

Determination of the Standard Entropy Changes of Ion Transfer for 1-Alkylpyridinium Ions by Thermal Modulation Voltammetry with Laser Heating at a Water/1,2-Dichloroethane Interface

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When laser light impinges upon a liquid-liquid interface between an optically transparent aqueous and opaque organic phase from the aqueous to organic phase, the temperature at the interface and the interfacial region rises. Using this rise in temperature, we have proposed and developed thermal modulation voltammetry at an interface between two immiscible electrolyte solutions (TMV-ITIES) and have determined the standard entropy changes of ion transfer, $\Delta S_{\text{tr}}^{\circ, \text{O} \rightarrow \text{W}}$. In this work, we have determined $\Delta S_{\text{tr}}^{\circ, \text{O} \rightarrow \text{W}}$ for four 1-alkylpyridinium ions, namely 1-methylpyridinium ion (MePy⁺), 1-ethylpyridinium ion (EtPy⁺), 1-propylpyridinium ion (PrPy⁺), and 1-butylpyridinium ion (BuPy⁺) by TMV-ITIES. As a result, we obtained the $\Delta S_{\text{tr}}^{\circ, \text{O} \rightarrow \text{W}}$ values of 108.0 ± 0.5 ($n = 3$), 75.8 ± 4.4 , 55.6 ± 1.2 , and 42.7 ± 0.9 J K⁻¹ mol⁻¹ for MePy⁺, EtPy⁺, PrPy⁺, and BuPy⁺, respectively. From these values of $\Delta S_{\text{tr}}^{\circ, \text{O} \rightarrow \text{W}}$, we have suggested that MePy⁺, EtPy⁺, and PrPy⁺ are classified as water structure-breaking ions and BuPy⁺ as a weak water structure-making ion. Further, we discuss the relationship between the standard free energy change, $\Delta G_{\text{tr}}^{\circ, \text{O} \rightarrow \text{W}}$, and $\Delta S_{\text{tr}}^{\circ, \text{O} \rightarrow \text{W}}$ of ion transfer for 1-alkylpyridinium ions and tetraalkylammonium ions.

Keywords Thermal modulation voltammetry, laser heating, water/1,2-dichloroethane interface, standard entropy change, ion transfer, 1-alkylpyridinium ion

(Received January 30, 2014; Accepted March 3, 2014; Published May 10, 2014)

Introduction

In spectroelectrochemistry, at an interface between two immiscible electrolyte solutions (ITIES), light has been used as a probe for monitoring electrochemical events at ITIES.¹⁻³ In contrast to such use of light in spectroelectrochemistry, we used light as a heating source and have proposed and developed thermal modulation voltammetry at ITIES (TMV-ITIES).^{4,5} In TMV-ITIES, we irradiate ITIES with laser light in the visible region from a transparent to opaque phase for heating the interface and the interfacial region. In this work, an aqueous solution served as a transparent phase and 1,2-dichloroethane solution containing crystalviolet tetrakis(4-chlorophenyl)borate (CVTCIPB) as an opaque phase. When the laser light serving as a heating source is chopped at a fixed frequency, electric currents of ion transfer voltammetry at ITIES (VITIES) are modulated at the same frequency to give an alternative voltammetry by using lock-in detection. In our previous papers,^{4,5} we have shown that the standard entropy change of ion transfer, $\Delta S_{\text{tr}}^{\circ, \text{O} \rightarrow \text{W}}$, can be determined from a TM voltammogram, and practically determined $\Delta S_{\text{tr}}^{\circ, \text{O} \rightarrow \text{W}}$ for tetraalkylammonium ions and some anions. In this work, remarking that the structure of 1-alkylpyridinium ions is more simple, unlike that of tetraalkylammonium ions, which is tetrahedral, (Figs. 1(a) and 1(b)), we determined $\Delta S_{\text{tr}}^{\circ, \text{O} \rightarrow \text{W}}$ for four 1-alkylpyridinium ions,

namely 1-methylpyridinium ion (MePy⁺), 1-ethylpyridinium ion (EtPy⁺), 1-propylpyridinium ion (PrPy⁺), and 1-butylpyridinium ion (BuPy⁺). Here we report the values of $\Delta S_{\text{tr}}^{\circ, \text{O} \rightarrow \text{W}}$ for these 1-alkylpyridinium ions, and discuss the hydration of 1-alkylpyridinium ions and the structure effect on $\Delta S_{\text{tr}}^{\circ, \text{O} \rightarrow \text{W}}$.

Experimental

Apparatus and procedure

Figure 2 shows the experimental arrangement for measuring linear sweep (LS) voltammograms and thermal modulation

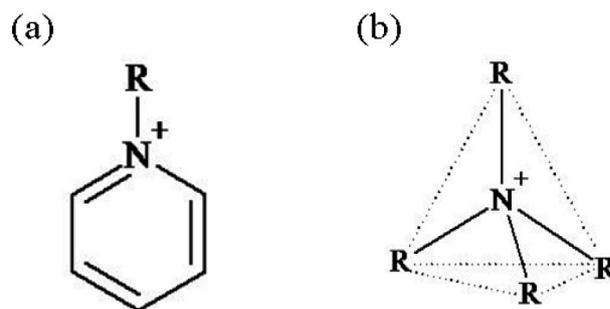


Fig. 1 (a) Simple structure of 1-alkylpyridinium ion, (b) Tetrahedral structure of tetraalkylammonium ion (R = methyl, ethyl, propyl, and butyl group)

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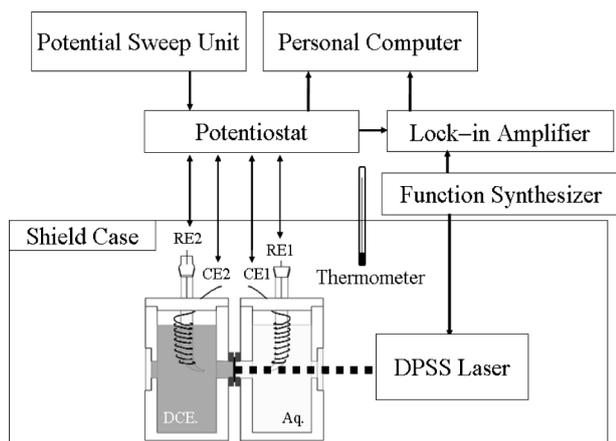


Fig. 2 Experimental arrangement of thermal modulation voltammetry at ITIES used in this work. The DCE phase looked purple when dissolving 10 mmol dm^{-3} (mM) CVTCIPB. The aqueous phase contained 10 mmol dm^{-3} LiCl. The ITIES was irradiated with the laser light from the transparent aqueous to purple DCE phase. RE1 and RE2 represent the Ag/AgCl electrodes, and CE1 and CE2 represent platinum wires.

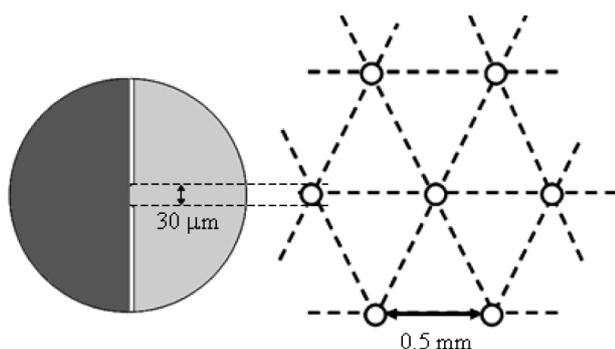
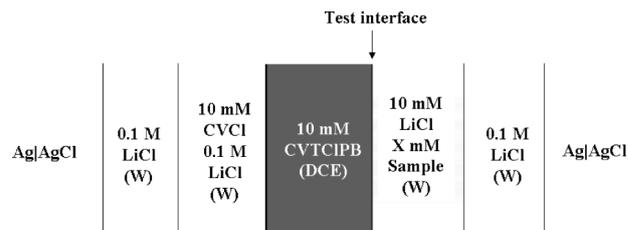


Fig. 3 Arrangement of microholes, serving micro-ITIESs, on a polyester film $16 \mu\text{m}$ thick. The film had 120 microholes $30 \mu\text{m}$ in diameter. The microholes were arranged at intervals of 0.5 mm .

(TM) voltammograms. A diode-pumped solid-state laser (DPSS, Phototechnica, JST, 532 nm , 30 mW) was used as a heating source. This laser beam was electronically modulated at 10 Hz by using a function synthesizer (NF, 1915), and was introduced from the aqueous to organic phase. The electrolytic cell was machined from poly(chlorotrifluoroethylene) resin blocks and composed of two compartments for the aqueous and 1,2-dichloroethane (DCE) phase. The cell was placed in a shield case in order to maintain the temperature and avoid electric noise. The two compartments were separated by a thin polyester film $16 \mu\text{m}$ thick with approximately 120 microholes $30 \mu\text{m}$ in diameter arranged as in Fig. 3. The microholes, bored into the film by an ultraviolet laser photoablation technique (Laserx Co., Ltd.),⁶ were employed as micro-ITIESs. The film was tightly held between two silicon rubber sheets together with the two compartments with screws. As shown in Scheme 1, the aqueous phase contained 10 mmol dm^{-3} (mM) LiCl as a supporting electrolyte and $X \text{ mmol dm}^{-3}$ 1-alkylpridinium ion as a sample, while the DCE phase contained 10 mmol dm^{-3} crystalviolet tetrakis(4-chlorophenyl)borate (CVTCIPB), which served not only as a supporting electrolyte but also as an optically absorbing substance. A visible absorption spectrum of



Scheme 1

CVTCIPB in DCE showed the absorption maximum at 591 nm and a molar absorption coefficient at 532 nm was $3.3 \times 10^3 \text{ m}^2 \text{ mol}^{-1}$. When the laser beam was modulated at 10 Hz , the temperature at the interface and interfacial region was also modulated, and consequently a current for ion transfer was modulated at the same frequency, depending on the standard entropy change of ion transfer and a temperature coefficient of a diffusion coefficient of a transferring ion. The modulated current was detected with a four-electrode type potentiostat (Hokuto Denko, HA1010mM1A) and amplified with a two-phase lock-in amplifier (NF, 5584A). The reference signal was supplied from the function synthesizer, which was used for driving the DPSS laser. The potential was swept at 5 mVs^{-1} with a potential sweep unit (Husou, Model 1104). A TM voltammogram and the corresponding LS voltammogram of ion transfer were simultaneously measured and recorded in a personal computer through a home-made interface. The ohmic drop compensation was not used in all the voltammetric measurements, and real parts of signals from the lock-in amplifier were recorded as a function of potential for measuring TM voltammograms. Only the real parts of signals were recorded because an analytical equation expressed with real numbers was used for determining the standard entropy changes of ion transfer, as described later. The reference electrodes of the aqueous and DCE phases were a silver/silver chloride (Ag/AgCl) and a crystalviolet ion-selective electrode, respectively. Platinum wires were used as counter electrodes. The measurements were carried out at room temperature, $25 \pm 2^\circ\text{C}$.

Reagents

In order to synthesize CVTCIPB, a methanol solution of crystalviolet chloride (CVCl, Tokyo Chemical Industry Co., Ltd.) and potassium tetrakis(4-chlorophenyl)borate (KTCIPB, Tokyo Chemical Industry Co., Ltd.) were mixed in a flask and the resulting precipitate was filtered.⁷ The precipitate of CVTCIPB was washed with a 1:1 v/v methanol-water solution more than five times and recrystallized twice from acetone. The DCE used was analytical grade (Nacalai Tesque, Inc.). DCE and deionized water were mixed in a large flask together and stirred with a stirring bar for 3 to 4 h for equilibration. After the equilibration, the DCE and aqueous solutions were prepared. All other reagents used were analytical grade and used without further purification.

Determination of the standard entropy change of ion transfer

The standard entropy change of ion transfer, $\Delta S_{\text{tr}}^{\text{O} \rightarrow \text{W}}$, for sample ions was determined according to the following equation,⁴

Table 1 Diffusion coefficients, D_w , and temperature coefficients of the diffusion coefficients, dD_w/dT , for four 1-alkylpyridinium ions

Ion	$D_w/10^{-10} \text{ m}^2 \text{ s}^{-1}$	$(dD_w/dT)/10^{-11} \text{ m}^2 \text{ s}^{-1} \text{ K}^{-1}$
MePy ⁺	8.4	2.5
EtPy ⁺	6.8	2.5
PrPy ⁺	5.4	1.9
BuPy ⁺	5.1	1.8

$$\Delta S_{\text{tr}}^{\circ, \text{O} \rightarrow \text{W}} = \frac{2RT}{D_w} \cdot \frac{dD_w}{dT} \cdot \frac{\Delta T_{\text{diff}}}{\Delta T_{\text{int}}} \cdot \left(1 - 2 \cdot \frac{\Delta I_{E_{1/2}}}{\Delta I_{E_L}}\right). \quad (1)$$

Here, D_w and dD_w/dT indicate a diffusion coefficient in the aqueous phase and its temperature coefficient, respectively. ΔT_{diff} and ΔT_{int} are temperature modulation widths in the diffusion layer and just at the interface, respectively. $\Delta I_{E_{1/2}}$ and ΔI_{E_L} are signal intensities of a TM voltammogram at the half-wave potential, $E_{1/2}$, and at any potential in the limiting current potential region, E_L , respectively. The half-wave potential was determined by the log-plot analysis of an LS voltammogram, which was recorded simultaneously with the TM voltammogram. R and T are the gas constant and the ambient temperature, which was $298 \pm 2 \text{ K}$, respectively. The diffusion coefficients of ions were estimated on the basis of the fact that a limiting-current of an LS voltammogram at a micro-ITIES, I_L , is proportional to a diffusion coefficient, *i.e.*, $I_L = 4NzFD_w r C^*$, where N , z , F , D_w , r , and C^* denote the number of the microhole (= 120), the charge of the transferring ion, the Faraday constant, the diffusion coefficient of the ion, the radius of the microhole, and the bulk concentration of the ion, respectively. Meanwhile, the temperature coefficients of the diffusion coefficients were determined by plotting the limiting currents against the temperatures from 293 to 313 K. Table 1 lists the diffusion coefficients and their temperature coefficients, dD_w/dT . The ratio of ΔT_{diff} to ΔT_{int} , $\Delta T_{\text{diff}}/\Delta T_{\text{int}}$, cannot be theoretically determined at present. Consequently, the ratio was experimentally estimated to be 0.182 by referring to a TM voltammogram for tetraethylammonium ion, TEA⁺, the standard entropy change for ion transfer of which is known as $16.8 \text{ J K}^{-1} \text{ mol}^{-1}$.⁸

Results and Discussion

Linear sweep voltammograms for 1-alkylpyridinium ions

Figure 4(a) shows linear sweep (LS) voltammograms for 1-alkylpyridinium ions, MePy⁺, EtPy⁺, PrPy⁺, and BuPy⁺, which were transferred from the aqueous to DCE phase. The results of the log-plot analyses for these LS voltammograms are summarized in Table 2. As can be seen in this table, the slopes were nearly equal to a theoretical value at 298 K, 0.059 V, which indicates that ion transfers of these cations are reversible. Since each LS voltammogram showed one well-defined S-shaped wave, it is supposed that secondary ion transfers for photodecomposed substances of crystalviolet (CV⁺) and tetrakis(4-chlorophenyl)borate (TCIPB⁻) ion do not occur in the potential range examined. On the other hand, the half-wave potential increases with decreasing alkyl-chain length of the 1-alkylpyridinium ion. This is because the hydrophilic nature of the ions increases with decreasing alkyl-chain length. Further, the limiting current increases with decreasing alkyl-chain length. This is attributed to the fact that the diffusion coefficient

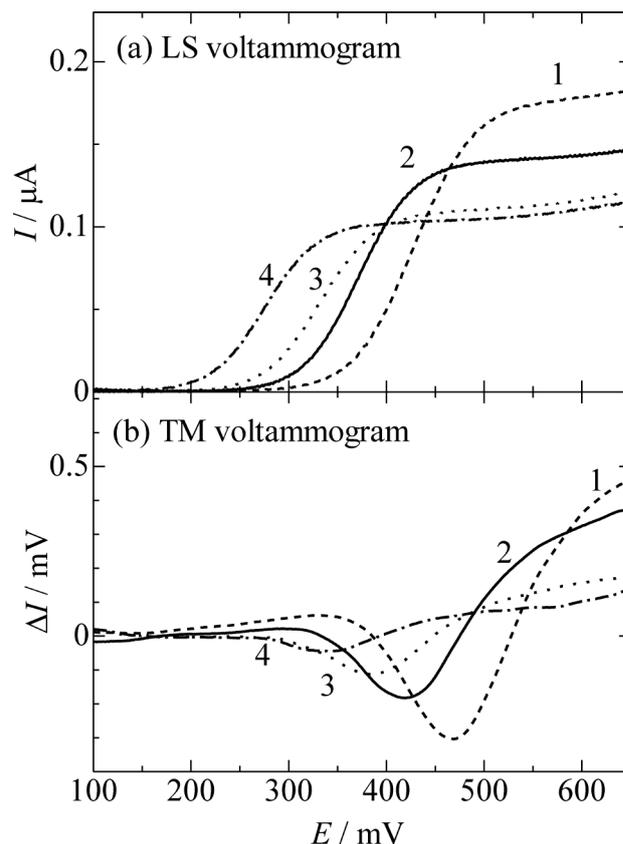


Fig. 4 Linear sweep (LS) (a) and thermal modulation (TM) (b) voltammograms. The concentrations of the four 1-alkylpyridinium ions were 0.3 mmol dm^{-3} . 1, MePy⁺; 2, EtPy⁺; 3, PrPy⁺; 4, BuPy⁺. The sweep rate was 5 mV s^{-1} . Both the voltammograms were corrected for the blank aqueous phases. The ΔI in the TM voltammogram are real parts (X components) of signals from the lock-in amplifier.

Table 2 Half-wave potentials for the 1-alkylpyridinium ions and slopes obtained by the log-plot analysis

Ion	$E_{1/2}/V$	E°/V^a	Slope/V
MePy ⁺	0.430	0.118	0.064
EtPy ⁺	0.374	0.062	0.062
PrPy ⁺	0.334	0.023	0.062
BuPy ⁺	0.279	-0.033	0.061

a. The values of E° are based on the TA-TB assumption. The value of E° for TEA⁺ is 0.02 V according this assumption.⁹

increases with decreasing alkyl-chain length (Table 1).

Thermal modulation voltammograms for 1-alkylpyridinium ions

Figure 4(b) shows thermal modulation (TM) voltammograms for the 1-alkylpyridinium ions. All the TM voltammograms displayed minima, suggesting that the standard entropy changes of ion transfer, $\Delta S_{\text{tr}}^{\circ, \text{O} \rightarrow \text{W}}$, for the ions are positive values.⁴ Further, the potentials of the minima increased with decreasing alkyl-chain length in a similar way to the half-wave potentials. Table 3 lists the thermodynamic parameters, such as the standard free energy change of ion transfer, $\Delta G_{\text{tr}}^{\circ, \text{O} \rightarrow \text{W}}$, $\Delta S_{\text{tr}}^{\circ, \text{O} \rightarrow \text{W}}$, and the standard enthalpy change of ion transfer, $\Delta H_{\text{tr}}^{\circ, \text{O} \rightarrow \text{W}}$, determined from the LS and TM voltammograms. Here, $\Delta G_{\text{tr}}^{\circ, \text{O} \rightarrow \text{W}}$ was calculated from the relation, $\Delta G_{\text{tr}}^{\circ, \text{O} \rightarrow \text{W}} = -FE^\circ$, and the standard potential for ion transfer, E° , was estimated from the half-wave

Table 3 Thermodynamic parameters for the four 1-alkylpridinium ions^a

Ion	$\Delta G_{tr}^{o,O \rightarrow W} / \text{kJ mol}^{-1}$	$\Delta S_{tr}^{o,O \rightarrow W} / \text{kJ mol}^{-1}$	$\Delta H_{tr}^{o,O \rightarrow W} / \text{kJ mol}^{-1}$
MePy ⁺	-10.0 ± 1.4	108.0 ± 0.5	22.7 ± 1.9
EtPy ⁺	-5.0 ± 1.5	75.8 ± 4.4	17.5 ± 0.9
PrPy ⁺	-3.2 ± 1.0	55.6 ± 1.2	14.7 ± 2.8
BuPy ⁺	-4.0 ± 0.8	42.7 ± 0.9	15.2 ± 3.0

a. The number of measurements was 3.

potential, $E_{1/2}$, according to the following equation for a liquid-liquid microinterface:¹⁰

$$E^o = E_{1/2} - \frac{RT}{zF} \ln \frac{\gamma_{D_w}^o}{\gamma_{D_o}^w} + \frac{RT}{zF} \ln \left(\frac{4d}{\pi r} + 1 \right), \quad (2)$$

then, the values of E^o were converted to ones based on the tetraphenylarsonium-tetraphenylborate assumption (TA-TB assumption; see Table 2). Here γ^o and γ^w denote the activity coefficient of the ion in the DCE and aqueous phases, respectively. In this work, it was assumed that γ^o is equal to γ^w . The ratio of D_w to D_o , D_w/D_o , was estimated from a viscosity ratio of water to DCE according to Walden rules.¹¹⁻¹⁴ The radius of the microhole and the film thickness are denoted by r and d . The standard enthalpy change of ion transfer, $\Delta H_{tr}^{o,O \rightarrow W}$, was calculated from the relation $\Delta H_{tr}^{o,O \rightarrow W} = \Delta G_{tr}^{o,O \rightarrow W} + T\Delta S_{tr}^{o,O \rightarrow W}$. As expected from the shapes of the TM voltammograms, the values of $\Delta S_{tr}^{o,O \rightarrow W}$ were positive, and increase with decreasing alkyl-chain length.

Assuming that solvation of the ions by DCE molecules hardly contributes to $\Delta S_{tr}^{o,O \rightarrow W}$, $\Delta S_{tr}^{o,O \rightarrow W}$ would be mainly attributed to hydration, that is, the structure of water. When $\Delta S_{tr}^{o,O \rightarrow W}$ ($= S_w - S_o$) is positive, the ion destroys the structure of water and has the opposite effect when $\Delta S_{tr}^{o,O \rightarrow W}$ is negative, that is, the ion promotes it. Based on the positive values of $\Delta S_{tr}^{o,O \rightarrow W}$ for 1-alkylpridinium ions, these ions are expected to be structure-breaking. According to a hydration model proposed by Frank and Wen,¹⁵ very hydrophilic ions such as Li⁺, Na⁺ and hydrophobic ions such as a tetrabutylammonium ion are classified as a water structure-making ions, and ions between very hydrophilic and hydrophobic ions serve as structure-breaking ions. Consequently, the decrease in $\Delta S_{tr}^{o,O \rightarrow W}$ with increasing alkyl-chain length can be explained by the fact that the ions with longer alkyl-chain have a more hydrophobic nature and a tendency to make the structure of water.

Relationship between $\Delta G_{tr}^{o,O \rightarrow W}$ and $\Delta S_{tr}^{o,O \rightarrow W}$

Figure 5 shows the relationships between $\Delta G_{tr}^{o,O \rightarrow W}$ and $\Delta S_{tr}^{o,O \rightarrow W}$ for 1-alkylpridinium ions (\blacktriangle) and tetraalkylammonium ions. The figure shows two separate values for $\Delta G_{tr}^{o,O \rightarrow W}$ and $\Delta S_{tr}^{o,O \rightarrow W}$ for tetraalkylammonium ions; those determined in an earlier study (\blacksquare)⁸ and those determined by TMV-ITIES in our laboratory (\bullet),¹⁶ respectively. The two sets of values are fairly in agreement each other, indicating that the determination of $\Delta S_{tr}^{o,O \rightarrow W}$ by TMV-ITIES is acceptable. Both the relationships for 1-alkylpridinium and tetraalkylammonium ions display straight lines with a similar slope, *i.e.*, approximately $-4.4 \times 10^{-3} \text{ K}^{-1}$. The minus sign of the slope indicates that $\Delta S_{tr}^{o,O \rightarrow W}$ decreases with increasing $\Delta G_{tr}^{o,O \rightarrow W}$. This finding is understandable because the hydrophobic tendency of the ions is enhanced by both decreasing $\Delta S_{tr}^{o,O \rightarrow W}$ and increasing $\Delta G_{tr}^{o,O \rightarrow W}$ except for very hydrophilic ions. The reciprocal value of the slope is around 230 K, which is very different from the ambient

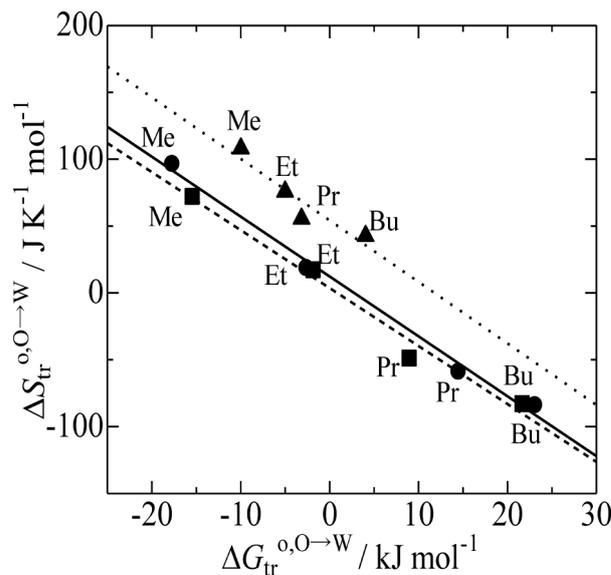


Fig. 5 Relationships between $\Delta S_{tr}^{o,O \rightarrow W}$ and $\Delta G_{tr}^{o,O \rightarrow W}$ for \bullet tetraalkylammonium ions,¹⁶ \blacksquare tetraalkylammonium ions,⁸ and \blacktriangle 1-alkylpridinium ions (this work).

temperature, $298 \pm 2 \text{ K}$. In our opinion, this slope value is a characteristic temperature of a monovalent cation with alkyl-chains, although the 1-alkylpridinium and tetraalkylammonium ions are considerably different in structure and in number of alkyl-chain. In order to verify our opinion on the characteristic temperature, we plan to conduct additional research to examine the relationship between $\Delta G_{tr}^{o,O \rightarrow W}$ and $\Delta S_{tr}^{o,O \rightarrow W}$ for divalent ions, such as 1,1'-dialkyl-4,4'-bipyridinium ions (methylviologen, ethylviologen, *etc.*).

The value of $\Delta S_{tr}^{o,O \rightarrow W}$ for a 1-alkylpridinium ion is larger than that of the corresponding tetraalkylammonium ion, suggesting that the 1-alkylpridinium ion is more destructive of the water structure than the tetraalkylammonium ion. This is probably because the charge of the 1-alkylpridinium ion with a more simple structure is relatively localized on the nitrogen atom. In contrast, the charge of the tetraalkylammonium ion with a tetrahedral structure is delocalized over all the ion, (Fig. 1). The changes in $\Delta S_{tr}^{o,O \rightarrow W}$ per one methylene group, $-\text{CH}_2-$, for the 1-alkylpridinium and tetraalkylammonium ion are calculated to be -21.8 and $-20.0 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. The difference of $\Delta S_{tr}^{o,O \rightarrow W}$ per one methylene group between the 1-alkylpridinium and tetraalkylammonium ion is very small. Consequently, the change in $\Delta S_{tr}^{o,O \rightarrow W}$ per one methylene group is not very dependent on the structure difference.

Conclusions

We determined $\Delta G_{tr}^{o,O \rightarrow W}$, $\Delta S_{tr}^{o,O \rightarrow W}$, and $\Delta H_{tr}^{o,O \rightarrow W}$ for four 1-alkylpridinium ions by thermal modulation voltammetry using crystalviolet as an optically absorbing substance. The values of $\Delta S_{tr}^{o,O \rightarrow W}$ were determined to be 108.0 ± 0.5 ($n = 3$), 75.8 ± 4.4 , 55.6 ± 1.2 , and $42.7 \pm 0.9 \text{ J K}^{-1} \text{ mol}^{-1}$ for MePy⁺, EtPy⁺, PrPy⁺, and BuPy⁺, respectively. The values of $\Delta S_{tr}^{o,O \rightarrow W}$ of the 1-alkylpridinium ions showed all positive values and increased with decreasing alkyl-chain length. This fact suggests that more hydrophilic 1-alkylpridinium ions have a tendency to destroy the structure of water. Both the relationships between $\Delta G_{tr}^{o,O \rightarrow W}$ and $\Delta S_{tr}^{o,O \rightarrow W}$ for the 1-alkylpridinium and

tetraalkylammonium ions displayed straight lines with a similar slope and the reciprocal value of the slope is thought to be a characteristic temperature of a monovalent cation with alkyl-chains. We will examine the relationship for divalent ions, such as 1,1'-dialkyl-4,4'-bipyridinium ions (methylviologen, ethylviologen, etc.).

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