Asian Journal of Chemistry Vol. 15, No. 1 (2003), 171-178

Viscometric Studies of Polybutadiene Based Liquid Rubbers in Benzene and its Derivatives

G. SHAKIL MUHAMMAD*, R. BALAKRISHNAN† and R. CHANDRASEKAR†
Department of Physics, Islamiah College, Vaniyambadi-635 752, India

Viscosities of the two liquid rubbers polybutadiene such as hydroxyl terminated polybutadiene (HTPB) and polybutyl acrylonitrile (PBAN) in four different organic solvents have been determined at various temperatures (303–323 K) over the concentration range (0.2–1%). The temperature and concentration dependences of the shear viscosity of these systems have been discussed. An equation that reproduces the viscosity as a function of temperature and concentration has been developed. The activation parameters of viscosity have also been calculated.

Key words: Viscosity, Activation parameters of viscosity, Viscosity equation.

INTRODUCTION

The flow behaviour of low molecular weight polybutadine rubbers, such as hydroxyl terminated polybutadiene (HTPB) and polybutyl acrylonitrile (PBAN), studied as a function of concentration and temperature provides vital information on molecular weight, chain dimension and polymer characterization[1, 2]. Although there is much literature on polymer-solvent mixtures of various kinds[3–6], data on viscosity of HTPB and PBAN in organic solvents is scarce. This paper reports the viscous behaviour of dilute solutions of HTPB and PBAN in benzene and its derivatives such as toluene, chlorobenzene and nitrobenzene. An equation that reproduces the viscosity as a function of temperature and concentration has been established for each system.

EXPERIMENTAL

HTPB and PBAN obtained as gift samples from the Vikram Sarabhai Space Centre, Thiruvanantapuram, India were used as received. Some of their physical properties relavant to this study are given in Table-1.

Benzene, toluene, chlorobenzene and nitrobenzene (AR grade, SD fine Chemicals, Mumbai) were purified by standard procedures. Solutions were prepared in the concentration range 0.2–1.0% by weight of the rubbers in the temperature range 303–323 K. The density (ρ) and absolute viscosity (η) of the solvents and the solutions were measured using a specific gravity bottle and a

†Madras Christian College, Tambaram, Chennai-600 059, India.

suspended type Ubbellohde viscometer respectively. Flow measurements were made at least on 5 replicates for each solution and the time measurements were averaged for calculating η. The accuracy of measurement of these parameters is ± 0.0001 g/cm^3 and $\pm 0.01\%$ respectively.

TABLE-1
PROPERTIES OF LIQUID RUBBERS*

	PBAN	HTPB
Average molecular weight M_n	4050	2530
Acid value mg KOH/g	36.5	0.35
Moisture content (%)	0.14	0.04
Density (g/cm^3)	0.93	0.82
Viscosity at 30°C (cPs)	3000	5210
Percentage of acrylonitrile	11.40	—
Hydroxyl value mg KOH/g	—	40.80

*as given by Vikram Sarabhai Space Centre report.

RESULTS AND DISCUSSION

The measured viscosities of HTPB and PBAN in benzene, toluene, chlorobenzene and nitrobenzene at five different temperatures are given in Tables 2 and 3 respectively. For all the systems studied, one finds that viscosity increases non-linearly with concentration and decreases with rise in temperature. The non-linear rise in viscosity with polymer concentration points towards the possibility of increasing molecular interactions between the polymer and solvent molecules[7,8].

The concentration coefficient of viscosity (η_c) defined for $\eta_c = \frac{\Delta\eta}{\eta} \times 100\%$ follows the order

HTPB+nitrobenzene>HTPB+chlorobenzene>HTPB+benzene>HTPB+toluene
(17%) (13%) (9%) (7.6%)

while the same for PBAN system is

PBAN+nitrobenzene>PBAN+chlorobenzene>PBAN+toluene>PBAN+benzene
(36%) (15%) (111%) (8%)

In both systems the change in viscosity with nitrobenzene as a solvent is observed to be maximum. This can be attributed to the fact that nitrobenzene with higher dipole moment (22.1) has the possibility of electrostatic attractions between N^+ and the electron rich —CH=CH— and hydrogen bonding between —COOH group of PBAN and O^- of the nitro group and the oxygen of the —COOH and N^+ of the nitrogen. Bagchi *et al.*[9] have demonstrated that H-bonding is responsible for an increase in viscosity by causing an increase in radius of gyration over-riding other solvent effects. However, in the HTPB + nitrobenzene system intermolecular attraction is possible between N^+ and the electron rich —CH=CH— and hydrogen bonding between OH and O^- of NO_2, which could possibly be the reason for smaller change in viscosity of this system.

TABLE-2
VISCOSITY VALUES (CPs) OF HTPB IN DIFFERENT SOLVENTS

Conc. (%)	Temp (K)	Benzene	Toluene	Chlorobenzene	Nitrobenzene
0.0	303	0.5980	0.5652	0.7150	1.6065
	308	0.5494	0.5309	0.6725	1.4509
	313	0.5032	0.4865	0.6310	1.3573
	318	0.4672	0.4547	0.5875	1.2104
	323	0.4218	0.4187	0.5450	1.1079
0.2	303	0.6036	0.5688	0.7202	1.6613
	308	0.5628	0.5346	0.7001	1.5101
	313	0.5242	0.4998	0.6509	1.3995
	318	0.4943	0.4762	0.6235	1.2466
	323	0.4557	0.4419	0.5885	1.1089
0.4	303	0.6082	0.5698	0.7394	1.7532
	308	0.5699	0.5457	0.7209	1.5626
	313	0.5326	0.5145	0.6661	1.4175
	318	0.5043	0.4879	0.6401	1.2801
	323	0.4649	0.4498	0.5991	1.1606
0.6	303	0.6140	0.5790	0.7639	1.7957
	308	0.5924	0.5586	0.7427	1.6251
	313	0.5504	0.5254	0.6861	1.4687
	318	0.5191	0.4965	0.6543	1.3135
	323	0.4754	0.4590	0.6112	1.2123
0.8	303	0.6233	0.5902	0.7812	1.8510
	308	0.6054	0.5729	0.7632	1.6987
	313	0.5602	0.5381	0.7094	1.5489
	318	0.5292	0.5091	0.6792	1.3947
	323	0.4853	0.4712	0.6248	1.2456
1.0	303	0.6517	0.6083	0.8079	1.8875
	308	0.6228	0.5895	0.7887	1.7503
	313	0.5802	0.5491	0.7385	1.5923
	318	0.5445	0.5239	0.7027	1.4759
	323	0.5043	0.4803	0.6467	1.2807

TABLE-3
VISCOSITY VALUES (CPs) OF PBAN IN DIFFERENT SOLVENTS

Conc. (%)	Temp (K)	Benzene	Toluene	Chlorobenzene	Nitrobenzene
	303	0.5980	0.5652	0.7150	1.6065
	308	0.5494	0.5309	0.6725	1.4509
0.0	313	0.5032	0.4865	0.6310	1.3573
	318	0.4672	0.4547	0.5875	1.2104
	323	0.4218	0.4187	0.5450	1.1079
	303	0.5998	0.5659	0.7429	1.7982
	308	0.5651	0.5362	0.7247	1.5740
0.2	313	0.5228	0.5015	0.6748	1.4034
	318	0.4879	0.4719	0.6354	1.2490
	323	0.4628	0.4506	0.6025	1.1087
	303	0.6102	0.5676	0.7631	1.8752
	308	0.5757	0.5479	0.7392	1.6494
0.4	313	0.5342	0.5127	0.6883	1.4778
	318	0.5009	0.4841	0.6479	1.3187
	323	0.4735	0.4618	0.6149	1.1595
	303	0.6163	0.5747	0.7818	1.9465
	308	0.5923	0.5609	0.7530	1.7159
0.6	313	0.5510	0.5230	0.7034	1.5483
	318	0.5155	0.4917	0.6618	1.3897
	323	0.4846	0.4671	0.6287	1.2114
	303	0.6412	0.5937	0.7966	1.9931
	308	0.6035	0.5724	0.7678	1.7993
0.8	313	0.5696	0.5368	0.7169	1.6565
	318	0.5246	0.5056	0.6747	1.4480
	323	0.4936	0.4794	0.6434	1.2890
	303	0.6643	0.6088	0.8201	2.1146
	308	0.6212	0.5886	0.7888	1.8826
1.0	313	0.5706	0.5491	0.7358	1.7429
	318	0.5387	0.5155	0.6906	1.4919
	323	0.5150	0.4910	0.6543	1.3627

The viscosity of many liquids varies with temperature in accordance with the classical Andrade's equation

$$\eta = A \exp\left(\frac{B}{T}\right) \quad \ldots (1)$$

where A and B are constants depending on the nature of the liquid. The viscosity of a solution in general depends on the concentration linearly or polynomi-

ally[10–12]. Combining the dependence of viscosity on temperature and concentration, an equation of the form

$$\ln \eta = a_0 + \frac{a_1}{T} + a_2 \frac{C}{T} \quad \ldots (2)$$

may be suggested. In this equation a_0, a_1 and a_2 are constants, which can be obtained using multiple correlation methods. The values of these regression coefficients obtained for the systems under study are given in Table-4. For each equation the standard deviation of the logarithm of the viscosity coefficient has been calculated from

$$\sigma = \left[\frac{\Sigma(\ln \eta \text{ exp} - \ln \eta \text{ cal})^2}{(n - n_p)}\right]^{1/2} \quad \ldots (3)$$

where n is the number of observations and n_p the number of parameters, following Brent Hawrylake *et al.*[15]

TABLE-4
VALUES OF REGRESSION COEFFICIENTS AND STANDARD DEVIATION

System	a_0	a_1	a_2	σ
HTPB + Benzene	–1.0966	16.5800	4.3600	0.0700
HTPB + Toluene	–1.0916	14.7700	4.0500	0.0700
HTPB + Chlorobenene	–0.7843	12.8400	5.3700	0.0800
HTPB + Nitrobenzene	–0.3221	23.7800	6.6600	0.0800
PBAN + Benzene	–1.0934	16.4800	4.6000	0.0600
PBAN + Toluene	–1.0683	13.9700	4.0100	0.0600
PBAN + Chlorobenzene	–0.7797	14.1300	4.0700	0.0700
PBAN + Nitrobenzene	–0.4418	28.7500	8.6400	0.0800

A perusal of Table-4 shows that the values of the coefficients a_1 and a_2 are larger for the system with nitrobenzene as solvent. The negative values of a_0 and the relative magnitudes of a_0, a_1 and a_2, however, need further exploration.

According to transition state theory[13] the dependence of absolute viscosity (at constant pressure) on temperature is given by

$$\ln \eta = \ln \eta^* + \frac{\Delta H}{RT} \quad \ldots (4)$$

where η^* is a constant, ΔH is the enthalpy of activation for viscous flow. The values of ΔH were obtained from plots of $\ln \eta$ *vs.* $1/T$ and are given in Table-5 for the two systems of 303 K. Fig. (1) gives the representative plots for the two cases and the plots are linear. The values of free energy and entropy of activation ΔG and ΔS of the viscous flow were also estimated using the equations[14]

$$\Delta G = RT \ln (\eta V/Nh) \quad \ldots (5)$$

$$\Delta S = \left(\frac{\Delta H - \Delta G}{T}\right) \quad \ldots (6)$$

where V is the molar volume and N and h are Avogadro number and Planck's constant respectively. The values of ΔG and ΔS are also included in Table-5. The positive values of the activation parameters ΔH normally reflect a degree of association in the liquid state[15]. The parameter ΔG when positive implies the existence of specific interactions between the molecules. This observation is in line with the work of Reed and Taylor[16] and Mayer *et al.*[17] The negative values of ΔS indicate the formation of an activated complex for the viscous flow involving comparatively increased molecular order[18]. Here again, one finds the system involving nitrobenzene as solvent to have larger values for ΔH, ΔG and ΔS. This brings us to the conclusion that nitrobenzene is the best solvent among the solvents studied for the liquid rubbers HTPB and PBAN.

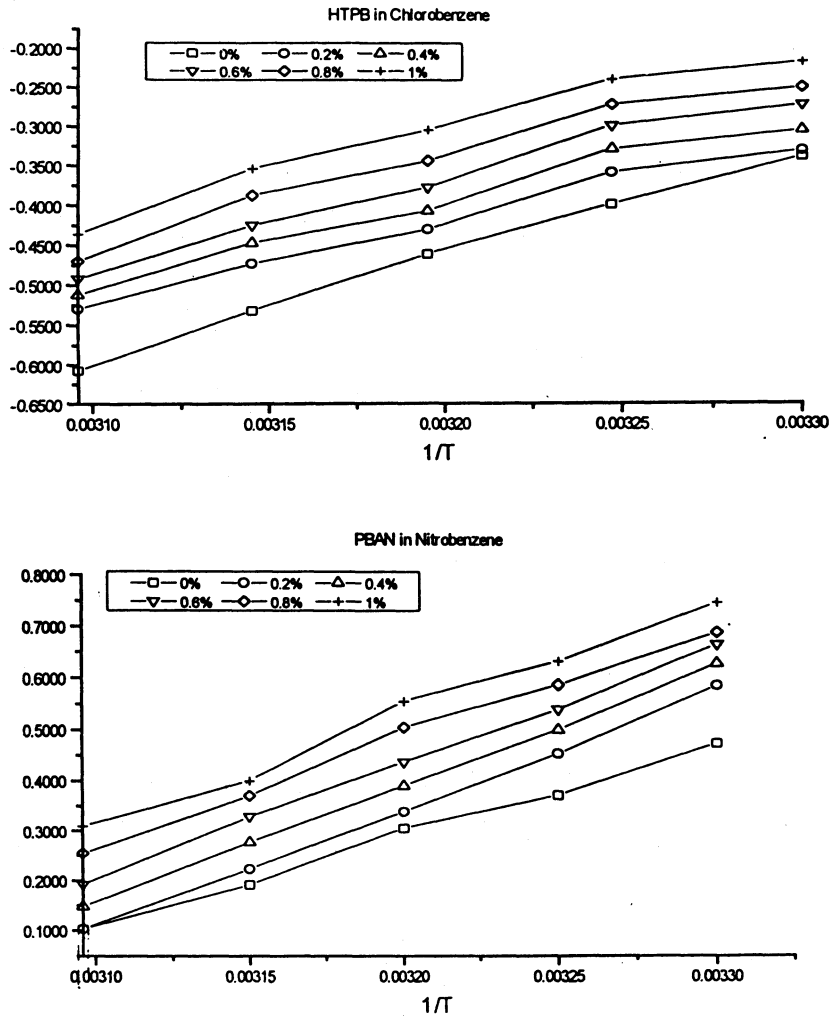

Fig. 1. Plots of (1/T) *vs.* ln (η) for HTPB in chlorobenzene and PBAN in nitrobenzene

TABLE-5
CALCULATED GIBB'S ENERGIES, ENTHALPIES AND ENTROPIES OF ACTIVATION OF VISCOUS FLOW FOR HTPB/PBAN POLYMERS IN NITROBENZENE, CHLOROBENZENE, BENZENE AND TOLUENE

Polymer/ Solvent	Concn. (%)	Temp. (K)	ΔH (kJ/mole)	ΔS (J/K/mole)	ΔG (kJ/mole)
Nitrobenzene	0	303		−0.1088	67.45
		323	34.47	−0.1129	70.94
HTPB	1	303		−0.1115	67.89
		323	34.10	−0.1154	71.37
PBAN	1	303		−0.0928	68.16
		323	40.05	−0.0975	71.53
Chlorobenzene	0	303		−0.1322	65.35
		323	25.28	−0.1353	68.98
HTPB	1	303		−0.1494	65.75
		323	20.47	−0.1519	69.54
PBAN	1	303		−0.1463	65.78
		323	21.44	−0.1490	69.57
Benzene	0	303		−0.1072	64.60
		323	32.11	−0.1111	67.98
HTPB	1	303		−0.1357	64.84
		323	23.72	−0.1386	68.49
PBAN	1	303		−0.1351	64.91
		323	23.97	−0.1381	68.57
Toluene	0	303		−0.1210	64.86
		323	28.19	−0.1244	68.40
HTPB	1	303		−0.1436	65.12
		323	21.60	−0.1462	68.82
PBAN	1	303		−0.1470	65.14
		323	20.61	−0.1496	68.92

REFERENCES

1. T.A. Litovitz, *J. Acoust. Soc. Am.*, **31**, 681 (1959).
2. Hiroshi Inagaki, Naboo Donkai, Akihisa Saitoh and Yukio Zeni Tani, *J. Appl. Polym. Sci.*, **29**, 3741 (1984).
3. K.K. Chee, *Eur. Polym. J.*, **26**, 423 (1990).
4. ———, *Eur. Polym. J.*, **31**, 155 (1995).
5. Y.P. Singh and R.P. Singh *Eur. Polym. J.*, **19**, 535 (1983).
6. ———, *Eur. Polym. J.*, **20**, 201 (1984).
7. William Bell, A. Richard, Pethrick, *Polymer*, **23**, 369 (1982).
8. S. Das, R.P. Singh and S. Maiti, *Polym. Bull.*, **2**, 400 (1980).
9. S. Bagchi, S.K. Nema and R.P. Singh, *Eur. Polym. J.*, **22**, 851 (1986).
10. A.S. Teja and P. Rice, *Ind. Eng. Chem. Fundamentals*, **20**, 77 (1981).
11. L. Grunberg and A.H. Nissan., *Nature*, **164**, 799 (1949).
12. P.K. Katti and N.M. Chaudri, *J. Chem. Eng. Data*, **12**, 514 (1967).
13. H. Eyring, R.E. Powell and W.E. Roseveare, *Ind. Eng. Chem.*, **33**, 837 (1941).
14. R.J. Moore, P. Gibbs and H. Eyring, *J. Phys. Chem.*, **57**, 172 (1953).
15. Brent-Hawrylak, Stacey Andrecy R, Carrie-Ellen Gabriel Kim Gracie, R. Paleper, *J. Sol. Chem.*, **27**, 827 (1998).
16. T.M. Reed and T.E. Taylor, *J. Phys. Chem.*, **63**, 58 (1959).
17. R. Meyer, M. Meyer, J. Metzer and A. Peneloux, *J. Chem. Phys.*, **62**, 405 (1971).
18. C. Ines Aceveo and Miguel Katz, *J. Sol. Chem.*, **19**, 1041 (1990).

(*Received*: 6 June 2002 *Accepted:* 14 August 2002) AJC-2814