

Synthesis and Some Properties of Anthracene and Anthraquinone Incorporated Poly(vinyl Chloride) and the Ion Exchange Resin Therefrom

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Synopsis

Poly(vinyl chloride) has been modified by chlorine displacement reaction with 2-anthrol and anthraquinone-2-ol. The condensates (PVC-ACOL and PVC-AQOL) are insoluble in all solvents common to PVC and have been characterized by elemental and IR spectra analysis. The initial decomposition temperature of these condensates follow the trend: PVC-AQOL (250°C) > PVC-ACOL (200°C) > PVC (190°C) and the overall thermal stabilities beyond 60% decomposition follows the same trend. Permittivity and dielectric loss of these condensates sharply fall with increasing applied frequency ($10\text{--}1.3 \times 10^7$ Hz) to a limiting constant value. In contrast, for unmodified PVC these values are low and remain independent of frequency in the same range. Sulfonation of these PVC condensates affords a weak acid resin with —COOH and —OH ionogenic groups, but no strong sulfonic acid groups due presumably to oxidative degradation of the PVC matrix.

INTRODUCTION

Recently, Biswas and co-workers¹⁻⁴ have shown that chlorine displacement reaction involving poly(vinyl chloride) (PVC) is a very convenient procedure for introducing desirable moieties in PVC, thereby inducing characteristic changes in the physicochemical properties of the base polymer. Thus, PVC has been reacted^{1,2} with *m*-aminophenol (MAP), bisphenol-A (BIS-A), phenolphthalein (PHEN), and 3,6-diaminocarbazole (NMDAC).⁴ In all these cases, the modified PVC condensates exhibit overall improved thermal stability and characteristically different dielectric behavior relative to unmodified PVC.

The selective studies as above indicate that the nature of the incoming moiety-aromatic or heterocyclic exerts a significant influence on the physicochemical properties of the modified PVC condensates. In this context, it has now been observed that introduction of condensed aromatic hydrocarbons like anthracene or anthraquinone through reaction of PVC with 2-anthrol (ACOL) and anthraquinone-2-ol (AQOL) (Fig. 1) further improves the thermal stability in the modified polymer. The dielectric properties also change significantly relative to those for unmodified PVC.

As part of a continuing program^{3,5} on the synthesis of PVC-based strong acid resins, PVC-ACOL and PVC-AQOL have further been sulfonated and the ion exchange characteristics of the resin evaluated. This article will

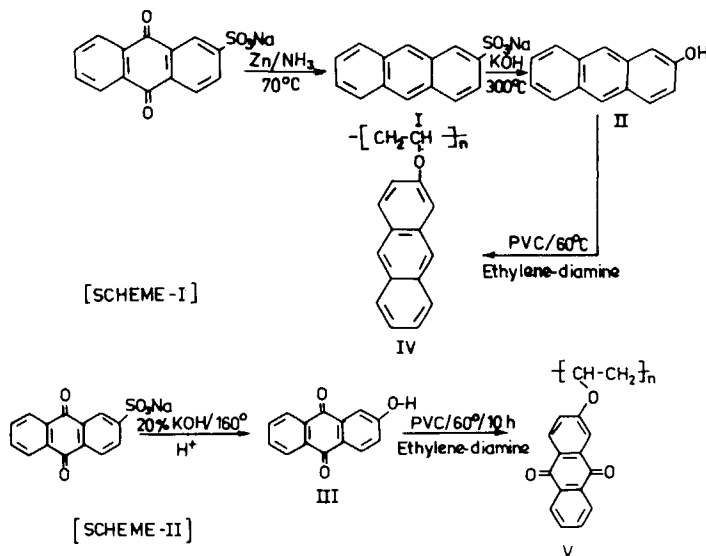


Fig. 1. Reaction scheme for the synthesis of PVC-ACOL and PVC-AQOL.

describe the synthesis and highlight some physicochemical properties of PVC-ACOL, PVC-AQOL, and the corresponding sulfonated resins.

EXPERIMENTAL

Materials

Poly(vinyl chloride) NOCIL ($\bar{M}_n = 8.6 \times 10^4$) was several times reprecipitated from THF by methanol. Anthraquinone-2-sulfonic acid, purified sodium salt (BDH, U.K.), Zn dust (AR), and potassium chloride (AR) were used without further purification. Ethylene-diamine (AR) and THF (AR) were distilled under vacuum.

Synthesis of 2-Anthrol (ACOL) II

A modified literature⁶ procedure was followed. Anthraquinone-2-sulfonic acid (sodium salt) (20 g) and zinc dust (16 g) were taken in a two-necked round-bottomed flask provided with a thermometer and a condenser. Twenty percent ammonia solution was poured into the mixture to obtain a thick mass. The color of the mass was instantaneously darkened. The mixture was vigorously stirred and heated to 70–80°C. Periodic addition of ammonia solution was needed frequently to prevent the system from becoming dry. After 5 h decoloration occurred, indicating completion of the reduction. To ensure complete reaction, about 10 g of zinc powder was added along with the ammonia solution and reaction was prolonged to 1 h. The mass was filtered and washed thoroughly with cold water. The residue thus obtained contained unreacted zinc and other zinc compounds. It was digested with excess of dilute acetic acid for 2 h, filtered, and washed thoroughly with water. The product, anthracene-2-sulfonic acid (I), was dried in oven at 120°C.

Anthracene-2-sulphonic acid (I), 1 part was fused with 3 parts potassium hydroxide in a nickel crucible at 300°C for 30 min. The molten mass was immediately extracted with distilled water. On acidification of the resulting solution with concentrated HCl, 2-anthrol (II), was immediately precipitated as a brown mass. The precipitate was filtered and washed thoroughly with hot water and dried at 60°C in vacuum and finally recrystallized from ethanol.

Synthesis of Anthraquinone-2-ol (AQOL), III⁷

Anthraquinone-2-sulfonic acid (10 g) was fused with 20% sodium hydroxide at 160°C under pressure. The fused mass was extracted with distilled water. The resulting solution was acidified with hydrochloric acid with constant stirring to precipitate the product. This was collected by filtration, washed with hot water, hot barium carbonate solution and again with hot water, dried at 60°C in vacuum and finally the product, anthraquinone-2-ol (III), was recrystallized from ethanol.

Condensation of PVC with 2-Anthrol (PVC-ACOL), IV

A solution of PVC (0.03M of repeating units) in THF (40 mL) and a solution of 2-anthrol (0.03M) in THF (25 mL) were introduced under nitrogen into a carefully dried 250 mL Pyrex flask. The mixture was stirred for 10 min at room temperature under nitrogen. About 10 mL ethylene-diamine was then added slowly to the stirred reaction mixture for 10 min. The reaction was carried out at 60°C for 10 h with vigorous stirring. The reaction mixture was poured slowly to methanol to precipitate the product which was collected by filtration, and repeatedly washed thoroughly with ethanol and benzene to remove unreacted II and PVC, respectively. The crude PVC-ACOL (IV) was digested in excess benzene solution at 60°C with occasional shaking for overnight, filtered, and dried at 60°C.

Condensation of PVC with Anthraquinone-2-ol (PVC-AQOL), V

For this synthesis the procedure was similar to that described for PVC-ACOL.

Sulfonation of PVC-ACOL and PVC-AQOL

The finely powdered polymer IV or V (2 g) was taken in a Pyrex conical flask and fuming H₂SO₄ (100 mL) was poured into it. The mixture was digested at 60°C for 12 h, cooled to room temperature, and poured into an ice-water mixture with constant stirring. The black resin thus formed was filtered and washed thoroughly with water until the filtrate was free from sulfate ion. The resin was dried at 100° for 3 h.

Characterization

Elemental Analysis

Estimation of carbon and hydrogen of the product was done by the Heraeus combustion apparatus (Micro).

Infrared Spectra

Infrared spectra of the samples dispersed in KBr pellets or in nujol mull were recorded on a Perkin-Elmer-237 B infrared spectrometer.

Thermal Stability

Thermal stability measurements were made on a Stanton Redcroft analyzer with the sample under air at a heating rate of 15°C/min. The temperature range was 0–1000°C.

Dielectric Measurements

Permittivity or dielectric constant (ϵ) and dielectric loss factor ($\tan \delta$) measurements were made with an impedance bridge (HP, A4192). The samples were used in pellet form coated (both surface) with silver paint.

Evaluation of Ion-Exchange Capacity

The total ion exchange capacity of sulfonated PVC-ACOL (PVC-ACOL-S) and sulphonated PVC-AQOL (PVC-AQOL-S) was evaluated by the following procedure. A known weight of the dried resin (about 0.3 g) was crushed and placed in a stoppered Pyrex conical flask. About 50 mL of NaOH solution (0.1*N*) was added, the mixture was kept with occasional shaking for 40 h to attain equilibrium. An aliquot (25 mL) of the supernatant liquid was withdrawn and titrated against standard HCL (0.1*N*). A blank experiment was also performed for determining the acid equivalent. From these data, the ion exchange capacity of the resin was calculated⁸⁻¹⁰ in meq/g.

pH-metric Titration

pH-metric titration characteristics of the PVC-ACOL-S and PVC-AQOL-S resins were determined by adding incremental quantities of NaOH solution (0.1*N*) to different mixtures containing a known weight of dry resin and 10 mL NaCl (1*N*), keeping the total volume at 50 mL by the addition of deionized water and measuring the equilibrium pH of the solution in each case. The capacities were evaluated¹⁰ after the attainment of a constant pH (after 40 h).

RESULTS AND DISCUSSION

General Features

The PVC-ACOL and PVC-AQOL condensates were recovered as deep colored powder, insoluble in THF, aromatic hydrocarbons, dimethyl sulfoxide and dimethylformamide. The sulfonated materials, PVC-ACOL-S and PVC-AQOL-S, were obtained as black powders, also insoluble in all the above solvents.

The probable mode of the condensation reaction between PVC and ACOL and AQOL is as suggested in structures IV and V. The presence of the aryl—C—O stretching, alkyl—C—O stretching, and the aromatic ring are well endorsed by the IR data (Table I).

TABLE I

Sample code	Compound	Color	Melting point (°C)	Solubility	C(%)		H(%)		Characteristic IR absorption (cm ⁻¹)
					Found	Calcd	Found	Calcd	
I	Anthracene-2-sulfonic acid	Light yellow	> 300	Slightly soluble in hot water	64.6	65.0	4.0	3.8	1045 (S=O sym stretching), 1200 (S=O asym stretching), 650 (S=O stretching)
II	ACOL	Brown	252	Ethyl-alcohol	86.2	86.5	5.23	5.14	1270 (O-H bending), 1320 (C-O stretching)
III	AQOL	Brown	302	Ethyl-alcohol	73.4	74.9	3.62	3.56	1640 (C=O stretching), 1275 (O-H bending), 1318 (C-O stretching)
IV	ACOL-PVC	Reddish brown	—	Insoluble in common organic solvent	61.5	89.62 ^a	5.1	5.5 ^a	1250 (aryl C-O stretching), 1070 (alkyl C-O stretching), 1610, 1420 (ar. ring vibration)
V	AQOL-PVC	Dark brown	—	Insoluble in common organic solvent	57.71	78.61 ^b	4.32	4.09 ^b	1260 (aryl C-O stretching), 1072 (alkyl C-O stretching), 1615, 1430 (aromatic ring vibration)

^{a, b}Calculated on the basis that each Cl in the PVC chain is replaced by the anthracene moiety.

The results of elemental analysis for C, H may now be analyzed in the light of structures IV and V. Taking into account the theoretical values for % C and % H (Table I), the observed % of C and H may be rationalized by supposing that Cl displacement occurs in the ratio 1 : 5.

Thermal Stability

Figure 2 represents the weight loss vs. temperature curves for unmodified PVC(1), PVC-ACOL(2), and PVC-AQOL(3), respectively. The initial decomposition temperatures of the modified polymer follow the trend: PVC-AQOL (270°C) > PVC-ACOL (210°C) > PVC (190°C). This feature is particularly significant in view of the previous experiences with PVC-aromatic and PVC-heterocyclic condensates, which revealed initial decomposition at around 100°C.¹⁻⁴

Up to 30% decomposition, PVC-AQOL exhibits higher stability than PVC-ACOL, both showing higher stability than unmodified PVC. Between 35 and 62% decomposition, PVC-ACOL exhibits a higher extent of stability than PVC-AQOL, but, beyond this temperature, PVC-AQOL exhibits much higher

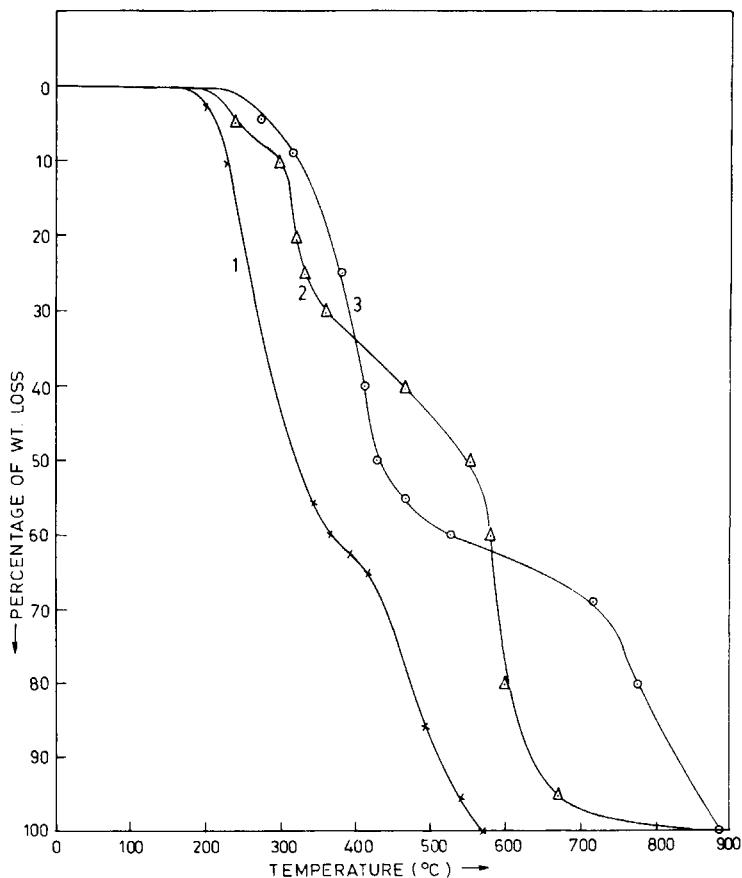


Fig. 2. Thermogravimetric analysis of: (1) PVC (X); (2) PVC-ACOL (Δ); (3) PVC-AQOL (○).

stability than PVC-ACOL or PVC itself. Thus, introduction of condensed hydrocarbon in the PVC chain improves the overall thermal stability as compared to unmodified PVC. The higher stability implies that PVC-AQOL possesses a comparatively more rigid network structure than PVC-ACOL. AQOL may exist in tautomeric equilibrium with the corresponding "enol" form (in presence of the base), which during reaction with PVC will form a more crosslinked structure with higher thermal stability.

Table II compares the thermal stabilities of PVC-containing aromatic, heterocyclic,^{1-4,11} condensed aromatic moieties and PVC grafted with polybutadiene and isobutylene.¹¹ PVC-ACOL and PVC-AQOL exhibit considerably higher stability than the corresponding carbazole and phenolphthalein modified PVC. On the other hand, bisphenol-A imparts an appreciable stability in the PVC chain which is more or less comparable to PVC-anthracene condensates. The bulkiness (PVC-PHEN) of the incoming moiety and the bond energy of the bond formed with incoming moiety ($C-O > C-N$) are important factors that control the overall stability.

Table II further reveals that thermal stabilities of anthracene incorporated PVC are appreciably better than the same for grafted and alkylated PVC.¹¹ According to Thame et al.,¹¹ the labile chlorine atoms are first removed by reaction with alkyl-aluminum compound producing carbonium ion centers in PVC, which attack the polymerizable olefin, to give the graft modification or undergo alkylation reaction with toluene. The enhanced thermal stability results from the replacement of the $C-Cl$ bond by the more stable $C-C$ bond. However, for PVC-anthracene and other related systems, the proposed chlorine displacement reaction may involve any available $-Cl$ atom—labile or not. Here, the enhanced thermal stability is due partly to the replacement of the $C-Cl$ unit by the more stable $C-OR$ bond.

The higher initial decomposition temperature of ACOL and AQOL implies that the initial dehydrohalogenation reaction is somewhat controlled, which is expected since some chlorine atoms are displaced by the incoming moiety.

TABLE II
A Comparison of the Thermal Stabilities of Chemically Modified PVC

Polymer	Temperature (°C) for the decomposition (%) of the polymer						Reference
	Initial (2-3%)	10	20	40	65	80	
PVC	190	225	250	275	420	475	This work
PVC-ACOL	210	300	320	460	590	600	This work
PVC-AQOL	270	325	365	410	625	775	This work
PVC-PHEN	120	140	250	375	500	600	3
PVC-NMCDA	100	110	275	410	490	525	4
PVC-BIS-A	200	290	340	410	645	780	3
PVC- <i>g</i> -polyisobutylene ^a	260	320	330	340	400	500	15
PVC- <i>g</i> -polybutadiene ^a	270	310	330	350	450	500	15
Alkylated PVC ^a	240	308	330	360	465	500	15
Toluene-modified PVC ^a	260	312	335	355	450	500	15

^aTGA was done in nitrogen with heating rate 6°C/min; all other analyses were performed in air with heating rate 10°C/min.

Solubility Characteristics of PVC-ACOL and PVC-AQOL

The general insolubility of the modified PVC may result from: (i) The incorporation of bulky anthracene moiety in place of the $-\text{Cl}$ atom (as in Fig. 1) thereby affecting chain flexibility. (ii) The possibility of interchain crosslinking in PVC-AQOL; the AQOL may undergo ketoenol tautomerism and thus behave as a triol in presence of base during reaction with PVC. (iii) The formation of conjugated double bond structures^{11,12} during dehydrohalogenation which, although reduced, can nevertheless be avoided completely.

Dielectric Characteristics

Figure 3 shows the variation of permittivity and dielectric loss ($\tan \delta$) with applied frequency for PVC, PVC-ACOL, and PVC-AQOL, respectively. Clearly, the permittivity values for the modified PVC polymers are dependent on the applied frequency and show a drastic fall in the frequency range ($f = 300\text{--}1000$ Hz), where after they vary very slowly with the applied frequency. For unmodified PVC, on the other hand, the permittivity remains essentially independent of the applied frequency in the same range ($10\text{--}10^7$ Hz), which behavior is in line with published reports.¹³ Dielectric loss parameters for both PVC-ACOL and PVC-AQOL are extremely broad and do not reveal any maximum corresponding to the inflexion in the permittivity-frequency curve. These features are reminiscent of what has earlier been

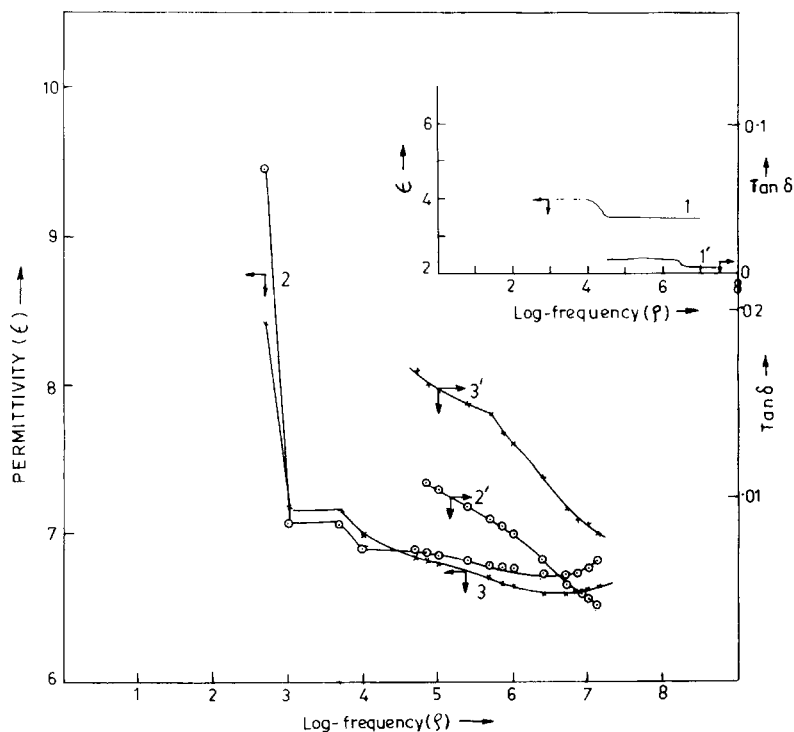


Fig. 3. Permittivity and $\tan \delta$ vs. frequency plots for (1,1')PVC; (2,2')PVC-ACOL (O); (3,3')PVC-AQOL (X).

observed with N-containing PVC condensates like PVC-MAP or PVC-NMCDA studied by Biswas et al.^{2,4}

The introduction of polar groups in the modified PVC will cause them to orient when placed in an electric field. If the polymer is very flexible or at least if the polar groups^{14,15} are flexibly attached to the polymer chain, they will orient easily and quickly. If the polymer is appreciably rigid and the polar groups are rigidly attached, they will orient very slowly with difficulty. Thus, in an alternating electric field, the polar groups in a polymer will orient and give high dielectric constant only when the frequency of alteration is low enough to permit motion and orientation of the polar groups. With increasing frequency in the alteration of the electric field, the polar groups will become less and less able to orient rapidly enough to effect the dielectric constant and at still higher frequency, they will hardly be able to orient at all. Consequently, the polymer will exhibit a low dielectric constant. In the light of this discussion, the typical behavior exhibited by PVC-MAP and PVC-NMCDA is perhaps rationalized. Pertinently, similar permittivity-frequency behavior was also experienced by Biswas and Das¹⁶ in the case of poly(*N*-vinylcarbazole-3,6-diphthalimide) containing *N*-heteroatoms. It seems therefore that the presence of *N*-heteroatom is important in realizing such dielectric polarization.

Typically, when modified with aromatic systems as PVC-BIS-A or PVC-PHEN,^{1,2} the dielectric frequency behavior is very similar to unmodified PVC. Interestingly however, the behavior of PVC-ACOL or PVC-AQOL is more similar to PVC-MAP or PVC-NMCDA rather than to PVC-BIS-A or PVC-PHEN. As is well known, the anthracene moiety because of its higher volume for the electrons to play around will exhibit greater electron polarizability compared to the PVC-aromatic system, hence the observed trend in permittivity frequency behavior (Fig. 3).

As for the $\tan \delta$ -frequency behavior of the PVC condensates, it seems that loss of electrical energy by conversion to thermal energy at low frequencies is too small to be detected, but it shows up only at some intermediate frequencies in the transition region, where the polar groups are able to orient at the rate and the frequency of alteration in the electric field. As a result, the broad relaxation manifests in place of the usual maxima in the loss tangent frequency curves.

Ion-Exchange Characteristics of Sulfonated PVC-ACOL or PVC-AQOL Resins

Table III presents all relevant ion exchange characteristics for PVC-ACOL-S and PVC-AQOL-S resins along with a comparative evaluation of some other PVC-based resins reported by Biswas and Moitra.¹ It may be readily understood from Table III that both PVC-ACOL-S and PVC-AQOL-S exhibit lower ion-exchange capacities ca. 1.4 ~ 1.7 meq/g dry resin. Further pH-capacity studies (Fig. 4) confirm that the resin possesses no strong acid groups (pK = 1-2) but only weak COOH (pK = 5-6) and OH (pK = 9-10) ionogenic groups.¹⁰ This behavior is strikingly similar to that experienced during the preparation of sulfonated resins from PVC-BIS-A or PVC-PHEN by direct sulfonation.¹ As reported in Table III, this procedure

TABLE III
 Ion Exchange Characteristics of PVC-Based Resins

Resin	Ion exchange capacity (meq/g)	pK values		Ionogenic group(s)	Reference
		pK ₁	pK ₂		
PVC-ACOL-S	1.41	5.14	9.25	-COOH, -OH	This work
PVC-AQOL-S	1.70	5.35	9.15	-COOH, -OH	This work
PVC-MAP-S	3.42	4.11	8.60	-COOH, -OH	1
PVC-PHEN-S	3.08	4.60	9.11	-COOH, -OH	1
PVC-BIS-A-S	3.20	4.90	8.48	-COOH, -OH	1

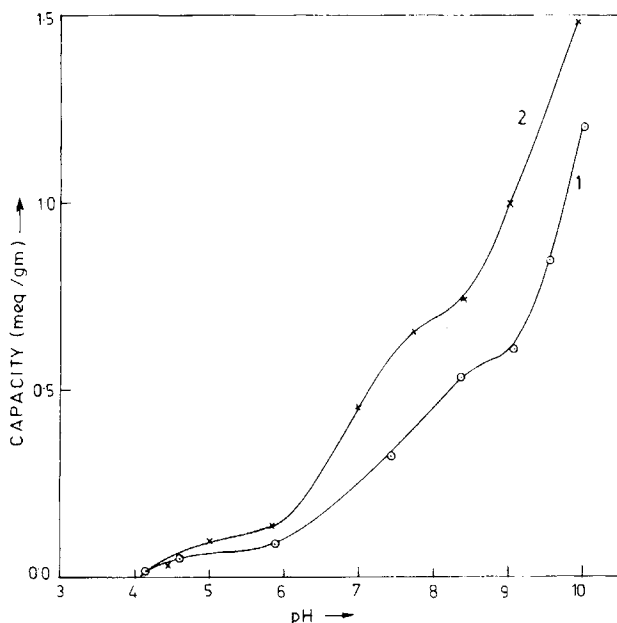


Fig. 4. Capacity versus pH for (1) PVC-ACOL (⊙) and (2) PVC-AQOL (X) sulfonated resin.

yields a weak acid resin in all these cases. A modified procedure,³ in which PVC is condensed with presulfonated BIS-A or PHEN, gives the resin which exhibits both strong ($-\text{SO}_3\text{H}$) as well as weak ($-\text{COOH}$) ionogenic groups. This behavior appears to be due to the possibility that during sulfonation of the PVC condensates oxidative degradation is favored in presence of concentrated H_2SO_4 disrupting PVC-O-R links as well as rupturing many weak links¹⁷ in the PVC network.

CONCLUSION

The incorporation of anthracene and anthraquinone moiety in PVC leads to a modified PVC matrix with higher initial decomposition temperature, overall thermal stability and distinct permittivity, and dielectric loss frequency behavior relative to unmodified PVC. Sulfonation of these condensates affords an ionexchange resin with $-\text{COOH}$ and $-\text{OH}$ ionogenic groups.

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