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5.6 Cellulose Acetate in Separation Technology

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Summary: Cellulose acetate has been utilized in a variety of separation and purification processes. In membrane separation, cellulosics, in particular cellulose acetate, have played important roles. Hemodialysis and desalination are the established fields where acetate membranes have been applied. Recently, a new application, that is the purification of drinking water, is growing. The history of cellulosic membranes, preparation of acetate membranes, and applications will be reviewed. Cellulose acetate is also useful in chromatography and related separation technologies. These application will also be reviewed and the relationship between the superstructure of cellulose triacetate and its adsorptive behavior is briefly mentioned.

Keywords: cellulose acetate, membrane, hemodialysis, dialysis, reverse osmosis, desalination, ultrafiltration, drinking water, cryptosporidium, membrane filter, chromatography, gel, cellulose beads, chiral separation, optical resolution, CTA I, CTA II, allomorph, plasmapheresis, granulocyte, ulcerative colitis

1. MEMBRANE SEPARATION

1-1. An overview of Membrane Separation

Selective transportation across membranes is one of the fundamental processes of life. Many biochemical processes *e. g.*, assimilation, urine excretion, respiration, nervous excitation, and so on take place across membranes. Therefore, it seems quite natural that modern technology sought membrane separation regardless to being aware of the role in life. It can be seen from the market forecast that membrane technology is growing rapidly. The subcategories of membrane technology and their main applications are listed in Tables 1 and 2.

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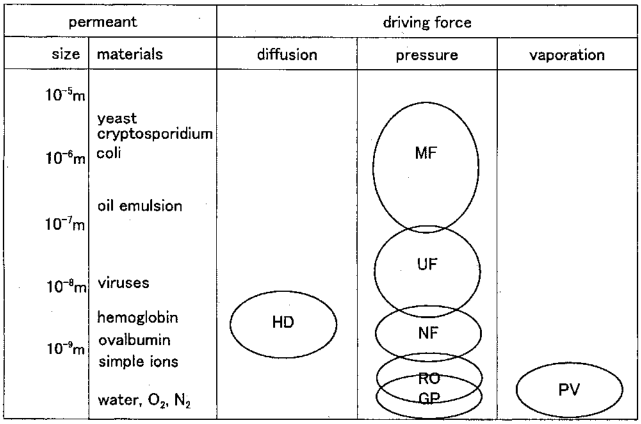
Table 1: Overview of membrane separation technology and its subcategories.



permeant		driving force		
size	materials	diffusion	pressure	vaporation
10^{-5}m				
	yeast cryptosporidium			
10^{-6}m	coli		MF	
	oil emulsion			
10^{-7}m				
			UF	
10^{-8}m	viruses			
	hemoglobin	HD	NF	
10^{-9}m	ovalbumin			
	simple ions		RO	
	water, O_2, N_2		GP	PV

GP; gas permeation, HD; hemodialysis, MF; microfiltration, NF; nanofiltration

PV; pervaporation, RO; reverse osmosis, UF; ultrafiltration.

Table 2: Application of membrane technology (example).

Medical care, Medical industry hemodialysis; hemofiltration; production of pyrogen-free water; purification of enzymes; hormones; antibiotics.
Food industry concentration of fruit juice, milk, and coffee; sugar purification; recovery of materials from cheese whey, soy bean whey, etc.; production of beer, sake, and wine; production of bottled water and drinks; waste water treatment.
Other industries desalination and salt production; preparation of ultra-pure water for semiconductor manufacture; waste water treatment and recovery of valuables (plating, grinding, pulping, oil emulsion, etc.); oxygen enrichment.
Life supply municipal waste water treatment; treatment of waste water of atomic power plant; drinking water purification.

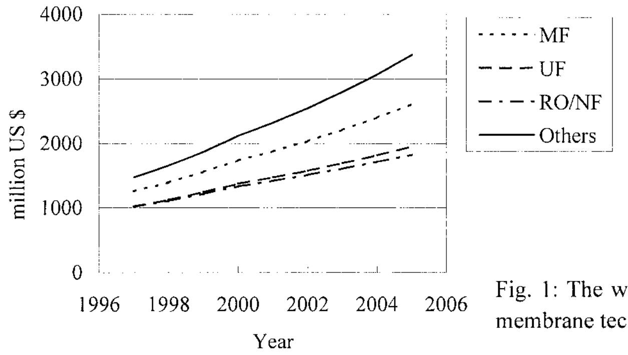


Fig. 1: The worldwide market profile for membrane technologies [1].

The most important property characterizing a membrane process is permeation vs. rejection for a material (permselectivity). In most cases, permselectivity is essentially controlled by the pore size of the membrane (capillary theory). However, in some cases, the affinity of the material to the membrane material profoundly affects the permselectivity (solution theory) like that of a cigarette smoke filter [2]. In actual systems, both factors are regarded to contribute more or less to the permselectivity.

1-2. The History of Acetate Membrane

Technology of synthetic membrane, which has been reviewed in detail by Presswood [3], developed along with cellulosic materials.

Schönbein invented cellulose nitrate in 1845. Fick made it into a membrane and used it in his study on dialysis in 1855. This was the start of synthetic membrane technology. Many researchers then prepared membranes from cellulose nitrate solution, so called collodion, and found that partially drying the solution and subsequently quenching it with water instead of completely drying it as had been first done results in a microporous membrane with a good permeability. It was also found that addition of a high boiling solvent or a salt into the solution further enhances the permeability. Bechhold prepared a membrane with pore diameters ranging from 1 to 5 μm and performed filtration with it under air pressure. He named the technology"ultrafiltration" and this term is now used as a standard. Cellulose acetate was made into membrane first by Brown in the 1910s. and the basic methodologies of controlling membrane permeability were established in the early 20th century. Sartorius Werke Aktiensgesellschaft, Göttingen, began the commercial production of membrane filters in 1927 though no one presumably imagined thes wide variety of applications as we know nowadays.

During World War II, German researchers searched for convenient methods to inspect the safety of drinking water as water supplies were damaged by bombing. Thus a method to collect microbes such as Coliform bacteria in water and cultivate them on a membrane was established by Müller. This technique was brought to the U.S.A. by the U.S. Army, developed by Goetz at Caltech, Pasadena, and was established as a method of drinking water inspection. It was kept secret because of bacteriological warfare concerns, but later became available to the public health field. This technology is now applied to drinking water purification as will be mentioned later.

An epoch of membrane technology was attained in the middle of the 20th century, that was the desalination by reverse osmosis. In 1952, Saline Water Act was legislated in the U.S.A. to promote research on preparing pure water from sea water or saline. Theory predicted that applying a reverse pressure exceeding the osmotic pressure (for example, 25 atm for sea water) could squeeze pure water if a suitable semipermeable membrane was available. An independent study was carried at the University of Florida and UCLA and both groups found that a cellulose acetate membrane can perform a good rejection of salt from water. Though a very low flux (rate of permeation) had kept the method far from practical application at the biginning, the UCLA group, Loeb and Sourirajan, attained a remarkable improvement by applying the casting method using an acetate solution in acetone/aq. magnesium perchlorate in 1960, that made desalination by reverse osmosis a promising technology [4].

1-3. Formation of Acetate Membrane

A cellulose acetate membrane is mostly made by the so-called phase-inversion method as well as many other synthetic ones are. The basic process is the gelation of a polymer solution by phase separation and the subsequent coagulation of the primary particles caused by evaporation of the solvent or contact with a nonsolvent. The outline of the prototypical preparation of an acetate RO membrane given by Loeb and Sourirajan [p.258 in ref. 4] is as follows.

An acetate solution comprising cellulose acetate (acetyl content 39.8%) 22.2 parts, acetone 66.7 parts, water 10.0 parts, and magnesium perchlorate 1.1 parts was casted in a cold box at 0 to

–10°C on glass at 0.025 cm thickness as cast. Evaporation of acetone for 3 to 4 minutes gave a semisolid mass, which was immersed into ice cold water for at least an hour. The resulting membrane, which is too porous to perform RO, was treated in water, which was heated gradually from ambient temperature to between 75 and 82 °C and kept for about one hour. After cooling, the membrane was pressurized in water at the operating pressure, *i.e.*, 10342kPag. The resulted membrane was stored in water.

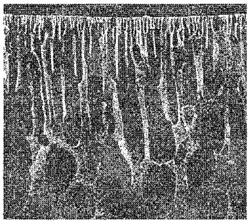


Fig. 2: Cross section of a CA asymmetric membrane (RO) (copied from Belfort [5]).

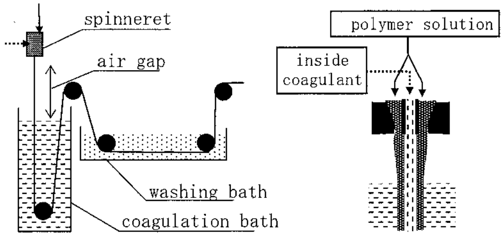


Fig. 3: A schematic diagram of a hollow fiber spinning machine (left) in dry-wet method and its spinneret (based on M. Mulder [6]).

The above described is the preparation of an RO membrane by a dry-wet phase inversion process (immersion process), and most acetate membranes are prepared similarly. The membrane thus formed has usually a depth dependent structure and called an asymmetric membrane. The surface which quickly gelatinizes forms a relatively continuous structure so-called surface layer. Once this layer is formed, mixing of the solvent and the coagulant becomes slower, phase separation develops, that result in a sponge-like structure sometimes accompanied by voids (a finger structure). The surface layer where the pore size is the smallest mostly determines the permselectivity and flux. The deeper part called the support layer, which has a much larger pore size than the surface, provides the mechanical strength. Such a structure can be seen in the cross section of an acetate membrane (Fig. 2) [5]. The pore size can be modified by the choice of solvent/coagulant, polymer concentration, the addition of a third component like a nonsolvent or a salt into the polymer solution, the contact with atmosphere prior to coagulation causing moisture uptake and/or partial vaporization of the solvent and so on.

Supplying vapor of a nonsolvent to the surface of casted solution before immersion or drying the solvent from a solution containing less volatile nonsolvent can make the pore size of the surface larger. Thus a membrane with a pore size rather independent of depth can also be made and used in microfiltration.

For the scientific description of the membrane formation process, see Sourirajan [4], Kesting [7], and so on.

The form of a membrane is chosen depending on the type of a module (mentioned later). A flat and a tubular membranes mostly with a support (*e.g.*, a nonwoven), and a hollow fiber membranes are common and the last one is dominant among them. In Fig. 3 is shown the basic constitution of a hollow fiber spinning machine by dry-wet method. Though coagulation takes place from the outer and inner surfaces of a hollow fiber, the permeability of each surface is independently designed by the choice of the coagulants and the air gap condition.

A unitary device including a membrane to perform separation is called a module, which is classified based on the form of the membrane into a hollow fiber, a plate and frame, a pleats, a tubular, and a spiral wound modules etc.

1-4. Application of Acetate Membrane

1-4-1. Desalination by Reverse Osmosis (RO)

There are two rationalizations regarding the mechanism of reverse osmosis. One is based on the different solubilities of water and salt in the membrane material. Another model by Sourirajan hypothesizes rejection of a salt from the boundary layer of the salt solution to lower the surface tension and predicts that only pure water should be soaked into the pores if the pore size of the membrane is smaller than twice the thickness of the layer (Fig.4) [ref.4, p.4]. Whichever is correct, the membrane material must have a suitable balance of hydrophilicity and hydrophobicity to attain a good balance between flux and rejection. For example, the degree of substitution of cellulose acetate has a profound effect on selectivity. An acetete of a higher degree ofsubstitution results in a higher rejection but a lower flux and *vise versa* (Fig. 5)[8]. This means that CTA is suitable for desalination from relatively concentrate salt solution like sea water, and CDA for a dilute solution like brackish water. In the field of desalination, cellulose acetates share the market with cross-linked aromatic polyamides and polyimides.

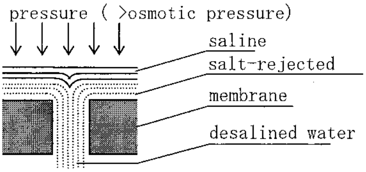


Fig. 4: The mechanism of reverse osmosis proposed by Sourirajan et al. [4].

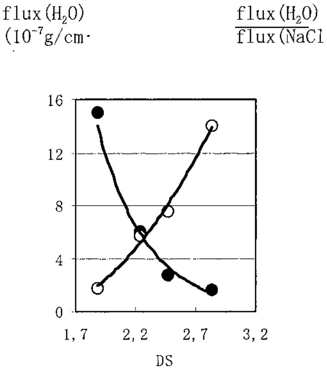


Fig. 5: The dependence of the flux of water and the rejection on the degree of substitution of cellulose acetate [8].

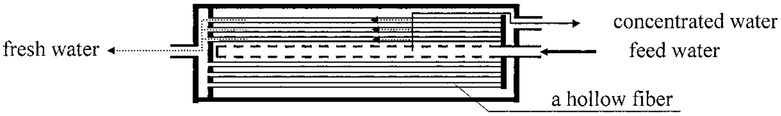


Fig. 6: A schematic diagram of an RO module (based on the web page of TOYOBO). A 1320 mm×295 mm$^{\varphi}$ single element module (HA-8130) can produce 60 m^3/day fresh water at 94% salt rejection operated at 30 kg/cm^2. A module including two elements operated at 60 kg/cm^2 can afford 99.4% salt rejection.

Fig. 6 shows an example of a CTA hollow fiber module supplied from TOYOBO. Salt water is supplied from the outside of the hollow fiber membrane and the fresh water is obtained from the inside. The feed water is suitably exhausted to keep the salt concentration not too high.

Industrial desalination by the membrane process started around 1970 and has developed so that today 20 million cubic meters of water is daily supplied worldwide. The evaporative method now occupying a more market will be soon overtaken. The application still limited to the areas like the Mideast countries and islands and to a ship will be extended along with the increasing water demand in the future and cost reduction attained by R&D.

Other than desalination, RO is applied in many fields (Table 1), but the use of the acetate membrane seems to be limited in those.

1-4-2. Hemodialysis [9]

Nowadays, nearly one million people worldwide need hemodialysis treatment.

The first artificial kidney was made using a collodion membrane by Abel et al. in 1913 and applied to an animal suffering uremia. A more suitable membrane and blood anticoagulant were then sought and the first successful clinical application was attained by Kolff and Berk in The Netherlands in 1943 during the World War II. They employed cellophane tubes for sausage casing. Cuprammonium cellulose membrane attracted attention by its success in lifesaving, *i.e.*, the treatment for acute renal failure of crash syndrome. Thus hemodialysis was established as a treatment for renal diseases. Cordis-Dow succeeded in making the artificial kidney much more compact by introducing hollow fibers. The membrane was first designed to permeate low molecular weight materials like inorganic ions, urea, creatine, and so on. However, it was then recognized that patients sometimes suffer a complication, carpal tunnel syndrome, after a long period of hemodialytic treatment and its cause is the accumulation of β_2-microglobulin, a low MW protein (11700 Dalton) being a metabolite of globulin. This drove the development of membranes with a larger cut-off molecular weight. On the other hand, for serious cases, a more rapid exchange of blood plasma, hemofiltration, is required. For those applications, an acetate membrane corresponding to the UF membrane was developed.

In Japan, CDA and CTA occupy one-third of the total market, the cuprammonium another one-third, and other synthetic materials, *e.g.*, polysulfone, EVA, and so on, do the remainder. In the US and European countries, synthetic materials occupy more of the market.

1-4-3. Drinking Water Purification by Ultrafiltration

Membrane filtration technology has recently been applied to the purification of surface water.

The conventional technique of water purification is comprised of flocculation, precipitation, and sand filtration processes that require a large facility floor space. The introduction of membrane filtration into water purification is expected to reduce the size of a facility and simplify the operation. In addition, the outbreak of massive infections by a microbe called cryptosporidium brought membrane technology into the spotlight. Cryptosporidium is very commonly distributed and causes diarrhea sometimes fatal to immunocompromised patients. As this microbe is resistant to chlorine sterilization, leakage through the filtration process caused massive outbreaks of cryptosporidiosis, in which one occurred in Milwaukee in 1993 (about 400 thousand people infected) is particularly well known. The diameter of the oocyst of C. parvum is about 5 μm and rejection of particles around this size by a UF membrane is estimated to be 10^3-10^4 times higher than by conventional systems. Thus membrane filtration is recognized as one of the promising technologies of removing microbes including this one.

Nowadays, up to 3 million m^3 of surface water is purified a day worldwide by membrane filtration systems and the amount is rapidly grawing. Though a variety of membrane materials are used, for example, polypropylene, polyacrylonitrile, polysulfone and so on, cellulose acetate is estimated to occupy about one-fourth of the total membrane market. The supplier of the CA hollow fiber membrane for water purification is Aquasource (France) and Daicel Chemical (Japan). Fig. 7 shows a membrane water purification facility in Japan.

Though the hollow fiber form is adopted regardless to the membrane material, the module and the total system are designed to be suitable for the characteristics of the membrane. For example, in the case of a Molsep FW50® module supplied by Daicen Membrane Systems, which includes the CA hollow fiber membrane produced by Daicel, feed water is supplied to the inside of the hollow fiber and the purified water is obtained from the outside. As the particle materials in the feed water deposit inside the hollow fiber and retard filtration, it is necessary to periodically wash away the sludge by a reversal flow.

The largest merit of the CA membrane in this field is its high flux (rate of permeation). Though the membrane is periodically cleaned to keep its flux as mentioned above, a certain initial loss of permeability from that of the virgin membrane is inevitable. Fig. 8 shows a comparison of the flux under constant pressure between the CA, PAN, and PES (polyethersulfone) membranes, in which the first one kept a higher flux throughout the experiment. Nakatsuka rationalized it due to the larger negative ζ potential, which may be advantageous to repel negatively charged colloid particles in surface water, rather than with the contact angle as a measure for the hydrophilicity (Table 3)[10].

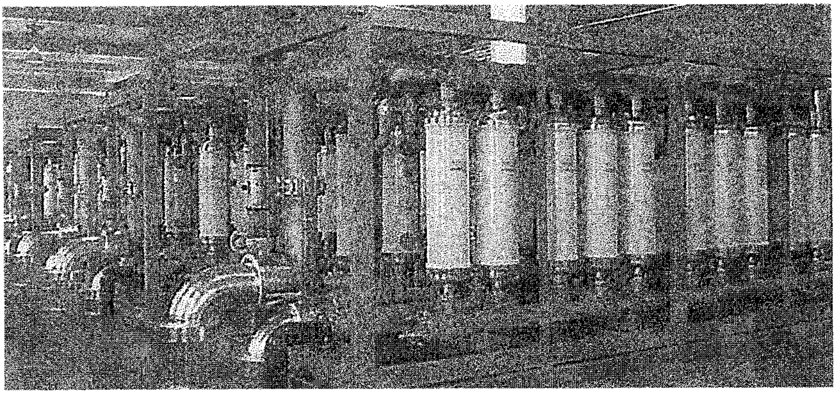


Fig. 7: The view of a water purification facility utilizing an acetate membrane (Japan).

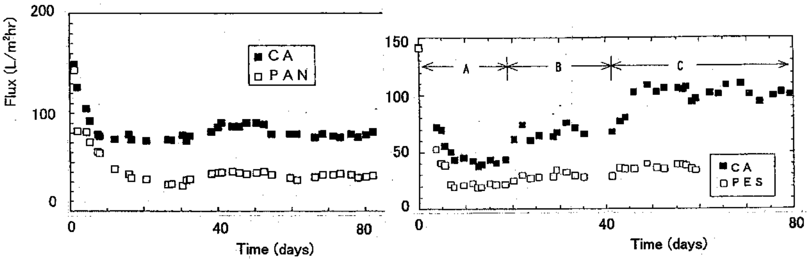


Fig. 8: The change of the flux for cellulose triacetate (CA), polyacrylonitrile (PAN), and polyethersulfone (PES) membranes. The water of Ibo river, Hyogo, Japan was treated at 50kPa. The notation A, B, and C indicate different operation conditions [10].

Table 3. Comparison of CA, polyethersulfone (PES), and polyacrylonitrile (PAN).

	CA	PES	PAN
Contact angle	50-55	65-70	52-58
ζ potential (mV at pH 7)	-30	-4.2	-7.5

1-4-4 Membrane Filter for Laboratory Use

A variety of flat microfiltration membranes for laboratory uses are commercially available (for example, from Sartorius, Apogent Technologies, Fuji Photofilm, and so on). Most of them have pore sizes between 0.1 and 10 μm and are used to remove particles like microorganisms, collect certain cells, and so on. The merits of the cellulose acetate membrane are said to be its inertness to proteins *i.e.*, a high recovery from a filtrate, and a high flux. Modified CA membranes are supplied from Millipore, which are a CA/cellulose nitrate blend membrane and a cellulose membrane prepared by the hydrolysis of a CA membrane.

1-5 Summary

Membrane technology has grown with cellulosic materials. This field is still in the development stage under active R&D and the membrane material is diversifying in order to adopt to the conditions of diversifying utilization. Even in such a situation, cellulose acetate consistently occupies an important position and will continue to do so. The comment by Kesting "Cellulose acetate is a versatile membrane polymer. Its low cost, availability in a wide variety of viscosity grades, outstanding tractibility, and reasonable resistance to oxidation by chlorine, guarantee its continued utility for the foreseeable future.“ [7] is lasting.

2. CELLULOSE ACETATE FOR CHROMATOGRAPHY AND APHERESIS

2-1. Overview

Chromatography is another important technology of separation and purification. In contrast to membrane separation, which utilizes the difference in the transportation rate for separation, chromatography utilizes difference in adsorption on or exclusion from a material called a stationary phase or a packing material. Cellulosic materials including acetate have been very often used as a stationary phase for chromatography. The adsorption of specific leukocytes on cellulose acetate offers a promising remedy for autoimmune disease.

2-2. Intermediate for Cellulosic Gel Beads

Cellulose powder has been utilized as an adsorbent or as a support for adsorbing ligands. In the 1980s, attempts were made to prepare microporous cellulose beads to improve column efficiency and capacity as a stationary phase. Among the methodologies is one via cellulose triacetate [11].

The point of the method is the formation of an o/w emulsion of a CTA solution in dichloromethane including a third material which is nonvolatile and inmiscible with CTA and the slow removal of the solvent. The third material causes phase separation to afford microporous CTA beads and hydrolysis of them reults in the formation of microporous cellulose beads.

The cellulose-based porous beads (50 to 100 µm$^{\varphi}$) prepared by this method has been commercialized by the Chisso Corporation (Japan) and supplied from the Biochemicals Corporation (Japan) under the CELLULOFINE® brand. It is applied to gel permeation chromatography in aqueous media as is and also to a variety of chromatographic separations by binding ligands (*e.g.*, an ion exchanging group, a hydrophobic group, or an affinity group) on it. They are used for the preparative purification of biomaterials like enzymes and antibodies.

Cellulose and cellulose acetate beads for cosmetic use, Celluflow®, are also supplied from the Chisso Corporation.

2-3. Cellulose Acetate as Adsorbent for Plasmapheresis [12]

The title word plasmapheresis may be unfamiliar to the readers. It is the compound of blood plasma and pheresis meaning separation, which means the separation of a particular constituent in blood plasma for therapeutic purposes. In the early 1990s, cellulose acetate was found to selectively adsorb granulocytes and monocytes. Though these have important roles in immunity, an unusual activation of them is concerned with autoimmune diseases. A column packed with cellulose diacetate beads (2mm$^{\varphi}$) named Adacolumn® was developed by Japan Immunoresearch Laboratory Co, Ltd. (Japan). The column can suitably remove those leukocytes from the blood of a patient circulated through it and mitigate the symptoms. It is an approved treatment for ulcerative colitis in Japan and also reported to mitigate rheumatoid arthritis and cachexia that appears in advanced cancer patients.

Though the origin of the selectivity for the particular leukocytes has not been rationalized, it is an intrisic property of cellulose acetate. In contrast, an adsorbent of a similar function based on a polyester fiber is available and the selectivity stems from the polyamine group bonded on it.

2-4. Chiral Separation

2-4-1. What is Chirality

Some of molecules cannot be superimposed with its mirror image like one's hand is. This property of the molecule is called "chirality" derived from the Greek word "keir" meaning a hand. When a molecule is chiral, the mirror image is called an enantiomer or an optical isomer. Though two enantiomers looks very similar to each other, their biological activities are sometimes dramatically different. That is because biological systems always consists mainly of one enantiomer, *e.g.*, the L-forms of amino acids, the D-form of glucose and so on. If a life is compared to an interior screw and the interacting enantiomeric molecules to right and left handed internal screws, the difference should easily be understood. Though the principle was underestimated until recent times, much learning has made people realize the importance of chirality in phamaceuticals [13]. Chirality is important not only in life science but also in physicochemical technology. For example, some liquid crystal displays need a pure enantiomer. However, the methodologies to prepare a pure enantiomer and to accurately analyze the enantiomeric composition were rather limited 20 years ago.

2-4-2. Cellulosic stationary phases and the two CTAs behaving differently

In the 1980s, a new convenient methodology to perform the separation of enantiomers was developed and quickly widespread, that is chromatography on a chiral stationary phase. Cellulosic materials are the most widely used family among chiral stationary phases as they can separate many enantiomeric pairs and be applied not only to analysis but also to preparative separation. Preparative separation requires a stationary phase of good durability and reasonable cost, both of which the cellulosic ones fulfill.

Eight kinds of cellulose and two kinds of amylose derivatives are now commercially supplied as a packed column or a stationary phase (packing material) from Daicel Chemical under the tradename CHIRALCEL O® series, CHIRALPAK A® series, and CHIRALCEL CA-1®. Two of them, CHIRALCEL OA® and CA-1® are both CTA based. Though the sales of the CTA phases are rather low compared to the other cellulose and amylose based ones, CTA not only played a very important role in the development of the polysaccharide phases as the prototype of cellulose esters, but also showed an interesting relationship between chiral recognition and the superstructure of a polymer [14]. The story below will answer why there are two kinds of CTA phases.

Hesse and Hagel at the University of Erlangen-Nürnberg reported the first complete separation of enantiomers by liquid chromatography in 1973 [15]. This separation was attained by using the particular kind of CTA so-called microcrystalline cellulose triacetate (MCT) (Fig.9a). It is noteworthy that this achievement was not attained suddenly but attained based on the accumulation of knowledge of chromatography on sugars, particularly on cellulosics [14]. A very interesting observation they reported was that once MCT had been dissolved in acetone and reprecipitated, the chiral recognition (the ability to separate enantiomers) was mostly lost (Fig. 8b). Therefore, chiral recognition was regarded by people as peculiar to MCT, presumably to its microcrystalline structure. Liquid chromatography columns based on MCT are supplied from E. Merck, Macherey-Nagel, and Daicel Chemical (CHIRALCEL CA-1®).

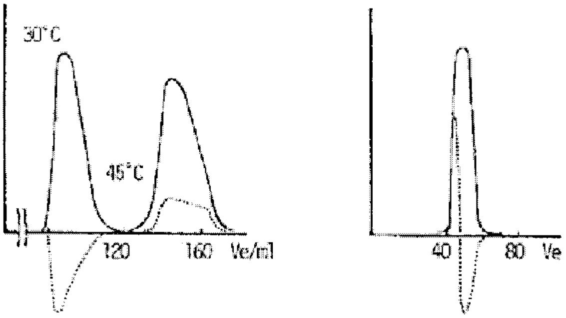


Fig. 9a (left): Chromatogram of Tröger's base on MCT.
Fig. 9b (right): Chromatogram on reprecipitated CTA from MCT.
Solid line denotes UV absorption and broken line does optical rotation [15].

Though MCT could separate many enantimeric mixtures, they are still only a part of many chiral molecules. Furthermore, MCT needs a long analysis time and the efficiency is still not very high. Those drove us to develop a novel way of applying cellulosics to chiral separation.

From the viewpoint of crystal structure, MCT, which is prepared by the heterogeneous acetylation of microcrystalline cellulose, belongs to CTA I. It is the metastable one of the two allomorphs of CTA [16] which irreversibly transforms to CTA II through dissolution in solvent. The novel way was the utilization of CTA II, which looked unpromising from the result of Hesse. Crystallization of CTA II was first attempted as people believed crystallinity is essential. However, it failed in stimulating chiral recognition but showed even a reverse effect. Instead, conformational regularity of CTA as the hysteretic memory of the casting solvent profoundly affected the chiral recognition [17]. This knowledge made it possible to employ macroporous silica beads as the support for CTA to realize a high performance stationary phase (CHIRALCEL OA®). The methodology established with CTA made possible the utilization of a variety of cellulose and other polysaccharide derivatives prepared in solution and resulted in the commercial supply of the most powerful family of chiral stationary phases.

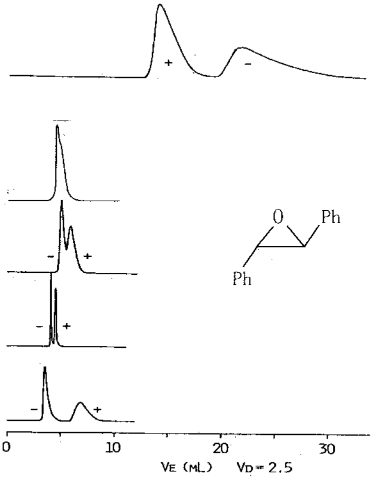


Fig. 10: Dependence of chromatogram on the states of CTA [14]. Sample: *trans*-1,2-diphenyloxirane.
The top: MCT (mobile phase: ethanol).
The 2nd: CTA II with a high crystallinity (mobile phase: ethanol).
The 3rd: CTA II with a low crystallinity (mobile phase: ethanol).
The 4th: CTA II coated on porous silica beads with dichloromethane (mobile phase: hexane/2-propanol 9:1v/v mixture).
The bottom: CTA II coated on porous silica beads with a phenol/dichloromethane mixture (mobile phase: hexane/2-propanol 9:1v/v mixture).
The +/- denote optical rotation.

Thus two stationary phases based on CTA were commercialized. However, the characteristics of these two phases are so different that one could hardly accept the identity of the chemical structure (Table 4). CTA I adsorbs many molecules stronger than CTA II, that is particularly clear for nonpolar aromatic compounds, and the enantiomeric elution order is often reversed between the CTAs (The +/- in parentheses in Table 4 indicates the optical rotation.). These facts, *i.e.*, the functional diversity between the allomorphs and that within an allomorph, shows a strong relation between functionality and superstructure.

The mechanism of chiral recognition on a cellulose derivative was clarified by Yashima et al. for a couple of binaphthol enantiomers and cellulose tris(5-fluoro-2-methylphenylcarbamate)[18]. However, many things are still unknown about chiral recognition by cellulosics, and the impact of the superstructure of CTA is the most interesting among them.

Table 4: The comparison of the retention behaviors of the two different CTAs.

Racemate	Stationary phase	k'_1	k'_2
Tröger's base	MCT	2.61 (-)	5.36 (+)
	CTA II	0.59 (+)	0.91 (-)
trans-1,2-Diphenyloxirane	MCT	7.82 (+)	11.3 (-)
	CTA II	0.94 (-)	1.23 (+)
Mandelamide	MCT	2.08	3.08
	CTA II	0.8 (no separation)	
Benzene (achiral)	MCT	10.3	
	CTA II	0.46	

The CTA II is the one giving the third chromatogram in Fig. 10. The mobile phase is ethanol.

2-5. Summary

Chiral recognition was spotlighted because of the novelty of the separation mode. However, it is just one of many interesting adsorptive properties cellulose acetate and other derivatives possess. For example, cellulosic phases are very potent in separating any structurally similar molecules like regioisomers and geometrical isomers. Adsorption of the specific kinds of leucocyte is also very interesting because not only of its usefulness but also of its mechanism. We believe that elucidation of what is occurring on and in cellulose acetate on a nanometer scale should allow us to find a larger variety of functionalities and applications.

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