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A Cationic Surfactant as a Phase-Transfer Catalyst for Reactions in Liquid/Liquid and Solid/Liquid Systems. Its Use in the Manufacturing of Trichlorobenzene from Lindane Wastes and Vitamin A Production

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Abstract:

The results of pilot plant experiments on phase-transfer-catalysed dehydrochlorination of hexachlorocyclohexane and vitamin A manufacturing using phase-transfer catalysis are discussed. A long-chain cationic surfactant (Katamine AB) was a suitable catalyst in these cases. Phase-transfer catalysis is shown to provide advantageous process results and characteristics for these two commercially important reactions under scaled up conditions.

The application of phase-transfer catalysis (PTC) in industry is widespread, but there are very few publications (aside from patents) describing particular processes.[1,2] Many processes are unique, and technical solutions are not so easily transferred from one process to another. Nevertheless, we think that the experience acquired in the process of development and scale-up of PTC-based technology is valuable.

Earlier we showed that long-chain ammonium salts are bifunctional catalysts, because in their presence a reaction proceeds by two catalytic pathways, i.e., a phase-transfer-catalysed pathway and a micellar-catalysed pathway.[3,4] These salts are therefore preferable, as they work in a wider range of reagent concentrations than the usual phase-transfer catalysts. Moreover, in our case the choice of catalysts was further limited by a narrow assortment of commercially available, inexpensive quaternary ammonium salts. As the catalyst for industrial applications of PTC we chose Katamine AB (52% aqueous solution of dimethylbenzylalkylammonium chloride, alkyl being in the range $C_{12}-C_{16}$).

Trichlorobenzene Production

It is well-known that the production of lindane (γ-isomer of hexachlorocyclohexane (HClCH)) is accompanied by the formation of large amounts of other isomers (so-called "nontoxic isomers" (NTI)).[5] These isomers are usually transformed to trichlorobenzene (TCB) by a thermal dehydrochlorination process.[6]

$$C_6H_6Cl_6 \xrightarrow[-3HCl]{\Delta} C_6H_3Cl_3 \qquad (1)$$

However, this process has a number of disadvantages, the most pronounced of them being formation of a significant amount of toxic wastes, containing polychlorinated polycondensed aromatic compounds. Thus PTC dehydrochlorination seems a good solution for overcoming these problems. The nontoxic isomers of HClCH consist mainly of α-isomer (about 80%) and β-isomer (about 10−12%). The reactivities of these isomers in alkaline dehydrochlorination differ sharply. The α-isomer at medium NaOH concentrations (10 wt % and higher) and high temperatures (about 150 °C) can be dehydrochlorinated even in the absence of a catalyst. However, the dehydrochlorination of the β-isomer demands drastic conditions and proceeds only in the presence of a catalyst. The full conversion of this isomer can be obtained only if the final NaOH concentration is more than 20 wt %. The usual PTC process would thus demand a large excess of alkali. This problem could be solved if the reaction were carried out in two steps with the counterflow of reagents. Preliminary laboratory experiments confirmed such a possibility. These results were checked at a batch pilot plant and are listed in Table 1.

The results obtained in the pilot plant showed the feasibility of catalysed alkaline dehydrochlorination of HClCH. Nevertheless, the residual NaOH concentration was still high (about 5−6 wt %), thus resulting in high NaOH consumption. Our laboratory experiments[7] showed that the α-isomer of HClCH in the presence of Katamine AB can be dehydrochlorinated at quite low NaOH concentrations (about $10^{-5}-10^{-3}$ M), and the rate of reaction is quite high (without the catalyst there is no reaction at these concentrations). This fact suggests the possibility of significant reduction of the amount of NaOH required. The rate constant at 100 °C was[7] 3.4×10^{-3} s^{-1}. Assuming that the final

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Table 1. **Some results of pilot plant dehydrochlorination of NTI catalysed by Katamine AB**

	run 1		run 2		run 3		run 4		run 5	
step no.	1_1	1_2	2_1	2_2	3_1	3_2	4_1	4_2	5_1	5_2
init NaOH concn, wt %	14.8	23.0	20.6	39.2	23.6	38.6	23.4	30.0	12.8	30.3
final NaOH concn, wt %	5.2	21.9	4.1	31.8	6.7	24.7	5.57	28.8	6.55	29.0
C_{cat}, wt %	0.22	0.22	0.2	0.12	0.15	0.07	0.18	0.09	0.16	0.08
time, h	2.5	2.5	4	3.3	4.2	4.2	7.25	3.25	3.75	4
mole ratio NaOH/NTI	3.09		4.8		2.91		2.07		2.4	
V_{aq}/V_{org}	1.56		2.27		1.2		0.6		0.79	
C_{NTI} (dissolved), wt % at the end	6.75	0.13	5.0	0.01		0.2	5.6	0.25		0.2
C_{NTI} (precipitate), wt % at the end								4.0		1.9
X_{NaOH}	0.85		0.8		0.72		0.72	0.2		
X_{NTI}								0.85		0.95

[a] The first-step temperature was 90−95 °C, and the second-step temperature was 100−105 °C.

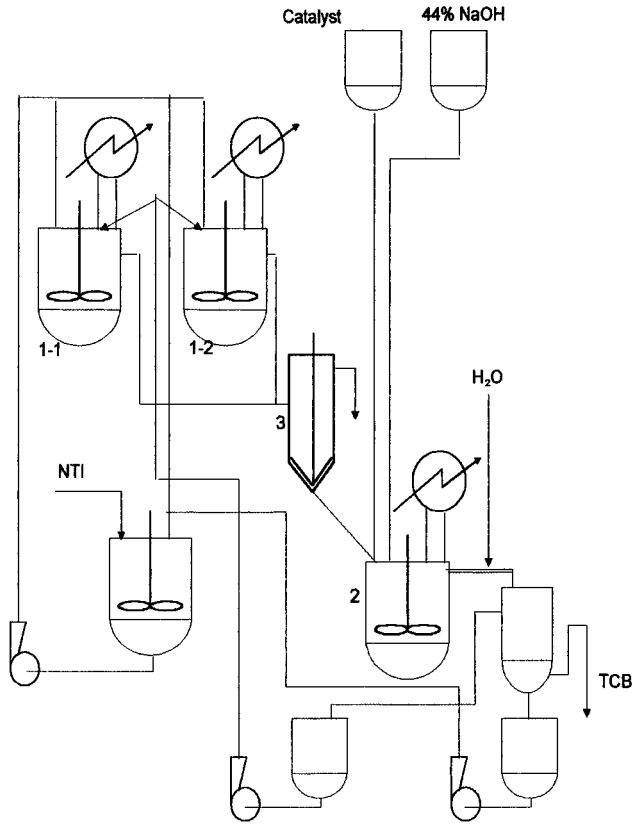


Figure 1. **Flow chart of TCB production process by two-phase alkaline dehydrochlorination of NTI. 1-1, 1-2: first-step reactors. 2: second-step reactor. 3: separation unit.**

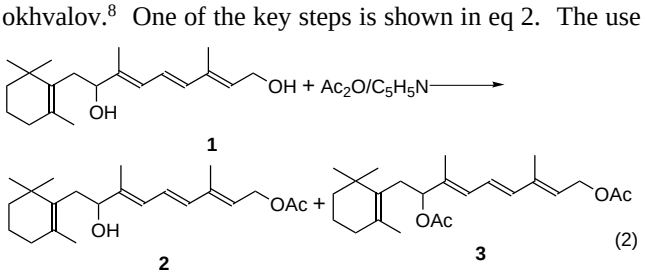
degree of conversion of the α-isomer of HClCH is 0.95, the residence time calculated by the equation $\tau = (1/k)(X/(1 - X))$ is equal to 1.5 h. The feed flow of a 50% NTI suspension in TCB is 3000 kg/h (1823 L/h). The corresponding feed flow of 10% NaOH solution is 4245 L/h. So the capacity of first-step reactor should not be less than 9500 L.

We decided to use two parallel reactors of 5500 L each in the first dehydrochlorination step. The flow chart is shown in Figure 1. The suspension of NTI in TCB is charged continuously in two reactors (1-1 and 1-2) that have high-speed stirrers and steam jackets. The 10% NaOH solution and Katamine AB solution are also fed to these reactors. The feed of NaOH is controlled by the pH value (about 7.5−11) in the output flow. From these reactors the reaction mixture goes to the separating unit, where organic and aqueous layers are separated. TCB containing the unreacted β-isomer of HClCH is fed to the second-step reactor (2). To this reactor are fed continuously 44% NaOH solution and catalyst solution. The reaction mixture leaving this reactor is fed to the florentine flask, where TCB is separated from the NaOH−NaCl solution. To the pipe leading to the florentine flask is also fed sufficient water to obtain a 10% NaOH solution. NaOH solution goes to the first dehydrochlorination step, and the TCB that is obtained is washed from the residual catalyst and goes to rectification. The first runs on this unit showed that after the first step the conversion of NTI was about 70−80%, and after the second step about 95%. The residual HClCH concentration in TCB was about 0.1−0.2%. So this method of HClCH processing appeared to be quite feasible also on a large scale. However, it must be noted that this process had a number of bottlenecks, the main one being the separation unit 3. It was very difficult to secure its stable performance. The most trouble was caused by the clockwork-driven dump valve (not shown in Figure 1) at the bottom of unit 3. It was designed for the dumping of the unreacted β-isomer suspension. It did not work properly, and the dump line was choked up quite often. In our opinion this difficulty and other ones resulting from it can be effectively overcome by combining the first and second dehydrochlorination steps and carrying them out in a reactor analogous to a rotary extractor. Preliminary laboratory experiments confirmed the feasibility of this solution.

Vitamin A Production

The next task that was solved using the long-chain ammonium surfactant was the improvement of the vitamin A production process.

Presently in Russian pharmaceutical plants vitamin A is produced by the method of Preobrazhensky and Samokhvalov.[8] One of the key steps is shown in eq 2. The use



(2)

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Table 2. **Results of pilot plant experiments on vitamin A manufacture**

run no.	load: Ac_2O, L	load: Na_2CO_3, kg	t, °C	reactn time, h	quality of vitamin A acetate: IU/g	quality of vitamin A acetate: content of retroisomer, %	quality of vitamin A acetate: content of *E*-isomer, %	yield of vitamin A acetate: kg	yield of vitamin A acetate: % of theory
1	85	70	37−40	4	2 293 000	7.8	71.5	120	85.2
2	100	70	37−41	7	2 261 000	9.6	66.0	87.1	62.1
3	85	70	37−40	5	2 193 000	8.1	65.5	96.6	68.7
4	75	70	47−49	5	2 123 000	8.1	67.6	99.6	71.0
5[b]	75	75[c]	37−40	5	2 124 000	11.1	67.7	96.2	68.1

[a] The load of **1** was130 kg, the load of the catalyst was 8 kg, and the load of CH_2Cl_2 was 260 L in all runs. [b] The run was carried out according to the conventional method with pyridine. [c] The amount of pyridine in liters.

of pyridine as the catalyst and solvent is not advantageous as this necessitates numerous washings of the reaction mixture. First it is washed by H_2SO_4, then it needs to be washed from this acid, and so on. This results in formation of an enormous amount of waste waters that contain pyridine, and in the loss of product. It is known that PTC is also used in O-acylation.[9] So we tried[10] to apply it in the acetylation of diol **1**. Preliminary experiments showed that **1** can be acetylated in the presence of solid Na_2CO_3 and Katamine AB. Also there is observed a sharp change in selectivity. In the presence of pyridine the **2**/**3** ratio is about 1/4−5; in the PTC reaction this ratio is about 8−10/1. This is also advantageous for the subsequent reactions of this mixture. The reaction in all probability proceeds through the intermediate complex of diol **1** absorbed on the surface of the solid sodium carbonate. The formation of such complexes on the solid salt surfaces was proved earlier.[11] In such a complex the approach to the secondary hydroxyl should be more hindered than to the primary one. So, in our opinion, this is a feasible explanation of the observed sharp change in selectivity. Laboratory experiments allowed us to determine the necessary ratio **1**/Na_2CO_3, optimal catalyst concentration, and other parameters. The results of pilot plant experiments are listed in Table 2. One can see that the new method gives product with yield and quality that are sometimes better than those of the old method. It should be noted that the product quality strongly depends on the quality of **1**, and this parameter strongly varied from batch to batch.

Experimental Section

1. TCB Production. The batch pilot plant consisted of the reactor (3 m^3 with jacket, stirrer, and reflux condenser), batch meters for the catalyst and alkali solutions, and tank for the washing of the obtained TCB from the catalyst. The reactor was charged with a suspension of NTI in TCB, NaOH solution, and catalyst. The first dehydrochlorination stage was carried out with a NaOH concentration of about 10−15 wt %. After the reaction the aqueous layer was separated. Concentrated alkali (about 30−40%) and catalyst were charged, and the second dehydrochlorination stage was carried out. The resultant TCB was separated, and a new portion of NTI suspension in TCB was charged. A defined volume of water was also charged to dissolve the precipitated NaCl. The concentration of NTI dissolved in TCB was determined according to the method in ref 5. The sample of TCB was refluxed with alcoholic NaOH solution, and the NaCl concentration was determined by Volhard titration. **CAUTION!** NTI and TCB are toxic substances, and all personnel should avoid skin contact. All laboratory work should be performed under a hood.

Degrees of conversion of alkali and NTI were calculated according to the following formulas:

$$C_{NTI} = 100W_{NTI}/(W_{TCB,0} + W_{TCB} + W_{NTI}) \quad (3)$$

where C_{NTI} is the sum of the concentrations of suspended and dissolved NTI; W_{NTI} is the current amount of NTI, kg; W_{TCB} is the amount of TCB formed in a given time, kg; $W_{TCB,0}$ is the amount of TCB initially loaded with the suspension of NTI, kg; and

$$W_{TCB} = (W_{NTI,0} - W_{NTI})(181.5/291) \quad (4)$$

Substituting eq 3 in eq 4 after the necessary transformations we obtain

$$X_{NTI} = C_{NTI}(W_{TCB,0} + 0.624W_{NTI,0})/(W_{NTI,0}(100 - 0.376C_{NTI}))$$

where X_{NTI} is the degree of conversion of NTI.

The conversion of alkali was calculated according to the equation

$$X_{NaOH} = 1 - C_{NaOH}(W_w + W_{NaCl} + 1.46W_{NaOH})/(W_{NaOH}(100 + 0.46C_{NaOH}))$$

where C_{NaOH} is the concentration of alkali, wt %; W_w is the overall amount of added water (including water charged with alkali), kg; W_{NaOH} is the amount of NaOH solution, charged into the reactor, kg; and W_{NaCl} is the amount of NaCl from the second step of the previous run (in the case of fresh NaOH solution, $W_{NaCl} = 0$).

2. Vitamin A Production. Laboratory experiments were carried out in a three-necked 250 mL flask with stirrer, reflux condenser, and thermometer. The reactor was charged with 13 g of **1**, 6−8 g of Na_2CO_3, 40−50 mL of hexane or CH_2Cl_2, and 0.5−1 mL of Katamine AB, and 8 mL of acetic anhydride at 35−40 °C was added for 4−4.5 h. The product obtained (a mixture of **2** and **3**) was used in the synthesis of vitamin A without isolation. The reaction was monitored

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by TLC on Silufol and by HPLC on a Milikhrom HPL chromatograph. The eluent was 1.5% *i*-PrOH in hexane, and the column, 2 × 64 mm, packed with Silasorb C 600; *p*-chlorophenol was used as an internal standard. The pilot plant reactor was a steel enameled tank of 1600 L capacity with stirrer and water jacket. Acetic anhydride and the solvent were loaded from the batch meter, and the catalyst and solid sodium carbonate were loaded through the access hatch. Loads and results are listed in Table 2.

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