

Solvent Extraction of Sodium Permanganate by Mono-benzo 3*m*-Crown-*m* Ethers (*m* = 5, 6) into 1,2-Dichloroethane and Nitrobenzene: a Method which Analyzes the Extraction System with the Polar Diluents

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Abstract

Analytical equations were derived for the extraction of univalent metal salts (MA) by crown ethers (L) into polar diluents. Then, NaMnO₄ was extracted at 25 °C by benzo-15-crown-5 and -18-crown-6 ethers (B15C5 and B18C6) from a water (w)-phase into a 1,2-dichloroethane (DCE)-one. So, the extraction constants of $K_{\text{ex}1}$ and $K_{\text{ex}2}$ were determined, where $K_{\text{ex}1} = [\text{NaLMnO}_4]_{\text{DCE}}/[\text{Na}^+][\text{L}]_{\text{DCE}}[\text{MnO}_4^-]$ and $K_{\text{ex}2} = [\text{NaL}^+]_{\text{DCE}}[\text{MnO}_4^-]_{\text{DCE}}/[\text{Na}^+][\text{L}]_{\text{DCE}}[\text{MnO}_4^-]$ ($= K_{\text{ex}1}/K_{\text{NaLMnO}_4}^{\text{DCE}}$). From the calculation processes of these K_{ex} values, $K_{\text{D,MnO}_4}$ and $K_{\text{MLA}}^{\text{DCE}}$ values with MLA = NaLMnO₄ were obtained and also $K_{\text{NaL}}^{\text{DCE}}$ values were estimated from the thermodynamic cycle of $K_{\text{ML}}^{\text{DCE}} = K_{\text{ex}2}/K_{\text{D,M}}K_{\text{D,A}}$. Here, the $K_{\text{MLA}}^{\text{DCE}}$, $K_{\text{D,A}}$ or $K_{\text{D,M}}$, and $K_{\text{ML}}^{\text{DCE}}$ values denote an ion-pair formation constant of MLA in the DCE-phase, a distribution constant of A⁻ or M⁺ between the w- and DCE-phases, and a complex formation one of a complex ion ML⁺ in the DCE-phase, respectively. The same values were obtained for the w/nitrobenzene (NB) extraction systems. By comparing the $K_{\text{NaL}}^{\text{org}}$ and $K_{\text{D,NaL}}$ ($= [\text{NaL}^+]_{\text{NB}}/[\text{NaL}^+]$: distribution constant into NB) values with those previously-reported by other methods, the validity of the equations was confirmed. Additionally, extraction-abilities of the extraction systems with DCE and NB were examined, using component equilibrium constants reported before.

Keywords: Extraction constant, Distribution constant, Pairing anion, Sodium permanganate, Crown ether, 1,2-Dichloroethane, Nitrobenzene

1. Introduction

Extraction of alkali metal salts (MA) by crown compounds (L) into less-polar diluents, such as benzene, chloroform, and 1,2-dichloroethane (DCE), has been studied in more detail by considering an ion-pair formation between a complex ion ML⁺ and a pairing anion A⁻ in water (w) and a distribution of the thus-formed ion pairs MLA into the diluents (Takeda et al., 2004; Yajima et al., 2000). In such extraction systems, especially the extraction into DCE has been also analyzed by taking other processes into account: a distribution of M⁺ or A⁻ between the w- and DCE-phases, a dissociation of MLA into ML⁺ and A⁻ in the DCE-one, and so on (Kikuchi and Sakamoto, 2000; 1998). These facts suggest that DCE makes treatments for chemical equilibria in the extraction systems either more-complicate or -simple, probably depending on experimental conditions. The former cases (Takeda et al., 2004; Yajima et al., 2000) are more-informative for the equilibria of species in the w-phase, while the latter ones (Kikuchi and Sakamoto, 2000; 1998) are more-informative for those in the diluent. Hence, if both the cases are combined, then it is more-convenient for the study of the extraction systems. Also, few systematic studies for data-handling of

the MA-extraction by L into polar diluents, such as nitrobenzene (NB) (Danesi et al., 1975; Makrlík et al., 1999), have been reported. However, these data-handlings seem to be either over-approximated (Kikuchi and Sakamoto, 2000; 1998; Danesi et al., 1975) or very complicate computation (Makrlík et al., 1999) for the determination of some equilibrium constants relevant to these extraction systems.

Moreover, the diluents, DCE and NB, have been well used for electrochemical studies of ion transfers of alkali and alkaline-earth metal ions across w/DCE and w/NB interfaces (Koryta, 1984; Sabera et al., 1992; Yoshida et al., 2002; Olaya et al., 2010) and of their transfers facilitated by L and other ligands (Sabera et al., 1992; Uehara et al., 2007; Kakiuchi, 2004). Especially, the ion-transfer behavior of univalent cations is very important for the determination of many equilibrium constants, such as complex formation (or stability) and acid-dissociation ones, in both the phases (Reymond et al., 2000), because standard potentials at the interfaces for the ion transfer (Koryta, 1984; Sabera et al., 1992) are always required for the calculation of these constants. Additionally, the potentials for A^- transfers across the w/DCE and w/NB interfaces are very interesting in examining properties of A^- -solvent and -w interactions and standardizing the ion-transfer behavior of M^+ and R_4N^+ at the interfaces (Sladkov et al., 2004).

In the present paper, we derived fundamental equations for a detailed analysis of the above extraction systems with DCE or NB as the polar diluent, examined usefulness of these equations, and then tried to elucidate extraction-abilities of the systems. Here, $NaMnO_4$ and benzo-15-crown-5 and -18-crown-6 ethers (B15C5 and B18C6, respectively) were employed as MA and L, respectively. In these processes, extraction constants ($K_{ex1}/mol^{-2} dm^6$ and $K_{ex2}/mol^{-1} dm^3$, respectively) for the extraction of $NaLMnO_4$ and sodium complex ions NaL^+ (with MnO_4^- as a counter ion) into the diluents, distribution constants ($K_{D,A}$ and $K_{D,NaL}$, respectively) of MnO_4^- and NaL^+ between the w-phase and the two diluents, and the ion-pair formation constants ($K_{MLA}^{org}/mol^{-1} dm^3$) of NaL^+ with MnO_4^- in the diluents were determined. Also, using the reported values for the distribution constant ($K_{D,M}$, converted into the potential at the interface) of Na^+ between the two phases, we estimated the complex formation constants ($K_{ML}^{org}/mol^{-1} dm^3$) of Na^+ with L in the w-saturated DCE and NB. The $K_{D,NaL}$ (into NB) and K_{NaL}^{org} values were compared with those reported previously, in order to examine the validity of the present method based on the equations derived here.

2. Theory

2.1 Fundamental equations

The following equilibria were considered for the analysis of the present extraction system with the polar diluent.



Here, the subscript "o" denotes the o-phase. For these equilibria, the corresponding equilibrium constants were

$$K_{D,L} = [L]_o/[L] \quad (E1)$$

$$K_{ML} = [ML^+]/[M^+][L] \quad (E2)$$

$$K_{MA} = [MA]/[M^+][A^-] \quad (E3)$$

$$K_{MLA} = [MLA]/[ML^+][A^-] \quad (E4)$$

$$K_{D,MLA} = [MLA]_o/[MLA] \quad (E5)$$

$$(K_{MLA}^{org})^{-1} = [ML^+]_o[A^-]_o/[MLA]_o \quad (E6)$$

Also, the entry of A^- and A^-_o or ML^+ and ML^+_o in Eqs. (2)–(4) and (6) means the presence of the distribution equilibrium of A^- or ML^+ into the o-phase, respectively (see 4.3). Equations of mass and charge balances for such equilibria were

$$[M]_t \approx [M^+] + [ML^+] + [MLA] + [MA] + [MLA]_o + [ML^+]_o \quad (7)$$

$$[L]_t = [L] + [ML^+] + [MLA] + [L]_o + [MLA]_o + [ML^+]_o \quad (8)$$

$$[A]_t = [A^-] + [MLA] + [MA] + [A^-]_o + [MLA]_o \quad (9)$$

and

$$[M^+] + [ML^+] = [A^-] \quad (10)$$

$$[ML^+]_o \approx [A^-]_o \quad (11)$$

It is assumed here that $[ML^+]_o \gg [M^+]_o$. Using Eqs. (10) and (11), the ionic strength-values of each phase were calculated from $[A^-]$ ($= I$) for the w-phase and $[ML^+]_o$ or $[A^-]_o$ ($= I_o$) for the o-phase, respectively.

Eqs. (7)–(9) were rearranged into

$$[M^+] = \frac{[M]_t - \sum [MLA_n]_o}{1 + K_{MA}[A^-] + (K_{ML}/K_{D,L})[L]_o(1 + K_{MLA}[A^-])} \quad (12)$$

$$[L]_o = \frac{[L]_t - \sum [MLA_n]_o}{1 + K_{D,L}^{-1} + (K_{ML}/K_{D,L})[M^+](1 + K_{MLA}[A^-])} \quad (13)$$

$$[A^-] = \frac{[A]_t - \sum [MLA_n]_o}{1 + [M^+]\{K_{MA} + (K_{ML}K_{MLA}/K_{D,L})[L]_o\}} \quad (14)$$

with $\sum [MLA_n]_o = [MLA]_o + [ML^+]_o \approx [MLA]_o + [A^-]_o$ {see Eq. (11)}.

2.2 For determination of compositions of extracted species

The overall extraction equilibria (Yajima et al., 2000; Danesi et al., 1975) are expressed as



and



The equilibrium constants for their mixtures are defined as follows:

$$K_{ex}^{mix} = \Sigma [MLA_n]_o / [M^+][L]_o[A^-] = K_{ex1} + K_{ex2}/[A^-]_o \quad (n = 0, 1) \quad (17)$$

with

$$K_{ex1} = [MLA]_o / [M^+][L]_o[A^-] = K_{ML}K_{MLA}K_{D,MLA}/K_{D,L} \quad (E15)$$

and

$$K_{ex2} = [ML^+]_o[A^-]_o / [M^+][L]_o[A^-] = K_{ex1}/K_{MLA}^{org} \quad (E16)$$

at I_o and I . Therefore, if the K_{ex1} and $[ML^+]_o$ $\{= (K_{ex}^{mix} - K_{ex1})([M^+][L]_o[A^-])$ in each run} values are determined (see 2.3 for K_{ex1}), then we can easily obtain the K_{ex2} from a set of $[M^+]$, $[L]_o$, $[A^-]$, and $[ML^+]_o$ and accordingly the K_{MLA}^{org} values at I_o .

By plotting $\log (D_{mix}/[A^-])$ or $2\log D_{mix}$ against $\log [L]_o$ based on Eq. (17), its slope generally gives the composition of the ion-pair complex or the complex ion (with the counter ion A^-) extracted into the o-phase, respectively. This detail is as follows. A distribution ratio of the mixtures with M^+ , D_{mix} , is defined as $\Sigma [MLA_n]_o / ([M]_t - \Sigma [MLA_n]_o) = \Sigma [MLA_n]_o / [M^+](1 + f_{AL})$ and, when $1 \gg f_{AL}$, it is nearly equal to $D_1 + D_2$, where f_{AL} , D_1 , and D_2 denote $K_{MA}[A^-] + (K_{ML}/K_{D,L})[L]_o(1 + K_{MLA}[A^-])$ in Eq. (12), $[MLA]_o/[M^+]$ in Eq. (E15), and $[ML^+]_o/[M^+]$ in Eq. (E16), respectively. One can see that, generally, D_{mix} becomes D_1 in the higher range of $[L]_o$, while it does D_2 in the lower range. In other words, the relation $\log \{(D_1 + D_2)/[A^-]\} \approx \log (K_{ex1} + K_{ex2}/[A^-]_o) + \log [L]_o$ is primarily derived from Eq. (17) and then becomes

$$\log (D_1/[A^-]) \approx \log K_{ex1} + \log [L]_o \quad (17a)$$

at the conditions of $D_1 \gg D_2$ and $K_{ex1} \gg K_{ex2}/[A^-]_o$. Similarly it becomes

$$2\log D_2 \approx \log K_{ex2} + \log [L]_o \quad (17b)$$

at the conditions of $D_1 \ll D_2$ and $K_{ex1} \ll K_{ex2}/[A^-]_o$ and by assuming that $[A^-]_o/[A^-] \approx [ML^+]_o/([M^+] + [ML^+]_o) \approx [ML^+]_o/[M^+] = D_2$ {see Eq. (11); $[M^+] \gg [ML^+]_o$ in Eq. (10)}. Therefore, in the plots based on Eqs. (17a) and (17b), their slopes have to show unity for the extraction of MLA and ML^+ into the o-phases, respectively.

2.3 For determination of K_{ex1} and $K_{D,A}$

From Eq. (17), we can obtain its other form:

$$K_{\text{ex}}^{\text{mix}} = K_{\text{ex1}} + K_{\text{D,A}}/[M^+][L]_{\text{o}}, \quad (18)$$

where $K_{\text{D,A}}$ refers to the distribution constant of A^- between the w- and o-phases and defined as $[A^-]_{\text{o}}/[A^-] \{ \approx [ML^+]_{\text{o}}/[A^-] \}$ from Eq. (11). Then, taking logarithms of both side of the equation, we have immediately

$$\log K_{\text{ex}}^{\text{mix}} = \log (K_{\text{ex1}} + K_{\text{D,A}}/[M^+][L]_{\text{o}}). \quad (19)$$

Therefore, a non-linear regression analysis of the plot of $\log K_{\text{ex}}^{\text{mix}}$ against $-\log [M^+][L]_{\text{o}}$ yields these K_{ex1} and $K_{\text{D,A}}$ values. Also, if the $K_{\text{D,M}}$ value, defined as $[M^+]_{\text{o}}/[M^+]$, is available, then we can easily estimate the $K_{\text{ML}}^{\text{otg}}$ value at I_{o} , using the thermodynamic cycle of

$$K_{\text{ex2}} = K_{\text{D,M}}K_{\text{D,A}}K_{\text{ML}}^{\text{otg}}. \quad (\text{E16a})$$

3. Experimental

3.1 Chemicals

Sodium permanganate solution was prepared from $\text{NaMnO}_4 \cdot \text{H}_2\text{O}$ (Aldrich, 97%) by the same procedure as that for the KMnO_4 solution (Kudo et al., 2003). Commercial B15C5 and B18C6 (Aldrich, 98%) were dried at room temperature under reduced pressure (Kudo et al., 2003). DCE or NB (Kanto, Guaranteed reagent) were washed three times with water and then saturated with water (Kudo et al., 2003). All other chemicals were analytical grade and used without further purification. Water, by which all the aqueous solutions were prepared, was obtained by distilling once tap water and then passing through a Milli-Q Lab system (Millipore).

3.2 Solvent extraction experiments

Initial concentrations of NaMnO_4 in w were in the range of 3.4×10^{-4} – 9.0×10^{-2} mol dm^{-3} ; those of L in w were in that of 9.2×10^{-5} – 2.5×10^{-2} mol dm^{-3} . The pH readings of the aqueous permanganate solutions at 25 °C were in the range of 5–6: these values were obtained with a Horiba pH/ion meter (type F-23), using a Horiba glass electrode (type 6366-10D).

Five cm^3 of the aqueous NaMnO_4 solution was mixed with 5 cm^3 of the aqueous L solution and then 10 cm^3 of DCE or NB was added into its mixture in the stoppered-glass tube of about 30 cm^3 . Its tube was agitated at 25 ± 0.3 °C about 10 minutes (Kudo et al., 2003) and then centrifuged. After the DCE- or NB-phase was subdivided by 2–9 cm^3 into another tube, 4–7 cm^3 of w was added into it, and then back-extracted into the w-phase by vigorously shaking the tube. The total concentration, $[\text{MnO}_4^-]_{\text{t}}$, of MnO_4^- back-extracted into the w-phase was spectrophotometrically determined at 525 nm (Kudo et al., 2003): absorbance = $2.40 \times 10^3 [\text{MnO}_4^-]_{\text{t}} - 2 \times 10^{-5}$ at correlation coefficient (R) = 0.9998. This $[\text{MnO}_4^-]_{\text{t}}$ was defined to be $[\text{NaLMnO}_4]_{\text{o}} + [\text{NaL}^+]_{\text{o}} \{ = \Sigma [\text{NaL}(\text{MnO}_4)_n]_{\text{o}} \}$, where it was assumed that $[\text{NaL}^+]_{\text{o}} \approx [\text{MnO}_4^-]_{\text{o}} \{ \text{see Eq. (11)} \}$. As the case may be, operations for the back-extraction from the DCE- or NB-phase and the spectrophotometric determination of MnO_4^- were repeated. The spectrophotometric measurements were performed at 25 °C by using a Hitachi U-2001 spectrophotometer equipped with a 1-cm quartz cell.

Decomposition of MnO_4^- was not detected spectrophotometrically and potentiometrically to 6 h after the dilution of the aqueous NaMnO_4 solution (Kudo et al., 2003) and accordingly the extraction experiments of NaMnO_4 by L into DCE or NB and the determination of amounts of MnO_4^- extracted were finished for about 6 h.

3.3 Computation of $[\text{Na}^+]$, $[\text{L}]_{\text{o}}$, and $[\text{MnO}_4^-]$ at extraction equilibrium

The molar concentrations at equilibrium, $[\text{Na}^+]$, $[\text{L}]_{\text{o}}$, and $[\text{A}^-]$ with $\text{A}^- = \text{MnO}_4^-$, were computed by the following successive approximation. First, $[\text{Na}^+]$ was computed by using Eq. (12) with the approximation (ap. 1) of $1 \gg K_{\text{MA}}[\text{A}^-] + (K_{\text{ML}}/K_{\text{D,L}})[\text{L}]_{\text{o}}(1 + K_{\text{MLA}}[\text{A}^-])$. Secondly, $[\text{L}]_{\text{o}}$ was computed by introducing $[\text{Na}^+]$ into Eq. (13) with the approximation (ap. 2) of $1 \gg K_{\text{MLA}}[\text{A}^-]$. Lastly, $[\text{A}^-]$ was computed by introducing $[\text{Na}^+]$ and $[\text{L}]_{\text{o}}$ into Eq. (14). Then, the second $[\text{Na}^+]$ was computed by introducing $[\text{L}]_{\text{o}}$ and $[\text{A}^-]$ into Eq. (12) without the ap. 1. Similarly, the second $[\text{L}]_{\text{o}}$ was computed by introducing $[\text{A}^-]$ and the second $[\text{Na}^+]$ into Eq. (13) without the ap. 2. Moreover, the second $[\text{A}^-]$ was computed by introducing the second $[\text{Na}^+]$ and $[\text{L}]_{\text{o}}$ into Eq. (14). These calculations were repeated until $[\text{Na}^+]$, $[\text{L}]_{\text{o}}$, and $[\text{A}^-]$ became constant values: namely, the $(N - 1)$ -th $[\text{Na}^+] =$ the N -th $[\text{Na}^+]$, where N means the number of run and $[\text{Na}^+]$ is replaced by $[\text{L}]_{\text{o}}$ and $[\text{A}^-]$. Using these values and the experimental $\Sigma[\text{NaLA}_n]_{\text{o}}$ one, we computed the $K_{\text{ex}}^{\text{mix}}$ value from Eq. (17). Such calculations were performed on other data sets. In the calculation of $[\text{Na}^+]$, $[\text{L}]_{\text{o}}$, and $[\text{A}^-]$, constant values were employed for K_{ML} and $K_{\text{D,L}}$, while K_{MA} and K_{MLA} were computed from their values at $I \rightarrow 0$, according to I for the w-phase.

4. Results and Discussion

4.1 Composition of the complexes extracted

The plots of $\log (D_{\text{mix}}/[\text{MnO}_4^-])$ versus $\log [\text{L}]_{\text{o}}$ based on Eq. (17a) yielded the slope of 0.92 and the intercept of 2.1

at $R = 0.997$ for $L = \text{B15C5}$, while those of $2\log D_{\text{mix}}$ versus $\log [L]_0$ based on Eq. (17b) yielded the slopes of 1.10 and the intercepts of -1.5 at $R = 0.993$ for B18C6 in the extraction into DCE, 1.10 and 0.4 at $R = 0.999$ for B15C5, and 0.99 and 0.9 at $R = 0.974$ for B18C6 in that into NB (Figure 1). According to Eqs. (17a) and (17b), these intercepts correspond to the $\log K_{\text{ex1}}$ value for the former system and the $\log K_{\text{ex2}}$ ones for the latter three systems, respectively. Also, the higher slopes of the NaMnO_4 extraction systems with both B18C6 into DCE and B15C5 into NB predict that the corresponding intercepts $> \log K_{\text{ex2}}$ and accordingly their experimental deviations from the prerequisite of $1 \gg f_{\text{AL}}$ in Eq. (17) are somewhat large, compared with the deviation for the extraction by B18C6 into NB. The results indicate the extraction of the complexes composed of $\text{Na:L:A} = 1:1:1$ and $\text{Na:L} = 1:1$. Taking the above facts into account, we determined the K_{ex1} and K_{ex2} values for MLA and ML^+ by using Eqs. (19) and (E16), respectively (see 4.2).

4.2 Extraction of NaLMnO_4 and NaL^+ into DCE and NB

Plots of $\log K_{\text{ex}}^{\text{mix}}$ versus $-\log [\text{Na}^+][L]_0$ for the w/DCE and w/NB extraction systems gave the K_{ex1} and $K_{\text{D,A}}$ values by the non-linear regression analysis based on Eq. (19) (Figure 2 as an example). Table 1 lists these values determined, together with other component equilibrium constants available in the references (Kudo et al., 2008; 2006a; 2007; 1991; 1996; Katsuta and Takeda, 2003); 15C5 and 18C6 in this table denote 15-crown-5 and 18-crown-6 ethers, respectively. In addition to the values in Table 1, the $\log K_{\text{NaMnO}_4}$ values at the given I , estimated from the value at $I \rightarrow 0$ (Kudo et al., 2003), were 0.82 for the DCE extraction systems with B15C5 and B18C6, 0.87 for NB with B15C5, and 0.89 for NB with B18C6 on the average.

In the w/DCE extraction, the $\log K_{\text{ex1}}$ value of Na(B15C5)A with $\text{A}^- = \text{MnO}_4^-$ was comparable with that of Na(B18C6)A (Table 1). We can see this result from the fact that a difference in $\log K_{\text{D,NaLA}}$ between Ls cancels out that in the sum of $\log K_{\text{NaL}}$ and $\log K_{\text{NaLA}}$ between them {see Eq. (E15)}. In the w/NB extraction, the $\log K_{\text{ex1}}$ value of Na(B18C6)A was larger than that of Na(B15C5)A . This difference ($= 1.24$) mainly comes from that $\{= 0.81 + 3.19 - (0.45 + 2.51) = 1.04\}$ between the sums of $\log K_{\text{NaL}}$ and $\log K_{\text{NaLA}}$, although there are differences between the experimental conditions of I and I_0 (see Table 1).

The K_{ex2} is immediately resolved as $K_{\text{ML}}K_{\text{MLA}}K_{\text{D,MLA}}/K_{\text{D,L}}K_{\text{MLA}}^{\text{org}}$ from Eqs. (E15) and (E16). Hence, we can see that a difference in K_{ex2} between $L = \text{B15C5}$ and B18C6 for the DCE extraction comes from that in $K_{\text{NaLMnO}_4}^{\text{DCE}}$ (see 4.4). For the NB extraction, differences in both K_{ex1} and K_{ex2} between their Ls are mainly due to those in the sum of K_{NaL} and K_{NaLMnO_4} (Table 1). On the other hand, we can adopt the cycle of Eq. (E16a). That is, fixing MA to NaMnO_4 , the extraction-ability depends on only the magnitude of $K_{\text{NaL}}^{\text{org}}$, because the product $K_{\text{D,Na}}K_{\text{D,MnO}_4}$ is an intrinsic value for NaMnO_4 and the diluent.

The $\log K_{\text{ex1}}$ values for Na(B15C5)MnO_4 and Na(B18C6)MnO_4 in the DCE extraction were smaller than those ($= 3.728$ at $I = 0.022 \text{ mol dm}^{-3}$ and 3.501 at $I = 0.081$) (Kudo et al., 2006b) for Na(B15C5)Pic and Na(B18C6)Pic , respectively: here Pic^- denotes picrate ion. Obviously, these differences are due to those in $\log K_{\text{D,NaLA}}$ between these systems: $\log (K_{\text{D,NaLPic}}/K_{\text{D,NaLMnO}_4}) = 1.37$ for $L = \text{B15C5}$ and 1.76 for B18C6. These results are the same as those reported previously for the extraction systems with 15C5 and 18C6 (Kudo et al., 2003; 2008).

The $\log K_{\text{D,NaLMnO}_4}$ values for the w/DCE extraction were much smaller than the $\log K_{\text{D,NaLPic}}$ ones which were reported to be 2.60 for $L = \text{B15C5}$ and 2.09 for B18C6 (Kudo et al., 2006b). These results indicate that an interaction of w-molecules with NaLMnO_4 in the w-phase is larger than that with NaLPic (Kudo et al., 2008). The same results for $K_{\text{D,NaLA}}$ with $L = 15\text{C5}$ and 18C6 have been reported (Kudo et al., 2008). Also, the $\log K_{\text{D,NaLMnO}_4}$ values for given L were in the relation of $\text{DCE} < \text{NB}$, suggesting that an interaction of NaLMnO_4 with NB is larger than that with DCE (see 4.3 for $K_{\text{D,MnO}_4}$ and $K_{\text{D,NaL}}$).

4.3 Distribution of single MnO_4^- and NaL^+ between water and DCE or NB

As can be seen from Table 1, the $K_{\text{D,MnO}_4}$ values for the extraction systems with B15C5 are somewhat smaller than those for the systems with B18C6. These findings suggest a pairing cation-dependence of $\log K_{\text{D,A}}$ in the present extraction experiments, as well as in the extraction ones of NaMnO_4 into the same diluents $\{\log K_{\text{D,A}} = -4.6$ (into DCE); -3.22 (NB), unpublished data by Kudo}. The $K_{\text{D,A}}$ -difference for the w/DCE extraction can be expressed as $\log \{K_{\text{D,A}}(\text{B15C5})/K_{\text{D,A}}(\text{B18C6})\} = \log \{([\text{Na}^+]_{\text{DCE}} + [\text{Na}(\text{B15C5})^+]_{\text{DCE}})/([\text{Na}^+]_{\text{DCE}} + [\text{Na}(\text{B18C6})^+]_{\text{DCE}})\}$, when $[\text{A}^-]$ has a common value between the extraction systems, and, according to Eq. (11), it becomes $\log (K_{\text{NaL}}^{\text{DCE}}[\text{B15C5}]_{\text{DCE}}/K_{\text{NaL}}^{\text{DCE}}[\text{B18C6}]_{\text{DCE}})$ (see 4.5 for $K_{\text{NaL}}^{\text{org}}$). Therefore, assuming that $[\text{B15C5}]_{\text{DCE}} = [\text{B18C6}]_{\text{DCE}}$, we obtained -0.8 as $\log \{K_{\text{D,A}}(\text{B15C5})/K_{\text{D,A}}(\text{B18C6})\}$, being equal to the experimental difference ($= -0.8$, see Table 1). The same is true of the w/NB distribution: the value was calculated to be -0.4 against the experimental value of -0.5 . These facts may mean that these values should be standardized by the $(\text{C}_6\text{H}_5)_4\text{As}^+\text{B}(\text{C}_6\text{H}_5)_4^-$ assumption (Rais, 1971). The $\log K_{\text{D,A}}$ values with $\text{A}^- = \text{MnO}_4^-$ were comparable with that ($\log K_{\text{D,ClO}_4} \approx -2.58$ at 20°C) measured at the w/DCE interface by cyclic voltammetry (Olaya et al., 2010). The same is true of the $\log K_{\text{D,ClO}_4}$ value (-1.4 at 25

°C) obtained from solvent extraction into NB (Rais, 1971). The K_{D,MnO_4} values indicate that an interaction of MnO_4^- with DCE is smaller than that with NB (Table 1), as well as that of ClO_4^- .

The complex-cation distribution constant can be calculated from the thermodynamic cycle of $K_{D,ML} = K_{D,L}K_{ex2}/K_{ML}K_{D,A}$ ($= [ML^+]_o/[ML^+]_w$). So, their values were $\log K_{D,NaB15C5} = 1.01$, $\log K_{D,NaB18C6} = 1.46$ in the w/DCE extraction, $\log K_{D,NaB15C5} = 2.62$, and $\log K_{D,NaB18C6} = 2.57$ in the w/NB one. As similar to the distribution of MnO_4^- , the $K_{D,NaL}$ values show that an interaction with NaL^+ was in the relation of DCE < NB. The $\log K_{D,NaL}$ values for the w/NB extraction are comparable with those recalculated from those determined by the ion-transfer polarography at the w/NB interface: $\log K_{D,NaL}(\text{recalculated}) = 2.1$ for L = B15C5 and 2.67 for B18C6 (Kudo et al., 1996). These facts indicate that the present method is comparable with the electrochemical method at the interface and also suggest that the $K_{D,NaL}$ values corresponding to the w/DCE extraction are valid ones.

For given L, the $\log K_{D,NaL}$ values were comparable with the $\log K_{D,NaLMnO_4}$ ones (Table 1), except for the extraction by L = B18C6 into DCE. These facts indicate that the interaction of NaL^+ with DCE or NB is similar to that of $NaLMnO_4$. On the other hand, a difference in L = B18C6 between $K_{D,NaL}$ and $K_{D,NaLA}$ suggests any change, such as a distortion of the $Na(B18C6)^+$ conformation, due to the ion-pair formation with MnO_4^- .

We estimated from the above values the $\log K_{D,A}$ and $\log K_{D,NaL}$ values at I and $I_o \rightarrow 0$ using the relation $\log K_{D,A}^0 \{= \log (y_-^{org}[A^-]_o/y_-[A^-])\} = \log K_{D,A} + \log (y_-^{org}/y_-)$ or $\log K_{D,ML}^0 = \log K_{D,ML} + \log (y_+^{org}/y_+)$. Here, $K_{D,A}^0$, y_-^{org} , and y_- (or $K_{D,ML}^0$, y_+^{org} , and y_+) denote $K_{D,A}$ at I and $I_o \rightarrow 0$, ionic activity coefficients of A^- (or ML^+) in the organic solvents (or diluents), and those in w, respectively; the extended Debye-Hückel law was applied for the y -calculation of MnO_4^- and the Davies equation, $\log y_+ = -(\text{constant})(+1)^2 \{\sqrt{I}/(1 + \sqrt{I}) - 0.3I\}$, for that of NaL^+ . Consequently, the $\log K_D$ values agreed with the $\log K_D^0$ ones within the error of about ± 0.01 . From this result, the $K_{D,A}$ and $K_{D,NaL}$ values seem to be independent of the I and I_o conditions under the present experimental concentration-ranges.

4.4 Ion-pair formation of NaL^+ with MnO_4^- in water-saturated DCE and NB

The $\log K_{NaLMnO_4}^{org}$ values estimated from Eq. (E16) are listed in Table 1 (see 4.2). Small I_o values suggest that these $\log K_{NaLA}^{org}$ values are very close to those at $I_o \rightarrow 0$. For a given L, $\log K_{NaLA}^{DCE}$ was larger than or nearly equal to $\log K_{NaLA}^{NB}$. Since DCE and NB have less-donor properties, this ion-pair formation seems to be affected by the amounts ($[w]_{t,o}$) of water saturated in both the diluents: $[w]_{t,DCE} = 0.127 \text{ mol dm}^{-3}$ (Kikuchi et al., 2001) and $[w]_{t,NB} = 0.178 \text{ mol dm}^{-3}$ (Iwachido et al., 1980) at 25 °C. That is, the above findings suggest that the hydration effect to Na^+ caught in L is stronger in NB than in DCE.

For a given diluent, the $\log K_{NaLMnO_4}^{DCE}$ values showed also the relation of L = B15C5 > B18C6. This fact reflects the degree of hydration to NaL^+ in the DCE-phase and its size (cavity size: B15C5 < B18C6). On the other hand, the same discussion does not hold for the same reaction in the w-saturated NB: its hydration number (h) for $NaL(OH)_2^+$ has been reported to be L = B15C5 ($h = 0.8$) \leq B18C6 (1.1) (Iwachido et al., 1980) and it is easily predicted that $Na(B15C5)^+ < Na(B18C6)^+$ in size. These fact and prediction are in conflict with the experimental result for $K_{NaLMnO_4}^{NB}$. This disagreement suggests, as described previously (Kudo et al., 2006a) for $\log K_{NaLMnO_4}$ in Table 1, that the shielding effect of B15C5 to the charge on Na^+ is greater than the size effect of B18C6; it is well known that Na^+ more size-fits the cavity of B15C5 than that of B18C6. Now, we can not explain the reason why the shielding effect to NaL^+ in the DCE-phase does not clearly function or the relation between the $K_{NaLMnO_4}^{NB}$ values is similar to those between the K_{NaLMnO_4} ones (see Table 1).

The $\log K_{NaLMnO_4}^{NB}$ values for L = B18C6 were much larger than those of the more-bulky ion-pair complex, $Na(DB18C6)A$ with $A^- = Pic^-$ and 2,2',4,4',6,6'-hexanitrodiphenylaminat (Dpa^-), where DB18C6 denotes dibenzo-18C6: $K_{Na(DB18C6)Pic}^{NB} = 10^{2.48} \text{ mol}^{-1} \text{ dm}^3$ at 22 ± 1 °C by solvent extraction experiments (Danesi et al., 1975) and $K_{Na(DB18C6)Dpa}^{NB} = 10$ at 25.00 °C by conductance measurements (Iwachido et al., 1980). From differences in size among these A^- , we can suppose easily the order in size of the ion-pair complex being $Na(B18C6)MnO_4 < Na(DB18C6)Pic < Na(DB18C6)Dpa$. These results indicate that a major interaction between NaL^+ and MnO_4^- in the diluents is the Coulombic force. This is also supported by the fact that the $\log K_{Na(B18C6)A}^{DCE}$ value ($= 4.5$) with $A^- = MnO_4^-$ (crystal radius: $r_c = 2.40$ Å) (Marcus, 1997) was a little larger than that ($= 4.38$ at $I_o \rightarrow 0$) (Kikuchi and Sakamoto, 2000) with $A^- = Pic^-$ ($r_c = 3.35$ Å) (Marcus, 1997).

4.5 Complex formation of L with Na^+ in water-saturated DCE and NB

When the $K_{D,Na}$ values of Na^+ into DCE and NB are available in some way, we can immediately calculate the K_{ML}^{org} values for Na^+ with L in these diluents using Eq. (E16a). The thus-obtained values were $\log K_{NaL}^{DCE} = 9.5$ for L = B15C5, 10.3 for B18C6, $\log K_{NaL}^{NB} = 7.4$ for B15C5, and 7.8 for B18C6, where $\log K_{D,Na} = -9.99$ at 25 °C for the ion transfer at the w/DCE interface (Sabela et al., 1992) or -10.502 at 22 °C (Ulmeanu et al., 2002) and -6.0 for the w/NB extraction (Rais, 1971). These relations, $K_{NaL}^{DCE} \gg K_{NaL}^{NB}$, suggest the hydration of w-molecules saturated in

the diluents to Na^+ or L (see 4.4). The $\log K_{\text{NaB18C6}}^{\text{DCE}}$ value was larger than that (9.43) reported previously (Kikuchi and Sakamoto, 2000). This fact can be due to a difference between the mass-balance equations: for example, $[\text{B18C6}]_{\text{DCE}}$ in the reference (Kikuchi and Sakamoto, 2000) must correspond to $[\text{B18C6}]_{\text{DCE}} + [\text{B18C6}] + [\text{Na}(\text{B18C6})^+] + [\text{Na}(\text{B18C6})\text{A}]$ in Eq. (8), namely $[\text{B18C6}]_{\text{DCE}}(\text{the ref.}) \geq [\text{B18C6}]_{\text{DCE}}\{\text{Eq. (8)}\}$. The $\log K_{\text{NaB18C6}}^{\text{NB}}$ value (7.8) thus-determined was in accord with that (7.91) determined at $I = 0.05 \text{ mol dm}^{-3} \{(\text{C}_4\text{H}_9)_4\text{N}^+\text{B}(\text{C}_6\text{H}_5)_4^-\}$ by ion-transfer polarographic measurements (Kudo et al., 1996). Similarly, the $\log K_{\text{NaB15C5}}^{\text{NB}}$ value (7.4) was close to that (6.8, 6.82, 6.9₂) determined by the same and voltammetric measurements (Kudo et al., 1991; 2001; Harris et al., 1992). The above results indicate that the present method is suitable for the estimate of some equilibrium constants at least.

5. Conclusion

It was demonstrated experimentally that the present method is useful for the determination of the composition of extracted species, MLA and ML^+ , and the equilibrium constants, K_{ex1} , K_{ex2} , $K_{\text{D,A}}$, $K_{\text{MLA}}^{\text{org}}$, $K_{\text{D,ML}}$, and $K_{\text{ML}}^{\text{org}}$, relevant to them. Comparable results with those by other measurements were obtained with respect to the $K_{\text{D,NaL}}$ and $K_{\text{NaL}}^{\text{org}}$ values. The method is effective for studying the extraction-ability of MA by neutral ligands into polar diluents. The pairing cation-dependence of $K_{\text{D,A}}$ shows that a further study will be required for the magnitude of $K_{\text{D,A}}$ and for other A^- (M^+ , and ML^+).

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Table 1. Equilibrium constants for the extraction of NaMnO₄ by L into DCE and NB and their component equilibrium constants at 25 °C

L	log K_{ex1}	log K_{ex2}	log K_{ML}	log $K_{MLA} (I)^a$	log $K_{D,MLA}$
Diluent: DCE					
15C5 ^b	2.02	--- ^c	0.70	1.49 (0.010)	-0.15
B15C5	2.24 ± 0.02 ^d	-3.7 ₅ ± 0.3 ₁ ^e	0.45 ^f	2.47 ^g (0.0084)	1.23
18C6 ^j	2.57	--- ^c	0.73	2.29 (0.0062)	-0.42
B18C6	2.26 ± 0.04 ^d	-2.2 ₃ ± 0.3 ₀ ^e	0.81 ^f	3.13 ^g (0.0077)	0.33
Diluent: NB					
B15C5	3.79 ± 0.08 ^d	-0.2 ₃ ± 0.2 ₁ ^e	0.45 ^f	2.51 ^g (0.0015)	2.4
B18C6	5.03 ± 0.09 ^d	0.6 ₁ ± 0.3 ₁ ^e	0.81 ^f	3.19 ^g (0.00031)	2.59

Table 1. Continued

L	$\log K_{D,L}$	$\log K_{D,A}$	$\log K_{MLA}^{org} (I_o)^a$
Diluent: DCE			
15C5 ^b	0.02	--- ^c	--- ^c
B15C5	1.910 ^b	-3.3 ± 0.3^d	6.0 ⁱ (4.5×10^{-6})
18C6 ^j	0.03	--- ^c	--- ^c
B18C6	2.009 ^b	-2.5 ± 0.2^d	4.5 ⁱ (2.3×10^{-5})
Diluent: NB			
B15C5	1.6 ^h	-1.7 ± 0.2^d	4.0 ⁱ (3.5×10^{-5})
B18C6	1.57 ^h	-1.2 ± 0.2^d	4.4 ⁱ (1.8×10^{-5})

a. Average values in each phase. b. Kudo et al., 2008. c. Not determined. d. Determined by the non-linear regression analysis. e. Calculated from each value. f. Katsuta and Takeda, 2003. g. Kudo et al., 2006a. h. Kudo et al., 2007; 1991; 1996. i. Calculated from $\log K_{MLA}^{org} = \log K_{ex1} - \log K_{ex2}$. See 4.4 in the text. j. Kudo et al., 2007.

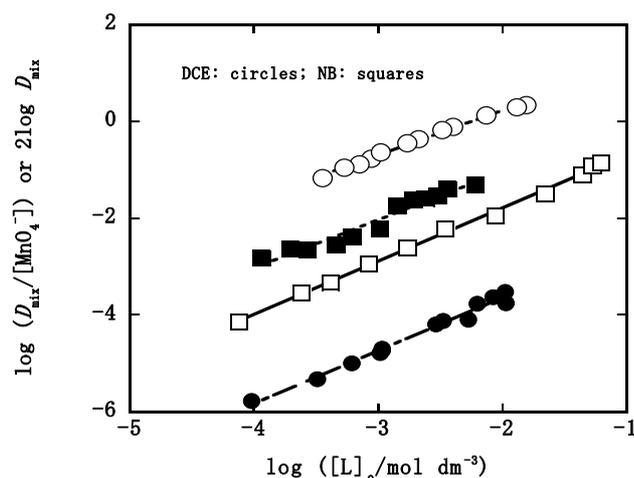


Figure 1. Plots of $\log (D_{mix}/[MnO_4^-])$ or $2\log D_{mix}$ versus $\log [L]_o$ for the $NaMnO_4$ -L extraction systems. The circles and squares refer to the extraction into DCE and NB, respectively. Also, the open and full symbols denote the extraction by $L = B15C5$ and $B18C6$, respectively. Only the open-circle symbol is the case for the $\log (D_{mix}/[MnO_4^-])$ -versus- $\log [L]_o$ plot.

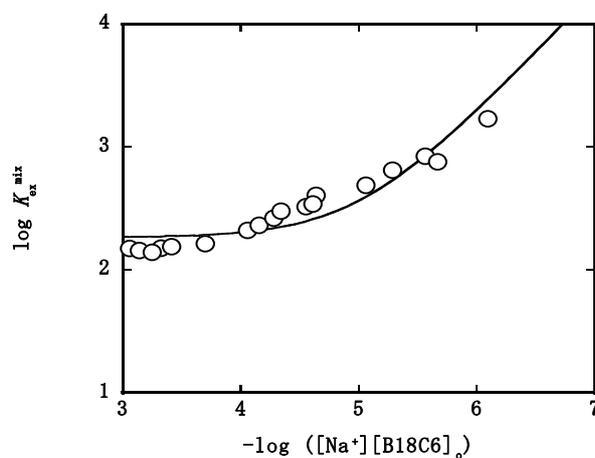


Figure 2. Plot of $\log K_{ex}^{mix}$ versus $-\log ([Na^+][L]_o)$ for the $NaMnO_4$ extraction by $L = B18C6$ into DCE. A curve shows the regression line of the plot analyzed by Eq. (19); $R = 0.936$.