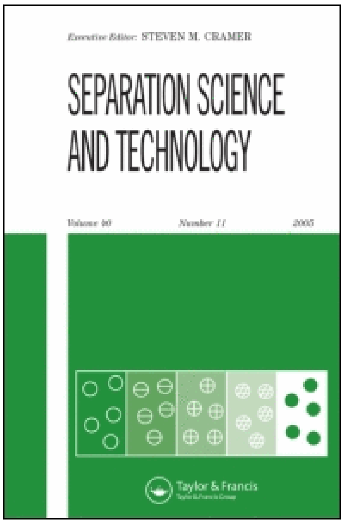

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Catalytic Extraction-Phase-Transfer Catalysis as a Separation Technique. Part I. Selective Esterification of Carboxylic Acid Salts

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COMMUNICATION

Catalytic Extraction–Phase-Transfer Catalysis as a Separation Technique. Part I. Selective Esterification of Carboxylic Acid Salts

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Abstract

Phase-transfer catalysis is applied for the separation of carboxylate salts in aqueous solutions.

Phase-transfer catalysis is a well-established synthetic method for reactions of ionic substances in aqueous solutions with organic compounds in hydrophobic media (*1*). Anions like halides (*2*), phenoxides (*3*), carboxylates (*4*), cyanide (*5*), hydroxide (*6*), and others (*7*) have been effectively extracted as ion pairs into organic solvents and were reacted in alkylations (*8*), substitutions (*9*), oxidations (*10*), eliminations (*11*), and other processes. Typical phase-transfer catalysts are quaternary ammonium and phosphonium salts, crown ethers, and related compounds (*1*).

We wish to describe the application of phase-transfer catalysis as a separation procedure. The procedure allows the separation of one anion from a mixture in an aqueous solution by contacting it with an organic phase containing a reactive substrate in the presence of a phase-transfer agent. This agent, which serves as an extracting reagent, is regenerated and recycled in situ by the reaction of the extracted ion pair with the substrate present in the organic phase.

A general system is described in the Scheme 1. A mixture of ions X^-,

Y^- in aqueous phase is contacted with an organic phase containing a functional substrate RZ, where R = alkyl or aralkyl and Z = active labile group (e.g., halide). A phase-transfer agent Q^+ is added to the system along with an inactive anion.

Organic phase

$$\frac{RZ + QX \rightarrow RX + QZ}{Q^+}$$

Aqueous phase X^- Y^-

SCHEME 1

The extraction constants of the ion pairs present in the system are defined as follows (*12*):

$$e_{QX} = \frac{[QX]_s}{[Q^+]_w[X^-]_w}, \qquad e_{QY} = \frac{[QY]_s}{[Q^+]_w[Y^-]_w}$$

where $[QX]_s$ and $[QY]_s$ are the concentrations of the ion pairs in the organic phase, and $[Q^+]_w[X^-]_w$ and $[Y^-]_w$ are the concentrations of the free ions in the aqueous phase. It is assumed that e_{QZ} is neglectable. If $e_{QX} \gg e_{QY}$, then we shall find that $[QX]_s \gg [QY]_s$. Furthermore, it can be shown that the selectivity of the extraction, defined as $[QX]_s/[QY]_s$, increases as the total amount of the extraction reagent (i.e., $[Q^+] + [QX] + [QY]$) decreases.

The ion pair QX will react in the organic phase with RZ to yield RX, Q^+ is recycled, and the extraction process is repeated. We call this process a catalytic extraction process.

In this report we wish to demonstrate the application of catalytic extraction to the separation of carboxylate ions in aqueous solution by two phases of selective esterification of butyl bromide in the presence of quaternary ammonium salts. For comparison, the same experiments were conducted in a homogeneous system by application of dimethylformamide (DMF) as a solvent.

EXPERIMENTAL

All the reactions were carried out using a 100-mL round-bottomed flask fitted with a water-cooled condenser and held in a thermostatic silicone oil bath at 120°. A 2-cm magnetic bar was used for mixing at a constant stirring rate of 150 rpm.

Reagents chemicals and solvents were commercial with purity >97%.

Product analysis was conducted using a Gow-Mac model 150 gas chromatograph with SS 6 ft × 0.125 in. 10% carbowax 20 M on a chromosorb W column.

Procedure

Heterogeneous Reaction

Sodium acetate (4.1 g, 50 mmol) and sodium formate (3.4 g, 50 mmol) were dissolved in 4 mL of water. *n*-Butyl bromide (6.85 g, 50 mmol) and Aliquat 336 (tricaprylmethylammonium chloride, 0.49 g, 1 mmol), dissolved in 25 mL o-xylene, were added to the aqueous solution. The mixture was refluxed at 120° with stirring for various lengths of time.

Homogeneous Reaction

Sodium acetate (4.1 g, 50 mmol) sodium formate (3.4 g, 50 mmol), and butyl bromide (6.85 g, 50 mmol) were dissolved in 25 mL DMF and heated to 120° for various lengths of time.

The products of the reactions were characterized by gas chromatography. In the case of heterogeneous reaction, a sample from the organic phase was injected into the chromatograph. The areas under the chromatographic peaks were determined manually.

RESULTS AND DISCUSSIONS

Several binary mixtures of carboxylate salts were reacted with *n*-butyl bromide to yield butyl esters according to

$$\mathrm{RCOO} + n\text{-}\mathrm{BuBr} \rightarrow \mathrm{RCOO{-}}n\text{-}\mathrm{Bu} + \mathrm{Br}^-$$

The reactions were carried out under phase-transfer conditions (PTC) and in homogeneous DMF solutions. The chromatograph data allow calculation of percent conversion of the salts to the esters, as well as of the amounts of each carboxylate extracted.

The selectivity of the catalytic extractions was calculated from the molar ratio of the major product to the minor product. The results of the study are shown in Table 1 where the conditions of each experiment, percent conversion to the ester, and the selectivity are given. For each experiment in the "Acid salts" column, the first salt is the minor product.

In order to demonstrate the effect of catalyst concentration on selectivity, we have conducted several experiments in which mixtures of acetate and formate ions were esterified in two-phase systems in the presence of tetrabutylammonium bromide. Selectivity as a function of catalyst concentration is presented in Table 2.

TABLE 1

Esterification of Carboxylic Acid Salts Mixtures with Butyl Bromide under Homogeneous and Phase-Transfer Conditions

Experiment	Acid salts	Mode	Time (h)	Conversion (%)	Selectivity
1	$HCOONa + CH_3COONa$	PTC	1	28	22
2	$HCOONa + CH_3COONa$	PTC	3	52	7
3	$HCOONa + CH_3COONa$	PTC	5	68	5
4	$HCOONa + CH_3COONa$	PTC	22	99	5
5	$HCOONa + CH_3COONa$	DMF	1/2	100	1.2
6	$HCOONa + CH_3COONa$	DMF	1/6	50	1.2
7	$HCOOK + CH_3COOK$	PTC	3	71	2
8	$HCOOK + CH_3COOK$	DMF	1	99	1
9	$CH_3COONa + C_2H_5COONa$	PTC	5	63	3
10	$CH_3COONa +$ *n*-C_3H_7COONa	PTC	5	90	8
11	$CH_3COONa + C_2H_5COONa$	DMF	2	99	1.7
12	$CH_3COONa +$ *n*-C_3H_7COONa	DMF	2	98	1.8
13	$HCOONa +$ *n*-C_3H_7COONa	PTC	5	100	99
14	$HCOONa +$ *n*-C_3H_7COONa	DMF	2	100	25
15	Iso-$C_3H_7COONa +$ *n*-C_3H_7COONa	PTC	5	100	1.2

TABLE 2

Effect of Catalyst[a] Concentration on Conversion and Selectivity of Esterification of Butyl Bromide with Mixture of Sodium Formate and Sodium Acetate

Experiment	Catalyst: substrate ratio	Conversion (%)[c]	Selectivity[b]
1	1: 10	90.6	2.5
2	1: 50	52.3	3.6
3	1: 100	44.9	4.0
4	1: 200	33.0	10
5[c]	1: 200	69.2	5

[a] Catalyst: tetrabutylammonium bromide.

[b] Molar ratio of butyl acetate to butyl formate.

[c] After 22 h.

Table 1 shows that the selectivity of conversion under catalytic extraction conditions is much better than in a homogeneous system. Several observations should be noted: (a) a longer reaction time gave greater conversion to the esters and usually worse selectivities and, hence, poorer separations; (b) the greater the hydrophilicity differences between the two salts, the greater the selectivity; and (c) sodium salts are easier to convert and separate than potassium salts.

It is quite clear from the above observations that the reactions in homogeneous systems are kinetically controlled and the selectivity therefore depends on the nucleophility of the carboxylate anions only. In the heterogeneous systems, on the other hand, the selectivity is mainly a function of thermodynamic factors, namely the extraction constants of the ion pairs involved in the system. In addition, the selectivity strongly depends on the degree of conversion (the higher the conversion, the lower the selectivity). The second factor is the catalyst concentration: in higher concentrations we observed lower selectivities.

Further applications of these systems are now under study.

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