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SEPARATION MECHANISM OF COPOLYMERS FROM STYRENE AND METHYL METHACRYLATE ACCORDING TO COMPOSITION BY LIQUID ADSORPTION CHROMATOGRAPHY

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ABSTRACT

Silica gel and a mixture of chloroform and ethanol were used as the stationary and the mobile phases, respectively. At the isocratic elution mode, the copolymers tended to adsorb on the column with increasing MMA content in the copolymers, with increasing column temperature, and with decreasing ethanol content in the mobile phase. The copolymers appeared always at the position proportional to the interstitial volume in the column, otherwise they adsorbed on the column. The equilibrium distribution of the copolymers between the mobile phase and the stationary phase cannot be considered in this system. Hydrogen bonding of carbonyl groups in MMA units of the copolymers to silanol groups on the surface of silica gel was considered to be the main interaction between the copolymers and the adsorbent. The hydrogen bonding increases with increasing the number of carbonyl groups per unit surface of copolymer coil in solution and with increasing free silanol groups on the silica surface. Ethanol in the stationary phase controls the content of the free silanol groups on the surface and is controlled by the content of ethanol in the

mobile phase in addition to column temperature. This phenomena can be explained by introducing the term of the adsorption energy of a copolymer segment with the silica surface. The adsorption energy is proportional to the strength of the hydrogen bonding. Above the critical adsorption energy which is defined to be equal to the dissolution energy of the copolymer to the mobile phase, the copolymers adsorb on the surface of silica gel and the desorption of the copolymers advances when the adsorption energy approaches to the critical adsorption energy. No adsorption of the copolymers is possible when the adsorption energy is equal or below the critical adsorption energy.

INTRODUCTION

In the previous papers[1-5], separation of styrene-methyl methacrylate random copolymers, P(S-MMA), according to chemical composition by liquid adsorption chromatography (LAC) was reported. The stationary phase was silica gel with a pore size of 30 Å[1], and the mobile phase was a mixture of chloroform and ethanol[2]. Copolymers having more MMA required more ethanol in chloroform to elute from the silica gel column. The copolymers tend to adsorb on the column at higher column temperature under the same composition of the mobile phase. The copolymers eluted at the interstitial volume in the column whenever they could elute from the column. The retention mechanism must be different from that of conventional adsorption chromatographic retention model.

In the present paper, the retention mechanism of the copolymers on the surface of silica gel is discussed. Ethanol in the mobile phase controls the content of silanol groups on the silica surface and the retention behavior of the copolymers can be understood from the retention behavior of ethanol on the stationary phase.

EXPERIMENTAL

LAC measurements were performed on a Jasco TRIROTAR-VI high-performance liquid chromatograph (Japan Spectroscopic Co., Ltd.,

Hachioji, Tokyo 192) with an ultraviolet absorption detector Model UVIDEC-100VI at a wavelength of 254 nm. Silica gel (Develosil-30) with a pore size of 30 Å and a mean particle diameter of 5 μm (Nomura Chemical Co., Seto, Aichi 489) was packed in a 50 mm x 4.6 mm I.D. column. This column was thermostated at a specified temperature by using a column jacket through which constant-temperature water was circulated.

Copolymer samples were prepared by solution polymerization at a low degree of conversion, and the compositions of the copolymers were between 15% and 85% by styrene mol%. The copolymers had narrow composition distributions. Polystyrene equivalent weight average molecular weights of the copolymers were between 1.2×10^5 and 1.5×10^5 and the polydispersity was about 2.0.

The mobile phase was a mixture of chloroform and ethanol. Ethanol contained in chloroform as a stabilizer was removed before use by washing the chloroform with water and drying by distillation. Henceforth, chloroform in this report means it does not contain any ethanol unless otherwise specified. Elution was first performed by the isocratic elution mode. The flow rate of the mobile phase was 0.5 ml/min. The gradient elution mode was explained in the next section.

RESULTS AND DISCUSSION

Effects of Ethanol and Column Temperature.

The elution behavior of the copolymers at the isocratic elution mode was summarized as follows[2]. The copolymers adsorbed on the column with the mobile phase of chloroform and by the addition of ethanol to chloroform, the copolymers having more styrene started to elute, and with increasing ethanol content in chloroform, those having less styrene could elute. At the constant composition of the mobile phase and at higher column temperature, the copolymers having more MMA tended to retain in the

column. However, eventhough the copolymers eluted from the column, the retention volume of the copolymers were unchanged with column temperature and with ethanol content in the mobile phase. They appeared always at the exclusion limit, which is proportional to the interstitial volume in the column, whenever they could elute from the column, or they adsorbed on the column. A pore size of silica gel was 30 \AA and was sufficiently small to prevent access to all copolymers, that is, separation of the copolymers by size exclusion was not possible.

Chloroform is a good solvent for polystyrene (PS) and polymethyl methacrylate (PMMA) homopolymers and their copolymers. However, PS eluted from and PMMA and the copolymers retained in the column with the chloroform mobile phase. The elution of the copolymers was controlled by the small addition of ethanol, which is a poor solvent for the homopolymers and the copolymers, to the mobile phase. Column temperature also affected the elution of the copolymers from the column. Examples of these observations are shown in Figures 1 and 2. Figure 1 represents that a copolymer having composition on the curve could elute from the column with the mobile phase including more ethanol than that correlated to the copolymer composition on the curve and adsorbed with the mobile phase having less ethanol than this value. Figure 2 represents that a copolymer having a composition below the curve adsorbed on the column over the column temperature correlated to the copolymer composition on the curve and eluted from the column below this column temperature.

PS did not adsorb on the column and eluted at the interstitial volume at any experimental conditions. Adsorption of the copolymers on the column was controlled by the MMA content in the copolymers. Hydrogen bonding of carbonyl groups in MMA units of the copolymers to silanol groups on the outer surface of silica gel may be considered as the main interaction between the copolymers and the adsorbent. In the case of silica gel, it is known that the adsorption sites are silanol groups of the surface of silica gels[6]. Hydrogen bonding may increase with increasing

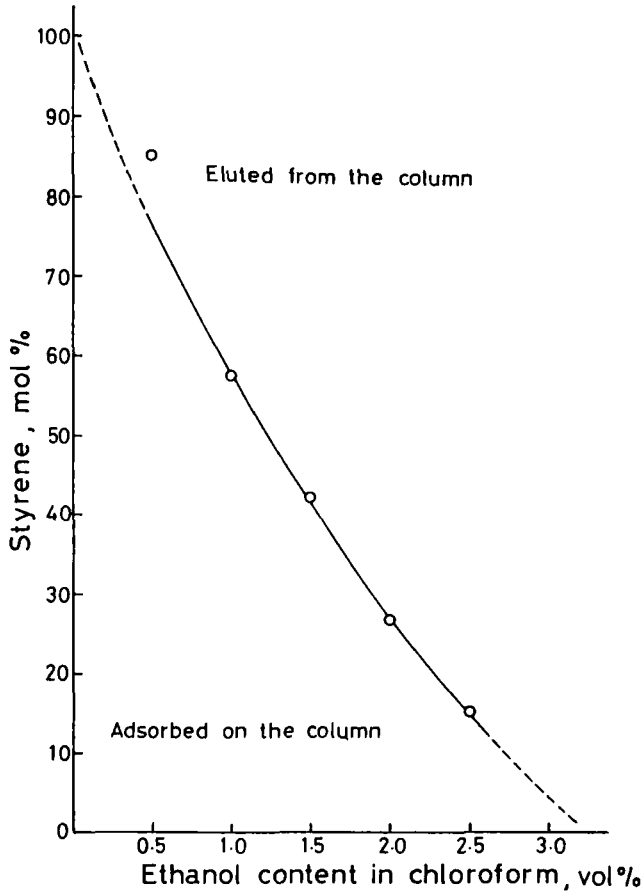


FIGURE 1. Effects of ethanol content in chloroform and styrene content in the copolymers on the elution of the copolymers from the column. Column temperature: 10 °C.

the number of carbonyl groups per unit surface of a copolymer coil in solution, that is, with increasing the density of carbonyl groups on the surface of a copolymer coil. In other words, the copolymers having more MMA have larger number of carbonyl groups per unit surface of a copolymer coil in solution and stronger hydrogen bonding to the silica gel surface than those having less

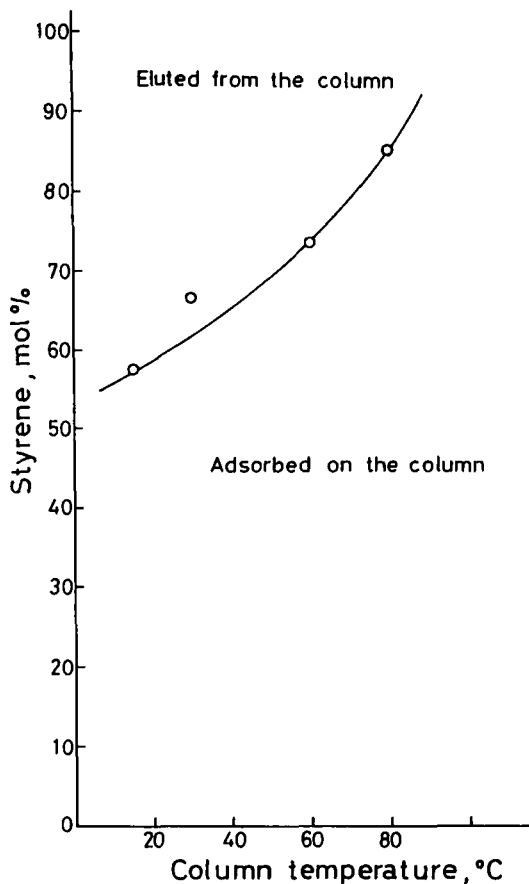


FIGURE 2. Effects of column temperature and styrene content in the copolymers on the elution of the copolymers from the column. The composition of the mobile phase: chloroform/ethanol, 99.0/1.0 (v/v%).

MMA. Moreover, the hydrogen bonding will increase with increasing free silanol groups on the silica surface (higher density of free silanol groups).

Ethanol in the mobile phase will make hydrogen bonding with silanol groups on the silica gel surface and will decrease free silanol groups on the surface. The content of ethanol in the stationary phase will be expressed in the term of k' as

$$k' = \frac{\text{number of ethanol molecules in the stationary phase}}{\text{number of ethanol molecules in the mobile phase}} \quad (1)$$

At a constant column temperature, k' should be constant. Therefore, number of ethanol molecules in the stationary phase will increase with increasing ethanol content in the mobile phase. As the results, free silanol groups on the surface of silica gel decrease and moreover, hydrogen bonding of the copolymers with silanol groups decreases. Consequently, the copolymers tend to elute from the column.

Column temperature influences k' values of samples. An increase in temperature should always shorten the retention volumes of samples as predicted by thermodynamics. With many mobile phases this is the case. In our experiment, the copolymers tended to retain in the column at elevated column temperature and this observation is hard to predict by thermodynamics. At elevated column temperatures ethanol content in the stationary phase decreases, resulting in the increase of free silanol groups of the surface of silica gel. The increase in column temperature, therefore, gives the same effect as the decrease of ethanol content in the mobile phase. Thus, the increase in adsorption of the copolymers on the column at elevated temperature is not because of the increase in adsorption energy of the copolymers, but because of the increase in silanol groups on the silica surface accompanied by the decrease in ethanol content in the stationary phase.

As a thermodynamic approach, the adsorption energy (E_{ad}) of the copolymer segment with the silica gel surface was introduced. The adsorption energy is a function of both the density of the carbonyl groups on the adsorption surface of a copolymer coil and the density of free silanol groups on the silica surface and increases with increasing these densities. This adsorption energy is proportional to the strength of the hydrogen bonding.

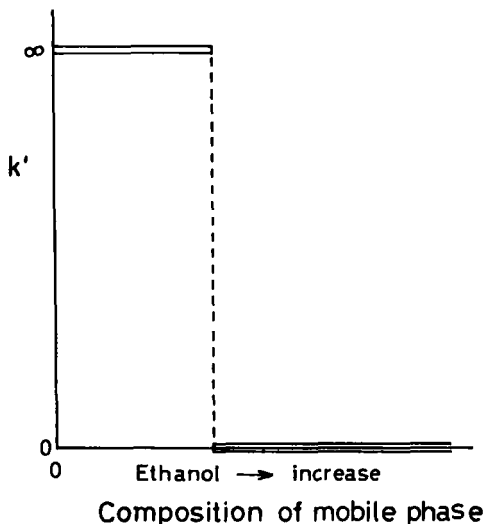


FIGURE 3. Illustration of adsorption on or elution from the column for the copolymers with changing the composition of the mobile phase.

Elution at the Interstitial Volume.

The other characteristic elution behavior of the copolymers in our system was that retention volume of the copolymers which could elute from the column was always at the position proportional to the interstitial volume in the column regardless of the copolymer composition, the ethanol content in the mobile phase, and the column temperature[2]. Schematic illustration is shown in Figure 3. The adsorption isotherm may be different from conventional adsorption chromatography.

A general expression for the chromatographic distribution coefficient K in adsorption system, where the interactions between the substance and the mobile phase are negligible, is expressed as[7]

$$\log K = \log V_a + \alpha(S^0 - A_s \epsilon^0) \quad (2)$$

where V_a is the surface volume of the adsorption layer, α is the surface activity of the adsorbent, S^0 is the adsorption energy of the substance on the surface of an adsorbent having an activity of unity, A_s is the adsorbent surface area occupied by the substance molecule adsorbed, and ϵ^0 is the elution strength of the mobile phase. This equation was applied to adsorption chromatography of PS oligomers to separate according to their degree of polymerization[8]. However, this equation cannot be applied to our system, because as shown in Figure 3, although the elution strength of the mobile phase was changed, k' value was 0 or ∞ , implying $\log K$ is not a function of the elution strength of the mobile phase nor the adsorption energy of the substance. This equation may be applied to low molecular weight materials such as ethanol, where the value of K decreases with increasing in column temperature[9].

Several retention models for oligomers and polymers for LAC have been proposed by Snyder and his co-workers: a model based upon displacement and localization phenomena[10], a precipitation-redissolution model and a normal chromatographic retention model ("sorption")[11]. However, these models cannot be applied to our system, either. Because their models also cause the change of retention volumes of solutes with the change of the mobile phase.

Belenkii et al.[12,13] presented the theory of adsorption chromatography of polymers: the change in the free energy of the system ($-\Delta G$) is equal to the change in the free energy of the polymers when adsorbed as

$$\frac{-\Delta G}{hT} = \ln k' + \ln \left(\frac{V_o}{V_p} \right) \quad (3)$$

where k' is the capacity factor, V_o is the mobile phase volume, V_p is the stationary phase volume available for adsorption, h is the Boltzmann constant, and T is the absolute temperature. The interaction energy ($-\mathcal{E}$) of a polymer segment with the surface of the adsorbent was introduced. When $-\Delta G$ is zero, then $-\mathcal{E} = -\mathcal{E}_{cr}$.

When $-\xi > -\xi_{cr}$, adsorption effects control the separation, when $-\xi < -\xi_{cr}$, the separation is controlled by size exclusion effects, and when $-\xi = -\xi_{cr}$, the above two effects cancel one another and k' is unity.

As already discussed, eq. 3 cannot be applied to our system, either. However, the similar approach to the interaction energy may be used to explain our system qualitatively. Instead of using the interaction energy, we already introduced the term of adsorption energy E_{ad} . To desorb the adsorbed copolymers from the silica surface, the dissolution energy (E_{dis}) of the copolymers to the mobile phase must be higher than the adsorption energy (E_{ad}). The value of E_{dis} is assumed to be nearly equal to all the mobile phases applied in this experiment, because the mobile phases, chloroform and a mixture of chloroform and ethanol up to 4.5% ethanol content are all good solvents for the copolymers. Therefore, the increase of ethanol content in the mobile phase or the decrease in column temperature result in the decrease in the density of silanol groups on the silica surface and consequently in the decrease in the adsorption energy E_{ad} . When $E_{ad} > E_{dis}$, adsorption effects are predominant and the copolymers adsorb on the surface of silica gel, that is, $k' = \infty$. The adsorbed polymers cannot be removed from the silica surface by dilution, and the desorption of polymers will advance if a competing substance with a higher level of adsorption energy such as ethanol is increased[14]. When E_{ad} decreases to E_{dis} , that is, $E_{ad} = E_{dis}$, or $E_{ad} < E_{dis}$, the copolymers cannot adsorb on the silica surface and eluted from the column. The critical adsorption energy (E_{cr}) is defined to be E_{ad} equal to E_{dis} .

Gradient Elution of the Copolymers.

One possibility to separate the copolymers according to their compositions was to use gradient LC by changing the content of ethanol in chloroform[3]. The initial mobile phase (A) was

chloroform/ethanol, 99.0/1.0 (v/v%) and the final mobile phase (B) was chloroform/ethanol, 95.5/4.5 (v/v%). The composition of the mobile phase was changed from 100% A to 100% B in 15 min and kept to 100% B for another 10 min. Samples were dissolved in the mobile phase (A). Column temperature was changed from 30 °C to 80 °C according to the sample compositions in question for separation. By the gradient LC, the copolymers having a styrene content below 73% could be separated in the order of decreasing a styrene content.

The adsorption of the copolymers on the silica surface occurred only at the inlet of the column and the copolymers which did not adsorb on the adsorbent there eluted at the interstitial volume without any interactions with the adsorbent. When the adsorbed copolymers desorbed from the silica surface, then the desorbed copolymers eluted from the column without interactions with the adsorbent any more.

Armstrong and Boehm[15] pointed out that in the LC separation of polymers, when strong adsorption occur between the polymer and the stationary phase, then the molecules are separated according to their chemical nature and that if adsorption is minimized, separation depends on molecular weight. The use of a well end-capped reversed-phase packing material simplifies the situation because strong adsorption effects are eliminated. As a results, separation of polymers by molecular weight is achieved. One possibility to separate polymers by molecular weight is to use a binary solvent mobile phase. One of the solvents must be a thermodynamically good solvent for the polymer, while the other must be a thermodynamically poor solvent. The retention of a homopolymer in gradient liquid chromatography (LC) was given by [16]

$$k' = \exp [AM(X - X_c)] \quad (4)$$

where k' is the capacity factor of a solute, M is the degree of polymerization of the solute, X is the mobile phase composition of

the good solvent, X_c is the critical mobile phase composition, and A is a constant for polymers with molecular weights $\geq 10^4$. X_c can be considered to be the composition of a binary solvent system that will dissolve an immobilized polymer or precipitate a dissolved polymer in the stationary phase. In other words, polymers are either infinitely retained above or tend to elute below the critical composition X_c .

The capacity factor k' of the copolymers in the gradient LC in our system is considered to be a function of MMA% in the copolymer (m_{MMA}), column temperature (T), and the chloroform content in the mobile phase (C) as follows:

$$k' = f(m_{MMA}, T, C) \quad (5)$$

The concept of this system was similar to that developed by Armstrong et al.[16], but actually there were several differences. The equation (4) is based on the equilibrium distribution of polymers between the mixed solvent mobile phase and the stationary phase, and the values of k' are not the same below the critical component X_c . In our system the equilibrium distribution of the copolymers between the mobile phase and the stationary phase could not be considered. In our system, both solvents, A and B , are thermodynamically good solvents for the homopolymers and the copolymers. Separation was independent on molecular weight[3]. The copolymers and PMMA retained in the column with the initial mobile phase (A) at appropriate column temperature.

At the constant column temperature, the capacity factor k' of the copolymers in the gradient elution may be expressed as

$$k' = t_c F / V_0 \quad (6)$$

where V_0 is the interstitial volume in the column, t_c is the time required for the mobile phase composition to become the critical composition, and F is the flow rate of the mobile phase. The copolymers remain at the column inlet until the mobile phase of

critical composition overtakes it, then the copolymer "pops off" the column packing and elutes through the column[17]. The gradient elution in our system plays a part of decreasing the adsorption energy E_{ad} of the copolymers down to E_{dis} or E_{cr} to elute the adsorbed copolymers at the inlet of the column through the outlet of the column.

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