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Evaluation of density and acoustical parameters of poly(2-methoxy) cyanurate of 1,1′-*bis*(3-methyl-4-hydroxy phenyl)cyclohexane [PCMBC]

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Abstract. The density of poly(2-methoxy)cyanurate of 1,1′-*bis*(3-methyl-4-hydroxy phenyl)cyclohexane [PCMBC] is determined by partial specific volume and floatation methods at 33° ± 0·1°C and compared with calculated values. Acoustical parameters such as viscosity (η), sound velocity (U), isentropic compressibilities (K_s), Rao's molar sound function (R), specific acoustical impedance (Z), solvation numbers (S_n), van der Waals constant (b) and relaxation strength (r) of PCMBC in two different solvents like chloroform (CF) and 1,2-dichloroethane (DCE) at 31°C are evaluated at different concentrations. The linear relationships of these parameters with the concentrations have been observed except the η vs concentration plots where upward curvature is observed after 1·5 g/dl indicating structural changes. The linear relationships indicate solvent–solute interactions.

Keywords. Density; acoustical parameters; poly(2-methoxy)cyanurate of 1,1′-*bis*(3-methyl-4-hydroxy phenyl)cyclohexane; chloroform; 1,2-dichloroethane.

1. Introduction

The density and specific volume data are most useful for the average distance between macro molecular chains and the extent of crystallinity in polymers. Acoustical parameters such as sound velocity, isentropic compressibility, Rao's molar sound function (Bagchi *et al* 1968) and solvation number (Passynsky 1943) are powerful means of characterizing the various aspects of physico-chemical behaviour of liquid mixtures and provide information about interactions occurring in the solution (Das *et al* 1980; Bandopadhyay *et al* 1982; Saraf and Samal 1984). To understand the structure of polymers and polymer-solvent interactions, acoustical parameters are of great importance. The present communication encompasses the evaluation of the density and acoustical parameters of poly(2-methoxy)cyanurate of 1,1′-*bis*(3-methyl-4-hydroxy-phenyl)cyclohexane [PCMBC] at 31°C.

2. Experimental

The solvents (Weissberger 1967) and polymer ($[\eta]^{30°}_{CHCl_3} = 0{\cdot}72$ dl/g) were purified prior to use by appropriate methods. The densities of the pure solvents and the polymer solutions were measured by employing a specific gravity bottle and a suspended level

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Ubbelohde viscometer with precisions of 0·01% and 0·02%, respectively. Ultrasonic velocity was measured with a Single Crystal Multifrequency Interferometer (Mittal Enterprise) operating at a frequency of 1 MHz with an accuracy of ± 0·2%. The density of PCMBC was determined by partial specific volume and floatation methods. All measurements were made at 31 ± 0·1°C.

3. Physical parameters

The various physical parameters were calculated from the measured values of density (ρ), viscosity (η) and ultrasonic velocity (U) according to standard equations.

$$\text{Isentropic compressibility: } K_s = 1/U^2 \cdot \rho; \tag{1}$$

$$\text{Rao's molar sound function: } R = (M/\rho)U^{1/3}; \tag{2}$$

$$\text{Specific acoustic impedance: } Z = \rho \cdot U; \tag{3}$$

$$\text{Solvation number: } S_n = M_2 \Big/ \left\{ M_1 (1 - K_s/K_{s1}) \frac{(100 - x)}{x} \right\}; \tag{4}$$

$$\text{Van der Waals constant: } b = \frac{M}{\rho}\left\{1 - \left(\frac{RT}{MU^2}\right)\left[\left(1 + \frac{MU^2}{3RT}\right)^{1/2} - 1\right]\right\}; \tag{5}$$

$$\text{Relaxation strength: } r = 1 - (U/U_\infty)^2,\ U_\infty = 1600\,\text{ms}^{-1}; \tag{6}$$

where M is the apparent molecular mass of the solution and is given by

$$M = M_1 W_1 + M_2 W_2. \tag{7}$$

Subscripts 1, 2 and 12 (see below) represent solvent, polymer and solution, respectively. x is the weight (g) of polymer in 100 g of the solution; and W is the weight fraction.

4. Results and discussion

The densities of polymer solutions of different concentrations in chloroform were determined by the usual method and fitted to the following equation

$$\frac{1}{W_1 \cdot \rho_{12}} = \frac{1}{\rho_1} + \frac{W_2}{\rho_2 \cdot W_1}; \tag{8}$$

the least squares equation is

$$\frac{1}{W_1 \cdot \rho_{12}} = 0{\cdot}6754 + 0{\cdot}859 \frac{W_2}{W_1}. \tag{9}$$

Thus, the least square densities of chloroform and PCMBC are found to be 1·4806 gcm^{-3} and 1·1642 gcm^{-3}, respectively. The correlation coefficient γ between $1/W_1 \cdot \rho_{12}$ and W_2/W_1 is 0·9809.

The density of PCMBC (thick film) was also determined by floatation method using CCl_4–*n*-hexane system of 33° ± 0·1°C. The compositions of the two solvents were adjusted in such a way that the film just remained suspended throughout. The density of the mixture was determined after 24 h by the usual method. The average of the three measurements was 1·2299 ± 0·001 gcm^{-3} for the film sample. The density

of PCMBC determined by this method is somewhat higher than that by the partial specific volume method and that might be due to the solvent molecules entrapped in the thick film.

4.1 *Theoretical calculation of density*

Theoretical density of PCMBC was calculated from the structural aspects (Slonimskii *et al* 1970; Askadskii *et al* 1987). Accordingly,

$$\rho = \frac{KM}{N_A \cdot \Sigma \Delta V_i}, \tag{10}$$

where K is the packing coefficient, M is the molecular mass of the polymer repeat unit, $\Sigma \Delta V_i$ is the instrinsic volume of the polymer repeat unit and N_A is Avogadro's number. For bulk and film samples the values of K are 0·681 and 0·695, respectively. In the present case, the values of $\Sigma \Delta V_i$ are calculated to be 381·6 Å. The calculated values of the density for bulk and film samples were 1·1941 gcm^{-3} and 1·2188 gcm^{-3}, respectively. Thus, the calculated and experimental density values are in excellent agreement with relative errors of $-2{\cdot}5\%$ and $+0{\cdot}91\%$ which suggest the right choice of the packing coefficients for the bulk and film samples.

4.2 *Acoustical parameters*

The density (ρ), viscosity (η) and ultrasonic sound velocity (U) for PCMBC in chloroform (CF) and 1,2-dichloroethane (DCE) at 31°C are reported in table 1. Using these data, the isentropic compressibility (K_s), Rao's molar sound function (R) (Bagchi *et al* 1968), the specific acoustic impedance (Z), solvation number (Passynsky 1943), Van der Waals constant (b) (Vigoureux 1952) and relaxation strength (r) (Johri and Misra 1985), were calculated according to the standard equations, (1)–(7), and

Table 1. The density (ρ), viscosity (η) and sound velocity (U) data of pure solvents and polymer solutions at 31°C.

Conc. (g/dl)	$\rho \times 10^{-3}$ (kg/m^3)	η (mPaS)	U (m/S)
$C_2H_2Cl_2$ + PCMBC			
0·0	1·2406	0·7470	1327·2
0·5	1·2401	0·9478	1349·6
1·0	1·2395	1·2430	1357·8
1·5	1·2390	1·5495	1363·8
2·0	1·2384	1·8643	1368·6
2·5	1·2380	2·2450	1376·4
$CHCl_3$ + PCMBC			
0·0	1·4695	0·5000	960·4
0·5	1·4680	0·7735	964·8
1·0	1·4667	1·0377	968·2
1·5	1·4652	1·3234	971·8
2·0	1·4637	1·6272	975·2
2·5	1·4622	2·0065	978·2

Table 2. The standard deviations (S_y), the correlation coefficients (γ) and correlation equations between various acoustical parameters (y) and the concentration (c). The standard deviation (S_c) of concentration is 0·7905 gdl^{-1}.

Parameter, y	S_y	γ	Correlation equation
1,2-Dichloroethane (DCE)			
U, ms^{-1}	10·221	0·9108	$U - 11{\cdot}78C = 1345{\cdot}57$
$Z{\cdot}10^{-3}$, $kgm^{-2}s^{-1}$	11·499	0·9940	$Z - 14{\cdot}459C = 1667{\cdot}27$
K_s, TPa	6·210	−0·9999	$K_s + 7{\cdot}855C = 446{\cdot}12$
$R.10^3$, $m^{10/3}.s^{-1/3}.mol^{-1}$	20·272	0·9998	$R - 25{\cdot}639C = 880{\cdot}36$
b	1·594	0·9998	$b - 2{\cdot}016C = 75{\cdot}32$
r	0·0109	−0·9964	$r + 0{\cdot}0137C = 0{\cdot}294$
S_n	0·293	0·9863	$S_n - 0{\cdot}366C = 0{\cdot}373$
Chloroform (CF)			
U, ms^{-1}	5·347	0·9997	$U - 6{\cdot}762C = 961{\cdot}50$
$Z.10^3$, $kgm^{-2}s^{-1}$	5·605	0·9973	$Z - 7{\cdot}071C = 1412{\cdot}97$
K_s, TPa	6·820	−0·9889	$K_s + 8{\cdot}515C = 735{\cdot}75$
$R.10^3$, $m^{10/3}.S^{-1/3}.mol^{-1}$	13·234	0·9861	$R - 16{\cdot}509C = 802{\cdot}70$
b	1·154	0·9999	$b - 1{\cdot}460C = 75{\cdot}81$
r	0·004	−0·9944	$r + 0{\cdot}005C = 0{\cdot}639$
S_n	0·171	0·9724	$S_n - 0{\cdot}210C = 1{\cdot}365$

correlated with concentrations. The standard deviations, the correlation coefficients and correlation equations of these parameters are reported in table 2. Excellent linear correlations between the parameters and the concentration are observed except for the η vs concentration plots where upward curvature is observed after 1·5 gdl^{-1} which is attributed to the structural changes (Das *et al* 1980; Bandopadhyay *et al* 1982; Saraf and Samal 1984).

The decrease of K_s and increase of Z with increase in concentration of PCMBC might be due to strong solvent–solute interactions. This is further supported by the increase of R and b and decrease of r with increasing concentration of PCMBC (Johri and Misra 1985; Rao *et al* 1989, 1993). It is also evident from table 2 that S_n and r are almost doubled in the chloroform system. The positive values of S_n suggest appreciable solvation of the solute, which again proves the structure- promoting tendency of PCMBC in both the systems (Woldan 1988). The increased value of S_n with concentration implies decreased solute–solute interactions. Thus, in conclusion solute–solvent interactions exist in PCMBC-CF and PCMBC-DCE solutions and structural changes also take place at 1·5 gdl^{-1} concentration.

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References

Askadskii A A 1987 in *Polymer yearbook* (4th edn) (ed.) R A Pethrick (London: Harwood Academic Publisher)

Bagchi S, Nema S K and Singh R P 1968 *Eur. Polym. J.* **22** 851

Bandopadhyay P C, Maiti A K, Chaki T K and Singh R P 1982 *Acoustica* **50** 75
Das S, Singh R P and Maiti S 1980 *Polym Bull.* **2** 400
Johri G K and Misra R C 1985 *Acoustica* **57** 292
Passynsky A 1943 *Acta Phys. Chem. USSR* **22** 317
Rao A V, Raman G K and Rajulu A V 1993 *Asian J. Chem.* **5** 582
Rao K Ch., Rajulu A V and Naidu S V 1989 *Acta Polym.* **40** 743
Saraf B and Samal K 1984 *Acoustica* **55** 60
Slonimskii G L, Askadskii A A and Kitagorodskii A I 1970 *Polym. Sci., USSR* **A12** 556
Vigoureux P 1952 *Ultrasonics* (London: Chapman and Hall)
Weissberger A 1967 *Techniques of organic chemistry* (New York: Interscience) vol. 3
Woldan M 1988 *Z. Phys. Chem.* **269** 628