

# A novel approach to determine the molecular overlap of polyelectrolyte using an ultrafiltration membrane

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## Abstract

The overlapping of charged polymers (e.g., polyelectrolyte) in the liquid phase is one of the key parameters affecting the processing of the macromolecular solutions. This work focused on the development of a novel method for determining the overlap concentration of polyelectrolytes with stirred cell ultrafiltration (UF) techniques. A new, simplified equation that incorporated the resistance-in-series UF model into the osmosis phenomenon caused by polymers was developed, and then applied to estimate the threshold concentration for macromolecular overlap. The overlap concentrations of model polymers, such as poly(dimethylamine-*co*-epichlorohydrin-*co*-ethylenediamine) and poly(diallyldimethylammonium chloride), were evaluated with different, initial polymer concentrations and membrane pore sizes. In the correlation between  $\ln R_i/C_i$  and  $\ln C_r$ , the concentration where  $\ln R_i/C_i$  had the minimal value was referred to as the overlap concentration. The gyration radius of polyelectrolytes was calculated using the overlap concentration, which can provide insight into the understanding of the size of polymers and their rejections by membranes. Determining the overlap concentration of polymers with a UF membrane appeared to be viable and practical.

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## 1. Introduction

The concentration of polymeric and colloidal solutions plays an important part in the interaction between solutes and also is in close association with their physicochemical and mechanical properties. Particularly, the transition concentration of polymer solutions from dilute to semi-dilute regimes, which is defined as the overlap concentration, affects the processing of the solutions. The macromolecular chains shove in the liquid phase while being in very close contact each other. Knowing the overlap concentration of polymeric solutions helps one understand the rheological and dynamic behavior of polymer processing including the spinning solution and casting films of synthetic and biological polymers and the interactions of polyelectrolytes [1–10]. For instance, in the dilute polymer solution, the complex reaction between borax and poly(vinyl alcohol) occurred in the intra-molecular chains, and thus no useful films were formed.

Whereas in the semi-dilute solution region, both intra- and inter-chain crosslink reactions may take place and make it possible to produce high modulus and strength polymer films with a gelation of polymers [11,12].

Several sophisticated techniques have been applied to determine the overlap concentration of polymeric solutions, such as small angle light scattering [1–3,11], osmometry, and pulsed field gradient nuclear magnetic resonance [13]. Recently, Cincu et al. [14] demonstrated that the overlap concentration could also be obtained with viscometry. The light scattering and nuclear magnetic resonance techniques could be powerful tools in the evaluation of kinetic properties of polymers, but they are very expensive and need lots of technical skills and experience. Osmometry and viscometry could be cost effective but labor intensive.

Thus, membrane filtration techniques including ultrafiltration (UF) membranes have been investigated for the characterization of polymers in recent years. During UF of polymeric solutions, the polymer solution is concentrated if polymers are retained by the membrane. The increase of polymer concentration leads to a decline in permeation flux, and an escalation in filtration resis-

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### Nomenclature

$a$	the exponent constant
$A_v$	constant-related interaction between polymer and solvent
$C_r$	polymer concentration in retentate ( $\text{g L}^{-1}$ )
$C^*$	polymer overlap concentration ( $\text{g L}^{-1}$ )
$F$	concentrate factor
$J_v$	membrane flux with a polymer solution ( $\text{L m}^{-2} \text{h}^{-1}$ )
$J_{wf}$	final water flux after flushing the used membrane ( $\text{L m}^{-2} \text{h}^{-1}$ )
$J_{wi}$	initial water flux with a virgin membrane ( $\text{L m}^{-2} \text{h}^{-1}$ )
$M$	molar mass of polymers ( $\text{g mol}^{-1}$ )
$M_w$	weight average molar mass of polymers ( $\text{g mol}^{-1}$ )
$N_A$	Avogadro's constant
$\Delta P$	transmembrane pressure (Pa)
$R_f$	filtration resistance due to pore clogging (fouling) ( $\text{m}^{-1}$ )
$R_g$	gyration radius (nm)
$R_m$	intrinsic membrane resistance ( $\text{m}^{-1}$ )
$R_p$	filtration resistance due to the formation of concentration polarization layers ( $\text{m}^{-1}$ )
$R_t$	total filtration resistance ( $\text{m}^{-1}$ )
$T$	absolute temperature (K)
<i>Greek symbols</i>	
$\eta$	permeate viscosity (Pa s)
$\Pi$	osmotic pressure (Pa)

tance. This phenomenon is ascribed to the effect of concentration polarization of polymers at the membrane surface [15–17]. The osmotic pressure caused by concentration polarization can be measured by osmometry [18]. Bowen and Williams [19] also tested a method to determine the osmotic pressure of an electrostatically stabilized colloidal dispersion (e.g., bovine serum albumin solution) by using a UF technique, along with the UF osmotic pressure model. The method, however, required the zeta potential, particle size, and ionic strength to be known. No direct estimation of overlap concentration was made based on the UF results.

In this work, therefore, we tried to estimate the overlap concentration of different polyelectrolyte solutions using the membrane flux data obtained during batch-stirred cell UF experiments along with a newly developed model equation. The effect of different, initial polymer concentrations and membrane pore sizes on permeation flux and hydraulic filtration resistance was examined to evaluate the overlap concentration by UF, as well as to establish the feasibility of a direct UF technique for the overlap concentration determination. The radius of gyration of polymers was also assessed using an empirical equation.

## 2. Materials and methods

### 2.1. Polymers and UF membranes

Copoly(dimethylamine-co-epichlorohydrin-co-ethylenediamine) with a weight average molecular weight ( $M_w$ ) of 75,000 Da (which was designated as P75k) and poly(diallyldimethylammonium chloride) (designated as PDADMAC) with a  $M_w$  of 288,000 Da purchased from Aldrich Chemical Co. were used as model polymers. The UF membranes used were YM10, YM30, and YM100 (Millipore, USA) with a molecular weight cutoff (MWCO) of 10,000, 30,000, and 100,000 Da, respectively. They were made of regenerated cellulose.

The initial polymer concentrations of P75k and PDADMAC that were applied for UF experiments ranged from 0.617 to 6.16 and 0.693–6.93 g/L, respectively. The background electrolytes in polymer solutions were a mixture of 4.29 mM  $\text{NaNO}_3$ , 0.50 mM  $\text{CaCl}_2$ , and 0.50 mM  $\text{NaHCO}_3$ .

### 2.2. UF unit and experimental procedure

The stirred cell UF unit used in this work was made of stainless steel as described elsewhere [9]. During UF, the transmembrane pressure was kept at  $1.0 \pm 0.05$  bar, while the stirring speed was fixed at 300 rpm. The temperature of feed solutions was maintained at  $25 \pm 1.0$  °C during experimental runs and the membrane flux was corrected to the flux value at 20.2 °C (where the viscosity of water corresponds to  $10^{-3}$  Pa s). The total volume of feed solution was approximately 180 mL and the sampling of permeate was made as follows: the volume of the first sample collected was approximately 10 mL and then the successive seven samples of permeate were collected with a volume of approximately 20 mL each. Thus the retentate volume remaining after UF was approximately 30 mL. The permeation flux was determined based on the variation of permeate volume over time during UF, while measuring the mass of permeate using an electronic balance connected to a personal computer. Initial and final water fluxes were measured using deionized water, in the same procedure as described above, in order to evaluate the variation of hydraulic filtration resistance. Before the measurement of final water flux, the membranes used were flushed by stirring them, with 100 mL of deionized water, to remove the polarized layer of polymers from the membrane surface.

### 2.3. Analytical methods

The polymer concentration was determined using a Sievers 820 total organic carbon (TOC) analyzer (Ionics, USA). The molecular weight of the polyelectrolytes used was measured using a gel permeation chromatograph (Alliance 2000, Waters, USA) equipped with a refractive index detector and Tosoh TSK columns (G4000PWXL and G5000PWXL, Japan).

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