Colloid Polym Sci (1995) 273:118–121
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ORIGINAL CONTRIBUTION

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Adsorption of 1,4 polyisoprene at solid-liquid interface

Received: 14 October 1993
Accepted: 19 April 1994

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Abstract The adsorption of trans 1,4 polyisoprene was studied on alumina and silica gel at four temperatures. The solvents were cyclohexane, toluene, and 1:1 mixture of the two. The adsorption was found to decrease from cyclohexane > toluene > mixed solvent. The amount of adsorption was an inverse function of temperature. For almost all the systems, the adsorption isotherms were of Langmuir type, though solvent characteristic seems to be a more dominating factor than adsorbent in determining the shape of the isotherm.

Key words Adsorption – Polymer – Interface – Solvent Isotherm

Introduction

Polymer adsorption is a widespread phenomenon, playing an important role in many industrial applications such as in adhesion [1], coatings [2], paints [3], as well as in fillers [4]. Therefore, in continuation of our previous studies [5, 6], the adsorption of trans 1,4 polyisoprene on silica gel and alumina at different temperatures of 25°, 30°, 35° and 40 °C was studied. The solvents were cyclohexane, toluene, and 1:1 mixture by volume of the two. The adsorption of polymer onto a solid surface is a complex phenomenon. The adsorption depends upon various interactions, i.e., polymer–solvent, adsorbent–solvent and polymer–adsorbent interactions. These factors determine the net adsorption. When a mixed solvent system is used, both the liquids which comprise the mixed solvent system experience separate interactions with the adsorbent and the adsorbate. The adsorption process therefore becomes more complex and understanding of that becomes more difficult. However, inspite of the tremendous complexity, adsorption from mixed solvents has long been routine in adsorption chromatography and various other processes [7].

Experimental

trans-1,4 Polyisoprene (GR) was obtained from Guyana. It was purified [8] by dissolving it in toluene and keeping the solution overnight. The clear supernatant solution was then filtered and poured in excess of methanol. This resulted in a pure white GR, which was vacuum dried to a constant mass at room temperature for later use. Toluene (T) and Methanol (Merck, India); cyclohexane (C) (HPLC grade, Spectrochem, India) were freshly distilled before use. The GR used for adsorption study was thoroughly characterized before use [9]. The $\bar{M}n$, $\bar{M}w$, and polydispersity ratio of GR being 1.4×10^5, 3.5×10^5 and 2.50, respectively. TLC grade silica gel (with 13% $CaSO_4$, mesh size > 100) was obtained from Acme Synthetic Chemicals, Bombay, India. Alumina (acidic, mesh size > 100) was obtained from BDH (Glaxo Laboratories), India. Surface areas of silica gel and alumina obtained by BET method under N_2 gas were 192.9 m^2/g and 97.1 m^2/g, respectively. The adsorbents were dried for 3 h at 125 °C, then cooled in a desiccator before use. The probability of the presence of surface impurities was checked by x-ray photoelectron spectroscopy and no impurity was observed [5].

1:1 mixture of cyclohexane and toluene was prepared by volume at room temperature. This was considered as stock solvent. Solution of highest concentration was made by dissolving the required weighed amount of GR in the appropriate solvent. The polymer concentration in solution was determined by both UV spectroscopy and gravimetry. For UV spectroscopy a Shimadzu 240 spectrophotometer was used. For cyclohexane system, absorbance was measured (λ max = 275 nm) for a series of known concentrations. The calibration curve so obtained was used for computing the concentration of solution after adsorption. The maximum error in polymer concentration was found to be 1%. UV spectroscopy could not be as well used for toluene as for mixed solvent systems [5] because of toluene's higher cut-off. Hence, the concentration of the polymer in solution was determined by gravimetric method in these cases. The procedure was described earlier [5, 6]. The concentration range of GR solution was from 0.05% (W/V) to 0.8%(W/V). The density of the polymer solutions of different concentrations was taken to be the same as that of the solvent [10]. The maximum error in gravimetric estimations was computed to be 2%. Wherever the concentration of polymer was checked by both gravimetric and spectrophotometric methods (only a few), the differences were less than 2% from each other.

Results and discussion

The adsorption isotherms of GR from cyclohexane solutions on both the adsorbents, at various temperatures, are given in Fig. 1 (a and b). The amount of adsorption increases with increase in equilibrium concentration of GR and then levels off to a plateau. The isotherm shapes are similar to Langmuir plots. The adsorption of GR from toluene on both the adsorbents, at various temperatures, are given in Fig. 2 (a and b). In all systems, the amount of adsorption decreased with increase in temperature, which is rather common [11–13]. The polymer solution has both the solvent and the polymer. In contact with the adsorbent, both polymer and solvent get adsorbed. The better the solvent (for polymer) the higher will be the affinity between the polymer and solvent and hence relatively less amount of polymer will be adsorbed. As the original concentration of the polymer increases in the solution, the tendency to replace the solvent from the adsorbent surface by the polymer will increase. That is, more polymer will get adsorbed. However, there will be a limit which is indicated by the plateau region. If the polymer–solvent affinity is not good, i,e., the solvent is a relatively poor one, then more polymer gets adsorbed on the surface. A comparison of Figs. 1 and 2 shows that adsorption from cyclohexane is higher than that from toluene. This is because of the different solvent strength, i.e., different polymer–solvent affinity. The intrinsic viscosity of GR is greater in toluene than in cyclohexane at all temperatures (Table 1). This indicates that toluene is a better solvent (more affinity)

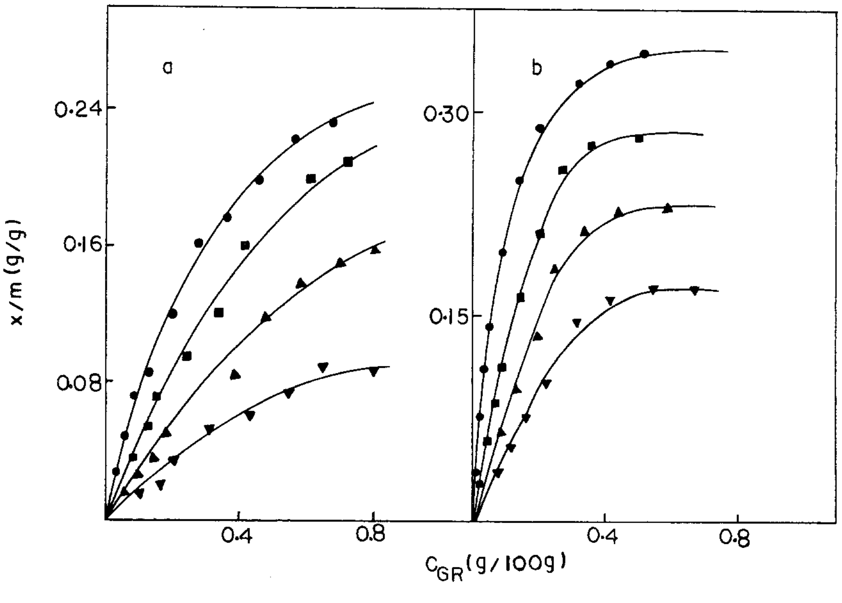


Fig. 1 Plot of specific adsorption (x/m) against equilibrium concentration of GR from cyclohexane at various temperatures. a) alumina; b) silica gel ● 25 °C; ■ 30 °C; ▲ 35 °C; ▼ 40 °C

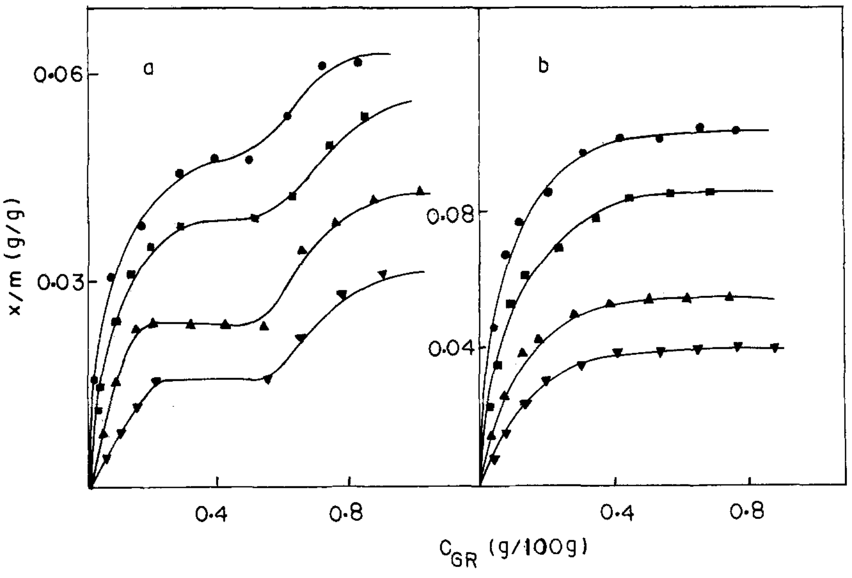


Fig. 2 Plot of specific adsorption (x/m) against equilibrium concentration of GR from toluene at various temperatures. a) alumina; b) silica gel. Symbols as in Fig. 1

Table 1. Variations in intrinsic viscosity with temperature for different solvent systems

Solvent systems	Intrinsic viscosity η (dl/g) 30 °C	35 °C	40 °C	45 °C
Toluene (T)	1.70	1.62	1.58	1.54
50:50 (v/v) C:T	1.83	1.77	1.70	1.64
Cyclohexane (C)	1.52	1.50	1.47	–

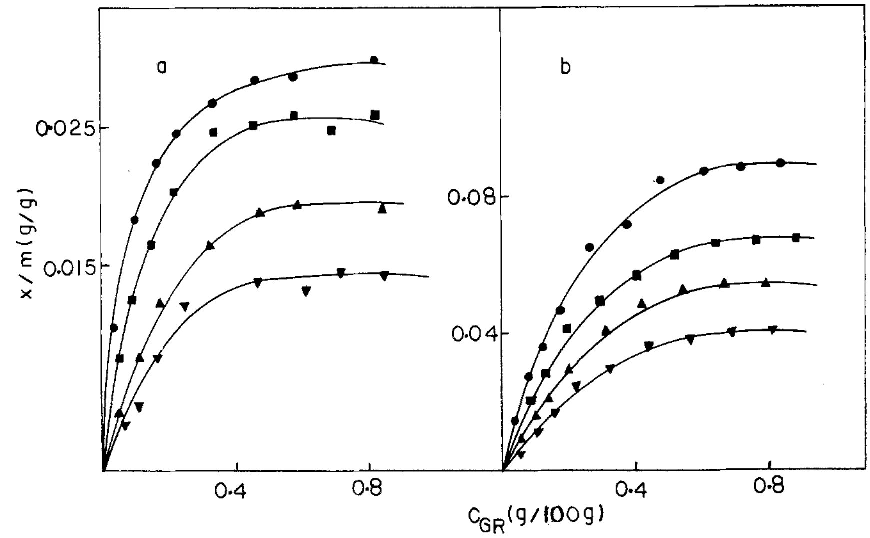
than cyclohexane for GR, hence, there is lower adsorption from toluene solution. Such higher adsorption from poor solvent and lower adsorption from relatively better solvent were reported earlier [14].

The solvent–adsorbent interaction can also be another reason for the above observation. The aromatics are adsorbed more on alumina and silica gel surfaces [15]. Therefore, this leads to preferential adsorption of solvent (toluene), leading to lower adsorption of GR from that particular solvent system. Figure 2(a) shows slightly different nature in comparison to the others. The semi-plateau is more pronounced at higher temperatures. Toluene being a better solvent, its replacement from adsorbent surface by polymer molecules is difficult. The appearance of these isotherms is because of polydispersity of polymeric samples and also because of specific interaction between the adsorbent and polymer. The polydispersity, as mentioned earlier, is 2.5. This indicates the presence of both low and high molecular weight species. The low molecular weight species get adsorbed first. These are later displaced by larger molecular weight species. This adsorption–desorption equilibrium is a function of polymer concentration. Overall, the amount adsorbed remains the same, only change in species occurs. However, at still higher concentration more polymer molecules get adsorbed because of the strong lateral attractive forces between adsorbed polymer molecules. The change in orientation as well as the formation of multilayers are the other possibilities [6]. We feel that the residual forces are more in the case of alumina providing an opportunity for further adsorption, whereas that is not so in silica gel in presence of GR. An experimental demonstration of adsorbed polymer multilayers was given by Johnson et al. [16] and such isotherms have been observed for protein and surfactant molecules [17], as well as in acrylates [6].

The isotherms obtained from mixed solvent system are shown in Fig. 3(a and b). In this particular mixture, cyclohexane has dominating influence on the overall solvent property. The adsorption of GR from mixed solvent system is much lower when compared to either of the pure solvent systems, on both the adsorbents. Table 1 shows that intrinsic viscosity of GR in mixed solvent system is highest, at all temperatures. This suggests that mixed solvent is a better solvent than either of the pure solvents, hence, there is the least adsorption of GR from the former solvent system.

Therefore, the amount of adsorption of trans-1,4 polyisoprene is more a function of solvent rather than adsorbent characteristics. This is because the amount of GR adsorbed (as seen from the values of specific adsorption, x/m, from the figures) on alumina or silica gel from any particular solvent remains almost the same. With change in the solvent, x/m values change drastically. However,

Fig. 3 Plot of specific adsorption (x/m) against equilibrium concentration of GR from cyclohexane–toluene (1:1) mixed solvent at various temperature a) alumina; b) silica gel. Symbols as in Fig. 1



polymer–adsorbent interaction, which is difficult to quantify, seems to be important for a proper explanation of the presence of the semiplateau.

Acknowledgement VV thanks University Grants Commission, New Delhi, for the financial assistance. Financial assistance from Department of Atomic Energy, Govt. of India is also acknowledged.

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