
Recent Progress in Surface Science and Its Application in Advanced Water Treatment by Membrane Processes

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RECENT PROGRESS IN SURFACE SCIENCE AND ITS APPLICATION IN ADVANCED WATER TREATMENT BY MEMBRANE

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Abstract

As environmental regulations become more stringent, water, used either as drinking water or as industrial process water, becomes increasingly better in its quality. As a result, an increasingly more advanced water treatment technology is required. It is believed that membrane technology will be able to satisfy such a requirement.

The heart of the membrane technology is membrane. The advancement in water treatment technology using membranes, therefore, depends on the development of novel membranes which are superior in performance to the currently available membranes. In this paper, a brief review will be made how the recent progress in surface science, such as surface modification and surface characterization, has aided to improve the performance of the membranes used for water treatment. Some suggestions will also be made regarding the future direction of the research in this area.

1. Membrane surface modification

The surface modification of polymeric materials is of growing interest, recognizing the fact that it is the property of membrane/feed solution interface which governs primarily the membrane transport.

The following methods have been attempted to modify the membrane surface.

1.1. Modification of membrane surface by forming a dense selective layer on top of a bulk porous sublayer. The chemical structure of the surface layer may or may not be the same as that of the sublayer. The following techniques are known.

- Lamination of ultrathin layer
- Formation of dynamic layer
- Dip and spin coating
- Plasma polymerization
- Interfacial polymerization
- Chemical vapor deposition

1.2. Modification of the chemical structure of the membrane surface while leaving the layer underneath intact. This modification technique can be applied to the surface of the dense selective layer which is formed by one of the techniques given above. The following techniques are known.

Surface cross-linking

Grafting

Surface chemical reaction such as fluorination

Blending surface modifying macromolecules

Mulherjee et al. applied surface chemical reaction on top of the FT-30 membrane which is one of the most widely used thin film composite membranes.¹⁾ The selective skin layer of FT-30 membrane is formed by interfacial polymerization. Thus, Mulherjee et al.'s technique is the combination of interfacial polymerization and surface chemical reaction. FT-30 membranes were cut into circular coupons of about 38.5 cm². The coupons were then soaked under controlled conditions of temperature in solutions of various concentrations of hydrofluoric acid (HF), fluosilicic acid (FSA) and their mixtures. The membranes were taken out after various intervals of time, rinsed with deionized water and then their performance in terms of flux and sodium chloride separation was determined. A dramatic effect of the surface modification on the membrane performance was observed when the membrane was soaked in 15 wt% HF solution for a period of seven days. The flux increased from 3.5 l/m² hr to 18 l/m² hr while sodium chloride separation increased from 94.5 to 95.3 % under the operating pressure of 250 psig. The surface characterization was done by X-ray photoelectron spectroscopy (XPS). The fluorine ratio (F/C) at the membrane surface increased from zero of a fresh FT-30 membrane to 0.012 of a membrane immersed in 15 wt% HF solution for 4 days and further to 0.044 of a membrane immersed in 15 wt% HF solution for 75 days. Thus, the surface fluorination of the FT-30 membrane is obvious. A ridge and valley network structure was observed at the membrane surface by the scanning electron microscope (SEM). The SEM pictures revealed further that the ridge thickness decreased on surface modification. This implies the thinning down of the polymeric network of the selective skin layer due to the etching of the surface by HF. Thus, both the chemical modification of the surface and the thinning of the selective skin layer contributed to the dramatic increase of the flux, while sodium chloride separation was practically unchanged. Similar effects were observed by Kulkarni et al. when hydrochloric, sulfuric, phosphoric and nitric acids were used instead of HF.²⁾ The contact angle measurement for octane-membrane-water systems revealed that the hydrophilicity of membrane surface increased after the surface modification.

Another attractive and simple method of membrane surface modification is to add or blend surface modifying macromolecular additive into the casting solution. Thermodynamic principles stipulate that the formation of the lowest possible energy status is a universal tendency. The principal characteristics of a surface modifying macromolecule (SMM) is that it has lower surface energy than that of a base polymer and thus the ability to migrate preferentially toward polymer-air interface. SMM molecules are synthesized using a two-step solution polymerization. First methylene bis-phenyl diisocyanate (MDI) is reacted with polypropylene diol (PPO) of average molecular weight 425 to form a prepolymer. Then, the prepolymer is reacted with

fluorotelomer (Zonyl BA-L™, DuPont). The MDI:PPO:BA-L ratio is either 2:1:2 or 3:2:2.³⁾ The molecular structure of SMM is given in Figure 1.

Membranes were cast using polymer solutions containing 17 wt% polyethersulfone (PES), 7 wt% polyvinylpyrrolidone (PVP) in dimethylacetamide solvent. In one solution 1 wt% of SMM was added (corresponding to M2 in Fig. 2) while in the other no SMM was added (corresponding to M10 in Fig. 2). In ultrafiltration experiments, the membranes were first compacted under pure water at 73 psig, until permeation rates levelled off. Then, a 10 % (by volume) cutting oil/water mixture was used as feed at the operating pressure of 53 psig. The feed was replaced with pure water after about eleven days of oil/water experiment and the pure water run was continued for about three days. Then, oil/water mixture was used again as a feed and the experiment continued for nearly seven days. The experiment was concluded with pure water as feed. Comparison between membranes M2 and M10 is shown in Fig. 2. The permeation rates through M2 are higher than those through M10 when the feed is oil/water, whereas for pure water permeation the order is reversed. This trend is observed during different oil/water and pure water cycles. The increased hydrophobicity of M2, resulting from incorporation of SMM in the casting solution, lowered the pure water permeation rate. On the other hand, the increased hydrophobicity reduced the gel formation, when oil was present in the feed, resulting in the higher flux of M2 as compared to M10.⁴⁾ The membranes were subjected to contact angle measurement of water/air/membrane system. As Fig. 3 shows both advancing and receding contact angles increased with an increase in the amount of SMM in casting solution, while PES and PVP concentrations were kept at 25 and 6 wt %, indicating that the surface hydrophobicity increased by adding SMM in the casting solution. Figure 4 shows the results of XPS experiments. In the figure, as the XPS take-off angle decreases, the distance from the membrane surface also decreases. Thus, the figure shows that the fluorine content increases toward the membrane surface, confirming the migration of fluorine containing SMM molecules toward the membrane surface.⁵⁾

2. Membrane surface characterization

2.1. Characterization methods

Advanced methods of surface characterization are necessary to examine and control the chemical structure and the morphology of the membrane surface. Typical examples of characterization methods are:

- a) To characterize the chemical properties of the membrane surface

X-ray photoelectron spectroscopy
FTIR-ATR
Raman spectroscopy

- b) To characterize the physical property of the membrane surface

Contact angle measurement
Inverse gas and liquid chromatography

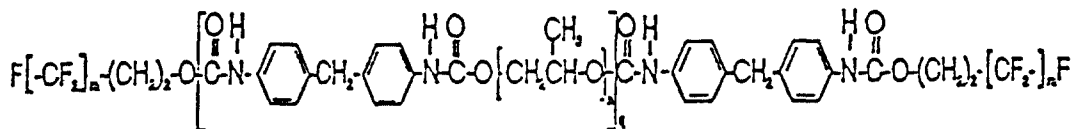


Figure 1. Structure of Surface Modifying Macromolecule

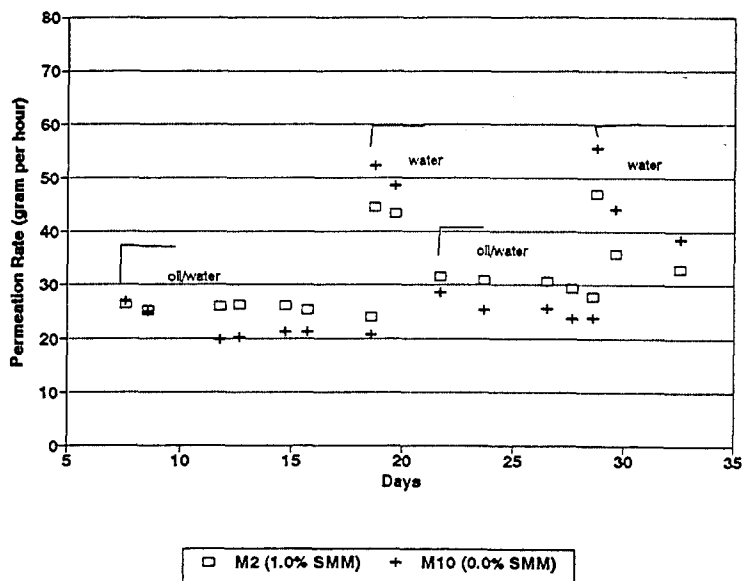


Figure 2. Performance of ultrafiltration membranes in the treatment of pure water and cutting oil/water mixture.

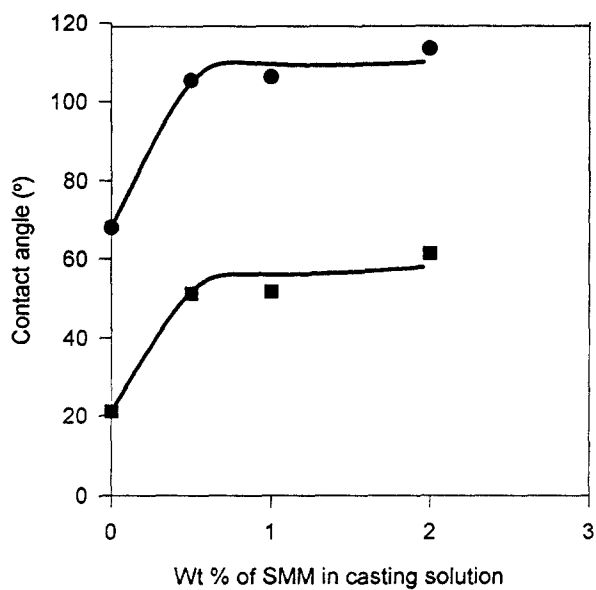


Figure 3. Contact angle versus SMM content
 Circle, advancing contact angle; square, receding contact angle

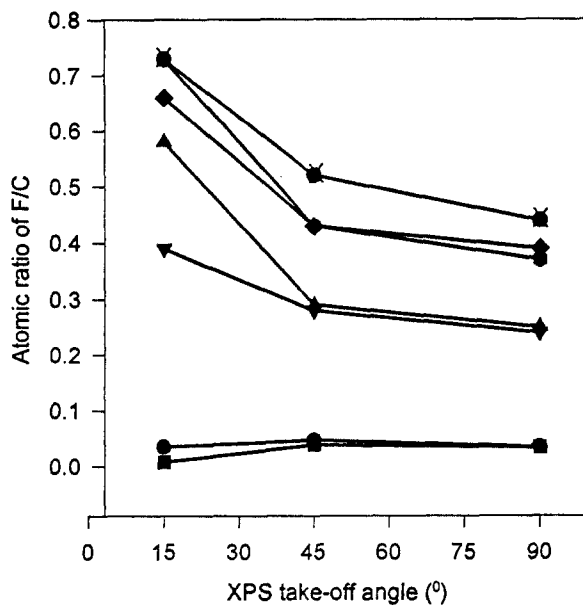


Figure 4. Results of XPS experiments
 SMM content ●, 0.5 %; ■, 1.0 %; ▲, 1.5 %; ▼, 2.0 %; ◆, 2.5 %; ●, 3.0 %; ✕, 3.5 %.

c) To characterize the surface morphology of the membrane

Scanning electron microscopy
Atomic force spectroscopy
Electron spin resonance
Gas adsorption measurement

Although all characterization methods have been used, progress in the area of atomic force microscopy is most remarkable in recent years. Some examples of surface characterization used to aid the surface modification have already been shown.

2.2. Surface characterization and membrane design

Hirose et al. found a relationship between the flux of reverse osmosis membranes and their roughness parameter determined by AFM. According to their experiments, an increase in surface roughness resulted in a higher water permeation flux. As an extension of this observation, they have prepared an aromatic polyamide composite membrane with an extremely rough surface. The roughness of the surface was confirmed by transmission electron microscope. The membrane so prepared, called ES 20 membrane, maintains a high salt rejection while the flux is double as high as the conventional low pressure RO membrane NTR-759HR.⁶⁾

Hamza et al. prepared thin film composite nanofiltration membranes by coating a thin layer of sulfonated polyphenylene oxide (Ion exchange capacity = 1.93 meq/g dry polymer) on top of a porous polyethersulfone substrate membrane. The coating solutions were prepared by dissolving 1 wt % of SPPO polymer in chloroform/methanol mixtures of different compositions.⁷⁾ The intrinsic viscosity of the polymer solution was measured for each solvent mixture and the results are given in Table 1.

The intrinsic viscosity decreases with an increase in chloroform in the solvent mixture, indicating that the polymer molecule is coiled more compactly in the solvent mixture with higher chloroform content. The surface investigation by AFM, on the other hand revealed its nodule-like structure. The diameter of the nodule is also reported in Table 1. The nodule size decreases also with an increase in chloroform content in the solvent mixture. This means the compactness of the polymeric coil in the coating solution is retained after the evaporation of the solvent from the solution.

The thin film composite membranes so prepared were tested for their performance in reverse osmosis separation of several electrolyte solutes. Figures 5 and 6 show the solute separation and product rate data. After the solute separation increased slightly with an increase in chloroform concentration in the solvent mixture from 0 to 42 %, the separation started to decrease with a further increase in chloroform concentration. The effect of the chloroform concentration in the solvent mixture on the membrane flux is more dramatic. In the separation experiment of sodium chloride solute, the flux decreased from 11 to less than $2 \times 10^{-6} \text{ m}^3/\text{m}^2 \text{ s}$ as the chloroform concentration increased from 0 to 66 %. These results offer a guideline for the choice of the solvent in the preparation of thin film composite membranes by the dip-coating method.

Table 1. Intrinsic viscosity of SPPO polymer solutions in different solvent mixtures and nodule size at the surface of thin film composite membranes

CHCl ₃ content in solvent mixture, wt %	Intrinsic viscosity, dL/g	Nodule size, nm
0	1.99	85-125
18	1.51	54-70
42	1.27	37-51
66	0.92	20-32

Table 2. The pore diameter measured by separation experiment and AFM technique

Membrane	40kDa	100kDa	200kDa	0.1 μm
d _{separation} (nm)	11	15.5	28.4	80.0
d _{AFM, min} (nm)		31	38	96
d _{AFM, max} (nm)		69	114	185

Table 3. The ratio of actual surface area to the geometric surface area

Membrane	Ratio
40 kDa	1.003
100 kDa	1.047
200 kDa	1.380
0.1 μm	1.154

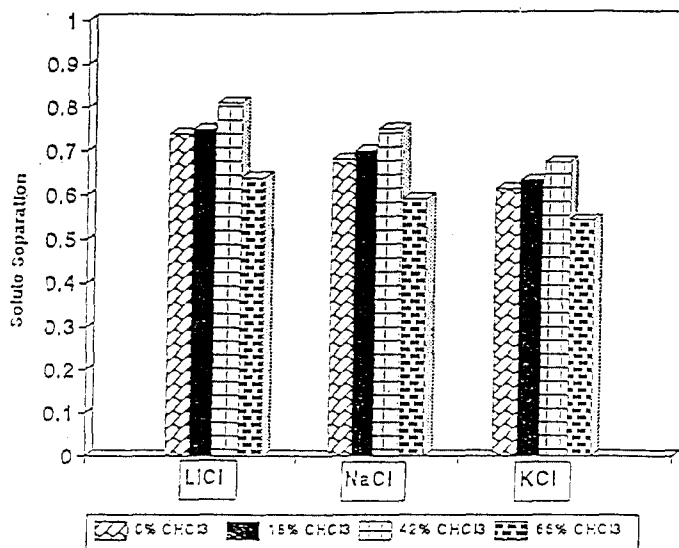


Figure 5. Effect of solvent in coating solutions on the separation of different electrolytes
 Operating pressure, 1379 kPa gauge; operating temperature, 25°C

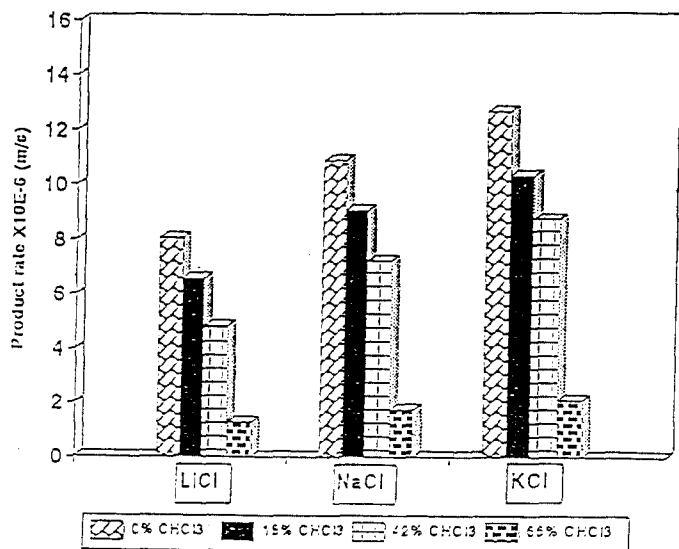


Figure 6. Effect of solvent in coating solution on the permeation rate
 Operating pressure, 1379 kPa gauge; operating temperature, 25°C

2.3. Surface characterization and membrane performance

Bessières et al. measured the pore sizes of sulfonated polysulfone ultrafiltration membranes with molecular weight cutoff values of 40,000, 100,000, and 200,000 Dalton and a polyvinylidene fluoride membrane with nominal pore diameter of 0.1 μm . The methods to determine the pore size were by separation experiments with polyethylene glycol solutes of different sizes and AFM.⁸⁾

In the former method, the sieving coefficient S was given by

$$S = (1 - \lambda)^2(2 - (1 - \lambda)^2)(1 - 2/3\lambda^2 - 0.163\lambda^3)$$

where λ is the ratio of the radius of ethylene glycol molecule, a , to the pore radius, r . The radius of polyethylene glycol was obtained from the intrinsic viscosity measurement, applying the following equation

$$a = (3[\eta]M_w/4\pi N)^{1/3}$$

where N is the Avogadro number.

Table 2 summarizes the data on pore diameter obtained from separation experiments and from AFM images. Minimum and maximum pore diameters are reported for the pore diameters obtained by AFM. The table shows that even though the pore diameters obtained by the AFM technique are consistently higher than those obtained by the separation experiments, a parallel relationship exists between both diameters, indicating that the AFM pores can be used to predict the separation data of polyethylene glycol. Another interesting conclusion in their work is that the actual membrane area can become considerably greater than geometric surface area when the surface roughness increases. As Table 3 indicates, the actual surface area for the ultrafiltration membrane of 200 kDa is almost 40 % more than the geometric surface area of the membrane.

2.4. Characterization of membrane fouling

A nanofiltration membrane was prepared by coating a thin layer of SPPO with ion exchange capacity of 2.0 meq/g dry polymer on top of a polyethersulfone ultrafiltration membrane to treat a solution which simulates white water, a wastewater from pulp and paper industry. The primary component of white water is clay, therefore the feed was made by dispersing clay particles in water. In some cases SBR latex was added to the feed. After treating the simulating solution the membrane surface was observed by AFM.⁹⁾ Figure 7 is the surface after treating the feed containing 0.87 % of clay. The surface is covered completely by clay layer and individual clay particles of about 0.2 μm can be observed. Figure 8 shows the membrane surface after treating 0.1 % of clay and SBR mixture. Clay particles are negatively charged and a repulsive force works between charged clay particles. In the presence of SBR, however, the clay particle is coated with SBR latex and tends to agglomerate. The size of each agglomerate is about 2.5 μm , containing 20 to 30 individual particles. Pores are formed between agglomerates. Thus, the mechanism of particle deposition is clearly seen by using AFM.

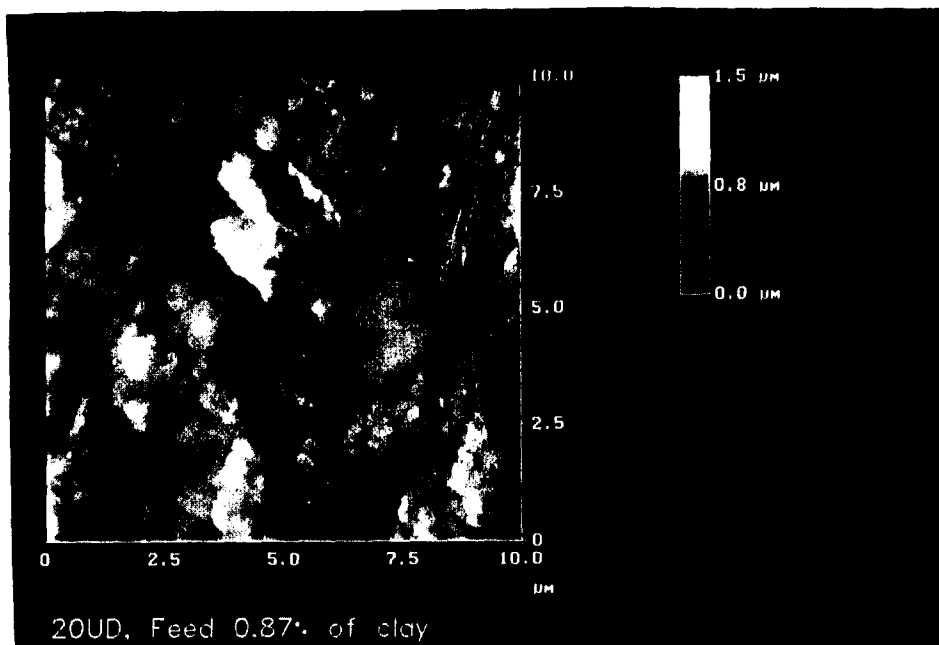


Figure 7. AFM picture of a nanofiltration membrane after treating a feed liquid containing 0.87 % clay particles

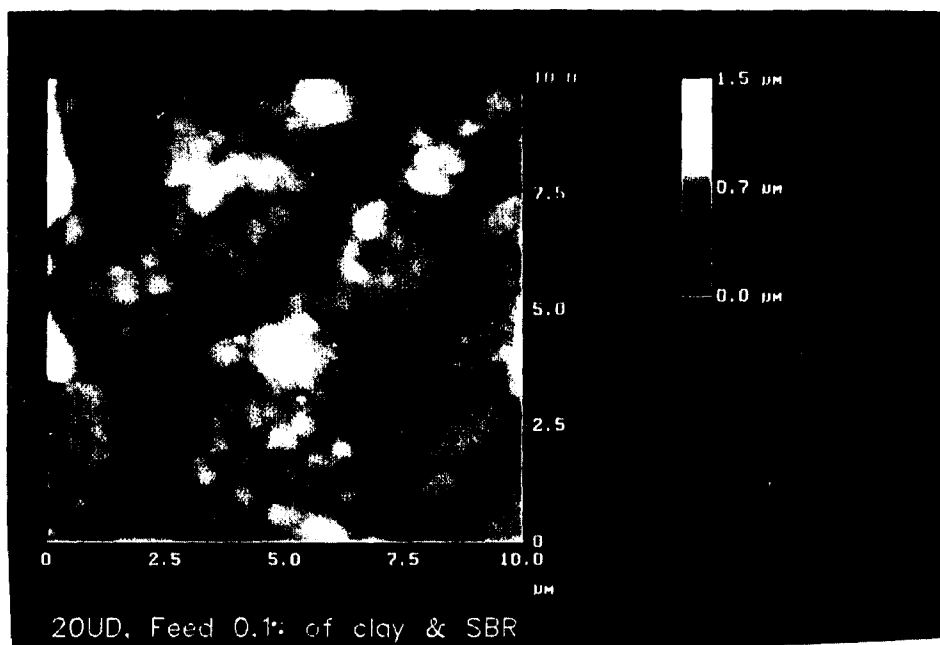


Figure 8. AFM picture of a nanofiltration membrane after treating a feed liquid containing 1 % of clay and SBR mixture

The membrane fouling by protein (bovine serum albumin) was studied by using electron spin resonance (ESR) technique.¹⁰⁾ A radical probe was added to 0.1 % bovine serum albumin solution in water and the solution was subjected to ESR analysis. Three signals of identical height and width could be observed (Fig. 9). When a membrane after treating the bovine serum albumin solution, which included the radical probe, was subjected to ESR analysis, three signals were also observed (Fig. 10). But the first and the third signals were much shorter than the central one, indicating that the movement of the spin probe was more restricted in the membrane than in the solution. This indicates also that the movement of bovine serum albumin molecules is restricted when they are adsorbed to the membrane surface. At present, the location of BSA molecules, either on the top surface of the membrane or in the pore, is not clear, but BSA is most likely in the membrane pore.

3. Future trend

The following areas of surface science and engineering are expected to progress rapidly in the near future.

- 1) The surface chemistry and morphology will be clarified more in detail, particularly for polymeric materials. The profiles of infrared, Raman, NMR and ESR spectra will be established to the direction perpendicular to the surface within a distance of nano-scale and they will help us understand the surface structure.
- 2) The contributions of the surface and bulk phases to the membrane transport will become known more clearly as the method of surface characterization progresses.
- 3) Regarding the phenomena occurring at the membrane-feed solution boundary, hydrodynamics of the feed solution should be affected by the microscopic roughness of the membrane considerably. Interfacial force starts to govern fluid dynamics. Computer simulation will enable us to understand concentration polarization and fouling more on a microscopic scale.
- 4) The coating of a selective layer on a porous sublayer is currently being done by trial and error. The flow of the viscous coating liquid on and/or into nano-scale pores should be more clearly understood in order to make the coating more effective. Again, the interfacial force starts to govern the nano-scale rheology. Computer simulation is desirable.

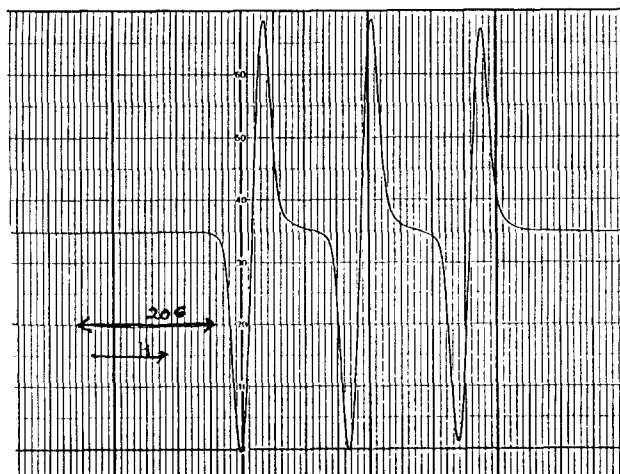


Figure 9. ESR spectra of 0.1 % BSA solution including radical probe

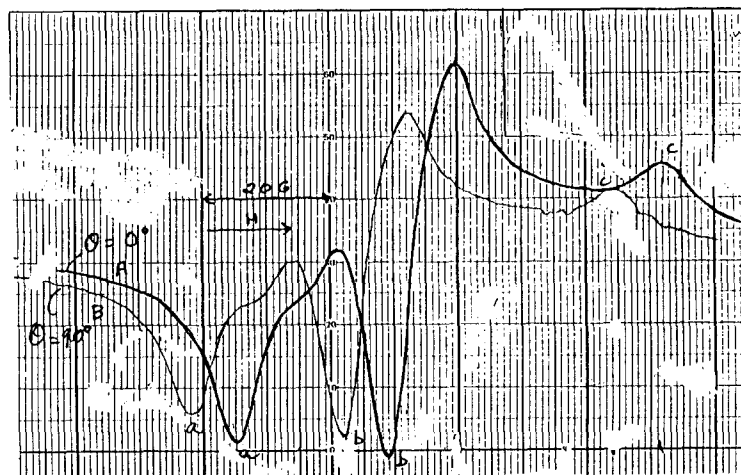


Figure 10. ESR spectra of Polyethersulfone ultrafiltration membrane after treating the solution 0.1 % BSA solution including radical probe

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