Micelle-related Heterogeneous Catalysis. Anion-activation by Polymer-linked Cationic Surfactants

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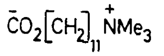
Summary Polymer-bound quaternary ammonium surfactants catalyse the *O*-alkylation of 2-naphthoxide.

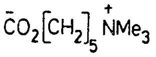
Synthetic applications of micellar catalysis are limited by problems of scale, since reactions must be carried out in dilute aqueous solution in the presence of an excess of surfactant.[1] We reasoned that the attachment of ionic surfactant chains to a rigid polymer backbone might obviate this limitation, creating phase-boundary conditions at an aqueous interface resembling those at the surface of a micelle, but much less prone to substrate saturation or deaggregation.

Preparation of the desired polymers was achieved by reaction of a 3-molar excess of carboxylates (**1**) and (**2**) with exhaustively substituted[2] cross-linked chloromethylpolystyrenes in dimethylformamide at 110 °C. In this way resins (**3a**) (based on 2% crosslinked 'Merrifield' polymer, 98% arene substitution by Cl and N analysis) and (**3b**) (based on Rohm and Haas XE305 macrorecticular resin,[3] 46% arene substitution by N analysis on Cl^- and NO_3^- salts) were prepared. The short-chain analogues (**4a**) and (**4b**) with respectively 100 and 40% substitution, were prepared similarly. For comparison purposes, the ion-exchange resin (**5**) was synthesised by conventional means. The amphiphilic nature of, for example, (**3a**) is demonstrated by its hygroscopicity, and ability to swell in both water (40% volume expansion) and organic solvents. Anion-exchange is rapid, and an aqueous solution of Methyl Orange is decolorised rapidly.



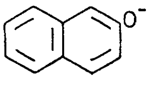
$\overset{-}{C}O_2[CH_2]_{11}\overset{+}{N}Me_3$

(1)

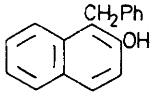


$\overset{-}{C}O_2[CH_2]_5\overset{+}{N}Me_3$

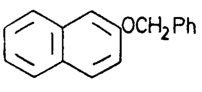
(2)



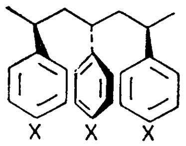
(6)



(7)



(8)



(**3a**); Merrifield resin, X = $CH_2OCO[CH_2]_{11}N^+Me_3Cl^-$
(**3b**); XE305 resin, X as in (**3a**)
(**4a**); Merrifield resin, X = $CH_2OCO[CH_2]_5N^+Me_3Cl^-$
(**4b**); XE305 resin, X as in (**4a**)
(**5**); Merrifield resin, X = $CH_2N^+Me_3Cl^-$

These resins, and particularly (**3a**) or (**3b**) promote the reaction of aqueous nucleophiles with organic substrates. Thus n-octyl bromide is quantitatively converted into n-octyl cyanide by stirring the neat liquid (2·2 mmol) with saturated aqueous sodium cyanide (5 ml) and (**3b**) (0·27 mmol, based on N^+Me_3) at 100 °C for 4 h. Under similar conditions, the conventional phase-transfer catalyst tetrabutylammonium bromide[4] displayed comparable reactivity. The resin-promoted reaction of benzyl bromide with sodium 2-naphthoxide (**6**) is of more immediate interest.

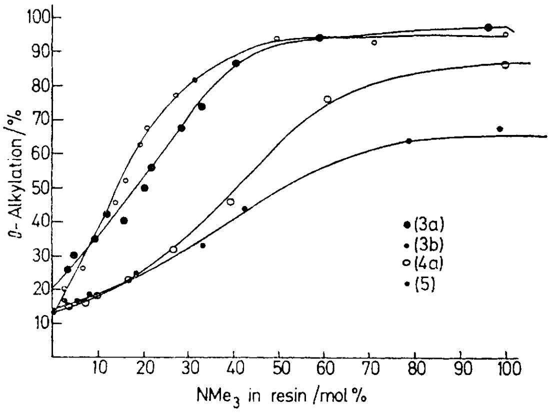


FIGURE 1. Variation of *O*-alkylation with resin quantity. Values were determined by n.m.r. spectroscopy in $CDCl_3$ from triple integration of the expanded region (δ 5·0—6·0) and are corrected for di-*C*-alkylation but not for traces of *O,C*-dialkylation. Standard conditions of experiment were: (**6**), 0·5 M, 1 ml; benzyl bromide, 15 μl; resin as indicated; stir for 5 h at 20 °C, extract with CH_2Cl_2, wash with D_2O, and evacuate at 0·1 mmHg.

It is already known that alkylation at C-1 giving (**7**) is predominant in water, but in dipolar aprotic solvents where specific *O*-solvation is lacking, (**8**) is formed exclusively.[5] Phase-transfer catalysts promote *O*-alkylation in CH_2Cl_2; in aqueous solution containing cetyltrimethylammonium bromide in comparable concentration to the reactants (**8**) is the predominant product.[6] The present study of this reaction (Figure 1) permits an assessment of the relative effectiveness of resins (**3a**)—(**5**) as anion-activation catalysts. From this it is clear that lengthening the alkyl chain promotes a marked improvement, although even the caproate derivative (**4**) is superior to the simple ion-exchange resin (**5**).[7] In addition, the macrorecticular resin (**3b**) is somewhat more efficient than the microporous resin (**3a**).

Given that reaction in pure water gives 14% (**8**) and that by extrapolation reaction on resin (**3a**) gives 98% and on (**3b**) 96% (**8**), relative rates of the aqueous and resin-based reaction may be calculated. The relative mole fractions of naphthoxide anion bound to the resin (x) and in bulk solution ($1 - x$) have been determined by independent spectrometric measurements, monitoring at 283 nm. Surprisingly, both (**3a**) and (**3b**) bind more than 1 equiv. of naphthoxide (1·52 and 1·27, respectively), behaviour not shared by (**4a**) or (**5**). Assuming that all the bound naphthoxide is kinetically active and that the rate of resin reaction increases linearly with the mole fraction of N^+Me_3 groups (y) (as more benzyl bromide is bound) then an empirical model (Figure 2) for the catalysed reaction may be made. Considering the obvious approximations in this, the fit of experimental data is surprisingly good.

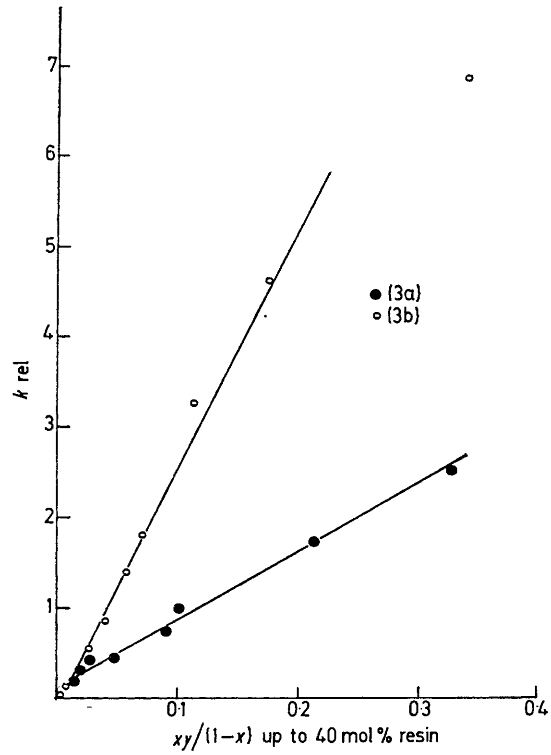


FIGURE 2. Variation of the relative rates of aqueous and resin-based reactions with variation in $xy/(1 - x)$ (defined in the text).

Although conditions are far from optimised, this work illustrates the potential of immobilised micelles in catalysis. We plan to study the reactivity of similar resins containing active functionalities in the head-group[8] or long alkyl-chain.[9]

We thank the S.R.C. Colloid Science Panel for support. J.A.J. is on leave from Otterbein College, Ohio.

(*Received*, 5*th April* 1976; *Com.* 369.)

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