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Effect of water removal on the textural properties of resorcinol/formaldehyde gels by azeotropic distillation

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The resorcinol/formaldehyde gels containing 5% (w/v) of reactants have been prepared. After curing for seven days, the gel is treated with trifluoroacetic acid to initiate the condensation of hydroxymethyl groups. Drying of the prepared gels is done by removing water with the help of vacuum heterogeneous azeotropic distillation using amyl acetate and *n*-butanol. The textural properties of the gels thus obtained are compared with the properties of the gel obtained from exchange of water by acetone (control experiment). The pore volume and average pore diameter of the gel obtained from the azeotropic distillation of water with amyl acetate are 0.7663×10^{-3} m^3/kg and 0.0145 μm, respectively. These values are 1.5 times higher than the values obtained by vacuum heterogeneous azeotropic distillation with *n*-butanol and about twice than the values obtained in the control experiment. The surface areas in all the three gels are almost constant.

1. Introduction

Resorcinol/formaldehyde gels are the precursors for the preparation of carbon aerogel electrodes in capacitive deionization of water [1]. Resorcinol/formaldehyde (abbreviated as R/F) gels are formed by the aqueous sol-gel polymerisation of resorcinol with formaldehyde under alkaline conditions. The reaction results in the formation of a mixture of addition and condensation intermediates. These intermediates combine to form a crosslinked polymer network [2, 3].

In order to obtain highly porous xerogels, water is usually removed by critical point drying technique [2]. Simple evaporation of water causes shrinkage of the gels due to surface tension effects [4]. However, critical point drying minimises shrinkage of the gel by eliminating vapour-liquid interface, thus resulting in zero surface tension.

Unfortunately, the critical point drying of hydrogels requires extreme process conditions (temperature and pressure). These extreme conditions may lead to potential hazards of mechanical, thermodynamic and chemical nature [5].

To avoid the above mentioned hazards, vacuum heterogeneous azeotropic distillation (abbreviated as VHAD) has been applied to remove water from R/F gels. This paper gives the textural data of R/F gels thus obtained by VHAD. Porosity results of these gels are then compared with that of control experiment gel.

2. Experimental

2.1. Chemicals

Resorcinol (99%) and *n*-butanol (99%) were from BDH Ltd. Formaldehyde (35%, methanol stabilised), sodium carbonate monohydrate and trifluoroacetic acid (99%) were from E. Merck. Amyl acetate (99%) was purchased from Fluka. Acetone used was of commercial grade. Stock solutions of 0.29 M resorcinol, 0.58 M formaldehyde and 0.003 M sodium carbonate were prepared in distilled water.

2.2. Preparation of gels

Gels were prepared according to the procedure given in the literature [2]. For the synthesis of gel containing 5% (w/v) reactants, equal volumes (100 ml each) of 0.29 M resorcinol and 0.58 M were mixed in a beaker and pH of the solution was adjusted to 5.72 with 62 ml of 0.003 M sodium carbonate solution. The pH adjusted R/F solution was then transferred to a flask which was stoppered. The contents of the flask were polymerised at 85 °C for about eight days in an oven.

After completion of the polymerisation, transparent orange red coloured gel was observed. The flask contents were cooled at room temperature and supernatant liquid was decanted off. The gel was transferred into a jacketed cylindrical glass vessel and soaked in 0.125% trifluoroacetic acid. The vessel was shaked mechanically and its temperature was kept at 45 °C for three

TABLE I Textural properties of different gels

Gel designation	Water removed from gel by	Pore volume, V (m^3/kg)	Total surface area, A (m^2/kg)	Average pore diameter, $4V/A$(μm)
G1	exchange with acetone[a] and subsequent evaporation	0.3431×10^{-3}	192.572×10^{3}	0.0071
G2	VHAD[b] with n-butanol	0.5051×10^{-3}	205.446×10^{3}	0.0098
G3	VHAD with amyl acetate	0.7663×10^{-3}	211.951×10^{3}	0.0145

[a] Exchange of water with acetone was done at 45 °C.

[b] VHAD stands for vacuum heterogeneous azeotropic distillation.

days. Trifluoroacetic acid treatment was given to cause further condensation of hydroxymethyl groups. After completion of the acid treatment, the gel was washed thoroughly with distilled water until neutral pH.

2.3. Water removal from hydrogels

Hydrogel was divided into three portions in order to apply different methods of water removal which are detailed below:

2.3.1. Exchange of water with acetone and subsequent evaporation

First portion of the hydrogel was taken in a cylindrical jacketed glass vessel maintained at 45 °C. To it added a sufficient quantity of acetone. After exchange for four days, excess acetone was decanted off and the gel was air dried. After air drying, colour of the gel changed from orange red to brownish black and a significant shrinkage of the gel was also observed. Air dried gel was then dried in an oven at 100 °C overnight. The gel obtained by this procedure is designated as G1 for further reference.

2.3.2. Water removal by VHAD using organic solvents (n-butanol and amyl acetate)

Second portion of the hydrogel of neutral pH was transferred to a quickfit round bottom flask and a calculated amount of *n*-butanol was added to it. The amount of *n*-butanol was estimated by its azeotropic composition with water [6] and assuming that hydrogel consists of 100% water. An azeotropic distillation of water with *n*-butanol was carried out in a rotary vacuum evaporator. During distillation, flask was rotated at a speed of 60 rpm in a water bath maintained at 60 °C. After completion of azeotropic distillation, gel was washed thoroughly with acetone in order to remove *n*-butanol present in the pores of the gel. After air drying, gel was further dried in an oven at 100 °C overnight. The xerogel obtained by this procedure is designated as G2.

A similar procedure was adopted for the removal of water from third portion of the hydrogel with amyl acetate. The gel was then given an identical washing and drying treatment. Air dried gel was further dried in an oven at 100 °C overnight. The brownish black coloured xerogel obtained by this procedure is designated as G3.

2.4. Characterisation of gels

Textural properties of R/F gels were measured by using mercury porosimeter (AUTOPORE II 9220, Micromeritics). Contact angle of 130° was used for pore diameter and surface area calculation. Textural properties of the gels G1, G2 and G3 are given in Table I.

3. Results and discussion

The measured textural properties of the R/F gels are given in Table I. R/F hydrogel contains a lot of water. To get a solid gel (xerogel), evaporation of this water is necessary. During evaporation, a liquid-vapour interface enters ultimately within the pores of the gel [5]. The surface tension of the liquid creates a concave meniscus and exerts compressive forces on the walls of the pore resulting in shrinkage of the gel. To minimise the effect of gel shrinkage, VHAD of water from the gels G2 and G3 with *n*-butanol and amyl acetate respectively (with surface tension values lower than water) was carried out. The gel G1 obtained in the control experiment was used to compare the effect of VHAD on the textural properties of gels.

The gel G1 shows the lowest pore volume and average pore diameter as compared to the gels G2 and G3. This indicates that less shrinkage occurred in gels G2 and G3 as compared to the gel G1. However, total surface area of the gels G1, G2 and G3 are almost similar. This is due to the reason that the same starting hydrogel (having same initial sol size) was used to prepare xerogels G1, G2 and G3. It may be mentioned that the surface tension values of *n*-butanol and amyl acetate are almost same. But the gel G2 obtained by using *n*-butanol has pore volume and average pore diameter 1.5 times less than that of the gel G3 obtained by using amyl acetate.

The solvent, *n*-butanol has higher hydrogen bonding tendency as compared to amyl acetate. Thus the former exerts greater attractive force (through hydrogen bonding) resulting in higher shrinkage as compared to the later one. Another way of explaining this phenomena is that *n*-butanol wets the gel more as compared to amyl acetate resulting in higher capillary pressure [7]. The magnitude of the capillary pressure (P_c) experienced by the network depends on the surface tension (γ), the cos of contact angle ($\cos\theta$) and the pore radius (r) and is equal to $2\gamma\cos(\theta)/r$. This means that $\cos(\theta)$ in case of *n*-butanol is larger as compared to amyl acetate.

Table I shows that VHAD has considerable effect on the textural properties of the gels. The pore volume and average pore diameter values of G3 are double as compared to the gel G1.

4. Conclusions

The results presented in this paper lead to the conclusion that VHAD is a better technique for removing water from the R/F gel as compared to simple exchange of water by acetone at 45 °C. By using amyl acetate as a solvent in VHAD, a two fold increase in values of pore volume and average pore diameter is observed as compared to the gel obtained in the control experiment. Total surface area values of the three gels G1, G2 and G3 are almost constant. By comparing the porosity data of R/F gels, it is obvious that amyl acetate is a better solvent for removal of water in VHAD than *n*-butanol. However, VHAD cannot produce gels with textural properties obtainable by supercritical drying.

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