (S_{exp}^i) and the MFs are varied until the residues (S_Δ^i) are minimized:

$$S_\Delta^i = S_{exp}^i - \sum_j MF_i^j \times S_P^j \qquad (1)$$

where S_P^j and MF_i^j are the principal spectrum and MF of species j retrieved in sample i. The best fit is monitored by the least-squares procedure.

The presence of supplementary species is revealed when the residues show some sigmoid that cannot be minimized satisfactorily.[29] These species are introduced into the FA procedure one at a time by taking the spectrum with the highest residues.

FA is restarted with the new set of principal spectra. The iteration procedure is pursued until the residues show only noise. The concentrations of the species are obtained by multiplying the MFs by the principal spectra concentrations.

2.2. Volumetric Titration Curves. For aqueous glycine, BOPA, sulfuric acid, and phosphoric acid, we have developed the titration equations based on the dissociation equilibrium, the species conservation, and the electroneutrality equations.[6–8,15] BOPA is a glycinate that contains two carboxylic groups whose dissociation equilibrium equations are

$$\begin{aligned}
&\underset{H^+AH_2}{R{-}NH^+(CH_2COOH)_2} \overset{K_1}{\rightleftharpoons} \\
&\qquad \underset{H^+ + H^+AH^-}{R{-}NH^+(CH_2COOH,CH_2COO^-)} \overset{K_2}{\rightleftharpoons} \\
&\qquad \underset{H^+ + H^+A^{2-}}{R{-}NH^+(CH_2COO^-)_2} \overset{K_3}{\rightleftharpoons} \underset{H^+ + A^{2-}}{R{-}N{-}(CH_2COO^-)_2}
\end{aligned} \tag{2}$$

with the following dissociation constants:

$$K_1 = \frac{[H^+AH^-][H^+]}{[H^+AH_2]} \tag{3}$$

$$K_2 = \frac{[H^+A^{2-}][H^+]}{[H^+AH^-]} \tag{4}$$

$$K_3 = \frac{[A^{2-}][H^+]}{[H^+A^{2-}]} \tag{5}$$

The titration equations for aqueous BOPA starting from any ionic state are given in ref 15. For aqueous glycine, which is an amino acid that contains one carboxylic group [$H_2N{-}CH_2{-}CO_2H$], the ionic form A^{2-} is not present and calculations in eq 2 are conducted with $K_3 = 0$. Aqueous betaine forms cationic and zwitterionic species [$(CH_3)_3{-}N^+{-}CH_2{-}COO^-$]; therefore, $K_2 = K_3 = 0$ are used in eq 2. Aqueous acetic acid [$CH_3CH_2{-}CO_2H$] and malic [$HO_2CCH(OH)CH_2{-}CO_2H$] acid do not have amino groups and cationic forms. For these, eq 2 uses $K_1 = \infty$. Aqueous acetic acid is only ionized once, so that $K_3 = 0$. The ionic concentrations are[15]

$$[H^+AH_2] = \frac{A}{1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2} + \frac{K_1K_2K_3}{[H^+]^3}} \tag{6}$$

$$[H^+AH^-] = \frac{A}{\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]} + \frac{K_2K_3}{[H^+]^2}} \tag{7}$$

$$[H^+A^{2-}] = \frac{A}{\frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2} + 1 + \frac{K_3}{[H^+]}} \tag{8}$$

$$[A^{2-}] = \frac{A}{\frac{[H^+]^3}{K_1K_2K_3} + \frac{[H^+]^2}{K_2K_3} + \frac{[H^+]}{K_3} + 1} \tag{9}$$

where A represents the total solute concentration. In the calculations, the lower and higher limits for K_i are set at 10^{-20} and 10^{+20}, respectively. At values of zero (0) and infinity (∞), these constants yield undefined numerical results. Equation 28 of ref 15 gives the relation between pH and the titrant mass from which the volumetric titration curves are obtained:

$$m_\delta = V \times \left\{ \frac{\rho_0\left(\frac{\epsilon_2}{M_2 + \alpha_\Delta M_{\Delta 3}}\right)\left(\frac{-1 + \frac{K_1K_2}{[H^+]^2} + 2\frac{K_1K_2K_3}{[H^+]^3}}{1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2} + \frac{K_1K_2K_3}{[H^+]^3}} - \Delta\alpha_\Delta\right) - [H^+] + \frac{K_0}{[H^+]}}{\delta\left(\frac{\epsilon_\delta}{M_\delta}\right) + (1 - \rho_\delta)\left(\frac{\epsilon_2}{M_2 + \alpha_\Delta M_{\Delta 3}}\right)\frac{\left(\frac{-1 + K_1K_2}{[H^+]^2} + 2\frac{K_1K_2K_3}{[H^+]^3}\right)}{1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2} + \frac{K_1K_2K_3}{[H^+]^3}} - \Delta\alpha_\Delta} \right\} \tag{10}$$

where the different symbols are defined in the List of Symbols.

3. Experimental and Data Treatment

3.1. Chemicals and Solutions. Table 1 provides a list of the nine carboxylic acids used in the present study. The following chemicals were used without further purification: glacial acetic acid (Baxter, No. C9800-70, ACS reagent grade, 99.7%, molecular weight (MW) of 60.05), betaine hydrochloride (Calbiochem Corporation, No. 200495, 97% purity, MW = 153.6), glycine (Sigma Chemical Company, No. G-7126, >99% purity, ammonia-free, MW = 75.07), D−L malic acid (Aldrich Chemical Company, No. M121-0, >99% purity, MW = 134.09), glycolic acid (Aldrich Chemical Company, No. 42,058-1, MW = 76.05, 70 wt % solution in water), chloroacetic acid (Aldrich Chemical Company, No. 40,292-3, ACS reagent grade, >99% purity, MW = 94.50), chloroacetic acid, sodium salt (Aldrich Chemical Company, No. 29,177-3, 98% purity, MW = 116.48), citric acid (Aldrich Chemical Company, No. 25,127-5, ACS reagent grade, >99.5% purity, MW = 192.12), and acrylic acid (Aldrich Chemical Company, No. 14,723-0, 99% purity, MW = 72.06). The synthesis of *N*,*N*-((butyloxy)-propyl)amino diacetic acid (BOPA) was conducted in our laboratory.[15]

Deionized water was used to prepare the aqueous solutions. Aqueous NaOH, (50.8% w/w) and concentrated HCl (37.0% w/w, density of 1.19 g/mL, Fisher Scientific) were used for the titration. These concentrations were used to maintain the high carboxylic acid concentrations in the sample. Neutral water, 1.54 M HCl, 2.23 M NaOH, and 5.13 M NaCl were used to obtain the reference spectra (or principal spectra) of neutral, acidic, basic, and salt-solvated water.[5]

Stock solutions of acetic acid (5.01 M), malic acid (1.85 M), betaine hydrochloride (1.63 M), glycine (1.33 and 2.66 M), and BOPA monosodium salt (0.95 M) were made. The samples were made by weighing the titrant in a 10-mL volumetric flask, with the volume being up to 10 mL stock solution and weighed. Solutions in the pH range of 0−14 were prepared: 16, 24, 20, 26, 48, and 27 samples for acetic acid, malic acid, betaine hydrochloride, 1.33 M glycine, 2.66 M glycine, and BOPA, respectively. The homogeneous solutions obtained were divided into two parts: one for the IR measurements and the other for the pH measurements.

The following compounds were prepared: 3.17 M chloroacetic acid, 2.58 M chloroacetic acid sodium salt, 3.94 M glycolic acid, 3.06 M glycolic acid sodium salt, 1.39 M citric acid (tri)sodium salt, and 2.12 M sodium acrylate. The sodium chloroacetate solution was measured immediately after it was

TABLE 1: List of Organic Acids

name	symbol	molecular weight, MW (g/mol)
Monocarboxylic Acids		
acetic acid	$H_3C{\cdot}CO_2H$	60.052
glycolic acid	$HO{\cdot}CH_2{\cdot}CO_2H$	76.052
chloroacetic acid	$ClCH_2{\cdot}CO_2H$	94.498
acrylic acid	$H_2C{=}CH{\cdot}CO_2H$	72.063
Dicarboxylic Acids		
D−L malic acid	$HO_2C{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H$	134.088
Tricarboxylic Acid		
citric acid	$HO_2C{\cdot}CH_2{\cdot}C(OH){\cdot}(CO_2H){\cdot}CH_2{\cdot}CO_2H$	192.125
Amino Acids		
glycine	$H_2N{\cdot}CH_2{\cdot}CO_2H$	75.067
N,N-((butyloxy) propyl) amino diacetic acid (BOPA)	$H_3C{\cdot}(CH_2)_3{\cdot}O{\cdot}(CH_2)_3{\cdot}N{\cdot}(CH_2{\cdot}CO_2H)_2$	247.291
Surfactants		
BOPA	$H_3C{\cdot}(CH_2)_3{\cdot}O{\cdot}(CH_2)_3{\cdot}N{\cdot}(CH_2{\cdot}CO_2H)_2$	247.291
betaine	$(H_3C)_3{\cdot}N^+{\cdot}CH_2COO^-$	117.147

prepared, to avoid its natural decomposition to glycolic acid and sodium chloride.[30]

3.2. pH Measurements. The pH was measured at ambient temperature (24 ± 2 °C) with a pH meter (Omega model PHH-253) that was equipped with a combination electrode (Analytical Sensors, Inc., model PH10107B-03-B). A two-point calibration was made, at pH 2.00 and 7.00 or pH 7.00 and 10.00, prior to any measurements.

3.3. IR Measurements. The IR measurements were obtained with a model 510P Nicolet Fourier transform infrared (FT-IR) single-beam spectrometer that was equipped with a DTGS detector. Two KBr windows isolated the measurement chamber from the outside. The spectra were obtained under a nitrogen flow, to ensure low residual CO_2 and H_2O vapors in the spectrometer. The samples were contained in a Circle cell (SpectraTech) with a ZnSe crystal rod (8 cm long) in an ATR configuration. The incident beam was oriented at an angle of 45° to the rod axis that made 6.6 reflections in contact with the sample. The spectral range was 4800−650 cm^{-1}. Twenty scans with a resolution of 4 cm^{-1} were accumulated for each spectrum. All spectra were obtained at 26.5 ± 0.3 °C. The cell was carefully dried before each measurement.

The IR measurements consisted of obtaining the following ATR intensities: background (R_0) and sample (R). The ratio of R/R_0 produced an intensity I for the spectra. Thereafter, the 2153 data points (I ($\tilde{\nu}$) vs $\tilde{\nu}$ (in cm^{-1})) of each spectrum were transferred to a spreadsheet program on a personal computer (PC), where the numerical treatment to obtain the ATR absorbances ($\log(1/I)$, expressed in absorbance units (abbreviated as au)) was conducted. The other mathematical operations were made in the spreadsheet. A small baseline correction (<0.005 au) was made to obtain a null mean absorbance in the 4600−4450 cm^{-1} region, where water absorbs very little.[31]

4. Results and Discussion

4.1. Water Spectrum Subtractions. The water spectrum subtraction is a critical point in these spectral data treatments. Details on the procedure have been reported elsewhere.[27] Increasing the water spectrum subtraction from the acidic solutions spectra produces a low-intensity absorption near 3200 cm^{-1} before a negative band appears near 3660 cm^{-1} (criterion (i), Section 2.1). This gives an absolute maximum water subtraction. The amount of water subtraction from the alkaline solutions is made such that no negative band appears near 3660 cm^{-1} (criterion (i), Section 2.1). After water subtraction, most spectra show residual water absorption that we attribute to water that is close-bound to the solutes. These are observed on the retrieved principal factor spectra in Figure 1.

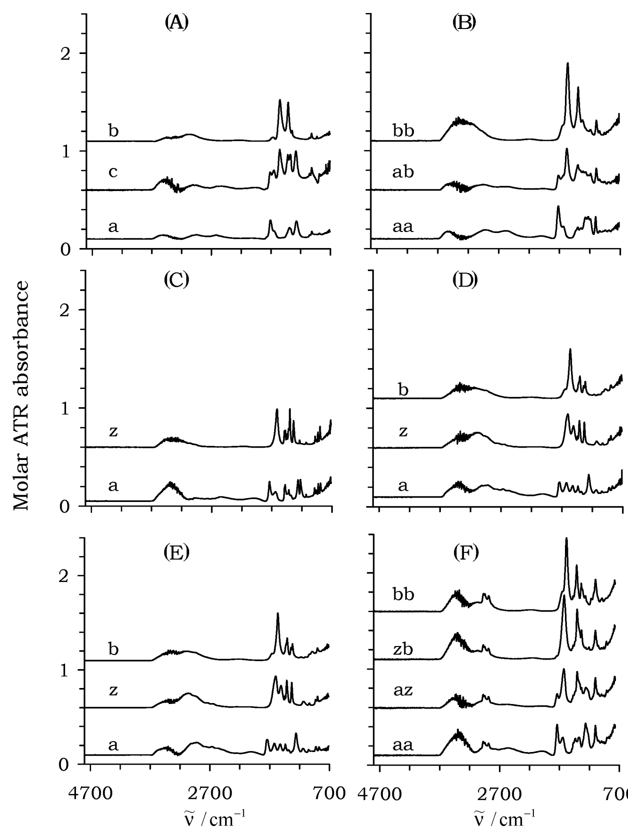

Figure 1. Factor analysis (FA) principal species spectra of carboxylic acids (using molar attenuated total relection−infrared (ATR−IR) spectroscopy): (A) acetic acid (spectrum a, 5.01 M; spectrum b, sodium salt; and spectrum c, aceto-acetate complex), (B) malic acid (spectrum aa, 1.80 M; spectrum ab, monosodium; and spectrum bb, disodium salts), (C) betaine (1.65 M) (spectrum a, hydrochloride; and spectrum z, zwitterion), (D) glycine (1.33 M) (spectrum a, hydrochloride; spectrum z, zwitterion; and spectrum b, sodium salt), (E) glycine (2.66 M) (spectrum a, hydrochloride; spectrum z, zwitterion; and spectrum b, sodium salt), (F) BOPA (0.95 M) (spectrum aa, hydrochloride; spectrum az, zwitterion; spectrum zb, monosodium salt; and spectrum bb, disodium salt). Note that the spectra are shifted.

4.2. IR Titration of Glycine. We use glycine to illustrate the IR titration of all carboxylic acids presented here. The

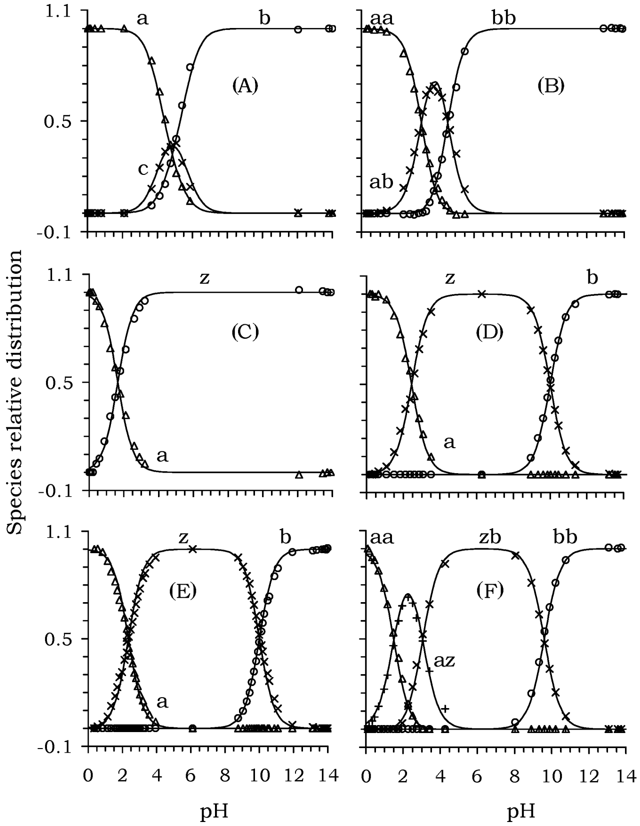

Figure 2. Relative distribution as a function of pH of the carboxylic acid principal species presented in Figure 1. Full lines represent theoretical calculations, and symbols represent the experimental results (see text).

procedure details are given in the Supporting Information and in ref 27 for malic acid.

4.2.1. Aqueous Glycine Factor Analysis. The three principal spectra retrieved by FA are presented in Figure 1D: glycine hydrochloride (D_a); zwitterion (D_z), and sodium salt (D_b). The residues obtained (in the Supporting Information) exhibit only noise that is similar to that of malic acid,[27] which indicates that the FA procedure operated adequately.

The relative distributions of the solute species are presented in Figure 2D, as a function of pH, which is the usual way of presenting titration results. Here, the experimental results (symbols) are situated exactly on the calculated curves (full lines). The glycine pK_a values obtained are located at pH 2.45 and 10.00; these are close to the literature values, which are 2.35 and 9.78, respectively.[32] The small differences come from the difference in the activity coefficient of the solutions. Figure 3D shows the normalized distribution of the solute species, as a function of equivalent titrant, along with that of the acidic and basic water, expressed as molar HCl and NaOH equivalents.[33] These curves, which show linear relationships, are a true advantage over the traditional relationships that give the relations as a function of pH. These are nonlinear (see Figure 2D).

The results obtained for the 48 solutions of 2.66 M glycine are presented in the same fashion as that of the 1.33 M solutions: principal spectra are shown in Figure 1E, and distributions are shown in Figures 2E and 3E). The pK_a values retrieved are 2.35 and 10.00, which are similar to the preceding pK_a values. The small differences come from the activity coefficient. The results obtained from this series are of better quality than those previously reported,[6] because the spectra extend to the full mid-IR region without any arbitrary baseline correction. In Figure 3E, all the experimental points fall on the calculated lines, whereas, previously (Figure 3A of ref 6), a few points were outside; this observation indicates that the present study gave better results.

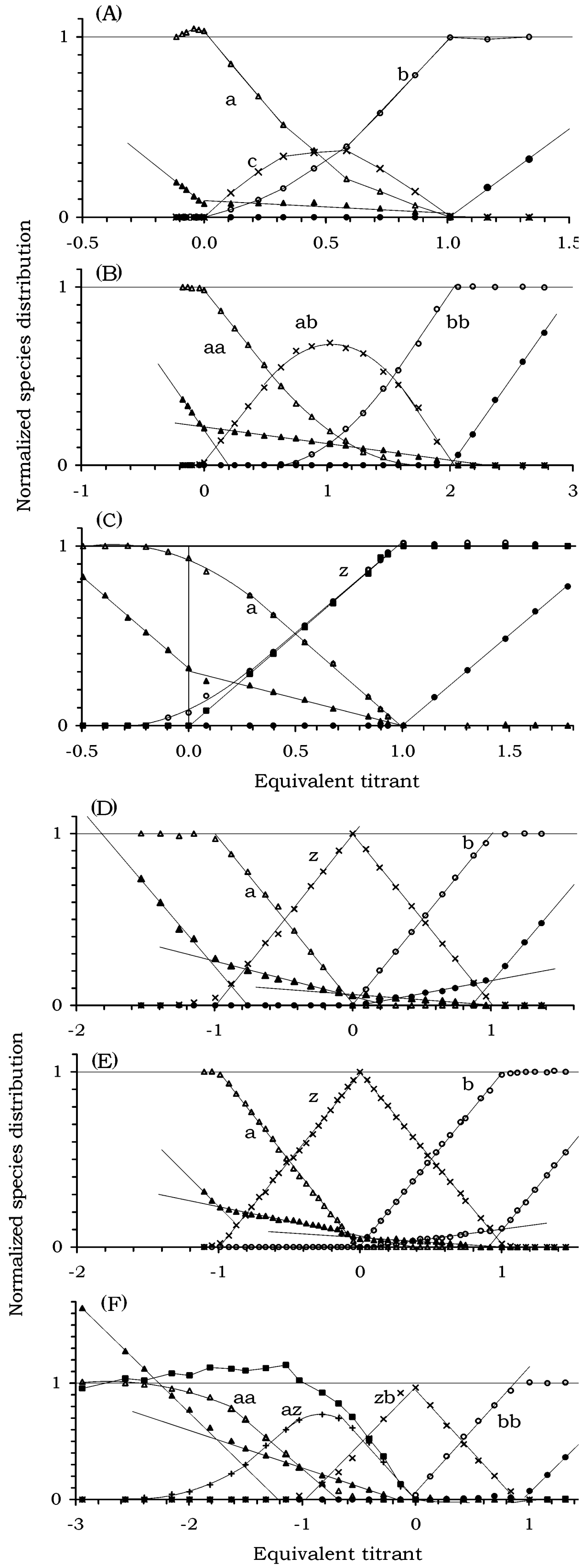

Figure 3. Relative distribution as a function of titrant equivalent for the carboxylic acid principal species presented in Figure 1. Water types are added: (●), 2.23 M NaOH; (▲), 1.54 M HCl; and (■) 5.1 M NaCl. Pure water is not shown.

TABLE 2: Characteristics of Acidic and Alkaline Water Titrants in Organic Acid Titrations

titrant equivalent	Acetic Acid		Malic Acid		Betaine		Glycine 1.33 M		Glycine 2.66 M		BOPA	
	slope[a]	origin	slope[a]	origin	slope[a]	origin	slope[a]	origin	slope[a]	origin	slope[a]	origin
$X < -2$											−0.949	−1.150
$-2 > X > -1$							−0.954	−0.733	−0.947	−0.719	nonlinear	
$-1 > X > 0$	−1.077	0.072	−0.993	0.197	−1.026	0.320	−0.167	0.064	−0.211	0.048	−0.324	−0.052
$0 > X > 1$	−0.069	0.092	−0.093	0.215	−0.304	0.304	−0.053	0.054	−0.055	0.062	0	0
							0.109	−0.007	0.150	−0.006		
$1 > X > 2$	0.991	−0.997	−0.093	0.215	1.008	−1.008	0.993	−0.901	0.947	−0.815	0.957	−0.902
$X > 2$			0.981	−1.966								

[a] Negative slopes are for acidic water (increasing with HCl added, that is, with decreasing titrant equivalent) and positive slopes are for alkaline water.

TABLE 3: pK_a, Concentration, and Zero-Titrant pH Values of Four Organic Acids

species	pK_a values: these results			pK_a values: literature values[a]		concentration (mol/L)	pH without added titrant
acetic acid		4.85			4.75	5.01	2.10
malic acid	3.20	4.60		3.40	5.11	1.80	1.35
betaine		1.65			1.83	1.65	0.60
glycine		2.45	10.00	2.35	9.78	1.33	6.27
glycine		2.35	10.00	2.35	9.78	2.66	6.10
BOPA	1.50	3.05	9.60			0.95	7.99

[a] From ref 32.

4.2.2. Abundance of Water Species in Aqueous Glycine. Because of the logarithmic relationship between pH and the related concentration, it is difficult to assess the direct relation between the water species abundance and the titrant equivalent. After the MFs are transformed into molar equivalents, the linear relationships are obtained. These, for acidic and alkaline water, are given in Figure 3D (legend is the same as that in Figure 2D) and their linear curve characteristics are presented in Table 2. The pure water concentration is not represented in the figure. Below a titrant equivalent of −1 (HCl added is negative), the curve of acidic water concentration (Figure 3D) is linear, with a slope of -0.95_4 (± 0.05). Similarly, above a titrant equivalent of +1 (NaOH added is positive), the curve of alkaline water concentration is linear, with a slope of 0.99_3 (± 0.05). Both curves are straight lines with slopes of 1, which indicates that the water subtraction procedure in these titrant equivalent regions accurately follows the addition of HCl (decreasing titrant equivalent below −1) or NaOH (increasing titrant equivalent above +1).[33,34] However, both acidic and alkaline water equivalent values obtained by IR differed from that calculated from the solute degree of ionization and pH values. This indicates that water molecules interacting strongly with the solute are perturbed in a manner similar to that with aqueous HCl (or NaOH).[27] Therefore, the solute principal spectra need to be corrected to address these differences.

4.2.3. Correction for Acidic and Basic Waters. The water subtraction that involves acidic, alkaline, or saline water represents the exact amount of these species, because these solvated waters are proportional to the amount of the related solute (HCl, NaOH, or NaCl) dissolved in the aqueous solution.[5] Therefore, when attempting to determine the principal spectra of the solute species, one must compare the amount of acidic, alkaline, and saline water retrieved by IR to that actually present in the solution. Any excess amounts are due to the solute and its spectrum must be corrected accordingly.[27] We use glycine to illustrate the procedure.

The pH of the 1.33 M glycine stock solution was 6.27 (Table 3). Because this solution is almost pure zwitterion (see Figure 2D), it does contain only a small amount of "free" protons (H^+ or H_3O^+): $[H^+] < 10^{-6}$ mol/L. According to FA of water subtraction, the stock solution contains 0.055 ± 0.005 mol/L equivalent HCl for each mol/L glycine (see Figure 3D); that is, $0.055 \times 1.33 = 0.073$ mol/L of acidic water (equivalent HCl). Because no HCl was added (0 titrant equivalent) and almost no H^+ is present in the solution (pH = 6.27), the acidic water retrieved by IR spectroscopy must be attributed to water in strong interaction with the glycine zwitterion. Excess acidic water has long been estimated by the so-called "continuum of absorption".[17−26] We also reported similar results for IR titrations of phosphoric and malic acids.[7,27] This acidic water cannot be attributed to free protons (H^+ or H_3O^+) and must be attributed to the solvated solute species. Hence, the aqueous glycine zwitterion spectrum (Figure $1D_z$) must be corrected for its acidic water, as well as for malic acid[27] (see Appendix A). Spectra d in Figure 6 shows the result.

When 1 equivalent HCl (−1 titrant equivalent) is added to the glycine zwitterion solution, it is completely transformed to glycine hydrochloride (see spectrum a in Figure 1D (spectrum $1D_a$)). The solution was observed to contain 0.228 mol/L equivalent HCl for each mol/L glycine. Again, this acidic water must be attributed to water that is strongly interacting with glycine hydrochloride. Therefore, spectrum $1D_a$ must be modified (see Appendix A). The resulting spectrum (Figure 4d) represents glycine hydrochloride in strong interaction with some water molecules.

Similarly, when 1 equivalent NaOH (equal to 1 titrant equivalent) is added to glycine zwitterion solution, it is completely transformed to sodium glycinate (see Figure 3D). The solution was observed to contain 0.132 mol/L equivalent NaOH for each mol/L glycine (see Figure 3D). This alkaline water is attributed to water that is strongly interacting with sodium glycinate (pH < 12) and must be added to the spectrum. Figure 5d shows the result after correcting the spectrum b of Figure 1D (spectrum $1D_b$) (see Appendix A).

The same situation prevails for 2.66 M glycine and is corrected accordingly. The spectra (Figure 1E) corrected for associated acidic and alkaline water are shown in spectra e in Figures 4−6.

4.2.4. Hydration Numbers in Aqueous Glycine. With quantitative subtraction of the water IR spectra, the hydration numbers of glycine ionic species were obtained by the method

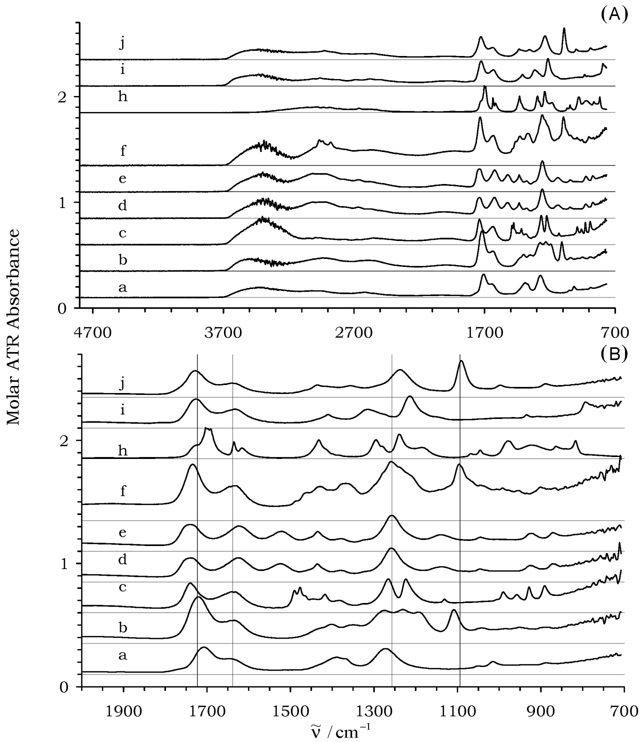

Figure 4. Molar ATR−IR spectra of protonated carboxylic acids (RCOOH): spectrum a, acetic acid; spectrum b, malic acid; spectrum c, betaine·HCl; spectrum d, 1.33 M glycine·HCl; spectrum e, 2.66 M glycine·HCl; spectrum f, BOPA·HCl; spectrum g, citric acid; spectrum h, acrylic acid; spectrum i, monochloacetic acid, and spectrum j, glycolic acid. Panel A shows the complete region, and panel B shows the expanded region. Spectra are shifted. Vertical lines at 1723, 1643, 1257, and 1094 cm^{-1}.

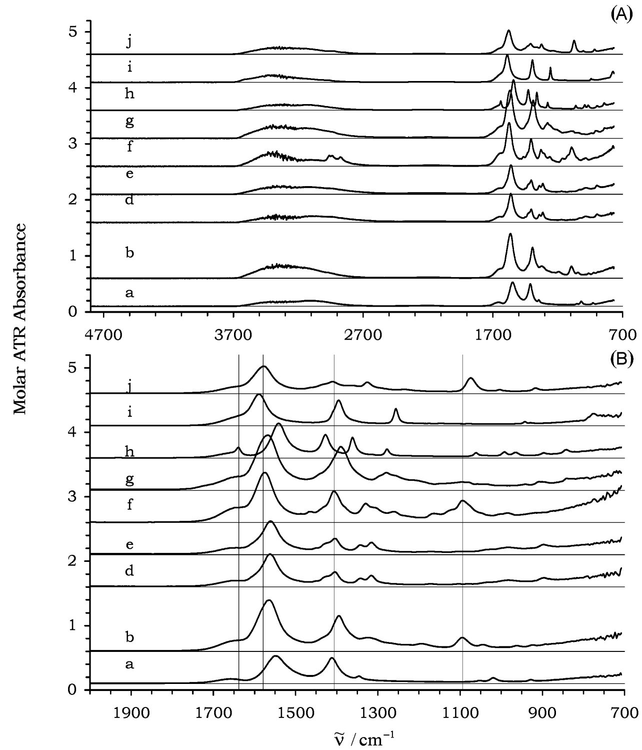

Figure 5. Molar ATR−IR spectra of dissociated carboxylates ($RCOO^-{\cdot}Na^+$) but no zwitterions: spectrum a, sodium acetate; spectrum b, disodium malate; spectrum d, 1.33 M sodium glycinate; spectrum e, 2.66 M sodium glycinate; spectrum f, disodium BOPA; spectrum g, trisodium citrate; spectrum h, sodium acrylate; spectrum i, sodium monochloacetate; and spectrum j, sodium glycolate. Panel A shows the complete region, and panel B shows the expanded region. Vertical lines at 1643, 1579, 1406, and 1094 cm^{-1}.

summarized in Appendix B.[27] For 1.33 M glycine, the hydration numbers were 5 ± 2, 2 ± 1, and 3.0 ± 0.5 for glycine hydrochloride, glycine zwitterion, and sodium glycinate, respectively. For 2.66 M glycine, the hydration number was 2 ± 1 for the three ionic species. Within the error limits, the two sets of values are the same.

4.3. IR Titration of Acetic Acid, Malic Acid, Betaine and BOPA. 4.3.1. IR Titration. The IR titrations of acetic acid, malic acid, betaine, and BOPA are made in the same manner as that for glycine. FA on these series of spectra gave the spectra presented in Figure 1. The residues (in the Supporting Information) are similar to those reported for malic acid.[27] Because these are at the zero level, it indicates that the FA procedure worked adequately. The high noise level in certain spectral regions is due to the strong water absorption. The titration curves, as functions of pH and equivalent titrants, are presented in Figures 2 and 3, respectively (see Supporting Information for details). Although FA results on malic acid have been reported elsewhere,[27] they are included here for comparison with the other acids. After correction for the acidic and basic waters, the spectra of the acids, salts, and special cases are presented in Figures 4, 5, and 6, respectively (see details in Supporting Information).

4.3.2. Hydration Numbers and pK_a Values. With quantitative subtraction of the water IR spectra, the hydration numbers of acid ionic species retrieved by FA were obtained using the method described in Appendix B.[27] The values are reported in Table 4, along with the pK_a values.

All six IR titrations of five carboxylic acids are made with principal FA over the entire MIR spectral range: 4800−700 cm^{-1}. The pK_a values of the acids (see Table 3) obtained from the IR spectra agree with the literature values.[32] The number of solute species and the abundance and complete spectra of each species have been obtained. In all cases, the species abundances obtained from the IR spectra agree with the thermodynamic calculations (see Figure 2). This indicates that the IR titration that is performed is quantitative and reliable.

4.4. Aceto-acetate Complex. The FA results deviate from those of the thermodynamic calculations obtained from eq 1 only when acetic acid and its sodium salt are used.[35] This indicated that another species is present in the solution. After adding it in the procedure, it was identified, by its spectrum, as an aceto-acetate complex. This complex has been observed previously in buffer solutions made of sodium acetate and acetic acid.[18] Our results indicate that such a complex also exists in acetic acid aqueous solutions and the surrounding water does not destroy it.

FA was applied to a series of 16 spectra that were obtained from the IR titration of 5.01 M acetic acid. The results are shown in Figures 1A, 2A, and 3A: spectrum A_a represents the acid, spectrum A_b represents aqueous sodium acetate, and spectrum A_c represents the 1:1 aceto-acetate complex. The pK_a value retrieved by IR spectroscopy is 4.85 (see Table 3). This value is similar to the literature value of 4.75.[32] The small difference is attributed to the activity coefficient, which is strongly dependent on the solute concentration.

The complex formation constant from the equilibrium reaction

$$CH_3COOH + CH_3COO^- \underset{K_{complex}}{\rightleftharpoons} CH_3COOH{\cdot}CH_3COO^- \qquad (11)$$

TABLE 4: Hydration Number, Acidic and Alkaline Water Equivalents, and pK_a Value of Organic Acids

acids/salts[a]	ionic species	Hydration Number total	Hydration Number per COO	Equivalent (mol/L) acidic water	Equivalent (mol/L) alkaline water	pK_a
BOPA						
$2F_{aa}$	$H_3C(CH_2)_3O(CH_2)_3{-}NH^+(CH_2{\cdot}CO_2H)_2$, $\cdot Cl^-$	3 ± 1	1.5 ± 0.5	0.765	0	1.50
$2F_{az}$	$R{-}NH^+(COOH, COO^-)$	2 ± 1	1.0 ± 0.5	0.137	0	3.05
$2F_{zb}$	$R{-}NH^+(COO^-)_2$, Na^+	2.0 ± 0.5	1.0 ± 0.5	0	0	9.60
$2F_{bb}$	$R{-}N(COO^-)_2$, Na^+	3.0 ± 0.5	1.5 ± 0.5	0	0	
betaine						
$2C_a$	$(H_3C)_3{\cdot}N^+{\cdot}CH_2{\cdot}CO_2{\cdot}H{\cdot}Cl$	2.5 ± 1.5	2.5 ± 1.5	0.256	0	1.65
$2C_z$	$(H_3C)_3{\cdot}N^+{\cdot}CH_2COO^-$	1.0 ± 0.5	1.0 ± 0.5	0	0	
glycine						
$2D_a$, E_a	$NH_3^+CH_2COOHCl^-$	5 ± 2	5 ± 2	0.228	0	2.35
$2D_z$, E_z	$NH_3^+CH_2COO^-$	2 ± 1	2 ± 1	0.055	0	10.00
$2D_b$, E_b	$NH_2CH_2COO^-$, Na^+	3.0 ± 0.5	3.0 ± 0.5	0	0.132	
acetic acid						
$2A_a$	CH_3COOH	2 ± 1	2 ± 1	0.082	0	4.85
sodium acetate						
$2A_b$	CH_3COO^-, Na^+	1.0 ± 0.1	1.0 ± 0.1	0	0	
aceto-acetic complex (pH 4.8)						
$2A_c$	$CH_3COOH{:}CH_3COO^-$, Na^+	1.0 ± 0.5	1.0 ± 0.5	0.144	0	
malic acid						
$2B_{aa}$	$HO{-}(CHCOOH,CH_2COOH)$	2.0 ± 1.0	1.0 ± 0.5	0.206	0	3.20
$2B_{ab}$	$HO{-}(CHCOOH, CH_2COO^-)$, Na^+	3.0 ± 2.0	1.5 ± 1.0	0.125	0	4.60
$2B_{bb}$	$HO{-}(CHCOO^-,CH_2COO^-)$, $2Na^+$	4.0 ± 0.5	2.0 ± 0.2_5	0	0	
acrylic acid	$CH_2{=}CHCOOH$	pure				4.25[32]
acrylate	$CH_2{=}CHCOO^-$, Na^+	2 ± 0.5	2.0 ± 0.5	0	0	
trisodium citrate	$HO{-}C(COO^-,(CH_2COO^-)_2)$, $3Na^+$	3 ± 0.5	1.5 ± 0.2_5	0	0	6.39[32]
monochloroacetic acid (MCA)	$Cl{-}H_2C{-}COOH$	2 ± 1	2 ± 1	0.24	0	2.85[32]
Na-MCA	$Cl{-}H_2C{-}COO^-$, Na^+	1 ± 1	1 ± 1	0	0	
glycolic acid	$HO{-}H_2C{-}COOH$	1 ± 1	1 ± 1	0.12	0	3.83[32]
sodium glycolate	$HO{-}H_2C{-}COO^-$, Na^+	1.0 ± 0.5	1.0 ± 0.5	0	0	
	average		1.7			

[a] Number refers to figure, and letter refers to spectrum; subscripts a, b, and z respectively refer to the acidic carboxylic form (−COOH), the salt form (−COO−), and the zwitterionic form (N^+COO^-).

is

$$K_{\text{complex}} = \frac{[\text{AH}{\cdot}\text{A}^-]}{[\text{AH}][\text{A}^-]} \qquad (12)$$

The resolution of simultaneous equilibrium reactions 2 and 11 gives the following:

$$[\text{CH}_3\text{COOH}] = \frac{-\left(1+\frac{K_2}{[\text{H}^+]}\right)+\sqrt{\left(1+\frac{K_2}{[\text{H}^+]}\right)^2+8A\left(\frac{K_2K_{\text{complex}}}{[\text{H}^+]}\right)}}{4\left(\frac{K_2K_{\text{complex}}}{[\text{H}^+]}\right)} \qquad (13)$$

$$[\text{CH}_3\text{COO}^-] = [\text{CH}_3\text{COOH}] \times \frac{K_2}{[\text{H}^+]} \qquad (14)$$

$$[\text{CH}_3\text{COOH}{\cdot}\text{CH}_3\text{COO}^-] = K_{\text{complex}}\,[\text{CH}_3\text{COOH}] \times [\text{CH}_3\text{COO}^-] \qquad (15)$$

where K_2 is the dissociation constant of acetic acid.

Equations 13−15 are used to evaluate the relative concentration of the species in the titration using K_{complex} as a parameter that is adjusted to provide the best fit between the FA results and the theoretical calculations. These are shown in Figure 2A (solid lines denote theory, whereas symbols denote the FA result). The experimental results fall on the calculated curves, which indicates that the description of this system is adequate. The resulting complex formation constant obtained is $K_{\text{complex}} = 1.8 \pm 0.4$ L/mol. This value is close to unity, which would have been obtained for a system with an equal probability for species AH and A^- (separated or complexed). Therefore, the aceto-acetate complex is neither a favored nor a disadvantaged species.

The maximum intensity of the complex is observed at the pK_a value of the acid and salt. We did observe similar results in the titration of H_3PO_4 by NaOH where three complexes were observed at the three pK_a values of the species.[8] The complex formations in acid−base titrations seem to be more frequent than those presented in textbooks. To obtain a complete picture of the species present in such titrations, the complexes must be included. This study indicates that IR spectroscopy is surely one of the best methods that can be used to observe them quantitatively.

4.5. Other Carboxylic Acids. To help in the spectral comparison, the ATR−IR spectra of several other carboxylic acids and some of their salts were obtained (see Table 1). These are pure acrylic acid and aqueous solutions of chloroacetic acid and its sodium salt, glycolic acid and its sodium salt, citric acid and its trisodium salt, and sodium acrylate.

After water subtractions, the real spectra of solvated solutes were obtained (see Figures 4 and 5). The amounts of equivalent acidic or alkaline water present in these species were evaluated with the spectra of 1.54 M HCl and 2.23 M NaOH. The amounts obtained are listed in Table 4. Acidic water was retrieved in both aqueous chloroacetic and glycolic acids. No acidic water was retrieved in pure liquid acrylic acid. The spectra of acrylic (pure), chloroacetic acid, and glycolic acid are shown in Figure 4, in traces h, i, and j, respectively. Those of sodium acrylate, sodium citrate, sodium chloroacetate, and sodium glycolate are shown in Figure 5, in traces h, g, i, and j, respectively. No acidic and alkaline waters were subtracted from these spectra.

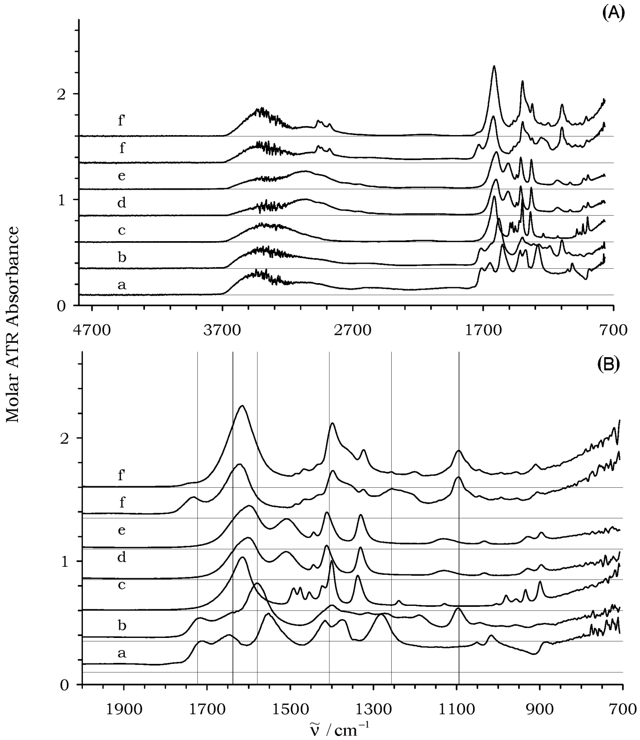

Figure 6. Molar ATR−IR spectra of zwitterionic carboxylic acids (N^+COO^-) and special cases: spectrum c, betaine; spectrum d, 1.33 M glycine; spectrum e, 2.66 M glycine; spectrum f, BOPA (one free carboxylic acid group); spectrum f′, BOPA (no free carboxylic acid group); spectrum a, sodium aceto-acetate complex; spectrum b, monosodium malate. Panel A shows the complete region, and panel B shows the expanded region. Vertical lines at 1723, 1643, 1579, 1406, 1257, and 1094 cm^{-1}.

4.6. Spectral Features. The corrected molar spectra of the protonated, dissociated, and zwitterion carboxylic acids are presented in figures 4, 5, and 6, respectively. Those of the sodium aceto-acetic complex and monosodium malate are presented in Figure 6. The top curves give the full spectra from 4800 cm^{-1} to 700 cm^{-1}, to have a bird's-eye view of the species spectra, to evaluate the continuum of absorption. The bottom curves give the spectra in the 2000−700 cm^{-1} region, to distinguish the details of the carbonyl region.

4.6.1. The Carbonyl Band: Position and Intensity. The carboxylic and carboxylate CO band positions and intensities are given in Table 5. The assignments of most of the bands are made with the use of glycine and malic acid.[6,27] This table give also the mean carbonyl band positions of 22 monocarboxylic and dicarboxylic acids, and their sodium salts.

For the acid species, the average carbonyl double bond ($\nu_{C=O}$) position is 1723 $\pm$ 12 cm^{-1}, with an approximate intensity of 0.25 molar au per vibrating group; the average single carboxyl bond (ν_{C-O}) position is located at 1257 $\pm$ 20 cm^{-1}, with an approximate ATR intensity of 0.20 molar au per vibrating group (see Figure 4B and Table 5). These values are comparable to those of Cabaniss et al.[37] The high position of the $\nu_{C=O}$ bands indicates that, for all these species, this group is not ionized: R−C(=O)−OH. This notwithstanding, the acetic and acrylic acid carbonyl bands are situated at 1706 and 1703 cm^{-1}, respectively. Compared to the average position of 1723 cm^{-1}, these low positions are attributed to the formation of dimers through hydrogen bonds that weaken the carbonyl bond.

The average position of the asymmetric ($\nu_{as}(COO^-)$) and symmetric ($\nu_s(COO^-)$) carbonyl bonds of the acid sodium salts are situated at 1579 $\pm$ 26 cm^{-1} and 1406 $\pm$ 12 cm^{-1}, with approximate intensities of 0.55 and 0.39 molar au per vibrating group, respectively (see Figure 5B and Table 5). Sodium acrylate has these bands situated at 1541 and 1427 cm^{-1}, respectively. The difference between these and the average values is due to the presence of a double bond (C=C), which increases the resonance between C=O and C−O groups. This weakens the $\nu_{as}(COO^-)$ and strengthens the $\nu_s(COO^-)$ bands.

For the zwitterionic molecules (betaine, glycine, and BOPA), the asymmetric ($\nu_{as}(COO^-)$) and symmetric ($\nu_s(COO^-)$) carbonyl bonds are situated at 1614 $\pm$ 7 cm^{-1} and 1402 $\pm$ 6 cm^{-1}, with approximate intensities of 0.47 and 0.40 molar au per vibrating group, respectively (see Figure 6B and Table 5). These values differ only slightly from the salt positions; therefore, they indicate that the behavior of the carbonyl groups is similar for these two ionic situations. However, the $\nu_{as}(COO^-)$ frequency is >30 cm^{-1} higher than the mean value, which indicates that a perturbation is acting on these molecules. This perturbation may originate from the presence of the N atom on these molecules or may be due to the net local charge on the ionized O atom that is not partly equilibrated by the surrounding cations. The situation is different for the aceto-acetate complex and monosodium malate (see Figure 6B_a and B_b), which is a situation that combines the acid and salt values.

For all the species studied, the ethoxy group ν(C−O−) in a noncarboxylic group (C−OC ethoxy or C−OH alcohol) is situated at 1094 $\pm$ 9 cm^{-1}, with an approximate intensity of 0.30 molar au per vibrating group.

The $\nu_{as}(COO^-)$ frequencies that have been obtained in the present study are plotted in Figure 7B against the pK_a value, along with the linear relation obtained by Cabaniss and McVey: $\nu_{as}(COO^-)$ (in cm^{-1}) = 1660 − 24.89 × pK_a.[37a] At pK_a < 5, our results follow the linear relationship. For pK_a > 5, $\nu_{as}(COO^-)$ remains almost unchanged near 1560 $\pm$ 25 cm^{-1}. This is because pK_a values above 5 are related to the charge lost on the N atom and not to the ionization of the carbonyl group that is already ionized. The $\nu_{as}(COO^-)$ frequency in a carboxylic group is strongly perturbed ($\Delta\nu$ is greater than +40 cm^{-1}) when in a zwitterionic molecule (betaine, glycine, and BOPA). Furthermore, the perturbation remains strong when two ionized carboxylic groups are present. These molecules have nitrogen with a positive charge; therefore, the perturbation of this mode may originate from this situation.

4.6.2. The CH Stretch Bands. The aliphatic CH stretch bands are situated in the 3100−2800 cm^{-1} region.[38] Because of the strong and large (3700−1700 cm^{-1}) OH stretch bands and weak CH band intensities, these are difficult to observe. Nevertheless, in frame A of Figures 4−6, we observe sharp weak bands in the CH region of some spectra that we assign to the asymmetric, symmetric CH_3 and CH_2, and CH stretch absorption. Their positions are given in Table 6. Malic acid (see Figure 4A_b) and sodium malate (see Figures 5A_b and 6A_b) do not show these bands, but the second-derivative techniques bring them out.[27] The same technique is used to determine the band positions of the other species. In Table 6, some of the bands are outside the normal regions of the aliphatic stretch bands. This is due to the perturbing nature of the adjoining groups. A complete evaluation of these is outside the scope of this study.

4.6.3. The OH Stretch Bands. The OH stretch bands of the carboxylic acids and their salts cover the region from 3700 cm^{-1} to 1700 cm^{-1} with large bands. Even at the lower-limit region, the absorption is not zero but it is weak. This indicates that the OH stretch absorption goes below 1700 cm^{-1}. On top of these bands are weak absorptions that we identified in the 2900 cm^{-1} region as the CH stretch bands (see previous discussion) and below 2800 cm^{-1} as combination bands. These bands are narrow

TABLE 5: CO Band Positions and Intensities of the Organic Acids in the 1800−800 cm^{-1} Region[a]

		st		def		st		def	def	st		def	st		def	def	st				st	def	st	
		–C=OOH		H_2O		–C=OO$^-$ asym		–NH_3 sc	CH_2 sc	–CO_2 symm		CH_2 r OH b	C–O			CNH_3 r CH_2 w	C–OH				CN CC	CH_2 tw CCOO w	CC, CN, CO	
species	formula	ν	I	ν	I	ν	I	ν	ν	ν	I	ν	ν	I	ν	ν	ν	I	ν	ν	ν	ν	ν	ν
BOPA H$^+$	$H_3C{\cdot}(CH_2)_3{\cdot}O{\cdot}(CH_2)_3\ NH^+(CH_2{\cdot}CO_2H)_2$, Cl^-	1734	0.46	1634	0.29								1259	0.48			1096	0.46						
BOPA$^\pm$	R–NH^+(COOH, COO^-)	1733	0.17	1650	0.04	1622	0.44			1397	0.39		1256	0.23			1095	0.33						
BOPA$^-$	R–$NH^+(COO^-)_2$, Na^+					1615	0.66			1399	0.52						1095	0.30						
BOPA^{-2}	R–$N(COO^-)_2$, $2Na^+$			1650	0.10	1575	0.77			1407	0.49						1094	0.35						
betaine acid	$(H_3C)_3{\cdot}N^+{\cdot}CH_2{\cdot}CO_2H$,$\cdot Cl^-$	1740	0.23	1635	0.15								1265	0.27	1223									
betaine$^\pm$	$(H_3C)_3{\cdot}N^+{\cdot}CH_2COO^-$					1615	0.44			1401	0.41	1337												
glycine acid	$NH_3^+CH_2COOH$, Cl^-	1736	0.20	1625	0.19			1524	1435			1379	1258	0.28		1137					1046			
glycine$^\pm$	$NH_3^+CH_2COO^-$			1640	0.05	1603	0.34	1510		1412	0.28	1331				1129					1033	928	897	
sodium glycinate	$NH_2CH_2COO^-$, Na^+			1646	0.07	1562	0.51		1343	1404	0.23	1316				1170				1082	1028	983	897	
acetic acid	CH_3COOH	1706	0.22	1647	0.10				1388				1271	0.21						1050	1015		886	
sodium acetate	CH_3COO^-, Na^+			1655	0.07	1548	0.43			1411	0.40	1346								1052	1020		928	
Ac–Ac, complex	CH_3COOH—CH_3COO^-, Na^+	1712	0.25	1646	0.15	1552	0.48			1416	0.43		1281	0.47										
malic acid	HO–(CHCOOH,CH_2COOH)	1721	0.38	1635	0.10				1402			1348	1274	0.27	1231	1194	1108	0.27	1273					
sodium malate	HO–(CHCOOH, CH_2COO^-), Na^+	1717	0.19	1640	0.05	1580	0.47			1400	0.30	1314	1270	0.23	1226	1190	1097	0.27	1273					
disodium malate	HO–($CHCOO^-$,CH_2COO^-), $2Na^+$			1652	0.05	1563	0.8			1395	0.55	1323				1193	1094	0.21			1046	963		
acrylic acid[b]	CH_2=CHCOOH	1703	0.25							1433	0.16		1238	0.2	1239	1184			1294					
sodium acrylate	CH_2=$CHCOO^-$, Na^+			1650		1541	0.54			1427	0.37	1361							1278	1061	992	965	896	841
trisodium citrate	HO–C(COO^-,(CH_2COO^-)$_2$), $3Na^+$			1650	0.07	1568	0.86			1390	0.69						masked		1280					
monochloroacetic acid (MCA)	Cl–H_2C–COOH	1725	0.23	1632	0.15				1414			1316	1215	0.26		1147				1277		934		
Na-MCA	Cl–H_2C–COO^-, Na^+					1589	0.49			1395	0.40									1257		943		
glycolic acid	HO–H_2C–COOH	1728	0.22	1635	0.10				1435			1356	1236	0.23			1091	0.30			998		888	
sodium glycolate	HO–H_2C–COO^-, Na^+			1655	0.10	1577	0.42		1360	1409	0.19				1235		1075	0.25	1325		1004		917	
	mean	1723	0.25	1643	0.11	1579	0.55	1517	1397	1406	0.39	1339	1257	0.28	1231	1168	1094	0.30	1287	1130	1020	953	901	841
	standard deviation	12	0.09	9	0.06	26	0.16	10	36	12	0.14	21	20	0.10	6	27	9	0.07	20	107	20	21	15	
	mean, Cabaniss et al.[c]	1719				1575				1377			1236											
	standard deviation	9				21				34			21											

[a] CO band positions given in units of cm^{-1}, and intensities given in units of molar absorbance units (au). Legend is as follows: asym, asymmetric; symm, symmetric; st, stretch; def, deformation; sc, scissors; r, rock; b, bend; tw, twist; and w, wag. [b] Pure anhydrous acrylic acid. [c] From ref 37.

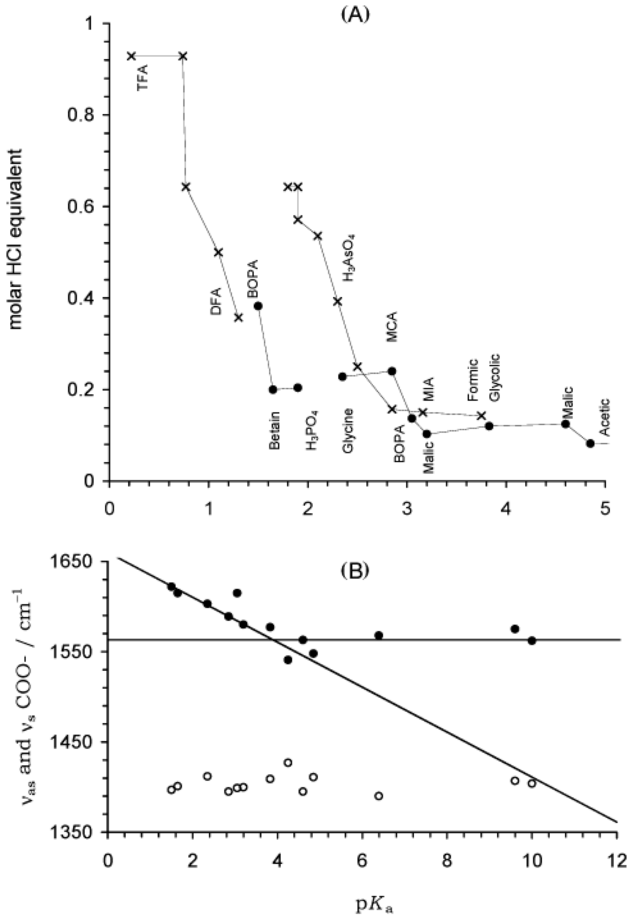

Figure 7. Relationship of pK_a with (A) acidic water (molar HCl equivalent or continuum of absorbance; (●) this work and (×) values from ref 26); (B) ν_{COO^-} ((●) asymmetric and (○) symmetric). Slanted straight line comes from the work of Cabaniss and McVey.[37a]

and weak; therefore, they do not bother our analysis of the OH stretch bands that are large and without much structure. The spectra of the acids, the salts, and the zwitterions and complex are presented on the top of Figures 4, 5, and 6, respectively. We could distinguish four large bands whose mean positions are located at 3391, 3022, 2584, and 2068 cm^{-1} with bandwidths of ~220 cm^{-1}. These values are large for two main reasons: (i) the hydrogen-bonding network weakens the OH force constant that causes many organizations, and (ii) as for the water situations,[12,29] the combination of the fundamental with the far-IR bands brings many satellites into the fundamental regions that broaden the bands. The bands are assigned in Table 7.

4.6.3.1. Carboxylic Acids. Figure 4 displays the spectra of the acid species. In these spectra, the carboxyl groups are not ionized (R−COOH). All the acids are in aqueous solutions, except acrylic, which is pure. This acid shows two broad, low-intensity bands, which are situated near 2900 and 2580 cm^{-1} (see Table 7). No absorption is observed near the OH stretch position of water and alcohol at 3391 cm^{-1}; therefore, the two bands must be assigned to the carboxyl OH stretch absorption. The difference of >450 cm^{-1} from the water OH stretch position indicates much stronger hydrogen bonding in the acid than in water. This indicates dimer or oligomeric formations, or both. The 2580 cm^{-1} band is approximately half the intensity of the 2900 cm^{-1} band; its greater displacement indicates stronger hydrogen bonding. On this basis, we assign the 2580 cm^{-1} band to the dimer and the 2900 cm^{-1} band to the oligomeric organization.

Although the other acids are in aqueous solutions, they show the same two bands at approximately the same positions as those for acrylic acid (see Figure 4 and Table 7) but with greater intensity. Since the spectra are molar, they indicate the presence of more OH bonds than in pure acrylic acid. These originate from their relation to the water molecules and would make hydrogen bonds with the acid carboxylic OH groups in close or open configurations for the 3022 and 3391 cm^{-1} bands, respectively.

The aqueous acids show two more bands near 3391 and 2068 cm^{-1}. The 3391 cm^{-1} band is near the OH stretch of pure water (~3320 cm^{-1}) or salt-solvated water (~3300 cm^{-1});[11,12] it is assigned to water that has not been strongly bonded to the carboxyl groups but bonded together. The 2068 cm^{-1} band is near the pure water 2100 cm^{-1} band and is assigned to the combination of the far-IR bands with the ν_2 frequency of water. This band in aqueous acids is broader than that in water, which indicates that the far-IR bands should also be broader than that in water.

4.6.3.2. Carboxylate Salts. The spectra of the sodium carboxylate salts are presented in Figure 5. The 2068 and 2584 cm^{-1} bands are absent. These salts are ionized because the carbonyl groups have two bands situated near 1579 and 1406 cm^{-1} (Table 5) that are typical of ionized groups (R−C═O O$^-$). The negative charge resonates between the two O atoms. Consequently, the absorption near 3391 and 3022 cm^{-1} is due to the solvated water, NH groups (glycine and BOPA), and OH alcohol (malic, glycolic). All these groups are hydrogen-bonded but less strongly than in the acid situation.

4.6.3.3. Zwitterions and Complex. The spectra of the aceto-acetic complex, sodium malate, betaine, glycine, and BOPA zwitterions are presented in Figure 6. The situation of the aceto-acetic complex, sodium malate, and BOPA monoacid are between the acid and salt situations because these molecules are half acids and half salts. Betaine is a zwitterion that has no OH group. Its spectrum (spectrum c in Figure 6) is almost the same as that of the salts (Figure 5). The glycine zwitterion (see spectra d and e in Figure 6) has three bands (at 3400, 3070, 2645 cm^{-1}) and a very small band (at ~2200 cm^{-1}). This zwitterion has no available OH group but does have three available NH groups. These could be responsible for the presence of the last two bands and the intensity of the 3070 cm^{-1} band, which is more intense than the other molecules of this series. The BOPA zwitterion is similar to that of glycine but with less-intense bands. This molecule has no available OH group but does have one available NH group.

4.6.4. Continuum of Absorbance. To evaluate the relationship between acidity and the continuum of absorption of the molecules, Leuchs and Zundel evaluated their intensities in terms of the HCl molar equivalent, as a function of pK_a.[25,26] The resulting relationship obtained for 14 species is plotted in Figure 7A. In the same fashion, we determined our series of carboxylic acids in terms of the HCl molar equivalent. The results given in Table 4 are plotted in Figure 7A. The results are comparable to those of Leuchs and Zundel. From this figure, we see that the variation in intensity of the acid continua is contrary to that of their pK_a values.

Because these acids are not deprotonated (the COOH groups are not ionized), the intensity of the continuum cannot be related to the acid anion and proton (H_3O^+), although the absorption pattern is similar. Therefore, it must be related to the hydrogen-bond network. The continuum is more intense when water is present, which is indicative that solvated water contributes to the continuum.

TABLE 6: Assignment of the CH Stretch IR Band Positions (in cm^{-1}) of Aqueous Carboxylic Species (1 M)[a]

species	formula	Comb. 3096−3000	Asymm. CH_3 2972−2952			Asymm. CH_2 2936−2916		CH 2899−2880	Symm. CH_3 2882−2862	Symm. CH_2 2863−2843	
BOPA H^+	$H_3C{\cdot}(CH_2)_3{\cdot}O{\cdot}(CH_2)_3NH^+(CH_2{\cdot}CO_2H)_2$, $\cdot Cl^-$	3010			2966	2938	2915		2877	2838	2815
$BOPA^{\pm}$	$R{-}NH^+(COOH, COO^-)$	3050			2963	2940	2910		2878	2850	2820
$BOPA^-$	$R{-}NH^+(COO^-)_2$, Na^+	3055			2965	2940	2907		2878	2850	2820
$BOPA^{-2}$	$R{-}N(COO^-)_2$, $2Na^+$	3100			2962	2939	2915		2876	2850	2815
betaine acid	$(H_3C)_3{\cdot}N^+{\cdot}CH_2{\cdot}CO_2{\cdot}H$, Cl^-		3060	3035	2993	2963					
betaine$^{\pm}$	$(H_3C)_3{\cdot}N^+{\cdot}CH_2COO^-$		3063			2970					
glycine acid	$NH_3^+CH_2COOHCl^-$	3010				2920					
glycine$^{\pm}$	$NH_3^+CH_2COO^-$					2970	2924				
sodium glycinate	$NH_2CH_2COO^-$, Na^+					2955	2935				
acetic acid	CH_3COOH		3020		2945						
sodium acetate	CH_3COO^-, Na^+										
Ac-Ac, complex	$CH_3COOH{:}CH_3COO^-$, Na^+		3010		2950						
malic acid	$HO{-}(CHCOOH,CH_2COOH)$					2940[b]		2895[b]		2840[b]	
sodium malate	$HO{-}(CHCOOH, CH_2COO^-)$, Na^+										
bisodium malate	$HO{-}(CHCOO^-,CH_2COO^-)$, Na^+					2970[b]		2925[b]		2889[b]	
acrylic acid[c]	$CH_2{=}CHCOOH$					2990		2935		2885	2805
sodium acrylate	$CH_2{=}CHCOO^-$, Na^+							2900			
trisodium citrate	$HO{-}C(COO^-,(CH_2COO^-)_2)$, $3Na^+$					2980	2935			2850	2815
monochloroacetic acid (MCA)	$Cl{-}H_2C{-}COOH$	3015				2960					2815
Na-MCA	$Cl{-}H_2C{-}COO^-$, Na^+					2960				2855	
glycolic acid	$HO{-}H_2C{-}COOH$					2925				2850	
sodium glycolate	$HO{-}H_2C{-}COO^-$, Na^+					2925				2850	
	mean	3040	3038	3035	2963	2952	2920	2914	2878	2855	2815
	standard deviation	36	27		15	21	11	19	1	16	5

[a] Assignment regions taken from Alpert et al.[38] [b] From second derivatives. [c] Pure anhydrous acrylic acid.

TABLE 7: Assignment of the OH Stretch IR Band Positions (in cm^{-1}) of Aqueous Carboxylic Species (1 M)

species	formula	$2\nu_{CO}$	ν_{O-H} (H_2O, $-CO_2H$, and R•O−H•R), ν_{N-H}	ν_{O-H} (carboxylic, hydrogen-bonded to water or other carboxylic groups)		H_2O comb.
BOPA H^+	$H_3C{\cdot}(CH_2)_3{\cdot}O{\cdot}(CH_2)_3NH^+(CH_2{\cdot}CO_2H)_2$, $\cdot Cl^-$		3410	2930	2560	1930
$BOPA^{\pm}$	$R{-}NH^+(COOH, COO^-)$		3400	∼2930	2560	1930
$BOPA^-$	$R{-}NH^+(COO^-)_2$, Na^+		3400			∼2140
$BOPA^{-2}$	$R{-}N(COO^-)_2$, $2Na^+$		3400	∼3100		∼2160
betaine acid	$(H_3C)_3{\cdot}N^+{\cdot}CH_2{\cdot}CO_2{\cdot}H$, Cl^-	3550	3400	∼2963	2550	1975
betaine$^{\pm}$	$(H_3C)_3{\cdot}N^+{\cdot}CH_2COO^-$		3320			2145
glycine acid	$NH_3^+CH_2COOHCl^-$	∼3500	3400	∼2965	2570	2010
glycine$^{\pm}$	$NH_3^+CH_2COO^-$		3400	3070	∼2645	∼2100
sodium glycinate	$NH_2CH_2COO^-$, Na^+		3350	3070	2645	2200
acetic acid	CH_3COOH		3450	3000	2612	2020
sodium acetate	CH_3COO^-, Na^+		3350	∼3100		2200
Ac-Ac, complex	$CH_3COOH{:}CH_3COO^-$, Na^+		3400	∼3100	2540	∼1935
malic acid	$HO{-}(CHCOOH,CH_2COOH)$		3500	2930	2580	1995
sodium malate	$HO{-}(CHCOOH, CH_2COO^-)$, Na^+		3400	2940	∼2540	−1960
bisodium malate	$HO{-}(CHCOO^-,CH_2COO^-)$, Na^+		3320	∼3000		2190
acrylic acid[a]	$CH_2{=}CHCOOH$			∼2900	∼2580	∼1950
sodium acrylate	$CH_2{=}CHCOO^-$, Na^+		3350	3120		2185
trisodium citrate	$HO{-}C(COO^-,(CH_2COO^-)_2)$, $3Na^+$		3350	∼3140		2180
monochloroacetic acid (MCA)	$Cl{-}H_2C{-}COOH$	3550	∼3420	3000	2575	1970
Na-MCA	$Cl{-}H_2C{-}COO^-$, Na^+	∼3620	3400	3000		2160
glycolic acid	$HO{-}H_2C{-}COOH$		3450	∼3100	2560	2000
sodium glycolate	$HO{-}H_2C{-}COO^-$, Na^+		3350	∼3000	2660	2165
	mean	3555	3391	3022	2584	2068
	standard deviation	49	44	75	40	105

[a] Pure anhydrous acrylic acid.

The absorption of the IR "continuum" was observed to be independent of the water/solute ratio (for a ratio sufficiently greater than 5). This indicates that there is a direct molecular relation between this continuous absorption and the carboxylic acid species with a fixed hydration number. The results of the present study confirm that the intensity of the continuum (evaluated as acidic water) decreases as the acid pK_a values increase.[26] Therefore, the IR measurements of the amount of acidic water gives an evaluation of the acid strength in water. Our results confirm that, at equivalent pK_a, the greater the number of OH acid groups in the acid, the greater the amount of acidic water present,[26] whereas the neat value per OH acid group seems to be only related to the corresponding pK_a value of the acid. An alcoholic OH group does not contribute to the acidic water. Finally, a molecular positive charge does not increase the intensity of the continuum, because of nondissociated OH acid groups, contrary to cases of negative charges.[26]

5. Conclusion

The present study shows that genuine results are obtained using a relatively inexpensive technique, compared to more-elaborate methods, such as neutron scattering. By adequately subtracting the water (acidic, basic, neutral, and saline) spectra of the solvent, we confirm, in this study, our previous results that flat baselines can be obtained directly without any artificial baseline correction. Even the OH stretch region, which is often overlooked because of the strong absorption of water, yield valuable quantitative information in all the IR regions: near-, middle-, and far-IR. Because IR spectroscopy is a technique that probes the species at the molecular level, we gain information at that level. Moreover, because this technique is a multispecies analytical tool, analytical protocols can be developed to give quantitative values on the fly for many substances in aqueous solutions. Compared to high-performance liquid chromatography (HPLC), which often requires >40 min to yield the same information, IR presents a real advantage.

Appendix A. Correction for Acidic and Basic Waters to Obtain Real Spectra of Solvated Species

An amount of 0.055 ± 0.005 mol/L equivalent HCl for each mol/L glycine zwitterion (Table 4) is subtracted to obtain spectrum D_z in Figure 1. Because this acidic water is solely due to the solvation of glycine zwitterion in water, it had to be added to spectrum D_z in Figure 1. Because the acidic water spectrum used is related to 1.54 M HCl, this spectrum, multiplied by (0.055/1.54), is added to spectrum D_z in Figure 1, yielding an intermediate spectrum. The acidic water spectrum contains part of a pure liquid water spectrum; thus, the latter was subtracted from the preceding intermediate spectrum, in accordance with the criterion listed in Section 2.1 for the maximum water spectrum subtraction. The resulting spectrum is displayed in spectrum d in Figure 6. The same strategy was applied to all solvated species spectra for which excess amounts of acidic or alkaline water were observed. Details are provided in the Supporting Information.

Appendix B. Hydration Number of Solute Species from IR Spectra

Previous work has given information about the hydration number of solute species from IR spectra.[27] After the acidic, basic, and pure water spectra are subtracted from the aqueous solution spectra, the resulting spectra indicate that water is still present. The hydration number of a solute species is defined as the amount of water strongly perturbed by the solute, giving a characteristic spectrum that is different from that of pure liquid water. To evaluate the hydration number, we calculate the exact composition of the species retrieved by FA. The principal water spectra (1.54 M HCl, 2.23 M NaOH, and 5.13 M NaCl) used for FA are not those of orthogonal species, because they contain some of the pure water spectra,[4,12] but their compositions are known.[32]

We extract the multiplying factors (MFs) related to the principal species spectra (Figures 4−6), $\mathbf{S}^{\mathrm{P}}$. Note that the carboxylic acid species spectra were normalized to 1.0 M (see Figures 4−6). The relationship between the experimental spectra used to calculate the principal ones ($\mathbf{S}_{\mathrm{P}}^{\mathrm{exp}}$) and principal spectra ($\mathbf{S}^{\mathrm{P}}$) is

$$\mathbf{S}_{\mathrm{P}}^{\mathrm{exp}} = \mathbf{P} \times \mathbf{S}^{\mathrm{P}} \tag{B1}$$

The MFs form matrix **P**. The principal spectra $\mathbf{S}^{\mathrm{P}}$ are obtained by multiplying both sides in eq B1 by the inverse of matrix **P**, giving

$$\mathbf{S}^{\mathrm{P}} = \mathbf{P}^{-1} \times \mathbf{S}_{\mathrm{P}}^{\mathrm{exp}} \tag{B2}$$

The water content of the principal solute species ($\mathbf{S}_i^{\mathrm{P}}$) is obtained by multiplying each coefficient of $\mathbf{P}^{-1}$ by the known water content of the corresponding experimental solution. The sums obtained by adding the results yield the water concentrations (in units of mol/L), and these, in turn, yield the hydration numbers when they are divided by the concentration of the solute species (1 mol/L). The error is greater on the hydration number of the acidic forms than on that of the anionic forms because in the former case, it is not possible to use the small water band near 3660 cm^{-1} for the water subtraction (criterion (i) in Section 2.1) that permit a more precise subtraction.

List of Symbols

BOPA = AH_2	*N,N*-(butyloxypropyl)amino diacetic acid, CH_3-$(CH_2)_3$−O−$(CH_2)_3$−N $(CH_2COOH)_2$
H^+AH_2	*N,N*-(butyloxypropyl)amino diacetic acid cation, R−$NH^+(CH_2COOH)_2$
AH_2 = H^+AH^-	*N,N*-(butyloxypropyl)amino diacetic acid zwitterion, R−$NH^+(CH_2COOH,CH_2COO^-)$
H^+A^{2-}	*N,N*-(butyloxypropyl)amino diacetic acid monoanion, R−$NH^+(CH_2COO^-)_2$
A^{2-}	*N,N*-(butyloxypropyl)amino diacetic acid dianion, R−N $(CH_2COO^-)_2$
Δ	Δ selects the counterion associated with dry BOPA, $\Delta = \pm 1$
α_1	mean number of counterions Na^+ associated with dry BOPA, $0 < \alpha_1 < 2$
α_{-1}	mean number of counterions Cl^- associated with dry BOPA, $0 < \alpha_{-1} < 1$
M_2	molar mass of BOPA in the neutral form (M)
M_Δ	mass added to the molar mass of BOPA when associated with the counterion
V	total volume of the sample (L)
A	total solute concentration in the sample (mol/L)
K_1, K_2, K_3	dissociation constants of BOPA in water
K_0	dissociation constant of water
δ	δ selects the titrant used: base, $\delta = +1$; acid, $\delta = -1$
ϵ_δ	relative concentration of the solution of titrant (w/w)
M_δ	molar mass of the titrant (M)
m_δ	mass of the titrant added to the sample (g)
ϵ_2	relative concentration of the stock solution of BOPA (w/w)
ρ_0	density of the stock solution of BOPA (g/L)
ρ	density of the sample (g/L)
ρ_δ	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)

Supporting Information Available: Description of the water spectrum subtraction methodology, spectra residues from

FA studies, and FA data (and corrections for acidic/basic waters) for various carboxylic acids (acetic acid, malic acid, betaine, and BOPA) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(33) The same situation prevails for all the carboxylic acid titrations presented here. Table 2 indicates that, in the titrant equivalent regions, where the solute does not overcome any change in its ionic form, the acidic and basic water slopes have the near unity values of −1 and +1, respectively. Therefore, as observed for glycine 1.33 M titration, the water subtraction procedure in these titrant equivalent regions accurately follows the addition of HCl (decreasing titrant equivalent below the limiting value corresponding to the most cationic form of the solute) or NaOH (increasing titrant equivalent above the limiting value corresponding to the most anionic form of the solute).

(34) The same is true for alkaline solutions: the continuous absorption measured as NaOH molar equivalent increases in proportion to the added NaOH after the neutralization is completed (see Figure 3).

(35) The curves obtained from eq 1 are not shown.

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