Metathesis Reaction between Hydroxo(tetraphenylporphinato)indium and Tetraphenylborate by Two-phase Reaction: Implication to Liquid Membrane Anion Selective Electrode

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The two-phase reaction of [In(OH)(tpp)] (tpp^{2-}: tetraphenylporphine) with sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB) gave ion-pairs of a cationic dimer, [In_2(OH)$(tpp)_2$]TFPB, and a cationic monomer, [In(tpp)]TFPB. In contrast, a stoichiometric metathesis was observed by the two-phase reaction with sodium tetraphenylborate (NaTPB) giving [In(Ph)(tpp)] and $PhB(OH)_2$.

In preparation of liquid membrane anion-selective electrodes using charged carriers, addition of a lipophilic anion to the membrane reduces the response induced by the purely electrostatic interaction, while highlighting some other interactions like hydrogen-bonding and Lewis acid–base reactions.[1] The effects of such ionic additives on the performances of ion-selective electrodes were discussed in detail.[2,3] With some metal–porphyrin complexes as the carrier, however, the addition induced an unexpectedly large potential response or super-Nernstian response. Recently, the super-Nernstian response of a gallium complex to fluoride or an indium complex to chloride was successfully explained by the spontaneous formation of a cationic dimer in the presence of a lipophilic counter anion in the membrane phase and its cleavage by a sample anion.[4] The cationic dimers of gallium and indium have been isolated and structurally characterized.[5] The same phenomena have been reported in other metal–porphyrin complexes.[6–10] The spectral characteristics of the dimers were appreciably different from the monomeric species and were effectively utilized for optical sensing of anions.[11,12] These have been reviewed and fully discussed.[13]

Commonly used as anionic additives are the derivatives of sodium tetraphenylborate (NaTPB), such as sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB) and potassium tetrakis(*p*-chlorophenyl)borate (KTCPB).[1] Especially, NaTFPB having high chemical stability and lipophilicity[14,15] has almost exclusively been used for porphyrin complexes.[9] In this paper, we have examined the two-phase reactions of [In(OH)(tpp)] (tpp^{2-}: tetraphenylporphine) complex with several lipophilic anions as the model for their interactions in the membrane phase of anion selective electrodes and have found completely different reaction patterns including an unusual metathesis reaction.

Examination of UV–vis spectra for a series of chlorobenzene solutions of [In(OH)(tpp)] in a concentration range of 2×10^{-5}–2×10^{-4} mol dm^{-3} indicated no intermolecular interactions as found for [Zr$(OH)_2$(tpp)].[9,16,17] A portion of 2.5×10^{-5} mol dm^{-3} chlorobenzene solution of [In(OH)(tpp)] was equilibrated with a series of aqueous solutions containing lipophilic anions (NaTFPB, NaTPB, and sodium dodecyl sulfate (NaDS)) at various concentrations and at pH 6.0 buffered by

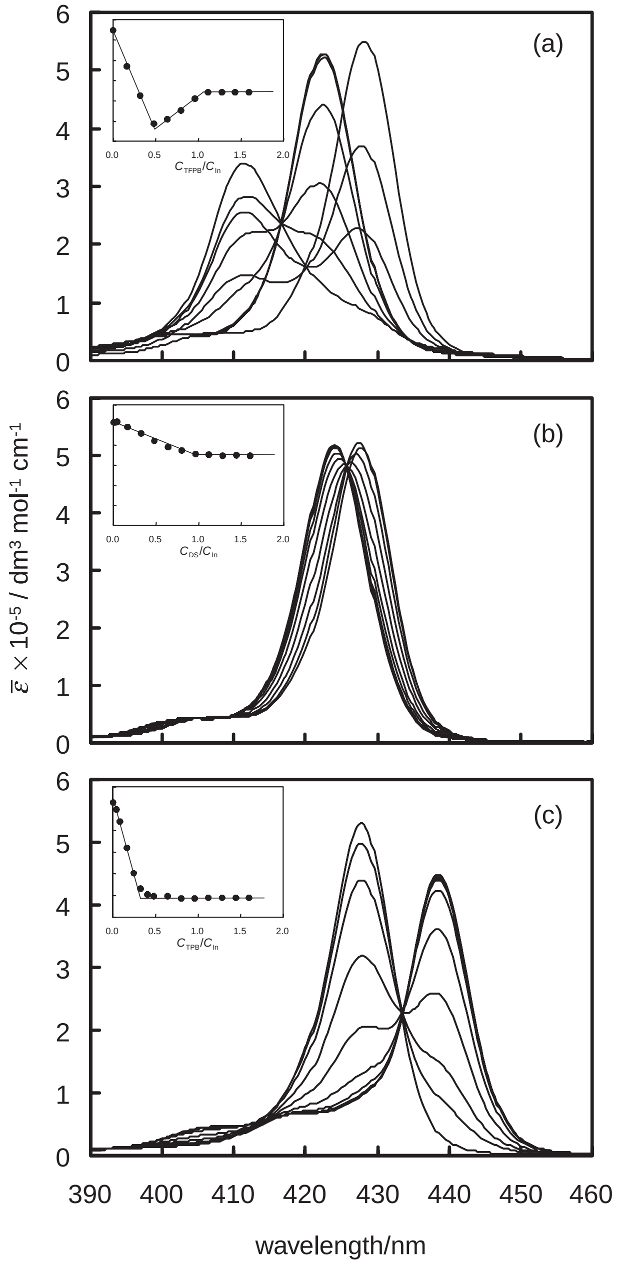

Figure 1. UV–vis spectral changes by two-phase reactions of [In(OH)(tpp)] with NaTFPB (a), NaDS (b), and NaTPB (c) and a molar ratio plot at 428 nm. Organic phase: chlorobenzene containing 2.5×10^{-5} mol dm^{-3} [In(OH)(tpp)]; aqueous phase: 0–4×10^{-5} mol dm^{-3} lipophilic anion and MES buffer at pH 6.0.

10^{-3} mol dm^{-3} 4-morpholinoethanesulfonate solution. Changes of absorption spectra are shown in Figure 1, where the apparent molar absorption coefficients at 428 nm are plotted against the molar ratio of the lipophilic anion to indium in insertion.

In the reaction with NaTFPB (Figure 1a), a Soret band of [In(OH)(tpp)] at 428 nm was shifted to a shorter wavelength of 411.5 nm up to the molar ratio of 0.5 and then to a longer wavelength of 422.5 nm up to the molar ratio of 1.0. The first reaction is assigned to the formation of a cationic dimer, based on the reaction stoichiometry and on the resemblance to the spectral shift (from 406 to 387 nm) induced by the formation of $[\mathrm{In_2(OH)(oep)_2}]$TFPB ($\mathrm{oep}^{2-}$: octaethylporphine) from [InCl(oep)].[4–6,11–13]

$$2[\mathrm{In(OH)(tpp)}]_\mathrm{o} + \mathrm{NaTFPB} = ([\mathrm{In_2(OH)(tpp)_2}]\mathrm{TFPB})_\mathrm{o} + \mathrm{NaOH} \tag{1}$$

The hydroxide expelled from the organic phase was accommodated in the aqueous buffer. In contrast, the product of the second reaction is assigned to the 1:1 ion-pair of [In(tpp)]TFPB.

$$([\mathrm{In_2(OH)(tpp)_2}]\mathrm{TFPB})_\mathrm{o} + \mathrm{NaTFPB} = 2([\mathrm{In(tpp)TFPB}])_\mathrm{o} + \mathrm{NaOH} \tag{2}$$

In the reaction with NaDS (Figure 1b), a Soret band was shifted only slightly to a shorter wavelength of 424 nm up to the molar ratio of 1.0. The reaction stoichiometry indicates formation of the 1:1 ion-pair.

$$[\mathrm{In(OH)(tpp)}]_\mathrm{o} + \mathrm{NaDS} = ([\mathrm{In(tpp)}]\mathrm{DS})_\mathrm{o} + \mathrm{NaOH} \tag{3}$$

The absence of a cationic dimer is not clearly reasoned at this stage but may be related to the less lipophilicity of DS^- than that of TFPB^-. The less spectral shift of [In(tpp)]DS from [In(OH)(tpp)] than [In(tpp)]TFPB suggests a stronger interaction of $[\mathrm{In(tpp)}]^+$ with DS^- than with TFPB^-.

In contrast to these systems, the reaction with NaTPB showed a shift of a Soret band to a longer wavelength of 438.5 nm up to the molar ratio of 0.33 (Figure 1c). Unlike the reaction with NaTFPB, further addition of NaTPB or the reaction in more acidic media caused no changes. Based on the comparison of the spectrum with those in literature, the product has been identified as [In(Ph)(tpp)] ($\lambda_\mathrm{max} = 439$ nm, $\mathrm{CHCl_3}$).[18,19] By taking the reaction stoichiometry, the following metathesis is expected:

$$3[\mathrm{In(OH)(tpp)}] + \mathrm{NaB(Ph)_4} = 3[\mathrm{In(Ph)(tpp)}] + \mathrm{PhB(OH)_2} + \mathrm{NaOH} \tag{4}$$

This reaction is confirmed by two more evidences. First, the same reaction was observed in chloroform; the aqueous phase showed a series of absorption maxima at 260.5, 265, and 271.5 nm characteristic of phenylboronic acid; tetraphenylborate had no peak in this region.[20] Second, ^{1}H NMR spectral characteristics of the product containing porphyrin [(300 MHz, $\mathrm{CDCl_3}$, δ) 8.99 (s, pyrrole), 8.14 (s, *m*-ph(py)), 7.77 (br, *o*-, *p*-ph(py)), 6.03 (t, *p*-ph), 5.72 (t, *m*-ph), 2.98 (d, *o*-ph)] agreed well with those of [In(Ph)(tpp)] in literature.[18,20]

The reaction with KTCPB is more complicated. Both 1:1 ion-pair formation and metathesis reactions were observed, but neither of these reactions proceeded quantitatively at any molar ratios.[20] When these salts of lipophilic anions were directly added to a solution of [In(OH)(tpp)] in chlorobenzene saturated with water, the same products were obtained immediately. Sodium hydroxide, phenylboronic acid, or sodium phenylborate is expected to precipitate or to dissolve into water saturated in chlorobenzene.

From the viewpoint of sensor development, we suggest the possibility of undesirable reactions of NaTPB as ionic additives with metal porphyrin complexes. In this respect, NaDS that causes neither ion-pair formation nor metathesis is a promising additive, although the lipophilicity is not so high. From the viewpoint of organic chemistry, such stoichiometric M–C bond formation under mild conditions has not been found in literature by our survey.[21] Further studies on the essential factors of this reaction are in progress in our institute.

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