Theoretical Investigations of Effective Debye Temperature, Pseudo-Gruneisen Parameter, and Bayer's Nonlinear Parameter of Some Polymers and Their Blends in Dimethylformamide at 303.15 K

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ABSTRACT

Theoretical investigations of effective Debye temperature, pseudo-Grüneisen parameters and Bayer's nonlinear parameter for four industrially important polymers viz. polyacrylonitrile (PAN), polyvinylpyrrolidone (PVP), polyvinyl chloride (PVC), polymethyl methacrylate (PMMA), using dimethylformamide (DMF) as solvent, have been done at 303.15K. The composition dependence of these parameters for three polymer blends viz; PAN/PVP, PAN/PVC and PAN/PMMA using DMF as solvent, have also been studied at 303.15K. The variation of these parameters, with change in concentration of the polymer solution, is explained in terms of nature, strength and type of intermolecular interactions, harmonicity and structural changes occurring in the bulk of these polymeric solutions.

Keywords: Intermolecular interactions, Harmonicity, Structural changes

BACKGROUND

Most of the polyacrylonitrile (PAN) produced is employed in acrylic fibers, which contain nearly 85 percent or more of it. PAN being almost insoluble in organic solvents and extremely difficult to dyeing, very little fiber is manufactured having PAN alone. However, a copolymer (like vinyl acetate) containing PAN can easily be spun into fibers, which are soft enough to allow the penetration of dyes. Another polymer, polyvinylpyrrolidone (PVP) has been used as a plasma volume expander for trauma victims since 1950s. In addition, it is used in medical products, hair care products and cosmetics. Its variant, PVP-I, a compound of PVP and iodine, is commonly used as an antibacterial agent and antiseptic. The polymer polyvinyl chloride (PVC) is extensively used in the construction sector. Having the properties of rigidity and low flammability, PVC is used in manufacture of pipes, conduits, sidings, door and window frames. Its blends with plasticizers are used in floor tiles, garden hoses, imitation leather upholstery and shower curtains. Another polymer, polymethyl methacrylate (PMMA) is employed in domed skylights, luminous ceilings, swimming pool enclosures, instrument panels and aircraft canopies. It is also injection-moulded into headlights, taillights and lighting-fixture covers [1].

Polymer blends are physical or mechanical mixtures of two or more polymers, which show large potential for the construction and development of novel surfaces with extraordinary properties. For the production of novel surfaces using polymer blends, numerous parameters have to be considered (e.g. nature of blend, solvent etc.) which permit us to transform and mold the final desired structure [2]. Polymer blends have assumed a very important status scientifically and technologically in recent years. Because of their extensive applicability, we report in this paper a comparative study of the various thermo-dynamic parameters for four polymers PAN, PVP, PVC, PMMA and their blends in dimethyl formamide (DMF). The aim of this study is to understand the polymer-solvent interactions and polymer-polymer compatibility through their thermodynamic properties.

During the past few decades, many researchers [3-5] have

made successful attempts to explain the intermolecular interactions in liquids by measuring the sound velocity and their thermo-acoustical parameters. Hughes et al. [6] showed that the atomic motion in water is similar to solids, instead of the gaseous phase. The study reveals that liquids are quasicrystalline materials as they acquire local order of the same type as that of the corresponding crystal. On the basis of atomic motion and quasicrystalline behavior of liquids, several attempts have been made to calculate the Debye temperature for the liquids [7-9].

The Bayer's nonlinear parameter *(B/A)* has a major role in non-linear acoustics. Its knowledge is immensely useful in the fields of underwater acoustics, medicines and biomaterials [10-12]. It provides information about internal pressure, structural behavior and acoustic scattering. Several researchers have done experimental and theoretical studies related to non-linearity of the liquid systems, using Bayer's nonlinear parameter. The anharmonicity and molecular order of Van der Waals bonds prevalent in the liquid mixtures can be assessed by measuring lattice Gruneisen parameter [12-14].

In the present study, effective Debye temperature (θ_D), pseudo-Gruneisen parameter (Γ) and non-linearity parameter (B/A) are determined for solutions of pure polymers viz. PAN, PVP, PVC, PMMA and their blends viz. PAN/PVP, PAN/PVC and PAN/PMMA, in DMF. The polymer blends, prepared by mixing the two polymers in equal (50/50) proportions, were dissolved in DMF, which acted as a solvent. The investigation of intermolecular interactions for these polymeric solutions have been done at various concentrations, and at a constant temperature of 303.15 K.

THEORETICAL BACKGROUND

Since PAN and other polymers, PVP, PVC, PMMA, chosen for current study, readily dissolve in DMF to produce solutions of low viscosity, so these solutions are useful to characterize the molecular interactions between the constituents of the solutions. The standard relations, as reported in literature [13-15] are used to determine effective Debye temperature (θ_D), pseudo-Grüneisen parameter (Γ) and Bayer's number (B/A). The experimental data for ultrasonic velocity (u), density (d), effective mass (M) and temperature (T) required for computation of θ_D, Γ and B/A are taken from literature [16].

The effective Debye temperature (θ_D) for solids can be calculated using following expressions:

$$\theta_D = \frac{h}{k}\left[\frac{\left(\frac{9N}{4\pi V}\right)}{(\rho\beta_a)^{3/2}\left\{\left(\frac{1}{1+\gamma}\right)^{3/2}+2\left(\frac{4}{3\gamma}\right)^{3/2}\right\}}\right]^{1/3} \quad (1)$$

where β_a can be calculated from the thermodynamic relation

$$\beta_a = \left(\rho_{mix}u_{mix}^2\right)^{-1}$$

and γ is defined as

$$\gamma = \frac{\beta_T}{\beta_a}$$

The parameter C_1 in terms of the linear thermal expansion coefficient (α) as

$$C_1 = \left(\frac{13}{3}\right)+\left(\frac{1}{\alpha T}\right)+\left(\frac{4\alpha T}{3}\right) \quad (2)$$

Bayer's nonlinearity and Lattice Gruneisen parameters in terms of C_1 are given by

$$\frac{B}{A} = C_1 - 1 \quad (3)$$

$$\Gamma = C_1 - 1 \quad (4)$$

RESULTS AND DISCUSSIONS

The computed values of θ_D, Γ, and B/A of pure polymers PAN, PVP, PVC, PMMA dissolved in DMF and the polymer blends PAN/PVP, PAN/PVC, PAN/PMMA dissolved in DMF as function of concentrations, at 303.15 K, are reported in the **(Tables 1-3)**. All the parameters are reported in SI system expect stated otherwise.

Most of the physical properties of the polymers and their variation with change in concentrations of the polymer solutions have been co-related with the dynamics of polymer chain. The change in θ_D, Γ, and B/A parameters with concentration of polymers are found to be important in studying the structural changes associated with the polymers in solution and makes way to identify the molecular interactions between the polymer and solvent. A perusal of **Table 1** reveals that the values of θ_D, Γ, and B/A fluctuate within a small range (For PAN+DMF, θ_D=45.3K-51.0K, Γ=7.35-7.55, B/A=6.85-7.05, and for PVP+DMF, θ_D=45K-50.5K, Γ=7.34-7.50, B/A=6.84-6.99), with rise in the polymers (PAN and PVP) concentrations in the binary solution. In case of blend, PAN/PVP (50/50), the values θ_D (45.69-47.44) is intermediate whereas the values of Γ (7.354-7.409) and B/A (6.854-6.909) is less than their pure counterparts with respect to the change in concentration in the solution. The consequence of addition of polymers is in the disruption of the structure of the pure components and restriction of their rotational motion. Interstitial accommodation and orientational order led to a more compact structure and to an observed decrease in the effective Debye temperature.

Table 1. Effective Debye temperature (θ_D), pseudo-Gruneisen parameter (Γ), and Bayer's number (*B/A*) values of PAN, PVP and PAN/PVP (50/50) blend dissolved in DMF at various concentrations at 303.15 K.

Conc. (g/l)	PAN			PVP			PAN/PVP (50/50)		
	θ_D	Γ	*B/A*	θ_D	Γ	*B/A*	θ_D	Γ	*B/A*
0.1	50.97	7.546	7.046	49.42	7.487	6.987	46.77	7.389	6.889
0.2	47.30	7.413	6.913	48.24	7.444	6.944	47.44	7.409	6.909
0.4	50.77	7.549	7.049	46.98	7.398	6.898	46.02	7.368	6.868
0.6	46.60	7.395	6.895	45.30	7.337	6.837	45.53	7.354	6.854
0.8	45.33	7.351	6.851	50.11	7.515	7.015	47.21	7.403	6.903
1	46.07	7.382	6.882	48.86	7.471	6.971	45.69	7.359	6.859
A.V.	**47.84**	**7.439**	**6.939**	**48.15**	**7.442**	**6.942**	**46.44**	**7.380**	**6.880**

Table 2. Effective Debye temperature (θ_D), pseudo-Gruneisen parameter (Γ) and Bayer's number (*B/A*) values of PAN, PVC and PAN/ PVC (50/50) blends dissolved in DMF, at various concentrations, at 303.15 K.

Conc. (g/l)	PAN			PVC			PAN/PVC (50/50)		
	θ_D	Γ	*B/A*	θ_D	Γ	*B/A*	θ_D	Γ	*B/A*
0.1	50.97	7.546	7.046	59.35	7.850	7.350	48.78	7.464	6.964
0.2	47.30	7.413	6.913	60.63	7.897	7.397	48.96	7.472	6.972
0.4	50.77	7.549	7.049	46.64	7.389	6.889	52.26	7.561	7.061
0.6	46.60	7.395	6.895	50.91	7.549	7.049	50.33	7.524	7.024
0.8	45.33	7.351	6.851	47.88	7.438	6.938	51.66	7.549	7.049
1	46.07	7.382	6.882	51.16	7.560	7.060	47.74	7.456	6.956
A.V.	**47.84**	**7.439**	**6.939**	**52.76**	**7.614**	**7.114**	**49.96**	**7.504**	**7.004**

Table 3. Effective Debye temperature (θ_D), pseudo-Gruneisen parameter (Γ), Bayer's number (*B/A*) values of PAN, PMMA and PAN/ PMMA (50/50) blends dissolved in DMF at various concentrations at 303.15 K.

Conc. (g/l)	PAN			PMMA			PAN/PMMA (50/50)		
	θ_D	Γ	*B/A*	θ_D	Γ	*B/A*	θ_D	Γ	*B/A*
0.1	50.97	7.546	7.046	51.04	7.551	7.051	52.86	7.614	7.114
0.2	47.30	7.413	6.913	48.83	7.470	6.970	59.67	7.819	7.319
0.4	50.77	7.549	7.049	49.05	7.479	6.979	42.02	7.229	6.729
0.6	46.60	7.395	6.895	50.84	7.547	7.047	48.51	7.457	6.957
0.8	45.33	7.351	6.851	48.94	7.478	6.978	58.06	7.781	7.281
1	46.07	7.382	6.882	49.06	7.484	6.984	52.15	7.596	7.096
A.V.	**47.84**	**7.439**	**6.939**	**49.63**	**7.502**	**7.002**	**52.21**	**7.583**	**7.083**

The lattice Gruneisen parameter is governed by the molecular order and structure. The Bayer's nonlinearity parameter (B/A) is strongly sensitive [17,18] and provides the information relating to internal pressure, clustering, intermolecular spacing. The decrease in θ_D, B/A and Γ values with rise in concentration of each solute indicates increase in intermolecular modes of vibration and harmonicity in the liquid state. This accounts for the associating nature in polymer solutions due to weak intermolecular attractive forces [12,19,20].

A perusal of **Table 2** reveals that the values of θ_D, Γ and B/A fluctuate within a small range (For PAN+DMF, θ_D=45.3-51.0, Γ=7.35-7.55, B/A=6.85-7.05 and for PVC+DMF, θ_D=46.5-60.7, Γ=7.39-7.90, B/A=6.89-7.40), with rise in the polymers (PAN and PVP) concentrations in the binary solution. In case of blend, PAN/PVC, the variation in the value of θ_D (51.66-47.74) is intermediate whereas the values of Γ (7.456-7.561) and B/A (6.956-7.049) is less than their pure counterparts with respect to change in concentration in the solution. These pure and blend polymers again exhibit similar behavior as reported for other polymers in **Table 1**. Consequently, the behavior of θ_D, Γ, and B/A parameters again indicate the increase in intermolecular modes of vibration and harmonicity in the liquid state and associating nature in polymer solutions due to weak intermolecular attractive forces [12,19,20].

A perusal of **Table 3** reveals that the values of θ_D, Γ, and B/A fluctuate within a small range (For PAN+DMF, θ_D=45.3-51.0K, Γ=7.35-7.55, B/A=6.85-7.05 and for PAMMA+DMF, θ_D=48.9K-51.1K, Γ=7.47-7.55, B/A=6.97-7.05) with rise in the polymers (PAN and PMMA) concentrations in the binary solution. It is interesting to notice that unlike other polymer blends (PAN/PVP and PAN/PVC) variation in the value of θ_D (42.02 -59.67) is greater than their pure counterparts with respect to change in concentration in the solution whereas the variation in the values of Γ (7.229-7.819) and B/A (6.729-7.319) are less than that of pure polymers solutions. The higher values of θ_D indicate that the addition of polymers results in the disruption of the structure of the pure polymers and restriction of their rotational motion. The interstitial accommodation and orientational order led to a less compact structure and to an observed increase in the range of θ_D. The decrease in θ_D, B/A and Γ values with rise in concentration of each solute indicates fluctuating behaviour in intermolecular modes of vibration and harmonicity in the liquid state. This accounts for the changes in associating nature of the polymer solutions due to weak intermolecular forces [12,19,20].

For a better understanding of molecular interactions prevalent in the polymer solutions, having DMF as a solvent, and solutes such as pure polymers e.g. PAN, PVC, PVP, PMMA, and polymer blends e.g. PAN/PVP, PAN/ PVC and PAN/PMMA, the average value (A.V.) of θ_D, Γ and B/A

respectively have also been reported **(Tables 1-3)**. The average magnitude of θ_D for polymer blends +DMF solutions follow the order; PAN/ PMMA >PAN/ PVC > PAN/ PVP. The order of the average values for Γ and B/A also follow a similar trend as reported for θ_D. Whereas, in case of pure polymers solutions the A.V. of θ_D, Γ, B/A of polymer solutions of PMMA lie between PVC and PVP. These trends indicate that PAN/PMMA+DMF is having more structural changes, higher intermolecular modes of vibration and harmonicity as compared to PAN/PVC+DMF and PAN/PVP+DMF whereas in case of pure polymer solutions PVC is found to have the highest values of θ_D, Γ, B/A.

The miscibility study of polymer blends PAN/PVP, PAN/ PVC and PAN/ PMMA are already reported in literature [2,13]. The previous reports indicate that PAN/PMMA blend is highly immiscible and PAN/PVP is completely miscible when polymers mix together in equal (50/50) proportions for preparation for blends with. Our study indicates that immiscible blends make more compact structure and having more intermolecular modes of vibration and harmonicity than miscible blends.

CONCLUSION

The variation of θ_D, Γ, B/A values, with rise in concentration of polymers in DMF, indicate considerable changes in intermolecular forces existing in the bulk of the solution. The present study helps in investigation of the miscibility characteristics of polymer blends, PAN/PVP, PAN/PVC and PAN/PMMA in DMF. The intermolecular interactions prevalent in the polymer solutions of four pure polymers and three polymer blends in a DMF solvent, have been explained in terms of θ_D, Γ, B/A. The reported average values of θ_D, Γ, B/A for polymer blends solutions under study reveal that immiscible blends (PAN/PMMA) exhibit more compact structure and higher intermolecular modes of vibration and harmonicity than miscible blends (PAN/ PVP and PAN/ PVC) in DMF solvent.

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