J. Am. Chem. Soc. **2000,** *122,* 8215−8219

Two-Phase Azo-Coupling Reactions Driven by Phase-Boundary Potential Across the Liquid|Liquid Interface

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Received November 8, 1999. Revised Manuscript Received March 20, 2000

Abstract: Phase-boundary-potential-driven azo coupling has been demonstrated for the reaction between hydrophilic arenediazonium ions and lipophilic coupling components in 1,2-dichloroethane (DCE)|water (W) two-phase systems. Instead of using phase-transfer catalysts, hydrophilic arenediazonium ions are driven into the DCE phase by externally controlling the potential drop across the polarized DCE|W interface. The diffusion-controlled transfer of arenediazonium ions across the interface is followed by azo-coupling reactions with coupling components in the DCE phase. The rate of the azo coupling in DCE has been accurately determined by using potential-step chronoamperometry for the transfer for four arenediazonium ions having different lipophilicity in the presence of one of four aromatic coupling components in DCE. No appreciable contribution of the adsorbed reactants to the overall azo-coupling process is detected. An electrochemical approach using liquid|liquid two-phase systems is advantageous in determining the rate of two-phase chemical reactions and is promising for elucidating the mechanism of phase-transfer catalysis.

Introduction

Phase-transfer catalysis, PTC, which facilitates chemical reactions between reactants in two immiscible phases, is one of the most important techniques in organic synthesis.[1−4] Much effort has been devoted to elucidate the mechanism of PTC, since its importance was widely recognized in the 1970s. The Starks ion-exchange mechanism[5] and the Makosza interfacial-reaction mechanism[6] are among the two well-known models for ion initiation reactions in liquid−liquid two-phase systems. However, little has been known about the molecular details of the mechanism of PTC, mainly owing to the complex interplay of mass transfer, adsorption, partitioning, and chemical reactions, all of which depend on the details of experimental conditions.[7−15]

From an electrochemical viewpoint, the role of phase-transfer catalysts is not necessarily to form ion pairs with hydrophilic reactants; the distribution potential between the two phases spontaneously formed by partitioning of ionic phase-transfer catalysts can act as the driving force for transferring charged reactants to the organic phase.[16,17] Such an electrochemical understanding of the mechanism of PTC can further be extended by applying the potential difference between the two phases to induce two-phase chemical reactions; chemical reactions can take place in the organic phase without phase-transfer catalysts if reactive cations or anions in the aqueous phase (W) are transferred to the organic phase in response to the applied potential. For this purpose, a polarized liquid|liquid interface where the electrical potential difference between the two phases is accurately controlled[18,19] is expedient for investigating two-phase chemical reactions, as a variety of electrochemical techniques[20] can be applied for obtaining kinetic parameters for the two-phase chemical reactions.

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10.1021/ja993937c CCC: $19.00

One notable advantage of using a polarized liquid|liquid interface is that one can focus on the charge transfer of only the reactant ions without any complication due to the partitioning of counterions, which are known to strongly influence the rate of PTC.[21] Moreover, mass transport, heterogeneous charge transfer, adsorption, and chemical reactions can be rigorously studied under the control of potential difference across the interface. S_N aryl reactions have been studied successfully using voltammetric techniques[22,23] at the nitrobenzene|W interface where the charge transfer of products across the interface takes place after the homogeneous chemical reactions. The present study is concerned with the azo-coupling reactions at the polarized 1,2-dichloroethane (DCE)|W interface. The azo coupling between diazonium ions and coupling components is an important reaction for synthesizing dye compounds.[24,25] Usually, this reaction proceeds in a homogeneous solution phase. However, in certain cases, the reaction in a two-phase system is advantageous, as many coupling components are lipophilic, while diazonium ions bearing positive charges are relatively hydrophilic. The two-phase azo coupling of this type is facilitated by the reverse-PTC in which hydrophilic cations are transferred from the water phase to the organic phase by ion-paring with large hydrophobic anions,[26−34] e.g., tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anion.[30,31] We will show that electrochemical techniques applied to the DCE|W interface are useful for quantitatively studying the mechanism of PTC.

Experimental Section

Reagent. 5-Diethylaminosulfonyl-2-methoxybenezenediazonium chloride hemi[zinc chloride] (Fast Red ITR), 5-butylaminosulfonyl-2-methoxybenezene diazonium chloride hemi[zinc chloride] (Fast Red PDC), and 4-chloro-2-methylbenzenediazonium chloride hemi[zinc chloride] (Fast Red TR) arenediazonium salt were from Merck. 2-Methoxy-4-nitrobenzenediazonium 1,5-naphthalene disulfonate (Fast Red B) diazonium salt, 1-naphthol, 2-naphthol, 1-naphthylamine (1-NA), and *N*,*N*-dimethyl-1-naphthylamine (DMNA) coupling components were of reagent grade from Wako Pure Chem. Co. Ltd. Zn^{2+}, Cl^-, and 1,5-naphthalene disulfonate contained in these reagents to stabilize arenediazonium ions did not transfer into the DCE phase in the potential window. Methods of the purification of water and tetrapentylammonium chloride (TPnACl) and the preparation of tetrapentylammonium tetraphenylborate (TPnATPB) have been described elsewhere.[35]

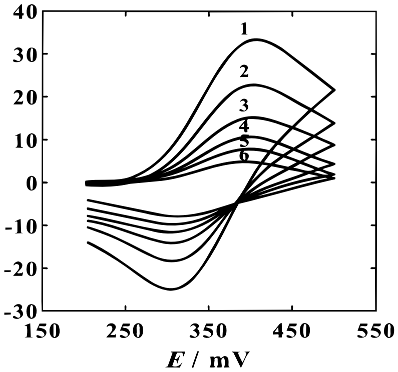

Figure 1. Cyclic voltammograms for the transfer of Fast Red TR ions across the DCE|W interface in the absence of coupling compounds in DCE. The concentration of Fast Red TR in W is 1 mM; the voltage scan rate is 1000 (curve 1), 500 (curve 2), 200 (curve 3), 100 (curve 4), 50 (curve 5), and 20 (curve 6) mV s^{-1}.

Cell. The electrochemical cell studied is represented as follows:

I	II	III	IV	V	VI	VII	
Ag	AgCl	5 mM TPnACl	20 mM TPnATPB	5 mM LiCl	AgCl	Ag	
		10 mM $MgCl_2$	*a* mM Coupling	50 mM $LiSO_4$			Cell(I)
			component	*b* mM Diazonium			
		(W2)	(DCE)	(W1)			

In the following, the potential of phase VII with respect to phase I is denoted as *E*, and the current flowing from phase V to phase IV is taken to be positive. This potential is approximately converted to the phase-boundary potential, $\Delta_{DCE}^{W}\phi$. The potential drop across the interface was controlled using a four-electrode potentiostat equipped with a positive feedback circuit for compensating the *iR* drop due to the solution resistance. Cyclic voltammetry and potential-step chronoamperometry measurements were made using a computer-controlled system. A four-electrode cell with a flat DCE|W interface whose area was 0.162 cm^2 was employed.[36] The temperature of the cell was maintained at 20 ± 0.5 °C. In potential-step chronoamperometry measurements, the time-dependent current was sampled at intervals of 10 ms. All experiments were done in a fume hood.

Results and Discussion

Potential-Sweep Measurements. Figure 1 shows cyclic voltammograms for the transfer of Fast Red TR ions across the interface at different scan rates when $a = 0$ and $b = 1$ in cell (I). The positive current corresponds to the transfer of Fast Red TR ions from W to DCE, and the negative current to the transfer of Fast Red TR ions back to the W phase. The peak separation was 75 mV and the midpoint potential was 360 mV. The linear dependence of the peak currents on the square root of the voltage scan rate, v, from 1000 to 20 mV s^{-1} and the negligible shift of the peak potential on v indicate that the transfer of Fast Red TR ions across the DCE|W interface is diffusion-controlled, as are other arenediazonium ions.[36] Although diazonium ions are known to gradually decompose in a solution at room temperature, the decomposition of arenediazonium ions we employed was negligible during the measurement of ca. 30 min, as no change in the height of the forward peak current was observed.

When a coupling component was present in the DCE phase, the shape of voltammograms in the reverse scan considerably changed. Figure 2 shows cyclic voltammograms for the transfer of Fast Red TR ions at 1 mM in W in the presence of 20 mM DMNA, a coupling component, in DCE at several values of v between 200 and 1000 mV s^{-1} (Figure 2a) and 20−100 mV

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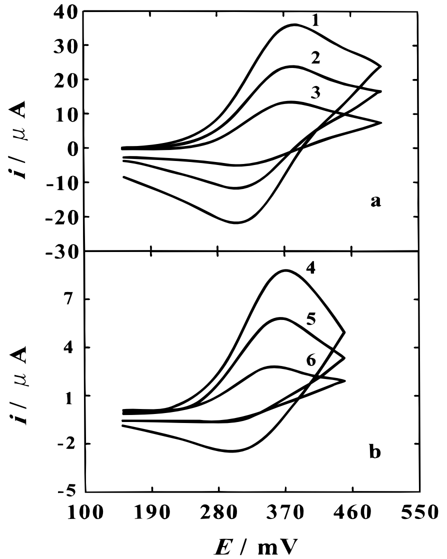

Figure 2. Cyclic voltammograms for the transfer of Fast Red TR across the DCE|W interface in the presence of 20 mM *N,N*-dimethyl-1-naphthylamine in DCE. The concentration of Fast Red TR in W is 1 mM; the voltage scan rate is 1000 (curve 1), 500 (curve 2), 200 (curve 3), 100 (curve 4), 50 (curve 5), and 20 (curve 6) mV s^{-1}.

s^{-1} (Figure 2b). The peak height in the forward scan was indistinguishable from that in the absence of DMNA in DCE within the range of v studied. When the voltage scan was fast, the peak in the reverse scan corresponding to the transfer of Fast Red TR ions from DCE to W appeared at 310 mV (Figure 2a), but its magnitude was smaller than that for the Fast Red TR ion transfer in the absence of DMNA in DCE. The height of the peak in the reverse scan decreased with decreasing v. The current in the reverse scan almost disappeared when v was as slow as 50 mV s^{-1} (Figure 2b, curves 5 and 6). Other coupling components, 1-NA, 1-naphthol, or 2-naphthol, also lowered the ion transfer current in the reverse scan.

The decrease in the peak current only in the reverse scan at a low scan rate strongly suggests that Fast Red TR ions are first transferred to the DCE and then react with DMNA to form either a neutral species or ionic products which are lipophilic enough to stay in the DCE phase within the potential window employed. After recording cyclic voltammograms, a purple color was visible on the DCE side of the interface. No coloring in the aqueous side of the interface was observed when the potential was kept at 150 mV, indicating that the coupling components did not appreciably partition into the W phase. The azo coupling therefore takes place in the DCE side of the interface.

Potential-Step Chronoamperometry Measurements. Figure 3 shows typical current−time curves in the absence of both Fast Red TR in W and DMNA in DCE (curve 1), in the presence of only 1 mM Fast Red TR in W (curve 2), and in the presence of both 1 mM Fast Red TR in W and 20 mM DMNA in DCE (curve 3). The initial potential was set at 150 mV where the transfer of Fast Red TR ions from W to DCE was negligible. Then the Fast Red TR ions were driven from the W phase to the DCE phase by stepping up the potential to 500 mV. After a certain time, τ, the potential was stepped back to the initial value. As the midpoint potential for the transfer of Fast Red TR was 360 mV, the potential at 500 mV was within the limiting current region where the surface concentration of the diazonium ions was very close to zero, ensuring that the current was diffusion-controlled.

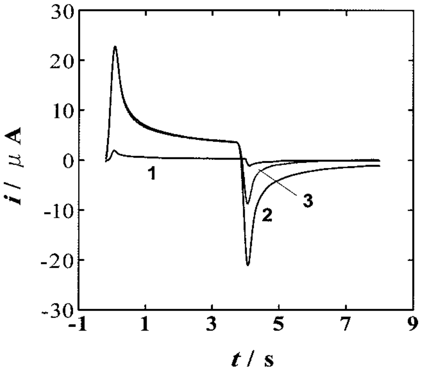

Figure 3. Chronoamperometry curves for a base supporting electrolytes in the absence of Fast Red TR and *N,N*-dimethyl-1-naphthylamine (curve 1), in the presence of 1 mM Fast Red TR in W (curve 2), and in the presence of 1 mM Fast Red TR in W and 20 mM *N,N*-dimethyl-1-naphthylamine in DCE (curve 3). The initial potential is 0.15 V; the second potential is 0.50 V; and the switching time is 4 s.

The positive current (curve 2 in Figure 3) corresponds to the transfer of Fast Red TR ions from W to DCE, and the negative current corresponds to the transfer of Fast Red TR ions back to W. In the presence of DMNA in DCE, the negative current in the second step decreased in comparison with the current in the absence of DMNA in DCE (curve 3), while the positive current in the first step was not affected by the presence of DMNA. The suppression of the current only in the potential reversal in potential-step measurements also suggests the decrease in the amount of diazonium ions transferred to DCE. Similar potential-step transients were observed in the presence of 1-NA, 1-naphthol, or 2-naphthol in DCE.

Mechanism of the Two-Phase Azo-Coupling Reaction. The mechanism of the phase-boundary-potential-driven azo-coupling reaction at the DCE|W interface may thus be represented by

$$\mathrm{Ar{-}N_2^{+}\ (W)} \underset{k_{\mathrm{DCE}}}{\overset{k_{\mathrm{W}}}{\rightleftharpoons}} \mathrm{Ar{-}N_2^{+}\ (DCE)} \tag{1}$$

$$\mathrm{Ar{-}N_2^{+}\ (DCE) + Y\ (DCE)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Ar{-}N{=}N{-}Y^{+}{-}H\ (DCE)} \tag{2}$$

$$\mathrm{Ar{-}N{=}N{-}Y^{+}{-}H\ (DCE) + B} \xrightarrow{k_2} \mathrm{Ar{-}N{=}N{-}Y\ (DCE) + HB^{+}\ (DCE)} \tag{3}$$

where Y is a coupling component, k_{W} and k_{DCE} are the rate constants of ion transfer in the forward and backward directions, k_1 and k_{-1} are the forward and backward rate constants of the formation of σ complex, Ar−N=N−$\mathrm{Y^{+}}$−H, B is a base, and k_2 is the rate constant for the release of the proton.[37] The mass transfer process, (1), may contain the adsorption of diazonium ions at the interface. However, the voltammograms in Figure 1 show no indication of the adsorption. The adsorption of both reactants and products has hence been disregarded in the above mechanism. When $k_{-1} \ll k_2[\mathrm{B}]$, which is presumably the present cases, the reaction in DCE is expressed by

$$\mathrm{Ar{-}N_2^{+} + Y} \xrightarrow{k_1} \mathrm{Ar{-}N{=}N{-}Y + H^{+}} \tag{4}$$

Such a heterogeneous charge transfer across the interface followed by a chemical reaction of the reactants formed by the preceding electrochemical process is known as the EC mech-

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anism, i.e., the heterogeneous charge transfer followed by a homogeneous chemical reaction, in electrode reactions.[38] The transfer of diazonium ions across the interface is electrochemically reversible within the experimental conditions, that is, the rate of ion transfer across the interface is limited by diffusion within the time scale of the present experimental conditions.[36] The mechanism is then described by the reversible charge transfer followed by an irreversible chemical reaction, i.e., E_rC_i.[39] At the DCE|W interface, Kontturi et al. found such a succeeding irreversible chemical reaction of H^+ ions with tetraphenylborate ions in DCE after the transfer of H^+ ions from W to DCE.[40] In the present study, we made the concentration of the coupling components much higher than that of the arenediazonium ions to ensure that the reaction is pseudo-first order with respect to the diazonium ions.

If H^+ ions formed by reaction 4 exist in the DCE phase as hydronium ions, they would be transferred into the W phase in the potential window we employed because of its high hydrophilicity: the standard Gibbs energy of the transfer of ion i from DCE to W, $\Delta G_{\mathrm{tr,i}}^{\mathrm{DCE}\rightarrow\mathrm{W},0}$, being 53 kJ mol^{-1} or the standard ion transfer potential, $\Delta_{\mathrm{DCE}}^{\mathrm{W}}\,\phi_i^{0'} = -\Delta G_{\mathrm{tr,i}}^{\mathrm{DCE}\rightarrow\mathrm{W},0}/\mathrm{ZiF}$, being 549 mV,[41] where z_i is the ionic charge and F is the Faraday constant. The resultant negative current due to the transfer of H^+ from DCE to W would reduce the net positive current in the forward scan due to the transfer of diazonium ions. In the reverse scan, the negative current of H^+ transfer would be added to the negative current due to the back transfer of arenediazonium ions. Experimentally, however, no significant decrease in the forward peak was observed in the case of Fast Red TR with DMNA. In the DCE phase, the H^+ ions formed by reaction 2 probably exist in the DCE phase as a protonated form which cannot be transferred to the W phase within the potential window. It is likely that H^+ ions attach to either coupling components or azo dyes in the DCE phase.[34] The protonated forms of coupling components or azo dyes are lipophilic enough to remain in the DCE phase within the potential window. The semiempirical calculation of the heat of formation of these protonated forms suggests that 1-NA and DMNA are more readily protonated than the azo dyes. Iwamoto et al. found the formation of protonated azo compounds in dichloromethane in dichloromethane−water two-phase azo-coupling reactions.[34]

In the case of the coupling of Fast Red TR or Fast Red PDC, the addition of a coupling reagent in DCE diminished the peak current of the diazonium ion transfer in the forward scan. This suggests that a certain fraction of H^+ ions formed in DCE moves to W. For simplicity, we disregard the transfer of H^+ in the following analysis. Strictly speaking, however, this effect has to be taken into account in accurately estimating the rate of the azo coupling reactions in DCE.

Rate of Azo Coupling Reactions. According to the theory of voltammetry for the E_rC_i mechanism,[42] the parameter which determines the voltammetric behavior is $\lambda = k_1RT/vnF$, where R is the gas constant, T is the absolute temperature, v is the scan rate, n is the number of charges transferred in the heterogeneous charge transfer, and F is the Faraday constant. The peak potential in the forward scan, E_p, shifts to the negative with decreasing the scan rate when $\lambda > 0.1$, while E_p and the peak current, I_p, are not affected by the irreversible succeeding reactions, when $\lambda < 0.1$. The observed constancy of E_p with v suggests that the latter condition is fulfilled in the range of v employed.[43] In other words, the ion transfer process can be regarded to be diffusion-controlled even in the presence of the following chemical reaction. In this case, however, the determination of the rate of the chemical reaction from cyclic voltammetry is impractical, as an extremely slow scan rate is required to determine k_1 from the shift of E_p with v. Instead, for determining k_1 values, we used the results of potential-step amperometry as illustrated in Figure 3.

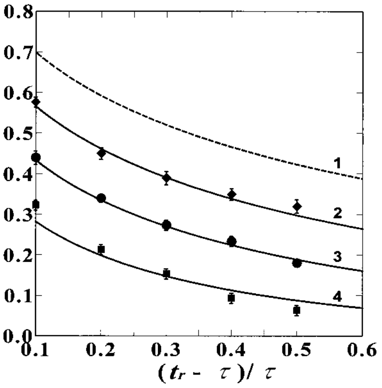

Figure 4. Plots of the ratio of negative current to positive current vs $(t_r - \tau)/\tau$ for the transfer of Fast Red ITR (◆), Fast Red TR (●), and Fast Red B (■) in the presence of 20 mM *N*,*N*-dimethyl-1-naphthylamine in DCE at 20 ± 0.5 °C: $\tau = 5$ s. The dashed line and solid lines are theoretical curves calculated using eq 5 for $k\tau = 0$ (curve 1), 0.3 (curve 2), 0.7 (curve 3), and 1.4 (curve 4).

The plots of the positive current as a function of the square root of time for several azo-coupling systems yielded straight lines, which again assured that the transfer of arenediazonium ions from W to DCE was diffusion-controlled. The analysis of a current−time curve for an E_rC_i mechanism is simplified by plotting the ratio of the current in the reverse step, i_b, at t_r to that at $t_r - \tau$ in the forward step, i_f, as a function of $(t_r - \tau)/\tau$,[42] where τ is the time of the potential reversal, and t_r is time after the second step but is measured after the first potential step. The ratio, i_b/i_f, for the E_rC_i process is expressed in terms of $k\tau$ and $(t_r - \tau)/\tau$, where $k = k_1[\mathrm{Y}]$ is the rate constant of the first-order irreversible chemical reaction, through[42]

$$-\frac{i_b}{i_f} = \phi[k\tau, (t_r - \tau)/\tau] - \left[\frac{(t_r - \tau)/\tau}{1 + (t_r - \tau)/\tau}\right]^{1/2} \qquad (5)$$

where ϕ represents a function involving the confluent hypergeometric series.[44] When reaction 4 is infinitely slow, ϕ becomes unity, corresponding to the simple diffusion-limited ion transfer.

The values of i_b/i_f at a given value of τ are plotted against $(t_r - \tau)/\tau$ for the transfer of Fast Red ITR (◆), Fast Red TR (●), and Fast Red B (■) in the presence of DMNA in Figure 4. The dashed line and solid lines are theoretical curves calculated using eq 5 for $k\tau = 0$ (curve 1), 0.3 (curve 2), 0.7 (curve 3), and 1.4 (curve 4). Figure 4 shows that the succeeding chemical reaction causes the downward shift of the plot and that the experimental points are well fitted to theoretical curves over the range of $(t_r - \tau)/\tau$ examined.

The values of k_1 calculated from k values are listed in Table 1 for the four diazonium ions and the four coupling components, together with the values of $\Delta_{\mathrm{DCE}}^{\mathrm{W}}\,\phi_i^{0'}$ for the diazonium ions.[36]

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Table 1. Values of k_1 for the Azo-Coupling Reaction in DCE Evaluated from Potential-Step Measurements at the DCE|W Interface at 20 ± 0.5 °C[a]

		k_1/M^{-1} s^{-1}			
	$\Delta_{\mathrm{DCE}}^{\mathrm{W}} \phi_i^{\mathrm{o}\prime}$/V	1-NA	DMNA	1-naphthol	2-naphthol
Fast Red B	−0.062	133.1 ± 6.5 2	31.1 ± 2.2	11.1 ± 0.5	3.4 ± 0.1
Fast Red TR	0.070	17.4 ± 0.5	13.3 ± 1.0	9.6 ± 0.6	1.6 ± 0.2
Fast Red ITR	−0.003	8.5 ± 0.4	5.6 ± 0.6	5.1 ± 0.3	4.4 ± 0.6
Fast Red PDC	0.049	2.8 ± 0.3	13.6 ± 0.4	2.4 ± 0.6	2.8 ± 0.3

[a] The concentration of a coupling component in DCE is 20 mM.

As might be expected, the rate of azo coupling is not correlated with the value of the standard ion-transfer potential (Table 1), i.e., the lipophilicity. This exemplifies the importance of separately evaluating the intrinsic lipophilicity of diazonium ions and their chemical reactivity with coupling components in organic solvents in analyzing the two-phase chemical reactions. In contrast, in actual PTC reactions, the degree of partitioning of reactants varies with not only their lipophilicity but other factors such as a coexisting ionic species, volume ratio, and the concentration of the chemical species involved,[45,46] which complicates the analysis of the data obtained from PTC experiments.[34]

Conclusion

Reverse phase-transfer catalysis has been achieved by electrochemically driving diazonium ions from W to DCE across the planar interface. The mechanism of the formation of lipophilic azo compounds is represented by E_rC_i, that is, the diffusion-controlled electrochemical charge transfer followed by the homogeneous chemical reaction. No evidence has been found for a significant role of the adsorbed species in the overall phase-transfer catalysis. Most of the arenediazonium ions have the transfer Gibbs energy ranging from 20 to −12 kJ mol^{-1}, which is within the potential window available in DCE|W two-phase systems.[36] It is therefore possible to study azo-coupling reactions for various diazonium ions using the electrochemical techniques. The present approach is useful and convenient for quantitatively studying the mechanism of PTC, because the contribution of the chemical reaction, mass transfer, partitioning, and the adsorption of reactants at the interface to the overall two-phase reactions are distinctively estimated. Introducing the concept of the phase-boundary potential into the study of PTC is of fundamental importance not only for externally controlling PTC through applied voltage but also for elucidating the mechanism of PTC even in the absence of applied potential, as the partitioning of ionic components is determined by the phase-boundary potential and vice versa.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research, No. 10440220, and a Grant-in-Aid for priority Research (No. 111 67246), from the Ministry of Education, Science, Sports and Culture, Japan.

JA993937C

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