

N-Vinylcarbazole-Divinylbenzene Copolymer. The Effect of Different Diluents on the Formation of Porous Structure in Suspension Polymerization

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Summary: N-Vinylcarbazole(NVC)-divinylbenzene(DVB) copolymer beads of porous structure were prepared by suspension polymerization in different solvating, non-solvating and mixture of diluents. These diluents having different affinities for the copolymers, produced changes in their morphology particularly with respect to porosity, pore size distribution and specific surface area and subsequently density and mechanical strength. It was observed that the use of relatively less solvating diluent results in more porous, large pore size distribution and large surface area and subsequently small density and poor mechanical strength copolymer beads and vice versa under the given experimental conditions. The use of a mixture of an appropriate solvating and non-solvating diluents could result in copolymer beads of desired characteristics.

The cation-exchange resins prepared by the sulfonation of the respective copolymer beads were checked for their Na⁺ ions capacity. The capacity varies from 3.45 to 4.10 meq/g. That means it does not change markedly with the change in diluent or mixture of diluents under the given experimental conditions.

Introduction

Ion-exchange resins are required in various purification circuits of moderators and coolants. Beside the basic functions of removing impurities it is also expected to remove the corrosion and fission products at trace levels. These resins are expected to withstand high radiation fields and oxidizing conditions prevalent in the reactor systems. The resins frequently used in the nuclear industry are mostly synthetic organic strong acid cation-exchangers and strong base anion-exchangers. Because of stringent specifications of the nuclear power plants the resins of improved characteristics different from that of the standard commercial products used in conventional water treatment are required. In order to meet these requirements a novel method has been developed by Sederel and De Jong [1]. In this method a mixture of solvating and non-solvating diluents has been used to produce a resin of required porosity mainly in the case of styrene and divinylbenzene system [2-5].

In view of this, it was of particular interest to synthesize strong acid cation-exchange resins of desired characteristics using NVC as a monomer and DVB as a crosslinking agent. The synthesis of

NVC-DVB copolymers by using anhydrous AlCl₃ as a catalyst [6] and their subsequent conversion into cation-exchange resins [7] by sulfonation have been reported in the literature. The resulting NVC-DVB copolymers and their respective cation-exchange resins have been mainly characterized for their thermal stability.

In this work copolymers were prepared by the radical polymerization of NVC with DVB by using the technique of suspension polymerization. The diluents of different chemical nature and combination of different solvating and non-solvating diluents were used in these polymerization experiments as an organic phase in a hope to obtain the desired results. The effect of these diluents was studied on the resulting copolymers with respect to their apparent density, porosity, surface area and mechanical strength. The copolymers were then converted into their respective cation-exchange resins by sulfonation. The ion-exchange capacity of these resins was determined with respect to Na⁺ ions. The results thus obtained are presented and discussed in this paper.

Results and Discussion

A series of NVC-DVB suspension copolymerization experiments were carried out using diluents of different solvating and non-solvating nature and functional groups. The resulting copolymer beads were characterized for their apparent density, porosity, surface area and mechanical strength. The experimental data is given in Table I. It can be seen from this Table that the density of the respective copolymer beads prepared by using hydrocarbons as a diluent decreases in the following order: Benzene > Toluene > Cyclohexane > Dodecane > Petroleum ether. In view of these results petroleum ether should be considered the most non-solvating and benzene a least non-solvating diluent in this work. This trend is also observed in their results of porosity and surface area whereas it is reverse in the case of mechanical strength. The density of the copolymer beads

prepared in the halogenated hydrocarbons decreases in the following order: Chlorobenzene > Dichloroethane > Bromobutane > Bromobenzene. The same trend is observed with respect to the mechanical strength whereas it is reverse in the case of porosity and surface area. These results are complementary to one another that means the decrease in density and mechanical strength is due to an increase in porosity and surface area of the respective copolymer beads. It is worth mentioning here that the use of chlorobenzene as a diluent yields copolymer beads of relatively high density (0.62) than the bromobenzene (0.5). This is most probably due to the fact that bromobenzene occupies relatively less space between nuclei, developed due to entanglement and crosslinkage of growing copolymer chain and microspheres (agglomerated nuclei), which agglomerate further to form the resulting copolymer beads than chlorobenzene under the given experimental conditions. The results

Table 1: The apparent density, porosity, surface area, mechanical strength and capacity of the NVC-DVB copolymers / resins, synthesized in different solvating / nonsolvating diluents.

Cross-linkage, DVB = 20%, Solvent fraction, $F_s = 0.6$

Diluents	Density (g/ml)	Capacity (meq/g)	Porosity Vp by Mercury Porosimeter (ml/g)	Surface area by BET Method (m ² /g)	Mechanical strength (Bead size = 200µm) (Newtons)
HYDROCARBONS					
Benzene	0.60	3.45	0.13	9	1.60
Toluene	0.53	3.50	0.18	13	1.29
Cyclohexane	0.48	3.48	0.40	—	0.60
Dodecane	0.26	3.90	1.20	87	0.20
Petroleum ether	0.25	4.00	1.26	89	0.18
HALOGENATED HYDROCARBONS					
Dichloroethane	0.58	3.70	0.18	15	1.30
Bromobutane	0.55	3.69	0.27	54	0.93
Chlorobenzene	0.62	3.57	0.15	13	1.40
Bromobenzene	0.50	3.87	0.31	74	0.83
ESTERS					
Methylpropionate	0.60	3.74	0.15	14	1.35
Isobutylpropionate	0.49	4.10	0.30	47	0.80
Dimethylphthalate	0.45	3.90	0.32	49	0.73
Diethylphthalate	0.39	3.95	0.40	73	0.64
Dioctylphthalate	0.34	3.89	0.59	90	0.45
ALCOHOLS					
2-Butylalcohol	0.59	3.58	0.16	19	1.37
Tertiaryamylalcohol	0.56	3.64	0.18	21	1.25
Benzylalcohol	0.32	3.90	0.84	30	0.27
KETONES					
Cyclohexanone	0.55	3.99	0.19	10	1.20
Methylisobutylketone	0.58	4.00	0.18	11	1.34
ETHERS					
Dioxane	0.70	3.79	0.12	10	1.69
Diisopropylether	0.52	4.20	0.28	68	—
Diisobutylether	0.48	3.91	0.37	48	0.73

NVC = N-Vinylcarbazole, DVB = Divinylbenzene, Solvent fraction = Amount of diluent / (Amount of diluent + Monomers)

obtained for the NVC-DVB copolymer beads prepared in a suspension containing ester as a diluent show that the density and mechanical strength decrease in the following order: Methylpropionate > Isobutylpropionate > Dimethylphthalate > Diethylphthalate > Dioctylphthalate whereas the porosity and surface area increase in the reverse order. These results are very interesting in a way to demonstrate that a slight increase in substituted alkyl group increases the porosity and surface area whereas it decreases the density and mechanical strength of the respective copolymer beads. A similar effect is also observed in the characteristics of these beads prepared in cyclic esters as compared to aliphatic ones (Table I). The density and mechanical strength of the copolymer beads prepared in a suspension containing alcohols decrease in the following order: 2-Butylalcohol > Tertiaryamylalcohol > Benzylalcohol whereas porosity and surface area increase in the reverse order. The characteristics of the copolymer beads prepared using ketones as an organic phase are somewhat similar to one another. The NVC-DVB copolymer beads were also prepared by using ethers

as diluents. The density and mechanical strength of these copolymer beads decreases in the following order: Dioxane > Diisopropyl ether > Diisobutyl ether whereas the porosity and surface area increase in the reverse order. These results are in agreement with the above mentioned explanation that the size of functional group of a diluent play an important role in the preparation of copolymer beads.

It can be concluded in general on the basis of these results that the mechanical strength (crushing load, L) of the copolymer beads of a given diameter decreases asymptotically with the increase in pore volume V_p (Figure 1). In other words the porous copolymer beads of relatively small porosity exhibit better mechanical strength and vice versa whereas in turn porosity depends on the solvating/non-solvating nature of the diluent.

Figure 2 shows the dependence of crushing load on $(1-V_p)/V_p$. The resulting straight line of this Figure validates the relationship between the different characteristics of porous copolymer beads already reported in the previous paper [14].

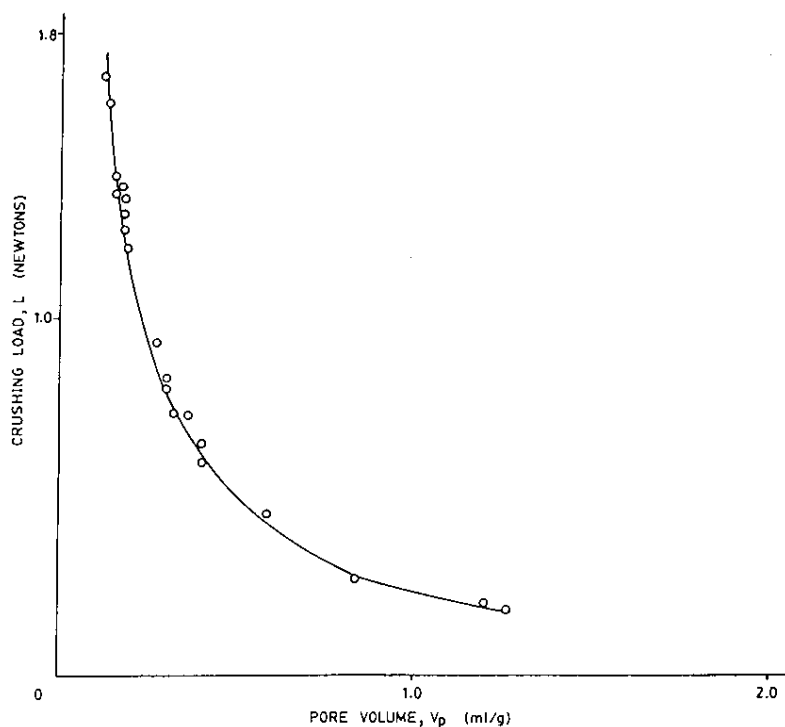


Fig. 1: The dependence of crushing load, L (Newtons) on the porosity, V_p (ml/g) using different diluents (Table I).

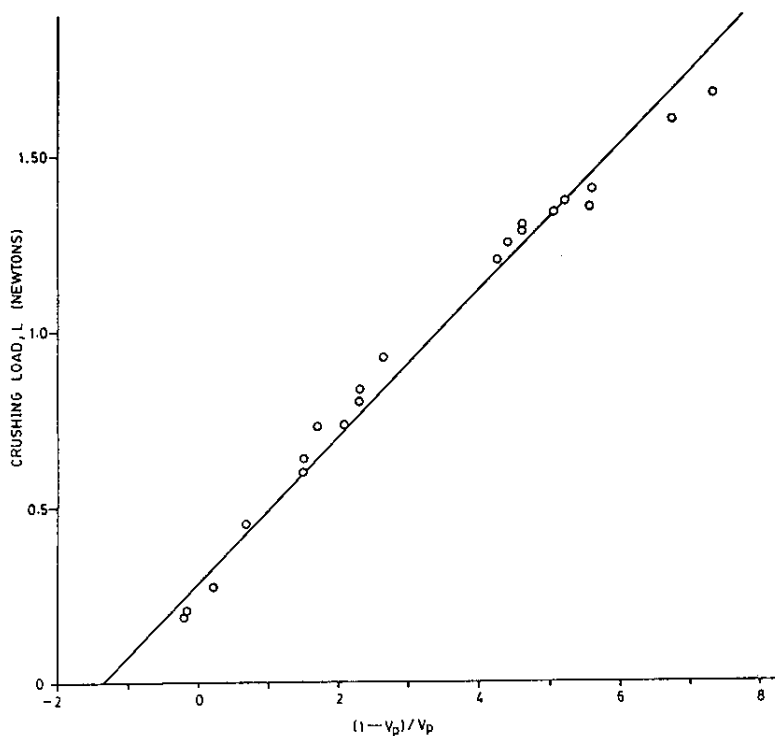


Fig. 2: The dependence of crushing load, L (Newtons) on $(1-V_p)/V_p$ using different diluents (Table I).

$$\frac{L}{D^2} = 4k \frac{(1-V_p)}{V_p} \frac{T}{r} + C$$

Here

L = Mechanical strength of copolymer bead

D = Overall bead diameter

V_p = Pore volume (porosity)

T = Surface tension

k = Constant

C = A factor represents the chain breaking with catalyst, monomers, diluents, other components of polymerization system and impurities such as inhibitors of polymerization.

r = Radius of constituent particles (nuclei). This is independent of D, much smaller in

magnitude and nearly constant for a given copolymer bead, irrespective of bead size.

This equation further shows that as the porosity increases, so the mechanical strength of a copolymer bead of given diameter will decrease.

Figure 3 shows the dependence of percentage pore volume on the pore diameter of copolymer beads synthesized in different diluents, generally known as pore size distribution curves. The distribution curves (Figure 3 a) are of those copolymer beads synthesized in toluene, chlorobenzene, bromobenzene, cyclohexane and dodecane. It can be seen from these curves that a change in the functional group of benzene causes a slight but persistent shift from small pore size to relatively large pore size in the following order: Toluene < Chlorobenzene < Bromobenzene. It is also worth mentioning here that the distribution curves tend to shift towards larger pore size when the diluent of copolymerization experiment changed from aromatic (bromobenzene) to cyclic aliphatic (cyclohexane) to straight chain aliphatic (dodecane)

compounds. The distribution curves (Figure 3 b) are of those copolymer beads synthesized in a suspension containing different esters. Here too, the relatively large functional group in phthalates tends to shift the pore size distribution curve towards a larger pore

size. A similar behaviour can also be seen when methyl propionate and isobutylpropionate are used as diluents. The pore diameter of copolymer beads synthesized using phthalates and isobutylpropionate mainly vary from 0.03 to 0.12 μm whereas the

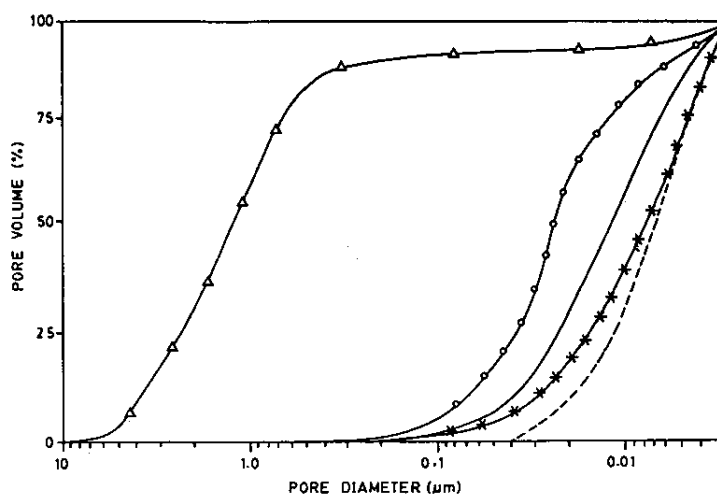


Fig. 3(a): The dependence of pore volume(%) on pore diameter (μm) of NVC-DVB copolymer beads synthesized using different hydrocarbons as diluents.

- - - - - Toluene, *-*-* Chlorobenzene, — Bromobenzene, —○—○— Cyclohexane,
—△—△— Dodecane.

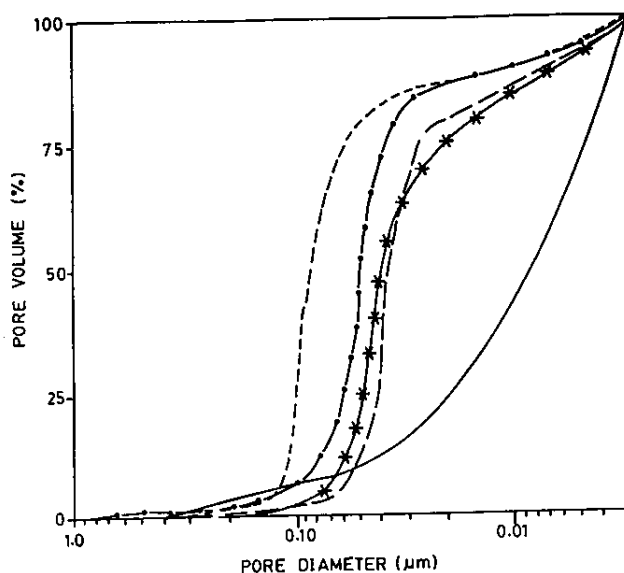


Fig. 3(b) The dependence of pore volume (%) on pore diameter(μm) of NVC-DVB copolymer beads synthesized using esters as diluents.

- - - - - Diethylphthalate, —●—●— Diethylphthalate, *-*-* Dimethylphthalate,
———— Methyl propionate, — — — Isobutylpropionate

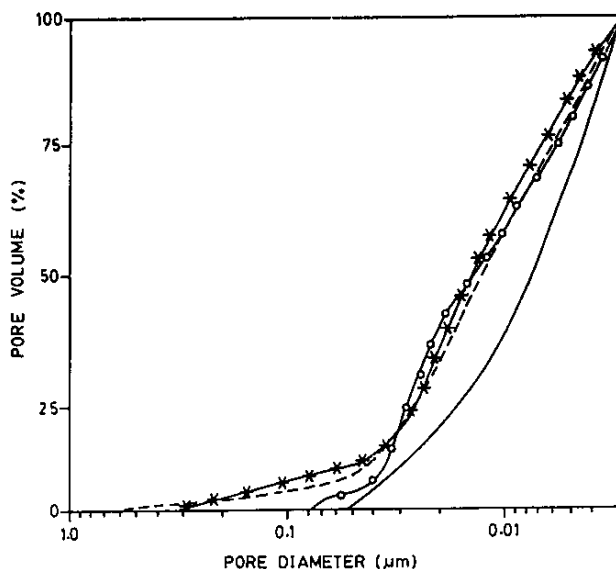


Fig. 3(c) The dependence of pore volume(%) on pore diameter(μm) of NVC-DVB copolymer beads synthesized using ethers and ketones as diluents.
 - - - - Diisopropylether, ——— Dioxane, —○—○— Methylisobutylketone,
 —*—*— Cyclohexanone

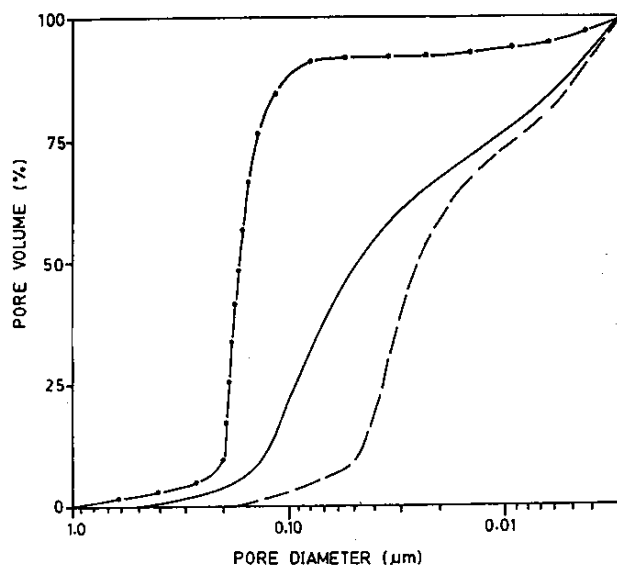


Fig. 3(d) The dependence of pore volume(%) on pore diameter(μm) of NVC-DVB copolymer beads synthesized using alcohols as diluents.
 —●—●— Benzylalcohol, — — — 2-Butanol, ——— Tertiary amylalcohol

respective copolymer beads (subsequent resin) have a reasonably narrow range of pore size particles (nearly mono-pore size particles) required for better

resolution. The distribution curves (Figure 3 c) are of those copolymer beads synthesized using ketones and ethers as diluent. The curves are very similar to one

another except for the one where dioxane was used as a diluent. The pore diameter of copolymer beads prepared in these diluents varies mainly from 0.005 to 0.03 μm . This range of pore size suggests that the relatively small pore size particles are formed as compared to the above mentioned systems under the same experimental conditions. The distribution curves (Figure 3 d) are of those copolymer beads synthesized using alcohols as diluents. It can be seen from these curves that they tend to shift from small pore size to relatively large pore size in the following order: 2-Butanol < Tertiaryamylalcohol < Benzylalcohol. The pore size is almost uniform for most of those beads prepared in benzylalcohol as diluents.

Scanning electron microscopy (SEM) was employed in order to know the morphology of the copolymer beads. Figure 4 shows SEM photographs of copolymer beads prepared in the presence of dioctylphthalate: (a) spherical shape of a bead (b) presents a surface of a bead consisting of agglomerates of various sizes, separated by large interstices (c) presents a cross-section of macroporous copolymer bead indicating mostly through channels, separated by interstices.

In view of the porosity data in conjunction with SEM findings it can be suggested that the pores are the interstices and their dimensions depend on the nature of diluent used in the synthesis of copolymer beads. The intermediate pores are those spaces which exist between the microspheres that form agglomerates whereas the micropores are the voids between the nuclei those form the microspheres. In turn the nuclei are developed due to the entanglement and crosslinkage of growing copolymer chains after a certain extent of conversion from monomers to the copolymer, a phase separation occurs between copolymer and diluent phases.

The copolymers (NVC-DVB) prepared by using different diluents were subsequently converted into respective cation-exchange resins by sulfonation and they were characterized for their Na^+ ions capacity (Table I). It can be seen from these results that the change of diluent does not cause a significant difference in capacity (3.45 to 4.20 meq/g) under the given experimental conditions.

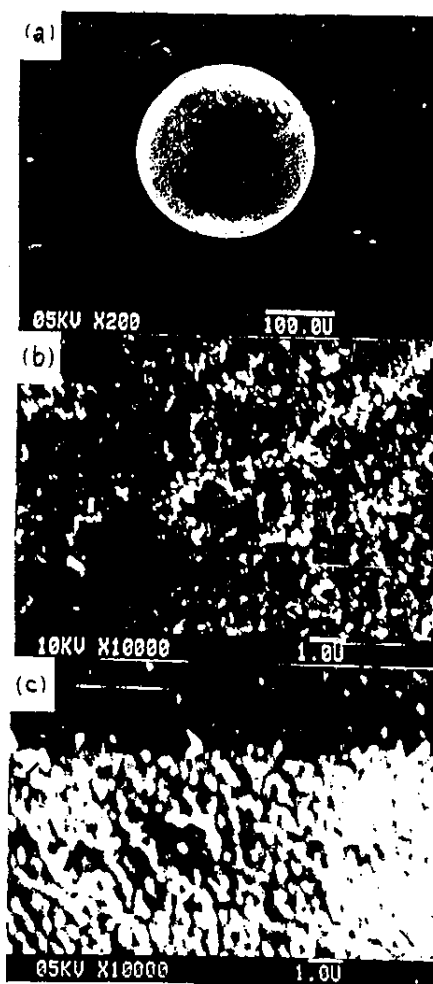


Fig. 4: SEM photographs of copolymer beads prepared in the presence of dioctylphthalate: (a) shape; (b) surface; and (c) cross-section of copolymer bead.

Certain polymerization experiments were also carried out using 1:1 combination of solvating and non-solvating diluents. In one set of experiments, petroleum ether, a well known non-solvating diluent was used in combination with solvating diluents such as dioctyl-, dibutyl-, diethyl-, dimethylphthalate, bromobenzene, cyclohexanone, toluene, chlorobenzene, dioxane and benzene whereas in the second set cyclohexanone (solvating diluent) was used in combination with non-solvating diluents such as dodecane, benzylalcohol, isobutylpropionate, methyl isobutylketone, 1-butanol, diisobutylether and

methylpropionate. The experimental data is presented in Table II. It can be seen from the results of first set of copolymerization experiments that the density of the copolymer beads increases from 0.28 to 0.38g/ml with the change in solvating diluents in the following order: Dioctylphthalate < Bromobenzene = Dibutylphthalate < Cyclohexanone = Diethylphthalate < Toluene < Dimethylphthalate = Chlorobenzene < Dioxane = Benzene whereas the porosity decreases slightly but consistently from 0.98 to 0.61 ml/g in the following order: Benzene < Dioxane < Chlorobenzene < Dimethylphthalate < Toluene = Diethylphthalate < Cyclohexanone < Dibutylphthalate < Bromobenzene < Dioctylphthalate. These results are complementary to one another in a sense that the increase in density causes the decrease in porosity of a given sample of copolymer beads. It can also be seen from Table II that the increase in porosity means subsequent increase in surface area of copolymer beads prepared under the given experimental conditions.

Figure 5 shows the dependence of crushing load, L (mechanical strength) on the porosity, V_p of the copolymer beads of a given diameter (200 μ m). These results demonstrate the fact that increase in porosity decreases the mechanical strength of a given

macroporous copolymer beads. The resulting straight line developed from the dependence of crushing load on $(1-V_p)/V_p$ also demonstrate the validity of the relationship between different characteristics of macroporous copolymer beads as mentioned above.

Figure 6 shows the pore size distribution curves of those copolymer beads prepared by using petroleum ether in combination with phthalates as diluents. It can be seen that these curves tend to shift from small pore size to relatively large pore size in the following order: Dimethylphthalate < Diethylphthalate < Dibutylphthalate < Dioctylphthalate. These pore size distribution curves are very similar to those curves of copolymer beads prepared in the respective phthalates except that the combination of phthalates with petroleum ether tends to shift them towards larger pore size. These results are complementary to the porosity data of the respective copolymer beads (Table I and II).

The Na^+ ions capacity of NVC-DVB cation-exchange resins varies from 3.80 to 4.03 meq/g. These results suggest that the change in solvating diluents does not cause a significant difference in the capacity of resins under the given experimental conditions.

Table 2: The apparent density, porosity, surface area, mechanical strength and capacity of the NVC-DVB copolymers / resins, synthesized in different solvating - nonsolvating diluents.

Cross-linkage, DVB = 20%, Solvent fraction, $F_s = 0.6$

Diluents		Density (g/ml)	Capacity (meq/g)	Porosity V_p by Mercury Porosimeter (ml/g)	Surface area by BET Method (m^2/g)	Mechanical strength (Bead size = 200 μ m) (Newtons)
1st Set of Experiments						
Petroleum ether	Dioctylphthalate	0.28	3.88	0.98	150	0.26
"	Bromobenzene	0.33	3.90	0.91	132	0.30
"	Dibutylphthalate	0.33	3.80	0.82	130	0.32
"	Cyclohexanone	0.35	3.90	0.77	128	0.43
"	Diethylphthalate	0.35	4.01	0.75	110	0.45
"	Toluene	0.36	3.98	0.75	80	0.45
"	Dimethylphthalate	0.37	4.10	0.69	75	0.57
"	Chlorobenzene	0.37	4.03	0.66	74	0.59
"	Dioxane	0.38	3.98	0.65	67	0.60
"	Benzene	0.38	4.03	0.61	65	0.70
2nd Set of Experiments						
Cyclohexanone	Dodecane	0.26	3.90	0.83	97	0.35
"	Benzylalcohol	0.33	3.81	0.71	64	0.45
"	Diisobutylether	0.37	3.59	0.58	27	0.53
"	Isobutylpropionate	0.41	3.69	0.45	60	0.60
"	Methylisobutylketone	0.48	3.87	0.38	33	0.80
"	1-Butanol	0.50	3.73	0.29	30	1.11
"	Methylpropionate	0.58	3.80	0.23	5	1.40

NVC = N-Vinylcarbazole, DVB = Divinylbenzene, Solvent fraction = Amount of diluent / (Amount of diluent + Monomers)

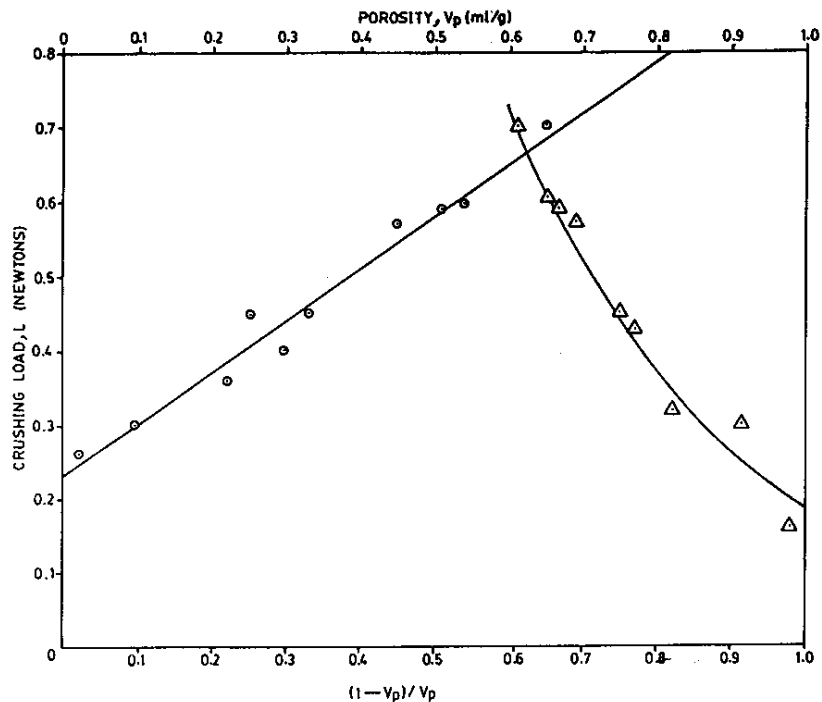


Fig. 5: The dependence of crushing load, L (Newtons) on porosity, V_p and $(1-V_p)/V_p$ using different diluents in combination with petroleum ether.
 —○—○— Crushing load vs. $(1-V_p)/V_p$, —△—△— Crushing load vs. V_p

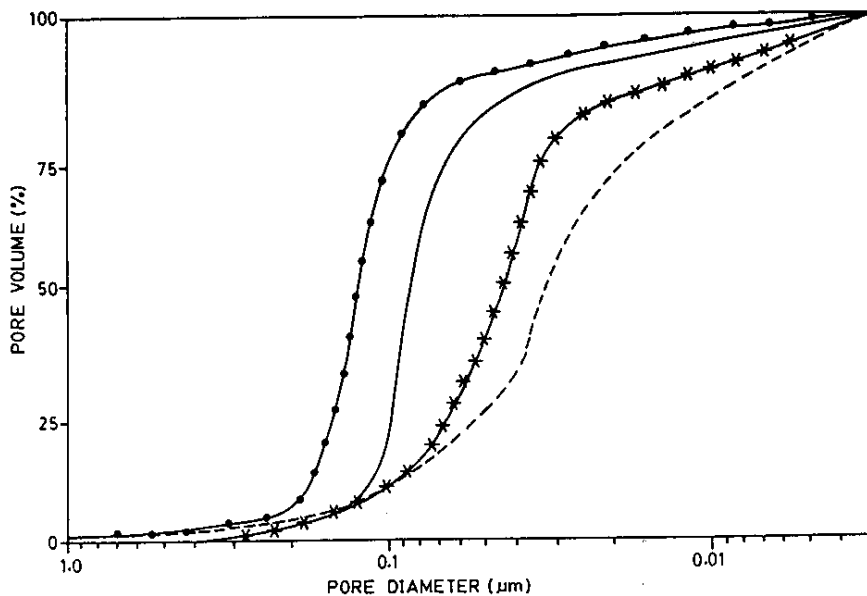


Fig. 6: The dependence of pore volume(%) on pore diameter(μm) of NVC-DVB copolymer beads synthesized using phthalates in combination with petroleum ether.
 - - - - Dimehylphthalate, —●—●— Dioctylphthalate, —*—*— Diethylphthalate,
 ———— Dibutylphthalate

In the second set of experiments, cyclohexanone, a well recognized solvating diluent was used in combination with non-solvating diluents such as dodecane, benzylalcohol, isobutylpropionate, methylisobutylketone, 1-butanol, diisobutylether and methylpropionate to synthesize NVC-DVB copolymer beads. The experimental data is given in Table II. The density of the copolymer beads increases with respect to non-solvating diluents in the following order: Dodecane < Benzylalcohol < Diisobutylether < Isobutylpropionate < Methylisobutylketone < 1-Butanol < Methylpropionate whereas the porosity and surface area decreases in the reverse order. These characteristics are complementary to one another as expected for macroporous copolymer beads. Figure 7 shows the pore size distribution curves for the copolymer beads. It can be seen from these curves in comparison with those presented in Figure 3 for the respective diluent that the combination of diluents placed them at an intermediate position. In another words the combination of solvating and non-solvating diluents influence the resulting copolymer beads in such a way that it can be exploited to prepare copolymer beads of desired characteristics.

Figure 8 shows the dependence of crushing load, L on the porosity, V_p and $(1-V_p)/V_p$ of the copolymer beads of a given diameter ($200 \mu\text{m}$). The observed trends are in agreement with the above mentioned results of the first set of copolymerization experiments and can be interpreted in a similar fashion.

It can be seen from Table II that the Na^+ ions capacity (3.59 to 3.90 meq/g) of the NVC-DVB cation-exchange resins subsequently prepared from the respective copolymer beads does not change significantly by the change of non-solvating diluent in the given combination of solvating and non-solvating diluents.

In the light of these results it can be concluded that relatively porous copolymer beads can be synthesized by using a non-solvating diluent (bad solvent) as compared to a solvating diluent (good solvent). It can be further stated that NVC-DVB copolymer beads and subsequently cation-exchange resin of desired density, porosity, pore size distribution, surface area and mechanical strength

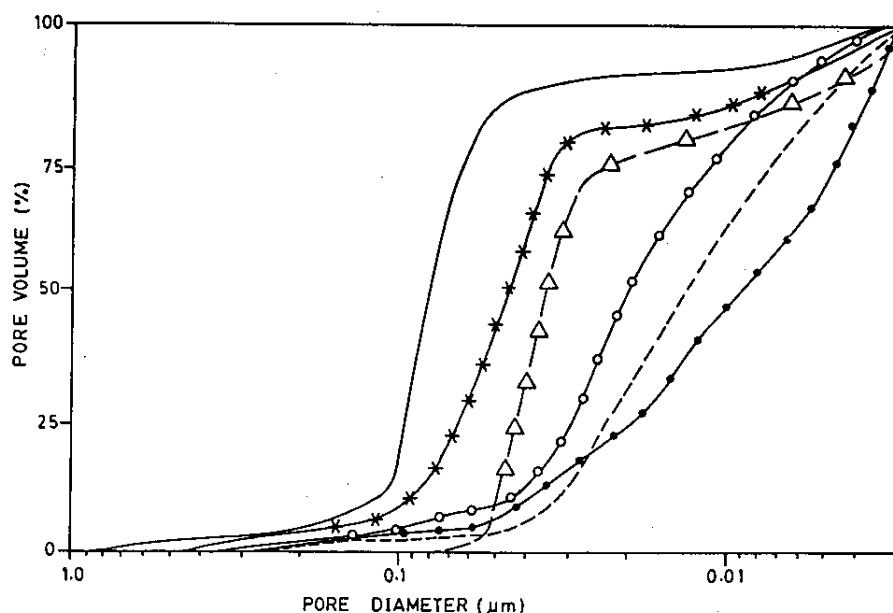


Fig. 7: The dependence of pore volume(%) on pore diameter(μm) of NVC-DVB copolymer beads synthesized using different diluents in combination with cyclohexanone.

—●—●— Methylpropionate, — — — Methylisobutylketone,
—○—○— Isobutylpropionate, —Δ—Δ— Butanol, — — — Dodecane,
—*—*— Benzylalcohol

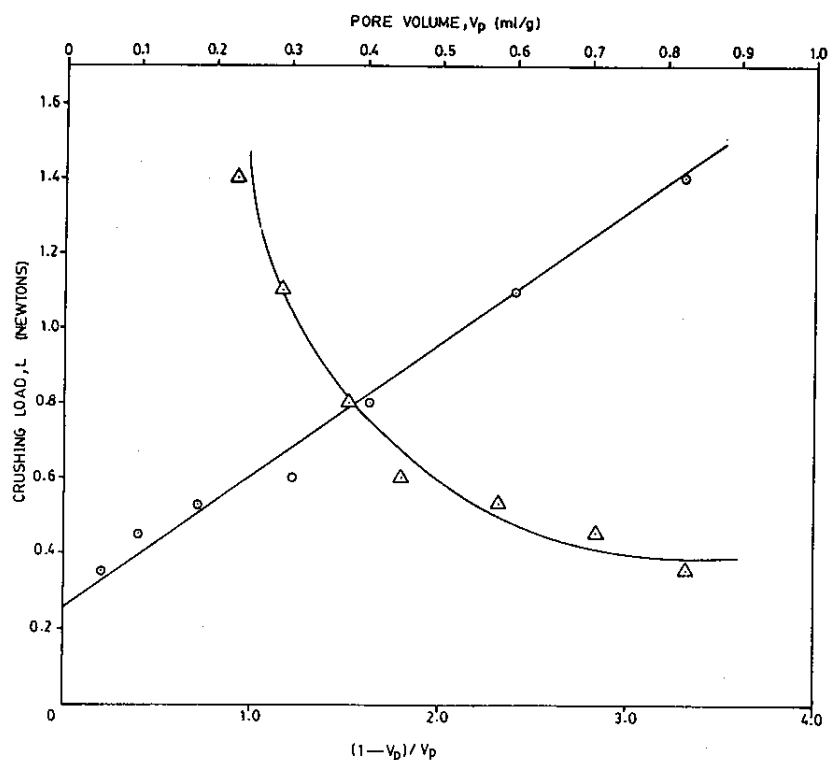


Fig. 8: The dependence of crushing load, L (Newtons) on porosity, V_p and $(1-V_p)/V_p$ using cyclohexanone in combination with different diluents.

—○—○— Crushing load vs. $(1-V_p)/V_p$, —△—△— Crushing load vs. V_p

can be synthesized by the use of right combination of solvating and non-solvating diluents under the given experimental conditions.

Experimental

N-Vinylcarbazole 95% pure supplied by Fluka Chemicals, Switzerland was recrystallized from n-hexane thrice and the final product about 70% of the starting material was dried in a vacuum oven at 30°C for 24 hours as reported in the previous paper [8].

Divinylbenzene supplied by Reidel-de-Häen, Germany, contains 60% DVB isomers and 35% ethylvinylbenzene was purified prior to its use adopting the procedure reported in the literature [9].

Azo-bisisobutyronitrile (AIBN) supplied by Merck, Germany was recrystallized from methanol prior to its use as described in the literature [10].

Benzene, diethylphthalate, dioxane, petroleum ether and butanol of technical grade supplied by Fluka Chemicals, Switzerland were used as such without further purification.

Toluene, cyclohexane, bromobutane, methylpropionate, dibutylphthalate, tertiaryamyl alcohol, benzyl alcohol, diisopropyl ether, dodecane, bromobenzene and dioctylphthalate of technical grade supplied by Merck, Germany were used as such without further purification.

Chlorobenzene, dimethylphthalate, cyclohexanone, diisobutyl ether and dichloroethane of technical grade supplied by BDH, Britain were used as such without further purification.

Isobutylpropionate and methylisobutyl ketone of technical grade supplied by Reidel-de-Häen were used as such without further purification.

Synthesis of Copolymers

Copolymers of NVC-DVB were prepared employing the suspension polymerization technique in aqueous medium. The aqueous phase consists of gum arabic, gelatin (3% each of water) and sodium chloride (6% of water) whereas an organic phase consists of NVC, DVB, a diluent or a mixture of solvating and non-solvating (1:1) diluents of required quantity. Aqueous to organic ratio was 6:1. Solvent fraction, F_s [Amount of diluent(s)/(Amount of diluent(s) + Amount of monomers)] was kept at 0.6. The percentage crosslinking agent, DVB used in the polymerization experiments was 20%. AIBN, 1% of the polymerization material was added to the organic phase prior to mixing the two phases. The two phases were then mixed and stirred for about half an hour at room temperature under nitrogen atmosphere. The temperature of the reaction mixture was then raised to 80°C. This process was continued for 24 hours. The resulting copolymer beads were successively washed with demineralized water (DMW), methanol and DMW. The copolymer beads were then sieved, certain fractions were collected, dried and used for their characterization.

The copolymer beads thus prepared were converted into cation-exchange resin by their sulfonation with concentrated sulphuric acid (98%) at 80°C for three hours.

Characterization of Copolymer Beads

Surface Area

Surface area of the copolymer beads was determined by using Brunauer-Emmett-Teller (BET) apparatus, Model No. QS-II, Serial No. 1170 supplied by Quantachrome Corp. 6-Aerial Way, Syosset, N.Y. 11791-U.S.A. This technique works on the principle of adsorption and desorption of nitrogen gas at a given temperature and pressure. The process of adsorption and desorption was monitored by measuring the change in the thermal conductivity of the gas as described in the BET method [11]. Helium was used as a carrier gas in this process.

Porosity

The volume distribution of pores in copolymer beads was determined by using

Micromeritics Porosimeter, Autopore II 9220 supplied by Micromeritics Instrument Corporation, 5680 Goshen Springs Road, Norcross, Georgia 30093, U.S.A. This instrument works on the principle of intrusion and extrusion of mercury in the pores of a material at a given pressure.

Apparent density

The apparent density of the copolymer beads was determined by measuring the volume and weight of its dry sample.

Mechanical strength of copolymer beads

The copolymer beads of 200 μ m size were selected to measure their mechanical strength. The apparatus used to measure the mechanical strength was constructed in our laboratory, was very similar to the one reported in the literature [12] by Golden and Irving. In this technique the resin bead is subjected to a compressive force which is monitored by a potentiometric chart recorder connected to the load cell output. Eventually the bead breaks which subsequently releases the pressure on the load cell platform, with the result the recorder trace shows a peak whose height corresponds to the crushing load of the bead.

Capacity of cation-exchange resin

The Na⁺ ions capacity of the cation-exchange resin was determined by following a method similar to that reported in the literature [13]. Air dried resin was weighed in two equal lots of 1g each. One lot was loaded onto a column (1cm X 5cm) whereas the other was dried in a vacuum oven at 100°C for 24 hours to determine its moisture contents. The resin bed thus made in the column was impregnated with 200ml of 0.1N NaOH solution and then it was washed with 40ml DMW (flow rate 150ml/h). The column effluent was collected in a flask. The liquid retained in the voids of the resin beads was forced down under pressure. The total volume of the effluent was then made upto 250ml by the addition of DMW. The concentration of NaOH in the effluent was determined by a standard analytical method. The quantity of NaOH consumed by the resin was considered as its capacity for Na⁺ ions.

References

1. W. L. Sederel and G. J. De Jong, *J. Appl. Polym. Sci.*, **17**,2835(1973).
2. A. Guyot and M. Bartholin, *Prog. Polym. Sci.*, **8**,277(1982).
3. R. L. Albright, *Reactive Polym.*, **4**,155 (1986).
4. A. Guyot, *Pure and Appl. Chem.*, **60**,365(1988).
5. a) R. Arshady, *J. Chromatogr.*, **586**,181(1991).
b) R. Arshady, *J. Chromatogr.*; **586**,199(1991).
6. M. Biswas and G. C. Mishra, *Makromol. Chem.*, **261**,182(1980).
7. M. Biswas and G. C. Mishra, *J. Appl. Polym. Sci.*, **26**,1719(1981).
8. M. A. Hamid, *Pak. J. Sci. Ind. Res.*, **31**,609(1988).
9. I. Poinescu, C. D. Vlad and A. Carpov, *Reactive Polym.*, **2**,26(1984).
10. F. M. B. Countinho and R. C. A. Cid, *Eur. Polym. J.*, **26**,1185(1990).
11. S. Brunauer, L. S. Demming, W. S. Demming and E. Teller, *J. Am. Chem. Soc.*, **62**,1723(1940).
12. L. S. Golden and J. Irving, *Chemistry and Industry*. p 837, (1972).
13. M. Marhol, "Comprehensive Analytical Chemistry, G. Svehl (ed), Vol. XIV." Elsevier Scientific publishing Company. Amsterdam-Oxford-New York. Ion Exchangers in Analytical Chemistry. Their properties and use in Inorganic Chemistry p 99, (1982).
14. M. A. Hamid, R. Naheed and E. Rehman. *The Nucleus.*, **33**,119(1996).