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► To cite this version:

B. Sharma. Relationship between the Gruneisen parameter, Flory-Huggins interaction parameter and other thermoacoustic parameters in dilute polymer solutions. *Journal de Physique IV Proceedings*, 1994, 04 (C5), pp.C5-713-C5-716. 10.1051/jp4:19945153 . jpa-00252832

HAL Id: jpa-00252832

<https://hal.science/jpa-00252832>

Submitted on 1 Jan 1994

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Relationship between the Gruneisen parameter, Flory-Huggins interaction parameter and other thermoacoustic parameters in dilute polymer solutions

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ABSTRACT: The parameter S_0 which is characteristic of melts, liquids and polymers, has also been shown to be characteristic of polymer solutions. Calculated data, using the volume expansivity of the polymer solution, establish the constancy of the S_0 -parameter which retains, on an average, a constant value of 1.11 in polymer solutions. The parameter S_0 has also been shown to be related to the anharmonic Gruneisen parameter, fractional free (available) volume, solubility parameter and Flory - Huggins interaction parameter χ in dilute polymer solutions. The results have been used to develop further understanding of the significance of fractional available volume and the S_0 -parameter in describing various thermo-acoustic properties and the anharmonic behaviour in polymer solutions.

1. INTRODUCTION

The Sharma parameter S_0 which is characteristic of molten substances at the solid-liquid phase transition, polymers and liquids at various temperatures and pressures, has, on the average, a constant value of 1.11 ± 0.01 in a wide variety of substances [1 - 4]. In this paper, it is shown that the S_0 -parameter retains its value even in polymer solutions. There is a significant contribution of the isochoric temperature derivative of internal pressure to the thermo-acoustic and anharmonic properties of dilute polymer solutions. An attempt has also been made to relate the S_0 -parameter to the anharmonic microscopical isothermal Gruneisen parameter γ' (as a measure of anharmonicity of normal mode frequency) of molecular vibrations, the dimensionless Gruneisen-like parameter Γ_0 , fractional free (available) volume f (as a measure of disorder due to increased mobility of molecules), Flory - Huggins thermodynamic interaction parameter χ (as a measure of polymer - solvent interaction) and the solubility parameter representing the square root of the cohesive energy density (as a measure of molecular cohesion) and evaluate them for dilute polymer solutions. Further understanding of the significance of the parameters f , S_0 and χ in describing the anharmonic behaviour with regard to molecular order and intermolecular interactions in dilute polymer solutions has been developed.

2. THEORETICAL

The anharmonic microscopic isothermal Gruneisen parameter Γ' , the dimensionless Gruneisen - like parameter Γ'_0 , Moelwyn - Hughes parameter C_1 , fractional free (available) volume f , isothermal volume derivative of intermolecular energy $\bar{\Phi}$ and the thermodynamic Gruneisen parameter $\bar{\Gamma}$, using the expressions obtained [1 - 4] for the anharmonic and thermo-acoustic parameters, S_0 -parameter, employing only the volume expansivity α for a polymer solution are given as

$$\Gamma' = -(\partial \ln V / \partial \ln V)_T = (4/2) [B(\partial \ln B_s / \partial p)_T - 1] = (2/3)(4 + \alpha T) + (1 - 2 S_0 / 3 + 4 \alpha T) / 2 \alpha T \quad (1)$$

$$f = (V_a / V) = (\Gamma' + 1)^{-1} = [3 + (2 \alpha T)^{-1} + (2/3)(1 + \alpha T) - S_0 / \alpha T (3 + 4 \alpha T)]^{-1} = (4/2) [(C_1 + 3) - 2 S_0 / \alpha T]^2 \quad (2)$$

$$S_0 = -(X/2)(3 + 4 \alpha T) = (4 + 2 \alpha T)(3 + 4 \alpha T) / (\tilde{V})^{C_1} = \Gamma'_0 \alpha T (1 + 2 \alpha T) / (\tilde{V})^{C_1} \quad (3)$$

$$(\partial \ln \bar{\Phi} / \partial \ln V)_T = \bar{\Gamma} X = -2 S_0 \bar{\Gamma} / (3 + 4 \alpha T) = -2 S_0 \bar{\Gamma} / \Gamma'_0 \alpha T \quad (4)$$

$$\Gamma'_0 = (\partial \ln B / \partial R) = \tilde{V}^{1/3} / (\tilde{V}^{1/3} - 1) = (3 + 4 \alpha T) / \alpha T = -2 S_0 / X \alpha T = 3(C_1 - 2) / (1 + \alpha T) \quad (5)$$

$$C_1 = (\partial B / \partial p)_T = (13/3) + (\alpha T)^{-1} + 4 \alpha T / 3 = 2 + \Gamma'_0 (1 + \alpha T) / 3 \quad (6)$$

$$X = (\partial \ln P_i / \partial \ln T)_V = -2(1 + 2 \alpha T) / (\tilde{V})^{C_1} \quad (7)$$

$$\tilde{V} = (V / V^*) = [(3 + 4 \alpha T) / 3(1 + \alpha T)]^3 \quad (8)$$

$$\alpha = \phi_1 \alpha_1 + \phi_2 \alpha_2 \quad (9)$$

where α_1, α_2 represent respectively the volume expansivities of the liquid(solvent) and polymer and ϕ_1, ϕ_2 are their respective mole fractions, R is the universal gas constant, V is the reduced specific volume, P_i the internal pressure, V_a the available volume of the molecules, V^* the hard core specific volume, and V, α, B and B_s are respectively the specific volume, the volume expansivity, isothermal and adiabatic bulk modulus of the polymer solution at absolute temperature T and pressure p .

Using eqs. (1) - (3) and (6) - (9), the parameters X, Γ', f and S_0 have been evaluated for several equimolar polymer - solvent systems ($\phi_1 = \phi_2 = 0.5$) at 298 K. The necessary experimental data on α_1 and α_2 to evaluate α are taken from literature [3 - 6]. The results are presented in Table 1.

Table 1: Calculated values of S_0 and other anharmonic parameters of polymer - solvent systems at 298 K

System	α ($10^{-3} K^{-1}$)	X	Γ'	f	S_0
Polymethylene + polyisobutylene	0.623	-0.599	3.87	0.20	1.12
Natural rubber + benzene	0.938	-0.544	3.67	0.21	1.12
Polystyrene + toluene	0.825	-0.563	3.72	0.21	1.12
Polystyrene + methyl ethyl Ketone	0.940	-0.543	3.67	0.21	1.12
Polystyrene + ethyl benzene	0.795	-0.568	3.74	0.21	1.12
Polyisobutylene + n - pentane	1.082	-0.520	3.62	0.22	1.12
Polyisobutylene + n - hexane	0.970	-0.538	3.66	0.21	1.12
Polyisobutylene + n - heptane	0.904	-0.549	3.68	0.21	1.12
Polyisobutylene + n - Octane	0.857	-0.557	3.70	0.21	1.12
Polyisobutylene + n - decane	0.802	-0.567	3.73	0.21	1.12
Polyisobutylene + n - hexadecane	0.728	-0.580	3.78	0.21	1.12
Polyisobutylene + benzene	0.889	-0.552	3.69	0.21	1.12
Polyisobutylene + cyclohexane	0.886	-0.552	3.69	0.21	1.12

The Flory - Huggins thermodynamic polymer - solvent interaction parameter χ , using the expression obtained [7] for χ , may be related to the S_0 - parameter, using eq. (3), for a dilute polymer solution as

$$\chi = (1/Z') + (V_1/RT)(\delta_2 - \delta_1)^2 = (1/Z S) - (2 S_0/\chi_1 \alpha_1 T)(\delta_2 - \delta_1)^2/\delta_1^2 \quad (10)$$

in which the solubility parameter δ_1 of a liquid can be written as [8]

$$\delta_1^2 = (RT/V_1) [\tilde{V}_1^{1/3}/(\tilde{V}_1^{1/3} - 1)] = (RT/V_1) [(3 + 4\alpha_1 T)/\alpha_1 T] = RT(\Gamma_0)_1/V_1 \quad (11)$$

where α_1 is the volume expansivity and $(\Gamma_0)_1$ the dimensionless Gruneisen - like parameter for the liquid (solvent), $Z' = ZS$ the effective coordination number, Z the coordination number taken equal to 4 in dilute polymer solutions, S represents the ratio $(V_1/V_2) \text{ or } (V_2/V_1)$ such that $S \leq 1$, V_1 , δ_1 and V_2 , δ_2 are respectively the molar volume and solubility parameter of the solvent and the polymer segment in dilute polymer solutions.

Using eq. (10) and taking $Z = 4$ the parameters Z' , S and χ have been evaluated for several polymer - solvent system at 298 K. The necessary experimental data on V_1 , V_2 (in cm^3/mol) and δ_1 , δ_2 [cal/cm^3]^{1/2} are taken from literature [6,9,10]. The results are presented in Table 2.

Table 2: Calculated Values of Flory-Huggins thermodynamic interaction parameter χ of polymer - solvent Systems at 298K

System	V_1	V_2	δ_1	δ_2	S	Z'	χ
Polystyrene + toluene	106.8	97.75	8.90	9.10	0.92	3.66	0.28
Polytetrahydrofuran + benzene	89.4	70.68	9.20	8.55	0.79	3.16	0.38
Polytetrahydrofuran + toluene	106.8	70.68	8.90	8.55	0.66	2.64	0.40
Polychloroprene + Carbon tetrachloride	97.1	71.95	8.60	8.50	0.74	2.96	0.34
Polyisobutylene + n - pentane	116.2	61.18	7.00	8.05	0.53	2.11	0.69
Natural rubber + benzene	89.4	74.58	9.20	8.10	0.83	3.34	0.48
Natural rubber + cyclohexane	108.7	74.58	8.20	8.10	0.67	2.74	0.37
Butyl rubber + toluene	106.8	61.0	8.90	8.05	0.57	2.28	0.57
GR-S + chlorobenzene	102.1	107.0	9.50	8.93	0.95	3.82	0.32
GR-S + cyclohexane	108.7	107.0	8.20	8.93	0.98	3.94	0.35

3. RESULTS AND DISCUSSION

Calculated values of the quantity X for several polymer - solvent systems in table 1 are negative. However, the absolute values of X range from about 0.52 to 0.60 which are of the same order, as observed for melts, polymers and liquids [1-4]. It may be interesting to note that although the values of χ and X depend on the nature of the polymer - solvent system, the parameters S_0 and f have, on the average, constant values of 1.11 ± 0.01 , 0.21 ± 0.01 respectively for these systems. Table 2 shows that the calculated values of the molar volumes ratio S range from about 0.53 to 0.98 and those of effective coordination number Z' from about 2.11 to 3.94

in several polymer - solvent systems at 298K, in close agreement with the range from about 2 to 4 as proposed by other workers [11,12]. The calculated values of the interaction parameter χ are of the same order as observed earlier [9], in good agreement with experimental values. For Natural rubber + cyclohexane system, the value of χ is 0.37 as the contribution of molar volumes ratio ϕ is significant while that of $(\delta_1 - \delta_2)^2$ is nearly zero. However, in case of polyisobutylene + n - pentane system, both the factors ϕ and $(\delta_1 - \delta_2)^2$ contribute significantly to the value of 0.69 for χ in this system.

The treatment offers a further evidence to support the constancy of the ϕ - parameter and for investigating several thermo-acoustic and anharmonic properties by relating it to the solubility parameter, the Gruneisen parameter, fractional available volume and the Flory-Huggins interaction parameter in dilute polymer solutions.

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