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Ion-Pair Formation of Sodium Salts of Several Oxo Anions and Cadmium Halides in Water and the Distribution of Monovalent Sulfate Ion Pairs in Nitrobenzene

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Ion-pair formation constants (K_n^0, $n = 1, 2$) of Na_2SO_4, $Na_2S_2O_3$, Na_2CrO_4, $CaCl_2$, $CdCl_2$, $CdBr_2$, and CdI_2 in water were determined at 298 K and an ionic strength of 0 $mol \cdot dm^{-3}$ by potentiometry with Na^+-, Cl^--, Br^--, and I^--selective electrodes. Simultaneously, equations for the K_n^0 determination based on the DeFord−Hume method were derived. The thus-obtained K_1^0 values for Na_2SO_4, $Na_2S_2O_3$, $CdCl_2$, and $CaCl_2$ were compared with those reported before, and the validity of their values was confirmed. Interactions of Na^+ with oxo anions (X^{2-}) and Cd^{2+} with the halide ions in water were characterized by considering hydration to and Coulombic forces acting between these ions. Then, a difference in K_1^0 between CdI^+ and $NaSO_4^-$ was interpreted as that in the Coulombic force between the pairing ions. Also, the K_1^0 difference between $Na^+BPh_4^-$ and $Ph_4As^+Cl^-$ or $CaCl^+$ and $NaSO_4^-$ was examined by using a thermodynamic cycle of these salts in a water/nitrobenzene (NB) distribution system. Furthermore, the distribution constants in the NB phases were evaluated.

Introduction

Many studies have reported ion-pair (or complex) formation constants (K_n) for CdX_2 with $X^- = F^-, Cl^-, Br^-$, and I^- in water at given values of ionic strength (I).[1,2] There are, however, few studies for the direct determination of their formation constants (K_n^0) at $I \rightarrow 0$. Recently, we reported a potentiometric determination of K_n^0 for $CdCl_2$ in water with $n = 1$ and 2 and accordingly tried an application of the DeFord−Hume method[3] for K_n^0 determination.[4] Although the K_n^0 values were determined in the study,[4] there was an assumption for deriving an analytical equation, namely, it was assumed that the sum of activities of some species, such as Cd^{2+}, $CdCl^+$, and $CdCl_2$, is equal to a mean activity of $CdCl_2$: it was defined as $[y_{Cd}(y_{Cl})^2]^{1/3}.(4)^{1/3}$-$[CdCl_2]_t$ (ref 5). Here, y and $[CdCl_2]_t$ denote an ionic activity coefficient and the total molar concentration of $CdCl_2$ in water. However, the basis for this assumption is unclear, and thereby the reliability of the K_n^0 determination method[4] described before becomes unclear.

In the present paper, to rule out the above assumption[4] on the K_n^0 determination, we improved a previously derived analytical equation and also extended it to the ion-pair formation of Na^+ with several oxo anions (X^{2-}). By applying the equation to the ion-pair formation of Na_2SO_4, $Na_2S_2O_3$, and Na_2CrO_4 in water as well as that of $CdCl_2$, $CdBr_2$, CdI_2, and $CaCl_2$, we determined at 298 K their K_1^0 and K_2^0 values and then compared them with K_1^0 values reported before.[4,6,7] Using a thermodynamic cycle for the ion-pair formation in water, the characteristics of these salts in water were also discussed on the basis of hydration around the anion X^{n-} or a cation (M^{n+}) and Coulombic interaction between M^{n+} and X^{n-} with $n = 1$ and 2. Furthermore, these results were used for estimations of $K_{D,MX}$ values of $Ph_4As^+Cl^-$, $Na^+BPh_4^-$, MSO_4^- ($M = $ Li to Cs), and $CaCl^+$ from water into nitrobenzene (NB) phases at 298 K, where $K_{D,MX}$ denotes a distribution constant of M^+X^-, M^+X^{2-}, or $M^{2+}X^-$ into the NB phase. Here, Ph_4AsCl and $NaBPh_4$ are important materials for the electrochemistry of ion transfer at liquid−liquid interfaces,[8−10] and particularly, for Ph_4AsCl we performed the electromotive force (emf) measurements of its aqueous solutions in comparison with a K_1^0 value reported by solvent extraction.[11]

Theory

Ion-Pair Formation of 1:2 Electrolytes in Water. Let us consider the following equilibria for M_2X in water.

$$M^+ + X^{2-} \rightleftharpoons MX^- \tag{1}$$

$$M^+ + MX^- \rightleftharpoons M_2X \tag{2}$$

To these reactions, the ion-pair formation constants based on the molar concentration are defined as $K_1 = [MX^-]/[M^+][X^{2-}]$ and $K_2 = [M_2X]/[M^+][MX^-]$. The corresponding mass and charge balances are

$$2[M_2X]_t = [M^+] + [MX^-] + 2[M_2X] \text{ for M} \tag{3}$$

$$[M_2X]_t = [X^{2-}] + [MX^-] + [M_2X] \text{ for X} \tag{4}$$

and

$$[M^+] = 2[X^{2-}] + [MX^-] \tag{5}$$

From eq 5 and the definition of K_1, we obtain easily

$$[X^{2-}] = \frac{[M^+]}{2 + K_1[M^+]} \tag{6}$$

Also, the concentration of MX^- is derived from a rearrangement of eq 6 and the definition of K_1 as

$$[MX^-] = \frac{K_1[M^+]^2}{2 + K_1[M^+]} \tag{7}$$

Using eqs 4, 6, and 7, furthermore, we can obtain

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$$[M_2X] = [M_2X]_t - \frac{[M^+](1 + K_1[M^+])}{2 + K_1[M^+]} \qquad (8)$$

Therefore, determining experimentally $[M^+]$ and assuming initially a K_1 value, we can easily calculate self-consistent $[X^{2-}]$ and K_1 values from eq 6 and the K_1 definition, respectively, by a successive approximation (see Experimental Section). Simultaneously, the I values are calculated from $I = [X^{2-}] + [M^+]$ $\{= (1/2)(4[X^{2-}] + [MX^-] + [M^+])$ with eq 5$\}$.

We can take a sum of activities (a_j) as

$$a_X + a_{MX} + [M_2X] = \sum_j a_j = a_X(1 + K_1^0 a_M + K_1^0 K_2^0 (a_M)^2) \qquad (9)$$

and then rearrange it to

$$(\sum_j a_j)/a_X = 1 + K_1^0 a_M + K_1^0 K_2^0 (a_M)^2 \qquad (9a)$$

with $K_1^0 = a_{MX}/a_M a_X$ and $K_2^0 \approx [M_2X]/a_M a_{MX}$. Here, the activity coefficient, y, of a neutral M_2X in water is assumed to be unity, and the subscript j, on which its formal charges are omitted, denotes the species M^+, MX^-, and X^{2-}. Hence, being able to obtain $\sum a_j$, a_M, and a_X values, a nonlinear regression analysis for a plot of $(\sum a_j)/a_X$ versus a_M due to eq 9a immediately yields the K_1^0 and K_2^0 values.

In the potentiometric determination of K_n^0, effects of the parameters, such as the Bjerrum distance of the closest approach ($\mathring{a}$) and an ion size parameter (a),[5] seem to be smaller than from its conductometric determination, because the potentiometry contains the parameters a in the function $\sum a_j$ with the activity coefficients. On the other hand, the conductometry usually contains the parameter $\mathring{a}$ more directly. Accordingly, the conductometric K_1^0 values are more dependent on the parameter $\mathring{a}$ than are the potentiometric values on a.[17] This can be an advantage of the present method.

Ion-Pair Formation of 2:1 Electrolytes in Water. We also consider the same equilibria as those described previously[4] for MX_2 in water. From the mass- and charge-balance equations,[4] the following equations are derived:

$$[X^-] = \frac{2[M^{2+}]}{1 - K_1[M^{2+}]} \text{ for } M^{2+} \text{ analysis} \qquad (10)$$

or

$$[M^{2+}] = \frac{[X^-]}{2 + K_1[X^-]} \text{ for } X^- \text{ analysis} \qquad (10a)$$

$$[MX^+] = \frac{2K_1[M^{2+}]^2}{1 - K_1[M^{2+}]} \qquad (11)$$

and

$$[MX_2] = [MX_2]_t - \frac{[M^{2+}](1 + K_1[M^{2+}])}{1 - K_1[M^{2+}]} \qquad (12)$$

Similarly, from a rearrangement of the mass-balance equation $[MX_2]_t = [M^{2+}] + [MX^+] + [MX_2]$ for M^{2+} (see eqs 9 and 9a), we can derive

$$(\sum_j a_j)/a_M = (a_M + a_{MX} + [MX_2])/a_M = 1 + K_1^0 a_X + K_1^0 K_2^0 (a_X)^2 \qquad (13)$$

with $K_1^0 = a_{MX}/a_M a_X$ and $K_2^0 \approx [MX_2]/a_X a_{MX}$ at an activity coefficient $y_{MX2} \approx 1$ and $I = [M^{2+}] + [X^-]$ $\{= (1/2)(4[M^{2+}] + [MX^+] + [X^-])$ from the charge-balance equation, $2[M^{2+}] + [MX^+] = [X^-]$; see ref 4$\}$. Like eq 9a, eq 13 gives the K_1^0 and K_2^0 values by the nonlinear regression analysis of the $(\sum a_j)/a_M$ versus a_X plot.

Experimental Section

Chemicals. Cadmium bromide and iodide, which were guaranteed reagents (GR), were purchased from Wako Pure Chemical Industries, Ltd. (Tokyo, Japan) and the Kanto Chemical Co., Inc. (Tokyo, Japan), respectively. Their purities for Cd^{2+} were checked by a chelatometric titration with ethylenediaminetetraacetic acid (EDTA).[4] The purity of cadmium chloride (GR, Kanto) was checked by the same method.[4] Sodium salts of SO_4^{2-} (99.9 %, Wako), Br^- (99.9 %, Wako), CrO_4^{2-} (tetrahydrate; GR, Kanto), $[IrCl_6]^{2-}$ (hexahydrate; > 97 %, Kanto), and Ph_4AsCl (99 %, Aldrich) were used without any purification. The purity of $Na_2S_2O_3 \cdot 5H_2O$ (GR, Kanto) was checked by iodometry with KIO_3 and KI. Sodium chloride {(99.99 or 99.98) %, Wako} was dried at about 160 °C for 5 h. The purity of KI (extra pure reagent, ≥ 99.5 %, Kanto) was checked by a precipitation titration with $AgNO_3$ and fluorescein. Other chemicals were GR and used without any purification. Water which was used for preparing all aqueous solutions was obtained by distilling once tap water and then passing its distilled water through a Milli-Q Lab system (Millipore).

emf Measurements. The following cell was employed for emf measurements at (25.0 ± 0.4) °C: Ag|AgCl|0.1 $mol \cdot dm^{-3}$ KCl|1 $mol \cdot dm^{-3}$ KNO_3|test solution|ISE (ion-selective electrode). Here, the liquid junction potentials of the 1 $mol \cdot dm^{-3}$ KNO_3|test solution interface were disregarded, because their values for the present emf measurements were estimated to be (+1 to +3) mV by the Henderson equation.[13] The test solutions were aqueous solutions of NaCl, NaBr, or KI for calibration curves and those of Na_2SO_4, $Na_2S_2O_3$, $Na_2[IrCl_6]$, Na_2CrO_4, $CaCl_2$, Ph_4AsCl, $CdCl_2$, $CdBr_2$, or CdI_2 for the K_n^0 determination. With the reference electrode (Horiba type 2565A-10T), Br^--(Horiba type 8005-10C), I^-- (type 8004-10C), and Na^+-selective electrodes (type 1512A-10C) were used for the emf measurements of the solution of $CdBr_2$, that of CdI_2, and those of Na_2SO_4, $Na_2S_2O_3$, $Na_2[IrCl_6]$, and Na_2CrO_4, respectively. Unfortunately, as a response to the $CdCl_2$ solution,[4] a Cd^{2+}-selective electrode did not respond well to the $CdBr_2$ and CdI_2 solutions. As Figure 1 shows, the electrode seems to respond to I^-, particularly in the higher concentration range of I^- in water. Hence, we measured again the emf for the $CdCl_2$ solution using a Cl^--selective electrode (Horiba type 8002-10C) and redetermined the K_1^0 and K_2^0 values. The K_1^0 determination of Ph_4AsCl or $CaCl_2$ in water was also performed by using the Cl^--selective electrode against the same reference electrode.

The experimental calibration curves at 298 K were slopes (S) of (52 to 63) mV/decade and intercepts (E^*) of (−101 to −82) mV at correlation coefficients (R) of 0.999 to 1.00 for $Na_2X = Na_2S_2O_3$, $S = 38$ to 59 and $E^* = -152$ to -81 at $R = 1.00$ for Na_2SO_4, $S = 53$ to 61 and $E^* = -108$ to -98 at $R = 1.00$ for Na_2CrO_4 using the Na^+ electrode, $S = -62$ to -57 and $E^* = -83$ to -68 at $R = 0.999_5$ to 1.00 with the Cl^- electrode for $CdCl_2$, $S = -66$ to -56 and $E^* = -102$ to -70 at $R = 0.998$ to 1.00 with the Cl^- electrode for $CaCl_2$, $S = -64$ to -58 and $E^* = -249$ to -228 at $R = 0.998$ to 1.00 with the Br^- electrode for $CdBr_2$, and $S = -62$ to -59 and $E^* = -464$ to -449 at $R = 1.00$ with the I^- electrode for CdI_2, with all units of S being mV/decade and those of E^* mV.

Calculation of $\sum a_j$ and K_1^0 from emf Measurements. We will describe here the case of the Na_2X system as an example.

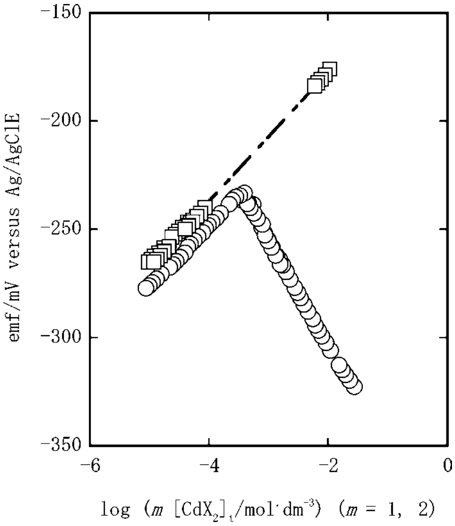

Figure 1. □, calibration curve prepared for the aqueous $Cd(NO_3)_2$-solutions ($m = 1$) and ○, plot of emf values measured for the aqueous CdI_2-solutions against $\log(2[CdI_2]_t)$ ($m = 2$) at 298 K, by using the Cd^{2+}-selective electrode. The curve depicted by a broken line is emf $= 30 \log [Cd(NO_3)_2]_t - 118$ at $R = 0.999$. The slope of the plots is -49 mV/decade in the $\log(2[CdI_2]_t)$ range of -3.5 to -1.5, suggesting an electrode response to I^-.

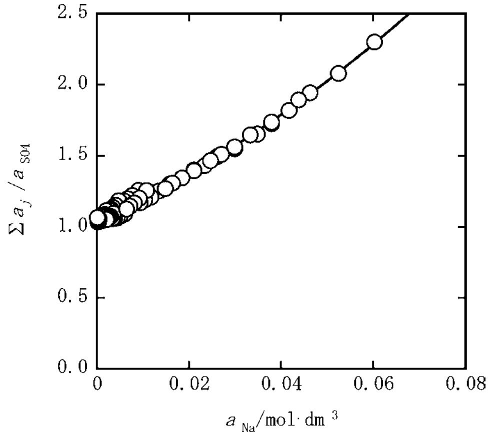

Figure 2. Plot of $(\sum a_j)/a_{SO4}$ versus a_{Na}. The solid line is a curve obtained from the regression analysis with eq 9a.

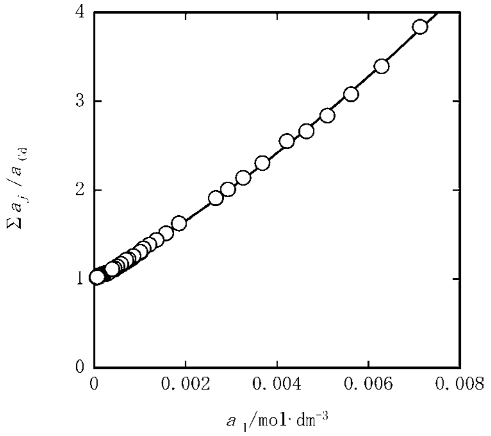

Figure 3. Plot of $(\sum a_j)/a_{Cd}$ versus a_I. The solid line is a curve obtained from the regression analysis with eq 13.

The molar concentrations, $[Na^+]$, of Na^+ in water were easily obtained from introducing directly the measured emf values into equations of the calibration curves with NaCl.

The thus-obtained $[Na^+]$ and first-approximated K_1 values, K_1^{first}, were introduced into eq 6, where an initial K_1^0 value was presumed from a value at any I reported previously, and thereby the K_1^{first} value was calculated. Then, from this estimated $[X^{2-}]^{first}$, $[Na^+]$, and K_1^{first}, the first-approximated $[NaX^-]$ value, $[NaX^-]^{first}$, was computed using the definition of K_1^0. Next, by introducing the $[X^{2-}]^{first}$, $[Na^+]$, and $[NaX^-]^{first}$ values into the K_1 definition, the second value, K_1^{second}, was estimated, and then the second value, $[X^{2-}]^{second}$, was computed from eq 6. Furthermore, using the K_1 definition, the second value, $[NaX^-]^{second}$, was computed from $[X^{2-}]^{second}$, $[Na^+]$, and K_1^{second}. So, these computations were repeated, until each of the $[X^{2-}]$, $[NaX^-]$, and K_1 values become a constant. The thus-obtained $[X^{2-}]$, $[NaX^-]$, and experimental $[Na^+]$ values gave the $[Na_2X]$ value, and also the activity coefficients, y_X, y_{MX}, and y_M, were computed from $I = [X^{2-}] + [Na^+]$ (see Theory Section) using the extended Debye−Hückel law for y_X and y_M or the Davies equation[5,7] for y_{MX}. From the above, we can immediately calculate the sum, $\sum a_j$, of activities a_X, a_{NaX}, and a_{Na2X} ($\approx [Na_2X]$) in each case by the left-hand side of eq 9. Basically, the above computations were performed by using Microsoft Excel 2002 as software, and the following nonlinear regressions were done by KaleidaGraph J (Hulinks Co. Japan, version 3.501). A nonlinear regression analysis of the plot of $\sum a_j/a_X$ versus a_{Na} yielded K_1^0 and $K_1^0K_2^0$. This K_1^0 value becomes the second estimate, and then the above processes were repeated until the N_r-th K_1^0 value was in accord with the $(N_r - 1)$-th K_1^0 value, where the symbol N_r denotes the number of the run. Other procedures were the same as those described previously.[4,14]

Similar calculations were performed for the $CdCl_2$, $CdBr_2$, and CdI_2 systems, and then their corresponding $\sum a_j$ values were computed by eq 13. For the $CaCl_2$ system, the K_2^0 value was not determined because of lower precision in the measured emf values. So, we analyzed the plot by using the linear equation $(\sum a_j)/a_{Ca} = 1 + K_1^0 a_{Cl}$.

Results and Discussion

Determination of K_1^0 and K_2^0 for 1:2 and 2:1 Electrolytes in Water. Strictly speaking, the present ion-pair formation constants are defined to mixtures of the solvent-separated ion pairs with the contact ion pair (CIP) in water,[14] because the ISE detects practically the free Na^+, Cl^-, Br^-, or I^- and does not detect the ion pairs themselves. Therefore, properties for the ion-pair formation of such mixtures are discussed in the present study. However, we can predict that the fraction of CIP in the mixture is very low because of the strong hydration of water molecules to Na^+, Cd^{2+}, or SO_4^{2-} (refs 4 and 15).

Figure 2 shows a plot of $(\sum a_j)/a_{SO4}$ versus a_{Na} due to eq 9a. From the nonlinear regression analysis of the plot, the equation $(\sum a_j)/a_{SO4} = (1.05 \pm 0.00_4) + (14.3 \pm 0.7)a_{Na} + (106 \pm 14)(a_{Na})^2$ was obtained with $R = 0.996$. Similar equations were determined for the plots of the other Na_2X systems: $(\sum a_j)/a_{S2O3} = (1.05 \pm 0.00_6) + (14.4 \pm 0.6)a_{Na} + (45.6 \pm 9.0)(a_{Na})^2$ at $R = 0.996$ and $(\sum a_j)/a_{CrO4} = (1.14 \pm 0.03) + (12.1 \pm 2.1)a_{Na} + (95.6 \pm 30.2)(a_{Na})^2$ at 0.994. The same is true of the CdX_2 and $CaCl_2$ systems: $(\sum a_j)/a_{Cd} = (1.09 \pm 0.00_5) + (91.6 \pm 3.7)a_{Cl} + (1236 \pm 410)(a_{Cl})^2$ at $R = 0.998$ for $X^- = Cl^-$, $(\sum a_j)/a_{Cd} = (1.04 \pm 0.04) + (118 \pm 19)a_{Br} + (3004 \pm 2244)(a_{Br})^2$ at 0.991 for Br^-, $(\sum a_j)/a_{Cd} = (0.99_1 \pm 0.00_3) + (308 \pm 5)a_I + (12348 \pm 756)(a_I)^2$ at 0.999_6 for I^- (Figure 3), and $(\sum a_j)/a_{Ca} = (1.07 \pm 0.00_7) + (41.1 \pm 2.5)a_{Cl}$ at 0.961 for $CaCl^+$. From the above values analyzed for the intercepts, the unity of the right-hand sides of eqs 9a and 13 was confirmed within experimental errors,

Table 1. Ion-Pair Formation Constants of Some 1:2 and 2:1 Electrolytes in Water at $T = 298$ K and $I \rightarrow 0$ and Standard Hydration Free-Energies of the Individual Ions Constituting Their Electrolytes

	K_1^0	K_2^0	ΔG_h^0 [b]/kJ·mol^{-1}	
electrolytes (N^a)	mol^{-1}·dm^3	mol^{-1}·dm^3	M^{n+}	X^{n-}
Na_2SO_4 (70)	$14 \pm 0._7$	7.4 ± 1.0	–375	–1090
$Na_2S_2O_3$ (68)	$14 \pm 0._6$	3.2 ± 0.6		*c*
Na_2CrO_4 (25)	12 ± 2	7.9 ± 2.8		–958
$CdCl_2$ (35)	92 ± 4, 89[d], 86[d]	13 ± 5, 8.7[d]	–1763	–347
$CdBr_2$ (27)	118 ± 19	25 ± 19		–321
CdI_2 (55)	308 ± 5	40 ± 3		–283
$CaCl_2$ (24)	41 ± 3, 40[d]	*e*	–1515	–347

[a] Number of data. [b] Ref 16. [c] Not available. [d] Values determined by potentiometry with the Cd^{2+}- or Ca^{2+}-selective electrode. See ref 4. [e] Not determined.

although the value of the Na_2CrO_4 system has a somewhat larger error than do those of the others.

The emf differences between the NaCl and the $Na_2[IrCl_6]$ solutions in the equivalent concentration ranges were so small that we could not determine the K_n^0 values. The same was true of the Ph_4AsCl system, namely, the differences in emf between the NaCl and the Ph_4AsCl solutions were not observed. The ionic radii[16] of X^{2-} are in the order SO_4^{2-} (2.30 Å) < CrO_4^{2-} (2.40 Å) < $S_2O_3^{2-}$ (2.50 Å) < $[IrCl_6]^{2-}$ (3.35 Å); this fact suggests that the ion-pair formation ability of $[IrCl_6]^{2-}$ with Na^+ in water is very weak. Table 1 summarizes the thus-determined K_n^0 values, together with hydration free energies[16] (ΔG_h^0) of the individual ions, constituting the electrolytes, at the standard state.

The K_1^0 value determined for Na_2SO_4 was slightly larger than or equal to that $\{1/0.094 = 11$ mol^{-1}·dm^3 (ref 17) or $1/0.086 = 12$ (ref 7) at 25 °C$\}$ reported by Fisher and Fox and two or three times larger than $10^{0.82}$ ($= 6.6$) by Reardon[18] or $1/0.19$ ($= 5.3$) by Jenkins and Monk.[19] Similar deviations have been reported for other MSO_4^- with M = Li, K to Cs.[18,20] Also, the value for $Na_2S_2O_3$ was three times larger than $1/0.21$ ($= 4.8$) mol^{-1}·dm^3 at 25 °C described before.[5] Considering the dependence of these K_1^0 values on $\mathring{a}$, a, or an equivalent conductivity (Λ) used in the data analysis, namely, the large differences among the above K_1^0 ones[7,17] by selected values of the parameters, such as a and Λ, we can see that their values are in agreement with our K_1^0 values within experimental error. As can be seen from Table 1, the K_1^0 value of $CdCl_2$ in water is in good agreement with those ((89 and 86) mol^{-1}·dm^3 in Table 1)[4] determined previously by potentiometry with the Cd^{2+}-selective electrodes. The same is true of the case of $CaCl^+$ in water (Table 1). These results indicate that the present potentiometric method has a satisfying validity and the previously reported method[4] also gives adequate results.

Resolution of K_n^0 into Component Constants Based on a Thermodynamic Cycle. The above results for K_1^0 can be explained as follows. From the thermodynamic cycle[21] of

$$M^+ \rightleftharpoons M^+(\text{g: gas phase}) \tag{14}$$

$$X^{n-} \rightleftharpoons X^{n-}(\text{g}) \tag{15}$$

$$MX^{(n-1)-} \rightleftharpoons MX^{(n-1)-}(\text{g}) \tag{16}$$

$$M^+(\text{g}) + X^{n-}(\text{g}) \rightleftharpoons MX^{(n-1)-}(\text{g}) \tag{17}$$

and

$$M^+ + X^{n-} \rightleftharpoons MX^{(n-1)-} \tag{1a}$$

with $n = 1$ or 2, we obtain immediately the relation

$$K_1^0 = K_{D,M}K_{D,X}K_1^g/K_{D,MX} \tag{18}$$

Here, $K_{D,M} = [M^+]_g/a_M$, $K_{D,X} = [X^{2-}]_g/a_X$, $K_1^g = [MX^-]_g/[M^+]_g[X^{2-}]_g$, and $K_{D,MX} = [MX^-]_g/a_{MX}$ as an example with $n = 2$, and the symbol $[\ ]_g$ denotes a concentration or an amount of the species, such as M^+ and MX^-, in a gas phase. These $K_{D,M}$, $K_{D,X}$, and $K_{D,MX}$ values can be considered to be apparent Henry's constants. Of course the gas phase is replaced by various organic phases.

The $K_{D,NaX}$ values in eq 18 were not available for the employed X^{2-}. It will be, however, important to consider properties of the ion-pair formation between Na^+ and X^{2-} in water, using $K_{D,Na}$, $K_{D,X}$, and K_1^g. Here, $K_{D,Na}$ can be expressed as $\exp\{\Delta G_h^0(Na^+)/RT\}$ with the hydration free energy, $\Delta G_h^0(Na^+)$, of Na^+, and then the same holds for $K_{D,X}$ and $K_{D,NaX}$. Essentially, the K_1^g value should reflect the Coulombic energy expressed by $|z_1z_2|/r$, where z_1 and z_2 denote the formal charges of ions j_1 and j_2, respectively, and r is the distance (Å) between the ions j_1 and j_2,[22] being calculated here as the sum, $r_{j1} + r_{j2}$, of their ionic radii. So, assuming that differences in $K_{D,NaX}$ among the employed X^{2-} are small, we can easily see from eq 18 that K_1^0 is fairly proportional to the product of $K_{D,X}$ and K_1^g. Also, eq 18 can be applied into the CdX_2 and $CaCl_2$ systems (see below).

Interaction between Na^+ and X^{2-} or Cd^{2+} and X^- in Water. The $K_1^0(CdI^+)$ value was much larger than the $K_1^0(NaSO_4^-)$ value (Table 1). The ionic radius (0.95 Å)[16,23] of Cd^{2+} is close to that (1.02 Å)[16,23] of Na^+ and similarly that (2.20 Å)[16] of I^- to that (2.30 Å) of SO_4^{2-}. Accordingly, to clarify a difference between the reactivity of M^{2+} and that of X^{2-} in water, it is interesting to compare the interaction between Cd^{2+} and I^- with that between Na^+ and SO_4^{2-}. The K_1^0 values at 298 K are in the order NaI $\{K_1^0 \approx \exp(-2.3) = 0.1$ mol^{-1}·dm^3: calculated for CIP using molecular dynamics simulations[24]$\}$ $\leq$ $NaSO_4^-$ < $CdSO_4$ (221)[25] $\leq$ CdI^+. It has been reported that the K_1^0(LiI) value determined by conductometry is about 100 times larger than that calculated from the simulations;[24] we supposed the K_1^0 order to be NaI $\leq$ $NaSO_4^-$, although M^+ differs from Na^+. The K_1^g relation is in the order NaI ($|z_1z_2|/r = 0.310$ Å^{-1}) < $NaSO_4^-$ (0.602) < $CdSO_4$ (1.23) > CdI^+ (0.635 or 0.714 at $r = 2.80$ Å[26]), suggesting $K_1^0(NaI) < K_1^0(NaSO_4^-) < K_1^0(CdI^+) < K_1^0(CdSO_4)$. Also, the $\Delta G_h^0(X^{n-})$ relations are $X^{n-} = I^- > SO_4^{2-}$ at a fixed Na^+, $Na^+ > Cd^{2+}$ at a fixed SO_4^{2-}, and $SO_4^{2-} < I^-$ at a fixed Cd^{2+} (see Table 1), suggesting $K_1^0(CdSO_4) < K_1^0(NaSO_4^-) < K_1^0(NaI)$ and $K_1^0(CdSO_4) < K_1^0(CdI^+)$. The relation, $\Delta G_h^0(SO_4^{2-}) < \Delta G_h^0(I^-)$ (that is, $K_{D,SO4} < K_{D,I}$), mainly contributes to $K_1^0(CdSO_4) \leq K_1^0(CdI^+)$ at a fixed Cd^{2+}. $|\Delta G_h^0(Na^+) - \Delta G_h^0(I^-)|$ ($= 92$ kJ·mol^{-1}) is much smaller than $|\Delta G_h^0(SO_4^{2-}) - \Delta G_h^0(Cd^{2+})|$ ($= 673$ kJ·mol^{-1}) at the fixed $|z|$ (see Table 1), where we compared ΔG_h^0 between the ions with the same $|z|$, since it is difficult to find out the value of its comparison between ions with the different charges. This fact indicates that the latter combination is more dominant than the former one for K_1^0. Therefore, the latter relation for ΔG_h^0 makes us predict $K_1^0(CdI^+) < K_1^0(NaSO_4^-)$, but this prediction differs from the experimental fact. Consequently, the K_1^0 relation of $NaSO_4^-$ < CdI^+ should be explained in terms of a difference in K_1^g between $NaSO_4^-$ (0.602 Å^{-1}) and CdI^+ $\{(0.635$ or $0.714)$ Å$^{-1}\}$. Here, we will bear in mind that the K_1^g value for CdI^+ contains a covalent-bond character.[2]

Equation 18 holds for the CdX_2 system, exchanging M^+ and X^{2-} for X^- and M^{2+}, respectively, in reactions 1a and 14 to 17. Simply, K_1^g predicts the $K_1^0(CdX^+)$ order $X^- = I^- < Br^- < Cl^-$ from $|z_1z_2|/r = 0.635$ Å^{-1} for CdI^+, 0.687 Å^{-1} for $CdBr^+$, and 0.725 Å^{-1} for $CdCl^+$, where $r_{Cl} = 1.81$ Å and $r_{Br} = 1.96$ Å.[16]

On the other hand, $K_{D,X}$ predicts the K_1^0 order $I^- > Br^- > Cl^-$ {see $\Delta G_h^0(X^-)$ in Table 1}. Although the $K_{D,CdX}$ values are unknown, the $K_{D,X}$ value, namely, $\Delta G_h^0(X^-)$, can be a major factor for determining the experimental K_1^0 order of CdX^+ (see Table 1) at least, and the K_1^g value is not a major one. Also, the order $K_1^0(CdCl^+) < K_1^0(CdBr^+) < K_1^0(CdI^+)$ was in agreement with that[2] reported in $I = 3\ mol \cdot dm^{-3}$ with $NaClO_4$; the same order has been described (see p 426 in ref 5).

The K_2^0 values for Na_2X were in the range of (3 to 8) $mol^{-1} \cdot dm^3$ (Table 1) and are somewhat smaller than the K_1^0 corresponding values. These facts indicate that the charge effect due to $|z_1z_2|/r$ is reduced by the NaX^- formation, although the size of NaX^- is not estimated. This is supported by the fact that the K_2^0 values are practically close to $K_1^0(Na^+X^-)$ (see below for the K_1^0 values).

Comparison of the NaX^- Formation to NaX in Water. The K_1^0 values at a fixed Na^+ were in the orders $X^{n-} = CrO_4^{2-} \leq SO_4^{2-} \approx S_2O_3^{2-}$ and ReO_4^- ($K_1^0 = 4.3\ mol^{-1} \cdot dm^3$ at 25 °C)[12] $< MnO_4^-$ ($8.0\ mol^{-1} \cdot dm^3$)[25] $< BPh_4^-$ ($14.3\ mol^{-1} \cdot dm^3$),[25] respectively. The ΔG_h^0 values are in the orders $SO_4^{2-} < CrO_4^{2-}$ (see Table 1) and ReO_4^- ($-338\ kJ \cdot mol^{-1}$) $< MnO_4^-$ ($-245\ kJ \cdot mol^{-1}$) $< BPh_4^-$ ($42\ kJ \cdot mol^{-1}$).[16] These facts suggest that $K_{D,X}$ is not dominant for an interaction of the divalent anion X^{2-} with Na^+ in water, while it is dominant for that of the univalent anion X^- with Na^+. The K_1^g relation seems to be dominant for ion-pair formation with Na^+, since CrO_4^{2-} ($|z_1z_2|/r = 0.585\ Å^{-1}$) $< SO_4^{2-}$ ($0.602\ Å^{-1}$). The same can be true of $K_1^g(NaX)$, since $X^- = ReO_4^-$ ($0.276\ Å^{-1}$) $< MnO_4^-$ ($0.292\ Å^{-1}$) from $r_{MnO4} = 2.40$ Å and $r_{ReO4} = 2.60$ Å.[16]

For BPh_4^-, there should be a hydrophobic interaction of its ion pair with water molecules, as discussed previously.[25] The predicted $|z_1z_2|/r$ order of X^-, BPh_4^- {$0.191\ Å^{-1}$ at $r_{BPh4} = 4.21$ Å (ref 16)} $< ReO_4^- < MnO_4^-$, means that the hydrophobic property of BPh_4^-, based on $K_{D,BPh4}$ in eq 18, is dominant for its ion-pair formation with Na^+, because the $K_{D,NaX}$ relation is presumed to be $NaX = NaReO_4$ or $NaMnO_4 < NaBPh_4$ from $\Delta G_h^0(X^-)$ (see below for the cases of MSO_4^- and $R_4N^+X^-$).

Application of the Above Results to Interaction between Na^+ and BPh_4^- or Ph_4As^+ and Cl^-. It is interesting to apply the discussion on the relation of $K_1^0(NaSO_4^-) < K_1^0(CdI^+)$ to that on $K_1^0(Ph_4AsCl) \leq K_1^0(NaBPh_4)$. These salts are important as materials related to a potential standardized by the $Ph_4As^+BPh_4^-$ or extra-thermodynamic assumption for ion transfer at liquid−liquid interfaces (for example, refs 8−10). The assumption[10] $K_{D,BPh4} \approx K_{D,Ph4As}$ is employed here without any limitations. Although we could not determine the $K_1^0(Ph_4AsCl)$ value potentiometrically as described above, it had been reported to be 1/0.079 (= $12._6$) $mol^{-1} \cdot dm^3$ at 25 °C by solvent extraction into $CHCl_3$.[11] The K_1^0 values are in the order NaCl {$K_1^0 \approx \exp(-1.0) = 0.4\ mol^{-1} \cdot dm^3$: calculated for CIP[24]} $<$ $Ph_4AsCl \leq NaBPh_4$. It has been reported that the $K_1^0(LiCl)$ value determined by conductometry is the same magnitude as that calculated from the simulations;[24] hence, we supposed NaCl $<$ Ph_4AsCl as the K_1^0 order. The facts that $\Delta G_h^0(Na^+)$ is slightly smaller than $\Delta G_h^0(Cl^-)$ and both are much smaller than $\Delta G_h^0(BPh_4^-)$ suggest the order $K_1^0(NaCl) < K_1^0(NaBPh_4) \leq K_1^0(Ph_4AsCl)$. These $|z_1z_2|/r$ values were calculated to be $0.165\ Å^{-1}$ for Ph_4AsCl, $0.191\ Å^{-1}$ for $NaBPh_4$, and $0.353\ Å^{-1}$ for NaCl from $r_{Ph4As} = 4.25$ Å (ref 16), $r_{Cl} = 1.81$ Å, $r_{Na} = 1.02$ Å, and $r_{BPh4} = 4.21$ Å. These results suggest that $K_{D,M}$ dominantly contributes to the K_1^0 relation of NaCl $<$ Ph_4AsCl, while K_1^g to that of $Ph_4AsCl \leq NaBPh_4$ (see the next section). Especially, the former should mean the hydrophobic interaction of Ph_4As^+ with water molecules as well as that of BPh_4^-.

Table 2. Logarithmic Component-Equilibrium Constants of Some Electrolytes in the Water/NB Distribution System at 298 K

$MX^{n\pm}$	$\log K_1^0$	$\log K_{D,M}$[a]	$\log K_{D,X}$[b]	$\log K_1^{NB}$[c]	$\log K_{D,MX}$[d]
$NaBPh_4$	1.15_5[e]	−6.0	6.3	1.66_3	0.8
Ph_4AsCl	1.10_0[f]	6.3	−5.2	1.64_5	1.6
NaCl	-0.3_9[g]	−6.0	−5.2	1.77_6	−9.0
$CaCl^+$	1.61_7	-11.799_9	−5.2	2.02_5	−16.6
$LiSO_4^-$	1.01_7[h]	-6.677_5	$< -17.92_0$	1.98_7	< −23.63
$NaSO_4^-$	1.15_5	−6.0	$< -17.92_0$	1.95_0	< −23.1
KSO_4^-	1.02_9[h]	−4.1	$< -17.92_0$	1.90_9	< −21.1
$RbSO_4^-$	1.11_7[h]	−3.4	$< -17.92_0$	1.89_6	< −20.5
$CsSO_4^-$	1.07_9[h]	-2.214_5	$< -17.92_0$	1.88_2	< −19.33

[a] Calculated from the $\Delta\phi_M^{0\prime}$ values for M = Li, Cs. See the text and refs 10 for Na, K, and Rb and 9 and 28 for other M values. [b] Calculated partially from the $\Delta\phi_X^{0\prime}$ values. See the text and refs 8 and 9. [c] Estimated from the Gilkerson equation. See ref 22. [d] Calculated from $\log K_{D,MX} = \log K_{D,M} + \log K_{D,X} + \log K_1^{NB} - \log K_1^0$. [e] Ref 25. [f] Ref 11. [g] Calculated for CIP. See ref 24. [h] Ref 6.

Comparison of $NaBPh_4$ with Ph_4AsCl in Distribution into the NB Phase. For the distribution of $NaBPh_4$ into the NB phase,[10] we have easily obtained $\log K_{D,NaBPh4} = \log K_{D,Na} + \log K_{D,BPh4} + \log K_1^{NB}(NaBPh_4) - \log K_1^0(NaBPh_4)$ from eq 18. When $K_{D,Na}$, $K_{D,BPh4}$, and $K_1^{NB}(NaBPh_4)$ are available, $K_{D,NaBPh4}$ can be immediately calculated from this equation. Into the equation, introducing $\log\{K_1^0(NaBPh_4)/mol^{-1} \cdot dm^3\} = 1.15_5$, $\log K_{D,Na} = -6.0$ (ref 10), $\log K_{D,BPh4} = 6.3$ (ref 10), and $\log\{K_1^{NB}(NaBPh_4)/mol^{-1} \cdot dm^3\} \approx 0.6990 \cdot 0.191 + 1.53 = 1.66_3$, which was computed from the Gilkerson equation,[22] we could obtain $\log K_{D,NaBPh4} \approx 0.8_0$. According to Gilkerson,[22] $K_1^{NB}(NaBPh_4)$ is expressed as $\log K_1^{NB}(NaBPh_4) = 0.6990|z_1z_2|/(r_{Na} + r_{BPh4}) - A$ at 298 K. Here, A is a constant dependent on the NB-ion and -ion pair interactions and was estimated to be -1.53 on average within ± 0.09 from the experimental K_1^{NB} values[27] of $(C_4H_9)_4N^+ClO_4^-$, $(C_4H_9)_4N^+I^-$, and $(C_2H_5)_4N^+ClO_4^-$ at 25 °C and their ionic radii: $r_{(C4H9)4N} = 4.13$ Å, $r_{ClO4} = 2.40$ Å, and $r_{(C2H5)4N} = 3.37$ Å.[16] The equation was also used for the estimation of $\log K_1^{NB}(Ph_4AsCl)$. Similarly, the $\log K_{D,Ph4AsCl}$ value was calculated to be 1.6_4.[10] Table 2 lists the thus-obtained values, with the corresponding ones of NaCl. The component-equilibrium constant (K) order in magnitude is $\log K_{D,Na} < -\log K_{D,NaBPh4}$ (< 0) $< \log K_1^{NB}(NaBPh_4) < \log K_{D,BPh4}$. We can see easily from this order and $\log K_1^0$ that $\log K_{D,BPh4}$ primarily controls the magnitude of $\log K_1^0(NaBPh_4)$; also $\log K_1^{NB}(NaBPh_4)$ secondarily contributes to its magnitude. In other words, these facts mean that the magnitude of $K_1^0(NaBPh_4)$ is controlled by the hydrophobic effect of BPh_4^-. Replacing $K_{D,BPh4}$ by $K_{D,Ph4As}$, the same is true of $K_1^0(Ph_4AsCl)$, while both $\log K_{D,Na}$ and $\log K_{D,Cl}$ control the magnitude of $\log K_1^0(NaCl)$ (see Table 2).

For the water/NB distribution system, we have the equation $\log(K_{D,Na}/K_{D,Cl}) + \log(K_{D,BPh4}/K_{D,Ph4As}) + \log\{K_1^{NB}(NaBPh_4)/K_1^{NB}(Ph_4AsCl)\} - \log(K_{D,NaBPh4}/K_{D,Ph4AsCl}) = \log\{K_1^0(NaBPh_4)/K_1^0(Ph_4AsCl)\} = 0.06 \geq 0$. These component K ratios are in the order $\log(K_{D,Na}/K_{D,Cl})$ (= −0.8) $< \log(K_{D,BPh4}/K_{D,Ph4As})$ (= 0.0) $\leq \log\{K_1^{NB}(NaBPh_4)/K_1^{NB}(Ph_4AsCl)\}$ (≈ +0.02) $< -\log(K_{D,NaBPh4}/K_{D,Ph4AsCl})$ (= +0.8). This finding shows that the $K_{D,NaBPh4}/K_{D,Ph4AsCl}$ value contributes most positively to the $K_1^0(NaBPh_4)/K_1^0(Ph_4AsCl)$ value of all of the ratios. The dependence of $K_1^0(NaBPh_4)/K_1^0(Ph_4AsCl)$ on $K_1^{NB}(NaBPh_4)/K_1^{NB}(Ph_4AsCl)$ also results from the fact that $K_{D,NaBPh4}/K_{D,Ph4AsCl}$ actually cancels out $K_{D,Na}/K_{D,Cl}$. This supports partly the above $|z_1z_2|/r$ discussion on $K_1^0(Ph_4AsCl) \leq K_1^0(NaBPh_4)$. The component K ratios between Ph_4AsCl and NaCl were in the order $-\log(K_{D,Ph4AsCl}/K_{D,NaCl})$ ($= -10.6$) $< \log\{K_1^{NB}(Ph_4AsCl)/K_1^{NB}(NaCl)\}$ (≈ -0.13) $\leq \log(K_{D,Cl}/K_{D,Cl})$ ($= 0.0$) $< \log(K_{D,Ph4As}/K_{D,Na})$ ($= +12.3$). This is consistent with the above $K_{D,M}$ discussion on $K_1^0(NaCl) < K_1^0(Ph_4AsCl)$, namely, $K_1^0(Ph_4AsCl)/K_1^0(NaCl) \gg 1$.

Taking the deviation ($\pm$ 0.09) of the estimated A value into account, the logarithmic ratio, $\log\{K_1^{NB}(NaBPh_4)/K_1^{NB}(Ph_4AsCl)\}$ ($= 0.01_8$) within $\pm$ 0.13, is actually in accord with that $\{= 0.6990(0.137 - 0.134) = 0.00_2\}$ computed from hydrated radii in the NB phase, $r_{Cl} = 3.22$ Å and $r_{Na} = 3.07$ Å, estimated by Osakai et al.[28] This finding indicates that the K_1^{NB} values of these salts are less sensitive to the hydration of Na^+ and Cl^- in the NB phase under the assumption that the A value for the NB phase equals that for the water-saturated NB one.

Comparison of $NaSO_4^-$ with $CaCl^+$ in Distribution into the NB Phase. Next we compared the distribution behavior of $CaCl^+$ with that of $NaSO_4^-$ between the NB and water phases, because the $K_{D,Ca}$ value had been available. From eq 18, $\log(K_{D,NaSO4}/K_{D,CaCl})$ is expressed as $\log(K_{D,Na}/K_{D,Cl}) + \log(K_{D,SO4}/K_{D,Ca}) + \log\{K_1^{NB}(NaSO_4^-)/K_1^{NB}(CaCl^+)\} - \log\{K_1^0(NaSO_4^-)/K_1^0(CaCl^+)\}$. Since $\log(K_{D,SO4}/K_{D,Ca}) = \log_{10}[\exp(-(z_{SO4}F/RT)\Delta\phi_{SO4}^{0\prime}) \exp((z_{Ca}F/RT)\Delta\phi_{Ca}^{0\prime})] = (2(\Delta\phi_{SO4}^{0\prime} + \Delta\phi_{Ca}^{0\prime})/0.05916) < -6.11_8$ (ref 29) with $\Delta\phi_{Ca}^{0\prime} = 0.349$ V (ref 8) and $\Delta\phi_{SO4}^{0\prime} < -0.53$ (ref 8) versus TPh(As/B)E at 25 °C, $\log\{K_1^{NB}(NaSO_4^-)/K_1^{NB}(CaCl^+)\} \approx 0.6990(0.602 - 0.712) = -0.077$, and $\log\{K_1^0(NaSO_4^-)/K_1^0(CaCl^+)\} = -0.46_2$, the relation between $K_{D,NaSO4}$ and $K_{D,CaCl}$ became $\log(K_{D,NaSO4}/K_{D,CaCl}) < -6.5_3$. Here, $\Delta\phi_j^{0\prime}$ versus TPh(As/B)E, z_{Ca}, and z_{SO4} denote the ion-transfer formal potentials of j (denotes Ca^{2+}, SO_4^{2-}) between the water/NB interface standardized by the $Ph_4As^+BPh_4^-$ assumption, a formal charge of Ca^{2+}, and that of SO_4^{2-} with signs, respectively. This result indicates that $K_{D,NaSO4} \ll K_{D,CaCl}$ for the water/NB distribution system, namely, the interaction of $NaSO_4^-$ with NB (or water) molecules must be much weaker (or stronger) than that of $CaCl^+$. When we tentatively regard $K_{D,SO4}/K_{D,Ca}$ as $7.6 \cdot 10^{-7}$, namely, $\Delta\phi_{SO4}^{0\prime}$ as -0.53 V, an order of the component K ratios becomes $\log(K_{D,SO4}/K_{D,Ca})$ (≈ -6.12) $< \log(K_{D,Na}/K_{D,Cl})$ ($= -0.8$) $< \log\{K_1^{NB}(NaSO_4^-)/K_1^{NB}(CaCl^+)\}$ (≈ -0.08) $< -\log(K_{D,NaSO4}/K_{D,CaCl})$ ($= +6.5$). Therefore, the relation $K_1^0(NaSO_4^-) < K_1^0(CaCl^+)$ is explained mainly in terms of a difference between $K_{D,Ca}$ and $K_{D,SO4}$. This does not necessarily correspond with the above K_1^g discussion on $K_1^0(NaSO_4^-) < K_1^0(CdI^+)$. However, although the pairing ions to react with Cd^{2+}, Ca^{2+}, or SO_4^{2-} are different, these results suggest that the reactivities of Cd^{2+} and Ca^{2+} are superior to that of SO_4^{2-} in water. This suggestion is supported by the fact of $K_1^0(LiSO_4^-) < K_1^0(CdI^+)$ (see Tables 1 and 2), because calculated r values are in the order $LiSO_4^- < CdI^+ < NaSO_4^-$.

Assuming that the A value can apply to the water/NB distribution systems with MX^- and MX^+ and $\Delta\phi^{0\prime}_{SO4} \approx -0.53$ V, we can immediately obtain the $K_{D,CaCl}$ and $K_{D,NaSO4}$ values from the procedure described above, that is, $\log K_{D,CaCl} = \log K_{D,Ca} + \log K_{D,Cl} + \log K_1^{NB}(CaCl^+) - \log K_1^0(CaCl^+) \approx -16.6$ and also $\log K_{D,NaSO4} \approx -23.1$ at 298 K. These values are summarized together with logarithmic component K ones in Table 2. The component K order for $CaCl^+$ was $\log K_{D,Ca} < \log K_{D,Cl}$ (< 0) $< \log K_1^{NB} < -\log K_{D,CaCl}$. This result indicates that the $K_{D,CaCl}$ value mainly controls the magnitude of $K_1^0(CaCl^+)$. Consequently, the weaker (or stronger) interaction of $CaCl^+$ with NB (or water) molecules rather than the interaction of Ca^{2+} or Cl^- seems to enhance their ion-pair formation in water. The same is true of $NaSO_4^-$.

Distribution of MSO_4^- into the NB Phase. Similarly, we calculated the $\log K_{D,MSO4}$ values for the other MSO_4^- systems with M = Li, K, Rb, and Cs. As an example, using the equation $\log K_1^0(LiSO_4^-) = \log K_{D,Li} + \log K_{D,SO4} + \log K_1^{NB} - \log K_{D,LiSO4}$, we obtained $\log K_{D,LiSO4} \approx -23.6$. Other logarithmic values are listed in Table 2. We estimated here the $K_{D,Li}$ $\{= \exp(-\Delta\phi_{Li}^{0\prime}/0.02569)\}$ and $K_{D,Cs}$ values from $\Delta\phi_{Li}^{0\prime} = 0.395$ V versus TPh(As/B)E at 25 °C (ref 28) and $\Delta\phi_{Cs}^{0\prime} = 0.131$ (ref 9), respectively, and the K_1^{NB} values from $|z_1z_2|/r = 0.654$ Å^{-1} for $LiSO_4^-$, 0.543 Å^{-1} for KSO_4^-, 0.524 Å^{-1} for $RbSO_4^-$, and 0.504 Å^{-1} for $CsSO_4^-$ using the Gilkerson equation.[16,22,23] The $\log K_{D,MSO4}$ values were much smaller than those of $\log K_{D,M}$ and $\log K_{D,SO4}$. Now, we cannot explain why the interaction of NB molecules with MSO_4^- becomes much weaker than that with M^+ or SO_4^{2-}, taking account of the generally accepted idea that the interaction of water molecules with MSO_4^- becomes weaker than that with M^+ or SO_4^{2-}. However, this fact of $K_{D,LiSO4} \ll K_{D,SO4}$ can give the reason that the cyclic voltammogram of $LiSO_4^-$ is not observed on the ion transfer at the water/NB interface.[8] Considering $K_{D,CaCl} \ll K_{D,Ca}$, the same is also true of the ion transfer of $CaCl^+$ at the interface.[29]

The $\log K_{D,MSO4}$ values were in the order M = Li ≤ Na < K < Rb < Cs, fairly reflecting the $\log K_{D,M}$ order in the water/NB distribution system (Table 2): $\log K_{D,MSO4} = 0.9_7 \log K_{D,M} - 17.1_9$ at $R = 0.9_9$. The value at $\log K_{D,M} = 0$ in this equation is going to deviate from -17.2 to the lower value, because of less precision of $\Delta\phi_{SO4}^{0\prime}$. A similar relation has been reported for the distribution of $R_4N^+X^-$ into CH_2Cl_2 at X^- = picrate ion.[21] These relations may hold also for a plot of $\log K_{D,NaX}$ versus $\log K_{D,X}$. Comparing the equation with the logarithmic form of eq 18, the finding indicates that $\log K_{D,MSO4} = \log K_{D,M} + \log K_{D,SO4} + \log\{K_1^{NB}/K_1^0(MSO_4^-)\} \approx \log K_{D,M} + \log K_{D,SO4}$ in the distribution system. In other words, this fact suggests that the solvation effects around MSO_4^- reflect essentially the solvation effects of M^+.

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