

Effects of Salts, Acids, and Phenols on the Hydrogen-Bonding Structure of Water–Ethanol Mixtures

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The effects of salts, acids, and phenols on the hydrogen-bonding structure of water in 20% (v/v) EtOH–H₂O solution were investigated on the basis of ¹H NMR chemical shifts of the OH of water and ethanol. It was found that many salts caused structure breaking of water while a few metal salts, such as MgCl₂ and KF, had a strengthening effect. The OH proton chemical shifts caused by the presence of alkali-metal and alkaline-earth-metal ions or anions (halides, NO₃[−], ClO₄[−], SO₄^{2−}) from strong acids were related to the sizes and charges of the ions. Not only acids (H⁺ and HA, undissociated acids) but also bases (OH[−] and A[−], conjugate-base anions from weak acids) had the effect of strengthening the structure of water; the degree of the effect was dependent on the acid strength (pK_a). The proton exchange between water and ethanol molecules in 60% (v/v) EtOH–H₂O solution was examined, on the basis of the coalescence of two signal peaks of water and ethanol as well as the further low-field shift in ¹H NMR spectra with increasing concentration of solutes. Although it has been already reported that the proton exchange between water and ethanol molecules is promoted by strong acids and bases, a distinct proton exchange was also observed in the neutral solution, i.e., by the addition of phosphate pH buffer solution (pH 6.86). It was also discovered that NaCl had the effect of breaking the structure of water in 20% (v/v) EtOH–H₂O solution; however, in 60% (v/v) EtOH–H₂O solution the same salt at lower concentrations strengthened the water–ethanol structure, promoting the proton exchange between water and ethanol molecules. Hydrogen bond donors as well as acceptors seemed to cause the intimate (or tight) interaction between H₂O and EtOH molecules even in alcoholic beverages.

Introduction

The study of water and ethanol has attracted many solution chemists. The structural properties of the mixtures of water and ethanol have been reviewed by Franks and Ives.¹ They examined the “abnormalities” shown by the alcohol–water mixtures in classical physicochemical and thermodynamic properties. Coccia et al.² investigated chemical shifts and line shapes in ¹H NMR spectra over the entire composition range of the two cosolvents at 20 °C. Wen and Hertz³ investigated the effect of alcohols on the structure of solvents in mixed solvents; they paid attention to the contribution of polar and nonpolar groups. By means of the mass spectrometric technique, Nishi et al.⁴ examined the properties of clusters composed of water–ethanol and ethanol–ethanol in water–ethanol mixtures. The ¹H NMR chemical shift values have been reported for aqueous binary mixtures of DMSO, acetone, and *tert*-butyl alcohol.⁵

The degree of hydrogen bonding in pure water has been experimentally examined with ¹H NMR chemical shifts.^{6,7} Other studies have also been reported for the relation between the degree of hydrogen bonding in water and the temperature.^{8–12} It has been concluded that water being a liquid phase still keeps hydrogen bonds as the state of ice and the degree of the bonds changes with the temperature. Hindman⁶ assumed that water is

an equilibrium mixture of a hydrogen-bonded icelike species and a monomer species. Samoilov¹³ and Narten et al.¹² proposed an ice I model containing vacancies and interstitial molecules. Pauling¹⁴ suggested that liquid water may have a clathrate structure similar to that of the gas hydrates. Nemethy and Scheraga⁸ proposed a model of water containing a cluster structure and a monomer molecule with statistical thermodynamic theories; the size of the clusters has been reported.¹⁵ With ¹H NMR^{16,17} and ¹⁷O NMR¹⁸ chemical shifts, the effects of some salts and acids on the hydrogen-bonding structure of water have been examined.

The water–ethanol mixture is one of the most familiar solvents to human beings in the form of alcoholic beverages. Alcoholic beverages are luxury goods; sufficient studies have been done on their flavor and taste components; however, only a few studies on the “structure” of water and ethanol have been reported.^{19–21} In whiskey, which needs a long-term maturation process in wood barrels or casks, the reduction of the stimulative taste of ethanol after maturation has been regarded as the result of tight association between water and ethanol molecules.²² Despite all these studies on the relation between the maturation and the structure of water and ethanol in distilled liquors, we can hardly find a study on the structure of water and ethanol in brewed liquors such as beer, wine, and Japanese sake, which usually need no long-term maturation. These liquors include various kinds of components, especially acidic and phenolic

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components (concerned much to the taste) other than water and ethanol. It may be quite natural to explore whether such components can affect the structure of water and ethanol in alcoholic beverages.

In the present paper, the effects of acids, phenols, or salts on the hydrogen-bonding structure of water (and ethanol) were examined by analyzing the chemical shift of ¹H NMR mainly in 20% (v/v) EtOH–H₂O solution. For the effects of solutes on the proton exchange between water and ethanol, 60% (v/v) EtOH–H₂O solutions were utilized. The effects of some acids, esters, or aldehydes, which are sparingly soluble in lower alcoholic content solution, were examined in 60% (v/v) EtOH–H₂O solutions. One of our goals is to make it clear how acids or phenols, which are the essential components of alcoholic beverages, affect the hydrogen-bonding structure among water and ethanol molecules. Our final destination is to elucidate the common principle lying in the “aging”, “maturation”, or origin of mellowness of every kind of alcoholic beverage.

Experimental Section

Procedure. ¹H NMR chemical shifts of the hydroxyl groups in EtOH–H₂O solutions containing acids or salts were obtained with a JEOL JNM-LA 400 NMR spectrometer at 25 ± 0.1 °C in Wilmad coaxial tubes. D₂O (99.9% D, Aldrich) in the inside tube served as the locking solvent. According to the method of Wen and Hertz,³ the chemical shift of the hydroxy proton resonance was determined relative to the peak due to the methyl group of EtOH. The center peak of the triplet peak of the methyl group was utilized as the standard (CH₃, 1.164 vs TMS). Incidentally, Funasaki et al.²³ reported NMR chemical shift references in aqueous solution. Mizuno et al.^{5,24} also demonstrated that ¹H chemical shifts of CH₃ protons are dependent on the composition of solvents. Our measurements have been carried out for solutions of constant EtOH–H₂O composition. So, in our case, the position of the CH₃ protons of ethanol is reliable enough as an internal standard to investigate the effects of various kinds of solutes. The chemical shifts per 1.0 mol dm⁻³ solutes were estimated after confirmation of the linearity between chemical shifts and their concentrations. In the 20% (v/v) EtOH–H₂O solution, the OH peaks of water and ethanol are observed as a single peak; i.e., the OH peaks cannot be given separately. In 60% (v/v) EtOH–H₂O solution, on the other hand, two OH peaks appear separately; the proton chemical shift of the water is observed at higher magnetic field than that in 20% (v/v) EtOH–H₂O solution.²

Chemicals. Commercially obtained acids of analytical grade were used without further purification: acetic (99.0%, Nacalai), propionic (98%, Wako), L-(+)-lactic (98%, Sigma), succinic (99%, Aldrich), malic (99%, Aldrich), L-(+)-tartaric (99.5%, Wako), citric (98%, Wako), trifluoroacetic (99.5%, Aldrich), methanesulfonic (98%, Wako), chloroacetic (99%, Wako), dichloroacetic (98%, Wako), trichloroacetic (99.0%, Wako), benzoic (99.5%, Wako), gallic (97%, Aldrich), vanillic (98%, TCI), syringic (97%, TCI), 2-hydroxybenzoic (99.5%, Wako), 3-hydroxybenzoic (98.0%, TCI), and 4-hydroxybenzoic (98.0%, TCI) acids. Other acids and chemicals were also of analytical grade: tannic acid (ACS reagent, Aldrich), (–)-epigallocatechin gallate (95.0%, Sigma), chlorogenic acid (predominantly the *trans* form (extracted coffee seeds), 99%, ACROS), phosphoric acid, crystals (99.999% Aldrich), methyl 3,4,5-trihydroxybenzoate (98%, Aldrich), phenol (99%, Wako), pyrogallol (99%, Wako), vanillin (98.0%, Wako), syringaldehyde (98%, TCI), NaOH (Wako, GR grade), pH 6.86 buffer solution (0.025 mol dm⁻³ KH₂PO₄ and 0.025 mol dm⁻³ Na₂HPO₄,

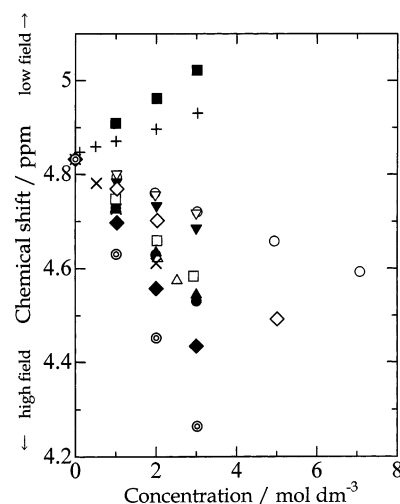


Figure 1. OH proton chemical shifts in 20% (v/v) EtOH–H₂O mixtures containing various salts: (○) LiCl; (●) NaCl; (△) KCl; (▲) RbCl; (□) CsCl; (■) MgCl₂; (▽) CaCl₂; (▼) NH₄Cl; (◇) LiBr; (◆) NaBr; (×) LiI; (⊙) NaI; (+) KF.

Wako, JCSS), C₂H₅OH (Wako, GR grade), 2,2,2-trifluoroethanol (98.5%, Wako), 1,1,1,3,3,3-hexafluoro-2-propanol (99.8%, Aldrich), NH₄Cl (99%, Wako), Me₄NBr (98%, Aldrich), Et₄NBr (Wako), Pr₄NBr (98%, Aldrich), sodium methanesulfonate (98%, Aldrich), sodium trifluoroacetate (98%, Aldrich), sodium chloroacetate (98%, Aldrich), sodium acetate (98.5%, Wako), sodium propionate (97.0%, Wako), sodium benzoate (98.0%, Wako), *p*-nitrophenol sodium salt (TCI), *o*-nitrophenol sodium salt (99%, TCI), sodium phenoxide trihydrate (99%, Aldrich). Commercially obtained inorganic salts of analytical grade were used as received. Bu₄NBr was prepared as described previously.²⁵ Sodium dichloroacetate and trichloroacetate were prepared following the method for sodium acetate.²⁶ Water was purified by means of the MilliQ system (Millipore Corp.).

Results and Discussion

1. Effects of Salts. Figure 1 shows the OH proton chemical shifts in 20% (v/v) EtOH–H₂O solution containing various kinds of metal halides. Only MgCl₂ and KF caused the chemical shift of the OH proton to shift toward low field, while all the other salts caused a high-field shift, compared with the water–ethanol solvent without salts. The contribution of each ion from the salts was evaluated following the method of Hindman:¹⁶ the value of the chemical shift caused by the NH₄⁺ ion was assumed to be zero. Thus, from the shift value of –0.048 caused by 1.0 mol dm⁻³ NH₄Cl, compared with that of no salt solution, the value for the 1.0 mol dm⁻³ chloride ion was attributed to be Δδ(Cl⁻) = –0.048 because of Δδ(NH₄⁺) = 0.

Figure 2 shows the relation between the chemical shifts (Δδ) caused by ions at (or per) 1.0 mol dm⁻³ and the crystal ionic radii^{27–29} per electric charge (*r/z*). Each ion of Mg²⁺, Ca²⁺, Li⁺, F⁻, or SO₄²⁻ caused a low-field shift, while all the other ions analyzed caused a high-field shift. Linear relations were found between the chemical shifts and *r/z* not only for metal cations (Mg²⁺, Ca²⁺, Li⁺, Na⁺) but also for anions (F⁻, Cl⁻, Br⁻, I⁻, ClO₄⁻, NO₃⁻, SO₄²⁻). As for alkali-metal ions of larger ionic sizes, Na⁺, K⁺, Rb⁺, and Cs⁺, the chemical shifts remained a constant value; the chemical shift value at 1.0 mol dm⁻³ of Na⁺ was evaluated to be –0.056 (Δδ(Na⁺) = –0.056) in 20% (v/v) EtOH–H₂O solution.

Coccia et al.² have reported that the structure of water is strengthened by the presence of small amounts of ethanol,

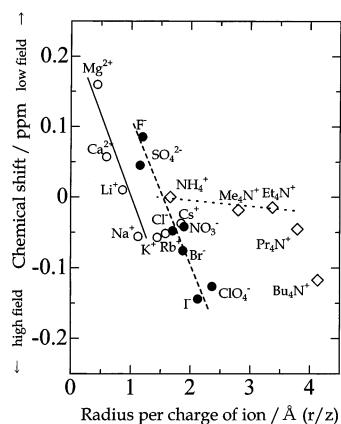


Figure 2. Relationship between the OH proton chemical shift and the crystal ionic radius per charge (r/z): (○) metal cations; (●) anions; (◇) ammonium ions.

accompanied by the formation of new water–ethanol H-bonds or the increased water–water association in the region of the ethanol mole fraction, 0–0.08, in water–ethanol mixtures. The 20% (v/v) ethanol content in water–ethanol mixtures at 25 °C corresponds to an ethanol mole fraction of 0.069, where the water structure is most strengthened in all ranges of ethanol content. As shown with the model of Frank and Wen,³⁰ the hydrating power for ions in aqueous solution becomes stronger as the radius of ions (per charge) decreases, and vice versa. Proton NMR chemical shifts may account for the average property or condition of water with ions. In 20% (v/v) EtOH–H₂O solution, almost all the salts, excluding MgCl₂ and KF, caused high-field chemical shifts, which should result in weakening of the water structure. As shown in Figure 2, the effect of strengthening the water structure was recognized for some ions, Mg²⁺, Ca²⁺, Li⁺, F[−], and SO₄^{2−}, the radii per charge of which are rather small (less than 1 Å for metal ions). Recently, on the basis of Raman spectra, the structure-breaking effects of anions (Cl[−], Br[−], I[−], ClO₄[−], NO₃[−]) on the hydrogen-bonded structure in alcoholic solutions were reported.³¹

The observed effects of the salts or ions on the water structure in 20% (v/v) EtOH–H₂O solution have the same tendency as observed in pure water.^{16,17,32,33} Therefore, the structure of water in 20% (v/v) EtOH–H₂O solution should be subject to effects of salts similar those in (pure) water despite the fact that the structure of water in 20% (v/v) EtOH–H₂O solution is beforehand strengthened in the presence of ethanol. The chemical shift values caused by the Me₄N⁺ and the Et₄N⁺ ions were nearly zero (Figure 2), supporting the assumption that the value of the NH₄⁺ ion is 0. However, the larger tetraalkylammonium ions, Pr₄N⁺ and Bu₄N⁺, caused structure-breaking effects in the solution at higher concentrations. We have demonstrated the breakdown of the water structure in the presence of concentrated Et₄NBr in D₂O by means of Raman spectroscopy,³⁴ although tetraalkylammonium (R₄N⁺) salts are usually regarded as having structure-making properties because of their “hydrophobic” effects.

2. Effects of Acids and Phenols. *2.1. Chemical Shifts Caused by the Addition of Acids.* The effects of carboxylic and other acids on the OH proton chemical shifts in 20% (v/v) EtOH–H₂O solution were also investigated (Figure 3). All the acids examined caused low-field shifts in proportion to their concentrations. In Table 1 are listed the chemical shift values caused by these acids at (or per) 1.0 mol dm^{−3}. The chemical shift of an acid may be divided into two factors: the undissociated acid molecule (HA) and H⁺ from the acid. The value of the chemical shift caused by the proton ([H⁺] = 1.0 mol dm^{−3}) was

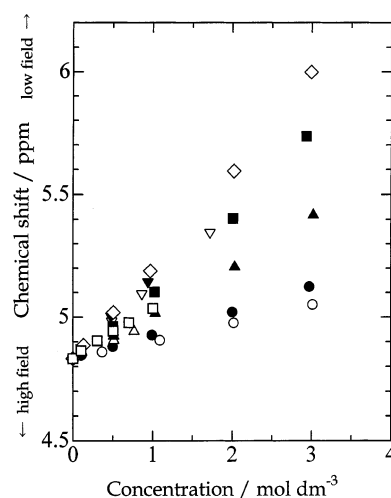


Figure 3. OH proton chemical shifts in 20% (v/v) EtOH–H₂O mixtures containing various acids: (○) acetic acid; (●) lactic acid; (Δ) succinic acid; (▲) malic acid; (□) tartaric acid; (■) citric acid; (▽) phosphoric acid; (▼) trifluoroacetic acid; (◇) methanesulfonic acid.

determined to be 0.424 ($\Delta\delta(\text{H}^+) = 0.424$). The proton concentrations dissociated from 1.0 mol dm^{−3} weak acids in the solution were evaluated by adopting dissociation constants of acids in pure water. The contribution of the proton to the whole value of the chemical shift of an acid was properly dependent on the acidity. The ratio of the contribution of the proton to the whole value of an acid was at most 3–7% for acetic and succinic acids and α -hydroxy acids. These acids have carboxyl groups and/or hydroxyl groups. The value of the chemical shift based on a carboxyl group (–COOH) was estimated to be 0.069 by subtracting the contribution of the proton (0.002) from the value of the chemical shift caused by 1.0 mol dm^{−3} acetic acid (0.071). Lactic acid has one carboxyl group and one hydroxyl group. So, by subtracting the chemical shift based on undissociated acetic acid (0.069) from the chemical shift based on undissociated lactic acid (0.086), the value of the chemical shift based on a hydroxyl group (–OH) was defined as 0.017. Using these values for the carboxyl group and hydroxyl group, the values of the chemical shift of succinic acid (number of –COOH groups/number of –OH groups = 2/0) and α -hydroxy acids, i.e., malic (2/1), tartaric (2/2), and citric (3/1) acids, were calculated according to the number of these two groups in each acid molecule. The calculated value for each acid was found to be close to the observed one. A similar consistency was found for the chemical shift value based on the whole acid, which should include the small contribution of the proton (cf. Table 1). As a summary of the above sections, in 20% (v/v) EtOH–H₂O solutions, acids strengthen the water structure, while salts (except for a few salts) weaken the structure.

2.2. Relation between Chemical Shifts and pK_a Values of Acids. The relation between OH proton chemical shifts and pK_a values of acids was investigated for acetic, chloroacetic, dichloroacetic, and trichloroacetic acids. Figure 4 shows the OH proton chemical shifts in 20% (v/v) EtOH–H₂O solutions caused by 1.0 mol dm^{−3} acids. In principle, with the smaller pK_a , the larger shift toward low field was observed among the chloroacetic acids (entry numbers 3–5). As for conjugate-base anions of acids (evaluated from the data of CH₃COONa, for instance), the values shifted toward higher field as the basicities of the conjugate-base anions decreased: the values of pK_a of the mother acids become smaller.

Similar examinations were performed for many acids and phenols with various acidities as follows: methanesulfonic (pK_a

TABLE 1: OH Proton Chemical Shifts in 20% (v/v) EtOH–H₂O Mixtures for Various Acids and Contributions through H⁺ or Undissociated Acid Molecules (HA)

component	pK _a in H ₂ O ^a	chemical shift value ^b (ppm)					
		whole acid		HA		H ⁺ ^c	H ⁺ /whole acid (%)
		obsd	estimated ^d	obsd	estimated ^d		
acetic acid	4.75	0.071	(0.071)	0.069	(0.069)	0.002	2.5
lactic acid	3.86	0.091	(0.091)	0.086	(0.086)	0.005	5.5
succinic acid	4.16, 5.61	0.134	0.142	0.130	0.138	0.004	2.6
malic acid	3.40, 5.11	0.192	0.162	0.184	0.155	0.008	4.3
tartaric acid	2.98, 4.34	0.191	0.182	0.177	0.172	0.014	7.1
citric acid	3.14, 4.77, 6.39	0.263	0.233	0.252	0.224	0.011	4.3
phosphoric acid	2.12, 7.21, 12.67	0.294		0.259			
trifluoroacetic acid	0.30	0.319		0.107			
methanesulfonic acid	−1.20	0.375 ^e		0			

^a Reference 35, except for trifluoroacetic acid (ref 36) and lactic and methanesulfonic acids (ref 37). ^b $\Delta\delta$ per 1.0 mol dm^{−3} acid. ^c The contribution through H⁺; the equilibrium concentration of H⁺ was calculated with the pK_a in H₂O (cf. the text). ^d Estimated by the values of acetic and lactic acids with the assumption of additivity for −COOH and −OH. ^e The complete dissociation was assumed; $\Delta\delta(\text{H}^+) + \Delta\delta(\text{CF}_3\text{SO}_3^-) = 0.375$, where $\Delta\delta(\text{H}^+) = 0.424$ and $\Delta\delta(\text{CF}_3\text{SO}_3^-) = -0.049$.

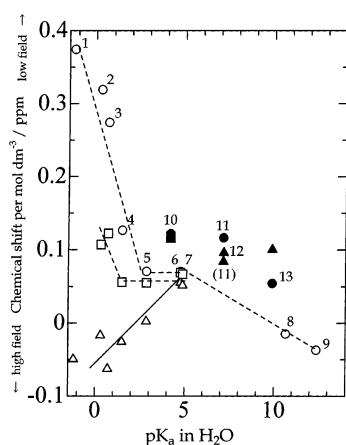


Figure 4. OH proton chemical shifts in 20% (v/v) EtOH–H₂O mixtures containing acids and conjugate-base anions as a function of pK_a in H₂O: (○) acids; (□) evaluated values for undissociated acids; (△) conjugate-base anions (solid symbols show acids having a benzene ring); (1) methanesulfonic acid; (2) trifluoroacetic acid; (3) trichloroacetic acid; (4) dichloroacetic acid; (5) chloroacetic acid; (6) acetic acid; (7) propionic acid; (8) 1,1,1,3,3,3-hexafluoro-2-propanol; (9) 2,2,2-trifluoroethanol; (10) benzoic acid; (11) *p*-nitrophenol; (12) *o*-nitrophenol; (13) phenol.

= −1.2), trifluoroacetic (pK_a = 0.3), benzoic (pK_a = 4.20), and propionic (pK_a = 4.87) acids, *p*-nitrophenol (pK_a = 7.15), *o*-nitrophenol (pK_a = 7.17), phenol (pK_a = 9.89), 1,1,1,3,3,3-hexafluoro-2-propanol (pK_a = 10.66: Henne, A. L.; Francis, W. C. *J. Am. Chem. Soc.* **1953**, *20*, 991), and 2,2,2-trifluoroethanol (TFE; pK_a = 12.37).³⁸ Results on these components were also plotted in Figure 4. Chemical shifts caused by acids (excluding acids having a benzene ring, shown in solid symbols) were almost constant in the region where pK_a is from 2.5 to 5.0. With values of pK_a lower than 2.5, the values for acids shifted linearly to low field. With pK_a values larger than 10, on the other hand, the chemical shift of an acid seemed to shift toward higher field and the value turned to a negative one. Harris et al.³⁹ have reported the ¹H chemical shift of H₂O in water–TFE mixtures.

It may be of interest to point out that the pK_a value of NH₄⁺ in H₂O is close to 10; the shift value of NH₄⁺ is assumed to be zero, as mentioned previously. Although the effects of the conjugate-base anions were found to be close to those of the mother acids around a pK_a of 5.0, the anions seemed to lose their structure-making effects with decreasing pK_a value. Some acids and phenols, such as benzoic acid and nitrophenols, gave

apparently a larger effect (+0.05 ppm) than acids without a benzene ring.

Although there would be several factors in the effect of acids on the structure of water, such as the steric structure of molecules, the kind of groups, and the strength of polarity, we demonstrated that the effects of acids as well as conjugate-base anions or the contribution of undissociated acids can be related to pK_a (in H₂O solution). Strong acids expressed by small pK_a values (less than zero) are thought to dissociate completely, and the conjugate-base anions from them have no ability to accept the proton, which may result in breaking the structure of water. In fact, the chemical shift value of the conjugate-base anion of methanesulfonic acid is around −0.05, and this value is nearly the same as the value of Cl[−] or Br[−] (cf. Figure 2).

From the above results, it can be suggested that, through donating the proton, acids exhibit an ability to strengthen the water structure while conjugate-base anions do through accepting the proton. In the X-ray diffraction study of tetrabutylammonium benzoate hydrate (Bu₄NC₆H₅COO·39.5H₂O), Bonamico et al.⁴⁰ have concluded that the oxygen atoms of the benzoate anions are hydrogen-bonded to the water framework and form part of the polyhedral structure. Engel and Hertz⁴¹ have reported that the anions HCOO[−], CD₃COO[−], CF₃COO[−], and CCl₃COO[−] showed a structure-forming effect in aqueous solutions. In 20% (v/v) EtOH–H₂O solution, the salt effects on the water structure were found to be related to crystal ionic radii and ionic charges. In this case, no proton transfer with cations or anions should be concerned. As for the effects of weak acids (HA) or of the salts from weak acids (NaA), however, the hydrogen-bonding interaction and proton-transfer with acid molecules or conjugate-base anions seem to play an important role.

Table 1 has verified that the estimated values for succinic acid and α -hydroxy acids are close to the observed ones. The pK_a values of these acids are around 3–6. As shown in Figure 4, the chemical shift values of the monoprotic acids were almost constant in this pK_a range. Accordingly, the reason for the accordance between the estimated and the observed values in the di- or triprotic acids should be brought by the fact that the carboxyl group or the hydroxyl group of each acid exhibits an almost constant value of chemical shift likewise as the result with the monoprotic acids (acetic and lactic acids).

2.3. Effects of Benzenecarboxylic Acids and Phenols in 20% and 60% (v/v) EtOH–H₂O Solutions. Figure 5 shows the effects of benzenecarboxylic acids and phenols on OH proton chemical shifts in 20% (v/v) EtOH–H₂O solution. Phenol and pyrogallol caused a low-field shift of the OH proton to a small extent.

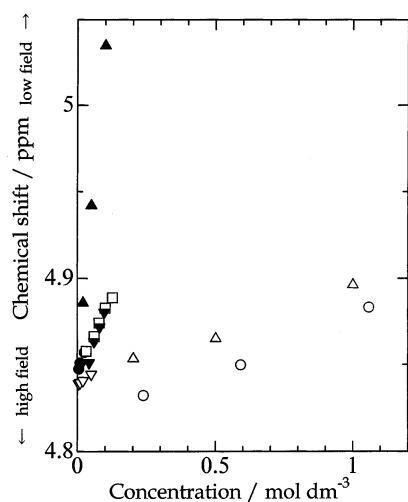


Figure 5. OH proton chemical shifts in 20% (v/v) EtOH–H₂O mixtures containing phenols or acids having benzene rings: (○) phenol; (△) pyrogallol; (▽) benzoic acid; (□) gallic acid; (●) epigallocatechin gallate; (▲) tannic acid; (▼) chlorogenic acid.

TABLE 2: OH Proton Chemical Shifts in 60% (v/v) EtOH–H₂O Mixtures Containing Acids and Aldehydes Having a Benzene Ring

component	pK _a in H ₂ O	chemical shift value ^a (ppm)
gallic acid	4.46 ^b	0.348
methyl 3,4,5-trihydroxybenzoate	8.87 ^c	0.099
vanillic acid	4.47 ^c	0.261
vanillin	7.62 ^c	0.114
syringic acid	4.34 ^b	0.250
syringaldehyde	7.62 ^c	0.070
benzoic acid	4.20 ^b	0.231
2-hydroxybenzoic acid	2.96 ^d	0.327
3-hydroxybenzoic acid	4.07 ^c	0.326
4-hydroxybenzoic acid	4.58 ^c	0.312

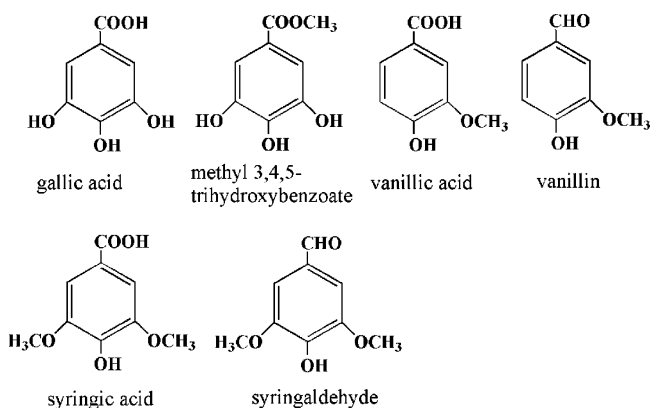
^a $\Delta\delta$ per 1.0 mol dm⁻³ acid, ester, or aldehyde. ^b Reference 42. ^c Reference 43. ^d Reference 44.

However, the other acids or “polyphenols”, such as gallic and chlorogenic acids and epigallocatechin gallate, caused a low-field shift to a great extent; e.g., $\Delta\delta = 0.363$ for 1.0 mol dm⁻³ gallic acid. An extremely large value ($\Delta\delta = \text{ca. } 2.0$) was given by tannic acid, the ester of a glucose with many gallic acids (molecular weight of 1701.23).

Next, the effects of substituent groups in benzene rings were examined in 60% (v/v) EtOH–H₂O solution. In Table 2 are listed the OH proton chemical shifts of 1.0 mol dm⁻³ acids, an ester, and aldehydes (cf. Chart 1). The value of the chemical shift of gallic acid (0.348) was more than 3 times as large as that of methyl 3,4,5-trihydroxybenzoate in which the carboxyl group was replaced with an ester group. The value of vanillic acid is larger (ca. 0.15) than that of vanillin, and a similar difference was observed between syringic acid and syringaldehyde. The existence of a carboxyl group on a benzene ring should cause a drastic low-field shift of the OH proton. Indeed, aldehydes give distinct chemical shifts toward low field, though.

Gallic acid has three hydroxyl groups in the compound, while two hydroxyl groups are replaced with methoxyl groups in syringic acid. The value of the chemical shift of syringic acid (0.250) was smaller than that of gallic acid or 4-hydroxybenzoic acid (0.312). The value of the chemical shift of syringaldehyde (0.070) was smaller than that of vanillin (0.114). These data suggest that methoxyl groups (hydrophobic groups) on a benzene ring can bring about the breaking of the water–ethanol

CHART 1: Structural Formulas of the Acids and Aldehydes for Which Data Are Shown in Table 2



structure. In fact, a methoxyl group on the benzene ring was found to reduce the OH proton chemical shift value by >0.04 .

Hydroxybenzoic acids, 2-, 3-, and 4-derivatives, have a hydroxyl group at the ortho, meta, and para positions, respectively, of benzoic acid. However, regardless of the substituted position, these three acids gave larger values of the chemical shift than benzoic acid (0.231). The existence of a hydroxyl group on the benzene ring of benzoic acid caused an additional chemical shift (ca. 0.1) toward low field without changing the pK_a so much, except for the 2-derivative (cf. Table 2).

2.4. Relation between Chemical Shifts and Ethanol Content. Figure 6 shows the OH proton chemical shifts caused by 1.0 mol dm⁻³ acetic, benzoic, and gallic acids and phenol in different ethanol contents. The values of the chemical shift of acetic acid remained constant in the region from 3.0% to 40% (v/v), and then the values increased with increasing ethanol content at $\geq 60\%$ (v/v). However, the values of the chemical shift of benzoic acid increased with the ethanol content at the beginning. Contrastively, the chemical shift values of gallic acid and phenol did not vary so much in the whole ethanol content range, although values at 3.0% (v/v) and pure ethanol were a little smaller than those at the other contents.

The chemical shift value for gallic acid or phenol was not as affected by the ethanol content as the other acids without the hydroxyl group. The hydroxyl group in gallic acid seemed to not only contribute to strengthening of the hydrogen-bonding structure by itself but also support an appropriate interaction between the acid and the solvent (cf. Chart 2). Thus, gallic acid may exhibit its effective ability of strengthening the structure of water (and ethanol) at any ethanol content.

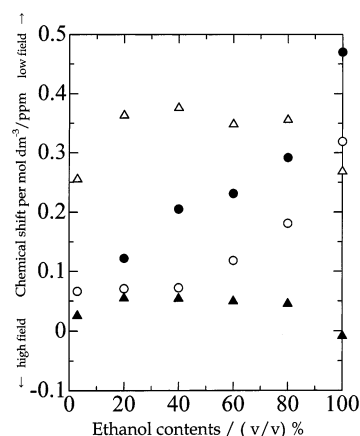
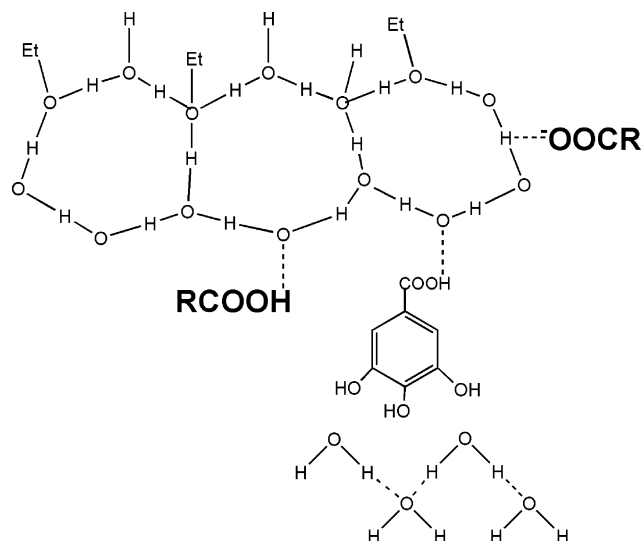


Figure 6. OH proton chemical shifts in EtOH–H₂O mixtures containing acids as a function of ethanol content: (○) acetic acid; (●) benzoic acid; (△) gallic acid; (▲) phenol.

CHART 2: A Model for the Intimate Association among Water and Ethanol Molecules with the Assistance of Stronger Hydrogen-Bonding Donors (Acids) or Acceptors (Conjugate-Base Anions)



3. Proton Exchange between Water and Ethanol. 3.1.

Effects of Acids and Phenols. At first, phenol of a wide concentration range was examined for the exchange of OH protons of water and ethanol in 60% (v/v) ethanol solution. The 60% (v/v) ethanol content in a water–ethanol mixture at 25 °C corresponds to an ethanol mole fraction of 0.31. The OH peak of ethanol was located at a much lower field ($\delta = 5.38$) than that of water ($\delta = 4.73$). As the phenol concentration increased, the peak of water shifted toward lower field and the peak of ethanol shifted oppositely. When the phenol concentration reached 1.5 mol dm^{-3} , the proton exchange between water and ethanol was much promoted: the two peaks coalesced to a single peak in the spectrum. The merged peak shifted to lower field as the phenol concentration increased further. For pyrogallol, the chemical shift jumped up and two peaks merged at $1.0 \times 10^{-1} \text{ mol dm}^{-3}$ (cf. Figure 7). We note that the merged signal was observed as a very broad peak when a small amount of the acidic component was added; however, the half-width of the peak decreased suddenly with further addition of the component.

Similar analyses were performed for acids: acetic, benzoic, and gallic acids showed similar behaviors. In the solution containing a concentration of an acid of $1.0 \times 10^{-5} \text{ mol dm}^{-3}$ and less, both peaks of water and ethanol existed still separately. At $1.0 \times 10^{-4} \text{ mol dm}^{-3}$, the peaks of water and ethanol merged into a single peak, and the chemical shift value increased suddenly. The merged peak shifted further toward low field, and the half-width of the peak decreased with increasing acid concentration.

Sodium hydroxide, a strong base, gave effects similar to those by acids: the two peaks of water and ethanol merged into unity at $1.0 \times 10^{-3} \text{ mol dm}^{-3}$. It has already been reported that H^+ and OH^- promote the proton exchange between water and ethanol.⁴⁵ Strange to say, upon the addition of the neutral buffer solution (pH 6.86, $0.025 \text{ mol dm}^{-3} \text{ KH}_2\text{PO}_4$ and Na_2HPO_4) to a 60% (v/v) ethanol solution, two peaks of water and ethanol also merged into a single peak at $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ phosphate. For the first time, the chemical shift of the OH proton toward low field (cf. Figure 7) and the coalescence of the water and ethanol signals were observed with increasing concentration of solutes (Na^+ , K^+ , H_2PO_4^- , and HPO_4^{2-}) in 60% (v/v) EtOH–H₂O solution, which should not be subjected to the effects of H^+ or OH^- .

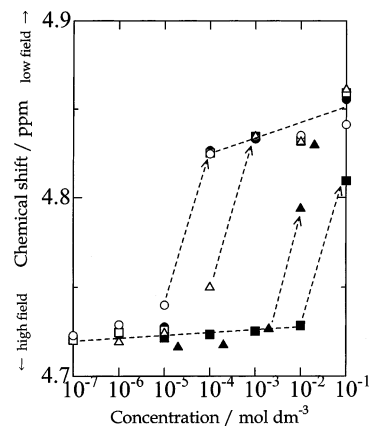


Figure 7. OH proton chemical shifts in 60% (v/v) EtOH–H₂O mixtures containing acids or bases: (○) acetic acid; (●) benzoic acid; (□) gallic acid; (■) pyrogallol; (△) NaOH; (▲) pH 6.86 buffer solution.

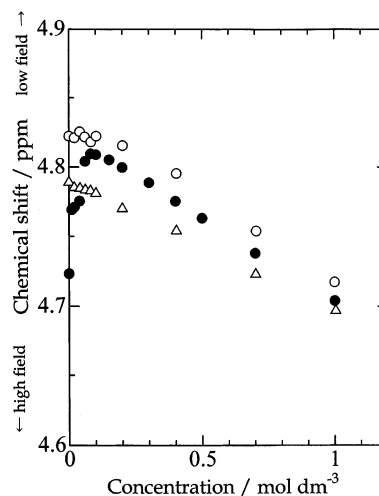


Figure 8. OH proton chemical shifts in various EtOH–H₂O mixtures with NaCl concentration. The ethanol contents are (△) 3.0%, (○) 20%, and (●) 60% (v/v).

The acid concentration at which the water and ethanol peaks combined into a single peak really increased as the acidity decreased, which suggests that the proton dissociated from acids may affect the proton exchange between water and ethanol. However, the prompted proton exchange has been observed even upon the addition of the neutral buffer solution (pH 6.86). Therefore, it may be concluded that not only H^+ or OH^- but also acid molecules (including ionic acids and bases, such as H_2PO_4^- and HPO_4^{2-}) can promote the proton exchange between water and ethanol.

3.2. Effects of Salts. Surprisingly, the OH peaks of water and ethanol shifted in opposite directions to merge when NaCl was added to a 60% (v/v) EtOH–H₂O solution. Two peaks existed separately at 1.0×10^{-4} or $10^{-3} \text{ mol dm}^{-3}$ NaCl and then coalesced to a single peak at $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ NaCl. Moreover, the merged peak shifted further to lower field at 0.1 mol dm^{-3} NaCl. In Figure 8, we notice that the combined peak shifted toward high field for $>0.1 \text{ mol dm}^{-3}$ NaCl in 60% (v/v) EtOH–H₂O solution and that the slope is almost the same as that in 20% (v/v) EtOH–H₂O solution. The chemical shift toward low field was also observed in 40% and 50% (v/v) EtOH–H₂O solutions in the presence of less than 0.1 mol dm^{-3} NaCl. In a 3.0% (v/v) EtOH–H₂O solution, just a normal behavior was observed for NaCl.

Next, the effects of MgCl_2 were examined in three different contents of ethanol (Figure 9). MgCl_2 showed chemical shifts

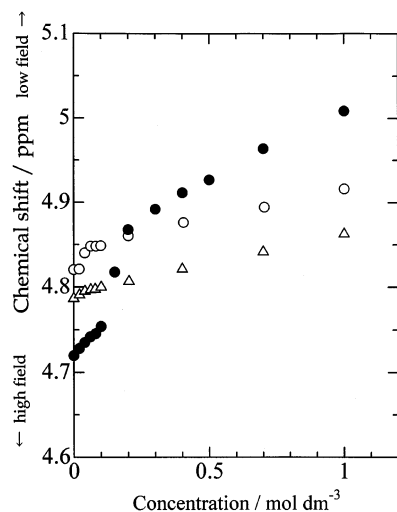


Figure 9. OH proton chemical shifts in various EtOH–H₂O mixtures with MgCl₂ concentration. The ethanol contents are (Δ) 3.0%, (○) 20%, and (●) 60% (v/v).

to low field in 3.0% and 20% (v/v) EtOH–H₂O solutions. In 60% (v/v) EtOH–H₂O solution, the peak of water shifted to low field with increasing concentration of MgCl₂, and then the peaks of water and ethanol coalesced into unity at 0.15 mol dm⁻³. After that, the merged water–ethanol peak shifted toward low field with increasing MgCl₂ concentration.

In 20% (v/v) EtOH–H₂O solutions, MgCl₂ caused a low-field chemical shift of the OH proton, while NaCl caused a chemical shift in the opposite direction. In 60% (v/v) EtOH–H₂O solution, however, both salts caused the merging of the water and ethanol OH signals, shifting the peak toward lower field at lower salt concentrations; finally, the merged signal was affected in different directions by NaCl and MgCl₂ at higher concentrations.

Conclusion and Scope

It was demonstrated that acids or phenolic components could strengthen the water–ethanol structure and also promote the proton exchange between water and ethanol in EtOH–H₂O solutions. With the assistance of the stronger hydrogen-bonding force by acids or phenols, ethanol molecules are supposed to be taken into the “water network” to associate with water molecules tightly. Chart 2 illustrates the intimate (or tight) interaction between water and ethanol molecules caused by acids as well as conjugate-base anions. The appropriate interaction between gallic acid and the solvent molecules supported by the phenolic part of the acid compound is also proposed.

We have analyzed the ¹H NMR chemical shift values for many kinds of spirits manufactured in factories. So far, it has been confirmed that the water–ethanol structure of whiskies matured in wood casks for 0 to more than 20 years is strengthened by acidic and phenolic components. We believe that hydrogen-bonding donors as well as acceptors in alcohol beverages, which exist as the initial components or are gained later on (e.g., in wood casks), should cause the tight association between water and ethanol molecules to give rise to the reduction of the stimulation of ethanol.

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