



Template Effect in Caesium Selective Phenolic Resins

ALAIN FAVRE-RÉGUILLON, BRANKO DUNJIC, NATHALIE DUMONT and MARC LEMAIRE*

Institut de Recherches sur la Catalyse, Laboratoire de Catalyse et Synthèse Organique, Université Claude Bernard, Lyon I, CPE, 43 Bld du 11 Novembre 1918, 69622 Villeurbanne, France

(Received: 4 September 1997; in final form: 15 January 1998)

Abstract. Two new phenolic resins have been synthesised by alkaline polycondensation of resorcinol and acetaldehyde using template polymerisation. The extraction properties of the resins have been evaluated in competitive extraction and show a selectivity in favour of Cs^+ . This selectivity is enhanced for the template resins. Structural data of the resins are discussed on the basis of ^{13}C -NMR CPMAS spectra. In particular, for caesium template resins, a structure similar to resorcinarene has been evidenced.

Key words: phenolic resins, caesium, resorcinol, resorcinarene, template polymerisation, competitive extraction, ^{13}C CPMAS solid state NMR

1. Introduction

The molecular imprinting technique is a promising way of preparing highly selective host polymers since it requires no multistep synthesis. This direct polymerisation method, called "template polymerisation" has been reported for the synthesis of ion-selective polymeric reagents [1]. Nishide et al. [2] have prepared a resin by crosslinking poly(4-vinylpyridine) in the presence of a transition metal ion. The resin selectively adsorbed the metal ion which was used as a template. This promising technique has been known for 20 years [2], but few applications dealing with imprinting resins have been described. This can be explained because resins prepared in such a way suffer from fundamental problems. The capacities of the resins are low, extractions are limited to transition metal ions and the polymer-metal complex is formed in organic media whereas the extractions are performed in aqueous solutions. The presence of organic solvents during the cross-linking process could modify the cavity conformation. Thus, in aqueous phase, cavity and template ions may not match.

In order to overcome these disadvantages, new metal ion template resins have been prepared by surface template emulsion polymerisation in water [3]. Increasing adsorption has been found but selectivity, in relation to non targeted metal ions,

* Author for correspondence.

remains low [4]. Furthermore this methodology can only be applied to multivalent ions.

In this study, an improvement of the selectivity of phenolic resins towards caesium by template polymerisation is presented. The ionoselective properties of the resins are then evaluated via a competitive extraction of five alkali-metal cations. In neutral solution this selectivity is found to be $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ \gg \text{Na}^+ \approx \text{Li}^+$. Furthermore, ^{13}C -NMR CPMAS of the resins are studied and compared with a macrocycle selective of caesium, resorcinarene. These studies have been carried out to provide information on the structural modification in the bulk of the phenolic resins.

2. Experimental

2.1. MATERIALS AND METHODS

All chemicals were purchased from Janssen, Aldrich or Prolabo and used as received. Resorcinarene was synthesised according to the method previously described [5].

^{13}C -NMR CPMAS solid-state spectra were obtained using a Bruker MSL-300 spectrometer operating at 75.47 MHz. The samples were packed into a 7 mm rotor that was spun at the magic angle with a spinning rate of the order of 3.5 kHz. For the cross-polarisation, contact times of 2 ms were used, while the recycle delay for CP experiments was 5 s and the number of transients required to achieve good signal to noise ratios varied with the circumstances. The chemical shifts were scaled to TMS.

^{13}C -NMR liquid-state spectra of resorcinarene were recorded at 50 MHz with a Bruker AC 200 spectrometer in $\text{D}_2\text{O}/\text{NaOD}$ 0.5 M: 155.86 ($\text{C}_{\text{arom.}}\text{-OH}$), 127.06 ($\text{C}_{\text{arom.}}\text{-C}$), 121.37 ($\text{C}_{\text{arom.}}\text{-CH meta}$), 106.62 ($\text{C}_{\text{arom.}}\text{-CH ortho}$), 29.12 (CH), 19.08 (CH_3).

Competitive extractions were performed according to the method previously described [6]. A known amount of resin was shaken for 5 hours with the solution of the five alkaline salts. The distribution coefficient was calculated as follows:

$$D = \frac{[M^+]_i - [M^+]}{[M^+]} \times \frac{V}{m}$$

The concentration of the metal cations before and after adsorption was determined by atomic emission spectroscopy. The subscript *i* refers to initial conditions, *V* (mL) to the volume of solution and *m* (g) to the mass of resin. Standard deviations were determined from six independent ion-exchange experiments.

2.2. SYNTHESIS OF THE RESINS

The polymers were synthesised using a polycondensation reaction between the phenolic compounds and acetaldehyde in the presence of alkaline hydroxide as catalyst according to the method previously described [6]. The phenolic compound/acetaldehyde/base/H₂O mole ratio was 1 : 2.5 : 1.5 : 50. After curing, the polymers were crushed, sieved to -80 +200 ASTN mesh size particles, washed and conditioned by subjecting them to two 1 N HCl/0.1 N NaOH cycles. The resins were finally converted to acid form and washed thoroughly with water until neutral.

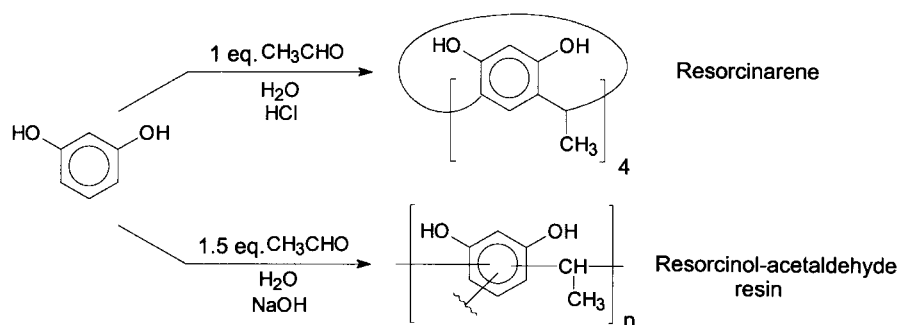
3. Results and Discussions

3.1. SYNTHESIS OF NEW PHENOLIC RESINS

To evaluate further the potential for template polymerisation and to increase both efficiency and selectivity of ion-exchange resins, an improvement of the selectivity toward caesium for phenolic resins was undertaken.

Phenolic ion-exchangers have been known to possess high affinity for caesium for many years. This property was used for the ¹³⁷Cs recovery from radioactive alkaline waste solutions [7, 8]. We have recently reported the successful extraction of caesium from an alkaline leaching solution of spent catalysts [6]. Template polymerisation with resorcinol-formaldehyde resins have been studied [9], but despite the use of radio tracers the effect on ionoselective properties could not until now be brought to the fore.

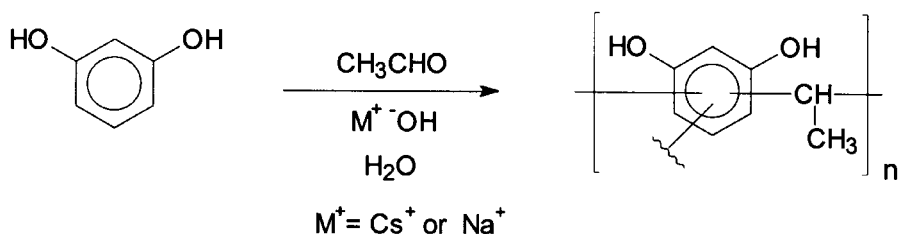
Unlike phenol, the high reactivity of resorcinol with formaldehyde did not allow the formation of a definite product. Nevertheless, with acetaldehyde resorcinol forms in high yields via simple, one-step procedures in acidic media and without using templates or high dilution techniques a cyclotetramer, resorcinarene [10, 11] (Scheme 1). Furthermore, the selective complexation of caesium by resorcinarene has been recently described [12, 13]. It is conceivable that, the possibility of forming resorcinarene in the resorcinol-acetaldehyde resin could make the characterisation of template effects easier, although the presence of macrocyclic structures in phenolic resins remains conjectural [14]. No template effect could be found if resorcinol-acetaldehyde resins were synthesised in acidic conditions because there are only weak interactions between alkali metal ions and the phenolic groups of resorcinol. No resorcinarene could be synthesised in basic media, only resorcinol oligomers were obtained. By using excess of acetaldehyde (i.e. 1.5 eq.) resins were obtained (Scheme 1). So, an investigation into the influence of the nature of the base (alkali hydroxide), which serves as the basic catalyst upon the alkali-metal sorption properties of phenolic resins, was undertaken.



Scheme 1. Synthesis of resorcinarene and resorcinol-acetaldehyde resin.

3.2. EVALUATION OF THE IONOSELECTIVE PROPERTIES OF THE RESINS

In this study, two resorcinol-acetaldehyde resins were compared. They were synthesised using sodium and caesium hydroxide as respective catalysts via methods which have been previously described (Scheme 2) [6]. The ionoselective properties of the two resins were then evaluated.



Scheme 2. Synthesis of resorcinol-acetaldehyde resins.

The high affinity of these resins towards caesium in strong basic condition make difficult the evaluation of their ionoselective properties. In order to decrease the value of the distribution coefficient for caesium, low pH and high concentration of others alkali metal ions (Li^+ , Na^+ , K^+ , Rb^+) were used. The result achieved for the resins with this competitive extraction are detailed in Figure 1.

The selectivity series for the alkali metal ions is as follows: $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ \geq \text{Li}^+$. This is in accordance with extraction studies on high molecular weight phenols [15] and with the values of the thermodynamic equilibrium constants and free energy changes for ion-exchange equilibria between alkali metal cation pairs determined on resorcinol-formaldehyde resins [16].

The extraction of caesium and to less extent the extraction of rubidium and potassium could be explained because the hydration effects have a predominant role in determining the affinity of resorcinol-formaldehyde [16]. But the differences of hydration could not explain the selectivity series observed for resins synthesised with different substituted phenol [6] as well as, in our case, resins synthesised with different base.

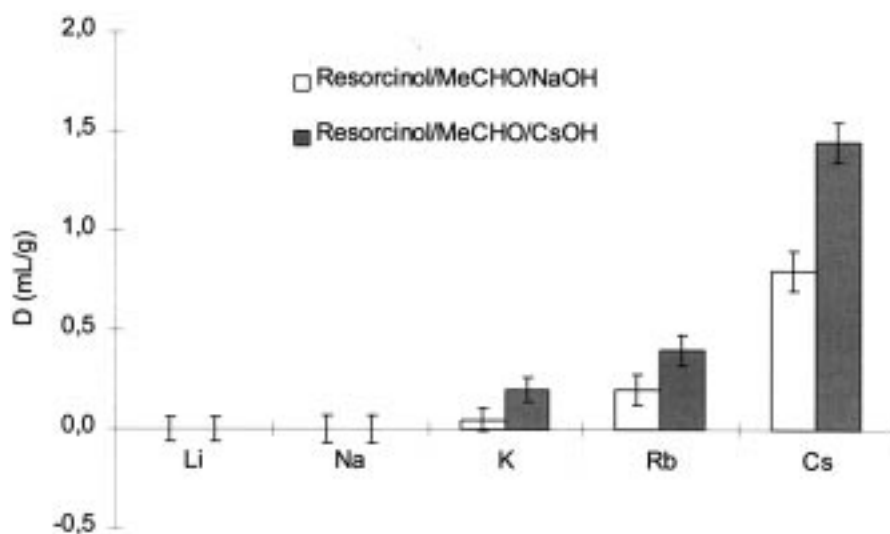


Figure 1. Distribution coefficients of the alkali metal ions using different resins. Conditions: resin (100 mg) was equilibrated five hours with 5 mL of a solution containing $[\text{LiNO}_3] = [\text{KNO}_3] = [\text{RbNO}_3] = [\text{CsNO}_3] = 0.25 \text{ M}$; $[\text{NaOH}] = 0.1 \text{ M}$. pH varied from 13 to 6 due to ion-exchange processes.

One can suggest that structural modification of the resins could explain the improvement of extraction of caesium by the resin synthesised with caesium hydroxide as base. In order to verify this assumption the two resins were compared by ^{13}C solid-state NMR spectroscopy.

3.3. COMPARISON OF STRUCTURAL DATA

The aim of this study was to establish whether ^{13}C CP-MAS (cross polarization magic angle spinning) NMR [17,18] is capable of detecting changes in structure as a function of the nature of the base. Peaks in the ^{13}C CPMAS NMR spectra obtained in this study were assigned on the basis of comparisons with solution-state and solid-state ^{13}C NMR data of resorcinarene. The ^{13}C solid-state NMR spectrum of resorcinarene is showed in Figure 2. Knowing these peak assignments, we were able to compare them with the spectra obtained from the different resins.

The NMR spectra of the two resins were compared (Figure 3). When caesium hydroxide was used for the cross-linking of resorcinol with acetaldehyde (Figure 3a) the spectra were similar to that of resorcinarene. The peak around 155 ppm was assigned to carbon bearing the OH group and the peak around 125 ppm was assigned to unsubstituted carbons in *meta* position to hydroxy. Intensity in the 105 ppm region was assigned to the remaining *ortho* phenol-ring carbons. Those peaks in the 35–20 ppm region can be assigned to the sp^3 carbons, CH and CH_3 respectively. The chemical shift of the aromatic carbons did not change but a slight alteration appears in the region of aliphatic carbons that could be attributed to a

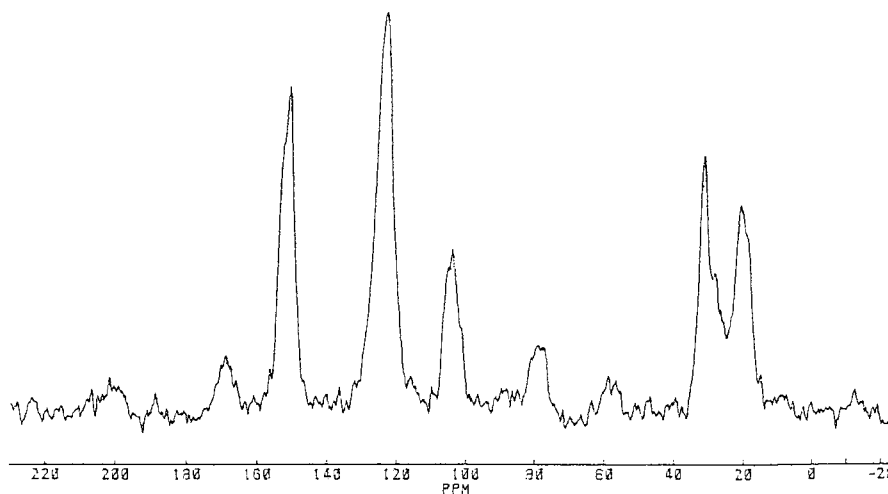


Figure 2. ^{13}C solid-state NMR spectrum of resorcinarene.

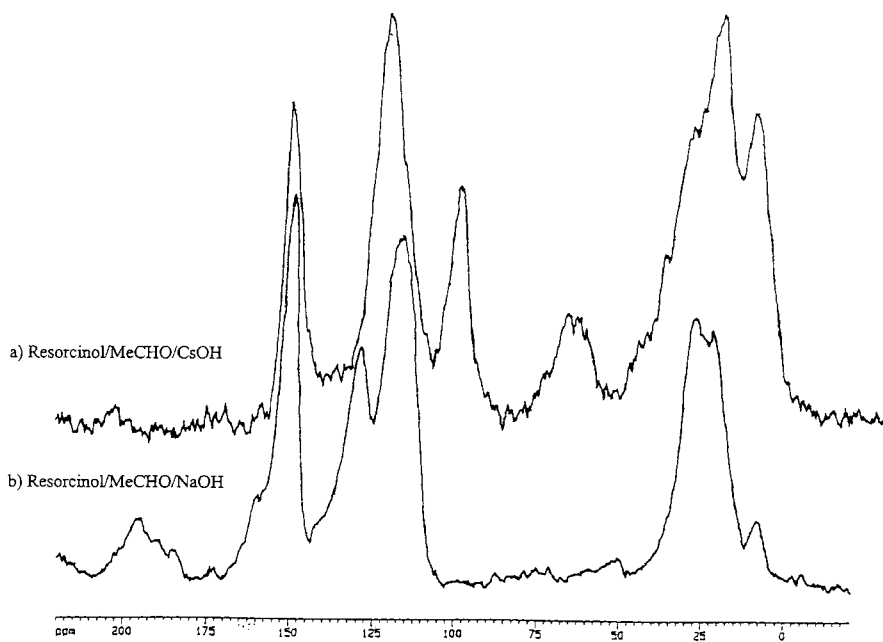


Figure 3. Comparison of ^{13}C solid-state NMR spectra of the different resins. (a) Resorcinol/MeCHO/CsOH, (b) Resorcinol/MeCHO/NaOH.

higher degree of cross-linking. With the resin synthesised using sodium hydroxide many more differences are observed in the region of aromatic carbons (Figure 3b). These differences indicate different types of substitution.

Thus, one can conclude that the process of polymerisation is affected by the nature of the base. In the case of caesium, this could be achieved with the aid of specific interactions of the resorcinol groups with the caesium ions. In particular "cation- π interaction", described as a new type of secondary valence force [19], could play a crucial role. Furthermore, it has been found that these interactions could change calixarene conformation in solution [20]. Thus an oligomer, selective of caesium, could be pre-organised around this cation and then cross-linked with acetaldehyde. The structure could be close to resorcinarene as shown by NMR spectra. In this macrocycle, Li^+ , Na^+ and K^+ ions cannot interact with all four benzene rings. Rb^+ and particularly Cs^+ can rest exactly in the cavity and interact with the four benzene walls simultaneously in η^4 fashion [19].

4. Conclusions

In conclusion, the results presented here underline further the potential of template polymerisation in ionoselective material synthesis. In this report, novel metal ion-imprinted resins were prepared by alkaline polycondensation of resorcinol and acetaldehyde. Caesium template resins exchange the caesium ions more selectively in comparison with no template resins. Furthermore, it is the first time that the guest-induced modification of the structure in the case of phenolic resins was demonstrated. Data from ^{13}C solid state NMR and extraction studies gave prominence to the presence of a structure similar to resorcinarene that could be introduced in the bulk of the resins in one step, leading to an improvement of the ionoselective properties. The selective extraction of caesium may occur because of its dimensional matching to the cavity of, cooperative caesium-arene interaction and the selectivity of the phenolic group for caesium.

References

1. G. Wulff: *Angew. Chem., Int. Ed. Engl.* **34**, 1812 (1995).
2. H. Nishide, J. Deguchi, and E. Tsuchida: *Chem. Lett.* 169 (1976).
3. K. Y. Yu, K. Tsukagoshi, M. Maeda, and M. Takagi: *Anal. Sci.*, **8**, 701 (1992).
4. K. Tsukagoshi, K. Y. Yu, M. Maeda, and M. Takagi: *Bull. Chem. Soc. Jpn* **66**, 114 (1993).
5. A. G. S. H. Högberg: *J. Org. Chem.* **45**, 4498, (1980).
6. N. Dumont, A. Favre-Réguillon, B. Dunjic, and M. Lemaire: *Sep. Sci. Technol.* **31**, 1001 (1996).
7. M. A. Ebra, R. M. Wallace, D.D. Walker, and R. A. Wille: *Scientific Basis for Nucl. Waste Manag.* **6**, 633 (1982).
8. K. Samanta, M. Ramaswamy, and B. M. Misra: *Sep. Sci. Technol.* **27**, 255 (1992).
9. J. R. Kaczvinsky, J. R. Fritz, D. Walker, and M. A. Ebra: *J. Radioanal. Nucl. Chem., Articles* **116**, 63 (1987).
10. A. G. S. Högberg: *J. Org. Chem.* **45**, 4498 (1980).
11. P. Timmerman, W. Verboom, and D. N. Reinhoudt: *Tetrahedron*, **52**, 2663 (1996).

12. E. Gaubert, H. Barnier, L. Nicod, A. Favre-Réguillon, J. Foos, A. Guy, C. Bardot, and M. Lemaire: *Sep. Sci. Technol.* **32**, 2309 (1997).
13. Y. Koide, T. Oka, A. Imamura, H. Shosenji, and K. Yamada: *Bull. Chem. Soc. Jpn* **66**, 2137 (1993).
14. C.D. Gutsche: *Progress in Macrocyclic Chemistry*, in R.M. Izatt and J.J. Christensen (eds.), Vol. 3, Chap. 3, J. Wiley & Sons (1987).
15. L.A. Bray: *Nucl. Sci. Eng.* **20**, 362 (1964).
16. S.K. Samanta and B.M. Misra: *Solv. Extr. Ion Exch.* **13**, 575 (1995).
17. T.G. Neiss and E.J. Vanderheiden: *Macromol. Symp.* **86**, 117 (1994).
18. C.A. Fyfe, M.S. McKinnon, A. Rudin, and W.J. Tchir: *Macromol.* **16**, 1216 (1983).
19. F. Inokuchi, Y. Miyahara, T. Inazu, and S. Shinkai: *Angew. Chem. Int. Ed. Engl.* **34**, 1364 (1995).
20. R. Ungaro, A. Casnati, F. Ugozzoli, A. Pochini, J.F. Dozol, C. Hill, and H. Rouqueete: *Angew. Chem. Int. Ed. Engl.* **33**, 1506 (1994).