Influence of Structure Breaking and Structure Forming Ions on the Dissociation Mechanism of Acetic Acid in Aqueous Solutions

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Dedicated to Professor W. Vielstich on the Ocassion of his 65th Birthday.

Using a rotating disc electrode, the dissociation rate of acetic acid in various aqueous electrolyte solutions is studied. Li^+, Cs^+ and $(CH_3)_4N^+$ at 1 M concentration considerably modify the activation enthalpy and entropy of the reaction. Evidently the interaction between the cations and water influences the dissociation mechanism of the weak acid. In the presence of 1 molar Li^+ the activated complex of acetic acid seems to contain only one water molecule instead of two in the other cases.

Keywords: Dissociation mechanism, weak acids, structure breaking and structure forming ions.

Introduction

The dissociation of weak acids in aqueous solutions has already been studied in previous papers [1, 2]. The dissociation seems to take place after formation of an activated complex [3, 4] in which two orientated water molecules allow for the formation of long-distance ion pairs. If the ionic strength is close to zero, the critical charge separation seems to be 7.5 Å [5], i.e. about three times the length of a hydrogen bond in water. This charge separation enables the dissociation of the ion pair. Thus, the dissociation step requires the previous orientation of two water molecules, this orientation being a process competing with the tendency of the water molecules to acquire their usual short range order.

Introduction of ions influences the ordering of the water molecules. Some ions are structure-breaking, others, such as ions with hydrophobic groups [6] are structure-forming.

Thus, when the solution contains structure-breaking ions, e.g., Na^+ or K^+, the orientation of the two water molecules needed for the formation of the activated complex should become easier. The contrary should be the case if the ions are structure-promoting.

In our work we have studied with a rotating disc electrode, how the formation of the activated complex is influenced by the presence of Li^+, Na^+, K^+, Cs^+ and $(CH_3)_4 N^+$ at different concentrations. The counterion was Cl^- in all cases. The obtained results are discussed within the framework of the water structure theories of Samoilov [7] and Nemethy and Scheraga [8].

The limiting currents obtained on a Pt rotating disc electrode can be described with the Dogonadze equation [9], and the necessary diffusion coefficient data can be deduced from Gregory and Riddiford's description [10]. According to Dogonadze's equation a plot of $i_L^r/\sqrt{\omega}$. vs. i_L^r should yield a straight line from whose slope the value of k_r can be obtained, provided the values of D_{H^+} K_{AH}, v, C_{A^-} and K_i are known. The symbols used here have their usual meaning. Gregory and Riddiford's aproximation allows to obtain the necessary values of D_{H^+} and D_{AH}. From measurements at different temperatures (which requires also the measurement of D_{H^+}, D_{AH}, v, K_i at different temperatures) plots of ln k_r vs. $1/T$ can be made, or of ln k_f vs. $1/T$, since k_f and k_r are related to the dissociation constant by:

$$K_i = k_f/k_r\,. \tag{1}$$

Supposing the expression (11)

$$k_f = \frac{k_B\,T}{h}\exp\left(\frac{\Delta S^{\neq}}{R}\right)\exp\left(-\frac{\Delta H^{\neq}}{R\,T}\right) \tag{2}$$

to be valid, a plot of ln k_f vs. $1/T$ should give, approximately, a straigt line with the slope $\Delta H^{\neq}/R$, and from the intercept a $T^{-\infty}$ the activation entropy for acetic acid dissociation could be obtained.

Experimental

The cell (glass, 500 cm³ capacity) consisted of three compartments, one for the PINE INST. Co, rotating Pt disc electrode, one for the SCE reference electrode, which communicates with a Luggin capillary, and one

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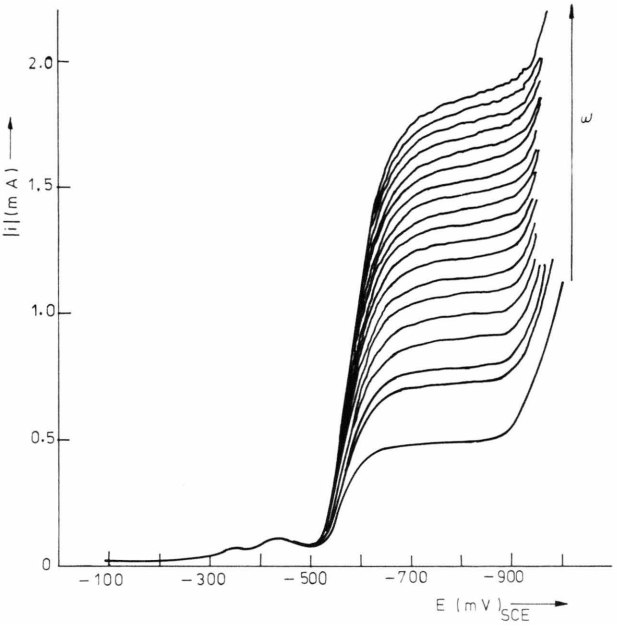


Fig. 1. Limiting current for H_3O^+ reduction at increasing rotation rate in solution of 1 M KCl, $3 \cdot 10^{-2}$ M NaAc and $3 \cdot 10^{-3}$ M HAc. $T = 5$ °C. $v = 50$ mV sec^{-1}.

for the Pt counter electrode (a 1 cm^2 Pt plate). The disc electrode had an area of 0.5 cm^2 and was inserted in a Teflon cylinder of 1.83 cm diameter. An MS 120 Model Fabelle potentiostat for the potential control and a PAR Mo. 175 Universal Programmer as function generator were used. The voltammograms and limiting currents were recorded on a Hewlett-Packard Mod. 7047A X-Y Recorder. The viscosity was measured with a Pobel glass pycnometer and the K_i value of acetic acid with a Beckman Expandomatic pH meter-Potentiometer. A Heto thermostat and a Colora Tauchkühler served for controlling the temperature. The Na^+, K^+, Cs^+ and $N(CH_3)_{4^+}$ chlorides were from Merck (p.a) and the Li^+ chloride from Carlo Erba (p.a.).

The concentrations of acetic acid and sodium acetate were $3 \cdot 10^{-3}$ M and $3 \cdot 10^{-2}$ M, respectively, and the chloride concentrations were 0.5 and 1 M.

The measurements of the diffusion coefficient for the free proton were made for a $3 \cdot 10^{-3}$ M HCl solution at 0.5 or 1.0 M concentrations of the electrolytes used.

The solutions were prepared with bidistilled water cleansed through a Millipore System and deaireated by stirring with N_2 previous to each experiment. The Pt disc working electrode was activated by application of triangular potential sweeps between hydrogen and oxygen evolution until the same voltammogram, taken as a reference, was obtained. Before every experiment and before activation, the working electrode was polished with 0.05 μ alumina powder.

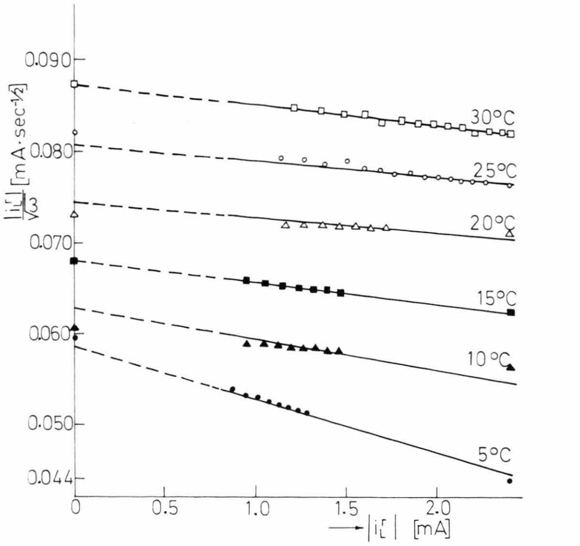


Fig. 2. $i_L^r \sqrt{\omega}$ vs. i_L^r for solution of 1 M Li Cl, $3 \cdot 10^{-2}$ M NaAc and $3 \cdot 10^{-3}$ M HAc.

Table 1. Diffusion coefficients of undissociated acetic acid molecules obtained from the intercepts of $i_L^r/\sqrt{\omega}$ vs. i_L^r plots in the presence of 0.5 M and 1.0 M MCl solutions.

	$D_{AH} \times 10^6$					
	t (°C)	LiCl	NaCl	KCl	CsCl	$(CH_3)_4NCl$
0.5 M MCl	5	5.68	6.46	6.27	6.01	6.27
	10	7.45	7.31	7.58	6.73	6.88
	15	8.34	7.90	8.41	7.80	8.30
	20	9.35	9.35	9.68	8.11	9.21
	25	10.20	10.40	10.60	9.59	9.94
	30	11.40	10.90	11.40	11.10	11.50
0.1 M MCl	5	6.01	6.29	6.25	6.26	5.68
	10	6.10	6.36	7.47	6.20	6.19
	15	7.15	7.18	8.76	6.95	7.31
	20	7.91	8.45	8.94	7.40	8.15
	25	9.05	9.05	10.60	9.84	9.51
	30	9.79	9.58	11.80	10.60	10.90

Results

Figure 1 shows the limiting currents obtained in a special case. The potential sweep rate was 50 mV sec^{-1}.

Table 2. Values of k_f (sec^{-1}) and k_r (1 mol^{-1} sec^{-1}) for the dissociation of acetic acid in the presence of 0.5 M and 1.0 M MCl.

Reaction: $CH_3-COOH+HOH \underset{k_r}{\overset{k_f}{\rightleftarrows}} CH_3-COO^-+H_3O^+$.

	0.5 M MCl	LiCl		NaCl		KCl		CsCl		$(CH_3)_4NCl$	
	T (°C)	k_f (sec^{-1})	k_r (1 M^{-1} sec^{-1})	k_f (sec^{-1})	k_r (1 M^{-1} sec^{-1})	k_f (sec^{-1})	k_r (1 M^{-1} sec^{-1})	k_f (sec^{-1})	k_r (1 M^{-1} sec^{-1})	k_f (sec^{-1})	k_r (1 M^{-1} sec^{-1})
0.5 M MCl	5	$2.4\cdot10^5$	$8.0\cdot10^9$	$3.1\cdot10^5$	$1.2\cdot10^{10}$	$3.4\cdot10^5$	$1.5\cdot10^{10}$	$2.0\cdot10^5$	$8.9\cdot10^9$	$2.7\cdot10^5$	$8.9\cdot10^9$
	10	$2.8\cdot10^5$	$9.1\cdot10^9$	$3.6\cdot10^5$	$1.4\cdot10^{10}$	$3.8\cdot10^5$	$1.6\cdot10^{10}$	$2.3\cdot10^5$	$1.0\cdot10^{10}$	$3.5\cdot10^5$	$1.1\cdot10^{10}$
	15	$3.3\cdot10^5$	$1.0\cdot10^{10}$	$4.2\cdot10^5$	$1.6\cdot10^{10}$	$4.3\cdot10^5$	$1.8\cdot10^{10}$	$2.8\cdot10^5$	$1.0\cdot10^{10}$	$4.2\cdot10^5$	$1.3\cdot10^{10}$
	20	$4.0\cdot10^5$	$1.2\cdot10^{10}$	$5.0\cdot10^5$	$1.7\cdot10^{10}$	$5.3\cdot10^5$	$2.2\cdot10^{10}$	$3.2\cdot10^5$	$1.4\cdot10^{10}$	$4.8\cdot10^5$	$1.5\cdot10^{10}$
	25	$4.8\cdot10^5$	$1.5\cdot10^{10}$	$5.3\cdot10^5$	$1.9\cdot10^{10}$	$5.8\cdot10^5$	$2.4\cdot10^{10}$	$3.6\cdot10^5$	$1.5\cdot10^{10}$	$5.0\cdot10^5$	$1.6\cdot10^{10}$
	30	$5.6\cdot10^5$	$1.7\cdot10^{10}$	$5.6\cdot10^5$	$2.0\cdot10^{10}$	$6.0\cdot10^5$	$2.5\cdot10^{10}$	$3.6\cdot10^5$	$1.6\cdot10^{10}$	$5.4\cdot10^5$	$1.7\cdot10^{10}$
1.0 M MCl	5	$8.5\cdot10^4$	$1.4\cdot10^{10}$	$4.3\cdot10^5$	$1.5\cdot10^{10}$	$4.5\cdot10^5$	$1.8\cdot10^{10}$	$1.5\cdot10^5$	$6.0\cdot10^9$	$4.3\cdot10^5$	$1.3\cdot10^{10}$
	10	$2.6\cdot10^5$	$1.6\cdot10^{10}$	$4.9\cdot10^5$	$1.7\cdot10^{10}$	$4.9\cdot10^5$	$1.9\cdot10^{10}$	$1.6\cdot10^5$	$6.3\cdot10^9$	$6.3\cdot10^5$	$1.6\cdot10^{10}$
	15	$5.9\cdot10^5$	$1.7\cdot10^{10}$	$5.8\cdot10^5$	$1.9\cdot10^{10}$	$5.0\cdot10^5$	$1.9\cdot10^{10}$	$1.9\cdot10^5$	$7.5\cdot10^9$	$9.8\cdot10^5$	$1.7\cdot10^{10}$
	20	$6.2\cdot10^5$	$1.8\cdot10^{10}$	$6.8\cdot10^5$	$2.2\cdot10^{10}$	$5.6\cdot10^5$	$2.1\cdot10^{10}$	$2.3\cdot10^5$	$8.8\cdot10^9$	$1.2\cdot10^6$	$1.8\cdot10^{10}$
	25	$6.9\cdot10^5$	$1.9\cdot10^{10}$	$7.2\cdot10^5$	$2.3\cdot10^{10}$	$6.1\cdot10^5$	$2.3\cdot10^{10}$	$2.8\cdot10^5$	$1.4\cdot10^{10}$	$1.5\cdot10^6$	$1.9\cdot10^{10}$
	30	$8.5\cdot10^5$	$2.4\cdot10^{10}$	$7.3\cdot10^5$	$2.4\cdot10^{10}$	$6.4\cdot10^5$	$2.5\cdot10^{10}$	$3.3\cdot10^5$	$1.8\cdot10^{10}$	$1.8\cdot10^6$	$2.2\cdot10^{10}$

Table 3. Activation enthalpy and entropy for the formation of the activated complex in the presence of 0.5 M and 1.0 M MCl solutions of the cations mentioned.

Cation	r_{Stokes} (Å)	$\Delta H_f^{\neq}$ (kJ mol^{-1})		$\Delta S_f^{\neq}$ J mol^{-1} K^{-1}	
		0.5 M	1.0 M	0.5 M	1.0 M
Cs^+	1.19	18.1	24.3	−78.1	−58.9
K^+	1.25	17.0	9.9	−77.7	−100.9
Na^+	1.83	17.9	15.9	−75.5	−79.5
$(CH_3)_4N^+$	2.04	19.2	39.7	−70.9	+6.5
Li^+	2.37	23.9	58.5	−55.8	+64.2

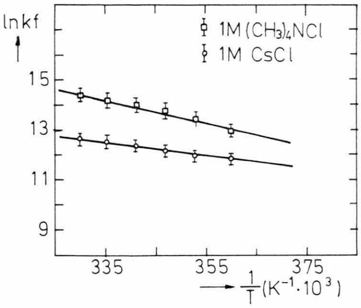


Fig. 3. ln k_f vs. $1/T$ for 1 M CsCl and 1 M $(CH_3)_4$ NCl solutions.

The limiting currents extend over a potential range of around 250 mV. Similar plots are obtained in all cases. In this way i_L^r (mA) was measured. A plot of $i_L^r/\sqrt{\omega}$ vs. i_L^r is shown in Figure 2. According to Dogonadze's equation, the slopes and intercepts of the straight lines of Fig. 2 allow to obtain values for k_r and, therefore, for k_f, provided the values of K_i (dissociation constant of the weak acid), D_{H^+} D_{AH}, and the viscosity have been measured. C_{A^-} has been previously fixed. Table 1 shows the obtained D_{AH} values and Table 2 the obtained k_r and k_d values. Figure 3 shows plots of ln k_d vs. $1/T$ obtained for solutions containing 1 M C_sCl and 1 M $(CH_3)_4$ NCL. The slopes of these plots lead to the activation energies 24.3 and 39.7 kJ mol^{-1}, respectively, for the acetic acid dissociation process. Table 3 shows the activation enthalpies and entropies deduced from plots analogous to those given in Figure 3. In Figs. 4 and 5 the activation enthalpies $\Delta H_d^{\neq}$ and entropies $\Delta S_d^{\neq}$ for acetic acid dissociation are plotted vs. the Stokes radii of the corresponding cations.

Before carrying out the measurements it was necessary to make sure that the obtained results were not influenced by effects of the field in the diffusion layer and perhaps in the diffuse double layer [12]. Mihelcic and Vielstich [13] studied the influence of the field effect on the acetic acid dissociation. They showed that k_f for acetic acid dissociation and, therefore, k_r is a function of δ_R (reaction layer thickness) only when δ_R is smaller than a critical value of around 30 Å. Taking a value for k_r of $2.1 \cdot 10^{10}$ (of the same order of magnitude as the k_r values shown in Table 2), application of the equation

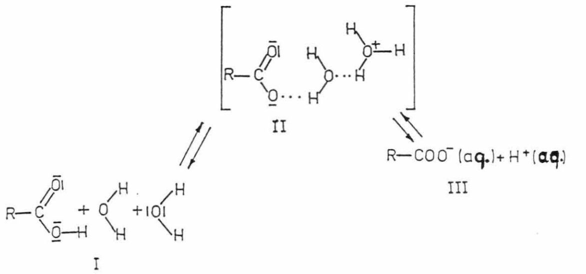
$$\delta_R\,(\text{cm}) = \sqrt{\frac{D}{k_r(\text{Ac}^-)}} \qquad (3)$$

gives a δ_R value of around 34.8 Å (13).

At 25 °C the layer is already so thick that with further increase of δ_r the constant k_f does not change any more. Furthermore, the fact that [Ac$^-$] was maintained constant means that the field effects on the acetic acid dissociation were the same, so that no influence on the reaction kinetics could be expected.

Discussion

Provided two water molecules are necessary to obtain an activated complex, the dissociation process of any weak acid takes place according to the following steps:



Configuration II corresponds to the activated complex; the positive and negative charges are separated by 7.5 Å [5].

The number of hydrogen bridges which must be broken for the formation of an activated complex depends on the structure of the solvent, i.e. on the type and concentration of the ions present [6].

Activation Enthalpy Values

Table 3 and Fig. 4 show that the most significant effect on $\Delta H_f^{\neq}$ is brought about by $(CH_3)_4N^+$ and Li^+ at 1.0 M concentration. For the other ions at 1.0 M and all ions at 0.5 M $\Delta H_f^{\neq}$ has a value around 18 kJ mol^{-1}, i.e. about for times the value 1.32 kcal mol^{-1} = 5.52 kJ mol^{-1} calculated [8] for the breaking of one of the four distorted hydrogen bonds with which a water molecule is bound in liquid water. This corresponds to the breaking of about 2 hydrogen bonds for each of the two water molecules in the activated complex. Only the Li^+ ions show also at 0.5 M a little effect ($\Delta H_f^{\neq} \simeq 24$ kJ mol^{-1}), due to the high capacity of these small ions for orientating water molecules in their solvation shells.

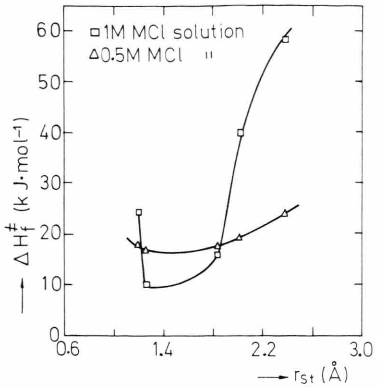


Fig. 4. The activation enthalpy for acetic acid dissociation in the presence of 0.5 M and 1.0 M MCl vs. the Stokes radius of the cation of the electrolyte.

Effect of Structure Forming Ions on the $\Delta H_f^{\neq}$ Value

In case of the structure promoting ion $(CH_3)_4N^+$ the big size and the methyl hydrophobic group give rise to a high structuration of the solvent. The presence of such ions in a 1.0 M solution requires breaking of almost 2 hydrogen bonds of an "icelike" structure (in ice the energy per hydrogen bond is twice that in liquid water) for every water molecule entering the activated complex.

Effect of Structure Breaking Ions on the $\Delta H_f^{\neq}$ Value

The small Li^+ ions have the greatest Stokes radius [7]. In the case of the 1.0 M Li^+ solution, the two water molecules necessary for the formation of the activated complex have to be snatched from the solvation shells of the Li^+ ions, so that coulombic interac-

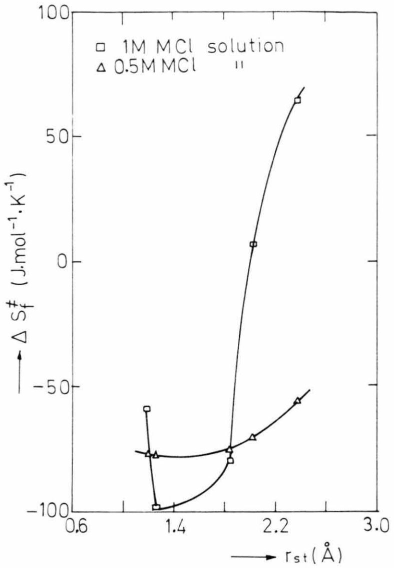
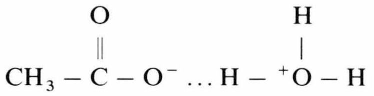


Fig. 5. The activation entropy for acetic acid dissociation in the presence of 0.5 M and 1.0 M MCl vs. the Stokes radius of the cation of the electrolyte.

tions beside hydrogen bond breaking must be overcome.

On the other hand, in the presence of highly orientating ions, possibly, dissociation of acetic acid via a complex containing only one water molecule could be preferred. The dissociation of such a structure, gives rise to two electrical charges close to each other, so that their coulombic interaction would be determining the dissociation step:



$$\mathrm{CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - O^- \ldots H - {}^{+}\overset{\overset{\displaystyle H}{|}}{O} - H}$$

For 0.5 M and 1.0 M solutions of $\mathrm{Na^+}$ and $\mathrm{K^+}$ ions the obtained $\Delta H_\mathrm{f}^{\neq}$ values agree with the small hydration capacity of both ions, or, according to Samailov's ideas [7] to their slight positive ($\mathrm{Na^+}$ ions) or negative ($\mathrm{K^+}$ ions) hydration. As for the $\mathrm{Cs^+}$ ions, their negative hydration [7] can explain their low Stokes radius. Their large size contributes significantly to the structuring of water, whenever the concentration is high enough. This explains the high $\Delta H_\mathrm{f}^{\neq}$ value obtained in the presence of 1 M $\mathrm{Cs^+}$ ions.

It is clear that the $\mathrm{Cl^-}$ ions cannot affect the $\Delta H_\mathrm{f}^{\neq}$ or $\Delta S_\mathrm{f}^{\neq}$ values since they were the common counterions. Only a specific adsorption could play a role, but not in the used potential range in which they have to compete with H atoms for the Pt sites.

Activation entropy values

The obtained activation entropies are given in Table 3 and Figure 5. For the 0.5 M solutions $\Delta S_\mathrm{f}^{\neq} \simeq -75\ \mathrm{J\ mol^{-1}\ K^{-1}}$ with the exception of the $\mathrm{Li^+}$ ions ($\Delta S_\mathrm{f}^{\neq} = -56\ \mathrm{J\ mol^{-1}\ K^{-1}}$). The negative values of $\Delta S_\mathrm{f}^{\neq}$ indicate an increase of order on activated complex formation. This increase can be atributed: a) to the conversion of translational and rotational degrees of freedom in the reactants into vibrational degrees of freedom in the activated complex: and/or b) to the separated electrical charges in the activated complex which bring about an additional orientation of water dipoles around them.

In the 1.0 M solutions $\Delta S_\mathrm{f}^{\neq}$ is negative for the $\mathrm{Cs^+}$, $\mathrm{K^+}$ and $\mathrm{Na^+}$ ions. The value $-59\ \mathrm{J\ mol^{-1}\ K^{-1}}$ for the $\mathrm{Cs^+}$ ions may be due to their big size, which has an ordering effect on the water structure making the orientation of the water dipoles more difficult. The value $-100\ \mathrm{J\ mol^{-1}\ K^{-1}}$ for the $\mathrm{K^+}$ ions could be a consequience of their negative hydration (7), which also lowers the value for $\Delta H_\mathrm{f}^{\neq}$ (Table 3). The most significant effect, is shown by the $\mathrm{(CH_3)_4N^+}$ and $\mathrm{Li^+}$ ions at 1.0 M concentration. For the $\mathrm{(CH_3)_4N^+}$ ions $\Delta S_\mathrm{f}^{\neq}$ is slightly positive. It seems that the water molecules pass from one to an other structure with a balance of almost no entropy change. The above discussed $\Delta H_\mathrm{f}^{\neq}$ value agrees with this interpretation.

The $\mathrm{Li^+}$ ions at 1.0 M show a high positive $\Delta S_\mathrm{f}^{\neq}$ value: If only one water molecule takes part in the activated complex, the electrical charges in the complex remain close to each other so that their interaction could partly hinder water dipole orientation around them. These ideas are in agreement with the high $\Delta H_\mathrm{f}^{\neq}$ value obtained.

Acknowledgement

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