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Effect of organic electrolyte on chloromethylation of 2-bromoethylbenzene in micellar catalytic system

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Abstract

A small amount of organic electrolyte tetrabutylammonium bromide (TBAB) was added into the micellar catalysis system in which chloromethylation reaction of 2-bromoethylbenzene (BrEtBz) was carried out, and the effect of TBAB on the catalytic reaction was investigated. The decrease in critical micelle concentration (CMC) and the increase in solubilization of BrEtBz in the micelles formed by surfactant and TBAB were observed. The chloromethylation reaction of BrEtBz exhibited higher conversion and higher selectivity for mono-chloromethylation in the surfactant micelles containing TBAB than in the single surfactant micelle. The mechanism of chloromethylation reaction and the synergistic mechanism between organic electrolyte (TBAB) and three types of surfactants were discussed.

Keywords: Organic electrolyte; Micellar catalysis; 2-Bromoethylbenzene; Chloromethylation

1. Introduction

2-Bromoethylbenzyl chloride (BEBC), especially the para-isomer, is a promising key intermediate for fine-chemicals, pharmaceuticals, polymers, etc. [1–5], because of its easy transformation to many chemicals. BEBC is mainly prepared by chloromethylation of 2-bromoethylbenzene (BrEtBz) in the presence of chloromethyl methyl ether and/or bis-chloromethyl ether (or reagent combinations which can result in the formation of these ethers) and Lewis acid [6–8]. Selectivity and yield of the mono-chloromethyl derivatives are determined by the consecutive formation of the polychloromethylation byproducts, and the formation of diphenylmethane derivatives and other byproducts, because of the Friedel–Crafts alkylation catalyzed by the same Lewis acid [9], and are often not so high [7]. Moreover, the hazards associated with these chloromethylethers are apparently so severe that classical procedures for the direct or indirect chloromethylation under Friedel–Crafts conditions are essentially no longer used, and other methods have been employed in order to develop alternative procedures which do not utilize extremely hazardous materials, but with no real success [10]. Micelles composed of surfactant molecules are the simplest of the aggregates to locally concentrate both lipophilic and hydrophilic reactants near them by micellar solubilization and electrostatic forces, often resulting in dramatic increases in reaction rates [11–13]. In addition, micellar catalysis can make reaction conditions gentle, can effectively avoid side reactions to occur, and enhance the efficiency of organic synthesis. At present, micellar catalysis has been applied in various organic syntheses, such as electrophilic substitution reaction, nucleophilic substitution reaction, oxidation reaction, hydrolysis and so on [14–22]. The objectives of the present work are to perform chloromethylation of BrEtBz catalyzed by micelles in aqueous surfactant solutions to avoid the formation of carcinogenic chloromethylethers [23], and to compare the effect in the presence and the absence of organic electrolyte on chloromethylation of BrEtBz in the micellar catalytic system.

2. Experimental

2.1. Materials

Tetrabutylammonium bromide (TBAB), cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfonates (SDS) and nonylphenol polyoxyethylene ether (NP-10) purchased from Aldrich Chemical Co., Inc. were of analytical grade and

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used without further purification. 2-Bromoethylbenzene and other reagents employed were commercial samples (ACS grade) and used without further purification. Distilled water was used for all the reactions.

2.2. *Determination of critical micelle concentration*

While a small amount of electrolyte was added into aqueous surfactant solutions, the critical micelle concentration (CMC) was determined by the ring method [24] with a JZHY-180 surface tension meter with the temperature kept constant (15 °C). The break point which indicated CMC was obtained by plotting the surface tension γ against the surfactant concentration. With the electrolyte concentration changed, the same experiments as the aforementioned one were repeated, and the curves of CMC versus the electrolyte concentration were plotted.

2.3. *Measurements of 2-bromoethylbezene solubilization*

The solubilization of BrEtBz in aqueous surfactant solution in the presence or the absence of TBAB was measured after equilibrium was reached using a UV-2602 ultraviolet–visible spectrophotometer at 259 nm. When BrEtBz was fully solubilized, the aqueous surfactant solution became cloudy. The break point was obtained by plotting absorbance against BrEtBz volume. With the surfactant concentrations changed, the same experiments as the aforementioned one were repeated, and the solubilization curves of BrEtBz were plotted.

2.4. *Chloromethylation experiment*

The chloromethylation reactions were carried out in a 250 mL round flask with a mechanical stirrer. A typical reaction procedure was as follows: BrEtBz, surfactant, 36.5% aqueous formaldehyde and 36% aqueous hydrochloric acid were added into the flask and the mixture was stirred. Then PCl_3 was added dropwise when the temperature reached to 80–82 °C At the end of the experiment the organic products were extracted with chloroform (3× 200 mL) and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo and organic residue was analyzed by HLPC using Waters 600 E $\varphi 4.5 \times 250$ mm.

3. Results and discussion

3.1. *Effect of adding electrolyte on the critical micelle concentration*

Fig. 1 shows the changes of CMC with the addition of TBAB or NaBr into ionic surfactants (CTAB and SDS).

At the beginning, CMC decreased sharply and there was a lowest point in the curve. The decrease in CMC was connected with the synergistic effect of electrolyte and surfactant [25], which was named "nonideality" or "negative deviation from ideality" [26]. When cation TBA^+ or Na^+ was inserted into the surfactant (SDS) micelle, the charge of anionic hydrophilic groups was partly counterbalanced. This would cause the increase in the micelle size and the reduction of the electrical repulsion in the Stern layer of the micelle [12,27]. In other words, the charge density at the micelle surface decreased, and thereby the absolute value of the electrical potential was also reduced [12]. This charge separation effect would be more favorable for the formation of the micelle at lower concentrations of anionic surfactant (SDS). In addition to electrostatic forces, another contribution to nonideality was due to the hydrophobic interaction [28] between hydrophobic groups of SDS and additive TBAB. It can be concluded that there must be hydrophobic interaction between hydrophobic groups of nonionic surfactant (NP-10) and TBAB. However, for cationic surfactant (CTAB), the effect of TBAB on CMC was the same as that of NaBr because there was only electrostatic interaction between cationic hydrophilic groups and Br^- and no hydrophobic interaction between hydrophobic groups of CTAB and TBAB.

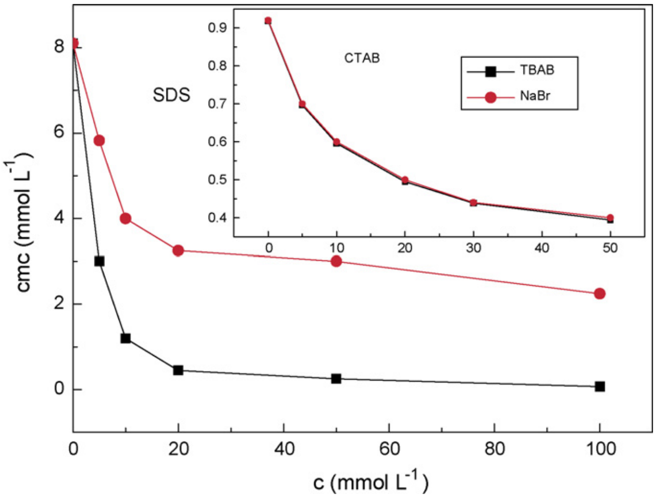

Fig. 1. Effect of adding electrolyte on the critical micelle concentrations of ionic surfactants.

3.2. *Solubilization of 2-bromoethylbenzene in micelle*

The solubilization capacity of BrEtBz in the aqueous solutions of three types of surfactants at 15 °C in the presence or the absence of TBAB is shown in Fig. 2. The curves in Fig. 2 are plots of the solubilization capacity of BrEtBz versus logarithm of surfactant concentrations. All the aqueous solutions containing surfactant but no TBAB could not make BrEtBz solubilize when surfactant concentrations were below CMC; once their concentrations reaching to CMC, BrEtBz could be solubilized in the micellar solutions significantly, and the solubilization capacity increased with the increasing surfactant concentrations rapidly. The solubilization abilities of the surfactant micelles were distinctly different at the same concentration, and decreased in the order: NP-10 > CTAB > SDS in accordance with the general rule of solubilization abilities of different types of surfactants for different organic reagents [25]. The difference should be attributed to the different compact extents of the surfactant micelles and the different CMC of these surfactants.

When a small amount of organic electrolyte (TBAB) was added into the solution containing ionic surfactant (SDS or CTAB), the solubilization capacity of BrEtBz was higher in