

A Proton Nuclear Magnetic Resonance (^1H NMR) Investigation of NaCl-Induced Phase Separation of Acetonitrile-Water Mixtures

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Abstract

The microscopic properties of NaCl-induced phase separation of acetonitrile (ACN)-water mixtures have been studied by proton nuclear magnetic resonance (^1H NMR). Acetonitrile-rich phase increases with increasing NaCl concentration (c_{NaCl}) at $x_{\text{ACN}} \approx 0.25$. ^1H chemical shift of water for acetonitrile-rich phase rapidly decreases with decreasing NaCl mole concentration and that for water-rich phase quickly increases with increasing c_{NaCl} . However, ^1H chemical shift of acetonitrile has nothing to do with the molar concentration of NaCl, and it keeps relatively stable for all solutions (± 0.002). These results reveal that Na^+ and Cl^- are rapidly hydrated by water, not by acetonitrile. The change of ^1H chemical shift of water has shown that the number of hydrogen bond increases or hydrogen bond strengths with increasing NaCl molarity in mixtures. But hydrogen bond is broken or weakened with the temperature rising. ^1H chemical shifts of pure water and the water in acetonitrile-rich phase have been investigated at 293 K, 298 K and 303 K. The hydration number of Na^+ (6.05) in water-rich phase is determined by an empirical equation involving ^1H chemical shift, temperature and NaCl molarity, which is in good agreement with the literatures.

Keywords

^1H NMR, NaCl, Phase Separation, Acetonitrile-Water Mixtures, Hydrogen Bond

1. Introduction

Acetonitrile (ACN) and water (W) are miscible at any ratio, but acetonitrile-

trile-water mixtures can be separated into acetonitrile-rich (ACN-R) and water-rich (W-R) two phases by addition of salts such as NaCl. Much attention has been paid to the salt-induced phase separation behavior on the basis of macroscopic parameters, such as electrical conductivity [1], viscosity [2] [3] [4], electrostatics [5], pH values [6] and refractive index [1] [7] [8] [9]. Only a few of studies have focused on microheterogeneity [10] of different mixtures by large angle X-ray scattering, small angle neutron diffraction, Infrared spectroscopy [10] [11] [12] [13]. However, few investigations about the microscopic properties of salt-induced phase separation by nuclear magnetic resonance (NMR) were explored until now.

To investigate the microscopic properties for NaCl-induced phase separation of acetonitrile-water mixtures, proton nuclear magnetic resonance (^1H NMR) has proven to be a useful approach. The NMR chemical shift carries a wealth of information regarding the environment and the local electronic structure in the vicinity of the nucleus under study. Polar functional groups make the chemical shift of under studied proton to move to downfield, while nonpolar functional groups have the opposite effect. For nuclear magnetic resonance, the change of chemical shift reflects the electronic environment experienced by the nucleus. Upfield shifts, negative in the sense of chemical shift, are linked to the increase in shielding tensor. On the contrary, downfield shifts, in a positive direction of chemical shift, are results of “deshielding”. Hydrogen bond in solutions leads to downfield NMR chemical shift (increased chemical shift effect). So downfield shifts are often taken as evidence of hydrogen bond formation, and upfield shifts are considered as hydrogen bond break or becoming weak. The proton chemical shift changes of water for the NaCl-induced phase separation of acetonitrile-water mixtures can support the changes of hydrogen bond of $\text{CH}_3\text{CN}-\text{H}_2\text{O}-\text{NaCl}$ ternary mixtures. The hydration number of Na^+ is one of all-important microheterogeneity in $\text{CH}_3\text{CN}-\text{H}_2\text{O}-\text{NaCl}$ ternary mixtures. In metal salt aqueous solution, the hydration number of the metal ion can be determined by the ^1H chemical shift changes of pure water and metal salt aqueous solutions with different concentrations at different temperatures [14] [15] [16] [17].

In this paper, we firstly investigated the effect of NaCl concentration in acetonitrile-water mixtures of 1:1 volume ratio of acetonitrile to water ($x_{\text{ACN}} \approx 0.25$) on chemical compositions after phase separation by atomic absorption spectroscopy, ion chromatography, moisture-determining instrument and gas chromatography. Secondly, volumes and ^1H chemical shift of water for both acetonitrile-rich and water-rich phases were measured to clarify ion preferentially hydrated and the effect of NaCl concentration on hydrogen bond. Finally, the effect of temperature on hydrogen bond and the hydration number of Na^+ in water-rich phase were studied by ^1H NMR.

2. Experimental Procedure

Chemical Reagents. HPLC-grade acetonitrile was purchased from Tedia Com-

pany (USA). Doubly distilled water was prepared by the Milli-Q purification system (Millipore Corp., Bedford, MA). Analysis-grade sodium chloride (Tianjin, China) was dried in an electric oven at 473 K for 8 h. Dimethyl sulfoxide-d₆ (DMSO-d₆, Cambridge Isotope Laboratories, INC, D 99.9%) was used without further purification.

Determination of chemical compositions for phase separation. Chemical compositions of acetonitrile-water mixtures at $x_{\text{ACN}} \approx 0.25$ ($V_{\text{ACN}}:V_{\text{W}} = 1:1$) after phase separation by addition of different quality of NaCl were determined as follows. First, 5 mL doubly distilled water and 5 mL pure acetonitrile were mixed in a graduated tube with a stopper. Then, the different quality of the dried sodium chloride was added to the mixture. The mixture in the tube was shaken in a constant temperature water bath oscillator for 30 min and left still at 293 ± 0.2 K for 24 h to reach a complete equilibrium. A volume of each separated phase was measured by the calibrated graduated tube. The concentration of Na⁺ in the upper acetonitrile-rich phase was determined by using an atomic absorption spectrometer (GBC Avanta, GBC Company, Australia) [18] [19] [20]. The concentration of Cl⁻ in the lower water-rich phase was determined by ion chromatography (Metrohm MIC). The concentration of Na⁺ in the upper phase stoichiometrically calculated from that of Cl⁻ in the lower phase is in basic agreement with that of experiment. The concentration of H₂O in the upper phase was determined by Karl-Fisher titration method (831 KF Couloeter, Metrohm) [21]. The content of CH₃CN in the lower phase was determined by GC-MS (Agilent7890A-5975C MSD stratum purge & trap) [22] [23].

¹H NMR Measurements. 0.05 mL sample solution was mixed with 0.5 mL (DMSO-d₆) to provide a locking signal and 0.03% tetramethylsilane (TMS) as internal standard. All NMR experiments were carried out on a Bruker (Germany) Avance 500 MHz spectrometer, employing an inverse detection probe (5 mm) with z-gradients. Solvent suppression was achieved by applying the standard “noesyprsat” pulse sequence. The spectrum was obtained with 16 scans over a spectral width 10,330.578 Hz, and each with a relaxation delay of 1 s, an acquisition time of 3.17 s. Spectra were processed with Bruker Topspin 2.1 NMR software.

3. Results and Discussion

Phase Separation Behavior. To describe the phase separation behavior of CH₃CN-H₂O-NaCl mixtures, the changes in composition and volume of each phase with the molar fraction of NaCl were measured. Ten mixtures were studied with NaCl molar fraction from 3.23×10^{-3} to 5.44×10^{-2} . As expected, phase separation depended on the molar fraction of NaCl. When x_{NaCl} is lower than 0.01 no phase separation takes place. Thus phase separation was observed in only the seven mixtures. The compositions of the CH₃CN-H₂O-NaCl ternary mixtures without phase separation and of the upper acetonitrile-rich and lower water-rich phases after phase separation are shown in **Table 1**. From **Table 1** we

Table 1. Concentrations (mol·dm⁻³), Molar Fractions and ¹H Chemical shift of Water in the solutions.

Solution	[ACN]	[H ₂ O]	[NaCl]	x_{ACN}	x_{W}	x_{NaCl}	$\delta_{\text{W}}/293 \text{ K}$	$\delta_{\text{W}}/298 \text{ K}$	$\delta_{\text{W}}/303 \text{ K}$
W		55.56					3.738	3.676	3.609
1	9.574	27.78	0.0606	0.256	0.741	3.23×10^{-3}	3.378		
2	9.574	27.78	0.0936	0.255	0.74	4.98×10^{-3}	3.421		
3	9.574	27.78	0.141	0.254	0.738	7.48×10^{-3}	3.466		
4-ACN-R	19.78	12.49	0.0325	0.612	0.387	1.00×10^{-3}	3.385	3.366	3.346
4-W-R	5.988	33.15	0.501	0.151	0.836	1.26×10^{-3}	3.479	3.465	3.449
5-ACN-R	21.45	11.69	0.0242	0.647	0.352	7.30×10^{-4}	3.368	3.349	3.342
5-W-R	3.458	36.06	0.845	0.0857	0.893	0.0209	3.502	3.49	3.477
6-ACN-R	21.47	11.21	0.023	0.657	0.343	7.03×10^{-4}	3.359	3.34	3.342
6-W-R	2.883	37.1	1.178	0.07	0.901	0.0286	3.526	3.516	3.506
7-ACN-R	21.58	9.84	0.0195	0.686	0.313	6.20×10^{-4}	3.347	3.329	3.319
7-W-R	1.898	39.25	1.889	0.0441	0.912	0.0439	3.536	3.531	3.526
8-ACN-R	21.63	8.079	0.015	0.728	0.272	5.05×10^{-4}	3.339	3.325	3.312
8-W-R	1.537	40.91	2.585	0.0341	0.908	0.0574	3.54		
9-ACN-R	21.91	6.419	0.0126	0.773	0.226	4.45×10^{-4}	3.339	3.322	3.306
9-W-R	1.002	42.62	3.265	0.0214	0.909	0.0696	3.544		
10-ACN-R	21.95	6.262	0.0122	0.778	0.222	4.32×10^{-4}	3.338	3.319	3.301
10-W-R	0.8876	43.36	3.697	0.0185	0.904	0.0771	3.547		

can see the concentration of NaCl is much higher in water-rich phases than that of in acetonitrile-rich phase. There is only trace NaCl in acetonitrile-rich phase and the concentration of NaCl decreased with increasing the total NaCl added to the solution. The more NaCl added, the more acetonitrile and less water is in acetonitrile-rich phase, instead the more water and less acetonitrile in water-rich phases. These results indicate that acetonitrile and water are separated more thoroughly with increasing added sodium chloride.

The change in volume for both acetonitrile-rich and water-rich phases with the total molar fraction of NaCl which was initially added is shown in **Figure 1**, a conclusion which is supported by Toshiyuki T, *et al.* at 298 K. The volume of acetonitrile-rich phase increases with increasing NaCl molar fraction, and it is worth noting that the volume of acetonitrile-rich phase quickly increases up to $x_{\text{NaCl}} = 1.49 \times 10^{-2}$ and then does slowly. On the contrary, the volume of water-rich phase decreased in the opposite way with increasing the total molar fraction of NaCl. These results suggest that acetonitrile molecules are rapidly exuded from the CH₃CN-H₂O-NaCl mixtures and the hydration of Na⁺ and Cl⁻ rapidly increase with increasing the total NaCl concentration.

¹H NMR Measurements. The change in ¹H chemical shift of water (δ_{W}) for both acetonitrile-rich and water-rich phases with the initial added NaCl molar concentration at 293 K is shown in **Figure 2**. It should be noted that δ_{W} for acetonitrile-rich phase decreases rapidly up to $C_{\text{NaCl,tot}} = 1.13 \text{ mol/dm}^{-3}$ ($x_{\text{NaCl}} = 1.49 \times 10^{-2}$) and then keeps stable roughly with increasing the NaCl concentration. On

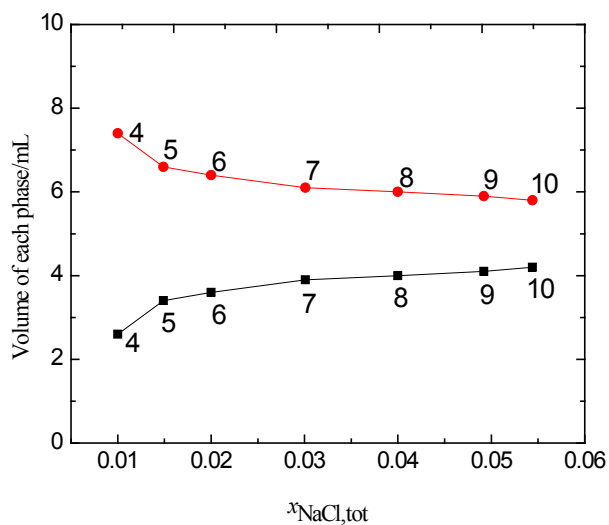


Figure 1. Volumes for acetonitrile-rich (■) and water-rich (●) phases after separation as a function of mole fraction of total NaCl, $x_{\text{NaCl,tot}}$.

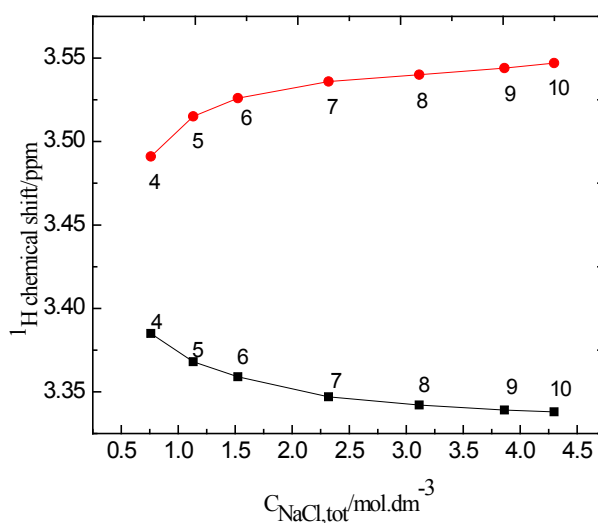


Figure 2. ^1H chemical shift for acetonitrile-rich (■) and water-rich (●) phases after separation as a function of concentration of total NaCl, $C_{\text{NaCl,tot}}$.

the contrary, the δ_{w} of water-rich phase increased in the opposite way with increasing the total NaCl molar concentration. These ^1H chemical shift changes of water have shown that hydrogen bond in acetonitrile-rich phase decreased or became weak and that in water-rich phase increased or strengthened. But ^1H chemical shift of acetonitrile for all solutions keeps relatively stable. These results suggest that Na^+ and Cl^- are not rapidly solvated by acetonitrile, but by water molecules. These also indicate that the number of hydrogen bond around water in mixtures rapidly increases with increasing NaCl concentration.

^1H chemical shifts of water for acetonitrile-rich phase with NaCl molar concentration after separation at 293 K, 298 K and 303 K are shown in **Figure 3**. δ_{w}

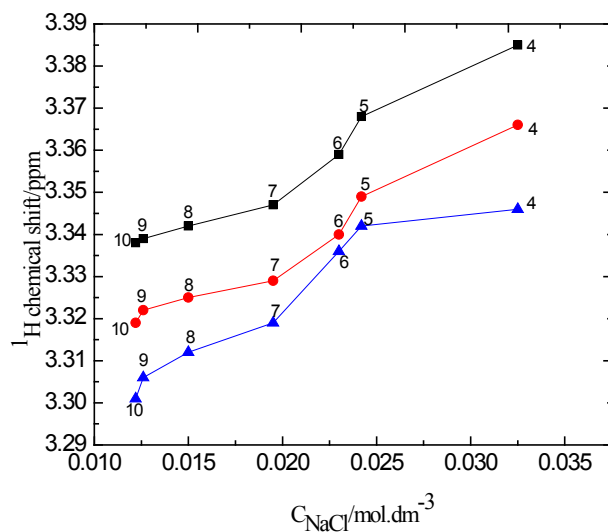


Figure 3. ^1H chemical shift for acetonitrile-rich phase at 293 K (■), 298 K (●) and 303 K (▲) after separation as a function of concentration of NaCl, C_{NaCl} .

for acetonitrile-rich phase decreases with temperature rising. It means that δ_w moves to the upfield with temperature rising. This result indicates that the hydrogen bond around water has been destroyed or weakened with temperature going up.

To investigate the influence of hydrogen bond between DMSO and solution on ^1H NMR chemical shift of water, ^1H NMR chemical shift of water for an acetonitrile-rich phase of different volume (0.025, 0.05, 0.075, 0.10 and 0.125 mL) and acetonitrile-water binary solution of different acetonitrile mole fraction (from 0.1 to 0.9) were measured. There are more hydrogen bonds between DMSO and solution with added more amount of solution to DMSO. The results are shown in **Figure 4**. As seen in the figure, for a fixed acetonitrile and water ratio of acetonitrile-rich phase, ^1H NMR chemical shift of water for five different volume solutions only has a little change. While ^1H NMR chemical shift of water for acetonitrile-water binary solution decreases obviously with increasing acetonitrile mole fraction and decreasing water mole fraction. These results suggest the change of ^1H NMR chemical shift of water in DMSO solution mainly relates to the water mole fraction and little to the hydrogen bond between DMSO and solution.

Na^+ is hydrated in both phases. For hydration structure of Na^+ , the water-rich phases which contain most of the Na^+ shows structures are similar to those of NaCl solutions at the same NaCl concentrations. The hydration number of Na^+ in water-rich phase was measured by ^1H NMR. Generally δ_f and T were fitted with a linear relationship, in which a_0 and b_0 are both empirical constants [14] [24].

$$\delta_f = a_0 T + b_0 \quad (1)$$

In general, metal ion may be hydrated in salt solutions. So water has two

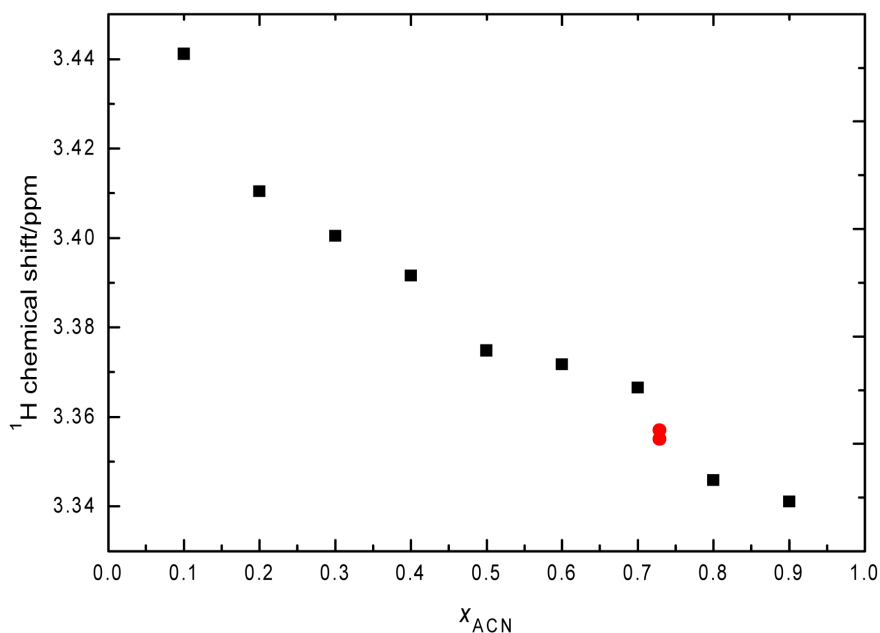


Figure 4. 1H chemical shift for acetonitrile-rich phase (●) and acetonitrile-water binary solution (■) as a function of mole fraction of acetonitrile, x_{ACN} .

forms, non-hydrated and hydrated water. Then 1H NMR chemical shift of water (δ_e) is fitted to Equation (2)

$$\delta_e = \frac{55.56 - nC_m}{55.56} \delta_f + \frac{nC_m}{55.5} \delta_h \quad (2)$$

where δ_e is a measured value, δ_f is the chemical shift of no hydrated water and δ_h is that of hydrated water. C_m represents concentration of metal ion and n is the number of hydration.

Equation (3) can be readily obtained from Equations (1) and (2)

$$\delta_e = \left(1 - \frac{nC_m}{55.56}\right) a_0 T + \frac{nC_m}{55.5} (\delta_h - b_0) + b_0 \quad (3)$$

where δ_e is linear dependent against T . And the linear correlation coefficient, c , is expressed as

$$c = \left(1 - \frac{nC_m}{55.56}\right) a_0 \quad (4)$$

In Equation (4), the linear correlation coefficient of c against C_m , d is

$$d = -\frac{n}{55.56} a_0 \quad \text{or} \quad n = -55.56d/a_0 \quad (5)$$

The hydration number n can be obtained from Equation (5).

δ_e of water and four water-rich solutions (4-W-R, 5-W-R, 6-W-R and 7-W-R) are detected by NMR at 293.2, 298 and 303.2 K (Table 1). The linear correlation coefficient, c can be obtained by plotting δ_e vs. T . Then in the similar way we can get d value, and the linear correlation coefficient of c against C_m . The coefficient d is calculated as 0.00146. C_m of pure water is zero, so c is equal to a_0 , -0.0134.

The values d and a_0 are fitted into Equation (5).

$$n = -55.56d/a_0 = 6.05 \quad (6)$$

The hydration number of Na^+ is 6.05, which is consistent with the values (5.9 and 6.0) [11] [25].

4. Conclusions

In this article, some microscopic properties for the NaCl-induced phase separation of acetonitrile-water mixtures are discussed. Acetonitrile-rich phase increases with increasing added NaCl concentration. The volumes of acetonitrile-rich phase increase quickly, contrary to variety in water-rich phase. These make clear that acetonitrile molecules are rapidly exuded from the $\text{CH}_3\text{CN-H}_2\text{O-NaCl}$ mixtures and the hydration of Na^+ and Cl^- rapidly increases with increasing the total NaCl concentration. From ^1H NMR measurements, we know that ^1H chemical shift of water increases with increasing the molar concentration of NaCl in both phases, however ^1H chemical shift of acetonitrile for all solutions keeps relatively stable. These indicate ions prefer solvating by water molecules in acetonitrile-water mixtures to doing by acetonitrile molecules. That is to say, water aggregates easily, but acetonitrile does not aggregate. The reason may be that water is higher than acetonitrile in both electron donor and acceptor properties or that acetonitrile aggregates have no strong interactions, for example hydrogen bond. So the preferential hydration of Na^+ and Cl^- to form water aggregates may be a major cause for NaCl induced phase separation of acetonitrile-water mixtures. Hydrogen bond strengthens with increasing NaCl concentration and weakens with temperature rising, because hydrogen bond in solution results in downfield NMR chemical shifts (increasing chemical shift). We calculated the hydration number of Na^+ by ^1H NMR, and the number of 6.05 is in good agreement with literatures.

The mechanism of NaCl induced acetonitrile-water phase separation can be applied to extraction, separation of food, plant and drug. Firstly the target component is extracted from food or plant using acetonitrile-water binary solvent, and then phase separation happens by adding salt revulsants. The result is that the polar compounds are kept in the water-rich phase and the compounds of relatively weak polarity are in acetonitrile-rich phase. So the separation of the corresponding analytes is realized. In addition, this method has the advantages of simple step, quick separation, high recovery rate and low production cost. Our study group has extracted pesticide residues in foods and separated flavones and flavone glycosides from ginkgo biloba extract using salt induced acetonitrile-water phase separation [26] [27] [28]. The results of our study can help researchers to better understand the mechanism of salt induced phase separation and better apply it to practical applications.

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