

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/37424515>

# Determination of the Entropy of Ion Transfer between Two Immiscible Liquids Using the Water|Oil|Water Thermocouple

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY B · SEPTEMBER 2003

Impact Factor: 3.3 · DOI: 10.1021/jp026797t · Source: OAI

---

CITATIONS

18

---

READS

42

4 AUTHORS, INCLUDING:



Hubert H Girault

École Polytechnique Fédérale de Lausanne

556 PUBLICATIONS 13,980 CITATIONS

SEE PROFILE

# Determination of the Entropy of Ion Transfer between Two Immiscible Liquids Using the Water|Oil|Water Thermocouple

Toshiyuki Osakai,<sup>\*,†</sup> Hajime Ogawa,<sup>†</sup> Toru Ozeki,<sup>‡</sup> and Hubert H. Girault<sup>§</sup>

Department of Chemistry, Faculty of Science, Kobe University, Nada, Kobe 657-8501, Japan,  
Hyogo University of Teacher Education, Shimokume, Yashiro-cho, Kato-gun, Hyogo 673-14, Japan,  
and Laboratoire d'Electrochimie Physique et Analytique, Ecole Polytechnique Fédérale de Lausanne,  
CH-1015 Lausanne, Switzerland

Received: August 20, 2002; In Final Form: April 27, 2003

A nonisothermal galvanic cell comprising two interfaces between two immiscible electrolyte solutions has been employed to determine the standard entropy ( $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$ ) of ion transfer at the nitrobenzene (NB)|water (W) interface. Under the conditions that only one ion ( $i$ ) can partition between the NB|W interface, the nonisothermal emf has been measured. A nonequilibrium thermodynamic treatment has shown that the peak value ( $E_0$ ) of the nonisothermal emf, being usually observed within 1 min, is related to  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  for ion  $i$ . However,  $E_0$  has also been shown, both experimentally and theoretically, to be influenced by thermal diffusion potentials arising in the bulk phases. Nevertheless, the contributions from the thermal diffusion potentials can be corrected for if the parameters for the ionic heats of transport are available, or they can be minimized by using adequate supporting electrolytes. Thus, accurate values of  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  have been determined for various cations and anions. The determined values of  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  for relatively hydrophobic cations (i.e., tetraalkylammonium ions,  $\text{Cs}^+$ , and  $\text{Rb}^+$ ) have been found to show a good correlation with the hydration entropies ( $\Delta S_{\text{hydr}}^{\text{o}}$ ), suggesting that  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  should reflect greatly the structure-making and -breaking effects of the ions in W. On the other hand, however, relatively hydrophilic ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , and  $\text{SCN}^-$ ) showed no correlation between  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  and  $\Delta S_{\text{hydr}}^{\text{o}}$ , probably because they are preferentially hydrated in NB.

## Introduction

The standard entropy ( $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$ ) of ion transfer between two immiscible liquids, as well as the corresponding Gibbs energy ( $\Delta G_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$ ) and enthalpy ( $\Delta H_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$ ), is fundamentally important for understanding ion-transfer processes across the oil (O)|water (W) interface. In comparison with  $\Delta G_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$ , however,  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  has not been extensively studied. There have been only a few reports on the determination of  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$ .<sup>1</sup> In a previous study,<sup>1</sup> the extraction of alkali metal dipicrylaminates into nitrobenzene (NB) was studied at 0–45 °C, and the entropy values ( $\Delta S^*$ ) for extraction of the alkali metal salts were reported. Assignment of  $\Delta S^*$  to the individual ions, however, requires an extrathermodynamic assumption such as the tetraphenylarsonium tetraphenylborate (TATB) assumption.<sup>2</sup> On the other hand, the values of  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  for individual ions were reported based on voltammetric measurements.<sup>3,4</sup> The reversible half-wave potential ( $E_{1/2}^{\text{rev}}$ ) of the transfer of an ion across the NB|W interface was measured at different temperatures, and the  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  of the ion was evaluated from the temperature dependence of  $E_{1/2}^{\text{rev}}$ . However, the voltammetric measurements were carried out using a water jacket to maintain the temperature around the NB|W interface at a selected value, while all the other parts, including the reference electrodes, were at the ambient temperature. Under these conditions, however, the thermal diffusion potential arising

from the temperature gradients in the electrolytic cell should be estimated to obtain accurate values of  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$ .

In 1988, Girault<sup>5</sup> presented a nonisothermal galvanic cell that comprises two O|W interfaces (Figure 1) and showed that if only one ion can partition across the O|W interface, the W|O|W cell behaves as a performant thermocouple. The objective of this study is to show that the W|O|W thermocouple can be utilized for determining accurate values of  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  for various ions.

## Theoretical Section

Schematically, the W|O|W thermocouple used in this study can be represented by the following cell (cell A):

terminal	reference electrode	W phase I	O phase	W phase II	reference electrode	terminal
(Cu)	(Ag AgCl)	ion $i$	ion $i$	ion $i$	(Ag AgCl)	(Cu)
$T_0$	$T_0$	$T_0$	$T_1$	$T_2$	$T_0$	$T_0$
1	12	23	45	67	89	910 10

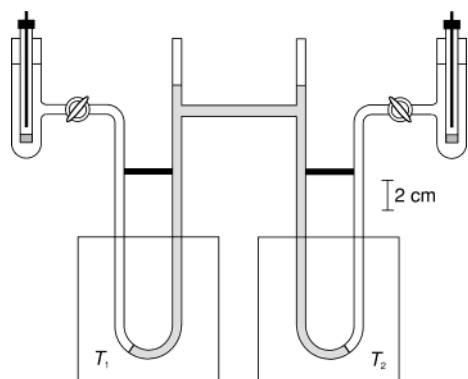
In this cell, the solution compositions of the two W phases (I and II) are initially the same. The temperatures of the left-hand and right-hand O|W interfaces are controlled at  $T_1$  and  $T_2$ , respectively, while the temperature around the two reference electrodes is the ambient temperature ( $T_0$ ). It is assumed that the two O|W interfaces are reversible for an ion  $i$  only. The two reference electrodes, being immersed in the respective W phases, are Ag|AgCl (saturated KCl) electrodes with porous Vycor glass (Corning no. 7930).

\* Author for correspondence (e-mail: osakai@kobe-u.ac.jp).

<sup>†</sup> Kobe University.

<sup>‡</sup> Hyogo University of Teacher Education.

<sup>§</sup> Ecole Polytechnique Fédérale de Lausanne.



**Figure 1.** W|O|W thermocouple with Ag|AgCl electrodes.<sup>5</sup> The U-tubes were made of Pyrex glass tubes of 5 mm diameter.

The measured emf,  $E$ , is taken as the difference between the electric potential in the right-hand terminal and that in the left-hand terminal (i.e.,  $E = \phi_{10} - \phi_1$ ), measured with no current flowing. Because the two electrode|terminal junctions are at the same temperature  $T_0$ , the differences  $(\phi_{10} - \phi_9)$  and  $(\phi_2 - \phi_1)$  cancel out. So do the differences  $(\phi_9 - \phi_8)$  and  $(\phi_3 - \phi_2)$ , if we assume that the solution composition in the vicinity of the electrodes remains unchanged. This assumption can be satisfied experimentally by interposing an electrolyte-sealed tap between the O|W interface and the reference electrode (see Figure 1) to ensure that the breakdown of the molarity homogeneity by the Soret effect occurs mainly between the tap and the O|W interface. Consequently,  $E$  can be given by

$$E = (\phi_8 - \phi_7) + (\phi_7 - \phi_6) + (\phi_6 - \phi_5) + (\phi_5 - \phi_4) + (\phi_4 - \phi_3) \quad (1)$$

The differences  $(\phi_8 - \phi_7)$ ,  $(\phi_6 - \phi_5)$ , and  $(\phi_4 - \phi_3)$  are thermal diffusion potentials given by<sup>6</sup>

$$F \text{ grad } \phi = - \sum_j \tau_j \left( (\text{grad } \mu_j)_{T,P} + \frac{{}^*Q_j}{T} \text{ grad } T \right) \quad (2)$$

where  $F$  denotes the Faraday constant,  $\tau_j$  and  $\mu_j$  are respectively the “reduced” transport number ( $\tau_j = t_j/z_j$ ; where  $t_j$  is the Hittorf transport number and  $z_j$  is the charge number) and the chemical potential of the different ionic species  $j$ , and  $(\text{grad } \mu_j)_{T,P}$  represents the gradient of chemical potential at constant temperature ( $T$ ) and pressure ( $P$ ), and refers therefore only to the change of chemical potential with concentration. The quantity  ${}^*Q_j$  denotes the heat of transport (in the Hittorf reference system<sup>6</sup>) of the ion  $j$  and is related to the transported entropy,  ${}^*S_j$ , by the definition

$${}^*Q_j = T({}^*S_j - S_j) \quad (3)$$

where  $S_j$  denotes the partial molar entropy.

Application of eq 2 for the O phase yields the thermal diffusion potential arising in the phase:

$$F(\phi_6 - \phi_5) = - \sum_k \tau_k \Delta_5^6(\mu_k^o)_{T,P} - \sum_k \frac{\tau_k {}^*Q_k^o}{T} \Delta T \quad (4)$$

where  $k$  stands for the different ionic species in the O phase, the superscript “o” refers to the O phase, and  $\Delta T = T_2 - T_1$ . For the sake of simplicity, the higher terms are omitted in eq 4. Similarly, the sum of the thermal diffusion potential in the two W phases is given by

$$\begin{aligned} & F[(\phi_8 - \phi_7) + (\phi_4 - \phi_3)] \\ &= - \sum_l \tau_l \Delta_7^8(\mu_l^w)_{T,P} - \sum_l \frac{\tau_l {}^*Q_l^w}{T} (T_0 - T_2) - \\ & \quad \sum_l \tau_l \Delta_3^4(\mu_l^w)_{T,P} - \sum_l \frac{\tau_l {}^*Q_l^w}{T} (T_1 - T_0) \\ &= - \sum_l \tau_l \Delta_7^8(\mu_l^w)_{T,P} - \sum_l \tau_l \Delta_3^4(\mu_l^w)_{T,P} + \sum_l \frac{\tau_l {}^*Q_l^w}{T} \Delta T \quad (5) \end{aligned}$$

where  $l$  stands for the different ionic species in the W phase, and the superscript “w” refers to the W phase. If the concentration of any ionic species is the same in positions 3 and 8 (this is valid before the tardy establishment of the concentration gradient; see below), eq 5 is reduced to

$$\begin{aligned} & F[(\phi_8 - \phi_7) + (\phi_4 - \phi_3)] = \\ & \quad - \sum_l \tau_l \Delta_4^7(\mu_l^w)_{T,P} + \sum_l \frac{\tau_l {}^*Q_l^w}{T} \Delta T \quad (6) \end{aligned}$$

As shown in eqs 4 and 6, the thermal diffusion potentials in the respective phases consist of contributions from different ionic species.

The differences  $(\phi_7 - \phi_6)$  and  $(\phi_5 - \phi_4)$  in eq 1 represent the two potential drops across the O|W interfaces. By assuming that the ion  $i$  is the only potential-determining ion across the O|W interface, these potential differences can be obtained from the electrochemical potential of the ion between the two phases:

$$\tilde{\mu}_i^w = \tilde{\mu}_i^o \quad (7)$$

to give

$$\begin{aligned} & z_i F[(\phi_7 - \phi_6) + (\phi_5 - \phi_4)] \\ &= [(\mu_i^o)_6 - (\mu_i^w)_7] + [(\mu_i^w)_4 - (\mu_i^w)_5] \\ &= \Delta_5^6(\mu_i^o) - \Delta_4^7(\mu_i^w) \quad (8) \end{aligned}$$

If we consider the system to be in mechanical equilibrium ( $\text{grad } P = 0$ ), the chemical potential gradient can be written as

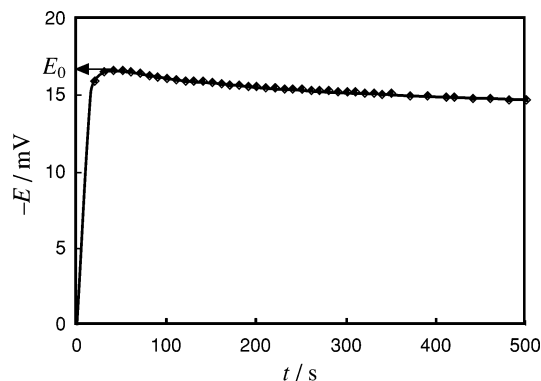
$$\text{grad } \mu_i = -S_i \text{ grad } T + (\text{grad } \mu_i)_{T,P} \quad (9)$$

and eq 8 therefore can be rewritten as

$$\begin{aligned} & z_i F[(\phi_7 - \phi_6) + (\phi_5 - \phi_4)] = \\ & \quad \Delta_5^6(\mu_i^o)_{T,P} - \Delta_4^7(\mu_i^w)_{T,P} - \int_{T_1}^{T_2} S_i^o dT + \int_{T_1}^{T_2} S_i^w dT \quad (10) \end{aligned}$$

By combining eqs 1, 4, 6, and 10, the total potential difference across the cell is given by

$$\begin{aligned} FE = & - \sum_k \tau_k \Delta_5^6(\mu_k^o)_{T,P} + \sum_l \tau_l \Delta_4^7(\mu_l^w)_{T,P} - \\ & \sum_k \frac{\tau_k {}^*Q_k^o}{T} \Delta T + \sum_l \frac{\tau_l {}^*Q_l^w}{T} \Delta T + \frac{\Delta_5^6(\mu_i^o)_{T,P} - \Delta_4^7(\mu_i^w)_{T,P}}{z_i} + \\ & \quad \frac{\int_{T_1}^{T_2} (S_i^w - S_i^o) dT}{z_i} \quad (11) \end{aligned}$$



**Figure 2.** Time dependence of the emf of the W|NB|W thermocouple. The W phases (I and II) contained 0.01 M TBACl and 0.1 M LiCl as a supporting electrolyte, whereas the NB phase contained 0.01 M TBATPB.  $T_1 = 25\text{ }^{\circ}\text{C}$ ;  $T_2 = 45\text{ }^{\circ}\text{C}$ .

The first four terms on the right-hand side (rhs) of eq 11 correspond to thermal diffusion potentials in the bulk solutions, whereas the last two terms on the rhs correspond to the thermal change in the Galvani potential difference across the O|W interfaces.

Usually, it takes a very long time for a thermocell to exhibit the steady-state response. In the case of the present W|O|W thermocouple, within 1 min after the temperature control was started, the thermo-emf reached a peak but gradually decreased (probably until the steady state would be attained). A typical time course is shown in Figure 2. Thus, the emf of the thermocouple is a function of time. For the steady state to be attained at the time  $t \rightarrow \infty$ , concentration gradients would be built up in the solution where concentration diffusion and thermal diffusion are balanced (i.e., the Soret effect). In the present experiments, however, the steady-state response (i.e., a constant  $E$  value) could not be observed, even after 3 h of measurement. Accordingly, in this study, the peak value of  $E$  (so-called the "initial" value, designated by  $E_0$ ) was measured. Under these conditions, no significant concentration gradients seem to be formed. Therefore, the first, second, and fifth terms in the rhs of eq 11 can be neglected:

$$FE_0 = - \sum_k \frac{\tau_k * Q_k^0}{T} \Delta T + \sum_l \frac{\tau_l * Q_l^w}{T} \Delta T + \frac{\int_{T_1}^{T_2} (S_i^w - S_i^0) dT}{z_i} \quad (12)$$

In a previous paper,<sup>5</sup> it was described that the steady-state response was reached well within 1 min. This value corresponded to the maximum before the slower variation reported in Figure 2.

As will be shown in the Results, the contributions of the thermal diffusion potentials to  $E_0$ , i.e., the first and second terms in the rhs of eq 12, may be reduced considerably by adding appropriate (supporting) electrolytes into the respective phases or may be compensated for by estimating them theoretically. If these conditions are met,  $E_0$  can be given by

$$z_i FE_0 = \int_{T_1}^{T_2} (S_i^w - S_i^0) dT \quad (13)$$

By differentiating eq 13 with respect to  $T$ , we finally obtain

$$\epsilon_0 = \frac{dE_0}{dT} = \frac{\Delta S_{\text{tr},i}^{\text{O} \rightarrow \text{W}}}{z_i F} \quad (14)$$

with

$$\Delta S_{\text{tr},i}^{\text{O} \rightarrow \text{W}} = S_i^w - S_i^0 \quad (15)$$

Thus, the measurement of  $E_0$  enables us to determine  $\Delta S_{\text{tr},i}^{\text{O} \rightarrow \text{W}}$  for the potential-determining ion  $i$ , providing that the appropriate measurement conditions are met.

## Experimental Section

**Chemicals.** Aqueous stock solutions of tetra-*n*-butylammonium chloride (TBACl), tetra-*n*-propylammonium chloride (TPrACl), tetraethylammonium chloride (TEACl), and tetramethylammonium chloride (TMACl) were prepared by dissolving the analytical-grade reagents in distilled water and then purified by metathesis with silver chloride (a possible impurity being iodide ion); the concentrations of the stock solutions were determined by potentiometric titration with a standard silver nitrate solution.

The potassium, rubidium, and cesium salts of dipicrylamine (DPA<sup>−</sup>) were prepared by an equimolar mixing of an aqueous solution of sodium dipicrylamine (NaDPA; Tokyo Kasei Kogyo Co. Ltd.) with an aqueous solution of potassium nitrate, rubidium chloride, or cesium chloride, respectively; the resultant precipitate was washed with distilled water more than five times and recrystallized twice from water–acetone. In a similar manner, the TMA<sup>+</sup> salt of DPA<sup>−</sup> was prepared from aqueous solutions of NaDPA and the bromide salt of TMA<sup>+</sup>. The TBA<sup>+</sup> salt of DPA<sup>−</sup> was prepared by equimolar mixing of an aqueous solution of dipicrylamine ammonium salt (Wako Pure Chemical Industries, Ltd.) with an aqueous solution of TBABr (Wako). The resultant oily substance was solidified by leaving it for a few days, and the solid substance was ground into small pieces, washed with water more than five times, and then dissolved in hot ethanol. After evaporation of the solvent by heating, addition of water reproduced the oily substance, which was solidified and ground into small pieces in the same manner as above.

The tetra-*n*-pentylammonium (TPnA<sup>+</sup>), TBA<sup>+</sup>, TPrA<sup>+</sup>, and TEA<sup>+</sup> salts of tetraphenylborate (TPB<sup>−</sup>) were prepared by equimolar mixing of an ethanol solution of the iodide or bromide salt with an ethanol solution of sodium tetraphenylborate (Dojindo Laboratories); the resultant precipitate was washed more than five times with distilled water and twice with ethanol and then recrystallized from 1:1 (v/v) acetone–ethanol. The tetra-*n*-hexylammonium salt (THxA<sup>+</sup>) of TPB<sup>−</sup> was prepared and purified in a similar manner, but its precipitate could be obtained by addition of an appropriate amount of water followed by evaporation of ethanol by heating.

Sodium dicarbollyl cobaltate(III)<sup>7</sup> (C<sub>4</sub>H<sub>22</sub>B<sub>18</sub>CoNa; denoted by NaDCC) was purchased from AZmax Co., Ltd. and used as received. The TPnA<sup>+</sup> salt of DCC<sup>−</sup> was prepared by equimolar mixing of an aqueous solution of NaDCC and an ethanol solution of TPnAI and purified in a similar manner as the alkali metal salts of DPA<sup>−</sup>.

The TBA<sup>+</sup> salt of picrate (Pic<sup>−</sup>) was prepared by equimolar mixing of aqueous solutions of TBABr and NaPic. The resultant precipitate was washed with distilled water several times and recrystallized from acetone (since the dry picrate salt may be explosive, *do not heat the solution*; the recrystallization should be done by evaporating the solvent under a hood at ambient temperature).

Analytical-grade nitrobenzene (NB; Wako) was purified by treatment with activated alumina (200 mesh) for column chromatography before use. All other reagents were of analytical grade and used without further purification.

TABLE 1: Electrolyte Compositions of Cell A and Its Nernstian Responses to Ion  $i$  at  $T_1 = T_2 = 298.15$  K

ion $i$	W phase I	O phase	W phase II	Nernstian response range (M)	slope (V)
TBA <sup>+</sup>	0.01 M TBACl + 0.1 M KCl	0.01 M TBATPB	0.001–0.1 M TBACl + 0.1 M KCl	0.002–0.1	+0.0241
TPrA <sup>+</sup>	0.01 M TPrACl + 0.1 M KCl	0.01 M TPrATPB + 0.1 M TPnATPB	0.001–0.1 M TPrACl + 0.1 M KCl	0.001–0.1	+0.0249
TEA <sup>+</sup>	0.01 M TEACl + 0.1 M KCl	0.01 M TEATPB + 0.1 M TPnATPB	0.001–0.1 M TEACl + 0.1 M KCl	0.001–0.1	+0.0252
TMA <sup>+</sup>	0.01 M TMACl + 0.1 M KCl	0.01 M TMADPA + 0.05 M TBADPA	0.001–0.1 M TMACl + 0.1 M KCl	0.001–0.1	+0.0255
Na <sup>+</sup>	0.01 M NaCl	0.01 M NaDCC + 0.1 M TPnADCC	0.001–0.1 M NaCl	0.001–0.02	+0.0229
K <sup>+</sup>	0.01 M KCl	0.01 M KDPA + 0.05 M TBADPA	0.001–0.1 M KCl	0.001–0.1	+0.0223
Rb <sup>+</sup>	0.01 M RbCl + 0.1 M LiCl	0.01 M RbDPA + 0.05 M TBADPA	0.001–0.1 M RbCl + 0.1 M LiCl	0.001–0.1	+0.0251
Cs <sup>+</sup>	0.01 M CsCl + 0.1 M LiCl	0.01 M CsDPA + 0.05 M TBADPA	0.001–0.1 M CsCl + 0.1 M LiCl	0.001–0.1	+0.0231
Br <sup>−</sup>	0.1 M KBr	0.01 M THxABr + ~0.08 M THxATPB	0.01–1.0 M KBr	0.01–1.0	−0.0234
I <sup>−</sup>	0.01 M KI + 0.1 M KCl	0.01 M TPnAI + 0.1 M TPnATPB	0.001–0.1 KI + 0.1 M KCl	0.001–0.1	−0.0245
SCN <sup>−</sup>	0.05 M KSCN + 0.5 M KCl	0.01 M TBASCN	0.005–0.5 M KSCN + 0.5 M KCl	0.005–0.5	−0.0252
Pic <sup>−</sup>	0.01 M NaPic + 0.1 M NaCl	0.01 M TBAPic + 0.1 M TBATPB	0.001–0.1 M NaPic + 0.1 M NaCl	0.001–0.05	−0.0236

**Procedures.** The temperatures ( $T_1$  and  $T_2$ ) of the U-tubes in the thermocell shown in Figure 1 were controlled by means of two water baths equipped with thermostirrers having an accuracy of 0.1 °C. The room temperature ( $T_0$ ) was 18–30 °C.

The emf of the thermocell was measured with an electrometer (Advantest TR8652). Because of the relatively high impedance (a few mega-ohms) of the cell used, careful earthing was essential for adequate accuracy of the measurement (errors <0.1 mV).

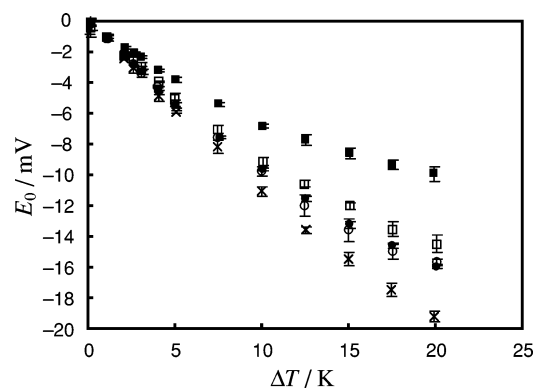
The aqueous solution for phases I and II and the NB solution were saturated in advance respectively with NB and W at 25 °C ( $T_1$ ). Using these mutually saturated solutions, the W|NB|W thermocouple was constructed. At the beginning of the measurement, the cell was placed in bath I with  $T_1 = 25$  °C, and the equilibrium emf ( $\sim 0$  mV) of the cell was recorded. The nonisothermal emf was measured by placing one of the U-tubes in bath II with a given temperature ( $T_2 > 25$  °C). Usually, the emf reached a peak value ( $E_0$ ) within 1 min. The cell was then replaced in bath I, and the emf soon returned again to the equilibrium value of  $\sim 0$  mV. In succession, the setup temperature of bath II was altered to another value. After waiting for about 5 min until the temperature reached the setup value, the nonisothermal emf was measured by moving again one of the U-tubes into bath II. In this manner, the values of  $E_0$  were determined at various  $T_2$ 's in the range of 25–45 °C.

## Results

**Nernstian Responses.** As described in the Theoretical Section, the determination of  $\Delta S_{w,i}^{O \rightarrow W}$  with the W|O|W thermocouple is based on the assumption that the respective O|W interfaces are reversible to ion  $i$  only; in other words, they show a Nernstian response to the ion. Under these conditions, the isothermal emf (i.e., at  $T = T_1 = T_2$ ) is approximately given by

$$E = \frac{RT}{z_i F} \ln \frac{c_i^{\text{II}}}{c_i^{\text{I}}} \quad (16)$$

where  $c_i^{\text{I}}$  and  $c_i^{\text{II}}$  are the concentrations of ion  $i$  in phases I and II, respectively, and  $R$  is the gas constant. Although eq 16 should



**Figure 3.** Effect of supporting electrolytes in the W phases on the value of  $E_0$  in the case when  $i = \text{TBA}^+$ . The W phases (I and II) contained 0.01 M TBACl and (○) 0.1 M KCl, (●) 0.1 M NaCl, (□) 0.1 M LiCl, (■) 0.1 M HCl, or (×) none as a supporting electrolyte, whereas the NB phase contained 0.01 M TBATPB. Vertical bars indicate the standard deviations for more than three repeat measurements.

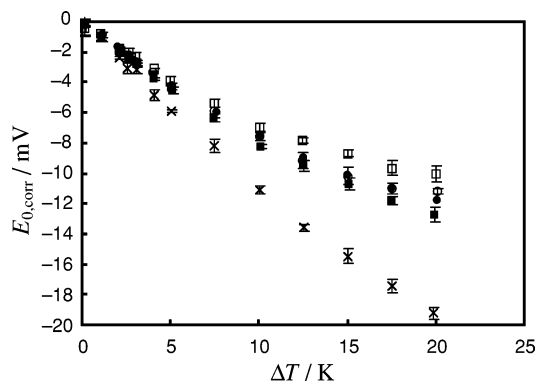
be written exactly using the activities rather than the concentrations, it would be valid to a relatively good approximation when only the concentration in the W phase is varied. In such cases, the value of  $E$  can be expected to depend linearly on  $\ln(c_i^{\text{II}}/c_i^{\text{I}})$ , with a slope of  $\pm(RT/F)$  ( $= \pm 0.0257$  V at  $T = 25$  °C) for a monovalent cation or anion. In practice, a Nernstian or near-Nernstian response was observed for all the monovalent ions tested in a definite range of concentrations (the unit M = mol dm<sup>−3</sup>). The results are summarized in Table 1. Nonisothermal measurements with the cell were performed on a proper choice of the value of  $c_i^{\text{II}}$  ( $= c_i^{\text{I}}$ , as shown in Table 1) ensuring such a Nernstian response.

**Effect of Supporting Electrolytes.** Figure 3 shows the effect of supporting electrolytes in the W phases on the nonisothermal emf ( $E_0$ ) in the case when  $i = \text{TBA}^+$ . As can be seen in the figure, there are some large differences in the  $E_0$  value among the supporting electrolytes employed. This seems to be due to differences in the thermal diffusion potential in the W phases. Since the thermal diffusion potential is given by the second term



**TABLE 2: Values of  $\lambda^\infty$ ,  $\tau$ , and  ${}^*Q^w$  for the Electrolytes in the W Phases at  $T = 298.15$  K**

electrolyte	$\lambda^\infty$ ( $10^{-4}$ S m <sup>2</sup> mol <sup>-1</sup> )		$\tau$		${}^*Q^w$ (cal mol <sup>-1</sup> )	
	cation	anion	cation	anion	cation	anion
HCl	349.65	76.31	+0.82	-0.18	+1550	+1700
LiCl	38.66	76.31	+0.34	-0.66	-1250	+1700
NaCl	50.08	76.31	+0.40	-0.60	-1010	+1700
KCl	73.48	76.31	+0.49	-0.51	-1340	+1700
KBr	73.48	78.1	+0.48	-0.52	-1340	+1640

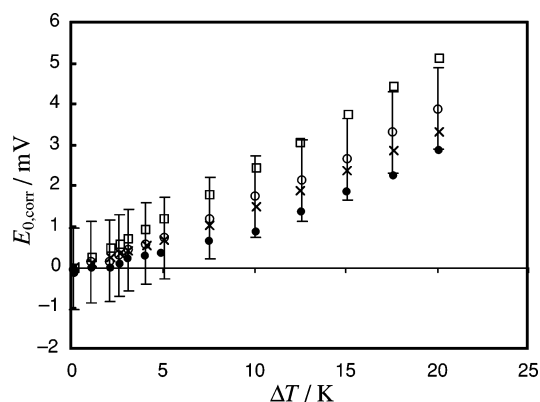
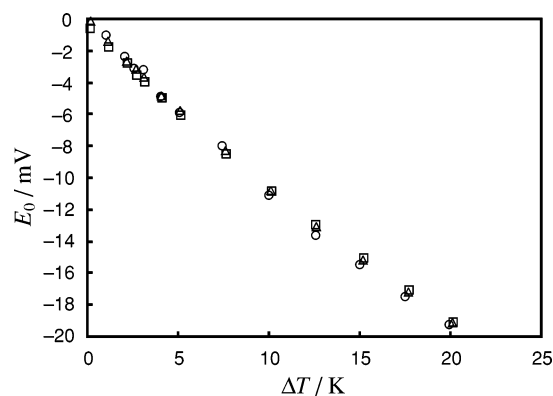
<sup>a</sup> Reference 8. <sup>b</sup> Reference 6.**Figure 4.**  $E_0$  values corrected for the thermal diffusion potential in the W phases. Experimental conditions and symbols are the same as in Figure 3. Note that in the case for no use of supporting electrolyte ( $\times$ ), no correction was made.

in the rhs of eq 12, it can be calculated from the values of  $\tau$  and  ${}^*Q^w$  for the electrolyte ions. The value of  $\tau$  for an ion is approximately given by

$$\tau = \frac{t^\infty}{z} = \frac{\lambda^\infty}{z\Lambda^\infty} \quad (17)$$

where  $t^\infty$  and  $\lambda^\infty$  are respectively the transport number and the limiting molar conductivity of the ion, and  $\Lambda^\infty$  is the limiting molar conductivity of the electrolyte, given by the sum of  $\lambda^\infty$  values of the cation and anion:  $\Lambda^\infty = \lambda^\infty_+ + \lambda^\infty_-$  (for a 1:1 electrolyte). The values of  $\tau$  thus evaluated for the respective electrolytes employed are shown in Table 2, along with the literature values of  $\lambda^\infty$ <sup>8</sup> and  ${}^*Q^w$ .<sup>6</sup> Using the values of  $\tau$  and  ${}^*Q^w$ , the measured  $E_0$  values shown in Figure 3 were corrected for the contribution of the thermal diffusion potential in the W phases. As shown in Figure 4, there are not very large differences in the corrected  $E_0$  values ( $E_{0,\text{corr}}$ ) among the supporting electrolytes; note that in the case of no use of supporting electrolyte, no correction was made because of the lack of a reported value of  ${}^*Q^w$  for  $\text{TBA}^+$ . This result shows that the thermal diffusion potential in W certainly affects the thermo-emf and that its contribution can be corrected for if the values of  $\tau$  and  ${}^*Q^w$  are available.

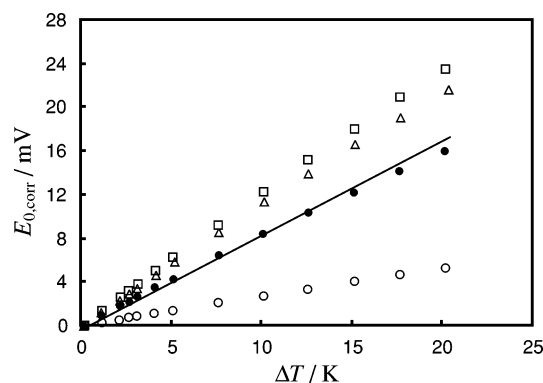
The effect of supporting electrolytes in the NB phase was also examined in the case of  $i = \text{TEA}^+$ . Figure 5 shows the  $E_{0,\text{corr}}$  values which were measured by using three different supporting electrolytes (0.1 M TPnATPB, 0.1 M TBATPB, 0.05 M TBADPA) or none. The figure shows some scatter, most probably due to the thermal diffusion potential arising in the NB phase (see the first term in the rhs of eq 12). Unfortunately, no correction could be made because of the lack of reported values for  ${}^*Q^w$ . Nevertheless, the differences in the  $E_{0,\text{corr}}$  values are as small as 2 mV, on the order of the experimental errors. This is probably because the electrolyte cation and anion are similar in their ionic sizes and thus in transport properties as

**Figure 5.** Effect of supporting electrolytes in the NB phase on the value of  $E_{0,\text{corr}}$  in the case when  $i = \text{TEA}^+$ . The NB phase contained 0.01 M TEATPB and ( $\circ$ ) 0.1 M TPnATPB, ( $\bullet$ ) 0.1 M TBATPB, ( $\square$ ) 0.05 M TBADPA, or ( $\times$ ) none as a supporting electrolyte, whereas the W phases (I and II) contained 0.01 M TEACl and 0.1 M KCl as a supporting electrolyte. The plots were made by using average values for more than three repeat measurements. Only for the  $\circ$  plot, standard deviations are shown by vertical bars.**Figure 6.** Concentration independence of  $E_{0,\text{corr}}$  in the case when  $i = \text{TBA}^+$ . The W phases (I and II) contained ( $\circ$ ) 0.01, ( $\Delta$ ) 0.005, or ( $\square$ ) 0.001 M TBACl and 0.1 M KCl as a supporting electrolyte, whereas the NB phase contained 0.01 M TBATPB as a supporting electrolyte. The plots were made by using average values for more than three repeat measurements.

well as solvation states in NB. Accordingly, in the determination of  $\Delta S_{\text{tr},i}^{\text{so} \rightarrow \text{w}}$  for an ion, any one of the above supporting electrolytes was normally used (see Table 1). For the case of  $i = \text{SCN}^-$ , however, no supporting electrolyte was added to the NB phase in order to avoid a possible interference to the Nernstian response of  $\text{SCN}^-$  from an electrolyte cation in NB.

**Concentration Independence.** The  $E_0$  value given by eq 12 is not a function of the concentration of any electrolyte ion in the W and NB phases. In practice, the measured values of  $E_0$  for  $i = \text{TBA}^+$  were entirely independent of the concentration of ion  $i$ , as shown in Figure 6. This strongly suggests the validity of either the theoretical treatment or the thermopower measurement.

**Determination of  $\Delta S_{\text{tr},i}^{\text{so} \rightarrow \text{w}}$ .** Figure 7 shows the plots of  $E_{0,\text{corr}}$  against  $\Delta T$  for alkali metal ions. The plot for the respective ion shows a (nearly) straight line with a different slope. The slopes increase in the order  $\text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$ . The slope at the origin (i.e.,  $\Delta T = 0$  K) should be given by eq 14; therefore, one can determine  $\Delta S_{\text{tr},i}^{\text{so} \rightarrow \text{w}}$  from the slope. However, the  $E_{0,\text{corr}}$  vs  $\Delta T$  plots for many ions showed some curvature, as represented by the plot for  $\text{K}^+$  in Figure 7. This is possibly due to the temperature dependence of partial molar entropy of an ion in W and/or NB. It should also be noted



**Figure 7.** Plots of  $E_{0,\text{corr}}$  against  $\Delta T$  for alkali metal ions: (○)  $\text{Na}^+$ , (●)  $\text{K}^+$ , (△)  $\text{Rb}^+$ , and (□)  $\text{Cs}^+$ . The electrolyte compositions are shown in Table 1. The plots were made by using average values for more than three repeat measurements.

**TABLE 3: Thermodynamic Quantities for the Transfer of Ions from NB to W at  $T = 298.15\text{K}$**

ion	$\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )			$\Delta G_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$ ( $\text{kJ mol}^{-1}$ )	$\Delta H_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$ ( $\text{kJ mol}^{-1}$ )
	this study <sup>a</sup>	lit. I <sup>b</sup>	lit. II <sup>c</sup>		
TBA <sup>+</sup>	-83.3		-92.6	+26.5	+1.7
TPrA <sup>+</sup>	-49.3			+16.4	+1.7
TEA <sup>+</sup>	+16.8		-8.3	+5.3	+10.3
TMA <sup>+</sup>	+71.7	+42.6	+27.4	-3.4	+18.0
Na <sup>+</sup>	+28.8	+28.9		-34.2	-25.6
K <sup>+</sup>	+84.3	+105.6		-23.5	+1.6
Rb <sup>+</sup>	+113.4	+91.1		-19.4	+14.4
Cs <sup>+</sup>	+121.3	+86.3		-15.4	+20.8
Br <sup>-</sup>	-35.3			-27.8	-38.3
I <sup>-</sup>	+16.8			-18.4	-13.4
SCN <sup>-</sup>	+26.7			-15.8	-7.8
Pic <sup>-</sup>	-37.2		+1.6	+6.7	-4.4
DPA <sup>-</sup>		+16.6		+39.4 <sup>d</sup>	+39.4

<sup>a</sup> The electrolyte compositions used in the thermopower measurements are as in Table 1. <sup>b</sup> Reference 3. <sup>c</sup> Reference 4, but at  $T = 293\text{K}$ . <sup>d</sup> Reference 9, except where otherwise noted. <sup>e</sup> Calculated from the relation:  $\Delta H_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}} = \Delta G_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}} + T \Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$ ; the  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  values used in the calculation are those determined in this study (except for DPA<sup>-</sup>). <sup>f</sup> Reference 7.

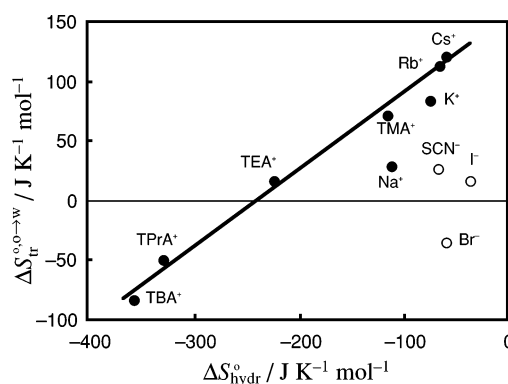
that there is a possible influence of the temperature dependence of mutual solubilities of W and NB. However, this effect on the value of  $\Delta S_{\text{tr},i}^{\text{o},\text{o} \rightarrow \text{w}}$  would not be serious, because  $\Delta S_{\text{tr},i}^{\text{o},\text{o} \rightarrow \text{w}}$  was determined from the slope at  $\Delta T = 0\text{K}$ .

In Table 3, the values of  $\Delta S_{\text{tr},i}^{\text{o},\text{o} \rightarrow \text{w}}$  thus determined for various ions are shown together with the literature values.<sup>3,4</sup> The literature values<sup>3</sup> for TMA<sup>+</sup> and Cs<sup>+</sup> were determined from the temperature dependence of  $E_{1/2}^{\text{rev}}$ , whereas those for the other ions were calculated from the entropy values<sup>1</sup> ( $\Delta S^*$ ) for extraction of alkali metal salts of DPA<sup>-</sup>. In the calculation,<sup>3</sup> it was assumed that  $\Delta S_{\text{tr},\text{metal}}^{\text{o},\text{o} \rightarrow \text{w}} = -\Delta S^* - \Delta S_{\text{tr},\text{DPA}^+}^{\text{o},\text{o} \rightarrow \text{w}}$ , where  $\Delta S_{\text{tr},\text{DPA}^+}^{\text{o},\text{o} \rightarrow \text{w}}$  ( $= +16.6\text{J K}^{-1} \text{mol}^{-1}$ ) was likewise determined from the  $\Delta S^*$  value of CsDPA<sup>1</sup> and the value of  $\Delta S_{\text{tr},\text{Cs}^+}^{\text{o},\text{o} \rightarrow \text{w}}$ . The literature values<sup>4</sup> of  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  for TBA<sup>+</sup>, TEA<sup>+</sup>, TMA<sup>+</sup>, and Pic<sup>-</sup> were determined from the temperature dependence of  $E_{1/2}^{\text{rev}}$ , measured by cyclic voltammetry. As can be seen in Table 3, the  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  values reported by two research groups<sup>3,4</sup> and those determined in this study are in rough agreement with each other. For most ions, however, there are rather large differences ( $\sim 40\text{J K}^{-1} \text{mol}^{-1}$  at largest) among the three data sets. From our standpoint, we recognize that the literature values<sup>3,4</sup> were determined by neglecting the thermal diffusion potential arising from the temperature gradients in the electrolytic cell. In general,

**TABLE 4: Some Ionic Properties Relevant to the Standard Entropy of Transfer of Ions from NB to W at  $T = 298.15\text{K}$**

ion	$\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$ <sup>a</sup> ( $\text{J K}^{-1} \text{mol}^{-1}$ )	$\Delta S_{\text{hydr}}^{\text{o}}$ <sup>b</sup> ( $\text{J K}^{-1} \text{mol}^{-1}$ )	$\Delta E_{\text{w}}^{\text{w}}$ <sup>c</sup> ( $\text{kJ mol}^{-1}$ )	$r^d$ (nm)	$r_h^e$ (nm)	$n^f$
TBA <sup>+</sup>	-83.3	-356	+3.50	0.413		0
TPrA <sup>+</sup>	-49.3	-327	+2.73	0.379		0 <sup>g</sup>
TEA <sup>+</sup>	+16.8	-222	+1.35	0.337		0
TMA <sup>+</sup>	+71.7	-114	+0.48	0.279		0
Na <sup>+</sup>	+28.8	-111	+0.59	0.116	0.307	3.8
K <sup>+</sup>	+84.3	-74	-1.46	0.152	0.220	1.0
Rb <sup>+</sup>	+113.4	-65	-1.79	0.166	0.212	0.7
Cs <sup>+</sup>	+121.3	-59	-1.89	0.181	0.206	0.4
Br <sup>-</sup>	-35.3	-59	-1.63	0.182	0.276	2.1
I <sup>-</sup>	+16.8	-36	-1.00	0.206	0.248	0.9
SCN <sup>-</sup>	+26.7	-66	-2.91	0.213	0.260	1.1
Pic <sup>-</sup>	-37.2			0.332		0 <sup>g</sup>
DPA <sup>-</sup>	+16.6					

<sup>a</sup> From Table 3. <sup>b</sup> Hydration entropies.<sup>10</sup> <sup>c</sup> Changes in the activation energy for water exchange.<sup>11</sup> <sup>d</sup> Radii of bare ions.<sup>9</sup> <sup>e</sup> Radii of hydrated ions in NB.<sup>9,12</sup> <sup>f</sup> Hydration numbers in NB.<sup>12</sup> <sup>g</sup> Assumed.



**Figure 8.** Plots of  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  against  $\Delta S_{\text{hydr}}^{\text{o}}$  for (○) cations and (●) anions. The regression line was drawn for the data points of TBA<sup>+</sup>, TPrA<sup>+</sup>, TEA<sup>+</sup>, TMA<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup>. For details, see the text.

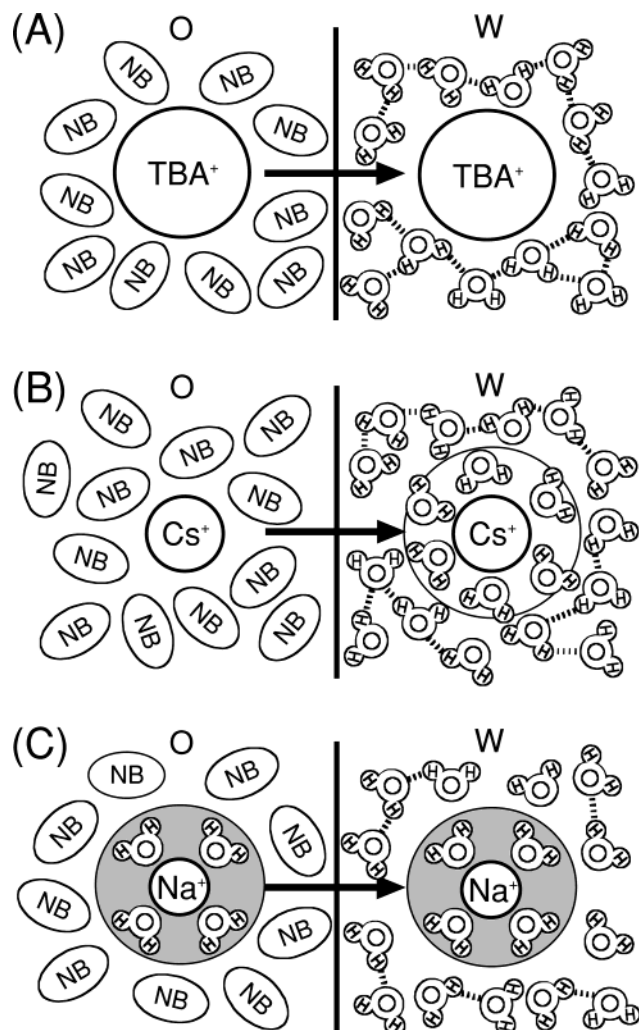
however, the thermal diffusion potential could not be bypassed, as clearly illustrated in Figure 3.

In Table 3, the values of  $\Delta G_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  and  $\Delta H_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  are also shown. Unless otherwise noted, the  $\Delta G_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  values are those compiled previously.<sup>9</sup> The  $\Delta H_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  values were not determined experimentally but were calculated from the measured values of  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  using the following general relation:  $\Delta H_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}} = \Delta G_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}} + T \Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$ . With regard to DPA<sup>-</sup>, its  $\Delta H_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  value was calculated by using the literature values of  $\Delta G_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$ <sup>7</sup> and  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$ .<sup>3</sup> From the  $\Delta H_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  values in Table 3, it follows that the transfers of the cations except for Na<sup>+</sup> from NB to W are endothermic to a greater or lesser extent, while those of the anions except for DPA<sup>-</sup> are exothermic. This conclusion is basically consistent with that reported previously.<sup>3</sup>

## Discussion

Table 4 shows some ionic properties relevant to  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$ , which include hydration entropies ( $\Delta S_{\text{hydr}}^{\text{o}}$ ),<sup>10</sup> changes in the activation energy for water exchange ( $\Delta E_{\text{w}}^{\text{w}}$ ),<sup>11</sup> radii of bare ions ( $r$ ),<sup>9</sup> radii of hydrated ions in NB ( $r_h$ ),<sup>9,12</sup> and hydration numbers in NB ( $n$ ).<sup>12</sup>

First, we examined the relationship of  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  with  $\Delta S_{\text{hydr}}^{\text{o}}$ . As shown in Figure 8, the  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  values for relatively hydrophobic cations (TBA<sup>+</sup>, TPrA<sup>+</sup>, TEA<sup>+</sup>, TMA<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup>) showed a good correlation with their  $\Delta S_{\text{hydr}}^{\text{o}}$  values:  $(\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}} / \text{J K}^{-1} \text{mol}^{-1}) = 0.648(\Delta S_{\text{hydr}}^{\text{o}} / \text{J K}^{-1} \text{mol}^{-1}) + 155.2$

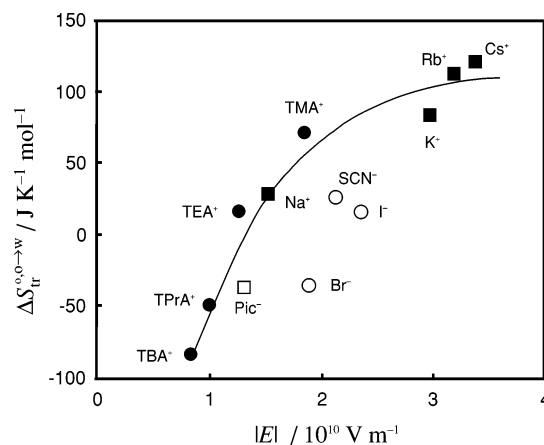


**Figure 9.** Models proposed for understanding the entropy changes of the interfacial transfer of three representative ions: (A)  $\text{TBA}^+$ , (B)  $\text{Cs}^+$ , and (C)  $\text{Na}^+$ . Dashed lines represent hydrogen bonds.

(the correlation coefficient = 0.996). For these ions, the entropy change in the hydration process seems to play a dominant role in determining the entropy change in the transfer process, i.e.,  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$ . It follows that the classical models<sup>13,14</sup> for ion hydration would give a qualitative interpretation to the  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  values of the ions.

As inferred by Frank and Wen,<sup>13</sup> a strongly hydrophobic ion such as  $\text{TBA}^+$  acts as a structure-promoter in water, because it has a low affinity for water. As shown in Figure 9A, water molecules around the  $\text{TBA}^+$  ion gather and form hydrogen-bonded water clusters. The hydrogen bonds thus formed are stronger than those in pure water; therefore, the  $\Delta S_{\text{hydr}}^{\text{o}}$  value of  $\text{TBA}^+$  is negatively large (see Table 4). Such an effect, generally called “hydrophobic structure-making”, was also suggested by Samoilov.<sup>14</sup> In his hydration model, ions are divided into two groups, i.e., water-structure-making and -breaking ions, according to whether the change in the activation energy ( $\Delta E_{\text{w}}^{\ddagger}$ ) of the exchange of the closest water molecules caused by an ion is positive or negative. Since the  $\Delta E_{\text{w}}^{\ddagger}$  value of  $\text{TBA}^+$  is positive (+3.50 kJ mol<sup>-1</sup>), it is considered that the water structure in the vicinity of  $\text{TBA}^+$  is strengthened by the ion. Such a hydrophobic structure-making effect of  $\text{TBA}^+$  in W would be responsible for the negative value of  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$ .

Relatively large alkali metal ions, i.e.,  $\text{Cs}^+$  and  $\text{Rb}^+$ , showed positively large values of  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$ . This corresponds to the less



**Figure 10.** Plots of  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  against  $|E|$  for (■) hydrated cations, (●) nonhydrated cations, (○) hydrated anions, and (□) a nonhydrated anion ( $\text{Pic}^-$ ). The additional line was drawn for the plots of hydrated and nonhydrated cations.

negative values of  $\Delta S_{\text{hydr}}^{\text{o}}$ . According to the model proposed by Frank and Wen,<sup>13</sup>  $\text{Cs}^+$  and  $\text{Rb}^+$  have a structure-breaking effect, so that the water molecules in the first solvation shell (indicated by a circle in Figure 9B) are more random in organization than the outer “normal” water molecules forming hydrogen-bonded clusters. This is also supported by the negative values of  $\Delta E_{\text{w}}^{\ddagger}$  for these ions.

Thus, the  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  values for relatively hydrophobic cations could be elucidated in terms of the structure-making and -breaking effects of the ions in W. However, it should be noted that relatively hydrophilic cations ( $\text{Na}^+$  and  $\text{K}^+$ ) as well as some inorganic anions ( $\text{Br}^-$ ,  $\text{I}^-$ , and  $\text{SCN}^-$ ) showed no correlation between  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  and  $\Delta S_{\text{hydr}}^{\text{o}}$ . This is most probably because such hydrophilic ions are preferentially hydrated in NB.

It is well known that water molecules are coextracted into water-immiscible organic solvents with hydrophilic ions such as  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Cl}^-$ , and  $\text{Br}^-$ .<sup>12,15–22</sup> Even water-immiscible organic solvents such as NB usually dissolve a considerable amount of water (e.g., 0.168 M  $\text{H}_2\text{O}$  in NB<sup>12</sup>). Accordingly, such phenomena can be elucidated in terms of selective hydration of ions in mixed solvents.<sup>23</sup> This concept has a fundamental significance for understanding a role of water in the transfer of hydrophilic ions between two “immiscible” liquids. To elucidate theoretically the  $\Delta G_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  values of hydrophilic ions, Osakai et al.<sup>9,12,22,24</sup> and Baruzzi et al.<sup>25</sup> proposed a new model in which a strongly hydrophilic ion transfers across the O|W interface as the hydrated ion (see Figure 9C).

In Table 4, the number of water molecules coextracted into NB by an ion, or the hydration number ( $n$ ) of the ion in NB, is shown for the ions studied. While the relatively large tetraalkylammonium ions have the  $n$  value of zero, the more hydrophilic, inorganic cations and anions have  $n$  values in the range from 0.4 to 3.8. For example, one of the most hydrophilic ions, i.e.,  $\text{Na}^+$ , has an  $n$  value of about 4. This means that  $\text{Na}^+$  transfers across the NB|W interface as a large hydrated ion, the radius of which is estimated to be  $r_h = 0.307$  nm (cf.  $r = 0.116$  nm).<sup>9,12</sup> In such a case, the contribution of the hydration shell (indicated by shadows in Figure 9C) to  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  is considered to be very small, provided that the transfer of the ion across the O|W interface does not cause any significant change in the structure of water molecules in the hydration shell. Accordingly, though  $\text{Na}^+$  is a water-structure-making ion (see the values of  $\Delta S_{\text{hydr}}^{\text{o}}$  and  $\Delta E_{\text{w}}^{\ddagger}$  in Table 4), its effect should be canceled out in



$\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$ . For this reason, it is thought that the plots for the comparatively hydrophilic ions (i.e.,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , and  $\text{SCN}^-$ ) deviated from the linear correlation line in Figure 8.

The recently proposed non-Bornian theory<sup>9,24</sup> showed that the  $\Delta G_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  of ions (exactly, its ionic-charge-dependent part) could be given by a quadratic function of the surface field strength ( $E$ ) of an ion. The value of  $E$  is obtained from the ionic charge ( $z$ ) and radius ( $r$ ) as

$$E = \frac{ze}{4\pi\epsilon_0 r^2} \quad (18)$$

where  $e$  is the elementary charge and  $\epsilon_0$  the permittivity of vacuum. It should be noted here that, for an ion being “hydrated” in the O phase,  $r$  in eq 18 should be replaced by  $r_{\text{h}}$ , which can be estimated from  $n$  and  $r$  as

$$r_{\text{h}} = \sqrt[3]{\frac{3}{4\pi} \frac{n}{d} + r^3} \quad (19)$$

where  $d$  is the density of water in the hydration shell (here assumed to be the same as that of bulk water, i.e.,  $3.33 \times 10^{28} \text{ m}^{-3}$ ). The estimated values of  $r_{\text{h}}$  are also shown in Table 4.

In Figure 10, the values of  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  determined for various ions are plotted against  $|E|$ . Although the anions had no well-defined dependence, the “nonhydrated” and “hydrated” cations were combined to have a certain correlation between  $\Delta S_{\text{tr}}^{\text{o},\text{o} \rightarrow \text{w}}$  and  $E$ , as shown by an additional line in Figure 10. This suggests that the electric field around a (hydrated) cation should dominate the organization of solvent molecules close to the ion. Increasing the electric field would cause destruction of the water structure around the (hydrated) cation.

## References and Notes

- (1) Rais, J.; Pacltová-Benešová, M.; Selucký, P.; Kyrš, M. *J. Inorg. Nucl. Chem.* **1973**, *35*, 633.
- (2) Marcus, Y. *Pure Appl. Chem.* **1985**, *57*, 1103.
- (3) Makrlík, E.; Hung, L. Q. *J. Electroanal. Chem.* **1983**, *158*, 269.
- (4) Wandlowski, T.; Mareček, V.; Samec, Z.; Fuoco, R. *J. Electroanal. Chem.* **1992**, *331*, 765.
- (5) Girault, H. H. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 2147.
- (6) Haase, R. *Thermodynamics of Irreversible Processes*; Addison-Wesley: Reading, MA, 1969.
- (7) Koryta, J.; Vanýsek, P.; Březina, M. *J. Electroanal. Chem.* **1977**, *75*, 211.
- (8) Lide, D. R., Ed. *Handbook of Chemistry and Physics*, 80th ed.; CRC Press: Boca Raton, FL, 1999.
- (9) Osaka, T.; Ebina, K. *J. Phys. Chem. B* **1998**, *102*, 5691.
- (10) Marcus, Y. *Ion Properties*; Marcel Dekker: New York, 1997; Chapter 8.
- (11) Marcus, Y. *Ion Solvation*; Wiley: Chichester, 1985; Chapter 5.
- (12) Osaka, T.; Ogata, A.; Ebina, K. *J. Phys. Chem. B* **1997**, *101*, 8341.
- (13) Frank, H. S.; Wen, W.-Y. *Discuss. Faraday Soc.* **1957**, *24*, 133.
- (14) Samoilov, O. Ya. *Discuss. Faraday Soc.* **1957**, *24*, 141.
- (15) Rais, J.; Kyrš, M.; Pivoňková, M. *J. Inorg. Nucl. Chem.* **1968**, *30*, 611.
- (16) Motomizu, S.; Tōei, K.; Iwachido, T. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1006.
- (17) Kenjo, T.; Diamond, R. M. *J. Phys. Chem.* **1972**, *76*, 2454.
- (18) Kenjo, T.; Diamond, R. M. *J. Inorg. Nucl. Chem.* **1974**, *36*, 183.
- (19) Yamamoto, Y.; Tarumoto, T.; Tarui, T. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1466.
- (20) Kusakabe, S.; Shinoda, M.; Kusafuka, K. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 333.
- (21) Kusakabe, S.; Arai, M. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 581.
- (22) Osaka, T. In *Interfacial Catalysis*; Volkov, A. G., Ed.; Marcel Dekker: New York, 2002; Chapter 4.
- (23) Osaka, T.; Hoshino, M.; Izumi, M.; Kawakami, M.; Akasaka, K. *J. Phys. Chem. B* **2000**, *104*, 12021.
- (24) Osaka, T.; Ebina, K. In *Liquid Interfaces in Chemical, Biological, and Pharmaceutical Applications*; Volkov, A. G., Ed.; Marcel Dekker: New York, 2001; Chapter 2.
- (25) Sánchez, C.; Leiva, E.; Dassie, S. A.; Baruzzi, A. M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 549.