Asian Journal of Chemistry Vol. 5, No. 3 (1993), 582–592

Acoustical Parameters of Polystyrene in Binary Mixture

AMARA VENKATESWARA RAO, G.K. RAMAN* and A. VARADA RAJULU†
Physico-chemical Laboratories
Department of Chemistry
S.V.U. College of Engineering, Tirupati–517502, India

Ultrasonic velocity, viscosity, density and refractive index measurements have been made for solutions of polystyrene (weight average molecular weight $\simeq$ 2,46,600) in the binary mixture (benzene + carbon tetrachloride) at various concentrations and temperatures. The molar compressibility (β), specific acoustic impedance (z), Rao number (R), van der waals constant (b) and the relaxation strength (r) have been computed. The variation of β, Z, R, b and r at 30 and 35°C have been studied from which the presence of solute-solvent interaction has been revealed.

INTRODUCTION

Ultrasonic velocity measurements in solutions of polystyrene in carbon tetrachloride (CCl_4), benzene (C_6H_6) and carbon disulphide (CS_2) at 29.7°C over a wide range of concentration have been reported by Saraf and Samal[1]. As there has been growing interest in the study of polymers dissolved in binary mixtures[2,3] the authors have studied the variation of molar compressibility (β), specific acoustic impedance (Z), Rao number (R) and relaxation strength (r) with concentration at 30° and 35°C in polystyrene in the binary mixture (C_6H_6 + CCl_4). The authors have determined the van der Waals constant (b) for these polymer solutions by refractive index and ultrasonic method and compared the results obtained by these methods.

EXPERIMENTAL

The ultrasonic velocity measurements have been made by a single frequency (2MHz) variable path interferometer with an accuracy of ±0.3% from measurements of the stationary wave pattern inside the liquid cell. The density, viscosity and refractive index have been measured by employing specific gravity bottle, Ostwald viscometer and Abbe's refractometer with an accuracy of ±0.01%, ±0.002% and ±0.02% respectively. The temperature has been maintained constant during the period of the measurement by a water circulation system from the thermostat with a thermal stability of ±0.05°C. The polymer sample used is polystyrene having the weight average molecular weight of 2,46,600. The solvents

---

†Polymer Physics Laboratories, Sri Krishnadevaraya University, Anantpur–515 003, In

are purified by the standard method[4] before use. The values of adiabatic compressibility (β_{ad}) and Rao number (R) are calculated using the following relations.

$$\beta_{ad} = (\rho v^2)^{-1} \tag{1}$$

$$R = (M/\rho)v^{1/3} \tag{2}$$

where M is the molecular weight, v is the ultrasonic velocity and ρ is the density. For solutions the molecular weight is given by the relation

$$M = M_{123} = [(n_1M_1 + n_2M_2 + n_3M_3)/(n_1 + n_2 + n_3)] \tag{3}$$

where M_1, M_2 and M_3 are the molecular weights and n_1, n_2 and n_3 are the number of moles of the components comprising the solution.

Schuyer[5] has derived a generalised expression of the Rao constant by including a correction factor.

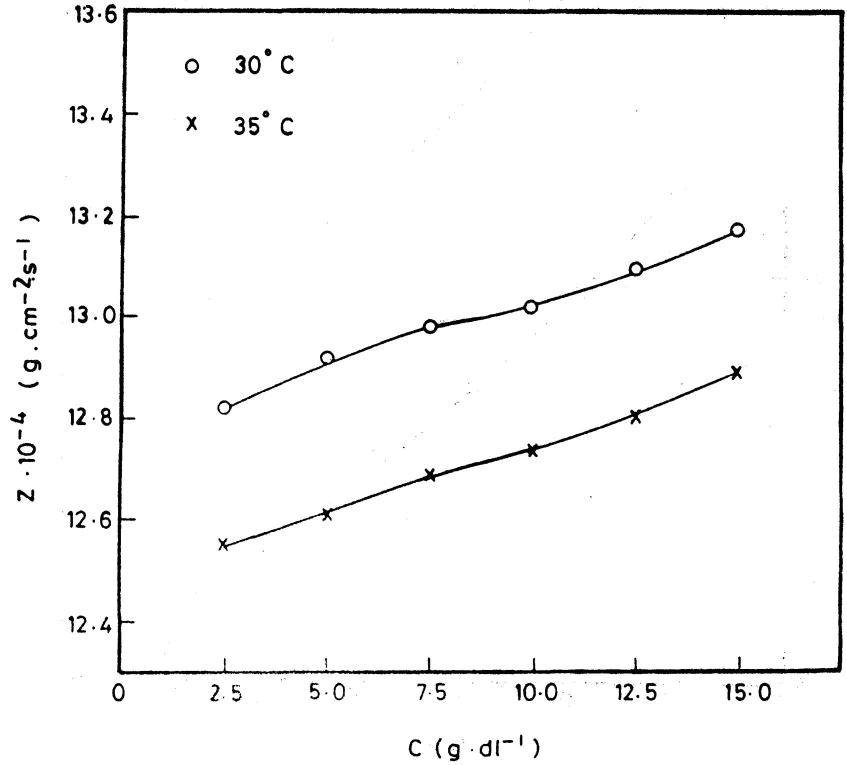

Fig. 1. Variation of specific acoustic impedance (Z) with concentration (C) for polystyrene: (C_6H_6 + CCl_4) solutions

$$R = \left(\frac{M}{\rho}\right) V^{1/3} \left\{\frac{(1+\nu)}{3(1-\nu)}\right\}^{1/6} \quad (4)$$

where ν is the Poisson's ratio of the polymer. The value of ν is taken from the literature[6] as 0.38 for polystyrene.

The theoretical value of Rao number for polymers in solution is given by the relation[7]

$$R = R_1X_1 + R_2X_2 \quad (5)$$

where R is the Rao constant of the solution, R_1, R_2 and X_1, X_2 are the Rao constants and mole fractions of the solute and solvent respectively.

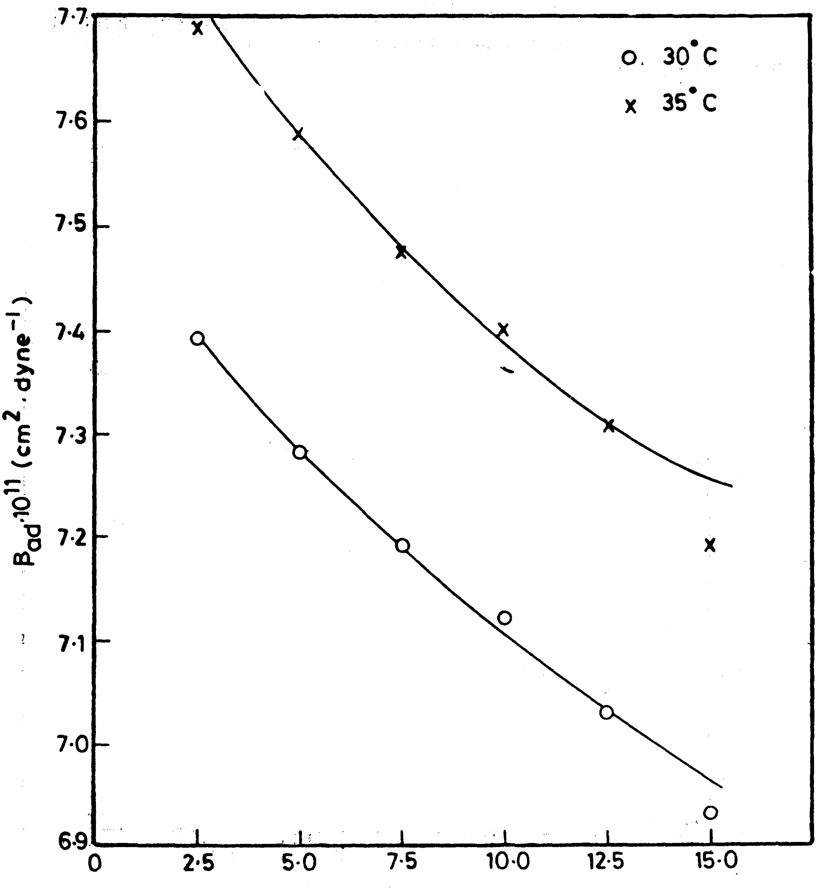

Fig. 2. Variation of adiabatic compressibility (β_{ad}) with concentration (C) for polystyrene: (C_6H_6 + CCl_4) solutions

TABLE 1: MEASURED VALUES OF DENSITY (ρ), VISCOSITY (η), ULTRASONIC VELOCITY (v) AND REFRACTIVE INDEX (n_D) FOR DIFFERENT CONCENTRATIONS (C) OF POLYSTYRENE: (C_6H_6 + CCl_4)

t°C	C g/dl	ρ g/cm^3	η cP	v m/s	n_D
30°C	0.0	1.2180	0.7140	1050.1	1.4730
	2.5	1.2174	2.8088	1054.1	1.4770
	5.0	1.2146	8.0155	1063.6	1.4810
	7.5	1.2119	16.6721	1071.1	1.4850
	10.0	1.2073	35.1074	1078.3	1.4900
	12.5	1.2053	66.2223	1086.3	1.4960
	15.0	1.2022	112.8663	1095.9	1.4990
35°C	0.0	1.2116	0.6670	1030.1	1.4730
	2.5	1.2111	2.5512	1036.2	1.4770
	5.0	1.2072	7.2826	1044.9	1.4810
	7.5	1.2050	15.2845	1053.0	1.4860
	10.0	1.2005	33.3098	1060.9	1.4885
	12.5	1.1985	55.7077	1068.6	1.4930
	15.0	1.1947	109.2929	1079.6	1.4990

Rao constant of polystyrene is taken from the literature[8] as 5980 cm$^{10/3}$ s$^{-1/3}$ mol^{-1}. The values of Rao constants calculated using eqns. (2) and (4) are presented in Table 2.

The molar compressibility (β) has been calculated using Wada's relation[9]

$$\beta = (M/\rho)(\beta_{ad})^{-1/7} \tag{6}$$

The specific acoustic impedance (Z) has been calculated by the relation

$$Z = \rho v \tag{7}$$

The van der Waals constant (b) has been calculated using the measured ultrasonic velocity by the relation[10]

$$b = (M/\rho)[1 - (RT/Mv^2)(\sqrt{1 + (Mv^2/3RT)} - 1)] \tag{8}$$

where R is the gas constant in ergs and T is the absolute temperature of the system. The van der Waals constant has also been calculated by the relation[11]

$$b = [(n_D^2 - 1)/(n_D^2 + 2)]4V_m \tag{9}$$

where V_m is the molar volume and n_D is the refractive index (Sodium D line) of the solution. The relaxation strength (r) defined by [11]

$$r = 1 - (v/v_\infty)^2 \tag{10}$$

has also been calculated, where V_∞ is a constant whose value is 1,600 m/s.

RESULTS AND DISCUSSION

Density (ρ), viscosity(η), ultrasonic velocity (v) and refractive index (n_D) for different concentrations of polystyrene in (C_6H_6 + CCl_4) at 30°C and 35°C are presented in Table 1. The computed values such as adiabatic compressibility (β_{ad}), Rao number (R), van der Waals constant (b) and relaxation strength (r) are calculated using the equations (1), (2 and 4), (8 and 9) and (10) respectively. The other characteristic parameters, *viz.* molar compressibility (β) and specific acoustic impedance (Z) have also been calculated for the present system under study and are listed in Table 2.

From Table 2, it is observed that the van der Waals constants b^1 and b^2 calculated

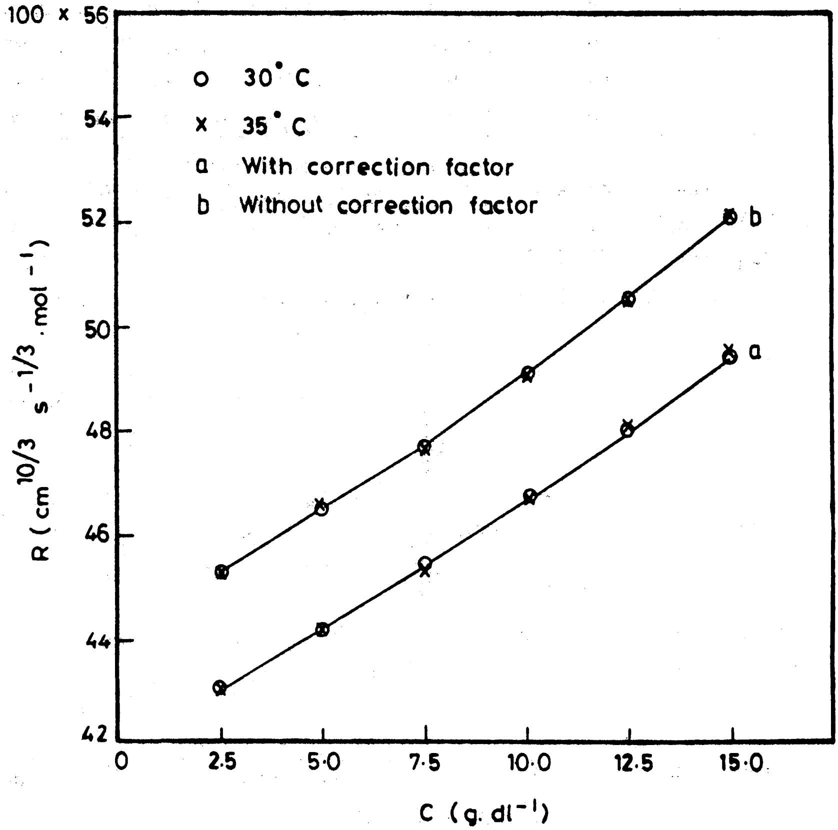

Fig. 3. Variation of Rao number (R) with concentration (C) for polystyrene: (C_6H_6 + CCl_4) solutions

TABLE 2: CALCULATED PARAMETERS, ADIABATIC COMPRESSIBILITY (β_{ad}), MOLAR COMPRESSIBILITY (β), RAO NUMBER (R) WITH AND WITHOUT CORRECTION FACTOR, VAN DER WAALS CONSTANT (b), RELAXATION STRENGTH (r) AND SPECIFIC ACOUSTIC IMPEDANCE (Z) FOR DIFFERENT CONCENTRATIONS (C) OF POLYSTYRENE: (C_6H_6 + CCl_4) AT 30°C AND 35°C

c g/dl	$\beta_{ad} \cdot 10^{11}$ cm^2/dyn	β $\left(\frac{g}{mol}\right)\left(\frac{cm^3}{g}\right)\left(\frac{cm^2}{dyne}\right)^{-1/7}$	R $cm^{10/3}\, s^{-1/3}\, mole^{-1}$ without ν factor	R $cm^{10/3}\, s^{-1/3}\, mole^{-1}$ with ν factor	b^1 cm^3/mol	b^2 cm^3/mol	r	$Z \cdot 10^{-4}$ $g/cm^2 \cdot s$
			Temperature 30°C					
0.0	7.45	2627.9	4431.1	4216.0	105.39	87.91	0.5693	12.79
2.5	7.39	2687.2	4531.7	4311.7	108.42	89.85	0.5659	12.83
5.0	7.28	2757.1	4653.5	4427.6	111.80	92.09	0.5581	12.92
7.5	7.19	2829.1	4777.7	4545.8	115.33	94.41	0.5519	12.98
10.0	7.12	2908.6	4916.1	4677.5	119.45	97.02	0.5458	13.02
12.5	7.03	2986.5	5051.0	4805.9	123.69	99.53	0.5390	13.09
15.0	6.93	3072.4	5200.8	4948.4	127.64	102.28	0.5309	13.17
			Temperature 35°C					
0.0	7.78	2625.5	4426.1	4211.3	105.95	88.25	0.5855	12.48
2.5	7.69	2686.2	4529.9	4310.1	109.01	90.22	0.5809	12.55
5.0	7.59	2758.4	4655.8	4429.9	112.52	92.56	0.5735	12.61
7.5	7.48	2830.5	4779.9	4547.9	116.25	94.87	0.5669	12.69
10.0	7.40	2910.7	4920.1	4681.3	119.89	97.50	0.5603	12.74
12.5	7.31	2989.0	5055.8	4810.4	123.85	100.05	0.5539	12.81
15.0	7.18	3079.1	5212.7	4959.7	128.57	102.91	0.5447	12.89

b^1 van der Waals constant calculated by refractive index method. b^2 van der Waals constant calculated by ultrasonic velocity measurement.

for the ploymer solutions from refractive index method and ultrasonic velocity method respectively differ from one another (the percentage deviation ranges from 17 to 20%) indicating the solute-solvent interaction. Similar conclusion is drawn by Rao *et al.*[12,13] in poly (vinyl pyrrolidone) solutions.

The variations of Z and β_{ad} with concentration are shown in Figs. 1 and 2 respectively. From Fig. 1 it is evident that Z increases linearly with concentration expect between the concentrations 7.5 g·dl^{-1} and 10.0 g·dl^{-1} showing a structural change in this range. Similar observation is made by Saraf and Samal[1] in the variation of η with concentration in the case of polystyrene: C_6H_6, CCl_4 and CS_2. From the Fig. 2, it is seen that β_{ad} decreases nonlinearly with concentration showing solute-solvent interaction[14].

The variations of R and β with concentration are shown in Figs. 3 and 4

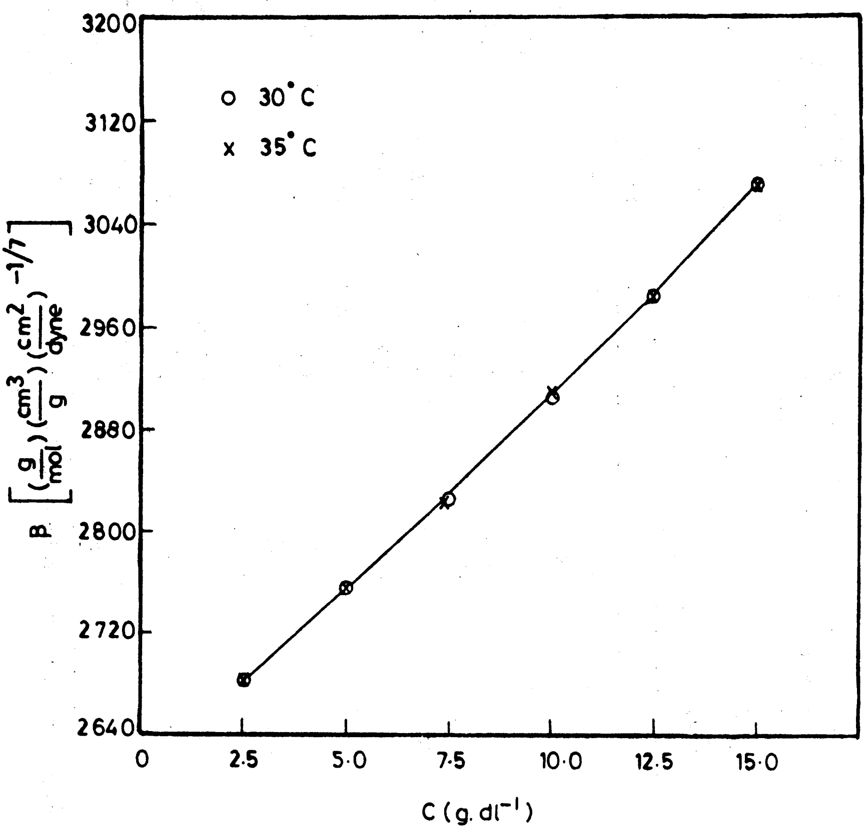

Fig. 4. Variation of molar compressibility (β) with concentration (C) for polystyrene: (C_6H_6 + CCl_4) solutions

respectively. From Fig. 3, it is evident that R changes almost linearly with concentration except for a slight nonlinearly between the concentrations 7.5 g·dl^{-1} and 10.0 g·dl^{-1}. It is also observed that the values of R at 30° and 35°C coincide with each other. This is in accordance with the theoretical expectation that Rao function is independent of temperature[15,16]. It is observed from the figure

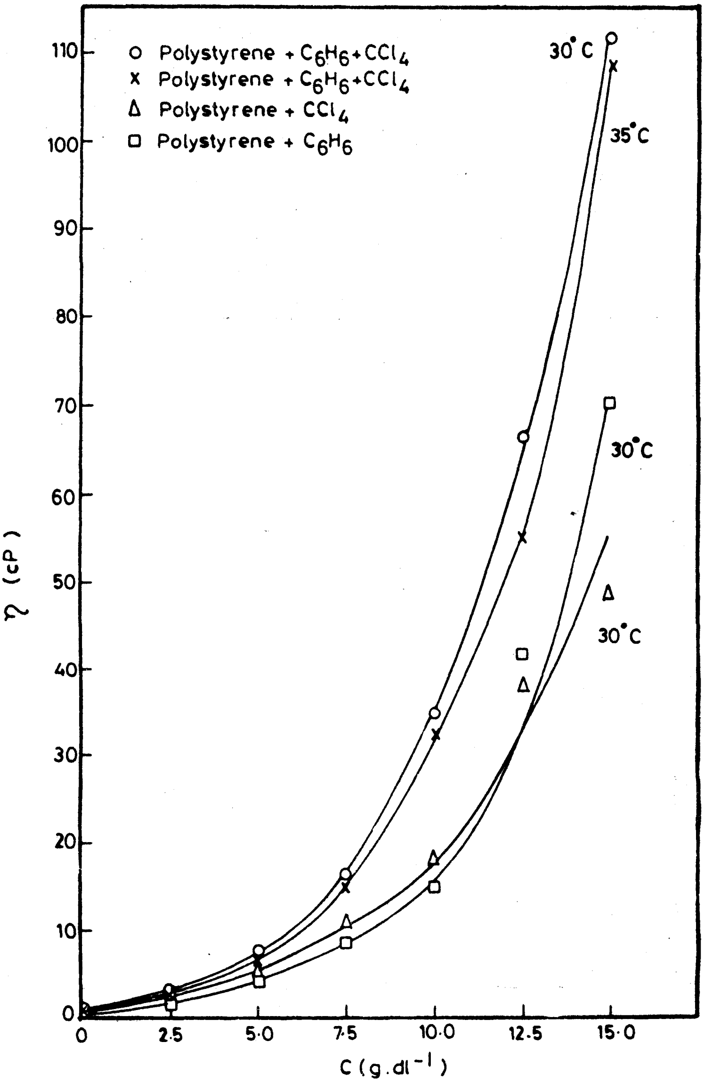

Fig.5. Variation of viscosity (η) with concentration (C) for polystyrene: (C_6H_6 + CCl_4), polystyrene: CCl_4 and polystyrene: C_6H_6 solutions

that the values of R calculated with v factor are lower than those calculated without v factor. The theoretical value of R calculated using eqn. (5) is 4431 $cm^{10/3} \cdot s^{-1/3} \cdot mol^{-1}$ at 30°C and 4426 $cm^{10/3} \cdot s^{-1/3} \cdot mol^{-1}$ at 35°C. The average values of R observed differ from the theoretical values by 9% and 4% without and with v factors respectively, showing a close agreement between theoretical and observed values. From Fig. 4, β increases with concentration but the relation is slightly nonlinear.

The variation of η with concentration is shown in Fig. 5. In the same figure the viscosities of polystyrene in C_6H_6 and polystyrene in CCl_4 at 29.7°C (available in the literature[1]) are also plotted for comparison sake. From the figure it is evident that η increases slowly upto the concentration of 7.5 $g \cdot dl^{-1}$ after which it increases rapidly in all three systems. Saraf and Samal[1] have attributed this to the structural changes. Similar conclusion can be drawn in the present case also.

The variations of b and r with concentration are presented in Figs. 6 and 7 respectively. From the figures it is clearly evident that the van der Waals

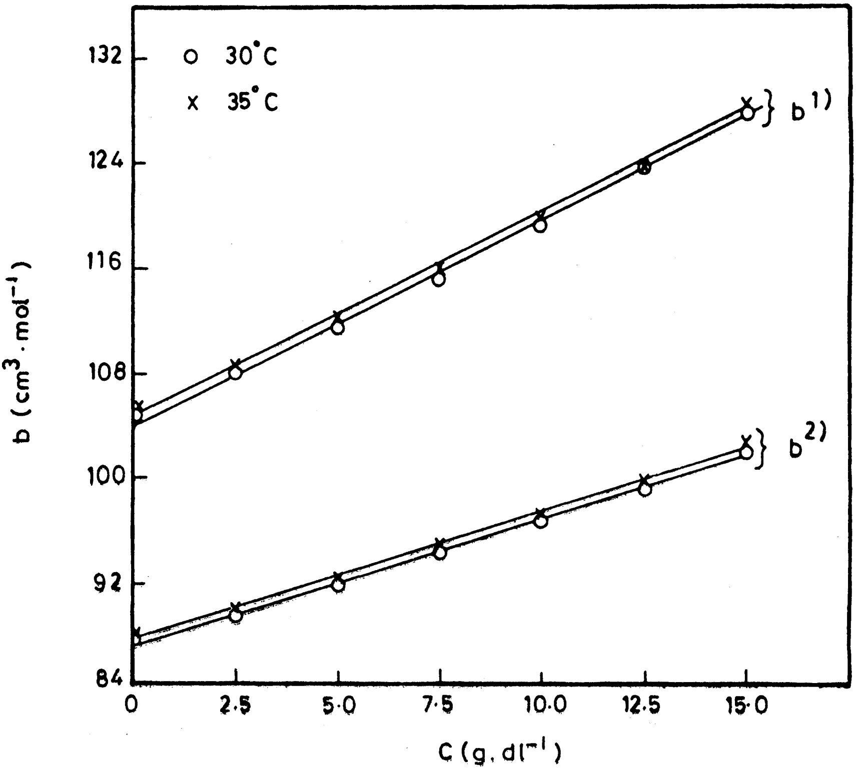

Fig.6. Variation of van der Waals constants b^1 (calculated by refractive index method) and b^2 (calculated by ultrasonic velocity measurement) with concentration (C) for polystyrene: (C_6H_6 + CCl_4) solutions

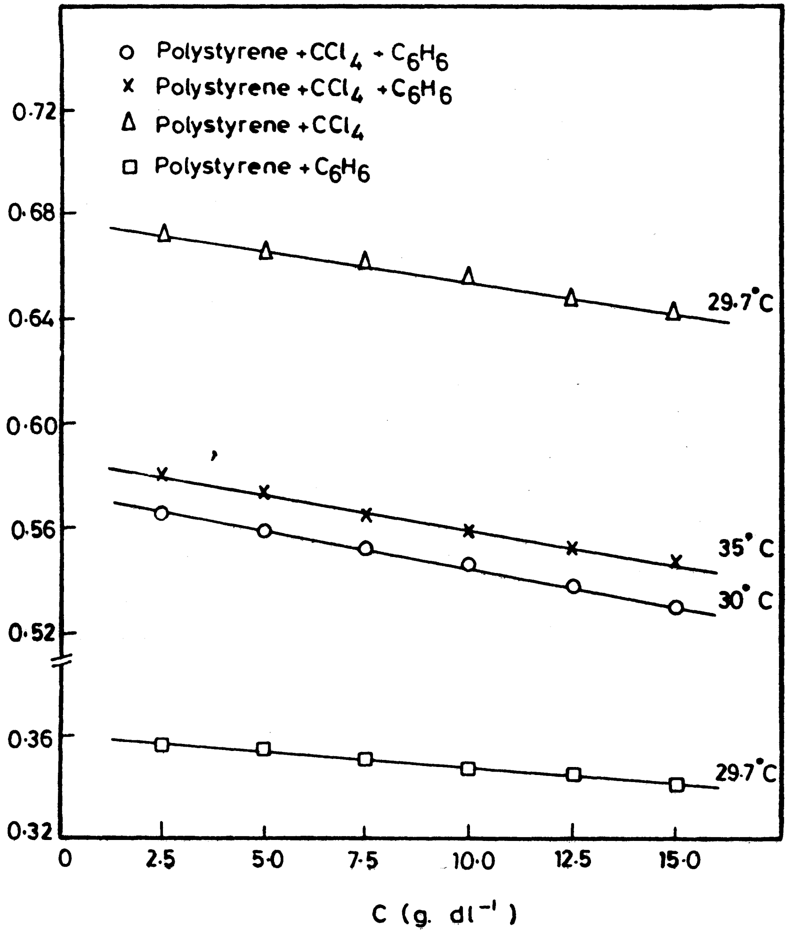

Fig. 7. Variation of relaxation strength (r) with concentration (C) for polystyrene:(C_6H_6 + CCl_4), polystyrene: CCl_4 and polystyrene : C_6H_6 solutions

constants b^1 and b^2 calculated differ from each other and b increases linearly with concentration, whereas r decreases linearly with concentration, which indicates solute-solvent interactions. Similar conclusions are drawn by Rao et al.[12,13] in the case of poly (vinyl pyrrolidone) solutions and by Johri and Misra[11] in the case of tertiary butyl alcohol in C_6H_6 and CCl_4 solutions. From all the above observations, the conclusion may be drawn that solute-solvent interactions exist in polystyrene: C_6H_6 + CCl_4) solutions and structural changes take place at 7.5 g.dl^{-1} concentration.

REFERENCES

1. B. Saraf and K. Samal, *Acustica*, **55,** 60 (1984).
2. I.A. Katime, F.J.J. Garica and P.M. Sasia, *European Polym. J.*, **24,** 557 (1988).
3. I.A. Katime, P.M. Sasia and B. Eguia, *European Polym. J.*, **24,** 1159 (1988).
4. A. Weissberger, Techniques of Organic Chemistry, Vol. 3, Interscience, New York (1967).
5. J. Schuyer, *Nature*, **181,** 1394 (1958).
6. J. Brandrup and E.H. Immergut (Eds.), Polymer-Hand Book, John-Wiley & Sons, New York (1975).
7. O. Nomoto, *J. Phys. Soc. Japan*, **13,** 1528 (1958).
8. G.V. Reddy, S. Majumdar and R.P. Singh, *Acustica*, **47,** 343 (1981).
9. Y. Wada, *J. Phys. Soc. Japan*, **4,** 280 (1949).
10. P. Vigoureux, "Ultrasonics", Chapman and Hall, London (1952).
11. G.K. Johri and R.C. Misra, *Acustica*, **57,** 292 (1985).
12. K.Ch. Rao, A.V. Rajulu and S.V. Naidu, *Acta Polymerica*, **40,** 743 (1989).
13. K. Chowdoji Rao, A. Varada Rajulu and S. Venkata Naidu, *European Polym. J.* (in press).
14. A. Varada Rajulu, K. Chowdoji Rao and S. Venkata Naidu, *Acta Polymerica* (in press).
15. P.A.K. Ekka, G.V. Reddy and R.P. Singh, *Acustica*, **46,** 341 (1980).
16. D.W.V. Krevelen and P.J. Hoftyzer, Properties of Polymers, Elsevier Sci. Publ. Co., Amsterdam (1976).

(*Received*: 16th December 1991; *Accepted*: 15th October 1992) AJC–490