ULTRAFILTRATION OF DYES IN THE PRESENCE OF SURFACTANTS

Georgeta Popescu *, **B. Albu***, **Demetra Nuta***, **Daniela Rata***, **E. Aldea** **, **G. Dinescu**** **and M. Olteanu*****

abstract: The wastewater from the dye synthesis facilities contains high concentrations of organic solutes and multivalent ions. This contribution evidences the influence of ionic surfactants on colloidal ultrafiltration of dyes. The surfactant-dye mixed aqueous solutions obtained by varying the dye and surfactant concentration respectively was characterized by UV-VIS spectroscopy. The interaction between these components and the ultrafiltration membrane determines the flow and retention values.

1. Introduction

The asymmetric membranes have determined a tremendous development of the separation processes involving membranes such as microfiltration, ultrafiltration and reverse osmosis.

In the 50'th period, the scientists have introduced the surfactants in the composition of the polymeric solution from which the membrane is formed, in view to maintain the characteristics of the membrane (for example, porosity, flux) both in wet and in dry state [1]. Recently the decisive role of the nature and concentration of the surfactant present in the casting solution to the morphology and membrane performances was emphasized [2].

The surfactants are also implied in the membrane processes, influencing flow through polymeric porous media [3,4], cleaning of membranes during the process and after use [5] or modifying the microstructure of the disperse system for separation [6,7].

In this work the influence of some surfactants upon the flow and retention of some pure water soluble dyes were studied.

---

* *Research Center for Macromolecular Materials and Membranes, Spl. Independentei 202B, 79611 Bucharest, e–mail: macromol@rnc.ro*

** National Institute for Lasers Plasma and Radiation Physics, Low Temperature Plasma Department, Atomistilor 1, Magurele-Bucharest - POB MG 36, 76900, Romania, e-mail: dinescug@alpha1.infim.ro

*** University of Bucharest , Department of Physical Chemistry, 13 Republicii Bld, 70346, Bucharest, e-mail: oltme@hotmail.com

Analele Universității din Bucureşti – Chimie, Anul XII (serie nouă), vol. I-II, pag. 49–54

2. Materials

Membranes: polysulfone membrane (PS) prepared by phase inversion method, immersion-precipitation technique from a casting solution 16% polysulfone in dimethylformamide, coagulated in water solution and a composite membrane (PSP) prepared by plasma polymerization conditioning of the PS membrane (monomer – styrene, working gas – air, pressure 100 Pa, conditioning time 8 min, exposure 100 W.min.) *Mercury porosimetry: Carlo-Erba* Computerized Microstructure Complex from Carlo-Erba (Italy). *Liquid porometry*: Coulter Porometer II from Coulter Electronics Limited (England) *Ultrafiltration device*: CELFA MEMBRANE SYSTEME P 28

Surfactants: dimethylbenzyl hexadecyl ammonium chloride (DBHAC) from Loba Feinchemie

Dyes: Yellow III (food dye, color index 15985) and Orange III (methyl orange) from Merck

All the reagents used were of analytical grade and the aqueous solutions were prepared with microfiltered water. The determination of dyes was performed by UV-VIS spectrophotometer (GBC 918), respectively.

3. Results

3.1. Membrane characterization

A complementary characterization of the PS membrane is presented below; the plots of pore size distribution given by mercury porosimetry, liquid porometry being represented in Figs. 1 and 2 respectively.

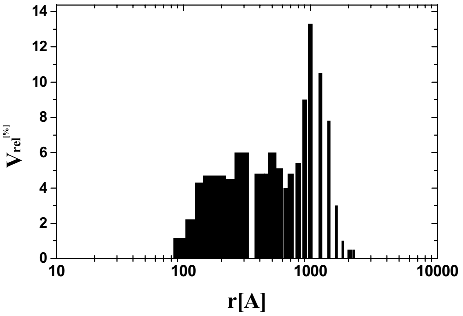

Fig. 1: *Pore size distribution carried out by mercury porosimetry*

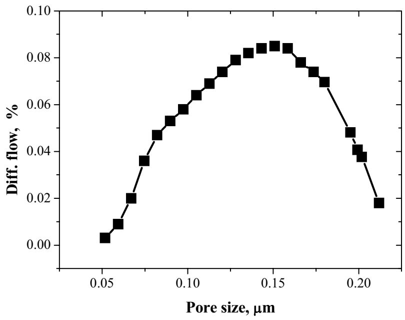

Fig. 2: *Pore size distribution carried out by liquid porosimetry*

The characteristics evidenced: pore size of the PS polymeric membrane having a Gaussian pore size distribution with maxims among 0.05÷0.1 μm.

The mean pore radii measured by a gas permeability method were 73 nm for PS and 21 nm for PSP membranes respectively, in accordance with the previous measurements.

The plot of the distilled water flux vs. pressure for the membranes PS and PSP is presented in Fig. 3. It is observed a linear plot flux – pressure, the hydraulic permeability for the PSP membrane being of 2.65×10^{-3} cm.s^{-1}.bar^{-1}.

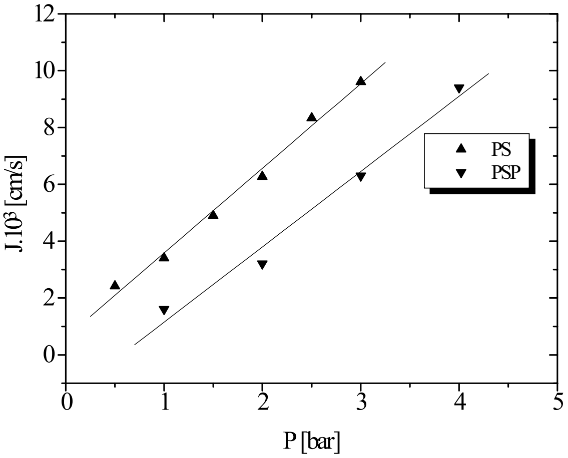

Fig. 3: *Plot of the distilled water flux vs. pressure for the membranes PS (▲) and PSP (▼).*

3.2. Dye characterization

In the absence of the surfactant, the Yellow III (Y) dye exhibits in the plot of the normalized flux vs. the solution concentration an extreme point at a concentration of 0.14 g/dL, both for PS and PSP membranes, which can be explained by an aggregation phenomenon. The Y dye shows also a maximum retention for small concentrations (0.01 g/dL). At greater concentrations, the retention on the PS membrane is zero, respectively 40% for the PSP membrane. The maximum point can be assigned to an adsorption phenomenon on the membrane, but the PSP membrane exhibits a real retention due to its hydrophilic surface (Fig. 4).

Adding in the Y dye solution a constant amount of DBHAC ([DBHAC]=0.05 g/dL) the normalized flux for the PSP membrane is diminishing its value in the aggregation zone followed by a strong decrease of it due to the adsorption phenomena of the complex in the porous structure. The introduction of DBHAC results an increase of the retention, due to the inclusion of the Y dye in the micelle, phenomenon also associated with a displacement of maximum adsorption in the visible (Fig. 5).

In the case of Orange III (MO) dye the observed phenomena are similar. Adding a constant amount of DBHAC ([DBHAC]=0.02 g/dL) in the MO solution micellar aggregates are formed, the PS membrane is fouled and hence the normalized flux is decreasing. The PSP membrane, which possesses smaller pore sizes as compared with PS membrane, retains the micellar associates only on the surface, as compared with the PS membrane where the adsorption occurs in the porous walls. This fact can explain the more pronounced discontinuity for the PSP membrane for an MO concentration of 0.025 g/dL (Fig. 6). The micellar association phenomenon leads to the displacement of the maximum adsorption wavelength from 470 nm, characteristic for MO solution to 362 nm specific to the micellar solution. The retention of MO increase with dye concentration (Fig. 6), attaining a 100% value for PSP membrane, the permeate UV spectra being specific to the surfactant, being possible to measure the surfactant concentration in permeate (Fig. 7).

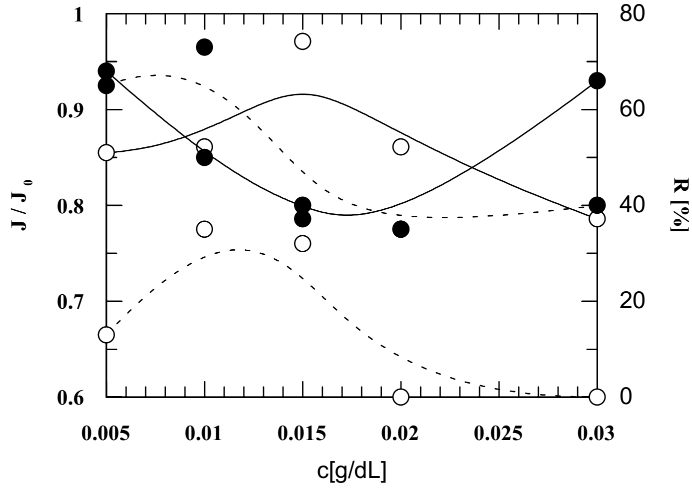

Fig. 1: *Dependence of the normalized flux (J/J0 —) and retention (R ·····) of Yellow III (Y) vs. concentration for ○- PS ●-PSP*

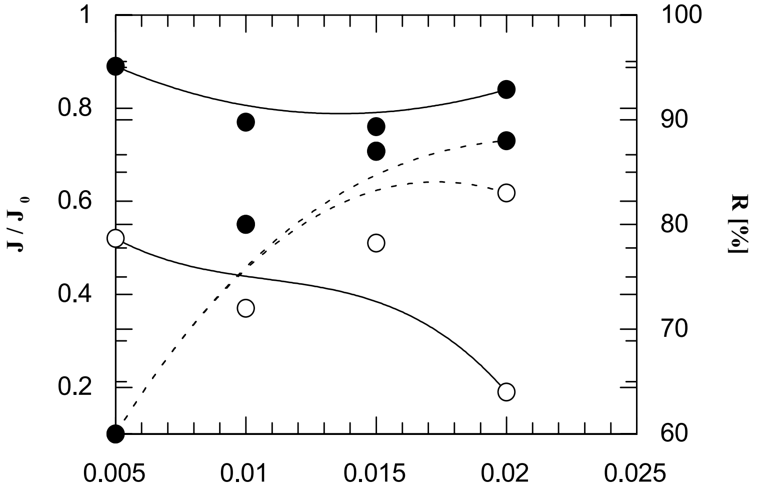

Fig. 2: *Dependence of the normalized flux (J/J0 —) and retention (R ···) of Yellow III (Y) / DBHAC ([DBHAC] = 0.05 g/dL) vs. concentration (○- PS ●-PSP).*

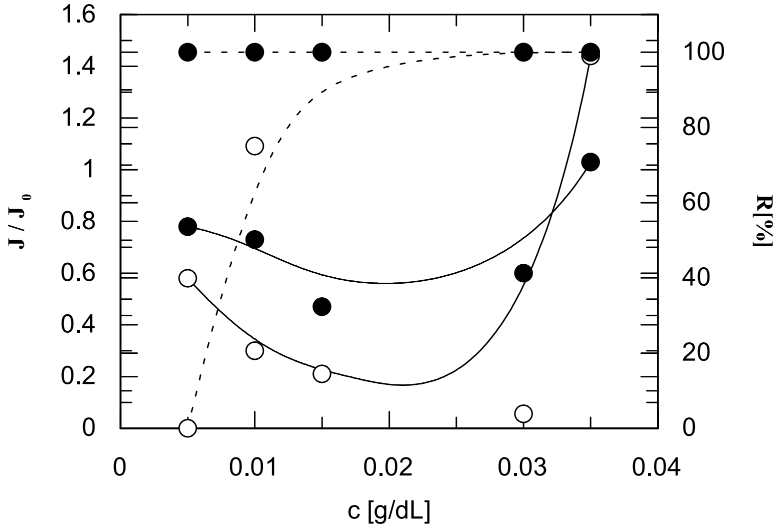

Fig. 3: *Dependence of the normalized flux (J/J0 —) and retention (R ···) of MO / DBHAC ([DBHAC] = 0.02 g/dL) vs. concentration (○- PS ●-PSP).*

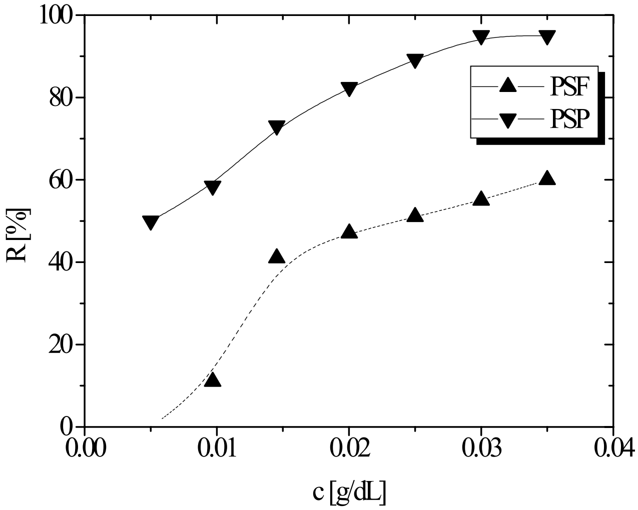

Fig. 4: *Plot of the DBHAC retention vs. MO concentration ([DBHAC]=0,02 g/dL) (▲- PSF, ▼ - PSP).*

4. Conclusion

The presence of the surfactant in the dye solution leads to the formation of some complexes in the initial solutions. These complexes may be swelled with an organic compound, or may be caused by the electrostatic interactions, favouring the increase of the retention both for the dye and the surfactant.

REFERENCE

1. Van Oss, G. J. (1970) **Progress in Separation and Purification**, Perry, E. S. and Van Oss, C. J., Eds., New York, Wiley - Interscience.
2. Nechifor, G., Luca, N., Albu, B. and Nechifor, A.M. (1993) *Roumanian Chemical Quarterly Reviews* **1**, 221-9.
3. Popescu, G., Nechifor, A.M., Albu, B. and Nechifor, G. (1989) *Proc. VIIth Jugoslav Symp. Surface Active Agents*, Tuzla.
4. Nechifor, G., Nechifor, A.M., Popescu, G. and Albu, B. (1990) *Proc. VIIIth Intern. Symp. Surfactants in Solution*, Gainesville, Florida.
5. Litner, K. and Bragulla, S. (1987) **Internationale Zeitschrift fur Lebensmittel - Technologie und Verfahrenstechnik**.
6. Albu, B., Gosa, K, Olteanu, M., Popescu, G., Nutã, D. and Dinescu, G. (1994) *Proc. VIIIth European Colloid and Interface Society Conference*, Montpellier, France.
7. Popescu, G., Albu, B.G., Ratã, D., Moise, L. and Nechifor G. (1994) *Interfiltra'94*, Intermembrane - Recentes progresses in genie des procedes.
8. Popescu, G., Nechifor, G., Albu, B., Luca, N. (1989) *Rev. Roum. Chim.* **34**, 577-92.
9. Nechifor, G., Luca, N., Popescu, G. and Nechifor, A.M. (1989) *Rev. Roum. Chim.* **34**, 2047-51.
10. Aldea, E., Dinescu, G., Musa, G., Catana, G., Albu, B., Nechifor, G., Popescu, G. (1995) *Proc. 12th International Symposium on Plasma Chemistry*.