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Thermodynamics of adsorption of polybutadiene on alumina and silica gel: effect of temperature and solvent

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Abstract The adsorption of polybutadiene (PBR) on alumina and silica gel was studied at different temperatures from cyclohexane and toluene solutions. It shows that the adsorption process was dependent on temperature and solvent The adsorption isotherm and the thermodynamic quantities of adsorption were determined and it was observed that the adsorption process from both solvents was similar and the amount of adsorption increased as temperature decreased. The silica gel-cyclohexane system was more exothermic than all other systems and was also relatively more ordered

Key words Adsorption, polybutadiene, thermodynamics, silica gel, alumina

Introduction

The adsorption of polymers on an adsorbent is an important phenomenon both from academic and industrial point of view. It is also different in many respects from the adsorption of small molecules [1]. A survey of literature shows that both the sophistication in theoretical developments and the range of experimental observation have been high, although they have not always kept pace with one another [2–10]. In the present study, we used the fundamental thermodynamics in the adsorption process of the title polymer, synthetic polybutadiene, on alumina and silica gel from toluene and cyclohexane solutions at 30, 35 and 40 °C.

Experimental

Polybutadiene (PBR) was obtained from Indian Petrochemicals, Vadodara, India Its composition was cis-1,4 (>96%), trans-1,4 (1-2%), and vinyl-1,2 (1-2%) [11] This was dissolved in toluene, filtered and then re-precipitated by adding methanol The polymer so obtained was vacuum dried before further use It has narrow molecular weight distribution [11] and its viscosity molecular weight was 4 14 \times 10⁵ Methanol (GPR, E Merck), toluene (synthesis grade, E Merck), and cyclohexane (chromatography grade, E Merck) were distilled before use Cyclohexane was passed through a column of activated silica gel and alumina to remove the traces of any olefinic impurities present

TLC grade silica gel (with 13% CaSO₄, 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 were 1929 m²/g and 97 1 m²/g, respectively, and were obtained by BET method using nitrogen gas Both were dried for 3 h at 125 °C before use The probability of the presence of surface impurities in silica gel and alumina was checked by X-ray photoelectron spectroscopy (Fig. 1) and no impurity was observed The spectra were recorded on a VG Scientific Escalab MK II spectrometer using Mg K α radiation under vacuum, which was better than 5×10^{-7} mbar [12] The SEM photographs were taken by a Jeol JSM-T3 scanning electron microscope after gold coating by using the usual procedure

PBR solution at highest concentration was made by dissolving weighed amount in a known volume of solvent. Other desired solutions were made from it by dilution The weighed amount of adsorbents were placed in a series of jacketed bottles and known amount of the desired solution was added to each one of them These were then placed on a shaker for continuous shaking Thermostated water (± 01 °C) was pumped through these jacketed bottles for about 3 h before the polybutadiene was estimated. The process was repeated a few times until two consecutive readings were within 2% of each other The same procedure was used at all temperatures Time required to get a reproducible value varied with system as well as temperature In most cases, it was more than 24 h In some preliminary runs, we determined the adsorption values at



Fig 1 X-ray photo electron spectra of a) alumina, b) silica gel

intervals of 3, 5, and 7 days to check on the probable quasiequilibrium of the systems We feel that such problem does not exist in this study

The concentration of the polymer in solution was determined by both UV spectroscopy and gravimetry For the cyclohexane solvent system, absorbance was measured at λ_{max} (240 nm) The concentration was computed from a calibration curve obtained earlier. This process was followed by gravimetry and the difference between the gravimetric and spectroscopic results was less than $\pm 1\%$. In the gravimetric procedure [13, 14], dry small-weighed beakers were taken To obtain complete dryness, 2 ml of solution was pipetted out in a beaker and placed under low vacuum at 50 °C. The beakers were then weighed to determine the amount of residual polymer present The process was repeated until two consecutive weighings gave the same result Each point was duplicated simultaneously to check for the reproducibility of the result Duplicate blank experiments were also conducted with pure solvents. PBR concentration studied ranged from 0.05% (w/v) to 1 2% (w/v) As UV spectroscopy could not be used when toluene was solvent, only the gravimetric procedure was used

Results and discussion

In Figs. 2–4, the amount of PBR adsorbed per gram of adsorbent are plotted against the equilibrium concentration of PBR (C_{PBR}). The effects of solvent and temperature in both cases are similar

although the amounts adsorbed are different. The amount of adsorption as a function of solvent is similar in both cases, with adsorption from cyclohexane being higher than that from toluene. These isotherms, which are relatively more sharp than rounded, show both maxima and minima and at higher concentration they finally become level. Such similarity of isotherms also was observed earlier [15]. It was suggested [16, 17] that as the polymer is adsorbed on the surface of the adsorbent, a second phenomenon, polymer spreading on the surface of the adsorbent, starts. The rate of adsorption is expected to be proportional to the concentration of the polymer in solution, and the rate of spreading is expected to be proportional to the concentration of the adsorbed polymer on the surface. Hence, the more the polymer spreads on the surface, the less is the amount adsorbed. The complicated nature of polymer isotherms is probably due to these two antagonistic effects, as well as some others. In Figs. 5 and 6, SEM photographs of the polymer adsorbed surface of alumina and silica gel are shown respectively. In both cases, the adsorbent was removed from the jacketed bottle after 24 h, dried, divided into two parts and then a SEM photograph was taken of one part. The SEM of the second part was taken after two more days. It can



Fig 4 Plot of adsorption per gram of alumina (x/m) against equilibrium concentration of PBR a) in cyclohexane and b) in toluene at different temperatures \bigcirc 30 °C, \triangle 35 °C, \Box 40 °C

adsorption processes are exothermic with negative entropy change. Both the enthalpy and entropy change values of the adsorption process in the silica gel-cyclohexane system are highly negative in comparison to those of other systems.

The adsorption process from a solution, as in these cases, are complicated due to the presence of many different phenomena. We have already mentioned the possibility of spreading of adsorbed polymer on the adsorbent surface. Moreover, the

Table 1 Free energy ΔG^0_{ads} , the enthalpy ΔH^0_{ads} and the entropy ΔS^0_{ads} of PBR adsorption at infinite dilution for different systems (Concentration is expressed in g/100 g solution)

System		Temp (°C)	ΔG_{ads}^0 (kJ)	ΔH_{ads}^0 (kJ)	$\Delta S^{0}_{ads}(\mathrm{JK}^{-1})$
1	Silica gel +	30 35	- 9 36 - 9 03	- 31 8	- 74 0
	toluene	40	- 8 66		
2	Alumina +	30 35	- 10 62 - 9 79	- 46 0	- 116 7
	toluene	40	- 9 49		
3	Silica gel + cyclohexane	30 35 40	16 48 14 14 11 79	158.5	468 4
4	Alumina + cyclohexane	30 35 40	- 8 95 - 8.61 - 8 32	- 28 7	- 65.2

1) polymer-solvent, 11) solvent-adsorbent and 111) polymer-adsorbent interactions also complicate the systems.

We are not in a position to compute the interaction parameter of the polymer-solvent systems. However, from the intrinsic viscosity of the solution we can qualitatively characterize the two solvents as good or poor [16, 24]. It is well known that the adsorption is more from a poor solvent than from a good solvent [25]. We determined that the intrinsic viscosities of the cyclohexane-PBR and the toluene-PBR systems are 2.38 and 2.48 at 30 °C, respectively [21], signifying that toluene is a good solvent and, hence, there will be less adsorption from this solvent system. The solubility parameter is another criterion used to characterize the solvent [26]. The solubility parameter of PBR, cyclohexane and toluene were calculated to be 8.13, 8.2 and 8.9, respectively, indicating that cyclohexane should be a better solvent for PBR [27, 28], which is contrary to what we expected from intrinsic viscosity. This type of conflicting observation was also observed earlier [6].

The other complicating factor is solventadsorbent interaction. The characteristics of adsorbent surfaces are important. It is a well-known fact that the aromatics are easily adsorbed on the alumina surface, and the adsorption occurs on the Al^{3+} site of the alumina [29]. Hence, qualitatively we expected that the toluene will be adsorbed on the authorities of IPCL, particularly Dr. T. S R. Prasada Rao, for a gift of polybutadiene as well as for measuring the surface area.

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Characterization of Natural Polyisoprenes and Synthetic Polybutadiene

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SYNOPSIS

Synthetic polybutadiene (PBR) and natural rubbers from India (InR) and Guyana (GR) have been characterized in detail. The characterization includes IR, NMR, GPC, DSC, TGA, contact angle, and viscosity measurements. Spectroscopic characterization helped in the differentiation of InR and GR. Viscosity data is used in the evaluation of activation parameters at infinite dilution of the viscous flow Viscosity data is also used for the de-

termination of the conformation of the macromolecules in various solvents. Surface characterization confirms the total hydrophobic nature of the three rubbers. Thermal analysis shows different degradation pattern for natural rubbers than for the synthetic rubber.

INTRODUCTION

As a part of our interest in polymer behavior, we decided to study the adsorption of polymers at the solid-liquid interface. The adsorption of synthetic polybutadiene was studied on inorganic substrates. for example, silica gel and alumina from solvents such as toluene and cyclohexane.¹ We are also studying copolymer adsorption, which will be published elsewhere We are presently studying the adsorption of different natural rubbers on these substrates. The natural rubbers chosen for the study were: (a) natural rubber obtained from Guyana and (b) natural rubber obtained from Kerala, India, To explain and understand the adsorption of all these rubbers on different substrates, detailed characterization is necessary. The characterization includes IR,² NMR, contact angle,² viscosity,¹ DTA, DSC, and GPC, as were performed earlier. The results are presented and discussed in this article.

EXPERIMENTAL

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FILAGE COMPLEXE Synthetic cis-1,4-polybutadiene (> 96%) (PBR) was obtained from IPCL, Baroda, India Guyana rubber (GR) was natural rubber from Guyana, and

was obtained as a gift from Dr. J. T. Guthrie, Department of Colour Chemistry, Leeds University, Leeds, UK. The Indian rubber (InR) was natural rubber obtained from Kerala, India, as ribbed, smoked sheet (RSS), from plant RRII 105. The polymers were purified by dissolving them in toluene and leaving them overnight. The insoluble matter was filtered out and the clear filtrate was poured in excess methanol with constant stirring. The pure white rubber obtained was vacuum dried to a constant mass at room temperature.

The solvents, that is, chlorobenzene, toluene, n-heptane, cyclohexane, methylcyclohexane, methanol, and chloroform, were obtained from Merck, India. The cyclohexane and methylcyclohexane used were chromatography grade. All the solvents were freshly distilled before use.

The IR spectra of the polymer films were taken on a Shimadzu IR-408 spectrophotometer. The films were made by dissolving the polymers in chloroform and then pouring the solution over mercury. The films were obtained by vacuum evaporation of the solvent. The NMR of the polymer solutions in CDCl, were recorded on a Varian XL a 300 MHz for PMR and 75 MHz for ¹²CNMR at the RSIC, IIT, Bombay, India. The GPC of the rubbers was run in tetrahydrofuran (THF) at ambient conditions ($\sim 27^{\circ}$ C) on "Waters" (150 C ALC, Millipore Corporation), with refractive index detector. DSC was recorded on a Dupont 2000) system in nitrogen atmosphere. TGA and DTA were recorded on the Shimadzu Thermal

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Analyzer DT 30B The contact angle²⁺ was determined with the help of a contact θ meter, fabricated at the department of color chemistry, Leeds University, Leeds, UK, and was obtained as a gift. Viscosity studies of different solutions were carried out with the help of an Ubbelohde Viscometer ¹ that was placed vertically in a thermostat at required temperature (± 0.05 °C).

RESULTS AND DISCUSSION

IR and NMR Spectra

The IR spectra of all three polymers are given in Figure 1 The GR films were opaque, hence the IR spectra was taken in chloroform solution. The spectra obtained compare favorably to those in literature.





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For lnR, the bands at 740, 1130, and 1310 cm⁻¹ are due to vibrations of cis-C(CH₂) = CH-group.⁴ For GR, the bands at 1150 and 1325 cm⁻¹ are due to vibrations of trans-C(CH₁) ~ CH-group ⁴ This suggests that lnR is a cis and GR is trans form of natural polyisoprene. The PBR spectra compare favorably with those in the literature.⁵

The PMR spectra of three rubbers are presented in Figure 2 and their ¹³CNMR spectra are presented in Figure 3 The resonance peaks suggest the arrangement of repeat unit, as shown in Figure 4. The symmetrical units of cis-1,4-polybutadiene (PBR) exhibit one resonance peak from equivalent ethylenic carbons (α peak) and one peak from equivalent methylene carbons (β peak) InR shows resonance peak at 5.12 ppm indicating that the sample is 1,4 adduct ⁶ The peaks at 2 03 and 1 67 ppm are given by α -CH₂ and α -CH₃, respectively The peak at 1.67 ppm indicates its cis structure The olefinic peak is observed at 5.12 ppm. In GR, the α -CH₃ peak is observed at 1 59 ppm. This suggests that the 1,4 unit is mainly trans in the repeat unit ⁷

The ¹¹CNMR spectra of InR and GR further contirms the configurational difference between them Both show five, clearly distinguishable, singlet resonance peaks, which are due to methyl, two methylene, and two ethylenic carbon atoms. From Figure 4, it can be seen that δ methylene molety, being in a similar environment in cis-and trans-1,4-polyisoprenes, shows similar chemical shift values in both cases. These values are 26.4 ppm for natural cis-1,4 and 26.8 ppm for natural trans-1,4, that is, for InR and GR, respectively.⁸ Unlike δ carbon, γ -methylene carbons resonate at 39.8 ppm for GR and 82.2 ppm for InR, that is, a difference of 7.6 ppm. The methyl carbons (ϵ carbons) also show a difference, that is, 23.37 ppm for InR and 16.03 ppm for GR. This confirms that InR is cis-1,4 polyisoprene and GR is trans-1,4-polyisoprene.⁹

Contact Angle Measurements

The contact angle, θ , of various liquids with polymer surfaces (films) was determined with the help of a contact " θ " meter, as mentioned earlier. The liquids used are listed in Table I. The surface tensions at

Table I The Surface Tension Values of the Liquids Used for Determing γ_e on Various Rubbers

Liquids Used	γ2°C <i>mN</i> m ⁻¹	Polymers		
Dioxane	32.59	PBR. GR 'nR		
Nitrobenzene	43 90	PBR, GR, InR		
Amhne	41.75	PBR, GR, InR		
Acetic acid	27.80	PBR, InR		
Acetone	23.70	PBR		
Glycerol	63 40	GR		
Ethylene Glycol	47 70	GR		
Formamide	58.20	GR		



Figure 2 PMR spectra of (a) PBR, (b) InR, and (c) GR.

20°C were taken from the literature and were used for determination of 'c. The Cos θ was plotted against the surface tension of the liquids. The linear plot obtained was extrapolated to Cos $\theta = 1$ ($\theta = 0$) and the corresponding surface tension was taken to be the critical surface tension 'c. The values were 165, 15.5, and 130 mN m⁻¹ for PBR, GR, and InR, respectively. This indicates that the liquids with surface tension than higher 'c will not easily spread on polymer surfaces. We can surmize that all three polymers are hydrophobic in nature.¹⁰

This conclusion indicates that liquids with hydroxyl or other hydrophilic groups will spread less on these rubbers. It is clear that synthetic polybutadiene and natural polyisoprenes show similar wetting behaviors.

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Figure 2 (Continued from the previous page)

Thermal Analysis

It is seen from the TGA of PBR, GR, and InR that the maximum weight loss is different for each rubber Weight loss is found to be 84%, 90%, and 94% for PBR, GR, and InR, respectively. From Figure 5. it can be seen that the DSC thermograph of PBR differs considerably from those of InR and GR. PBR falls into the class of elastomers, showing degradation by exothermic reaction in nitrogen atmosphere. This exotherm peak precludes oxidation and indicates crosslinking and cyclization reactions.¹¹ The energy change associated with this is found to be 965 4 J/g. InR and GR fall into another class, degrading both by the exothermic and endothermic reactions in nitrogen 1213 Both exothermic and endothermic reactions show a diffused exotherm up to about 255°C, followed by an endotherm, an exotherm, and finally a devolatalization endotherm be- . tween 330°C and 450°C. The absolute values associnted with individual transitions differ for both the

rubbers; the values are dependent on the molecular structure, configuration, and chemical composition

Viscosity Study of Polymer Solutions

The viscosity of rubbers was studied in different solvents and at different temperatures. This enabled us to calculate the viscosity average molecular weight for different rubbers. The values are listed in Table II. The values obtained from GPC analysis are also cited in Table II. GPC of InR could not be run because of its insolubility in THF. The intrinsic viscosities of all three rubbers in different solvents, and at different temperatures, are listed in Table III. The intrinsic viscosities were computed by a well-known procedure ¹⁴ It can be seen that the intrinsic viscosity linearly decreases with an increase in temperature The accuracy of the data was checked by calculating K', K⁻¹⁵ and their difference was 0.5, as expected.¹⁵

Table II Average Molecular Weights and Polydispersities of Rubbers

' lvmer	$K \times 10^{5}$	(† ⁴	<i>М</i> ,	<i>М</i> ь	М _п	D
PBR	.3.3 9	0.688	4.14 > 10	5.9 + 10	2.3×10^5	2 52
GR	50.2	0.667	5.61 + 10	$3.5 + 10^{'}$	$1.1 + 10^{6}$	2.50
InR	50/2	0.667	9 15 - 10			

* Mark-Houwink constants 17

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Figure 3 ¹¹C NMR spectra of (a) PBR, (b) InR, and (c) GR.

parameters of different solvents for each of the rubbers. The plots show maxima, corresponding to the solubility parameter of the rubber The solubility parameter of PBR was found to be 8 75 at 30°C and 8 4 at 35°C. The solubility parameter for GR was found to be 8.8 at 30°C The solubility parameter for InR was difficult to find because fewer solvents were used

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From the viscosity data, various activation parameters of the viscous flow were evaluated using the Frenkel-Eyring equation, ¹⁶ that is

$$\eta = (Nh/V) \exp(\Delta G_{\min}^{\sharp}/RT)$$
(1)

Where V is the molar volume of the solution, N is the Avogadro number, h is the Plank's constant, Ris the gas constant, T is the temperature, and



Figure 3 (Continued from the previous page)



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Figure 5 DSC curve of (a) PBR, (b) InR and GR.

 $\Delta G_{\rm vis}^I$ is the activation free energy change of the viscous flow. Equation (1) can be rewritten as

$$\ln(\eta V/Nh) = \Delta G_{yy}^{\dagger}/RT$$
$$= \Delta H_{yy}^{\dagger}/RT = \Delta S_{yy}^{\dagger}/R - (2)$$

Where $\Delta H_{\rm vis}^4$ and $\Delta S_{\rm vis}^4$ are the activation enthalpy and entropy change of the viscous flow. The linearity is observed by plotting ln $(\eta V/Nh)$ against T^{-1} . The slope and the intercept gave ΔH_{tigh}^4 and ΔS_{tigh}^4 , respectively. On plotting ΔS_{tigh}^4 against concentra-

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Table III Intrinsic Viscosities of Rubbers in Various Solvents and Temperatures

		Intrinsic Viscosity $[\eta]$ (dL/g)					
Solvent System	Type of Rubber	25°C	30°C	35°C	40°C	45°C	
n-heptane ($\delta^* = 7.4$)	PBR	1 60	1 56	1.51	1.48		
Methyl	GR	-	1 53	1.51	1.49	1.47	
Cyclohexane $(\delta^* = 7.8)$	InR		4 20	4.05	3 85	3.70	
Cyclohexane	PBR	2 4 1	2 37	2 34	2.30		
$(\delta^* = 8.2)$	GR	1.55	1.52	1.50	1.47	-	
Toluene	PBR	2.56	2.48	2.34	2.06	1.94	
$(\delta^* = 8.9)$	GR	1.73	1.70	1.62	1.58	1.54	
	InR	4.90	4.75	4.60	4.45	4.30	
Chlorobenzene	PBR	2.44	2.33	2.16	1.84		
$(\delta^* = 8.9)$	GR	1.70	1 57	1.50	1.46		
	InR	4.26	3.12	2.27	2.17		

* Solubility parameter, ö, as given in Ref 17

tion, and extrapolating to C = O, ΔS_{vis}^{\dagger} values were obtained. $\Delta H_{v_{10}}^{\frac{1}{2}}$ values were also similarly obtained. $\Delta G_{\rm vin}^{\dagger *}$ values were then computed at 30°C by wellknown thermodynamic relations. All these activation parameters, at infinite dilution, are complete in Table IV. It can be seen that the heats of activation of the viscous flow are positive for all systems The entropies of activation of the viscous flow are also positive. However, free energy of activation of viscous flow seems to be independent of polymer and solvent.

The relative viscosity data at different concentrations helps us in the calculation of the voluminosity (V_F) of polymer solutions at a fixed temperature. Recently, the data have been used 18 to determine the shape of the protein molecules in solution. that is, the so-called "shape factor " V_E was calculated by plotting Y against concentration C (in g/mL), where

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 $Y = (\eta_r^{0.5} - 1) / [C(1.35 \eta_r^{0.5} - 0.1)]$ (3)

The straight line obtained was then extrapolated to $\mathbf{C} = \mathbf{O}$ and the intercept yielded V_t . The shape factor " was obtained from the equation

$$[\eta] = \nu V_F \tag{4}$$

The shape factor gives an idea of the shape of the macromolecules in the solution.¹⁹ Values of shape factor in different solvents are listed in Table V. It is seen that the value for all the systems is around 2.5, suggesting that the macromolecules acquire spherical formations²⁰ in all solvents chosen for this study Moreover, v values were found to be almost independent of temperature, varying between 2.4 and 2.6, indicating that the ratio between the major axis and the minor axis varies by about 2%. Therefore, we suggest that the formations of these polymers are independent of temperature

Table IV Viscosity Activation Parameters at Infinite Dilution

	PBR			GR			InR		
Solvents	7H‡;" (F1)	(1K /) 72 t: "		2H‡;. (k1)	(1K_1) 78ti*	2G‡¦" (K1)30°C	ΔH‡; (kJ)	- 28‡%. - 28‡%.	(k1).8).c 7(]‡¦"
Toluene	11.4	9.0	87	10.1	57	8 5	9.6	-1 21	10.0
Chlorobenzene	9.6	3.8	84	93	27	85	11 ()	9.0	8.3
Cyclohexane	11.8	71	96	13.0	13.2	9.0	••		produces.
n-Heptane	8.8	28	80						
Methyl Cyclohexane				86	-08	8.6	9 1	17	99

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Table V Shape Factor, v, at 30°C

Solvents	PBR	GR	InR .
Toluene	2.54	2.48	, 2.48
Chlorobenzene	2.50	2.53	2.53
Cyclohexane	2.49	2.52	****
n-Heptane	251		
Mathyl Cyclohexane		9.63	2.54

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