Solvent, Temperature and Concentration Effects on the Adsorption of Poly(n-Butyl Methacrylate) on Alumina from Solutions

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Adsorption of poly(n-butyl methacrylate) (PnBMA) on alumina from solution was studied by UV and FT-IR Photoacoustic Spectroscopy techniques. The effects of the solvent, temperature, concentration, and molecular weight of the polymer on adsorption were investigated. Three solvents, cyclohexane, carbon tetrachloride and benzene, were employed. The adsorption was dependent on molecular weight and much more polymer was adsorbed in cyclohexane than in other solvents on the alumina surface. A decrease in adsorption was observed with increasing temperature. The results are in conformity with Langmuir's isotherm. The differences observed in Langmuir parameters were explained by polymer-polymer, polymer-solvent, polymer-adsorbent, and solvent-adsorbent interactions.

Key Words: poly(n-butyl methacrylate), solubility parameter, alumina, adsorption, solvent

Introduction

The adsorption of macromolecules is quite different in many aspects from that of small molecules. The difference arises from the obvious differences in the size and the resultant flexibility of macromolecules[1]. The adsorption of linear macromolecules from solution on solid surfaces is a complicated phenomenon with many problems to be clarified. This is mainly due to the constitution of macromolecules with a large number of repeating monomeric units. The determination of the conformation of the adsorbed macromolecules is one aspect still causing some difficulty. Several techniques such as viscometry, ellipsometry, IR and NMR spectroscopy, calorimetry and adsorption isotherm characteristics have been used to obtain valuable data concerning the nature of adsorbed macromolecules[2].

The adsorption of polymers at solid-liquid interfaces has been studied extensively in recent years[3−5]. Kawaguchi et al.[6] have studied the adsorption of PS and PMMA onto silica surfaces by IR. Adsorption of poly(dimethyl siloxanes) from solution on silica has been investigated by Brebner et al.[7]. Fontana and Thomas[8] have pioneered the development of a spectroscopic technique for the quantitative estimation of the fraction of adsorbed polymer segments. Lipatov et al.[9,10] have studied the adsorption of a mixture of PS and PMMA from solution onto silica surfaces. Polymer adsorption at solid surfaces is important in a variety of fields, such as material and food sciences, medical science, and stone conservation[11].

Moreover, adsorption of polymers is applied in coating, painting, glues, and chromatographic techniques. Nguyen and Berek[12] have studied the separation of six-component blends of chemically similar homopolymers such as poly(methyl methacrylate), polystyrene, poly(lauryl methacrylate) and poly(ethyl methacrylate), using the full adsorption-desorption process. They have carried out the separation of these homopolymer blends with successive and independent size-exclusion chromatography. In another study, for the purpose of water clarification, the adsorption of Rhodamine-B labelled cationic polyelectrolyte, as flocculants of negatively charged contaminants, onto colloidal silica were investigated[13]. We studied the adsorption of poly(2-hydroxypropyl methacrylate) on alumina from solutions for the purpose of stone conservation[14]. It would therefore appear that the adsorption behavior of polymers at the solid-liquid interface is of considerable technological importance, yet is not adequately understood due to the complexity of the adsorption process itself.

In this paper, we present UV spectroscopy studies of the adsorption of PnBMA onto alumina in various solvents, benzene, cyclohexane and carbon tetrachloride, at $25\pm1°$C. FT-IR spectroscopic evaluations of adsorbed PnBMA onto alumina depending on solvent type, temperature etc. were reported in our previous study[15]. The effects on adsorption of amounts of adsorbent, temperature, and concentration have also been investigated for cyclohexane. Various adsorption equations were applied to adsorption isotherms. The results are in conformity with Langmuir's isotherm. The differences observed in Langmuir parameters were explained by polymer-polymer, polymer-solvent, polymer-adsorbent and solvent-adsorbent interactions.

Experimental

Polymer: PnBMA was prepared by the suspension polymerization of n-butyl methacrylate obtained from Merck, using recrystallized benzoyl peroxide as the initiator. The viscosity-average molecular weight, $\overline{M}_v$, was determined in benzene at $30°$C with an Ubbelohde type viscometer. The viscosity-average molecular weight of two polymers synthesized having different molecular weights was found to be $\overline{M}_v$=150 000 and $\overline{M}_v$=400 000 using the equation[16] $[\eta] = 4 \times 10^{-5}$ M$^{0.77}$. PnBMA microspheres with 800μm average size were used for the adsorption studies.

Solvents: The solvents used for the adsorption experiments were spectroquality cyclohexane (C_6H_{12}), carbon tetrachloride (CCl_4), and benzene (C_6H_6), purchased from BDH and Merck.

Adsorbent: Alumina supplied by BDH was used as the adsorbent. Alumina, -χ-alumina-, was characterized by X-Ray Diffraction. Alumina was dried at $250°$C for one hour before use. It had a specific surface area of 111m^2/g as determined by BET analysis.

Procedure: The polymers were weighed into 100mL volumetric flasks, made up to volume, and kept at room temperature in darkness. Then 100mL of the solutions were added to alumina previously weighed (0.1-2.0g of alumina) and placed in flasks. The stoppered flasks were then placed in a thermostatically controlled water bath at $25\pm1°$C and continuously agitated. The supernatant solution was decanted to sediment the alumina particles with a centrifuge. The equilibrium concentration, C_{eq}, of the supernatant solution was determined by taking small aliquots and using a Philips PU 8715 UV-vis spectrophotometer. Calibrations of the absorbency values versus concentrations of polymer in the solvent of interest were made and the unknown supernatant concentrations interpolated from them.

The amount of adsorbed polymer (A in g polymer/g alumina) was calculated from

$$A = \frac{V}{m}(C_0 - C_{eq}) \qquad (1)$$

where V is the volume (mL) of polymer solution used, m is the weight of the alumina (g), and C_0 and C_{eq} are the initial and equilibrium concentrations of polymer solution (g/100mL), respectively. The *A* values were then plotted against their corresponding C_{eq} values to construct the adsorption isotherms.

Results and Discussion

In order to investigate the effect of various parameters on the adsorption of PnBMA on alumina, three solvents, namely benzene, cyclohexane and carbon tetrachloride, were used and the influences of temperature, polymer concentration and molecular weight in the PnBMA-C_6H_{12}-alumina system were studied. Adsorption isotherms of PnBMA in the three solvents used in this study are given in Figures 1-3. As can be seen from the equilibrium adsorption values, the lowest adsorption for PnBMA is observed in benzene for the same concentration values. The combinatory effect of solubility parameter values and solvent-adsorbent interactions causes this result. The solubility parameter values of the solvents and polymer used in this study are given in Table 1. As seen from these values, polar contributions are zero, and H-bonding contributions are negligible in these solvents. All solubility contributions can be attributed to dispersion forces. The conformation of adsorbed macromolecules is dependent on several factors, among which are the magnitudes of the interactions between polymer, solvent and adsorbent. Cyclohexane is a poor solvent for PnBMA and the macromolecules are highly coiled to give small size, and are usually adsorbed better than from good solvents because of the weaker polymer-solvent interaction. CCl_4 is a good solvent for PnBMA and the adsorption of PnBMA on alumina from CCl_4 is low because of strong polymer-solvent interactions[9,10]. However, adsorption from C_6H_6 is lower than from CCl_4. Differences observed in the effect of solvents on the adsorption can be explained by the dimensional changes in polymer coils. The Flory-Fox equation gives the relation between the average molecular weight of a polymer and polymer coil in the solution[17].
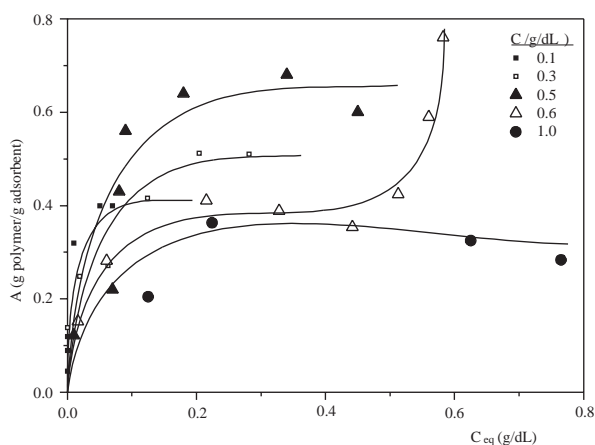
Figure 1. The change of adsorption in PnBMA-C_6H_{12}-alumina system with concentration (t=25°C)
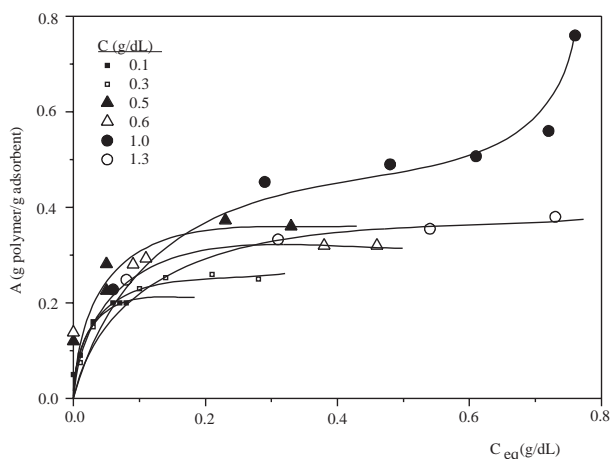
Figure 2. The change of adsorption in PnBMA-C_6H_6-alumina system with concentration (t=25°C)

Table 1. The solubility parameter values[16] of solvents and PnBMA

Solvents	[(MPa)$^{1/2}$]			
	δ_H	δ_D	δ_P	δ_T
Cyclohexane	0.2	16.8	0.0	16.8
Benzene	2.0	18.4	0.0	18.6
Carbon Tetrachloride	0.6	17.8	0.0	17.8
PnBMA	-	-	-	17.9

$$[\eta] = \frac{\phi\left[\langle r^2 \rangle\right]^{3/2}}{M})$$

$$(2)$$

where $[\eta]$ is the intrinsic viscosity, M is the average molecular weight of the polymer, Φ is the Flory constant, and $< r^2 >$ is the mean square end-to-end distance of the polymer coil.

$[\eta]$ and relative $< r^2 >$ values of PnBMA for the three solvents used in this study are given in Table 2. As can be seen from this table, the relative $< r^2 >$ value of C_6H_{12} is the smallest one among the solvents, that is, polymer coils expand less in C_6H_{12} than in the other two solvents. Our experimental findings conform to those in the literature.

**Table 2.** $[\eta]$ and relative $< r^2 >$ values of PnBMA for three solvents

Solvent	$[\eta]$, dL/g	Relative $< r^2 >$ values
Cyclohexane	0.46	1.00
Benzene	0.75	1.39
Carbon tetrachloride	1.27	1.97

The interaction of both the polymer and the solvent with the surface of the adsorbent is as important as the polymer-solvent interaction. A strong solvent-adsorbent interaction will decrease the adsorption of the polymer and may prevent diffusion of the macromolecules onto the adsorbent. The PnBMA-CCl$_4$-alumina system shows very good accordance with Langmuir type isotherms in all concentrations studied in this work. The PnBMA-C$_6$H$_6$-alumina and PnBMA-C$_6$H$_{12}$-alumina systems are very well described by Langmuir's isotherms up to a concentration of 0.5g/dL. However, above this concentration (0.6g/dL, 0.7g/dL, 0.9g/dL concentrations, data not shown), adsorption isotherms are represented by S-shape isotherms. It is assumed that above a certain critical concentration, the intermolecular interactions between macromolecules in solution lead to the formation of molecular aggregates or other supramolecular structures in solution. Therefore, during adsorption from concentrated solutions, both molecular aggregates and individual coils are transferred to the adsorbent surface. At higher concentrations, adsorption values are decreased because the polymer-polymer interaction has a greater effect than the polymer-surface interaction.

The adsorption isotherms of PnBMA on alumina from C$_6$H$_{12}$ solutions also indicate a decrease in adsorption with an increase in molecular weight. We have mentioned that the rate of adsorption of smaller molecules is higher than that of larger molecules due to diffusion. Therefore, smaller molecules are adsorbed from the polymer solution in the initial stage; these are then displaced by larger molecules, corresponding to the thermodynamic equilibrium state in Figure 4.
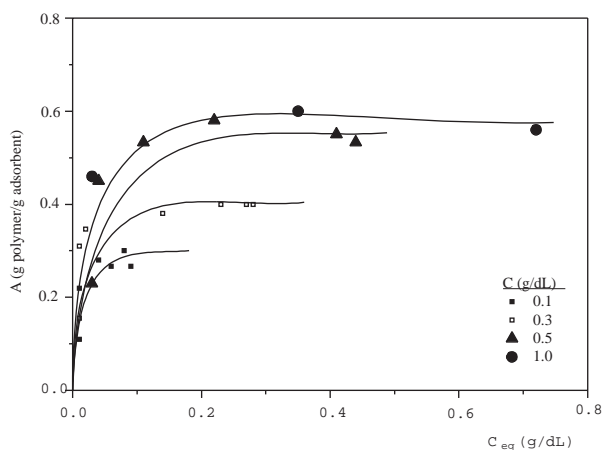
Figure 3. The change of adsorption in PnBMA-CCl₄-alumina system with concentration (t=25°C)
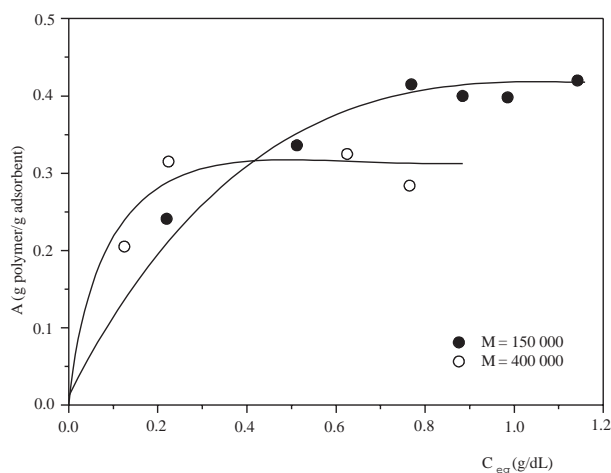
Figure 4. The effect of molecular weight of PnBMA on the adsorption of PnBMA in PnBMA-C_6H_{12}-alumina system (t=25°C, 1.0g/dL conc.)

It is our opinion that the polymer is not adsorbed layer-by-layer from concentrated solutions, but in molecular aggregates. Consequently, when analyzing the temperature dependence of adsorption, we must allow for the change in the character of structure formation in the solution under the effect of heat. Figure 5 shows that the adsorption of PnBMA on alumina from C_6H_{12} decreases with increases in temperature. This is confirmed by the increase in the intrinsic viscosity in Table 3. PnBMA shows UCST (upper critical solution temperature) in C_6H_{12} solution. Above the critical temperature, polymer coils are more expanded. Near the critical temperature, polymer coils are precipitated. As seen from Table 3, $[\eta]$ values increase with increasing temperature. Solvent is diffused into the polymer coil, which is more expanded. Therefore, only one polymer coil lies on a surface instead of more coils and the adsorption value decreases. In addition, the desorption of adsorbed macromolecules from the surface increases with increasing temperature. Because desorption is activated process in contrast to adsorption, which is a non-activated process, adsorbed polymers leave the surface easily with increasing temperature.

Table 3. The change of $[\eta]$ and adsorption equilibrium value with temperature

Temperature, °C	$[\eta]$	A, g/g
13	0.24	-
20	0.28	0.63
25	0.29	0.64
30	0.46	0.41
35	0.62	0.26
40	0.68	0.24

Various adsorption equations (Freundlich, Langmuir and B.E.T. equations) were applied to PnBMA adsorption isotherms. The results are in conformity with Langmuir's isotherm. C_{eq}/A values are plotted against C_{eq} with the following equation (Fig. 6) and the data obtained from the slope and intercept of Langmuir curves are shown in Tables 4-6.

$$\frac{C_{eq}}{A} = \frac{1}{\lambda.A_{mon}} + \frac{C_{eq}}{A_{mon}} \tag{3}$$

where C_{eq}=equilibrium concentration in the supernatant solution (g/dL), A=g adsorbed polymer per g alumina, A_{mon}=g adsorbed polymer per g alumina if monolayered adsorption occurs, and λ=constant term controlling the energetic interactions between the polymer and alumina.

**Table 4.** Langmuir parameters of PnBMA in various solvents

Solvents	λ	A, g/g	A_{mon}, g/g
Cyclohexane	362	0.40	0.42
Benzene	61	0.20	0.25
Carbon tetrachloride	217	0.27	0.31

Table 5. Langmuir parameters for PnBMA-C_6H_{12}-alumina system at various concentrations
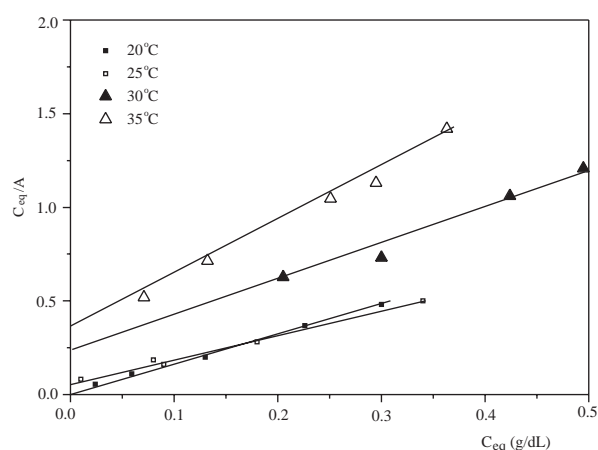
Concentration, g/dL	λ	A, g/g	A_{mon}, g/g
0.1	362	0.40	0.42
0.3	33	0.51	0.57
0.5	28	0.64	0.68
0.6	41	0.41	0.42
1.0	16	0.25	0.36

Table 6. Langmuir parameters for PnBMA-C_6H_{12}-alumina system at various temperatures

Temperature, °C	λ	A, g/g	A_{mon}, g/g
20	76	0.63	0.65
25	28	0.64	0.68
30	13	0.41	0.48
35	10	0.24	0.34
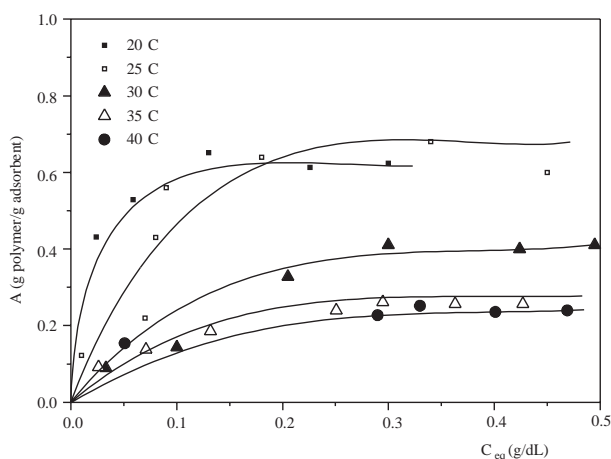
Figure 5. The effect of temperature on the adsorption of PnBMA in PnBMA- C_6H_{12}-alumina system (0.5g/dL conc.)

Figure 6. Langmuir plots of Figure 5

Adsorptivity increases with increasing polymer-adsorbent interactions. As shown in Table 4, the λ value of C_6H_{12} is larger than that of the other solvents. λ become smaller with increasing adsorption and A_{mon} increases. For the PnBMA-C_6H_{12}-alumina system given in Table 5, λ is decreased while A_{mon} values increase with increasing concentrations. At low concentrations, polymer-surface binding is strong;

λ has a higher value. When the concentration is increased, λ decreases considerably. Adsorption of the PnBMA-C_6H_{12}-alumina system decreases with increasing temperature because PnBMA has a UCST in C_6H_{12} solutions. Therefore, A_{mon} values of that system increase with decreasing temperature and λ is increased, as seen in Table 6.

Conclusions

PnBMA is synthesized by suspension polymerization. The adsorption of PnBMA onto alumina increases with increasing polymer concentration up to 0.5g/dL. However, adsorption decreases above this concentration due to the entanglement of polymer coils. Adsorption is investigated in various solvents: C_6H_{12}, C_6H_6 and CCl_4. It was observed that the adsorption of PnBMA from C_6H_{12} on alumina is higher than that from C_6H_6 and CCl_4. Adsorption is also studied in polar solvents: 2-propanol, methanol and tetrahydrofuran. However, no adsorbance was observed in these solvents, because these polar solvents have stronger affinity for the alumina surface. This study shows that the adsorption of PnBMA from C_6H_{12} on alumina surfaces can be achieved very efficiently at 25°C for the purpose of conservation of ancient stones like other methacrylate type polymers.

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