

Studies on Ultrasonic Velocity and Acoustical Properties of Poly (4, 4' - Cyclohexylidene diphenylene toluene - 2, 4-Disulfonate) in Different Solvents at 30⁰ C.

K. M Rajkotia

Department of Chemistry, M.M. Science College, Morbi, Gujarat, India

ABSTRACT

Various acoustical Parameters of Poly (4, 4'-Cyclohexylidene diphenylene toluene - 2,4-disulfonate) (PSBT) in Chloroform, 1,2-dichloroethane, 1,4-dioxane and tetra hydrofuran were evaluated at 30⁰ C using an interferometer operating at a frequency of 3 MHz. Some of these parameters, except the internal pressure, relaxation time, classical absorption coefficient and solvation number, were correlated with concentration. Excellent linear correlations between the parameters U, Z, K_S, R, b, L_f and v and concentration are observed.

Keywords : Solvent - polymer and polymer - polymer interactions exist in the solvent systems studied.

I. INTRODUCTION

Recently, ultrasonic studies on polymer solutions have been carried out extensively in order to understand the nature of molecular interactions occurring in solution.^[1-7] The change in ultrasonic velocity, relaxation time and relaxation amplitude with solute concentration are useful parameters for understanding the structural changes associated with formation of solutions and readily identifying the molecular interaction between polymer and solvent. A literature survey on ultrasonic studies of polymer solutions reveals that most of the work has been confined to addition polymers.^[8-11] acoustical properties of poly (4,4'-cyclohexylidene diphenylene toluene-2,4-disulfonate) in different solvents at 30⁰ C.

II. Experimental

The solvents used were of laboratory grade and purified prior to use by an appropriate method^[15] Poly(4-4'-cyclohexylidene diphenylene toluene-2,4-disulfonate) (PSBT) used for the study was synthesized according to ref.^[16]

Ultrasonic velocity (3 MHz), density (D) and viscosity (V) measurement were made at 30⁰ C. The ultrasonic velocity (U), density and viscosity

measurements were accurate to $\pm 0.05\%$, $\pm 0.0001 \text{ g/cm}^3$ and $\pm 0.1\%$, respectively.

III. RESULTS AND DISCUSSION

The experimental data on density (D), viscosity (V) and ultrasonic sound velocity (U) of pure solvents : chloroform (CF), 1,2-dichloroethane (DCE), tetrahydrofurna (THF), 1,4-dioxane (DO) and PSBT solutions (0.5-3.0%) at 30⁰C are presented in Table 1. The observed trend in U is CF < DCE < THF < DO. It is observed graphically that D and U varied linearly with concentration (C) but the relative viscosity. (V/V₀) varied nonlinearly with C (Fig. 1). We have also observed such behaviour in other polysulfonates^[12-13]. The curvature in the viscosity plots are attributed to the polymer-polymer chain entanglement for the linear flexible polymers.^[17]

Both the relative absorption factor and the relative viscous relaxation strength^[3] showed the curvature in the same concentration range and were exactly identical to the relative viscosity against C plots (Figure 1). The results can be explained in terms of motions of polymer molecules influenced by interchain forces. The viscosity is a relaxational property and the increase in viscosity with C is attributed to predominant interchain forces over solvent-solvent forces and this may be the reason for the increase in relaxation time and relaxation

amplitude with C. The existence of polymer-polymer entanglement are reported in the literature.^[14,17-18] and is due to entropic fluctuation associated in solution with dynamically formed interchain interactions.

Various acoustical parameters were evaluated in order to support solvent-polymer and polymer-polymer interactions. Some of these parameters varied linearly with concentration, except for the internal pressure (P) and the solvation number (Sn). The variation of P and Sn with C are reported in Table 1. The correlation coefficient (r) and the correlation equations are presented in Table 2. From Table 2, an excellent linear correlation between parameter y and C is observed.

The variation of ultrasonic velocity in a solution depends on the intermolecular free path length (L_f) on mixing. On the basis of a model proposed by Eyring and Kincaid^[19], U increases with decreasing L_f and vice versa. In the present case, L_f decreases linearly with increasing C and hence increase in U with C, indicating significant polymer-solvent interaction, suggesting a structure promoting tendency of the solute. Polymer-solvent interaction was further supported by an increase in acoustical impedance (Z). Rao's molar function (R), van der Waals constant (b) and decrease in isentropic compressibility (K_s), and relaxation strength (τ) with increasing concentration of PSBT. The nonlinear increase of P with C and positive values of Sn suggests an increase in cohesive forces which again supports the structure forming tendency of PSBT. In CF and DO systems, Sn decreases in the beginning and then increases with C, whereas in DCE and THF systems, Sn increase nonlinearly with C (Table 1). The resultant values of Sn are operative on the solvent-polymer and polymer-polymer interactions (intra- and intermolecular) occurring in the solution. The decrease in Sn with C indicates that polymer-polymer interaction is more powerful than polymer-solvent interaction and vice versa. At constant temperature, the concern traction and dielectric constant of the medium play an important role in deciding the polymer chain configurations and interactions occurring in the solutions which are reflected in Sn values.

In conclusion, solvent-polymer and polymer-polymer interactions exist in the solvent systems studied. Structural changes take place after about 1% concentration, except for the THF system where it is observed at about 2% concentration.

Table 1. The density (D), viscosity (V), sound velocity (U), internal pressure (P) and solvation number (Sn) data of pure solvents and PSBT Solutions

Conc. (g/dl)	Density (10^{-3} Kg/m ³) D	Viscosity (10^{-3} , Pas) V	Velocity (m/s) U	Int. pressure (10^8 , Pas) P	Solvation number Sn
CF					
0.0	1.4753	0.6027	969.6	4.0141	--
0.5	1.4752	0.6744	971.9	4.1825	2.95
1.0	1.4720	0.7599	975.1	4.3716	2.45
1.5	1.4750	0.9145	976.4	4.7259	2.99
2.0	1.4750	1.0256	978.5	4.9327	3.06
2.5	1.4749	1.2477	979.7	5.3655	3.40
3.0	1.4748	1.5918	982.4	5.9725	3.24
DCE					
0.0	1.2442	0.7570	1174.7	4.5460	--
0.5	1.2446	0.8842	1182.8	4.8111	1.38
1.0	1.2448	1.0271	1187.4	5.0863	1.79
1.5	1.2450	1.2565	1193.0	5.5143	1.90
2.0	1.2459	1.4640	1195.6	5.8495	2.19
2.5	1.2460	2.0865	1201.7	6.7570	2.16
3.0	1.2469	2.3286	1208.6	6.9912	2.08
THF					
0.0	0.8791	0.4856	1263.4	4.0382	--
0.5	0.8855	0.5763	1267.7	4.2996	2.70
1.0	0.8873	0.7038	1270.1	4.6341	3.85
1.5	0.8892	0.8286	1272.4	4.9039	4.50
2.0	0.8907	0.9706	1275.2	5.1798	4.89
2.5	0.8936	1.3245	1278.5	5.9202	4.86
3.0	0.8957	1.4334	1282.1	6.0104	4.90
DO					
0.0	1.0248	1.0906	1331.5	5.1591	--
0.5	1.0251	1.1265	1336.4	5.1287	3.49
1.0	1.0262	1.1539	1341.4	5.0815	3.33
1.5	1.0273	1.2069	1345.7	5.0881	3.44
2.0	1.0287	1.2460	1350.9	5.0649	3.34
2.5	1.0299	1.3190	1353.4	5.1118	3.66
3.0	1.0311	1.4197	1357.9	5.2001	3.66

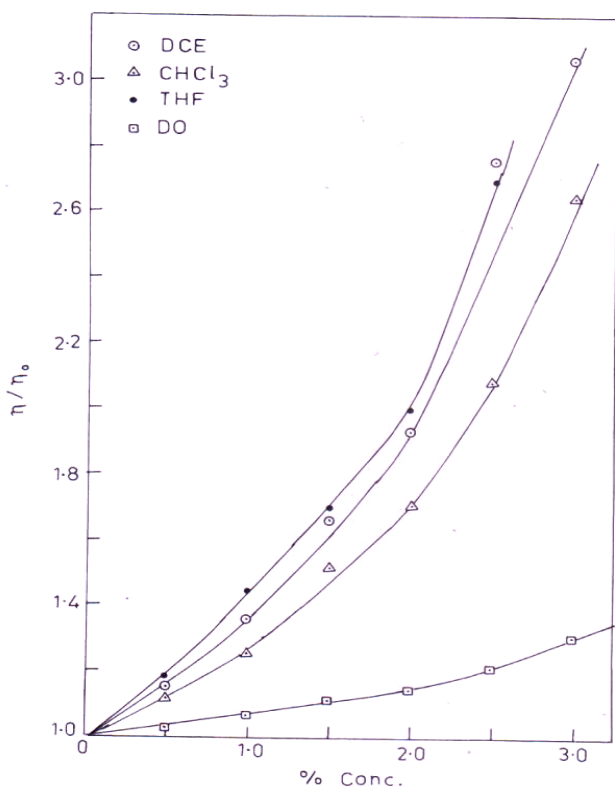


Figure 1. Plots of V/V_0 against C for PSBT in different solvents at 30°C

Table 2. The correlation coefficient (ρ) and the correlation equations for PSBT

Parameter y	Correlation Coefficient (ρ)	Correlation equation
CF		
U (m/s)	0.9912	$U - 3.9314C = 970.47$
Zx 10^{-3} (Kg/m ² s)	0.9906	$Z - 5.6514C = 1431.69$
K _s (T/Pa)	-0.9908	$K_s + 5.6331C = 719.63$
Rx 10^4 (m ^{10/3} /S ^{1/3} mol)	0.9999	$R - 0.2061C = 8.0187$
r	-0.9921	$r + 0.0030C = 0.6321$
L _f	-1.0061	$L_f + 0.0021C = 0.5353$
D (Kg/m ³)	-0.9613	$D + 0.1657C = 1475.31$
DCE		
U (m/s)	0.9936	$U - 9.9714C = 1177.50$
Zx 10^{-3} (Kg/m ² s)	0.9941	$Z - 13.4571C = 1464.63$
K _s (T/Pa)	-0.9947	$K_s + 9.7561C =$

		579.55
R x 10^4 (m ^{10/3} /S ^{1/3} mol)	0.999	$R - 0.2776C = 8.4032$
r	-0.9929	$r + 0.0093C = 0.4586$
L _f	-0.9937	$L_f + 0.0041C = 0.4804$
D (Kg/m ³)	0.9493	$D - 0.9257C = 1243.88$
THF		
U (m/s)	0.9957	$U - 5.7142C = 1264.33$
Zx 10^{-3} (Kg/m ² s)	0.9958	$Z - 10.2971C = 1116.58$
K _s (T/Pa)	-0.9966	$K_s + 9.3623C = 708.09$
Rx 10^4 (m ^{10/3} /S ^{1/3} mol)	0.9998	$R - 0.3668C = 8.8180$
r	-0.9953	$r + 0.0057C = 0.3756$
L _f	-0.9971	$L_f + 0.0036C = 0.5310$
D (Kg/m ³)	0.9957	$D - 4.0800C = 883.19$
DO		
U (m/s)	0.9964	$U - 8.4971C = 1332.75$
Zx 10^{-3} (Kg/m ² s)	0.9982	$Z - 12.0285C = 1364.37$
K _s (T/Pa)	-0.9971	$K_s + 8.0280C = 549.72$
Rx 10^4 (m ^{10/3} /S ^{1/3} mol)	0.9998	$R - 0.4105C = 9.9065$
r	-0.9966	$r + 0.0089C = 0.3062$
L _f	-0.9979	$L_f + 0.0035C = 0.4680$
D (Kg/m ³)	0.9997	$D + 2.4286C = 1023.80$

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