Ion Transfer from Aqueous to Mixed Organic Solution Studied by Polarography at the Electrolyte Dropping Electrode

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Organic mixed solvents composed of polar and non-polar solvents or protic and aprotic solvents are introduced as feasible organic solvents (Org) for the ion transfer voltammetry at the aqueous (W)/Org solution interface. The transfer energies of such univalent ions as tetraalkylammonium ions, ClO_4^- or I^- were discussed based on the half-wave potentials in voltammograms (polarograms) at the interface between W and acetonitrile-chloroform, acetonitrile-benzene or n-butanol-chloroform. The transfer of tetraalkylammonium ions, ClO_4^- or I^- from W to chloroform is facilitated by the addition of acetonitrile to chloroform, and the transfer of H^+ from W to Org is facilitated when butanol was added to chloroform.

KEY WORDS: Ion transfer/ Polarography at a liquid/liquid interface/ Acetonitrile-chloroform mixture/ Butanol-chloroform mixture

INTRODUCTION

The voltammetry for the ion transfer at the two immiscible electrolyte solutions interface (VITIES) has been recognized as one of the epoch-making branch in the field of electrochemistry, since the amount of ions transferred and the transfer energy (ΔG_{tr}) are measured simultaneously as the current (I) and the potential difference between two phases (ΔV). The voltammetry is very attractive from the viewpoint of the determination of ion, the interpretation of ion transfer in living organisms, the elucidation of interfacial phenomena accompanied with the ion transfer, etc. Hence, more than 400 papers have been published concerning with the voltammetry.[1]

Various organic solvents (Org) of dielectric constants (ε) between 5 and 34 have been examined as one of two immiscible liquids.[2] Little differences have been found, however, in transfer behaviors of ions with different Org, because Org employed have similar physico-chemical properties each other. As we can get organic solvents of wide variety of physico-chemical properties by mixing non-polar with polar solvents or protic with aprotic solvents at appropriate ratios, if organic mixture could be demonstrated to be feasible to the voltammetry, the information more useful for analytical chemistry or biochemistry will be gathered.

In the present paper, the ion transfer between aqueous and organic mixtures such as acetonitrile (AN) - chloroform ($CHCl_3$), AN - benzene (BN), AN - carbon tetrachloride (CCl_4), acetone (AC) - $CHCl_3$ or n-butanol (BuOH) - $CHCl_3$ mixtures has been investi-

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gated by current-scan polarography at an aqueous electrolyte solution dropping electrode.[2]

EXPERIMENTAL

Polarographic Measurement

The procedure for the measurement of the polarogram, the cell, potentiostat, galvanostat, function generator, X-Y recorder and the apparatus for IR drop compensation employed in the present work were identical to those described in the previous work.[2] The potential difference (ΔV) at the W/Org interface was measured with a silver/silver chloride electrode (SSE) and tetraphenylarsonium ion selective electrode (TPhAsE) set in W and Org, respectively. The cell configuration of TPhAsE has been given elsewhere.[2] For mixtures containing $CHCl_3$, TPhAsE made of pure $CHCl_3$ was used. Neglecting liquid junction potential between $CHCl_3$ and the mixtures of $CHCl_3$, ΔV measured between SSE and TPhAsE can be converted into a potential denoted as TPhE where the Gibbs transfer free energy is assumed to be zero.[3,4]

Polarographic measurements were carried out at $25 \pm 1°C$.

Chemicals

Tetrabutylammonium tetraphenylborate ($TBA^+ \cdot TPhB^-$), crystalviolet $TPhB^-$ ($CV^+ \cdot TPhB^-$) and tetraphenylarsonium dipicrylaminate ($TPhAs^+ \cdot DPA^-$) were prepared and recrystallized according to the procedures mentioned previously.[2] Organic mixtures were shaken for 1 h with the same volume of water containing 1 M $MgSO_4$ to attain partition equilibrium between W and Org before the preparation of electrolyte solutions.

All other chemicals used were of reagent grade quality.

RESULTS AND DISCUSSION

Potential Windows in Residual Currents

The supporting electrolytes (SE) in the aqueous and organic phases should have appropriate solubilities and dissociate well in each phase, and must be composed of ions stable in one phase and hardly transfer to the other since the final rise and the final descent in the residual polarogram are determined by the transfer of SE ions at the interface. As SE, 1 M $MgSO_4$ and 0.01 M $TBA^+ \cdot TPhB^-$ or $TPhAs^+ \cdot DPA^-$ were added into W and Org, respectively. The distribution of AN, AC or BuOH between W containing 1 M $MgSO_4$ and $CHCl_3$, BN or CCl_4 was studied since AN, AC and BuOH are soluble in both aqueous and organic phases.[5] Table 1 summarizes the results. When W contained 1 M $MgSO_4$, AN, AC or BuOH is excluded from W by the salting-out effect.

Residual currents were investigated at interfaces between W containing 1 M $MgSO_4$ and AN - $CHCl_3$, AN - BN, AN - CCl_4 or AC - $CHCl_3$ containing 0.01 M $TBA^+ \cdot TPhB^-$ and BuOH - $CHCl_3$ containing 0.01 M $TPhAs^+ \cdot DPA^-$. The polarized region in the residual polarogram, denoted as potential window (Pw) in the following, obtained are also listed in Table 1. Mixed solvents such as 10 to 50 mol% AN - $CHCl_3$, 10 to 20 mol% AN - CCl_4, 10 to 20 mol% AN - BN, 10 to 30 mol% AC - CCl_4 and 0 to 40 mol% BuOH - $CHCl_3$ are applicable to VITIES from viewpoints of low mutual solubilities and wide Pw. Here, $TBA^+ \cdot TPhB^-$ and $TPhAs^+ \cdot DPA^-$ are well known supporting electrolytes which

Table 1 Potential windows (Pw) at interfaces between aqueous (W) and various mixed organic solutions (Org). Supporting electrolyte (SE) in W: 1 M MgSO$_4$.

Org	SE in Org (0.01 M)	AN in Org (mol%)	AN in W (mol%)	Pw (V)
AN[a]-CHCl$_3$	TBA$^+$·TPhB$^-$	22	1.4	0.46
		35	1.8	0.42
		45	2.2	0.35
		61	2.5	0.28
		75	2.5	0.20
AN-benzene	TBA$^+$·TPhB$^-$	22	2.5	0.31
		35	2.5	0.26
		48	2.5	0.22
		56	3.9	0.20
AN-CCl$_4$	TBA$^+$·TPhB$^-$	20	3.7	0.32
		31	3.8	0.29
		46	3.9	0.28
		59	3.9	0.23
		69	3.9	0.21
BuOH[b]-CHCl$_3$	TPhAs$^+$·DPA$^-$	BuOH in Org	BuOH in W	
		0	0	0.54
		20	0	0.46
		40	0	0.36
AC[c]-CHCl$_3$	TBA$^+$·TPhB$^-$	AC in Org	AC in W	
		27	1.6	0.32
		37	2.0	0.28
		47	2.4	0.22

[a]acetonitrile, [b]n-butanol, [c]acetone.

give wide Pw in VITIES with pure organic solvents.

Final rises and final descents in polarograms at interfaces between W containing 1 M MgSO$_4$ as SE and 22 mol% AN - CHCl$_3$ or 22 mol% AN - BN containing 0.01 M TBA$^+$·TPhB$^-$ as SE, or at interfaces between W and 22 mol% AN - CHCl$_3$ or 20 mol% BuOH - CHCl$_3$ containing 0.01 M TPhAs$^+$·DPA$^-$ as SE were attributable to the transfer of Mg^{2+} from W to Org and TBA$^+$ or TPhAs$^+$ from Org to W, respectively, which was confirmed by varying the concentration of MgSO$_4$, TBA$^+$·TPhB$^-$ or TPhAs$^+$·DPA$^-$.

The Pw became narrower with the increase of mole fractions of polar solvents in organic solvents as seen in Table 1, and, hence, the transfer of Mg^{2+} from W to Org is considered to be facilitated in the presence of polar solvents in Org.

Polarograms for Ion Transfer from Aqueous to Mixed Organic Solutions

Curve 1 in Fig. 1 is the residual polarogram at the interface of W containing 1 M MgSO$_4$ and 10 mol% BuOH - 90 mol% CHCl$_3$ containing 0.01 M TPhAs$^+$·DPA$^-$. Curve 2 in Fig. 1 realizes the current-scan polarogram for the transfer of H$^+$, added as 10^{-4} M

H_2SO_4 in W, from W to 10 mol% BuOH - 90 mol% $CHCl_3$. The limiting current (I_{Lc}) is proportional to both the concentration of H^+ in W in the range 2×10^{-5} to 3×10^{-4} M and the square root of the height of the water reservoir. The logarithmic analysis of the polarogram, log (I_{Lc}-I)/I vs. ΔV gave straight line with a slope of 59 ± 5 mV, where I is the instantaneous current and ΔV the electrical potential difference at the interface. Hence, the transfer of H^+ was concluded to be polarographically reversible.
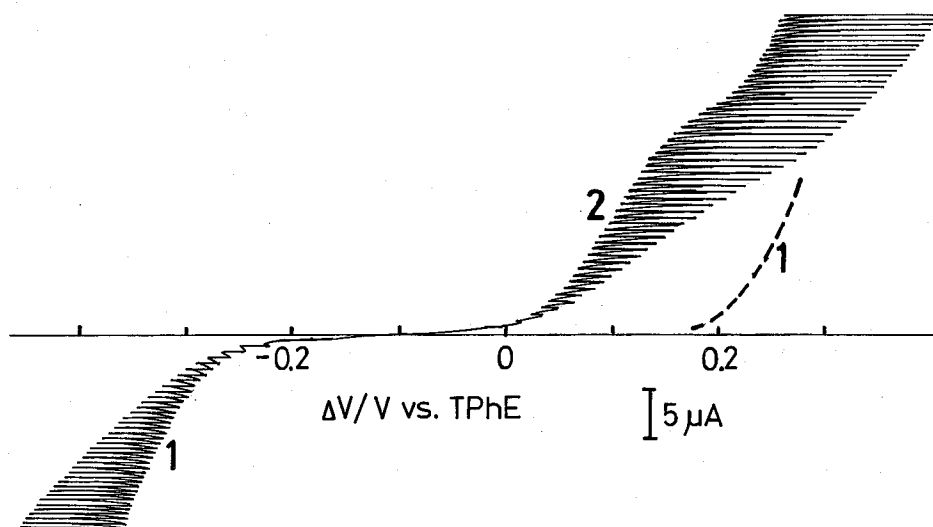
Fig. 1 Current-scan polarograms at the aqueous/10 mol% butanol-90 mol% chloroform interface. Supporting electrolyte: 1 M $MgSO_4$ in aqueous phase, 0.01 M $TPhAs^+ \cdot DPA^-$ in mixed organic phase. (1) Residual current. (2) The transfer of H^+ from aqueous containing 10^{-4} M H_2SO_4 to 10 mol% butanol-90 mol% chloroform.

The half-wave potential ($\Delta V_{1/2}$) of the reversible polarogram of univalent ion i^z ($z = 1$ or -1) from W to Org in the presence of ion-pair formation of i^z with SE ion, j^{-z}, in Org is expressed as eqn. (1) and can be related to the standard Gibbs transfer free energy (ΔG_{tr}^0) of i^z from W to Org through eqn. (2).[6]

$$\Delta V_{1/2} = \Delta_{Org}^W \varphi^0 - (RT/2zF)\ln(\bar{D}_{i^z,Org}/D_{i^z,W})$$
$$- (RT/zF)\ln(\gamma_W/\gamma_{Org}) - (RT/zF)\ln(1 + K_a c_{j^{-z}}\gamma_{Org}^2) \qquad (1)$$

where, $\Delta_{Org}^W \varphi^0$ is the standard Galvani potential difference, D the diffusion coefficient of i^z, $\bar{D}_{i^z,Org}$ the mean diffusion coefficient of i^z and ion-pair $i^z \cdot j^{-z}$ in Org, γ_α the activity coefficient of i^z in α phase, $c_{j^{-z}}$ the concentration of SE ion j^{-z} in Org and K_a the ion-pair formation constant. In eqn. (1), the ion-pair formation in W is neglected because of the high ε of W.

$$\Delta_{Org}^{W}\varphi^0 = \Delta G_{tr}^{0,W\to Org}/zF \; (= -\Delta_{W}^{Org}\varphi^0) \tag{2}$$

The standard Gibbs transfer free energy of an ion from W to Org is considered to be the difference between the solvation energies of the ion in both solutions.

$$\Delta G_{tr}^{0,W\to Org} = \Delta G^0_{solv,Org} - \Delta G^0_{solv,W} \tag{3}$$

The $\Delta V_{1/2}$ for Transfer of Various Ions from Aqueous to Mixed Organic Solutions Containing AN

The polarogram for the transfer of tetramethylammonium ion (TMA$^+$), tetraethylammonium ion (TEA$^+$), tetrapropylammonium ion (TPrA$^+$), H$^+$, ClO$_4^-$ or I$^-$ from W to AN - CHCl$_3$ mixture had characteristics of the reversible ion transfer[1,11]. As summarized in Table 2, $\Delta V_{1/2}$ of polarograms for the transfer of TMA$^+$, TEA$^+$ or TPrA$^+$ from W containing 1.4 mol% AN and 1 M MgSO$_4$ to 22 mol% AN - 78 mol% CHCl$_3$ containing 0.01 M TPhAs$^+$·DPA$^-$ were about 0.09 V more negative than those observed for the transfer from W to CHCl$_3$, and $\Delta V_{1/2}$ for H$^+$ from W to the mixed organic solution was almost identical with that from W to CHCl$_3$. The $\Delta V_{1/2}$ for ClO$_4^-$ and I$^-$ were about 0.04 V more positive. Employing 0.01 M TBA$^+$·TPhB$^-$ as SE in Org instead of TPhAs$^+$·DPA$^-$, similar effects of the addition of AN to CHCl$_3$ on $\Delta V_{1/2}$ for TMA$^+$, TEA$^+$, TPrA$^+$ and ClO$_4^-$ to that mentioned above were observed. Therefore, these ions except H$^+$ are considered to be solvated more weakly in CHCl$_3$ than in AN - CHCl$_3$ mixture. Here, the effect of 1.4 mol% AN in the aqueous phase on $\Delta V_{1/2}$ for the above ions is considered to be small and less than 20 mV (i.e. 2 kJ·mol^{-1}) referring to the standard Gibbs transfer free energies of Na$^+$, K$^+$, Cl$^-$, I$^-$, TPhB$^-$ or TPhAs$^+$ from W to AN - W mixture.[7,8]

Table 2   Half-wave potentials ($\Delta V_{1/2}$) for transfer of ions at interfaces between aqueous and various organic mixed solutions. Supporting electrolyte (SE) in W: 1 M MgSO$_4$.

Org	SE in Org (0.01 M)	$\Delta V_{1/2}$/V vs. TPhE						
		H$^+$	Cs$^+$	TMA$^+$	TEA$^+$	TPrA$^+$	ClO$_4^-$	I$^-$
CHCl$_3$	TPhAs$^+$·DPA$^-$	0.145		0.16	0.03	-0.11	-0.165	-0.195
	CV$^+$·TPhB^{-a}	0.30 <		0.15	0.02	-0.11	-0.15^b	-0.17^b
AN^c-CHCl$_3$	TPhAs$^+$·DPA$^-$	0.15		0.06	-0.06	-0.20	-0.12	-0.155
	TBA$^+$·TPhB$^-$	0.21 <	0.12	0.07	-0.06	-0.20	-0.13	
BuOH^d-CHCl$_3$	TPhAs$^+$·DPA$^-$	0.09	0.14 <	0.14 <	0.02	-0.12	-0.16	-0.195

[a]Crystalviolet tetraphenylborate. [b]SE in Org: 0.05 M. [c]Acetonitrile. [d]Butanol.

When mole fractions of AN in AN - CHCl$_3$ mixture were lower than 25 mol%, $\Delta V_{1/2}$ for TMA$^+$ were shifted more negative almost linearly with the increase of the mole fraction of AN as shown in Fig. 2, and when more than 30 mol% of AN, $\Delta V_{1/2}$ for TMA$^+$ were practically independent of the mole fraction of AN and at 0.025 V which was almost equal to the calculated $\Delta V_{1/2}$, 0.04 V, based on ΔG_{tr} from W to pure AN.[9]
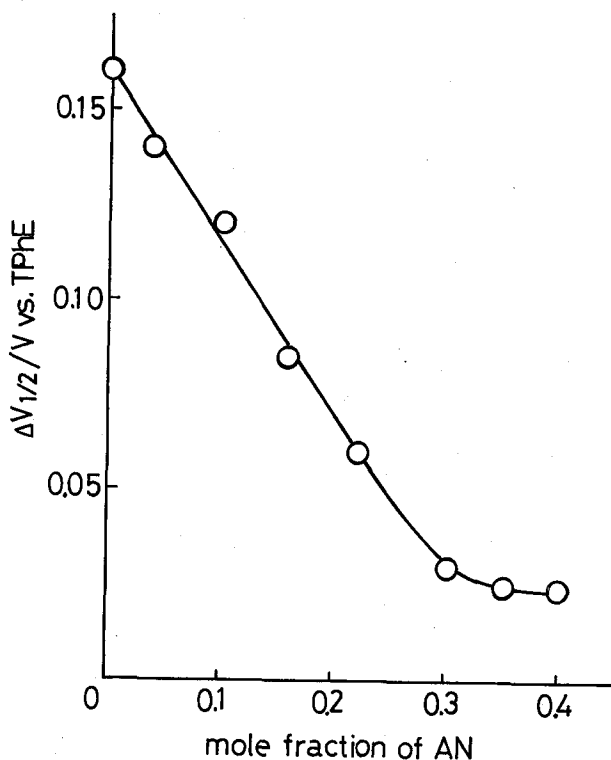
Fig. 2 Half-wave potentials for the transfer of TMA$^+$ from aqueous to acetonitrile-chloroform mixtures of various mole fractions. Supporting electrolyte: as Fig. 1.

The $\Delta V_{1/2}$ for TEA$^+$ from W to 22 mol% AN - 78 mol% CHCl$_3$ is about 0.13 V more negative than that for TMA$^+$ and 0.14 V more positive than that for TPrA$^+$. The difference between $\Delta V_{1/2}$ for TMA$^+$ and TEA$^+$ or that between TEA$^+$ and TPrA$^+$ are almost identical with those observed at W/nitrobenzene(NB) and W/1,2-dichloroethane(DCE) interfaces.[6,10] The difference is attributable to the difference between Gibbs energies required to form cavities to immerse uncharged moieties in these alkylammonium ions in W and those in Org.[11] Hence, the cavity formation energy required in the mixed organic solvent is identical with that in NB or DCE.

Polarographic waves for 3×10^{-4} M Na$^+$, K$^+$ and Rb$^+$ or Cl$^-$ and Br$^-$ from 1.4 mol% AN - W containing 1 M MgSO$_4$ to 22 mol% AN - 78 mol% CHCl$_3$ containing 0.01 M TBA$^+$·TPhB$^-$ could not observed since they merged into the final rise or final descent of the residual current. Adding 10^{-2} M ions in W instead of 3×10^{-4} M, final rises of polarograms were 0.025, 0.05, 0.11, 0.185 or 0.03 V more negative with Na$^+$, K$^+$, Rb$^+$, Cs$^+$ or H$^+$ and the final descents were 0 or 0.065 V more positive with Cl$^-$ or Br$^-$, respectively, than those of residual polarogram in the absence of objective ions (Fig. 3).
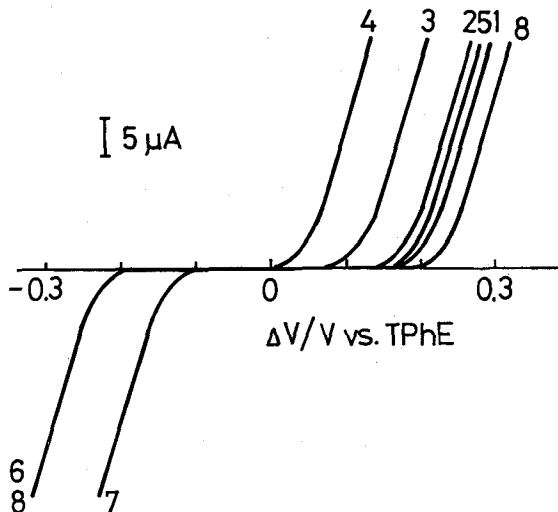
Fig. 3   Polarograms of 10^{-2} M of various ions at interfaces between aqueous containing 1.4 mol% of acetonitrile and 22 mol% acetonitrile-78 mol% chloroform. (1) Na^+, (2) K^+, (3) Rb^+, (4) Cs^+, (5) H^+, (6) Cl^-, (7) Br^-, (8) none. Supporting electrolyte: 1 M $MgSO_4$ in aqueous, 0.01 M TBA^+·$TPhB^-$ in Org.

Polarograms for the transfer of TMA^+, TEA^+ or Cs^+ from W containing 1 M $MgSO_4$ and 2.5 mol% AN to 22 mol% AN - 78 mol% BN containing 0.01 M TBA^+·$TPhB^-$ also have reversible characteristics (Fig. 4).   The difference between $\Delta V_{1/2}$ for TMA^+ and that for TEA^+ was almost identical with the difference from W to 22 mol% AN - 78 mol% $CHCl_3$.   Polarograms for the transfer of such univalent small anions as ClO_4^- or I^- merged into the final descent of the residual current when concentrations of ions were less than 3 × 10^{-4} M.   The ΔV at the interface of 22 mol% AN - 78 mol% BN was not converted into TPhE scale in the present case, since the transfer of $TPhB^-$ overlapped with the transfer of Mg^{2+} and it seemed difficult to determine the potential for the transfer of $TPhB^-$.

Here, it is interesting that even such a non-polar solvent as benzene is feasible to VITIES as Org if a polar solvent such as AN is added.

The $\Delta V_{1/2}$ for Transfer of Various Ions from Aqueous to Mixed Organic Solutions Containing BuOH

Employing 20 mol% BuOH - 80 mol% $CHCl_3$ as Org containing 0.01 M $TPhAs^+$·DPA^-, $\Delta V_{1/2}$ for the transfer of TEA^+, $TPrA^+$, ClO_4^- or I^- from W containing 1 M $MgSO_4$ to Org were almost identical with those from W to $CHCl_3$ containing 0.01 M $TPhAs^+$·DPA^- as seen in Table 2.   Polarographic waves for TMA^+ and Cs^+ merged into the final rise of the residual polarogram.   Here, the transfer of H^+ from W to Org is facilitated by the ion-pair formation of H^+ with DPA^- in Org, and, hence, the polarographic wave for H^+ can be observed in the presence of $TPhAs^+$·DPA^- as SE in Org.[12]   The
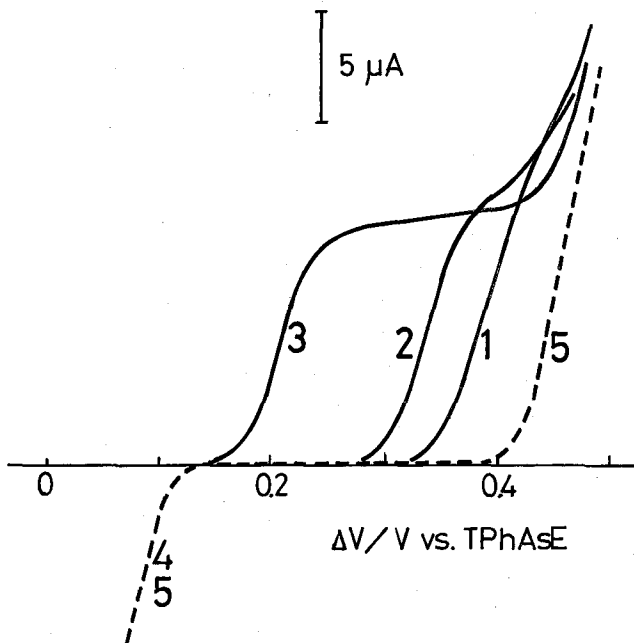
Fig. 4   Polarograms for the transfer of various ions from aqueous containing 2.5 mol% of acetonitrile to 22 mol% acetonitrile-78 mol% benzene.   (1) Cs^+, (2) TMA^+, (3) TEA^+, (4) ClO_4^-, (5) none.   Supporting electrolyte: as Fig. 3.   Ions in the aqueous: 2.5×10^{-4} M.

$\Delta V_{1/2}$ for H^+ from W to 20 mol% BuOH - 80 mol% $CHCl_3$ in the presence of 0.01 M $TPhAs^+ \cdot DPA^-$ was 0.055 V more negative than that from W to $CHCl_3$ containing 0.01 M $TPhAs^+ \cdot DPA^-$.   The association constant, K_a, of H^+ with DPA^- in BuOH - $CHCl_3$ mixture is expected to be smaller than that in $CHCl_3$, because dielectric constant of BuOH, ε = 17.5,[5] is larger than $\varepsilon = 4.8$ of $CHCl_3$[5] and ε of the mixture become larger with the increase of mole fraction of BuOH.   Considering K_a of $H^+ \cdot DPA^-$ only, the transfer of H^+ should be depressed and $\Delta V_{1/2}$ for H^+ should shift to more positive by the addition of BuOH, which is opposite to the result observed.   Therefore, the more negative $\Delta V_{1/2}$ for the transfer of H^+ from W to BuOH - $CHCl_3$ mixture is considered to be due to the strong solvation of BuOH to H^+ in the mixture.   In this connection, ΔG_{tr} reported for H^+ from W to methanol, ethanol, propanol or $CHCl_3$ are 10, 10, 9[13] or more than 30 kJ·mol^{-1} which suggest that H^+ is more stable and solvated more strongly in alcohols than in $CHCl_3$.

Since $\Delta V_{1/2}$ for H^+ from W to BuOH - $CHCl_3$ mixture shifted more negative almost linearly with the increase of mole fractions of BuOH up to 10 mol% but nearly constant with more than 10 mol% of BuOH (Fig. 5), H^+ is considered to be solvated preferentially by BuOH molecules in the mixture and the local mole fraction of BuOH molecules in the first solvation sphere of H^+ may be larger than the mole fraction in the bulk.
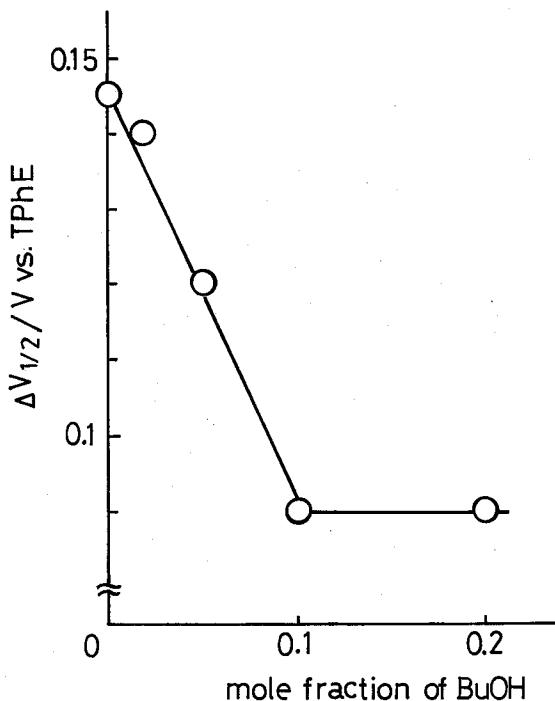
Fig. 5 Half-wave potentials for the transfer of H^+ from aqueous to butanol - chloroform mixtures of various mole fractions. Supporting electrolyte: as Fig. 1.

Using $CV^+ \cdot TPhB^-$ as SE in Org, the polarogram for 2×10^{-4} M H^+ from W to $CHCl_3$ or BuOH - $CHCl_3$ mixture merged into the final rise of the residual current. When 10^{-2} M H^+ was added as H_2SO_4 to W, final rises of polarograms at the interfaces between W and BuOH - $CHCl_3$ mixtures were more negative than that at the W/$CHCl_3$ interface, i.e. ΔV at the current of 15 $\mu A \cdot cm^{-2}$ in final rises in the presence of 10^{-2} M H^+ were 0.295, 0.115 or 0.09 V at the interface between W and $CHCl_3$, 20 mol% BuOH - 80 mol% $CHCl_3$ or 40 mol% BuOH - 60 mol% $CHCl_3$, respectively, and ΔV in the absence of H^+ were 0.295, 0.255 or 0.155 V. These results suggest that the transfer of H^+ is also facilitated even when a salt such as $CV^+ \cdot TPhB^-$ which hardly form ion-pair with H^+ is used as SE in Org.

The final rise in polarogram at the interface between W containing 0.1 M Na^+ or Cs^+ instead of H^+ and 20 mol% BuOH - 80 mol% $CHCl_3$ shifted 0.04 V or 0.05 V, respectively, more negative than that of residual currents in the absence of Na^+ or Cs^+, indicating that ΔG_{tr} for Na^+ and Cs^+ from W to the mixture are almost equal (Fig. 6). That is, ΔG_{tr} of Na^+ and Cs^+ become close each other by the addition of only 20 mol% of BuOH to $CHCl_3$. The remarkable effect of BuOH is very interesting compared with the effect of AN. The differences between the final rise of the polarogram for 10^{-2} M Na^+ and that for Cs^+ were 0.16 V or more than 0.15 V at interfaces between W and 22 mol% AN - 78

(534)

mol% CHCl₃ or between W and CHCl₃. Here, ΔG_{tr} reported for Na⁺ and Cs⁺ from W to BuOH are 18.8 and 18.5 kJ·mol⁻¹, respectively,[14] which are almost identical each other.
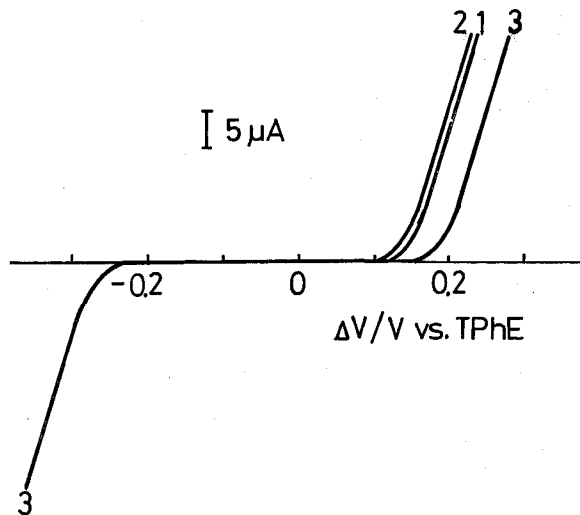

Fig. 6 Polarograms of 0.1 M of various ions at the interface be-
tween aqueous and 20 mol% butanol-80 mol% chloroform. (1)
Na⁺, (2) Cs⁺, (3) none. Supporting electrolyte: as Fig. 1.

In conclusion, it has been demonstrated in the present work that organic mixed sol-
vents are feasible to the ion transfer voltammetry as Org, and that the preferential solvation
of some ions with polar or protic solvents added in non-polar and/or aprotic solvents can be
elucidated based on the ion transfer voltammograms.

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