Functionalised Polyorganosiloxanes as Selective Liquid Extractants

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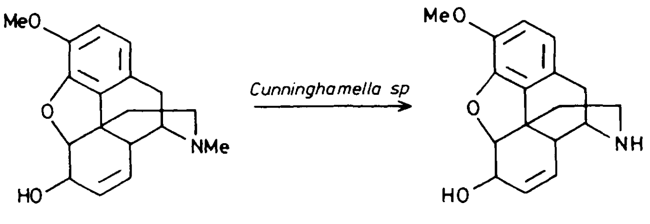
The cyclic ether 2-(hex-5-enyl)-1,4,7,10-tetraoxacyclododecane has been synthesised and attached to a siloxane backbone to produce linear polyorganosiloxanes functionalised with 12-crown-4 terminated alkyl chains, $Me_3SiO(Me_2SiO)_x[MeSiO(CH_2)_6\text{-12-crown-4}]_ySiMe_3$ ($x = 47$, $y = 1$, or $x = 286$, $y = 12$); the preferential complexation of 12-crown-4 for secondary amine salts in mixtures of protonated secondary and tertiary amines is maintained in the functionalised liquid polymers, which are thus effective selective extractants for the separation of secondary and tertiary amine mixtures including norcodeine and codeine present in low concentrations in bioreactor broth.

Polyorganosiloxanes functionalised with ligand terminated alkyl chains have been used to anchor a variety of metal species,[1] and the resulting materials have been used primarily as novel polymer-supported catalyst systems.[2] No attempt has been made to utilise low mole % functionalised linear polysiloxanes as selective liquid extractants, despite their low viscosities, immiscibility with water, and high thermal and chemical stability. We have been attempting to produce polyorganosiloxanes functionalised with receptors capable of molecular recognition which can act as selective extractants for fine chemicals of commercial importance. Here, we describe the use of 12-crown-4 functionalised polysiloxanes as extractants for protonated secondary amines from aqueous, acidic solutions containing mixtures of secondary and tertiary amines. This procedure has been developed into the basis of a liquid–liquid extraction process for the separation of norcodeine produced from codeine in an air-lift fermenter system[3] using alginate immobilised *Cunninghamella sp.*, see Scheme 1.



codeine norcodeine

Scheme 1

Previous studies[4,5] have shown that small crown ethers, such as diaza-12-crown-4 (I) and 12-crown-4 (II),† bind strongly to secondary amine salts *via* two bifurcated N–H · · N(O) hydrogen bonds (see Figure 1).[4] These are structurally specific interactions which are not possible for tertiary amine salts, and we have been unable to isolate definite complexes of (I) or (II) with R_3NH^+ cations under a variety of experimental conditions. By contrast, protonated secondary amine salts, including [piperidine–H]$^+$ and [norcodeine–H]$^+$, readily form 1 : 1 complexes with (I) or (II) which can be isolated as their PF_6^- or ClO_4^- salts from either hydroxylic or non-hydroxylic solvents.‡ Complexes of (I) slowly decompose on standing, and as the synthetic route to (I) and its derivatives is tedious,[6] we have concentrated our attention on 12-crown-4, which is readily prepared in a functionalised form (Scheme 2) suitable for attachment to a polysiloxane backbone (Scheme 3) using known methods.[7]

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† (I) 4,10-diaza-1,7-dioxacyclododecane, (II) 1,4,7,10-tetraoxacyclododecane.

‡ Satisfactory C, H, and N elemental analyses were obtained for all 1 : 1 complexes between the protonated secondary amine perchlorates and diaza-12-crown-4 or 12-crown-4. Selected n.m.r. data for $(C_8H_{18}O_2N_2\cdot NC_5H_{12})ClO_4$; $^1H(CDCl_3)$ δ 7.25 (s,4H,NH), 3.80 (m,8H,OCH_2), 3.20 (m,4H,CH_2) 3.05 (m,8H,NCH_2,crown), 1.90 (m,4H,CH_2), 1.72 (m,2H,CH_2); ^{13}C-(^1H) δ 67.0 (OCH_2), 47.8 (NCH_2,crown), 44.8 (CH_2), 22.6 (CH_2), 22.2 (CH_2). $(C_8H_{16}O_4\cdot NC_5H_{12})ClO_4$: $^1H(CDCl_3)$ δ 7.22 (s,2H,NH), 3.70 (m,16H,OCH_2), 3.28 (m,4H,CH_2) 1.85 (m,4H,CH_2), 1.68 (m,2H,CH_2); ^{13}C–(^1H) δ 68.1 (OCH_2), 45.6 (CH_2), 22.6 (CH_2), 22.1 (CH_2).

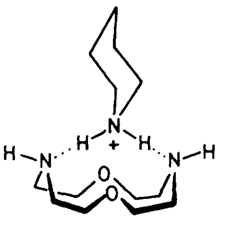
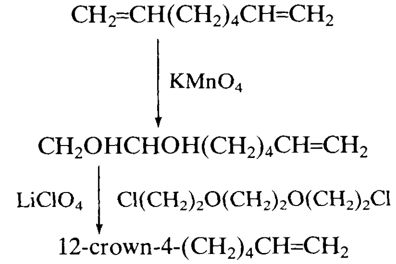
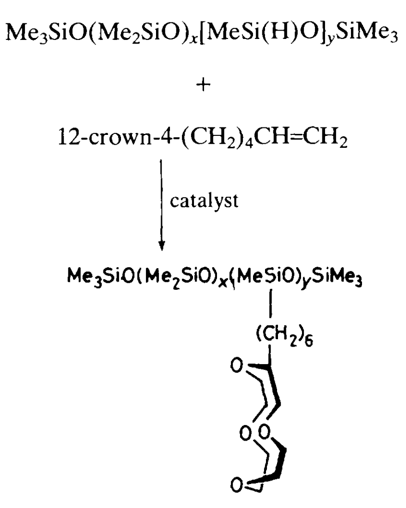


Figure 1



Scheme 2



Scheme 3

Polymers with a low $x:y$ ratio were readily soluble in aqueous media and hence unsuitable as extractants. However those with a crown ether functionality in the 2—4 mole % range, and M_r values up to 27 000, were mobile fluids which selectively complexed with secondary amine salts and extracted them into the hydrophobic polymer phase. Single stage extraction of aqueous, acidified equimolar mixtures of codeine and norcodeine at concentrations typical of those found in fermenter liquors (10^{-3}—10^{-4} M) by equal volumes of such a fluid resulted in a *ca.* 25% extraction of the total norcodeine content with no detectable codeine. Recovery of norcodeine was almost quantitative following separation and extraction of the norcodeine containing polymer by methanolic NaOH solution. No interference with nitrogen and carbon sources, or inorganic nutrient salts (mainly sodium and potassium phosphates) used in the bioreactor culture medium were detected.

Support for this research by the S.E.R.C. is gratefully acknowledged.

Received, 8th June 1987; Com. 782

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