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Selective Transport of Pb(II) Ion by Acyclic Polyethers Bearing Amide End-Groups

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A series of acyclic polyethers bearing amide end-groups and lipophilic alkyl chains (**3-5**) were successfully synthesized with quantitative yields. Based upon the transport experiment in a bulk liquid membrane (BLM) system and solvent extraction, a very high selectivity of Pb^{2+} over other transition metal cations was observed. Measurement of thermodynamic parameters for complexation in methanol at 25 °C gave a strong evidence for excellent selective complexation for lead ion over other transition metal ions.

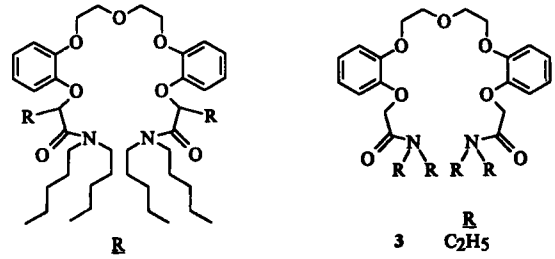
Introduction

Acyclic polyethers has been considerably studied due to an excellent complexation behavior although they do not have the pre-organized form to adopt metal ions as do cyclic polyethers.[1-4] So, selective transport of metal cations using acyclic polyethers has long been studied in viewpoints of selective separation, recovery, volume reduction, and selective instrumental sensor applied in most industrial field.[5-7] Especially, selective separation of heavy metal ion such as lead ion from the industrial waste has been remarkably focused.[8,9] We have reported that acyclic polyether **1** in ion selective electrode (ISE) system shows an excellent selectivity of Pb^{2+} over Cu^{2+}.[10] Also, we reported that when dipentyl chains are fixed in nitrogen atom of amide group, increase of lipophilicity e.g. two lipophilic $C_{14}H_{29}$ side chains were attached on α-carbon of carbonyl group (compound **2** in Figure 1) shows decreasing selectivity of Pb^{2+} over Cu^{2+}.[10] However, the thermodynamic parameters such as changes of equilibrium constants, enthalpy changes, and entropy changes of those acyclic polyethers diamide have been not determined so far. Therefore, herein we report the results for the selective transport of Pb^{2+} in bulk liquid membrane and in solvent extraction using organic carrier **3-5** where the hydrogen atom is fixed on the α-carbon of carbonyl group and the alkyl chain length varies from ethyl to propyl to butyl to study an influence of alkyl chain on amide end-group on metal ion complexation. We also report the results for the determination of thermodynamic parameter for the ligand-metal ion complexation by the use of calorimetric titration method.

Experimental

Chemical Analysis

IR spectra were obtained with a Perkin-Elmer 1600 Series FT-IR on potassium bromide pellet and are recorded in wave number. ^{1}H NMR spectra were recorded with an AF-300 spectrometer with the chemical shifts (δ) reported down-



	R
1	H
2	$C_{14}H_{29}$

	R
3	C_2H_5
4	C_3H_7
5	C_4H_9

Figure 1.

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field from the internal standard, tetramethylsilane. Elemental analysis was performed by Vario EL Elemental Analyzer in Korea Basic Science Institute in Seoul, Korea. The concentration of metal ions were determined by AAS, Model Perkin-Elmer 2380.

Chemicals

Unless specified otherwise, reagent grade reactants and solvents were obtained from chemical suppliers and used as received. Dry solvents were prepared as follows: benzene and pentane were stored over sodium ribbon; dichloromethane was freshly distilled from lithium aluminum hydride. 1,5-Bis[2-(carboxymethyloxy)phenoxy]-3-oxapentane (**6**)[11] is known compound. Deionized water was prepared by passing distilled water through an Organo G-10 cartridge.

Syntheses

1,5-Bis[2-(2'-*N*,*N*-diethylacetamidooxy)phenoxy]-3-oxapentane (3). Under nitrogen, a solution of 1,5-bis [2-(carboxymethyloxy)phenoxy]-3-oxapentane (**6**) (2.00 g, 4.90 mmol), oxalyl chloride (4.27 mL, 49.0 mmol), and 1 drop of pyridine in 100 mL of dry benzene was refluxed for 10 h. The solvent and excess oxalyl chloride were removed *in vacuo*. To this crude product was added 50 mL of dichloromethane and 50 mL of water. Organic layer was separated, washed with 1 N HCl solution (2×50 mL), and dried over $MgSO_4$. Removal of the solvent *in vacuo* gave a desired product 1,5-bis[2-(chloroacetyloxy)phenoxy]-3-oxapentane in quantitative yield as a yellowish oil. With spectroscopic evidences for the structural identification the obtained product was used without further purification. Under nitrogen, to a turbid solution of 1,5-bis[2-(chloroacetyloxy) phenoxy]-3-oxapentane (2.17 g, 4.90 mmol) and triethylamine (1.53 mL, 11.3 mmol) in 50 mL of dry benzene was added dropwise diethylamine (1.19 mL, 11.3 mmol) during a period of 30 min at 0 °C. Upon the complete addition, the reaction mixture was stirred for additional 3 hr at room temperature. Water (100 mL) was poured and organic layer was separated. Drying the benzene layer over $MgSO_4$ followed by filtration column chromatography of the residue on silica gel with ethyl acetate provided 1.77 g (88%) of desired product **3** as a colorless oil. IR (neat): 1651 (C=O), 1497, 1450, 1230, 1061, 1120 (C-O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.10-1.35 (2 t, 12H), 3.43 (q, 8H), 3.90-3.97 (m, 4H), 4.15-4.23 (m, 4H), 4.69 (s, 4H), 6.92 (s, 8H). Anal. calculated for $C_{26}H_{40}N_2O_7 0.5CH_2Cl_2$: C, 59.49; H, 7.67. Found: C, 59.31; H, 7.66.

1,5-Bis[2-(2'-*N*,*N*-dipropylcarbamidopentadecyloxy)phenoxy]-3-oxapentane (4). Synthetic procedures are same as that for compound **3**. Colorless oil was obtained in 89% yield. IR (neat): 1650 (C=O), 1495, 1450, 1061, 1120 (C-O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.25 (t, 8H), 3.88-4.20 (m, 4H), 4.15-4.25 (m, 4H), 4.71 (s, 4H), 6.91 (s, 8H). Anal. calculated for $C_{30}H_{48}N_2O_7$: C, 67.10; H, 8.45. Found: C, 67.19; H, 8.44.

1,5-Bis[2-(2'-*N*,*N*-dibutylcarbamidopentadecyloxy)phenoxy]-3-oxapentane (5). Synthetic procedures are same as that for compound **3**. Colorless oil was obtained in 90% yield. IR (neat): 1650 (C=O), 1497, 1453, 1211, 1257, 1060, 1118 (C-O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.79-1.10 (2 t, 12H), 1.11-1.80 (m, 32H), 3.22 (t, 8H), 3.88-3.97 (m, 4H), 4.15-4.23 (m, 4H), 4.70 (s, 4H), 6.92 (s, 8H). Anal. calculated for $C_{36}H_{56}N_2O_7$: C, 68.76; H, 8.98. Found: C, 68.61; H, 8.74.

Two Phase Extraction

Competitive solvent extraction was used as reported by Bartsch group.[12] This method has been known for special advantages in that usage of an only trace amount of organic ligand as well as easy and fast measurement. Each of 700 μL of 0.125 M solution containing transition metal ions were mixed together. Deionized water was added for total aqueous volume to be 2 mL. To centrifuge tube this aqueous solution and 2 mL of 0.01 M solution of organic carrier in chloroform were added. After centrifuging for 5 min, 1.0 mL of organic layer was taken and stripped with 1.0 mL of 0.1 N HCl solution. The concentration of metal ion in aqueous phase was determined by atomic absorption spectrometer.

Bulk Liquid Membrane

Membrane transport experiments were carried out using a bulk liquid membrane cell based on the concept of the Schulman bridge at 25 °C.[13,14] The bottom half of the cell was filled with 3.0 mL of 0.001 M solution of the organic ligand in chloroform and a glass tube is inserted. The interior of the tube above the organic media is filled with a 0.8 mL of 0.1 M metal ion solution as a source phase. The outer cylinder is filled with 5.0 mL of deionized water as a receiving phase. The details of the transport conditions are summarized in the footnotes of Table 2. The receiving phase was sampled after 24 hours stirring with 120 rpm at 25 °C and analyzed for cation concentration using an atomic absorption spectrometer.

Calorimetric Titration

Solution calorimeter (Model TRONAC 1250) used in this study composes of water bath, Dewar flask, auto-titration burette system, temperature measurement device, and cooling system. Methanol (Fisher HPLC grade) was used as a solvent. To precisely correct a reaction heat for the complex formation of a ligand with metal ion, heat of dilution was firstly measured. 1 mM of organic carrier dissolved in methanol was prepared. Nitrate salt (Aldrich) dissolved in methanol was used for metal ion solution. The addition of titrant to titrate solution produces one or more reactions where the extent of the reactions and the energy produced are related to the corresponding equilibrium constants and enthalpy changes for the reactions. Using Gibbs-Helmholtz equation, enthalpy change and stability constant, and entropy change is determined as follows,[15]

$$Q_c = \sum_{i=1}^{n} \Delta H_i \Delta n_i \tag{1}$$

$$U(K_i, \Delta H_i) = \sum_{p=1}^{m} (Q_{c,p} - \sum_{i=1}^{n} (\Delta n_{i,p} \Delta H_i))^2 \tag{2}$$

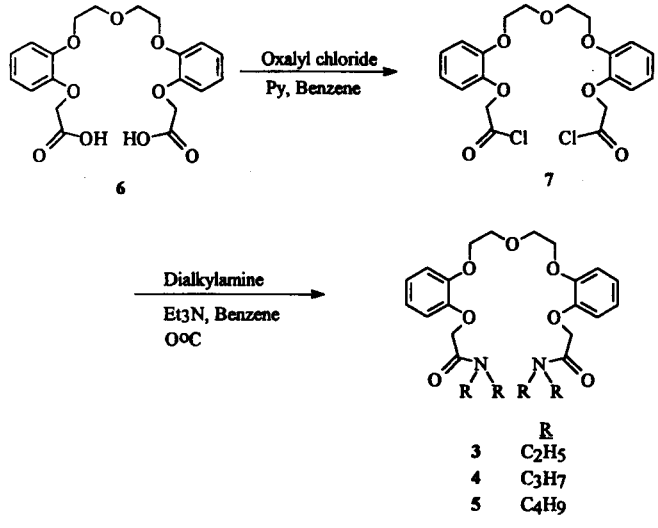
where Q_c is denoted as heat of reaction from the reaction of titrant and titrate, ΔH_i is an enthalpy change of complex formed, Δn_i is the change in moles of product, and K_i is for equilibrium constant.

Results and Discussion

Synthesis of Acyclic Polyether Diamides. Synthetic routes for the preparation of acyclic polyether diamides are described in Scheme 1. Previously we developed and reported synthetic procedures from dicarboxylic acid to diamide.[10] Chlorination of dicarboxylic acid **6** with oxalyl chloride in the presence of catalytic amount of pyridine provides 1,5-bis[2-(chloroacetyloxy)phenoxy]-3-oxapentane (**7**) with a quantitative yield as a yellowish oil. The corresponding acid chloride was used in next reaction step without any further purification. Subsequently, reaction of corresponding acid chloride with diethylamine and triethylamine as a base in benzene gave the compound **3** as a colorless oil. When the triethylamine was added, the reaction mixture immediately changed from transparent solution to turbid one. After the diethylamine was added dropwise, stirring the mixture for 1 hr at room temperature gave a transparent brown solution which indicates the reaction finished. Structural analogues such as compound **4** and **5** were prepared by the same method used in preparing compound **3**.

Complexation Studies. Solvent extraction as shown in Figure 2 indicates that the acyclic polyether amides **3-5** behave as an excellent organic carrier for Pb^{2+} over other transition metal ions. Interestingly, the detected amount of stripped Pb^{2+} from the organic phase was gradually decreased as the length of alkyl side chain on amide end-group is increased from ethyl (**3**) to propyl (**4**) to butyl (**5**) group. The shorter the alkyl chain attached on amide end-group, the better is the extraction ability for Pb^{2+}. This is probably ascribed to a steric disfavor of the large alkyl group when it forms pseudocyclic array with Pb^{2+}. In competitive solvent extraction as shown in Table 1, acyclic polyether diamides also behave as a selective lead ion carrier. Compared with other organic ligands compound **3** where diethyl group is substituted on amide end-group increase the selectivity and efficiency for Pb^{2+}.

To further study an influence of alkyl chain on the amide end-group considering transport amount from source phase to receiving phase by an organic medium, we used a bulk liquid membrane system.[11] The results are described in Table



Scheme 1. Synthetic routes for acyclic polyether diamide **3-5**.

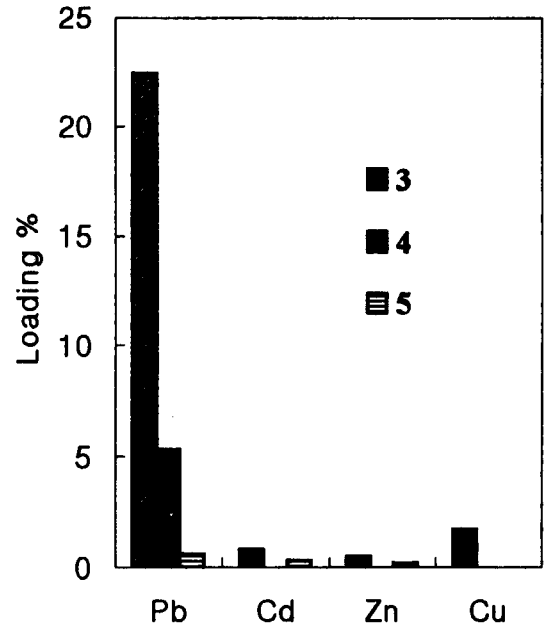


Figure 2. Loading percentage of transition metal ions in organic medium in solvent extraction.[a] [a]Loading percentage=concentration of extracted metal ion/concentration of organic ligand (0.001 M). Co^{2+}, Ni^{2+}, and Mn^{2+} were not extracted.

Table 1. Molar concentration of transition metal ions in chloroform phase for competitive extraction using acyclic polyether diamide **3-5**

Compound	Molar concentration ($\times 10^{-4}$ M)						
	Pb^{2+}	Zn^{2+}	Cd^{2+}	Cu^{2+}	Co^{2+}	Ni^{2+}	Mn^{2+}
3	2.24	0.05	0.08	0.17	0	0	0
4	0.53	0	0	0	0	0.05	0
5	0.06	0.02	0.03	0	0	0	0

Table 2. Flux values for single transport of transition metal ions by bulk liquid membrane[a] containing acyclic polyether diamides **3-5**

Compound	Flux ($\times 10^{-7}$ mole·m^{-2}·h^{-1})					
	Pb^{2+}	Zn^{2+}	Cd^{2+}	Co^{2+}	Ni^{2+}	Mn^{2+}
3	173.5	0	0	0	0	0
4	201.6	72.0	0	0	0	0
5	204.8	0	0	0	0	0

[a]Transport conditions: source phase (aqueous solution of nitrate, 0.8 mL), $M(NO_3)_2$=0.1 M; membrane phase ($CHCl_3$, 3.0 mL), (carrier)=1.0 mM; i.d. of glass vial=18 mm, stirred by 13 mm Teflon-coated magnetic stirring bar driven by a Hurst Synchronous motor; receiving phase (deionized water, 5.0 mL). The average value of three independent determinations. The experimental values deviate from the reported values by an average of 10%.

2. For all of compounds **3-5**, excellent selectivity for Pb^{2+} was observed. No other transition metal ions were transported. As increasing the chain length from ethyl to propyl to butyl on amide end-group, the transport amount of lead ion is found to increase, which exhibits an exactly reverse trend with that of the solvent extraction experiment. In ad-

Table 3. Flux values for competitive transport of transition metal ions (Pb^{2+} and M^{2+}) by bulk liquid membrane[a] containing acyclic polyether diamides **3-5**

Pb^{2+}/M^{2+}	Flux ($\times 10^{-7}$ mole·m^{-2}·h^{-1})		
	3	**4**	**5**
Pb^{2+}/Zn^{2+}	255.6 /b	346.7 /b	380.0 /b
Pb^{2+}/Cd^{2+}	518.4 /b	484.9 /b	534.6 /b
Pb^{2+}/Cu^{2+}	320.0 /b	480.0 /b	595.2 /b
Pb^{2+}/Co^{2+}	327.6 /b	457.4 /b	496.0 /b
Pb^{2+}/Ni^{2+}	306.0 /b	534.8 /b	512.6 /b
Pb^{2+}/Mn^{2+}	500.4 /b	678.2 /b	656.2 /b

[a] Experimental condition are same as shown in Table 1. The experimental values deviate from the reported values by an average of 10%. [b] No transport was observed.

Table 4. Thermodynamic parameters for the interaction between Pb^{2+} and acyclic polyether diamides in methanol at 25 °C

Ligand	logK	ΔG (kcal/mol)	ΔH (kcal/mol)	TΔS (kcal/mol)
3	>5	a	a	a
4	4.56(±0.04)	−6.22	−8.53(±0.01)	−2.31
5	3.16(±0.06)	−4.31	−15.29(±1.12)	−10.98

[a] The heat of reaction is measured. Log K and ΔH, however, are not able to be determined simultaneously due to the large value of logK. Heats of reaction for the complexation of other transition metal ions (Cu^{2+}, Cd^{2+}, Zn^{2+}, Co^{2+}, and Ni^{2+}) by the acyclic polyether diamide **3-5** are too small to be determined.

dition, competitive transport experiment indicates lead ion selectivity over other transition metal ions as well (Table 3). In bulk liquid membrane the transport amount is defined as competitive dissociation on the surface between organic medium and receiving phase. So, we could assert that the compound **3** complexes with Pb^{2+} more tightly than do other organic ligand **4** and **5**, resulting in more difficult dissociation from the organic medium to the receiving phase. On the other hand, in solvent extraction, better selectivity was observed in the case of compound **3** rather than other ligands **4** or **5** because the complexed ion is readily stripped by aqueous HCl solution followed by transporting from chloroform layer to the aqueous acid medium.

In determination of the complex stability there are many known methods such as potentiometry,[16] polarography,[17] calorimetry,[18] and spectrophotometry.[19] We have used the solution calorimeter to obtain the thermodynamic parameters which give an important and more detail information for the complexation behavior. In order to determine the log K, it should be ranged by $0 < \log K < 4$. Also, the temperature change should be over 0.02 °C. Calorimetric titration were conducted in methanol to determine stability constants (log K) for the complexation of Pb^{2+} and transition metal ions by the acyclic polyether diamides **3-5**. The thermodynamic parameters presented in Table 4 were calculated from the collected data by a program FS 101. The stability constant (log K) of Pb^2 complexation with ligand **3** was observed by over 5 resulting that we could not determine the appropriate values of log K and ΔH simultaneously. The log K of Pb^{2+} complexation by ligand **4** and **5** were observed with 4.56 and 3.16, respectively. However, heats of reaction for the complexation of other transition metal ions (Cu^{2+}, Cd^{2+}, Zn^{2+}, Co^{2+}, and Ni^{2+}) by the acyclic polyether diamide **3-5** are too small to be determined. The data strongly indicates that acyclic polyether bearing amide end-group complexes with Pb^{2+} much better than other transition metal ions. More interestingly, we could conclude that ligand **3** bounds more tightly with Pb^{2+} than do other ligand **4** and **5**, which is in good agreement with the results of solvent extraction and bulk liquid membrane experiment.

In conclusion, syntheses of novel acyclic polyethers bearing amide end-groups were successfully accomplished with quantitative yields. From the results of solvent extraction, bulk liquid membrane, and solution calorimetry, compound **3** containing diethyl group exhibits an excellent selectivity for Pb^{2+} over other transition metal ions. To further investigate the influence of length of the ring linkage on Pb^{2+} complexation, synthetic variation of structural analogues and their complexation studies are in progress and the results will be reported.

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Reactions in Surfactant Solutions(V): Dephosphorylation of *p*-Nitrophenyldiphenylphosphinate by Benzimidazole Catalyzed with Ethyltri-*n*-octylammonium Bromide

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The phase-transfer reagent (PTC), ethyl tri-*n*-octylammonium bromide (ETABr), strongly catalyzes the reaction of *p*-nitrophenyldiphenylphosphinate (*p*-NPDPIN) with benzimidazole (BI) and its anion (BI^-). In ETABr solutions, the dephosphorylation reactions exhibit higher than first order kinetics with respect to the nucleophile, BI, and ETABr, suggesting that reactions are occuring in small aggregates of the three species including the substrate, whereas the reaction of *p*-NPDPIN with OH^- is not catalyzed by ETABr. This behavior for the drastic rate-enhancement of the dephosphorylation is refered as 'aggregation complex model' for reactions of hydrophobic organic phosphinates with benzimidazole in hydrophobic quarternary ammonium salt solutions.

Introduction

We have reported a series of papers[1] for reactions in surfactant solutions of cetyltrimethylammonium halides (CTAX) with respect to micellar catalysis. This work deals with dephosphorylation of an organic phosphinate, *p*-nitrophenyldiphenylphosphinate (*p*-NPDPIN), catalyzed by a phase transfer catalyst, ethyltri-*n*-octylammonium bromide (ETABr) in aqueous solutions.

Micellar effects upon reaction rates in aqueous solutions have generally been analyzed in terms of a pseudophase model,[2-4] assuming reactants are distributed between the aqueous solvent and micelles, with reaction occurring in either pseudophase. It was first applied to micellar inhibited bimolecular reactions[5] and then to micellar catalyzed unimolecular reactions[6] and has been extended to bimolecular micellar catalyzed reactions.[3,4,7-9] It is implicit in this treatments that reactants do not perturb micellar structure and do not bind cooperatively to the micelle. These assumptions are reasonable, provided that surfactant is in large excess over reactants. However the quantitative treatments sometimes fail for [surfactant] near the critical micellar concentration (cmc), especially with hydrophobic reactants which may interact strongly with micelles or premicelles.[10,11]

Pskiewicz has developed an alternative model in which rate-surfactant profiles are explained by an equation similar to the Hill equation for enzyme kinetics,[11] which stresses cooperative binding. Kunitake and co-workers found that the phase-transfer catalyst, tri-*n*-octylmethylammonium chloride (TMAC), strongly accelerates deacylation of *p*-nitrophenyl acetate by hydrophobic hydroxamates or imidazoles in water.[12] The reactions in TMAC were faster than in micellized cetyltrimethylammoniun bromide (CTABr), showing that nonmicellar aggregates could be catalytically active and that rate effects in very dilute surfactant might also be due to the formation of submicellar aggregates. The rate enhancements by micellized surfactants and nonmicellized quarternary ammonium ions were ascribed to the formation of 'hydrophobic ion pairs' which were considered to be more nucleophilic than the free ions.[12] These observations were especially interesting because phase-transfer catalysis typically applied to biphasic reactions in which transport of ionic reactant across a phase boundary is of key importance.[13]

We have compared catalysis by a micellar forming surfactant, CTABr, with that by a phase-transfer catalyst, ethyl tri-*n*-octylammonium bromide (ETABr).[1a,1c,14] In the dephosphorylation reactions of *p*-nitrophenyldiphenylphosphate (*p*-NPDPP) and *p*-nitrophenyldiphenylphosphinate (*p*-NPDPIN) by benzimidazole (BI) or its anion. The anion of BI is an effective dephosphorylating agents in solutions of micellized CTABr[1a,1e] (Scheme 1). Except in very dilute CTABr, the rate enhancements are due wholly to the concentration of reactants in the micelles, and second-order rate constants in the micellar pseudophase are similiar to those in water and are independent of the total concentrations of the reactants. Reactions of benzimidazolide ion (BI^-) with *p*-NPDPP and *p*-NPDPIN are reversible (Scheme 1),[1a-1e] but the reverse reaction is unimportant in very dilute *p*-nitrophenoxide ion, return of the phosphorylated intermediate to reactants can be neglected when the concentration of *p*-nitrophenoxide ion is less than 10^{-5} M.[1a,1e]

There is extensive catalysis for the dephosphorylations of *p*-NPDPP and *p*-NPDPIN at [CTABr] below the cmc in water,[1a-1e] which could be due to induced formation of normal micelles in the presence of the hydrophobic reactants, or the reactants might combine with surfactant to form