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Selective separation of polymer mixtures by ‘bubble-flotation chromatography’

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The ‘bubble-flotation chromatography’ technique was proposed and successfully applied to the selective separation of chitosan samples of different hydrophobicity from their mixed aqueous solutions.

Well-known high-performance liquid chromatography (*e.g.*, gel permeation chromatography) is widely used for the determination of the molecular weights of polymers and for their fractionation.[1,2] Nevertheless, there are no effective methods for the separation of the fractions of individual polymers, which differ in the degree of hydrophobic modification. Moreover, hydrophobically modified (HM) polymers highly associate in their solutions that present some difficulties for their separation. Thus, the search for effective and accessible methods for the fractionation of these polymers is an urgent problem.

In this context, we used different adsorption activities of HM polymers at the air–water interface to separate the polymer mixtures from their aqueous solutions using the ascending bubbles of air. The well-known foam flotation method is widely employed in industry.[3] This method is successfully used to recuperate surfactants from industrial wastewater.[4] Here we propose ‘bubble-flotation chromatography’ for the separation of mixed polymer solutions, which is based on different rates of adsorption of the components of a mixture on ascending air bubbles. This technique is characterised by high effectiveness and possibility of its application at an industrial scale.

The schematic diagram of the technique is given in Figure 1. A mixed aqueous solution of two polymers, more hydrophobic P_1 and less hydrophobic P_2, flows with the rate J_1 ($\mathrm{m^3\,s^{-1}}$) through a cylindrical vessel (A) and joins a container (B). Simultaneously, the air flux J_2 ($\mathrm{m^3\,s^{-1}}$) is purged through a sintered glass filter to the vessel (A) in the form of ascending bubbles with the mean radius R. The macromolecules of the polymers are adsorbed on the surface of ascending air bubbles and concentrated in the foam layer formed at the top of the vessel A. Consequently, the concentrations C_1^{B} and C_2^{B} of both polymers in the container B will be higher than the corresponding initial concentrations C_1^{A} and C_1^{A} of these polymers in the vessel A. The parameter $K_i = (C_i^{\mathrm{B}} - C_i^{\mathrm{A}})/C_i^{\mathrm{A}}$ characterises the effectiveness of concentrating the *i*th polymer component by bubble chromatography. One can expect that the concentrating effect is more pronounced for the hydrophobic polymer P_1 than that for the less hydrophobic polymer P_2 ($K_1 > K_2$) because the adsorption activity of the former is higher than that of the latter.

A mixture of polymers can be separated according to their adsorption activity at the air/water interface. If the polymer concentration ratio in the vessel A before the separation was $\varphi_{\mathrm{A}} = C_1^{\mathrm{A}}/C_2^{\mathrm{A}}$ and, after the separation procedure, became $\varphi_{\mathrm{B}} = C_1^{\mathrm{B}}/C_2^{\mathrm{B}}$, the effectiveness of the separation of polymers may be expressed by the parameter

$$\alpha = (\varphi_{\mathrm{B}} - \varphi_{\mathrm{A}})/\varphi_{\mathrm{A}} = (K_1 + 1)/(K_2 + 1) \tag{1}$$

The detailed physico-chemical background of the proposed ‘bubble-flotation chromatography’ method will be published elsewhere.[5] One of the critical parameters, which are expected to affect the effectiveness of the separation of polymer mixtures, is the relative rate of adsorption (*i.e.*, of the irreversible capturing) of polymers by the surface of ascending air bubbles from the solution. This rate increases with the bulk concentration C_i^{A}, the mobility (the diffusion coefficient D_i) of macromolecules in the aerated solution, the time τ of contact between air bubbles and the solution (or the time of bubble lifting) and the energy of attraction of macromolecules to the interface.

The diffusion flux of macromolecules from the bulk of solution to the surface of air bubbles can be expressed as $J_i(\tau) \cong C_i^{\mathrm{A}}\sqrt{D_i/\pi\tau}$.[6] If all macromolecules that approach the surface are irreversibly captured by this surface, the adsorption amount $\Gamma_i(\tau)$ ($\mathrm{mol\,m^{-2}}$) has the known form of the Ward and Tordai equation[6]

$$\Gamma_i(\tau) \cong \int_0^\tau J_i(t)\mathrm{d}t = 2C_i^{\mathrm{A}}\sqrt{D_i\tau/\pi}. \tag{2}$$

In general, not all the macromolecules that arrive at the surface could be irreversibly captured by this surface because of kinetic restrictions and the existence of a potential barrier to adsorption. To be irreversibly adsorbed, the gain in the free adsorption energy $\Delta_{\mathrm{ad}}G$ per macromolecule must be sufficiently high, *e.g.*, $|\Delta_{\mathrm{ad}}G| >> kT$. Taking into account that, for the adsorption of one hydrophobic $\mathrm{CH_2}$ group at the air/water interface, this gain is of the order of $\sim kT$,[7] this signifies that only alkylated macromolecules with alkyl chains longer than $\sim\mathrm{C_{10}}$ could be retained by the interface and do not desorb after having been ‘anchored’ into the air phase. Macromolecules, which have less bulky hydrophobic groups distributed along the macromolecular backbone, could be desorbed after adsorption, and only macromolecules with sufficiently high numbers of these groups can be definitely ‘anchored’ to the surface of air bubbles. Another factor that decreases the probability of the irreversible adsorption of macromolecules is the association of sufficiently long alkyl chains into intra- and intermolecular aggregates *via* hydrophobic interactions. Taking into account that the free energies of aggregation and adsorption per alkyl chain are comparable, the hiding of these alkyl chains inside the aggregates makes them less accessible to adsorption at the interface. The electrostatic repulsion between the charged ionic groups of polyelectrolytes decreases this association; however, it creates an energetic barrier to the adsorption of macroions.

There is no quantitative theory for the kinetics of adsorption of macromolecules, which is able to account for the effect of

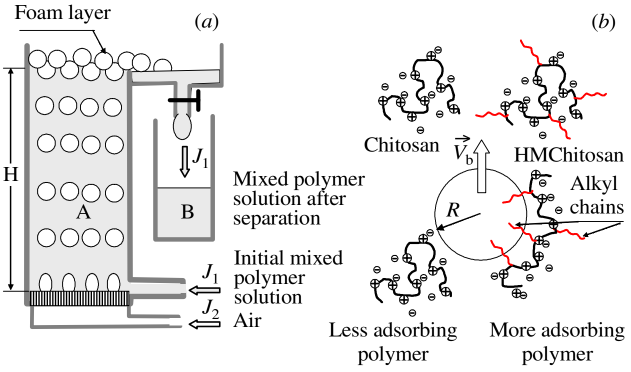

Figure 1 Schematic diagram of the bubble-flotation chromatography method.

the above physico-chemical parameters on the rate of adsorption.[8] The effectiveness of the adsorption of macromolecules can be formally described considering diffusion as an energetically activated process[9] and introducing the effective diffusion coefficient $D_i^* = D_i\exp(-E_i^a/kT)$, where E_i^a is the activation energy of diffusion. This is equivalent to the introduction of the probability β_i of the irreversible adsorption of macromolecules approaching the interface by diffusion, which is designated here as the capture coefficient $\beta_i = \exp(-E_i^a/2kT)$. Thus, equation (2) for the adsorption of macromolecules on the surface of air bubbles should be rewritten as

$$\Gamma_i(\tau) \cong 2\beta_i C_0\sqrt{D_i\tau/\pi}. \tag{3}$$

The mass m_i of the polymer of the ith type in the mixture captured from the solution during the time of lifting $\tau = 4.5\eta H/g\rho R^2$ (ref. 10) by one ascending bubble of the radius R can be expressed as

$$m_i = \Gamma_i(\tau)a_\mathrm{b} = 9\sqrt{\pi}\,\beta_i C_i^\mathrm{A}\sqrt{D_i\tau}\,R^2,$$

where $a_\mathrm{b} = 4\pi R^2$ is the area of the bubble, η and ρ are the viscosity and the density of the solution, respectively. The frequency n_1 (s^{-1}) of the formation of air bubbles in the vessel A is equal to $n_1 = J_2/v_\mathrm{b}$, where J_2 is the air flux, and $v_\mathrm{b} = 4/3\pi R^3$ is the volume of a bubble. During the time T_s of the separation process, the number n of all bubbles formed will be equal to $n = T_\mathrm{s}n_1 = T_\mathrm{s}J_2/v_\mathrm{b}$, and the mass $m_i(T_\mathrm{s})$ of the adsorbed polymer of the ith type is

$$m_i(T_\mathrm{s}) = m_iT_\mathrm{s} = \sqrt{\frac{162\pi\eta D_iH}{g\rho}}\;C_i^\mathrm{A}\frac{\beta_i}{R^2}J_2T_\mathrm{s}. \tag{4}$$

Taking into account that, during the time of the separation process T_s, the solution volume V in the container B becomes equal to $V_\mathrm{B} = J_1T$, where J_1 is the flux of the solution, the concentration coefficient k_i for the ith polymer can be written as

$$K_i = \frac{\Delta C_i}{C_i^\mathrm{A}} = \frac{m_i(T_\mathrm{s})}{V_\mathrm{B}C_i^\mathrm{A}} = \sqrt{\frac{162\pi\eta D_iH}{g\rho}}\;\frac{\beta_i}{R^2}\frac{J_2}{J_1}. \tag{5}$$

The separation efficiency α can be calculated using equation (1).

Equation (5) shows that the critical parameters, which influence the efficiency of concentration and separation of polymers, are the capture coefficients β_i of the macromolecules by the bubbles, as well as the size of bubbles and the ratio J_2/J_1 between air and liquid fluxes. Let us estimate the parameters K_i for hydrophobic polymers with high capture coefficients of the order of $\beta_i \cong 1$. Substituting the parameters $\eta \cong 10^{-3}$ Pa s, $D \cong 10^{-11}\ \mathrm{m^2\,s^{-1}}$, $g = 9.8\ \mathrm{ms^{-2}}$, $\rho \cong 10^3\ \mathrm{kg\,m^{-3}}$ and $R \cong 1$ mm into equation (5), we obtain $K_i \cong 10^{-2}\beta_iJ_1/J_2$. Thus, for the ratio $J_2/J_1 \cong 10$ and $\beta_i \cong 1$, we have the concentration coefficient $k_i \sim 10\%$.

The coefficient K_i may be considerably increased by decreasing the bubble radius on account for the scaling relation $K_i \sim R^{-2}$. Bubbles much smaller that 1 mm can be generated by ultrasonication or electrochemical methods.[11,12] A considerable increase in the coefficient k_i may be obtained even for a bubble size of ~1 mm by increasing the ratio J_2/J_1. Practically, this may be performed when the liquid flux J_1 tends to zero at a constant air flux J_2. This separation regime is possible only if the adsorbing hydrophobic polymer, *e.g.*, P_1, is an effective foam former and foam stabilizer. In this case, in the absence of the liquid flux J_1 the continuously formed stable foam is pushed out from the vessel A to the container B, carrying away the hydrophobic polymer P_1.

The 'bubble flotation chromatography' has been used for the separation of two polymers, chitosan (Ch) and a hydrophobically modified chitosan containing 5 mol% *n*-dodecyl side chains (HMCh) from their mixed aqueous solutions. The polymers (Ch and HMCh) have the same molecular weight ($M = 300\,000\ \mathrm{g\,mol^{-1}}$) and the same degree of deacetylation (DA = 0.85). The hydrophobically modified chitosan is a very powerful stabilizer of foams,[5] whereas chitosan is a poor foam former. The higher foaming capacity of HMCh correlates with its higher surface activity at the air/water interface in comparison with Ch. This is demonstrated by the dynamic surface tension measurements (Figure 2) of two polymers (Ch and HMCh) in aqueous solutions at the same bulk concentration $C_\mathrm{p} = 1.6\ \mathrm{g\,dm^{-3}}$ using a rising bubble tensiometer (Tracker, IT Concept, France).[13] The rising bubble (or pendent drop) method allow the determination of the dynamic surface tension $\sigma(t)$ during a long time by analysing the axial symmetric shape (Laplacian profile) of a rising air bubble in the liquid (or of a pendent liquid drop in air).[14,15] The surface tension isotherm for HMCh lies lower than that for Ch (Figure 2). This suggests higher surface activity and the rate of adsorption of the former polymer because of a higher hydrophobicity of HMCh.

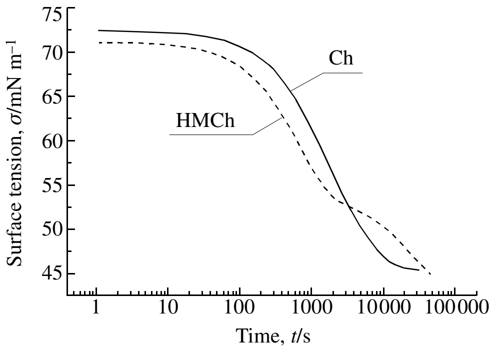

Figure 2 Dynamic surface tension curves $\sigma(t)$ for the aqueous solutions ($C_\mathrm{p} = 1.6\ \mathrm{g\,dm^{-3}}$) of hydrophobically modified (HMCh) and nonmodified (Ch) chitosans.

In order to determine quantitatively the concentration of polymers in mixed solutions, we labeled HMCh and Ch with different chromophore groups: fluoresceinisothiocyanate and remazol brilliant blue R (Sigma–Aldrich). The dye contents of HMCh and Ch were equal to 2.0 and 2.5 mol%, respectively. The procedures of HMCh preparation and chitosan labeling will be published elsewhere.[5] The solutions of the labeled HMCh were bright yellow and had an absorption maximum at $\lambda = 450$ nm. At the same time, the solutions of labeled Ch were bright blue and had an absorption maximum at $\lambda = 590$ nm. The mixed solutions of labeled HMCh and Ch were greenish and exhibited two absorption maxima (Figure 3, curve *1*).

During a separation process, the liquid flux J_1 was maintained constant and equal to 460 $\mu\mathrm{l\,s^{-1}}$, whereas the air flux J_2 was at least 10 times higher than J_1. The air bubble radius was 0.5–1 mm. The initial volume of the mixed solution was equal to 150 ml. Before the separation, the initial concentrations of HMCh and Ch in the mixed solution were equal to 0.066 and 0.23 $\mathrm{g\,dm^{-3}}$, respectively. After the separation, the concentrations of HMCh and Ch determined from the spectrum (Figure 3, curve *2*) increased by $K_1 = 12\%$ and $K_2 = 5\%$, respectively. From these data and equation (1) the separation coefficient was estimated to be $k_\mathrm{sep} \cong 1.07$.

Next, the flow of the initial solution to the vessel A was stopped, but the bubbling of air was continued for 30 min. This regime corresponds to $J_1 \rightarrow 0$ (or $J_2/J_1 \rightarrow \infty$). The initial solu-

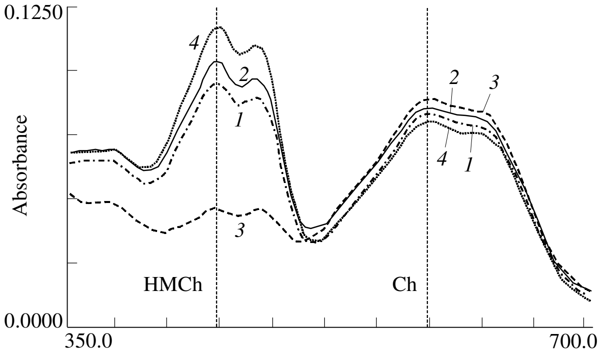

Figure 3 Spectra of different mixed solutions of labeled hydrophobically modified (HMCh) and nonmodified (Ch) chitosans. See the text for explanation.

tion volume was 90 ml. As a result of foam formation and transfer from the vessel A to the vessel B, the solution volume in the vessel B became equal to ~30 ml, while the solution volume in the vessel A was ~50 ml. Under these conditions in the vessel A the concentration of HMCh decreased to 0.032 g dm^{-3}, while the concentration of less hydrophobic Ch increased up to 0.24 g dm^{-3}. By contrast, in the vessel B the concentration of HMCh increased up to 0.082 g dm^{-3}, while the concentration of Ch decreased to 0.22 g dm^{-3}. Thus, the separation coefficient was $\alpha \cong 1.25$.

The numerical value of the concentration coefficient $K_i \cong 10\%$ estimated using equation (5) for similar separation conditions on the assumption of the high capture coefficient $\beta_i \cong 1$ correlates well with the experimental coefficients found for alkylated ($K_1 = 12\%$) and non alkylated ($K_1 = 5\%$) chitosans at the flux ratio $J_2/J_1 \cong 10$. This signifies that the capture coefficients for these chitosans in the mixed aqueous solution are $\beta_i \cong 1$, but $\beta_1 > \beta_2$ in accordance with the fact (see Figure 2) that the surface activity of HMCh is somewhat higher than that of Ch.

For the experimental regime at $J_1 = 0$ (or $J_2/J_1 \to \infty$), we found that the concentration of HMCh increased by ~25% in the vessel B but decreased by more than 50% in the aerated vessel A. Surprisingly, the concentration of Ch decreased by ~4% in the vessel B and increased by ~4% in the vessel A. This effect may be due to alkylated chitosan HMCh which is characterized by a high foaming capacity. The liquid volume V_B in the vessel B was obtained *via* the destruction of a foam, which contained this alkylated chitosan preferentially localized in thin liquid films of the foam, which was formed by the aqueous solution in the vessel A. Apparently, the less surface active chitosan Ch was repelled from the liquid films of the foam. This fact explains why the concentration in the vessel B decreased with regard to the initial concentration in the vessel A.

These preliminary results demonstrate the possibility of separation of a mixture of polymers according to their hydrophobicity by the proposed ‘bubble flotation chromatography’. A further development of this technique will concern the elaboration of more sophisticated procedure for the separation of polymer mixtures by introducing a small amount (~1%) of ionic and nonionic surfactants that form dynamic associates (non-stoichiometric polymer/surfactant or polyelectrolyte/surfactant complexes) selectively bound to some of the components of the polymer mixture.[16–19]

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