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Dynamic Structure of Water in Aqueous Solutions of Chloroacetate. I. Temperature Dependence of Limiting Mobilities of Mono-, Di-, and Tri-chloroacetate Ions

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Electric conductivities of the sodium salts of mono-, di-, and tri-chloroacetic acids were measured in water at 15, 25, and 35 °C. The molar conductivities were analyzed by the Fuoss-Onsager equation to obtain the limiting mobility. On the basis of the temperature dependence of the limiting mobilities, the dynamic structure of water around these anions was investigated by means of Samoilov's theory. Chloroacetate ions are structure maker and the degree of the positive hydration is in the order TCA$^-$>acetate ion>DCA$^-$>MCA$^-$. From the results, it is shown that a competition between the different orientation of water molecules in the surroundings of $-CH_2Cl$ and $-CHCl_2$ groups occurs, and consequently, shown that the water molecules around DCA$^-$ and MCA$^-$ ions more mobile than those around TCA$^-$ and acetate ions.

There have been many investigations on the hydration of aqueous solutions of organic electrolytes. The particular interest in the hydration is related to the interactions between water and the hydrophobic or ionized groups of these electrolytes.

The study of aqueous solutions of halogenized organic compounds is important from both theoretical and biochemical point of view. For example, trifluoroacetic and trichloroacetic acids cause denaturation of proteins and nucleic acids. The systematic investigations, however, have been scarecely made.

Robinson and Jencks[1)] determined the activity coefficient of acetyltetraglycine ethyl ester in the presence of various organic electrolytes. According to their results, trichloroacetate ion behaves as the structure breaker in contrast to acetate ion. On the other hand, Engel and Hertz[2)] showed that the trichloroacetate ion is structure maker by means of the measurement of proton relaxation rates in aqueous solutions of the various electrolytes. Recently, we have measured the turbidity of several proteins in aqueous solutions by some aromatic sulfonic acids and trichloroacetic acid.[3)] Only trichloroacetic acid gave a common profile for all of the proteins examined, *i. e.*, the turbidity of protein solutions increases abruptly with increasing the concentration of trichloroacetic acid, and above 0.5 mol dm^{-3} of trichloroacetic acid goes through a maximum. The values of maximum turbidity are similar for all of the protein solutions.

It is thought that the peculiar interaction between trichloroacetic acid and protein may be related to the nature of hydration of the precipitant. But on the hydration of trichloroacetate ion the above mentioned contradictory results are obtained. In a series of our studies of the effects of organic electrolytes on the dynamic structure of water, it was shown that the water structure around organic ions is affected by the individual interactions between water and the ionized, hydrophobic, or hydrophilic groups.[4—7)] From this point of view, in order to examine the interaction between trichloroacetate ion and water, we present here the electric conductivities of the sodium salts of mono-, di-, and trichloroacetate in water at 15, 25, and 35 °C. The dynamic structure of water around these anions are discussed on the basis of Samoilov's theory.[8)]

Experimental

Monochloroacetic and trichloroacetic acids (G. R., Wako Pure Chemicals) without further purification were neutralized with NaOH (G. R., Wako Pure Chemicals). Dichloroacetic acid (E. P., Wako Pure Chemicals) was once distilled before neutralization with NaOH. These sodium salts (NaMCA, NaDCA, and NaTCA) were recrystallized five times from ethanol for NaMCA, and from ethanol-water for NaDCA and NaTCA, and dried at 55 °C *in vacuo* over phosphorus pentoxide.

Water was deionized, glass-distilled, and the electrolytic conductivity of water was about $1\times10^{-6}\ \Omega^{-1}\ cm^{-1}$ at 25 °C. All the solutions were prepared by weighing and all the weights were corrected to those in vacuum. The molar concentrations of these solutions were calculated from solution densities. Electric conductivities of all the solutions were measured at 15, 25, and 35±0.001 °C. The procedure of the measurements of the conductivity and density are described elesewhere.[9)]

Results and Discussion

The molar conductivities of NaMCA, NaDCA, and NaTCA in water at 15, 25, and 35 °C are given in Tables 1, 2, and 3, respectively. The limiting molar conductivities of salts, Λ°, were determined by the Fuoss-Onsager equation,[10)]

$$\Lambda = \Lambda^\circ - S\sqrt{c} + Ec\log c + Jc, \qquad (1)$$

where c is a molar concentration and the other symbols are defined in Ref. 10. The plots of molar conductivities *vs.* $c^{1/2}$ at 25 °C are shown in Fig. 1, where the solid lines were calculated from Eq. 1.

The $\lambda_+^\circ(Na^+)$ used to calculate λ_-° from the Kohlraush rule were obtained from the literature.[11)] The temperature dependence of λ_-° for MCA$^-$, DCA$^-$, and TCA$^-$ ions are shown in Fig. 2.

According to Samoilov,[8,12)] the dynamic structure of water around an ion is described by the quantities τ_i/τ_0 and ΔE_i, and the following relation approximately holds between these quantities:

$$\tau_i/\tau_0 = \exp(\Delta E_i/RT), \qquad (2)$$

TABLE 1. MOLAR CONDUCTIVITIES OF SODIUM MONOCHLOROACETATE IN WATER AS FUNCTION OF TEMPERATURE

15 °C		25 °C		35 °C	
c (mol m^{-3})	Λ (cm^2 Ω^{-1} mol^{-1})	c (mol m^{-3})	Λ (cm^2 Ω^{-1} mol^{-1})	c (mol m^{-3})	Λ (cm^2 Ω^{-1} mol^{-1})
0	71.53	0	90.27	0	111.80
0.09446	70.62	0.18868	89.05	0.19857	110.44
0.20032	70.64	0.38206	88.83	0.35304	109.85
0.35782	70.43	0.55420	88.34	0.55159	109.83
0.55623	70.20	0.80334	88.11	0.79823	109.35
0.80029	70.04	1.08936	87.66	1.08461	108.91
1.10141	69.69	1.42188	87.59	1.41036	108.41
1.43009	69.63	2.22546	86.88	2.19660	107.83
2.21919	68.98	3.04732	86.66	3.18045	107.08
3.36991	68.55	4.43901	85.97		
4.37920	68.26	5.93186	85.26		
5.66748	67.82				

TABLE 2. MOLAR CONDUCTIVITIES OF SODIUM DICHLOROACETATE IN WATER AS FUNCTION OF TEMPERATURE

15 °C		25 °C		35 °C	
c (mol m^{-3})	Λ (cm^2 Ω^{-1} mol^{-1})	c (mol m^{-3})	Λ (cm^2 Ω^{-1} mol^{-1})	c (mol m^{-3})	Λ (cm^2 Ω^{-1} mol^{-1})
0	69.55	0	88.27	0	108.97
0.20595	68.61	0.19990	87.09	0.29099	107.10
0.35868	68.36	0.35322	86.72	0.47540	106.63
0.55703	68.11	0.55505	86.50	0.73606	106.31
0.80286	67.83	0.82304	86.13	1.06371	105.76
1.09032	67.61	1.08632	85.79	1.45131	104.97
1.42231	67.33	1.40913	85.39	1.90373	104.65
2.22863	66.82	2.221578	84.72	2.94811	103.85
3.20101	66.32	2.88883	84.23	4.20935	102.88
4.38957	65.80	4.36259	83.30		

TABLE 3. MOLAR CONDUCTIVITIES OF SODIUM TRICHLOROACETATE IN WATER AS FUNCTION OF TEMPERATURE

15 °C		25 °C		35 °C	
c (mol m^{-1})	Λ (cm^2 Ω^{-1} mol^{-1})	c (mol m^{-3})	Λ (cm^2 Ω^{-1} mol^{-1})	c (mol m^{-3})	Λ (cm^2 Ω^{-1} mol^{-1})
0	67.39	0	85.76	0	106.33
0.08473	66.83	0.19128	84.27	0.19092	105.02
0.18446	66.82	0.33988	84.30	0.33748	104.33
0.33866	66.26	0.53254	83.90	0.52748	103.68
0.52955	65.92	0.75835	83.67	0.76188	103.21
0.76237	65.73	1.04199	83.29	1.03524	102.74
1.03783	65.51	1.32992	82.94	1.35195	102.14
1.35270	65.29	2.12819	82.30	1.97345	101.54
2.11642	64.94	2.87635	81.68	3.04430	100.52
2.98928	64.33	3.93795	81.03		
4.15373	63.91	5.15951	80.49		
5.38978	63.44				

where τ_i and τ_0 are the mean residence times of a water molecule in the immediate neighbourhood of the ion in an aqueous solution and in the immediate vicinity of a water molecule in pure water, respectively. ΔE_i is the difference of the activation energies for the removal of a water molecule from the immediate neighbourhoods of the ion and the water molecule.

The value of ΔE_i is obtained from the temperature dependence of the limiting mobility of the ion. One of the authors (H. U.) together with Uedaira[4)] obtained the following equation for organic ions and molecules by extending the Samoilov's equation,[8)] which holds

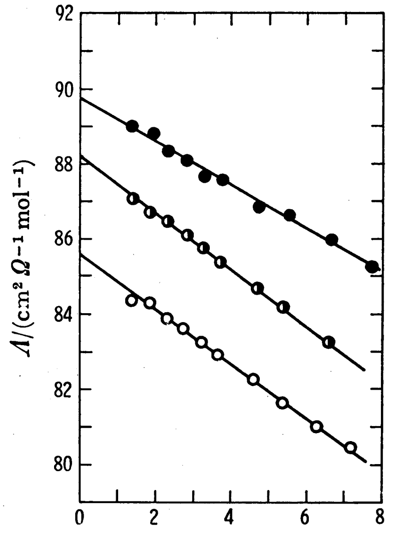

Fig. 1. Electric conductivities of NaMCA, NaDCA, and NaTCA in water at 25 °C.
—●— NaMCA, —◑— NaDCA, —○— NaTCA.

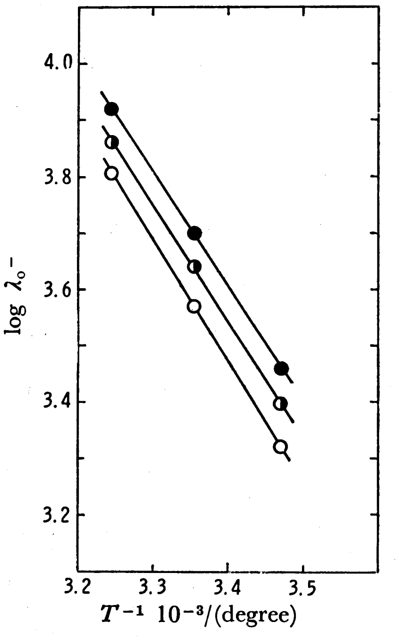

Fig. 2. Temperature dependence of limiting mobilities of MCA⁻, DCA⁻, and TCA⁻ ions.
—●— MCA⁻, —◑— DCA⁻, —○— TCA⁻.

for inorganic ions;

$$\frac{1}{\lambda_-^\circ}\frac{\mathrm{d}\lambda_-^\circ}{\mathrm{d}T}+\frac{1}{T}-\frac{1}{D_\mathrm{w}}\frac{\mathrm{d}D_\mathrm{w}}{\mathrm{d}T}=\frac{\Delta E_\mathrm{i}}{RT^2}, \tag{3}$$

where D_w is the self-diffusion coefficient of pure water. ΔE_i consists of two terms,

$$\Delta E_\mathrm{i}=\Delta E_1+\Delta E_2, \tag{4}$$

where ΔE_1 and ΔE_2 represent the effects of the ionized and the hydrophobic groups on the thermal motion of water molecule around the organic ion, respectively. In general, ΔE_2 represents the effect of any group except the ionized group.

Table 4. The values of ΔE_i and $\tau_\mathrm{i}/\tau_\mathrm{o}$ for mono-, di-, and trichloroacetate ions at 25 °C

Ions	$r(10^{-10}\,\mathrm{m})$	ΔE_i(J/mol)	$\tau_\mathrm{i}/\tau_\mathrm{o}$
MCA⁻	2.41	285	1.12
DCA⁻	2.54	582	1.26
TCA⁻	2.67	1247	1.65

From the results of Fig. 2 and the self-diffusion coefficient of water,[13] the values of ΔE_i and $\tau_\mathrm{i}/\tau_\mathrm{o}$ for MCA⁻, DCA⁻, and TCA⁻ ions at 25 °C were calculated by the Eqs. 2 and 3. The calculated results and the ionic radii estimated by the Pauling model[14] are presented in Table 4. The values of ΔE_i and $\tau_\mathrm{i}/\tau_\mathrm{o}$ for MCA⁻, DCA⁻, TCA⁻, and acetate ions[4] are shown in Fig. 3 as a function of the ionic radius.

It is seen from Table 4 that the residence times of a water molecule around MCA⁻, DCA⁻, and TCA⁻ ions are larger than that in pure water. That is to say, these anions are structure maker, and the structure making effect increases with an increase in the number of the chlorine atom.

As the result of the molecular motion, a water molecule change very rapidly its position and the momentary configurations between individual molecules. If the residence time of a water molecule in the hydration sphere of an ion is longer than that in pure water, also its reorientational time in the hydration sphere is longer than that in pure water. Hertz and Zeidler[15] showed that the residence time of the water molecule in the hydration sphere, τ_i, must be approximately equal to the reorientational correlation time. This concept was confirmed in the case of inorganic[16] and organic ions.[4] Engel and Hertz[2] obtained the value of 1.7, as the ratio of the reorientational correlation time in the hydration sphere to that in pure water

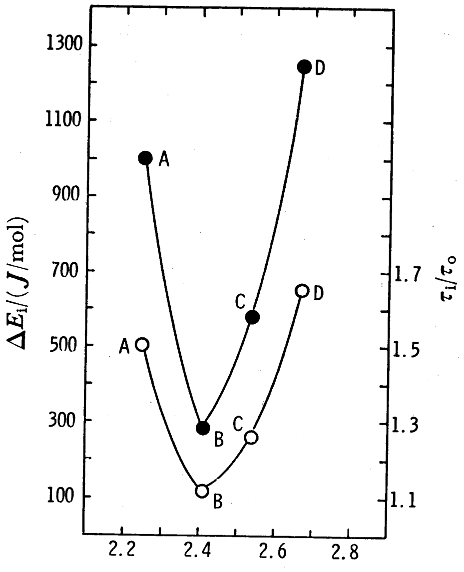

Fig. 3. The values of ΔE_i and $\tau_\mathrm{i}/\tau_\mathrm{o}$ of acetate, MCA⁻, DCA⁻, and TCA⁻ ions.
—●— ΔE_i, —○— $\tau_\mathrm{i}/\tau_\mathrm{o}$.
A; acetate ion, B; MCA⁻, C; DCA⁻, D; TCA⁻.

for TCA$^-$ ion at 25 °C. Their result coincides very good with the result of Table 4.

From Fig. 3 one sees that ΔE_1 and τ_1/τ_0 for acetate ion are larger than those for MCA$^-$ and DCA$^-$ ions. Since ΔE_1 and τ_1/τ_0 are the characteristic quantities of the hydration at infinite dilution, the difference in ΔE_1 among acetate and chloroacetate ions is attributed to the difference in ΔE_2 in Eq. 4. Consequently, the thermal motion of the water molecule around $-CH_3$ group is slower than those around $-CH_2Cl$ and $-CHCl_2$ groups.

The possible explanation for this result is made as follows. At present, it is not yet clear what kind of water structure is formed around the alkyl groups in water. According to Wen,[17)] there are two possibilities: ice-like and gashydrate-like types. The water molecule in the vicinity of the chlorine atom of MCA$^-$, DCA$^-$, and TCA$^-$ ions may turn its proton preferentially towards the chlorine atom during the residence in the hydration sphere. This orientation is different from that of the water molecule around $-CH_3$ group. In the surroundings of $-CH_2Cl$ and $-CHCl_2$ groups, therefore, a competition between the different orientatins of water molecules occurs, and on account of this competitive action the water structure around these two groups may be in a state more disturbed than those around $-CH_3$ and $-CCl_3$ groups. As a result, the thermal motion of the water molecules around $-CH_2Cl$ and $-CHCl_2$ groups are faster than those around $-CH_3$ and $-CCl_3$ groups. Taking account of the fact that ΔE_1 of TCA$^-$ ion is larger than that of acetate ion, the thermal motion of water molecule around $-CH_2Cl$ group is most vigorous (see Fig. 3).

If TCA$^-$ ion and a compound with the hydrophobic group coexist in an aqueous solution, the water structure around the hydrophobic group may be disturbed by $-CCl_3$ group. That is, TCA$^-$ ion behaves like a structure breaker and the hydrophobic compound is salted-in by TCA$^-$ ion. The result of Robinson and Jencks[1)] is accounted in this manner.

Both TCA$^-$ and acetate ions are structure maker, but the water structure around them is very different from each other. Probably, the chlorine atom does not from the hydrogen bond with the water molecule, taking account of the values of τ_1/τ_0. Actually, Walrafen[18)] found no evidence of the presence of the hydrogen bond between the water molecule and the chlorine atom by the measurement of Raman spectra of aqueous solution of NaTCA.

It is interesting to compare the dynamic structure of water around the chloro and methyl substituent groups of the protons in the methyl group of an acetate ion, since the van der Waals volume of the chlorine atom is equal to that of the methyl group. The limiting mobility is inversely proportional to both the ionic radius and the microviscosity of water around the ion, which depends on the water structure.[19)] MCA$^-$, DCA$^-$, and TCA$^-$ ions have the same volumes as propionate, isobutyrate, and trimethyl acetate ions, respectively. Therefore, the difference of the limiting mobilities of the ions can be ascribed in the difference in water structure around the ions. The limiting mobilities of propionate, isobutyrate, and trimethyl acetate ions at 25 °C are 35.82,[20)] 24, and 23[4)] Ω^{-1} cm^2 mol^{-1}, respectively.

From the values of the limiting mobilities, it is found that the microviscosities of water around MCA$^-$, DCA$^-$, and TCA$^-$ ions are smaller than those around the corresponding methyl substituents of the acetate ion. Thus, the degree of the structure making effect of the chloroacetate ions is lower than that of the corresponding methyl substituents. Recently, we found that the degree of hydrophobic hydration of isobutyrate and trimethyl acetate ions is very strong.[4)] These results support the existence of the competition between the different orientations of water molecules around $-CH_2Cl$ and $-CHCl_2$ groups.

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