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Note

Thin-layer chromatography on polyacrylonitrile

I. Effect of the *cis–trans* configuration of cobalt(III) complexes on their R_F values

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Polyacrylonitrile is a chain polymer of acrylonitrile of the general formula $-[CH(CN)CH_2]_n-$. Owing to the mutual repulsion of cyano groups, the macromolecule gains a spiral chain conformation with occasionally formed hydrogen bonds between cyano groups and α-methyne hydrogens of adjacent chains[1].

At present, the most readily accessible are commercial polyacrylonitrile fibres consisting of different copolymers which contain at least 85% of acrylonitrile monomer[1]. Its world production is very high[1], which makes this material cheap and easily available.

Polyacrylonitrile belongs to specific sorbents with localized negative charges on nitrile groups[2]. It is very resistant at room temperature to the action of most organic solvents applied in chromatography and also to dilute solutions of acids and bases[3]. Hence we consider that polyacrylonitrile could be more widely applied in chromatography.

Polyacrylonitrile has so far been applied as a sorbent in thin-layer chromatographic separations in only one instance, namely, Hesse *et al.*[4] used it for the separation of some monosaccharides and dicarboxylic and sulphonic acids. However, they stated neither the method of preparation of the sorbent nor its characteristics. Therefore, in this work, we wanted to consider the possibility of its laboratory preparation and to determine its most important characteristics. In addition, we wanted to check the applicability of the prepared sorbent to the separation of some *cis–trans* isomeric cobalt(III) complexes.

EXPERIMENTAL

Preparation of the polyacrylonitrile sorbent

The procedure for the preparation of the polyacrylonitrile sorbent involves dissolution of 50 g of white PAN fibres (OHIS, Skoplje, Yugoslavia) in 2 l of concentrated nitric acid (ρ = 1.40 g/cm^3) at room temperature, followed by dropwise addition of the solution obtained to 6 l of water with vigorous stirring. The voluminous precipitate obtained is then filtered off under slightly reduced pressure, washed with

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water and ethanol and dried in a porcelain dish at 50°C with occasional stirring. The yield is quantitative. In order to separate larger particles, the dried powder is then finely ground and suspended in 1 l of 96% ethanol. The suspension is left to stand at room temperature for 10 min and then the part of the suspension above the sediment, which contains about 25 g of the sorbent, is decanted. The sediment is dried, ground and treated again as described above. The decanted suspension is left to stand overnight at room temperature, by which time a white precipitate has settled to the bottom. The main part of the ethanol above precipitate is gently decanted, and the remaining part is shaken and applied to chromatographic plates.

Apparatus and methods for the determination of sorbent characteristics

Electron microscope analysis was performed on a JEOL (Peabody, MA, U.S.A.) J. SM-35 scanning microscope.

X-ray diffraction analysis of the sorbent was carried out on a Philips (Wavre, Belgium) PW 1051 powder diffractometer.

Infrared spectra were recorded on a Perkin-Elmer (Norwalk, CT, U.S.A.) 457 spectrophotometer using the potassium bromide technique.

The distribution of sorbent particles according to their size was determined by means of a CILAS (Marcoussis, France) E 715 granulometer.

The pore volume of the sorbent was determined by centrifugation with *n*-nonane[5].

The ion exchange capacity of the sorbent was determined by volumetric analysis[6].

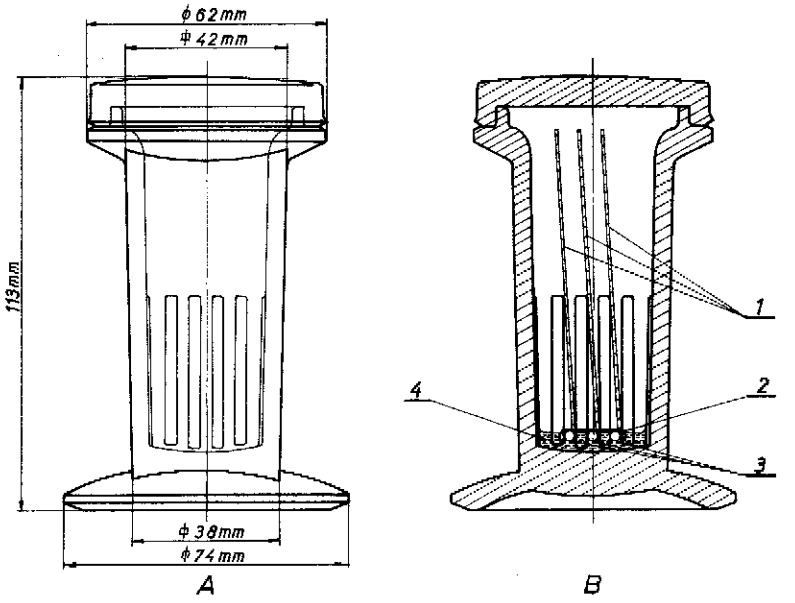

Fig. 1. Diagram of the apparatus. (A) Chromatographic chamber; (B) its cross-section. 1 = Microscopic plates; 2 = band made of Whatman 3MM chromatographic paper; 3 = glass rods; 4 = developing solution.

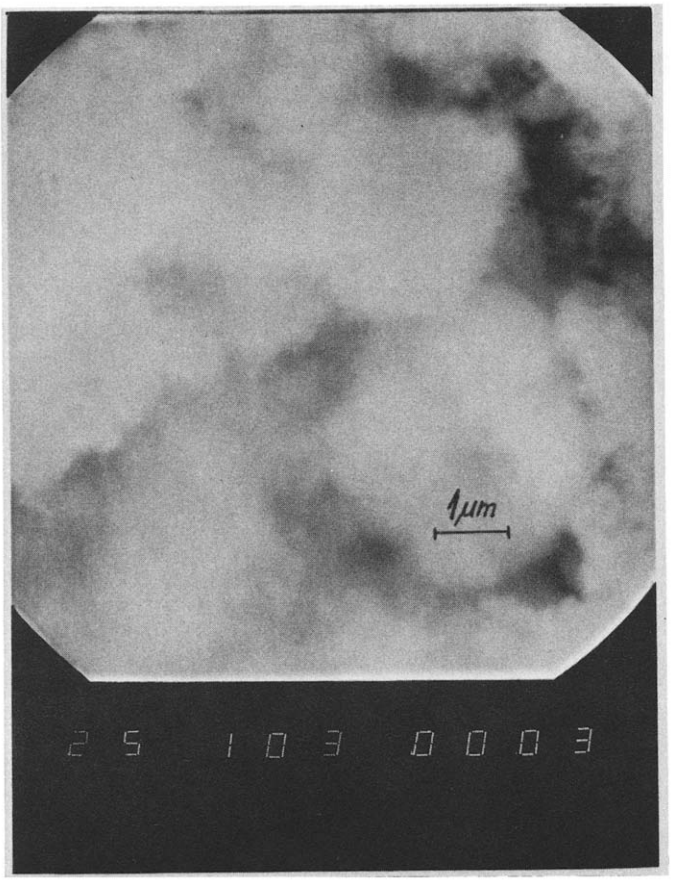

Fig. 2. Polyacrylonitrile sorbent examined by electron microscopy.

The specific surface area of the sorbent was determined, after drying at 70°C for 3 h, by the BET nitrogen adsorption method on a Flowsorb II 2300 apparatus (Micromeritics, Norcross, GA, U.S.A.).

For covering the plates with the sorbent, a Camag (Muttenz, Switzerland) hand-operated TLC plate coater was used.

Syntheses

All the investigated complexes were synthesized by described procedures (Table I).

Chromatographic data

Thin-layer chromatographic separations were carried out on microscope plates (26 × 76 mm); the layer thickness was about 0.25 mm. Before use, the plates covered with the sorbent were dried in air for about 1 h and then kept in a desiccator over calcium chloride. For each separation, 0.5 µl of a 0.01 *M* solution of the corresponding

TABLE I

$R_F \times 100$ VALUES OF THE INVESTIGATED COMPLEXES OBTAINED BY THIN-LAYER CHROMATOGRAPHY ON THE POLYACRYLONITRILE SORBENT

Complex[a]	*Isomer*	*Solvent*					*Ref.*[b]
		Water	*0.1% $KClO_4$*	*0.1% $HClO_4$*	*1% $KClO_4$*	*1% $HClO_4$*	
$[Co(NH_3)_4(NO_2)_2]^+$	*cis*		31	33	60	59	7, 8
	trans	–	45	54	76	69	7, 8
$[Coen_2(NO_2)_2]^+$	*cis*	–	27	38	50	53	9
	trans	–	43	52	70	69	9
$[Coen_2(NO_2)Cl]^+$	*cis*		34	27	52	52	10
	trans	–	49	33	64	67	10
$[Coen_2(SCN)Cl]^+$	*cis*	–	23	–	39	41	10, 11
	trans	–	37	–	47	55	10, 11
$[Coen_2(SCN)_2]^-$	*cis*	–	8	7	11	8	10, 11
	trans	–	20	18	24	23	10, 11
$[Cotn_2(NO_2)_2]^+$	*cis*	–	26	34	48	40	12
	trans	–	40	43	67	62	12
$[Copn_2(NO_2)_2]^+$	*cis*		33	25	46	50	13
	trans	–	50	43	72	70	13
$[Cotngly(NO_2)_2]$	*cis*	86	85	89	90	88	14
	trans	94	96	96	95	95	14
$[Cotn\beta\text{-ala}(NO_2)_2]$	*cis*	85	80	82	86	81	14
	trans	93	94	92	96	90	14
$[Coen\beta\text{-ala}(NO_2)_2]$	*cis*	89	87	79	88	84	14
	trans	96	95	92	99	94	14

[a] en = 1,2-Diaminoethane; tn = 1,3-diaminopropane; pn = 1,2-diaminopropane; glyH = glycine; β-alaH = β-alanine.
[b] Syntheses used.

Co(III) complex was used. The development of chromatograms was performed by the ascending method (Fig. 1). The developing time was 30–40 min, and the solvent front travelled about 5 cm. Detection was performed by keeping the plates for 10 min above 2 *M* ammonium sulphide solution. All investigations were carried out at room temperature (22 ± 1°C).

RESULTS AND DISCUSSION

Characteristics of the sorbent prepared

It has been established by electron microscopy that the sorbent prepared consists of grain-like particles grouped into agglomerates of different size (Fig. 2). On the basis of X-ray analysis, it can be concluded that the sorbent prepared is not completely amorphous, its pattern indicating a certain degree of an ordered structure.

Infrared spectra of the prepared sorbent and of ground PAN fibres used as the starting material were identical, which proves that no chemical changes take place in the course of sorbent preparation. The spectra clearly show the presence of carboxylic groups, which probably originate from comonomers possessing carboxylic groups (*e.g.*, itaconic acid[3]).

The mean particle size of the sorbent prepared was 4.7 μm; 80% of the particles had a diameter between 2 and 12 μm. The pore volume of the sorbent was 1.7 cm^3/g and its ion-exchange capacity was 1.0 mequiv./g. The specific surface area of the sorbent was 55 m^2/g.

From the above, it can be concluded that the polyacrylonitrile sorbent prepared fulfils all the conditions required for its successful application in thin-layer chromatography[15]. This is demonstrated by the fact that the isomer separations and spot shapes obtained were aproximately of the same quality as those which we obtained in a previous study[16] in which silica gel G-RS (Carlo Erba, Milan, Italy) was used.

Chromatographic separations

The R_F values obtained and the compositions of the solvent systems applied are given in Table I. To check the applicability of the sorbent prepared, seven pairs of *cis trans* isomeric cobalt(III) complexes of the cationic type and three pairs of the neutral type were chromatographed. The solvent systems used were water and aqueous solutions of different electrolytes having concentrations of 0.1% and 1%, respectively. In all instances it was been established that the *trans* isomers exhibit higher R_F values than the corresponding *cis* isomers, which is in accordance with the previously established rule[16], obtained by chromatographing the isomers on silica gel with single solvents. This analogy exists in spite of the fact that silica gel contains on its surface localized positive charges, originating from protons of silanol groups, whereas polyacrylonitrile contains negative charges, originating from cyano groups[2]. On this basis, it may be concluded that the same regularity exists regardless of the adsorbent surface charge. In this connection, it may be assumed that the adsorption mechanism, involving hydrogen bond formation, is dominant in the chromatographic separation process. In the former instance hydrogen bonds would be formed between silanol protons of the silica gel and markedly electronegative atoms of the ligands, whereas in the latter instance, where hydrogen bonds between polyacrylonitrile and the complexes are concerned, hydrogen atoms from the ligands would be bonded to cyano groups of the sorbent.

As regards the mechanism of separation of the investigated cationic complexes, when potassium perchlorate was used as the solvent, it may be assumed that in addition to adsorption, cation exchange at carboxylic groups of the sorbent also takes place. For check this assumption, we carried out elution with perchloric acid solution in order to prevent the protolysis of the sorbent carboxylic groups and thus render impossible the process of ion exchange. As the results obtained were analogous to those obtained with a solvent system that contained no acid, it may be assumed that in both instances adsorption is the dominant separation mechanism. However, with complexes of the neutral type, only the adsorption separation mechanism may be involved.

Taking into consideration the nature of our sorbent, containing cyano groups with localized negative charges, and also carboxylic groups capable of exchanging cations, cationic complexes would be expected to be more strongly sorbed and to exhibit lower R_F values than neutral complexes, which was observed in all instances studied. The former consideration is supported by the fact that when water was used as the solvent the cationic complexes could not be chromatographed, as the spots were elongated from the start, whereas the complexes of the neutral type gave well defined spots. In addition, a comparison of R_F values obtained with solvent systems containing 0.1% and 1% solutions of the same electrolyte revealed that the elution capacity of 1% solutions was considerably higher than that of 0.1% solutions when cationic complexes were chromatographed. However, with neutral complexes this effect was insignificant.

It is concluded that the polyacrylonitrile sorbent can be applied to thin-layer chromatographic separations.

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