Selective Hydration of a Carboxylate Group in Nitrobenzene

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Eight different carboxylate ions were extracted with Crystal Violet into nitrobenzene. The Karl Fischer method was employed to determine the numbers of water molecules co-extracted with the carboxylate ions, i.e., their hydration numbers (n_h) in nitrobenzene. The values of n_h for the carboxylate ions were little dependent on their chemical structures, being 2.4 ± 0.2 as the average value.

It is well known that water molecules are co-extracted into water-immiscible organic solvents with hydrophilic ions such as Li^+, Na^+, Ca^{2+}, and Cl^-.[1–9] Even water-immiscible organic solvents such as nitrobenzene (NB) usually dissolve a considerable amount of water (e.g., 0.168 M H_2O in NB;[9] 1 M = 1 mol dm^{-3}). Accordingly, such phenomena can be elucidated in terms of selective hydration of ions in mixed solvents.[10,11] This is a key concept intimately related to important ion-transfer processes not only in analytical systems (e.g., solvent extraction, membrane transport, ion-selective electrodes) but also in biological systems (lipid membrane, ion channels, etc.). In recent years the co-transport of water by ions has been dealt with in molecular dynamics simulations.[12–14]

Previous studies on the co-extraction of water by ions have been confined mainly to inorganic ions. In our latest paper,[15] however, it has been shown that primary to tertiary ammonium ions with Me, Et, and *n*-Bu groups co-extract some water molecules in the NB–water (W) system. The number of water molecules co-extracted into NB with an ion, i.e., the hydration number (n_h) in NB, has been found to be little affected by the alkyl chain length, but very dependent on the class of the ammonium ion: n_h = 1.64, 1.04, 0.66, and 0.00, respectively, for the primary, secondary, tertiary, and quaternary ammonium ions. In this study, measurements have been extended to carboxylate ions (RCO_2^-) in order to obtain insight into the biologically significant compounds such as amino acids.

Eight different carboxylate ions (RCO_2^-; R = (**1**) Ph, (**2**) *o*-, (**3**) *m*-, (**4**) *p*-Tol, (**5**) Ph_2CH, (**6**) *cyc*-$(C_6H_{11})CH_2$, (**7**) *n*-C_5H_{11}, and (**8**) *n*-C_7H_{15}) were extracted from W to NB with a cationic dye, Crystal Violet (tris(4-dimethylaminophenyl)methyl chloride). The sodium salts[16] of the carboxylates and Crystal Violet[17] were initially added, respectively, to the W and NB phases (volume ratio 1:1) at the same concentration in the range of 5–20 mM. Because Crystal Violet cation (CV^+) is very hydrophobic, it can draw RCO_2^- to NB by releasing Cl^- into W. In a similar manner as previously,[9,15] the equilibrium concentration of water in the NB phase was determined at 25 °C by means of a Karl Fischer coulometer (Kishida Chemicals CA-20).

Spectrophotometric determination[18] of CV^+ in the W phase showed that CV^+ almost completely remained in the NB phase. Potentiometric titration with a standard silver nitrate solution showed that a part (0.7–18%) of Cl^- initially added to the NB phase remained unexchanged with RCO_2^- in the W phase. The equilibrium concentration of RCO_2^- in NB was evaluated from its initial concentration and the concentration of Cl^- remaining in NB. Such distribution behavior of the ions in the NB–W system could be elucidated by using the proposed theory,[19] in which the standard ion-transfer potential ($\Delta_o^w\phi°$) is used as a measure of extractability of an individual ion. The literature values of $\Delta_o^w\phi°$ for the carboxylate ions[20] (except **5** and **6**), CV^+,[21] Cl^-,[22] and Na^+ [22] were successfully employed for theoretical prediction of distribution ratios of the ions. It can be thus concluded that in the present system, the ions are distributed as individual ions without forming ion-pairs.

In order to know the water extractability of CV^+, a distribution experiment was performed in advance with no addition of carboxylate ions. The results showed that 3.8 moles of water molecules were extracted with 1 mole of CV^+Cl^-, but all the water molecules should be allocated to Cl^- that is known to convey 4 water molecules.[9] Therefore, it can be assumed that CV^+ transports no water molecules to NB.

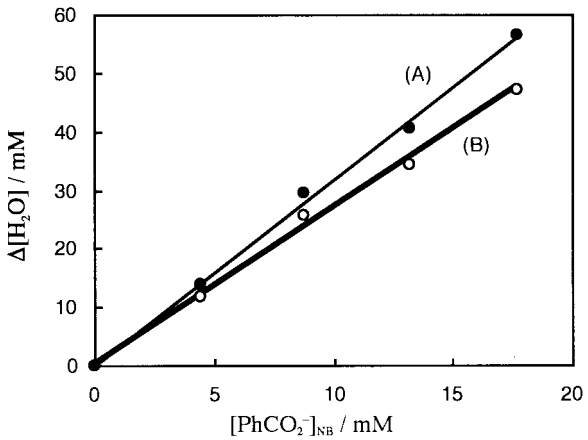

Figure 1. (A) Plots of the increase in water concentration in NB ($\Delta[H_2O]$) with extraction of carboxylate ion **1** with CV^+ against the equilibrium concentration of the carboxylate ion in NB. (B) Plots corrected for the contribution of Cl^- to $\Delta[H_2O]$. When $[PhCO_2^-]_{NB}$ = 0 mM, $[H_2O]$ was 185 mM in NB.

In Figure 1, the plots (A) shows a linear dependence of the increase in water concentration in NB ($\Delta[H_2O]$) on the equilibirium concentration of benzoate ion (**1**) in NB. However, since a part of Cl^- remained in NB as described above, its contribution to $\Delta[H_2O]$ should be evaluated to obtain the correct n_h-value for the carboxylate ion. Using the value of n_h (= 4.0) for Cl^-,[9] the value of $\Delta[H_2O]$ was corrected to obtain the plots (B). From the slope of the linear regression line, the n_h-value for **1** was evaluated to be 2.7 ± 0.2. Similar linear plots were obtained for other carboxylate ions, and their n_h-values thus determined are shown in Table 1.

Table 1. Hydration numbers of carboxylate ions (RCO_2^-) in NB at 25 °C

Entry	R	n_h
1	Ph	2.7 ± 0.2
2	*o*-Tol	2.4 ± 0.2
3	*m*-Tol	2.4 ± 0.2
4	*p*-Tol	2.5 ± 0.2
5	Ph_2CH	2.1 ± 0.4
6	*cyc*-$(C_6H_{11})CH_2$	2.4 ± 0.2
7	*n*-C_5H_{11}	2.5 ± 0.4
8	*n*-C_7H_{15}	2.3 ± 0.3

As seen in Table 1, the n_h-values for the carboxylate ions examined are little dependent on their chemical structures. There is no noticeable difference in n_h between the aromatic and aliphatic groups. Thus, it has been found that a carboxylate ($–CO_2^-$) group is selectively hydrated by 2.4 ± 0.2 water molecules in NB. The reason why this hydration number is not an integer is because it is always given as an averaged value over several species with different hydration numbers.[8,11]

The above hydration number determined for $–CO_2^-$ is larger than that observed for an amino group ($–NH_3^+$), i.e., n_h = 1.64 in NB.[15] As is well known generally, the larger water-holding capacity of $–CO_2^-$ has been confirmed in this study as well. It is expected that an amino acid having both $–CO_2^-$ and $–NH_3^+$ in its structure hold at least 4 water molecules in NB.

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16 The sodium salts of **1** and **8** were purchased from Wako Pure Chemical Industries, Ltd. and dried at 50 °C before use. The other sodium salts were prepared as follows: ethanol solutions of the acid types of **2**–**5**, **7** (Wako) and **6** (Aldrich) were mixed with an equimolar aqueous solution of sodium hydroxide, followed by concentration to one-fourth. An addition of acetone upon cooling induced crystallization of the sodium salts, which were then recrystallized from a small amount of hot water.
17 Purchased from Wako, and dried at 80 °C under reduced pressure.
18 The absorption coefficient of CV^+ in water is 9.745×10^4 at 589 nm.
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