Bull. Mater. Sci., Vol. 18, No. 3, June 1995, pp. 247–253. © Printed in India.

Acoustical parameters of polyethylene glycol/water mixtures

A VARADA RAJULU and P MABU SAB
Department of Polymer Science and Technology, Sri Krishnadevaraya University, Anantapur 515 003, India

MS received 12 September 1994; revised 17 February 1995

Abstract. Ultrasonic velocity (v) and density (d) have been measured for polyethylene glycol/water mixtures at 30°C. The adiabatic compressibility (β_{ad}), molar compressibility (β), specific acoustic impedance (Z), Rao number (R) and van der Waals constant (b) have been computed. The variations of v, d, β_{ad}, β, Z, R and b with mole ratio of water/ether group oxygen have been studied. The association between the components and the formation of tetrahydrate have been reported.

Keywords. Polyethylene glycol; acoustical parameters; van der Waals constant; molecular association; liquid mixtures.

1. Introduction

The variation of ultrasonic velocity and adiabatic compressibility of dilute aqueous solutions of solid polyethylene glycol (PEG) with concentration was studied by Gerecze (1977) who concluded that there was no solute–solvent interaction. Recently Graham and Chen (1993) studied the interaction of liquid and solid PEG (PEG-300, 400, 1000 and 3330) with water and revealed the formation of tetrahydrate in low molecular weight PEG (MW < 600) and tri- and hexahydrate formation for higher molecular weight PEGs using density data. In the present work we have measured the ultrasonic velocity and density of PEG-200 (MW ~ 200) at 30°C. The acoustical parameters molar compressibility β, specific acoustic impedance Z and Rao number R have been computed. The van der Waals constant b has also been determined by ultrasonic method. The variation of these parameters with the ratio of moles of water per ether oxygen in the PEG has been studied. We selected PEG as it has applications as hydrogel and PEG-200 was not covered in the interaction studies of Graham and Chen (1993).

2. Experimental

PEG-200 (S D Chemicals) was dried under vacuum at 65°C for 24 h before use. To known weight of the dry PEG in 50 ml standard flasks the appropriate amounts of double distilled water was added to give the desired ratio of moles of water per ether oxygen in the PEG and test samples with H_2O/–CH_2–CH_2–O of 1·5, 2·0, 2·5, ···, 7·0 were prepared. These mixtures were maintained in the oven for 6 h at 65°C to obtain thorough mixing, cooled to room temperature, and allowed to attain equilibrium for several days in sealed containers. The ultrasonic velocities of these mixtures were measured with a 2 MHz variable path interferometer at 30°C as described by Varada Rajulu *et al* (1990). The densities were measured with a precalibrated density bottle using a water bath thermostated at 30°C.

Table 1. Ultrasonic velocity (v), density (d), adiabatic compressibility (β_{ad}), molar compressibility (β), van der Waals constant (b), Rao number (R) and acoustic impedance (Z) of polyethylene glycol/water mixtures at 30°C.

Mole ratio (H_2O/ether group)	v (m/sec)	d (g/cm^3)	β_{ad} (cm. sec^2/g)	R (cm$^{10/3}$/mol/sec$^{1/3}$)	β (cm$^{20/7}$. sec$^{-2/7}$/mol g$^{-1/7}$)	Z (g/cm^2/sec)	b (cm^3/mol)
1·5	1722·2	1·0881	30·986	4643	2646·5	187392	83·45
2·0	1716·1	1·0855	30·281	4023	2293·0	186282	72·40
2·5	1709·9	1·0831	31·578	3586	2043·9	185199	64·62
3·0	1705·3	1·0806	31·822	3258	1856·6	184274	58·75
3·5	1699·2	1·0777	32·138	3001	1709·7	183122	54·18
4·0	1692·7	1·0769	32·409	2794	1591·8	182286	50·14
4·5	1685·3	1·0733	32·804	2629	1497·1	180883	47·59
5·0	1677·1	1·0693	33·249	2492	1419·1	179332	45·20
5·5	1670·8	1·0641	33·664	2380	1354·6	177789	43·22
6·0	1663·2	1·0610	34·072	2280	1297·2	176465	41·46
6·5	1652·9	1·0545	34·710	2199	1250·6	174298	40·08
7·0	1646·1	1·0518	35·088	2123	1207·1	173136	38·74

3. Results and discussion

The measured values of ultrasonic velocity (v) and density (d) are presented in table 1. The adiabatic compressibility (β_{ad}) was calculated using the relation (Varada Rajulu *et al* 1990)

$$\beta_{ad} = (dv^2)^{-1}. \quad (1)$$

The Rao number (R) was calculated using the relation (Rao *et al* 1989)

$$R = (M/d)v^{1/3}, \quad (2)$$

where M is the molecular weight of the liquid mixture given by

$$M = (n_1 M_1 + n_2 M_2)/(n_1 + n_2), \quad (3)$$

where M_1 and M_2 are the molecular weights and n_1 and n_2 are the moles of the components comprising the mixture. The molar compressibility (β) was calculated using Wada's (1949) relation

$$\beta = (M/d)(\beta_{ad})^{-1/7}. \quad (4)$$

The specific acoustic impedance (Z) was calculated using the relation

$$Z = (dv). \quad (5)$$

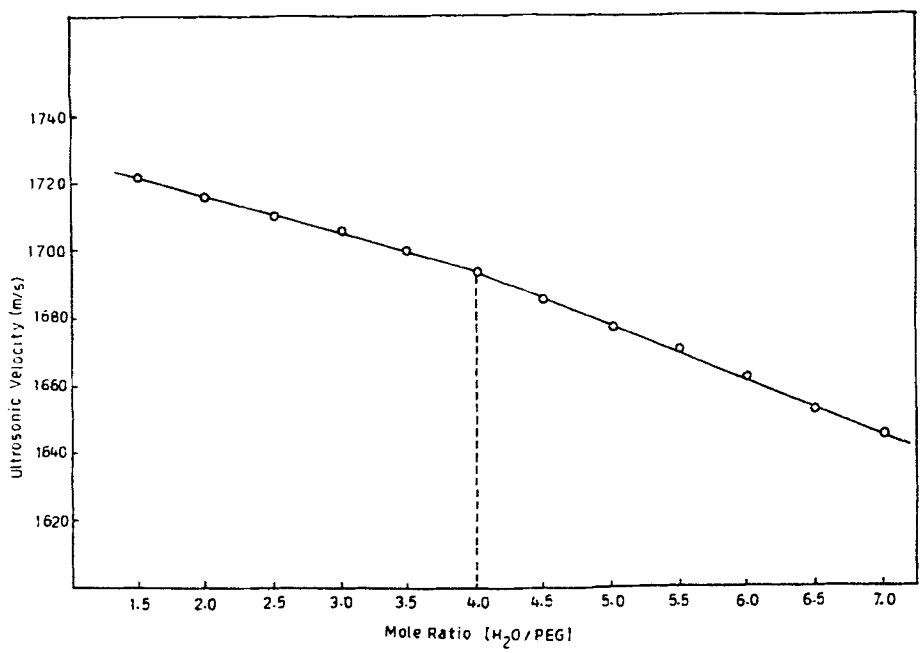

Figure 1. Variation of ultrasonic velocity (v) with moles of water per ether group in PEG-200/water mixtures at 30°C.

The van der Waals constant (b) was calculated using the measured values of v and d from the relation (Vigoureux 1952)

$$b=(M/d)[1-(RT/Mv^2)\sqrt{1+(Mv^2/3RT)}-1]. \quad (6)$$

Though (2) and (4) are empirical and additive in nature, (1) which has a semiempirical origin soon found theoretical support (Blitz 1967). Similarly (5) is written considering its anology to the mechanical and electrical impedance without reactive component (Blitz 1967). Equation (6) is semiempirical in nature (Flugge 1961).

The measured values of v and d and the computed values of β_{ad}, R, Z, β and b are given in table 1. The variation of v, d, β_{ad}, β, R, Z and b with mole ratio of H_2O/ether group is shown in figures 1, 2, 3, 4, 5, 6 and 7 respectively. From figures 1–3 and 6 it is evident that the variation of v, d, β_{ad} and Z show two linear portions with different slopes with a break at a mole ratio of 4. A similar observation was made by Graham and Chen (1993) in the case of PEG (MW < 600) by density measurements and this was attributed to the formation of tetrahydrate.

Nomoto (1953) established the validity of (2), (4) and (6) in a large number of liquid mixtures and stated that for unassociated components in the liquid mixtures the variation of R, β and b with mole ratio will be linear. In the present study a smooth nonlinear relation is observed indicating that association exists between PEG and water. The nonlinear behaviour is probably due to the fact that there will be a change of molecular weight due to the association and the weight of the associated groups is

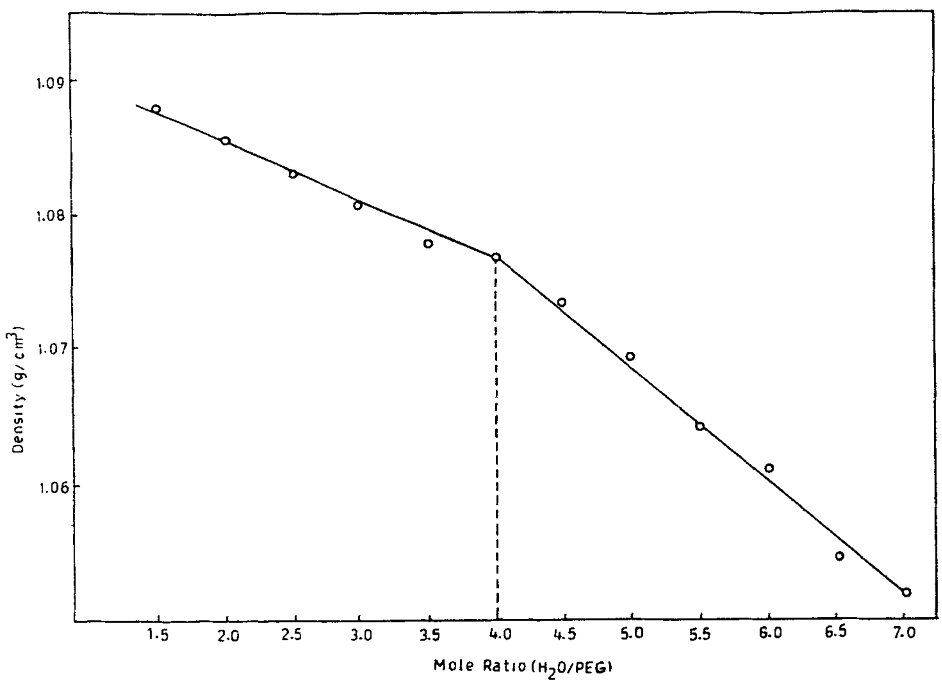

Figure 2. Variation of density (d) with moles of water per ether group in PEG-200/water mixtures at 30°C.

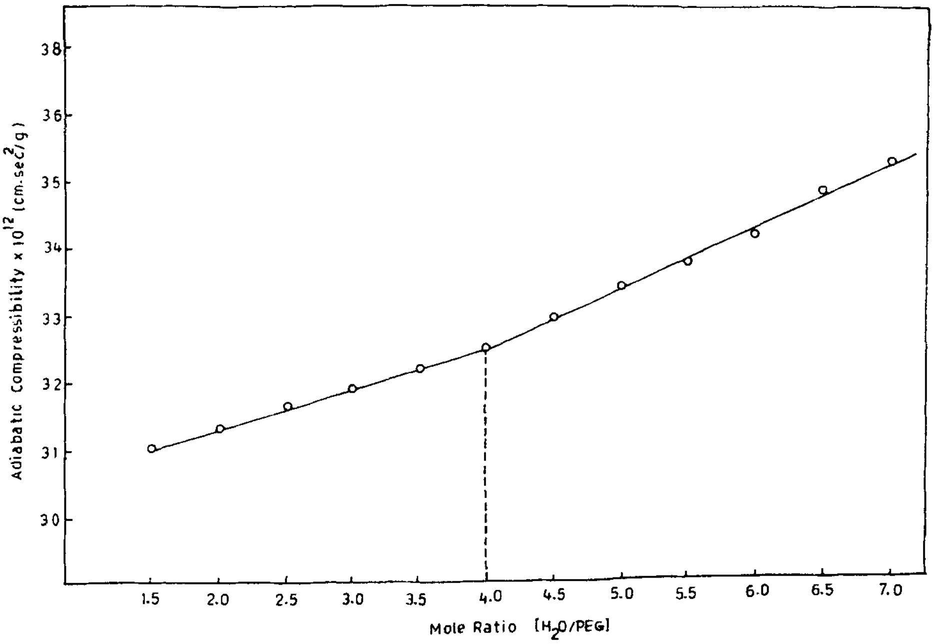

Figure 3. Variation of adiabatic compressibility (β_{ad}) with moles of water per ether group in PEG-200/water mixtures at 30°C.

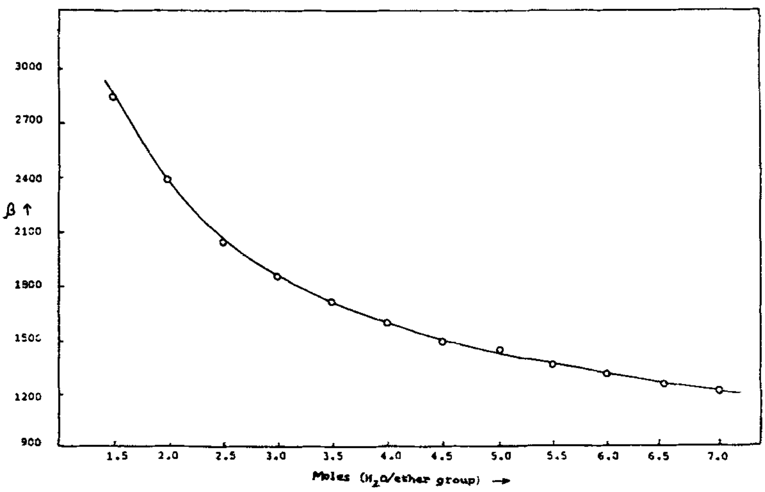

Figure 4. Variation of molar compressibility (β) with moles of water per ether group in PEG-200/water mixtures at 30°C.

different from that of the components (Nomoto 1953). Further the smooth nonlinear behaviour is observed only in the case of the variation of parameters β, R and b which involve the molecular weight term. Similar observations were also made by Chowdoji Rao *et al* (1990) and Varada Rajulu *et al* (1990) in the case of polyvinyl pyrrolidone

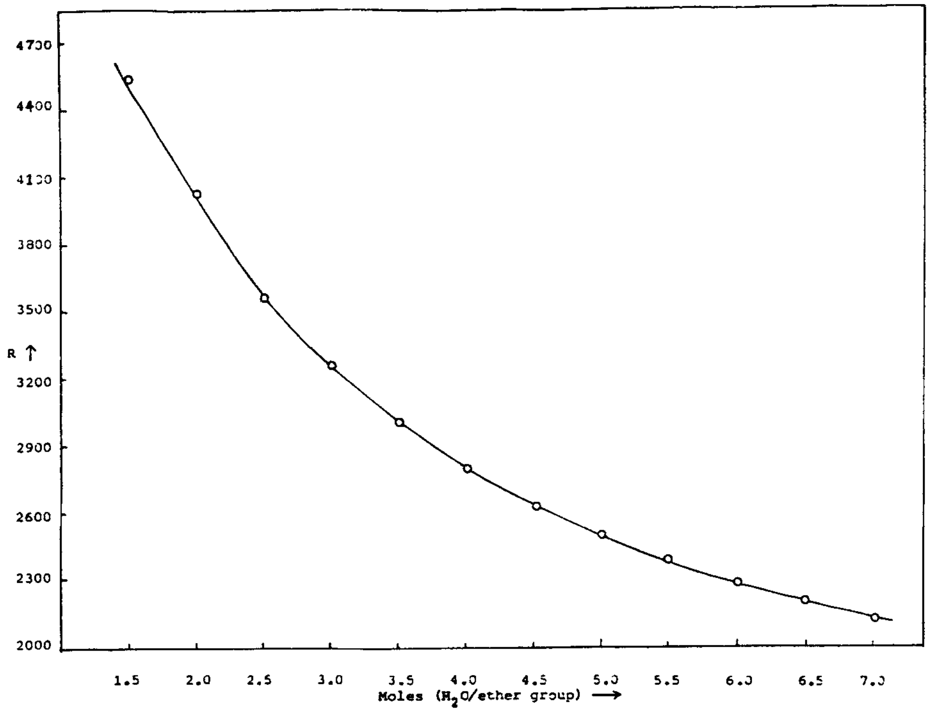

Figure 5. Variation of Rao constant (*R*) with moles of water per ether group in PEG-200/water mixtures at 30°C.

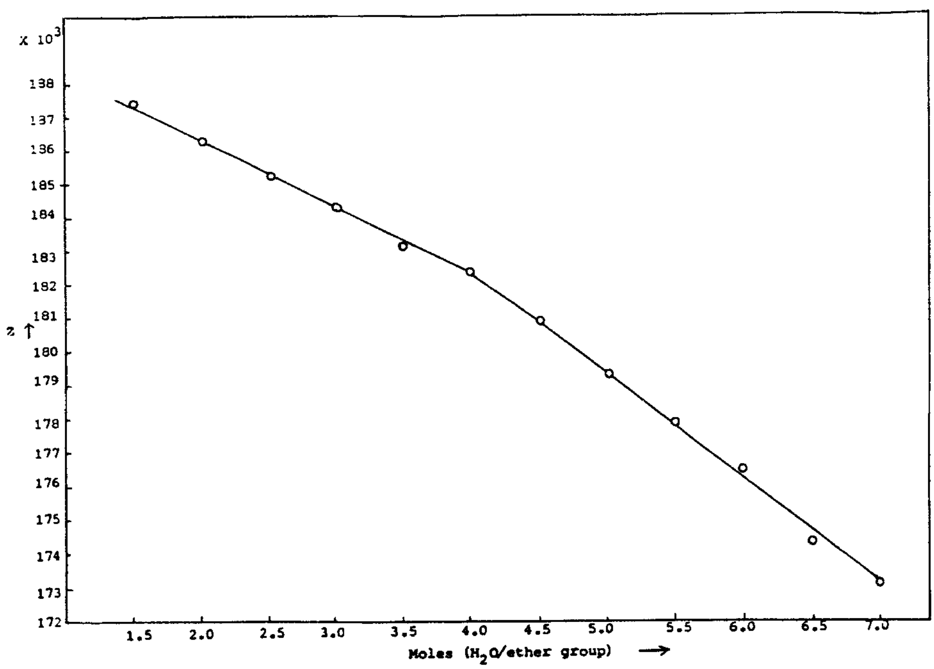

Figure 6. Variation of acoustic impedance (*Z*) with moles of water per ether group in PEG-200/water mixtures at 30°C.

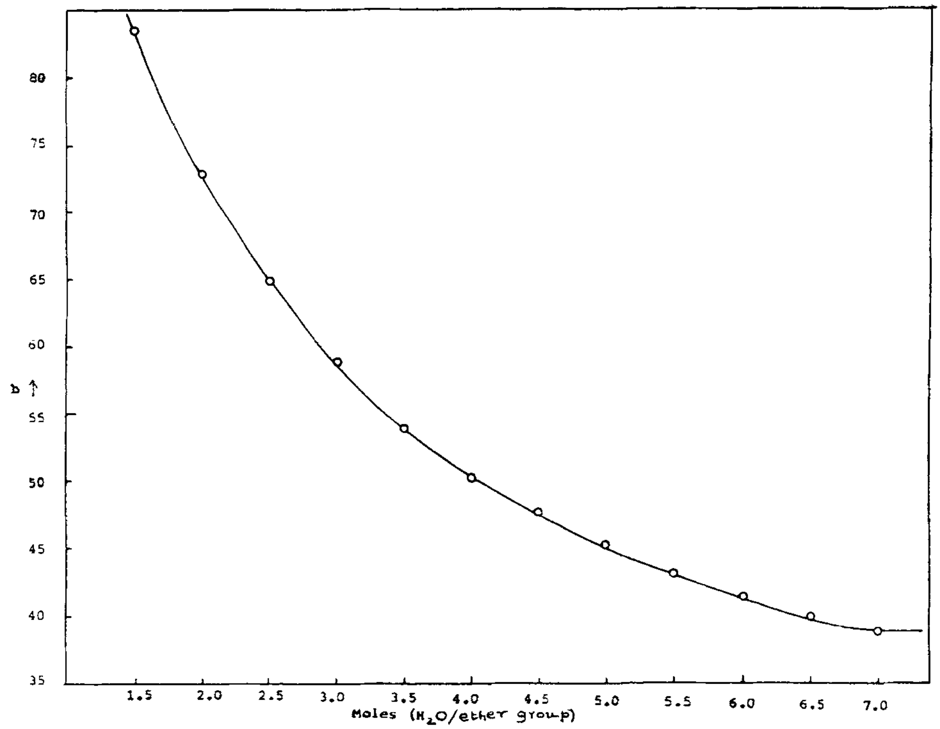

Figure 7. Variation of van der Waals constant (*b*) with moles of water per ether group in PEG-200/water mixtures at 30°C.

solutions. These observations help us to confirm the association. Thus the association between PEG-200 and water and the tetrahydrate formation can be confirmed using ultrasonic velocity data in the present case. The interaction of PEG (MW > 1000) with water was not observed by Gerecze (1977) as the solution concentration was maintained very low.

References

Blitz J 1967 in *Fundamentals of ultrasonics* (London: Butterworth Publishing Co. Ltd.)
Chowdoji Rao K, Venkata Naidu S and Varada Rajulu A 1990 *Eur. Polym. J.* **26** 657
Flugge S 1961 in *Encyclopedia of physics* (Berlin: Springer Verlag) Vol. XI/1
Gerecze N G 1977 *Acustica* **38** 51
Graham N B and Chen C F 1993 *Eur. Polym. J.* **29** 149
Nomoto O 1953 *J. Chem. Phys.* **21** 950
Rao K Ch, Rajulu A V and Naidu S V 1989 *Acta Polymerica* **40** 743
Varada Rajulu A, Chowdoji Rao K and Venkata Naidu S 1990 *J. Pure Appl. Ultrason.* **12** 115
Vigoureux P 1952 in *Ultrasonics* (London: Chapman and Hall)
Wada Y 1949 *J. Phys. Soc. Jpn.* **4** 280