

# THERMODYNAMIC AND VISCOMETRIC STUDIES OF POLYBUTADIENE RUBBER IN TOLUENE AT VARIOUS TEMPERATURES

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The behaviour of Poly (butadiene) rubber used in local tyre industry was studied in a common solvent in the temperature range of 288-348 K by viscosity technique. Huggins and Kraemers equations were used to determine the intrinsic viscosity which showed increase with temperature. Thermodynamic parameters like  $\Delta G_v$ ,  $\Delta H_v$  and  $\Delta S_v$  were determined showing orientation and uncoiling of molecules during flow and system becoming more ordered. Hydrodynamic volume values are reported at different temperatures.

**Key words:** Viscometric studies, Polybutadiene rubber, Toluene

## Introduction

Polybutadiene (PBR) is an important elastomer due to its outstanding abrasion resistance. It also exhibits high elasticity, low build up and good resistance to oxidation. Its processing properties can be improved when blended with natural rubber. In passenger tyres, PBR improves tread wear by about 1% for each percent of Polybutadiene in the tread compound. In truck tyres, its blended with natural rubber gives 14% more wear than natural rubber alone. Therefore, PBR ranks very high (Kirschner 1996) in the world wide synthetic rubber consumed.

In solution, properties depends not only on its molecular weight but also on the nature of solvent and temperature (Tager and Rheol 1974). From the previous study (Jurgin and Wolf 1982) of polymer solutions on the thermodynamic properties, it has been found that the intrinsic viscosity  $[\eta]$ , (a measure for the size of the isolated molecules), and Huggins constnat  $K_H$  (a measure of their mutual interaction) are both influenced by changes of solvent power and temperature. Two independent parameters (Mayer and Makramol 1963; Murata and Mayer 1963) i.e. long range and short range interactions parameter, describe the conformational and thermodynamic properties of macromolecules in dilute solutions. These parameters are respectively related to the excluded volume effect and unperturbed chain dimensions of a given polymer in a given environment. Various methods (Anoop 1987) are available to determine these parameters. Scott *et al* (1961) and Ambler (1980) worked on polybutadiene - toluene system and determined the molecular weight dependence of intrinsic viscosity.

It is very necessary to characterize the rubber before its use. Unfortunately no such work is done on polybutadiene rubber which is used in local industries of Pakistan. Therefore aim of the present work was to characterize the locally used polybutadiene rubber.

Viscosity measurements are conveniently made by comparing the time flow of the sample with liquid of known viscosity which yield the relative viscosity of the solution, from which the specific and reduced viscosities can be calculated. Well known Huggins and Kraemer's equations as given below are mostly used to determine the intrinsic viscosity.

$$\frac{\eta_{sp}}{C} = [\eta] + K_H [\eta]^2 C \dots\dots\dots (1)$$

$$\frac{\ln \eta_{rel}}{C} = [\eta] + K_K [\eta]^2 C \dots\dots\dots (2)$$

Where  $K_H$  is Huggins and thermodynamic parameters can be determined from the Frenkle and Eyring equation rearranged in the following form:

$$\Delta G_v = 2.303 RT \log (\eta/10^3) \dots\dots\dots (3)$$

$$\log \eta = (\log 10^3 - \Delta S_v / R) + (\Delta H_v / RT) \dots\dots\dots (4)$$

$$\Delta G_v = \Delta H_v - T \Delta S_v \dots\dots\dots (5)$$

## Experimental

The sample PBR was supplied by General Tyre Co. Ltd. Karachi, Pakistan. It was in yellow, elastic and semisolid form, readily soluble in toluene at room temperature. Dilute solutions were prepared in the concentration range  $0.2 \text{ gdl}^{-1}$  to 1

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gd<sup>-1</sup>. In addition to the effect of concentration on viscosity, temperature effect was also taken into account in the temperature range 288-348 °K. The viscosity of each solution was determined using Ostwald viscometer suspended in a constant temperature water bath. The precalibrated viscometer was used to take at least three readings of each sample at a given temperature.

## Results and Discussion

Figures 1-2 show plots of the reduced viscosity ( $\eta_{sp}C^{-1}$ ) i.e. Huggin's plot and in  $\eta_{rel}C^{-1}$  versus concentration Kraemer's plot at each temperature. The values of intrinsic viscosity were obtained from the intercept of these plots at zero concentration for all the solutions (Table 1).

Table 1 shows that the values of Huggin's intrinsic viscosity and those of Kraemer's intrinsic viscosity, though not exactly equal, are comparable, but their constants do not add upto 0.5 (Maron and Rezmik 1969; Seymour and Charrasher 1987), indicating the fact that toluene is not a theta solvent. However, values of Huggin's constant are low, a characteristics of good solvents, showing that toluene is a good solvent for PBR (Danussa *et al* 1961; Scott *et al* 1961; Ambler 1980; Yanovskii *et al* 1984; Tieliang and Hecheng Xian 1989). The values of Huggin's constant increase with the rise in temperature showing that the solvent quality deteriorates (Tager 1978). The intrinsic viscosity decreases with an increase in temperature following LCST (Lower critical solution temperature) phenomenon. In LCST system, interaction between polymer-solvent decreases with rise in temperature and so ( $\eta$ ) falls (Flory 1967; Baloch 1986).

The absolute viscosity is used to calculate various thermodynamic parameters from its temperature dependence and

**Table 1**

Values of Intrinsic viscosity, Huggins constant and Kraemers constant for solutions of polybutadiene rubber in toluene at different temperatures

Temp (°K)	$[\eta]$ (dl g <sup>-1</sup> )	$k_H$	$[\eta]$ (dl g <sup>-1</sup> )	$k_H$	$k_H + k_K$
288	2.677	0.285	2.524	0.126	0.411
298	2.302	0.379	2.289	0.122	0.501
308	2.245	0.403	2.240	0.118	0.521
318	2.261	0.433	2.172	0.113	0.546
328	2.059	0.470	2.103	0.111	0.546
338	1.952	0.540	2.036	0.103	0.643
348	1.804	0.637	1.921	0.089	0.726

are calculated according to equations 3-5 and shown in Tables 2-4. It would be seen from the Table 2 that energy of activation of viscous flow increases with concentration and temperature which may be due to some conformational change taking place during the course of flow (Ahmed and Rashad 1990). The values of  $\Delta H_v$  increase with the increase in concentration but the effect with the rise in temperature is irregular. Increase in  $\Delta H_v$  values with concentration may be due to the production of strong forces between the solute and solvent molecule (Tafer 1978). The entropy of all solutions at all temperature is found to be negative. The values of entropy decrease with the increase in concentration and above 318 °K indicate more order in the system. The negative entropies showed that uncoiling and orientation of molecules is taking place and the system is becoming more ordered in the course of flow (Tager 1978).

**Hydrodynamic volume.** When a polymeric molecule is dissolved in a solvent, it swells up due to solvation. Volume being occupied by the expanded coil alongwith the bound solvent is called as hydrodynamic volume ( $V_H$ ). The hydrodynamic volume of the polymer molecules was calculated using the following relationship (Brown and Zhon 1951).

$$V_H = \frac{[\eta] M_w}{0.025 N_A}$$

The values of hydrodynamic volume of PBR samples at different temperatures are summarized in Table 5. As is known that hydrodynamic volume is a function of quality of solvent and temperature, the better the quality of the solvent, more strong will be the polymer-solvent interaction and hence more expanded will be the polymer coil. The values show that toluene is a good solvent for PBR. The decrease in the values with temperature may be because of the decrease in interaction between polymer-solvent molecules leading to contraction of the coil.

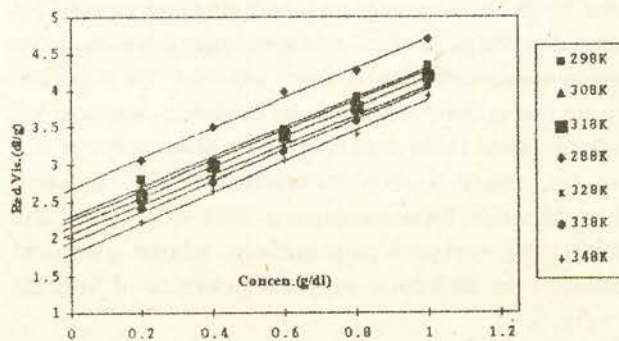


Fig 1. Huggin's Plots.



**Table 2**

Values of free energy of activation of viscous flow ( $\Delta G_v, \text{KJ.mol}^{-1}$ ) of Polybutadiene rubber in toluene at different temperatures ( $^{\circ}\text{K}$ )

Conc (g dL <sup>-1</sup> )	288	298	308	318	328	338	348
0.2	16.758	17.029	17.085	17.250	18.065	18.252	18.477
0.4	17.720	17.892	18.014	18.202	19.051	19.272	19.521
0.6	18.549	18.709	18.868	19.099	19.973	20.209	20.492
0.8	19.165	19.424	19.593	19.834	19.785	21.051	21.886
1.0	19.778	20.067	20.257	20.528	21.511	21.829	22.124

**Table 3**

Values of  $\Delta H_v (\text{KJ.mol}^{-1})$  of viscous flow of polybutadiene rubber in toluene at different temperatures ( $^{\circ}\text{K}$ ).

Conc (g dL <sup>-1</sup> )	288	298	308	318	328	338	348
0.2	11.630	11.699	11.577	11.564	11.631	11.634	11.672
0.4	12.094	12.071	11.997	11.990	12.042	12.061	12.108
0.6	12.346	12.289	12.232	12.249	12.280	12.292	12.351
0.8	12.185	12.202	12.128	12.187	12.182	12.196	12.194
1.0	11.927	11.942	11.859	11.858	11.892	11.929	11.941

**Table 4.**

Values of  $-\Delta S_v (\text{KJ.mol}^{-1})$  of viscous flow of polybutadiene rubber in toluene at different temperatures( $^{\circ}\text{K}$ )

Conc (g dL <sup>-1</sup> )	288	298	308	318	328	338	348
0.2	17.81	17.89	17.88	17.88	19.62	19.58	19.56
0.4	19.54	19.53	19.54	19.54	21.37	21.33	21.30
0.6	21.54	21.54	21.55	21.54	23.54	34.42	23.40
0.8	24.24	24.24	24.24	24.24	26.23	26.20	26.16
1.0	27.26	27.27	27.27	27.26	29.33	29.29	29.26

**Table 5**

Values of hydrodynamic volumes  $V_H (\text{E17 cm}^3)$  of PBR in toluene

Temperature( $\text{K}^{\circ}$ )	$[\eta]_{av}$	$V_H$
288	2.6005	4.3055
298	2.2955	3.8006
308	2.2425	3.7128
318	2.1665	3.5869
328	2.0810	3.4454
338	1.9940	3.3013
348	1.7130	2.8361

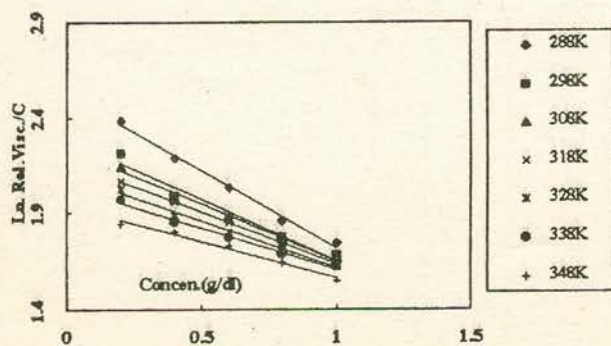


Fig. 2. Kraemer's Plots.

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