

A fresh study of optical and thermal properties of polystyrene solutions

S DURAI* and P RAMADOSS

P.G. and Research Department of Physics, A.M. Jain College, Chennai 600 114, India

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Abstract. Polymers have immense practical applications and one such polymer is polystyrene. It is a linear polymer and useful for plastic optical components. The optical and thermal properties of polystyrene solutions are investigated in this paper making use of the ultrasonic velocity and fluid parameters. The results reveal a number of significant informations.

Keywords. Polystyrene; Debye temperature; heat of mixing; molecular frelength; refractive index.

1. Introduction

A polymer of a particular group is characterized by the molecular weight of the monomer unit. To study the interactions in the solid state of the polymers few models have been suggested. One such model treats a polymer as an aggregate of fairly stiff tubes held together in approximately parallel bundles of forces arising from particle–particle potentials (Barker 1967). The structure of polymers has been related to internal pressure (Suryanarayana and Pugazhendhi 1986) and the same study has been extended to polystyrene solutions (Varadarajulu *et al* 1992). Some of the interesting properties of polystyrene like the Gruneissen parameter, specific heat and bulk modulus have also been reported. However, in this paper the authors have diverted their attention to the Debye temperature, relative association and optical property of polystyrene solutions. The three solvents considered are carbontetrachloride, benzene and carbondisulphide.

2. Theory

Three aspects have been given special attention.

(i) Relative association (RA) and heat of mixing: When a solution of polystyrene is prepared using a solvent (polar or non-polar), as the concentration increases there is a decrease in the availability of solvent molecules for polymer–solvent association. This is studied by the factor, RA, given by

$$RA = (\mathbf{r}_0/\mathbf{r}_{\text{mix}})(u_{\text{mix}}/u_0), \quad (1)$$

where \mathbf{r}_0 and \mathbf{r}_{mix} are the density of solvent and solution, respectively and u_0 and u_{mix} are the sound velocity in pure solvent and solution, respectively.

Polystyrene is a linear polymer. The theory of solubility based on the thermodynamics of polymer solutions is highly developed only for linear polymers in the absence of crystallinity. The heat of mixing per unit value can be approximated (Billmeyer 1984) as

$$\Delta H = \mathbf{n}_1\mathbf{n}_2(\mathbf{d}_1 - \mathbf{d}_2)^2, \quad (2)$$

where \mathbf{n} is the volume fraction and subscripts 1 and 2 refer to solvent and polymer, respectively. \mathbf{d} is known as the solubility parameter and \mathbf{d}^2 the cohesive energy density. ΔH has been calculated for these systems.

(ii) Debye temperature: The solid like behaviour of liquids and solutions has been studied in some cases (Durai and Ramadoss 2002). In a polymer–solvent interaction, the change in thermal energy is due to (i) translational, rotational and vibrational energies of the components and (ii) the interchange energy. The change in internal energy is predominant and next comes vibrational energy, which is characterized by the Debye temperature. It is calculated from a knowledge of mean sound velocity, u_m , using the formula

$$\mathbf{q}_D = (h/k_B)(3N/4pV)u_m, \quad (3)$$

and

$$u_m = [(1/3)(1/u_t^3 + 2/u_l^3)]^{-1/3},$$

where u_t and u_l are the transverse and longitudinal sound velocity, respectively.

(iii) Optical property: The density rule is available for the calculation of refractive index. The authors have related the ultrasonic velocity to viscosity and surface tension (Durai and Ramadoss 2003). This empirical relation has been extended to binary mixtures (recently communicated). In this work the relation has been tried for finding the refractive index of polystyrene solutions.

*Author for correspondence

Table 1. Carbontetrachloride + polystyrene.

| Conc. (g/l) | r^* | u^* | h^* | L_f | s | RA | I | X | n_1 | n_2 | q_D | ΔH |
|-------------|--------|-------|-------|--------|--------|--------|--------|--------|--------|--------|-------|------------|
| 0 | 1585.5 | 906.7 | 0.84 | 5.7550 | 0.0221 | 1.0000 | 0.8313 | 0.1444 | 1.1958 | 1.4607 | 46.60 | ** |
| 25 | 1575.6 | 914.7 | 2.34 | 5.7220 | 0.0224 | 0.9909 | 0.8235 | 0.1439 | 1.3838 | 1.4574 | 46.99 | ** |
| 50 | 1562.2 | 923.8 | 6.24 | 5.6900 | 0.0227 | 0.9792 | 0.8126 | 0.1428 | 1.5869 | 1.4529 | 47.41 | ** |
| 75 | 1553.7 | 930.9 | 10.49 | 5.6621 | 0.0229 | 0.9714 | 0.8059 | 0.1423 | 1.7061 | 1.4500 | 47.77 | ** |
| 100 | 1547.9 | 937.9 | 18.53 | 5.6300 | 0.0231 | 0.9653 | 0.8007 | 0.1422 | 1.8478 | 1.4479 | 48.15 | ** |
| 125 | 1537.4 | 946.8 | 37.99 | 5.5964 | 0.0234 | 0.9558 | 0.7925 | 0.1416 | – | 1.4446 | 48.57 | ** |
| 150 | 1531.2 | 955.8 | 48.38 | 5.5567 | 0.0237 | 0.9490 | 0.7887 | 0.1415 | – | 1.4425 | 49.03 | ** |

*Varadarajulu *et al* (1992); ** ΔH is zero for this system, since $d_1 = d_2$ (see text).

Various symbols, their meanings with units used in the tables 1–3: r , density (kg m^{-3}); u , ultrasonic velocity (ms^{-1}); h , viscosity (10^{-3}Nsm^{-2}); L_f , intermolecular frelength (10^{-11}m); s , surface tension (Nm^{-1}); RA, relative association; I , mean frepath (10^{-11}m); X , ratio of mean frepath and intermolecular frelength; n_1 , refractive index (using empirical relation); n_2 , refractive index (using density rule); q_D , Debye temperature (K); ΔH , heat of mixing (J/m^3).

Table 2. Benzene + polystyrene.

| Conc. (g/l) | r^* | u^* | h^* | L_f | s | RA | I | X | n_1 | n_2 | q_D | ΔH |
|-------------|-------|--------|-------|--------|--------|--------|--------|--------|--------|--------|-------|------------|
| 0 | 872.6 | 1278.3 | 0.56 | 5.5020 | 0.0233 | 1.0000 | 0.8023 | 0.1458 | 1.1777 | 1.5011 | 68.11 | – |
| 25 | 877.9 | 1281.4 | 1.77 | 5.4721 | 0.0236 | 1.0053 | 0.8064 | 0.1474 | 1.3959 | 1.5047 | 68.18 | 0.0180 |
| 50 | 883.5 | 1284.3 | 4.35 | 5.4297 | 0.0239 | 1.0117 | 0.8130 | 0.1497 | 1.6030 | 1.5085 | 68.44 | 0.0343 |
| 75 | 888.8 | 1287.8 | 8.80 | 5.4114 | 0.0242 | 1.0161 | 0.8171 | 0.1510 | 1.7875 | 1.5121 | 68.47 | 0.0500 |
| 100 | 893.1 | 1291.2 | 14.99 | 5.3842 | 0.0245 | 1.0201 | 0.8209 | 0.1525 | 1.9479 | 1.5151 | 68.52 | 0.0656 |
| 125 | 898.5 | 1294.3 | 41.87 | 5.3551 | 0.0247 | 1.0251 | 0.8250 | 0.1541 | – | 1.5188 | 68.62 | 0.0790 |
| 150 | 899.9 | 1297.8 | 70.36 | 5.3365 | 0.0250 | 1.0261 | 0.8279 | 0.1551 | – | 1.5097 | 68.71 | 0.0956 |

Table 3. Carbondisulphide + polystyrene.

| Conc. (g/l) | r^* | u^* | h^* | L_f | s | RA | I | X | n_1 | n_2 | q_D | ΔH |
|-------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|-------|------------|
| 0 | 1253.2 | 1127.0 | 0.34 | 5.2075 | 0.0231 | 1.0000 | 0.7147 | 0.1372 | 1.0730 | 1.6276 | 67.71 | – |
| 25 | 1251.7 | 1131.0 | 0.94 | 5.1943 | 0.0233 | 0.9976 | 0.7148 | 0.1376 | 1.2322 | 1.6266 | 67.76 | 0.0025 |
| 50 | 1247.0 | 1135.1 | 2.77 | 5.1831 | 0.0235 | 0.9927 | 0.7136 | 0.1377 | 1.4294 | 1.6237 | 67.77 | 0.0051 |
| 75 | 1245.5 | 1138.9 | 7.75 | 5.1689 | 0.0237 | 0.9904 | 0.7134 | 0.1381 | 1.6420 | 1.6228 | 67.83 | 0.0073 |
| 100 | 1241.0 | 1142.9 | 28.70 | 5.1602 | 0.0238 | 0.9857 | 0.7122 | 0.1380 | 1.9732 | 1.6199 | 67.84 | 0.0096 |
| 125 | 1236.1 | 1147.7 | 76.75 | 5.1511 | 0.0240 | 0.9805 | 0.7107 | 0.1379 | – | 1.6169 | 67.88 | 0.0119 |
| 150 | 1232.8 | 1151.2 | 120.00 | 5.1405 | 0.0242 | 0.9768 | 0.7097 | 0.1372 | – | 1.6149 | 67.93 | 0.0138 |

3. Results and discussion

The ultrasonic velocity and viscosity data for various concentrations of the systems are those obtained by Varadarajulu *et al* (1992). Surface tension (s), intermolecular frelength (L_f), mean frepath (I) and refractive index (n) obtained by us are given in tables 1–3 for carbontetrachloride + polystyrene, benzene + polystyrene and carbon-disulphide + polystyrene, respectively. It is observed that the relative association shows a continuous decreasing or increasing trend in the solutions. The observation is in accordance with the change in mean frepath.

The values of q_D in all the cases assume values in the range 46 K–68 K reflecting the low boiling point of the solute. Further, heat of mixing another thermal data has very small value and is zero in the case of polystyrene with carbontetrachloride. This indicates a readjustment of internal and vibrational energies.

The refractive index values calculated from density rule and the empirical relation are of the same order. However, in some cases the values are slightly high and

they are not reproduced in the tables. It may be due to the fact that the solutions become less transparent.

4. Conclusion

Thus the systematic analysis of polymer solutions presented here reveals interesting features. However, a decisive conclusion could be drawn only after several such investigations.

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