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# Properties of 2-Hydroxyethylamine Acylimide Aqueous Solution – Unusual Clouding Phenomenon

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## ABSTRACT

Surface active and solution properties of 2-hydroxyethylamine acylimides, such as dimethyl-2-hydroxyethylamine acylimides, bis(2-hydroxyethyl) methylamine acylimides, and tris(2-hydroxyethyl) amine acylimides were investigated. An unusual clouding phenomenon, which depends upon time after dissolving, concentration of aminimide, as well as temperature of the aqueous solution is discussed. The phenomenon may be explained by slow protonation to the negative center of the aminimide and slow rate to attain the equilibration of hydration by strong hydrogen bonding between a negative center and a hydroxyl group of the aminimide. The facts that the aminimide can exist in different forms in solid state as well as in solution, and that the forms are reversible by treating them with water or a nonpolar solvent, may also be explained by strong hydrogen bonding.

## INTRODUCTION

Many kinds of aminimides have hitherto been prepared and utilized in various industrial fields. Particularly, since McKillip reported a facile and quantitative synthetic method of aminimide preparation (1,2), studies of their applications became active. In spite of the fact that the aminimides are potential surfactants, only limited studies have been done on their basic surface chemical properties (3-6). Aminimides having a 2-hydroxyethylamine group may be expected to play an interesting role in an aqueous solution because of the interaction between a negative nitrogen (or a negative center) and a hydroxyl group.

During the authors' investigation on preparation (7) and properties of some 2-hydroxyethylamine acylmides, an unusual clouding phenomenon of the aminimide aqueous solution was observed. Clouding phenomenon of an aqueous solution of an usual nonionic surfactant is explained in terms of hydration to ether linkage of the oxyethylene group. This clouding property depends upon temperature, and the cloud point is given when the hydrophile and lipophile groups of a surfactant are settled.

On the contrary, this new clouding phenomenon is found to be dependent on time and concentration as well as temperature. In this report this phenomenon is fully discussed, and other surface active properties such as aqueous surface tension, critical micelle concentration (CMC), and efficiency of 2-hydroxyethylamine acylimides (8) are also reported.

## EXPERIMENTAL PROCEDURES

### Synthesis of 2-Hydroxyethylamine Acylimide

Lauroyl (12-MOH), myristoyl (14-MOH), and palmitoyl (16-MOH) derivatives of dimethyl-2-hydroxyethylamine acylimide (MOH) were prepared according to Slagel's method (2).

12-MOH: mp 57.5-59.5 C; IR (KBr) 3120, 1565 $cm^{-1}$; NMR ($CDCl_3$,δ) 0.86 (3 H, t), 1.24 (18 H, m), 2.00 (2 H, t), 3.45 (6 H, s), 3.57 (2 H, m), and 3.97 (2 H, m). Anal. Calcd. for $C_{16}H_{34}N_2O_2$: C, 67.09; H, 11.96; N, 9.78. Found: C, 66.78; H, 11.89; N, 9.64.

14-MOH; mp 66.0-67.5 C; IR (KBr) 3120, 1565 $cm^{-1}$; NMR ($CDCl_3$, δ) 0.87 (3 H, t), 1.24 (22 H, m), 2.00 (2 H, t), 3.46 (6 H, s), 3.56 (2 H, m), and 3.98 (2 H, m). Anal. Calcd. for $C_{18}H_{38}N_2O_2$: C, 68.74; H, 12.18; N, 8.91. Found: C, 68.56; H, 12.47; N, 8.85.

16-MOH: mp 71.5-73.5 C; IR (KBr) 3120, 1565 $cm^{-1}$; NMR ($CDCl_3$, δ) 0.87 (3 H, t). 1.24 (26 H, m), 2.01 (2 H, t), 3.46 (6 H, s), 3.56 (2 H, m), and 3.98 (2 H, m). Anal. Calcd. for $C_{20}H_{42}N_2O_2$: C, 70.12; H, 12.36; N, 8.18. Found: C, 69.77; H, 12.75; N, 8.20.

Bis(2-hydroxyethyl)-methylamine-acylimide (BOH) was synthesized as follows; methylhydrazinium sulfate (4.32 g, 0.03 mol) was suspended in an isopropanol (20 ml) solution containing an equivalent amount of potassium isopropoxide (K: 2.34 g, 0.06 mol) and allowed to stir for 2 days. Potassium sulfate, a white precipitate, was removed by filtration. An isopropanol (20 ml) solution of methyl carboxylate (0.006 mol) was added into a glass autoclave containing the isopropanol solution of methylhydrazine, and ethylene oxide (ca. 3.0 ml, 0.06 mol) was condensed into it under cooling at -60 to -70 C. The mixture was allowed to react at 100 C for 2 hr after sealing it. At the end of the reaction period, the solvent was removed in vacuo, and the crude product was recrystallized from hexane (50-70ml) or hexane-ethanol, then from hexane-benzene.

Myristoyl (14-BOH) and palmitoyl (16-BOH) derivatives were prepared.

14-BOH: mp 75.0-77.0 C; IR (KBr) 3160, 1575 $cm^{-1}$; NMR ($CDCl_3$, δ) 0.86 (3 H, t), 1.24 (22 H, m), 1.99 (2 H, t), 3.52 (3 H, s), and 3.9-4.0 (8 H, m). Anal. Calcd. for $C_{19}H_{40}N_2O_3$: C, 66.24; H, 11.70; N, 8.13. Found; C, 65.99; H, 11.91; N, 8.01.

16-BOH; mp 80.0-82.5 C; IR (KBr) 3160, 1575 $cm^{-1}$; NMR ($CDCl_3$, δ) 0.87 (3 H, t), 1.25 (26 H, m), 2.01 (2 H, t), 3.54 (3 H, s), and 3.9-4.0 (8 H, m), Anal. Calcd. for $C_{21}H_{44}N_2O_3$: C, 67.70; H, 11.90; N, 7.52. Found: C, 67.48; H, 12.04; N, 7.33.

Lauroyl (12-TOH), myristoyl (14-TOH), palmitoyl (16-TOH), and stearoyl (18-FOH) derivatives of tris(2-hydroxyethyl)amine-acylimide were prepared according to the reported method (7).

12-TOH: mp 85.0-87.5. 14-TOH: mp 88.5-91.0. 16-TOH: mp 93.0-95.0. 18-TOH: mp 95.5-97.0 C.

### Measurement of Surface Active Properties

The Krafft point of aminimide and its hydrochloride was measured in 0.2% aqueous solution. Surface tension was measured by du Noüy's method, and CMC and efficiency of hydrophilic group as defined by Rosen (8) were

TABLE I

Surface Active Properties of Aminimides

| Aminimide | KP$^a$ (°C) | CMC (μM/l) | $\gamma^b$ (dyn/cm) | Log$(1/C)_{\pi=20}$ |
|---|---|---|---|---|
| 12-MOH | < 0 | 750 | 32.5 | 3.96 |
| 14-MOH | < 0 | 92 | 32.5 | 4.82 |
| 14-BOH | < 0 | 65 | 34.0 | 4.85 |
| 12-TOH | 31 | 700 | 36.0 | 4.00 |
| 14-TOH | 47 | — | — | — |
| 12-MOHHCl | < 0 | 1400 | 30.0 | 3.62 |
| 14-MOHHCl | < 0 | 190 | 37.0 | 4.44 |
| 16-MOHHCl | 25 | 23 | 35.0 | 5.07 |
| 14-BOHHCl | < 0 | 75 | 40.5 | 4.49 |
| 16-BOHHCl | < 0 | 16 | 37.5 | 5.05 |
| 12-TOHHCl | < 0 | 1300 | 41.0 | 3.17 |
| 14-TOHHCl | < 0 | 250 | 40.0 | 4.66 |
| 16-TOHHCl | < 0 | 12 | 38.5 | 5.18 |

[a] Krafft point.

[b] Surface tension at critical micelle concentration (CMC), at 25 C.

determined from the surface tension curve. Results are listed in Table I.

## Clouding Phenomenon of Aminimide Aqueous Solution

*Change of cloud point with time:* One hundred milligrams of 14-MOH dried in vacuo at 40 C for 1 day before use was added to deionized water (D-water, 50 ml) with stirring and thermoregulated at specified temperatures (43 and 50 C). The solution was clouded at first. After becoming clear, an aliquot of the 14-MOH solution (5 ml) was taken in a test tube ($\phi$ = 20 mm), and the cloud point was measured with an oil bath maintained at 100 C. Subsequently, the same measurements were carried out at specified time intervals (Fig. 1).

*Clouding phenomenon at specified temperatures:* Aminimide dried in the same way as above was added to a test tube containing D-water (5 ml) kept at a specified temperature with stirring. The lengths of time required to get a clear solution after dissolving the aminimide and those required to get a clouded solution again were measured at various temperatures. In the case of being clear from beginning, only the latter lengths of time were measured (Fig. 2,3).

*Clouding phenomenon in HCl-, acetic acid-, NaOH-, and urea-aqueous solutions at specified temperatures:* Aqueous solutions of 0.2% 14-MOH containing 1/100, 1/10, or an equivalent amount of HCl to 14-MOH (0.01-HCl, 0.1-HCl, 1-HCl), 1/10 or an equivalent amount of acetic acid to 14-MOH (0.1-AcOH, 1-AcOH), 1/10 or an equivalent amount of NaOH to 14-MOH (0.1-NaOH, 1-NaOH), and 3% of urea (3-U) were prepared by use of distilled deionized water (DD-water); subsequently clouding phenomenon was explored in a similar manner under a nitrogen atmosphere (Fig. 4,5).

*Change of pH value of 14-MOH in 0.1-HCl with time:* One hundred milligrams of 14-MOH dried in the same manner as above was added to 0.1-HCl (50 ml) and thermoregulated at the specified temperatures (70 and 80 C). A pH meter (Hitachi-Horiba Type F-7) was used to measure pH of the solution at specified time intervals under a nitrogen atmosphere.

*Change of specific conductivity of 14-MOH DD-water solution with time:* One hundred milligrams of 14-MOH treated in the same manner as above was added to DD-water (50 ml, 60 C). Specific conductivity of the solution was measured with a universal bridge (Yokagawa Electric Works, Ltd., BV-Z-13A) at specified time intervals under a nitrogen atmosphere.

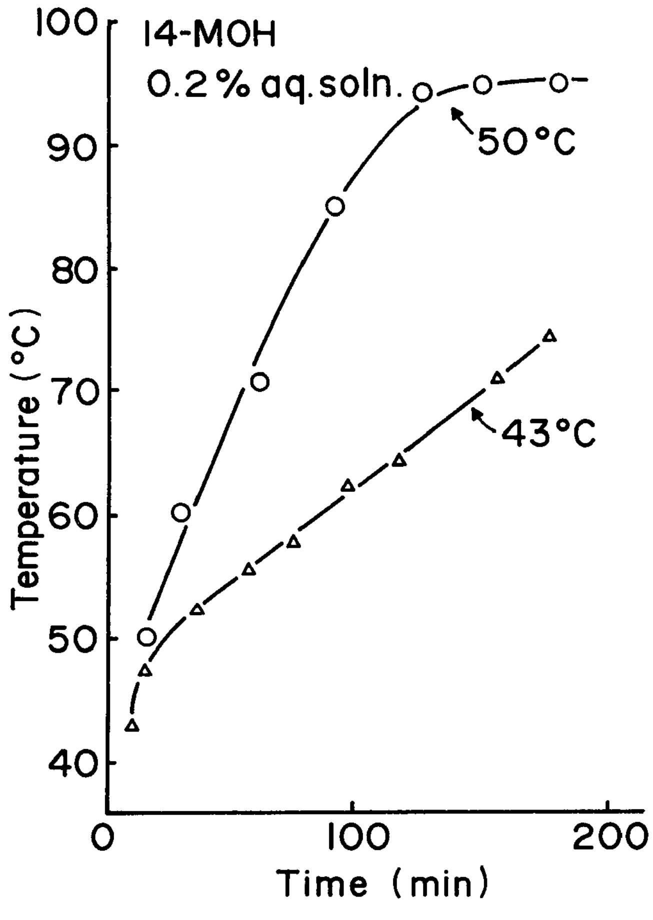


FIG. 1. Cloud points of dimethyl-2-hydroxyethylamine myristimide aqueous solutions after aging for the specified times.

## RESULTS AND DISCUSSION

Melting point of aminimide became higher as the number of 2-hydroxyethyl groups increased, indicating that the 2-hydroxyethyl group takes part in intermolecular hydrogen bonding of aminimides. The differences were also recognized among NMR spectra of MOH, BOH, and TOH. Thus, a signal of N-methylene protons ($\overset{+}{N}$-CH$_2$-C) was clearly isolated from that of O-methylene protons (O-CH$_2$-C) in MOH, but these signals overlapped slightly in BOH, and the complete overlap of these signals was observed in TOH. This can be explained in such a way that a signal of N-CH$_2$-C shifted to lower magnetic field because

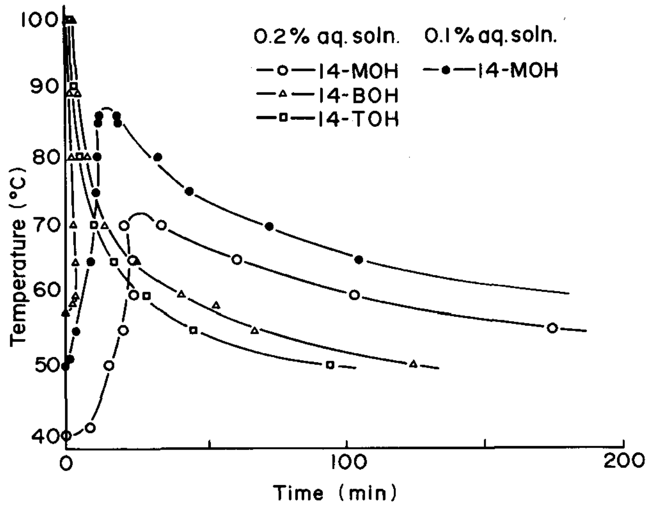


FIG. 2. Clouding phenomenon of mono-, bis-, and tris-2-hydroxyethylaminimide aqueous solution at specified temperatures (change in appearance, clouded→clear→clouded or clear→clouded).

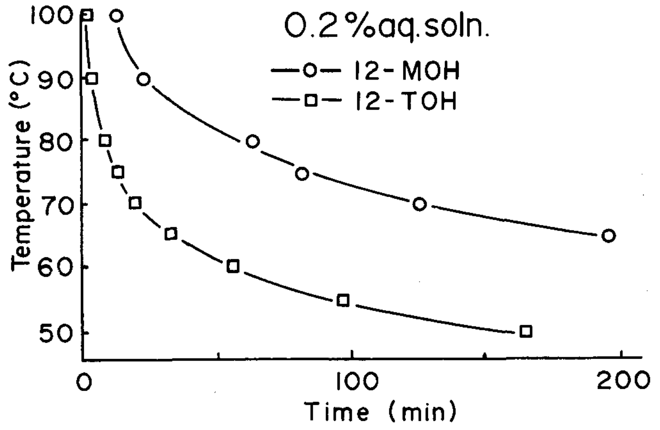
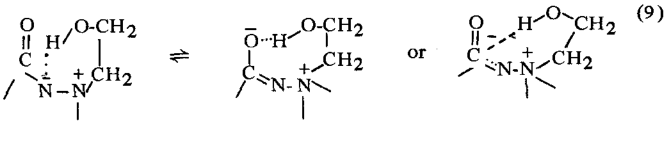


FIG. 3. Clouding phenomenon of mono- and tris-2-hydroxyethylamine laurimide aqueous solution at specified temperatures (change in appearance, clear→clouded).

its nitrogen atom was more electron deficient in proportion to the number of the 2-hydroxyethyl group and by intramolecular hydrogen bonding as shown in the following equation.


(9)

Hitherto, some surface active properties of MOH have been investigated, and some aminimides had been found to possess the Krafft point and the cloud point (3). The term "efficiency" in a quantitative fashion was defined, and its relationship to molecular structure of surfactant was explored by Rosen (8).

In the present work, to clarify the differences among MOH, BOH, and TOH in size and structure of hydrophilic groups, the Krafft point, the cloud point, and the surface tension of the aminimide solution were measured. CMC, surface tension reduction, and $\text{Log}(1/C)_{\pi=20}$, the logarithmic value of the reciprocal of the surfactant concentration necessary to produce a surface tension reduction of 20 dynes/cm, were determined from the surface tension vs. the concentration curve. These surface active properties of aminimide and its hydrochloride are shown in Table I.

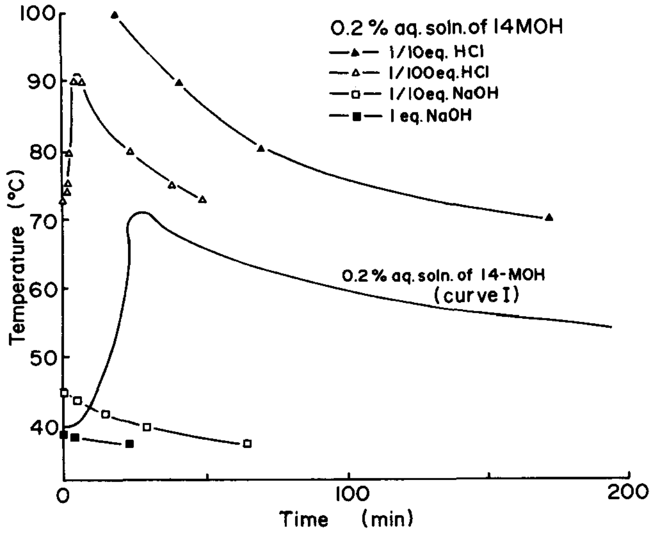


FIG. 4. Clouding phenomenon of dimethyl-2-hydroxyethylamine myristimide aqueous solution in the presence of HCl and NaOH (change in appearance, clouded→clear→clouded or clear→clouded).

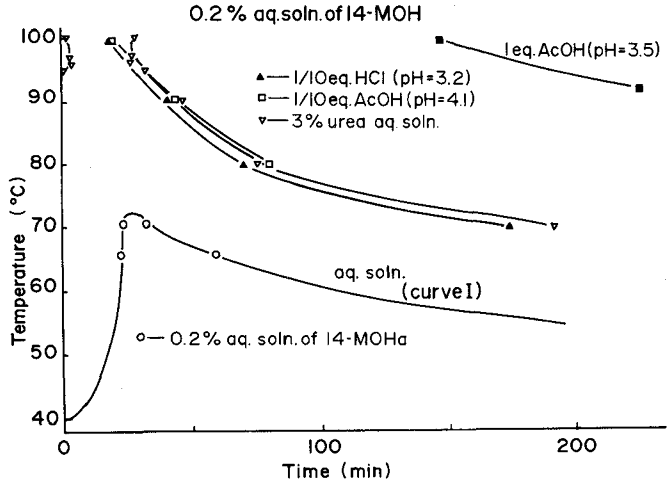


FIG. 5. Clouding phenomenon of dimethyl-2-hydroxyethylamine myristimide aqueous solution in the presence of acetic acid and urea and that of the recovered aminimide aqueous solution at specified temperatures (change in appearace, clouded→clear→clouded or clear→clouded).

These properties of palmitoyl and stearoyl aminimides aqueous solutions were not measured because of their poor solubility.

Three compounds, 12-TOH, 14-TOH, and 16-MOH HCl were found to have the Krafft point. CMC and surface tension reduction obeyed Traube's rule, and their values of hydrochloride were generally higher than those of aminimides. In comparing MOH, BOH, and TOH, CMC decreased in the order of MOH > BOH > TOH. CMCs of myristoyl and palmitoyl aminimide hydrochlorides were comparable to that of nonionic surfactant; especially palmitoyl derivatives showed low values, 12 μm/l in TOH HCl and 16 μM/l in BOH HCl. The value of $\text{Log}(1/C)_{\pi=20}$ increase with extension of the alkyl chain length in every case, and in comparing hydrophilic group, a slight tendency of MOH < BOH< TOH was observed.

The nonionic surfactant has the cloud point. Some aminimides have also been found to have it (3). However, MOH, BOH, and TOH were found to have "clouding phenomenon" which has not been reported yet. It is different

TABLE II

The Change "14-MOHb → 14-MOHa" by Organic Solvents[a]

| Solvent | Condition | a : b |
|---|---|---|
| Hexane | dissolved at 50 C | 10 : 0 |
| CC14 | dissolved at r.t. | 0 : 10 |
| | refluxed for 30 min | 3 : 7 |
| | refluxed for 1 hr | 9 : 1 |
| Benzene | dissolved at r.t. | 0 : 10 |
| | refluxed for 1 hr | 5 : 5 |
| Ethanol | refluxed for 1 hr | 5 : 5 |

[a] Figures estimated from IR spectra.

from the usual cloud point and dependent on temperature, time, and proton concentration of aqueous solution. Thus, when 14-MOH was added in water (0.2%, 50 C), the solution was clouded first for 14 min, and then it became clear. After 14 min, the cloud point of the aqueous solution rose with the passage of time. Figure 1 shows the changes of the cloud point of 0.2% 14-MOH aqueous solution with time. Moreover, then 0.2% 14-MOH aqueous solution was left to stand at 50 C, the solution clouded again. Then the clouding phenomena (change in appearance, clouded → clear → clouded or clear → clouded) of 14-MOH, 14-BOH, and 14-TOH at specified temperatures were explored, which are shown in Figure 2. The results of 12-MOH and 12-TOH are shown in Figure 3. As a result, the clouding phenomenon can be classified into three patterns in relation to the temperature: (a) "clear → clouded" below 40 C, (b) "clouded → clear → clouded" from 40 to 70 C, and (c) "clouded throughout" over 70 C were observed in 0.2% 14-MOH aqueous solution. Patterns (a) and (b) for 14-BOH aqueous solution and only (a) for 14-TOH, 12-MOH, and 12-TOH aqueous solutions were observed, respectively. The same observation for 0.1% 14-MOH aqueous solution resulted in expanding the clear part (Fig. 2).

IR spectra of two samples recovered from different states, one sample (14-MOHa) recovered by evaporation of water from the clear aqueous solutions, and another (14-MOHb) recovered by evaporation of water from the clouded aqueous solutions (secondary clouded), were different from each other, especially in the region from 700 to 1500 $cm^{-1}$. IR spectrum of 14-MOHa is the same as that of 14-MOH, and IR spectrum of 14-MOHb is different from that of any probable by-products such as hydrazinium salts $(\mathrm{RCOO^{-}\ NH_2\overset{+}{\underset{|}{N}}{\equiv}})$, acylhydrazides, or rearranged ester $(\mathrm{RCOOC_2H_4\underset{\|}{N}{-}NH_2})$.

When 14-MOHb was dissolved and heated in solvents shown in Table II, the change "14-MOHb → 14-MOHa" was found from IR spectra. The degree of this change depended upon solvents, namely spontaneous in hexane and gradual in carbon tetrachloride, benzene, and ethanol. But any change "14-MOHa → 14-MOHb" was not observed by heating 14-MOH under refluxing in any of these solvents for 1 hr. Moreover, when a sample from 14-MOHb treated with hexane, namely 14-MOHa, was dissolved in DD-water, and the clouding phenomenon at specified temperatures (65 and 70 C) was measured, DD-water solution of 14-MOHa showed the same behavior as that of 14-MOH (Fig. 5), indicating more directly that 14-MOHb was not generated by chemical change of 14-MOHa, namely 14-MOH.

The clouding phenomenon at specified temperatures in acidic and basic aqueous solutions of 14-MOH was examined. The result of DD-water solution of 14-MOH (curve I) is included in Figure 4 for comparison. The curve shifted upward with increase of HC1 concentration compared with curve I. Thus, clouding phenomenon of 14-MOH in 0.01-HC1 was similar to curve I, but in the case of 14-MOH in 0.1-HC1, only the clouding pattern (a) was observed in all temperatures, as observed in the aqueous solutions of 14-TOH, 12-MOH, and 12-TOH.

The clouding phenomenon of 14-MOH in 1-AcOH and 0.1-AcOH was also observed and shown in Figure 5. Curve I and the curve of 14-MOH in 0.1-HC1 are included in Figure 5 for comparison. The AcOH-aqueous solution of 14-MOH showed the same behavior as the HC1-aqueous solution of 14-MOH. The position of the curve of 14-MOH in 0.1-AcOH nearly corresponds to the curve of 14-MOH in 0.1-HC1, in spite of the difference in pH values of aqueous acids (0.1-HC1 vs. 0.1-AcOH). The curve of 14-MOH in 1-HC1 shifted more upward than that in 1-AcOH.

The curve shifted down as increase of NaOH concentration in NaOH-aqueous solution of 14-MOH (Fig. 4).

The changes of pH value and specific conductivity with time at specified temperatures were measured for 0.1-HC1 and DD-water solutions of 14-MOH, respectively. When 14-MOH was dissolved in 0.1-HC1, the pH value was ca. 5.5, and then it increased gradually like a neutralization titration curve. The ratio of specific conductivity of DD-water solution of 14-MOH to DD-water showed the similar tendency, linear increasing.

From the changes of pH value and specific conductivity with time, it may be concluded that this aminimide is subject to slow protonation because of a hydrogen bond of a 2-hydroxyethyl group and a negative center. On the other hand, the shift-up of curve I due to increase of the concentration of proton shows that hydration to the protonated aminimide may easily occur, and that the protonated aminimide aqueous solution is hard to cloud. Curve I was shifted down with increase of hydroxide ion (Fig. 4), because protonation to the aminimide is retarded and hydration to the aminimide is hard to occur.

There is stronger hydrogen bonding than usual in the prepared aminimide because of the presence of a negative divalent nitrogen (or negative center) and a 2-hydroxyethyl group; this is apparent from hydroxyl streatching absorption revealed at 3120-3260 $cm^{-1}$. Consequently, in formation of micelle of aminimide in the aqueous solution, the strong hydrogen bonding may play an important role, by which in turn the protonation and the hydration to aminimide may occur slowly. To clarify the participation of the hydrogen bonding of a negative center and a 2-hydroxyl group, the clouding phenomenon of 14-MOH in 3-U was explored and shown in Figure 5. As a result, the curve was shifted up to give the same shaped curve as the aqueous solution of 14-BOH. Probably, the aminimide was apt to hydrate more strongly by assistance of urea to hydrogen bonding between aminimide and water molecules or by changing the nature of the water structure in the presence of urea (10).

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