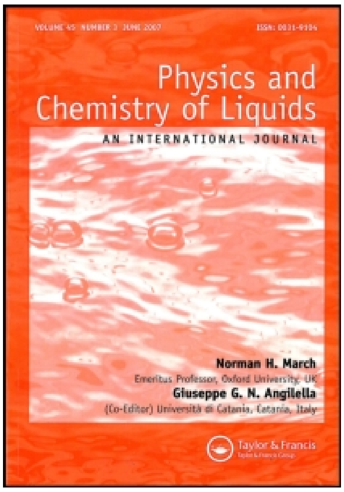

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Maimoona Yasmin[a]; Manisha Gupta[a]; Jagdish Prasad Shukla[a]
[a] Department of Physics, University of Lucknow, Lucknow 226007, India

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Acoustical study of molecular interactions in polymer solutions through various thermodynamical parameters and Flory's theory at 298.15 K

Maimoona Yasmin, Manisha Gupta* and Jagdish Prasad Shukla

Department of Physics, University of Lucknow, Lucknow 226007, India

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This study intends to portray the nature of polymer solutions by ultrasonic velocity and density data. Acoustical parameters, such as relaxation strength, relative association, molecular constant, fractional free volume, available volume, Beyer's non-linearity parameter, internal pressure, van der Waals' constants and molecular radius have been computed for the binary mixtures of PEG400 + methanol, PEG400 + ethanol, PPG400 + ethanol and PPG400 + 2-propanol systems at 298.15 K. Flory's theory has been used for computing ultrasonic velocity, surface tension, thermal expansion coefficient, thermal conductivity, excess heat capacity and excess isothermal compressibility. Isothermal compressibilities of mixtures have been theoretically evaluated using different theories. A new relation has been proposed by us for evaluating excess molar volume using ultrasonic velocity of the mixture which gives fairly good result when compared with the experimental values. Excess molar volume has been calculated using Flory's theory and Prigogine–Flory–Patterson theory. The partial molar volume and its excess value at infinite dilution have also been evaluated.

Keywords: polyethylene glycol 400; polypropylene glycol 400; Flory's theory; excess molar volume

1. Introduction

Several industrial applications make use of substances, such as polyethylene glycol (PEG), polypropylene glycol (PPG) and their copolymers. Because of their low toxicity, PEG, a hydrophilic non-ionic polymer is frequently used in the pharmaceutical and cosmetic industries as solvents, carriers, humectants, lubricants, binders, bases and coupling agents and also for extraction, separation and purification of biological materials. Since PEG is a flexible, water-soluble polymer, it can be used to create very high osmotic pressures (tens of atmospheres). It is also unlikely to have specific interactions with biological chemicals. These properties make PEG one of the most useful molecules for applying osmotic pressure in biochemistry experiments, particularly when using the osmotic stress technique. PEG is also commonly used as a polar stationary phase for gas chromatography, as a heat transfer fluid in electronic testers and in protein crystallography.

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*Corresponding author. Email: guptagm@rediffmail.com

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In recent years, numerous studies have been carried out on mixtures containing PPGs. PPG is used in many formulations for polyurethanes. It is used as a rheology modifier, in solid tires, in automobile seats, in foams and in membranes.

An understanding of the thermodynamics of the polymer solutions is important in practical applications, such as polymerisations, devolatilisation and the incorporation of plasticisers and other additives. Properties of mixtures are useful for designing many types of transport and process equipment in the chemical industry [1] and in studying the structure of such solutions. Thermodynamic properties are important means in studying the interaction in the mixtures [2].

Such importance of polymer solutions and its vast domain of industrial and biochemical applications have enforced us to study the means of predicting the properties of polymer solutions with minimum input data.

The fundamental forces between particles account for the existence of an atom, for the bonding of atoms to form molecules, for the shapes adopted by these molecules, and for the interaction between one molecule and another. It appears, therefore, of particular interest to study the presence of such forces in the mixture.

Various thermodynamic and acoustical parameters, such as relaxation strength, relative association, molecular constant, fractional free volume, available volume and Beyer's non-linearity parameter (B/A) for liquid and liquid mixtures at varying composition have been studied and correlated with molecular interaction using minimum input data for the systems PEG400 + methanol, PEG400 + ethanol, PPG400 + ethanol and PPG400 + 2-propanol. The experimental data required for this study have been taken from different sources [3–5]. Few molecular parameters, such as internal pressure (π_i), van der Waals' constants (a) and (b) and molecular radius (r) have been evaluated using thermodynamic relations. Flory's theory has been used to estimate the ultrasonic velocity (u), surface tension (σ), coefficient of thermal expansion (α) and thermal conductivity (λ) of the liquid mixture. Excess heat capacity at constant pressure (C_P^E) and excess isothermal compressibility (k_T^E) have also been calculated and discussed in terms of the intermolecular interactions between mixing components. Isothermal compressibility (k_T) of these binary mixtures have been evaluated in terms of pure components data using Flory's theory, Mc-Gowans' relation and hard sphere models and the results have been compared in terms of average percentage deviation. A comparative study on the evaluation of excess molar volume has been done and a new relation has been proposed considering the effect of molecular structure on ultrasonic velocity. The excess molar volume results have been used to estimate the partial molar volume ($\bar{V}^0$) and partial molar excess volume ($\bar{V}^{E,\infty}$) at infinite dilution of the components.

2. Theory

2.1. *Parameters using thermodynamic relations*

The parameters for the deduction of interaction have been evaluated using standard equations as reported earlier [6] and mentioned below:

Relaxation strength is given as

$$R_S = 1 - \left(\frac{u}{u_\infty}\right)^2, \tag{1}$$

where $u_\infty = 1.6 \times 10^5\ \mathrm{cm\,s^{-1}}$.

Relative association is given as

$$R_A = \frac{\rho}{\rho_0}\left(\frac{u_0}{u}\right)^{1/3}, \tag{2}$$

where u_0 and ρ_0 are ultrasonic velocity and density of solvent (alcohol).

The two van der Waals' constants, a and b, are characteristic properties of a particular liquid. The first of these constants which corrects for the force of attraction between particles is

$$a = \frac{\pi_i}{V^2}, \tag{3}$$

where V is the molar volume and π_i is the internal pressure of the mixture given by the thermodynamic relation [7]

$$\pi_i = \frac{(\alpha T)}{k_T}. \tag{4}$$

It is a measure of the resultant attractive and repulsive forces between the interacting components in the mixture.

The other van der Waals' constant, b, is computed as

$$b = \left(\frac{M}{\rho}\right)\left(1 - \frac{RT}{Mu^2\left(\sqrt{1 + Mu^2/3RT} - 1\right)}\right), \tag{5}$$

where R is the gas constant, M is the effective molar mass of the mixture, u is the ultrasouic velocity and T is the absolute temperature.

Determination of molecular radius of pure liquids and liquid mixtures is helpful in predicting the structural arrangement and mutual interaction. Molecular radius in the mixture depends on the properties of the mixture which is due to the interaction of two components. The study of variation of molecular radius with composition offers an indirect but convenient way to ascertain the nature and possibilities of microscopic interactions between the like as well as unlike species.

Molecular radius from the van der Waals' constant, b is

$$r = \left(\frac{3b}{16\pi N}\right)^{1/3}, \tag{6}$$

where N is Avogadro's number.

The thermoacoustical parameters, i.e. isochoric temperature coefficient of internal pressure (X) and isothermal acoustical parameter (K') as in Carnevale and Litovitz [8] have been used for the evaluation of molecular constant, fractional free volume, available volume and Beyer's non-linearity parameter as follows:

$$\text{The available free volume, } V_a = \frac{V}{K' + 1}, \tag{7}$$

$$\text{Molecular constant, } n_M = \frac{1}{1 + X/2}. \tag{8}$$

$$\text{Fractional free volume } f = \frac{1}{K' + 1}. \tag{9}$$

Most of the parameters involved in ultrasonic studies have been deduced by considering the propagation of acoustic waves of infinitesimal amplitude. But when sound waves of high amplitude propagate, non-linear effects, such as harmonic distortion and acoustic scattering occur. The measure of ultrasonic propagation constants becomes unreliable when sound waves of high intensity are made to propagate in fluids because non-linear effects occur due to greater attenuation of the high frequency components to low frequency ones. Wave propagation of ultrasound through condensed media is fundamentally non-linear in nature. The extent of non-linearity is related to the ratio of coefficients of the quadratic and linear terms of a Taylor series used to express an equation of state of the medium in terms of pressure and density [9,10]. This ratio B/A called Beyer's non-linearity parameter reflects the non-linearity effects efficiently. The importance of this parameter lies in obtaining certain information about the physical attributes of the liquid, such as internal pressure, clustering, intermolecular spacing and acoustic scattering [11], which play a significant role in non-linear acoustics ranging from underwater acoustics to medicine.

Here, the parameter B/A has been evaluated using isobaric acoustical parameter as in Ali et al. [12], isothermal acoustical parameter as in Carnevale and Litovitz and isochoric acoustical parameter as in Sharma [13]. The thorough description of the non-linearity parameter evaluation is given elsewhere [14].

$$\text{Beyer's non-linearity parameter } \frac{B}{A} = 2\gamma K'' + 2K, \tag{10}$$

where γ is the specific heat ratio.

2.2. *Parameters using Flory's theory*

The relation used to predict excess isothermal compressibility [15] using Flory's theory is given as

$$k_{\mathrm{T}}^{\mathrm{E}} = \frac{3\tilde{V}^2}{P*\left[\left(\tilde{V}^{1/3} - 1\right)^{-1} - 3\right]} - \frac{\sum_{i=1}^{2}\left(x_i \tilde{V}_i k_{\mathrm{T},i}\right)}{\tilde{V}}. \tag{11}$$

Patterson and Rastogi [16] have used Flory statistical theory (FST) theory to calculate surface tension which in turn is used to evaluate ultrasonic velocity in liquid mixtures.

Thus, the surface tension of a liquid mixture is given by the relation,

$$\sigma_{\mathrm{m}} = \sigma * \tilde{\sigma}(\tilde{V}), \tag{12}$$

where σ^* is the characteristic surface tension and $\tilde{\sigma}(\tilde{V})$ is the reduced surface tension given by Prigogine and Saraga [17].

The values of surface tension obtained by Flory's theory [17] have been used to evaluate ultrasonic velocity of liquid mixture, making use of the well known Auerbach relation [18],

$$u_\mathrm{m} = \left(\frac{\sigma_\mathrm{m}}{6.3 \times 10^{-4}\rho_\mathrm{m}}\right)^{2/3}. \tag{13}$$

The thermal conductivity and excess heat capacity of liquid mixture were evaluated using the following relations

$$\lambda = 2.8k\left(\sum_i n_i\phi_i\right)^{2/3}\left[\frac{P^*V^*\left[1 - 3\left(\tilde{V}^{1/3} - 1\right)\right]}{3\tilde{V}\left(\sum_i x_i m_i\left(\tilde{V}^{1/3} - 1\right)\right)}\right]^{1/2}, \tag{14}$$

$$C_\mathrm{P}^\mathrm{E} = \frac{P^*V^*}{T^*}\left[\frac{1}{\tilde{P}\tilde{V}^2 - 2/3\tilde{P}\tilde{V}^{5/3} + 4/3\tilde{V}^{1/3} - 1} - \sum_i\left\{\frac{x_i}{\tilde{P}_i\tilde{V}_i^2 - 2/3\tilde{P}_i\tilde{V}_i^{5/3} + 4/3\tilde{V}_i^{1/3} - 1}\right\}\right]. \tag{15}$$

2.3. *Isothermal compressibility*

FST gives the following relation for the isothermal compressibility [12]

$$k_\mathrm{T} = T\tilde{V}^2\frac{\alpha}{P^*}. \tag{16}$$

Mc-Gowan [19] suggested the following relationship between isothermal compressibility k_T and surface tension σ,

$$k_\mathrm{T}\sigma^{3/2} = 1.33 \times 10^{-8}\ \text{(CGS units)}. \tag{17}$$

The values of isothermal compressibility k_T for the binary mixtures were predicted by the rigid sphere equations [20] based on various hard sphere models: Thiele–Lebowitz model [21,22], Guggenheim model [23] and Carnahan–Starling model [24]. The experimental k_T values were calculated using the relation

$$k_\mathrm{T} = k_\mathrm{S} + \frac{T\alpha^2 V}{C_\mathrm{p}}, \tag{18}$$

where C_p is the heat capacity at constant pressure.

2.4. *Excess molar volume*

Flory's model [26] and other works that have resulted in the Prigogine–Flory–Patterson (PFP) model are the most popular theoretical approaches to describe and predict some thermodynamic properties of many liquid multicomponent systems. Excess molar volume (V^{E}) has been calculated from Flory's equation of state [26] as

$$V^{\mathrm{E}} = \left(\sum_{i=1}^{2} x_i V_i^*\right)\left(\frac{\tilde{V}^o 7/3}{\left[4/3 - \tilde{V}^o 1/3\right]}\right)(\tilde{T} - \tilde{T}^o). \tag{19}$$

The PFP approach represents the class of phenomenological thermodynamic models of phase equilibrium calculations that are based on the reduced equation of state. Thus, one of the main features of PFP equations is the ability to determine the free volume effect. The detailed description of the computation methodology is given by Gepert et al. [25].

The variation of excess molar volume with polymer concentration provides us useful information regarding the polymer–solvent interactions and deviation of polymer solution from ideal solution.

Ultrasonics offer the possibility to detect and characterise microstructural properties as well as deformation process in materials controlling material behaviour based on the physical mechanism to predict future performance of materials. The ultrasonic waves interact indirectly by vibrating perturbations of the weak bonds between molecules. The following relation has been proposed by us and is used to estimate the V^{E} values.

$$V^{\mathrm{E}} = \left[\frac{(x_1 m_1 + x_2 m_2)}{\left(x_1 m_1 u_1^{1/3} + x_2 m_2 u_2^{1/3}\right)/((x_1 m_1/\rho_1) + (x_2 m_2/\rho_2))u^{1/3}}\right] - \left(x_1 \frac{m_1}{\rho_1} + x_2 \frac{m_2}{\rho_2}\right). \tag{20}$$

2.5. *Partial molar volume at infinite dilution*

Partial molar volumes ($\bar{V}_1^0$, $\bar{V}_2^0$) and partial molar excess volumes ($\bar{V}_1^{\mathrm{E},\infty}$, $\bar{V}_1^{\mathrm{E},\infty}$) at infinite dilution for each component in both the mixtures were calculated from the excess molar volume $V_{\mathrm{m}}^{\mathrm{E}}$ values using the Redlich–Kister coefficients. The partial molar volumes $\bar{V}_1$ and $\bar{V}_2$ in these mixtures were evaluated [27,28] over the entire composition range by the following equations.

$$\bar{V}_1 = V^{\mathrm{E}} + V_1^* + (1 - x_1)\left(\frac{\partial V^{\mathrm{E}}}{\partial x_1}\right)_{P,T}, \tag{21}$$

$$\bar{V}_2 = V^{\mathrm{E}} + V_2^* + (1 - x_2)\left(\frac{\partial V^{\mathrm{E}}}{\partial x_1}\right)_{P,T}. \tag{22}$$

The derivatives of these equations were obtained by differentiation of $V_{\mathrm{m}}^{\mathrm{E}}$ from Redlich–Kister polynomial and these equations reduce to

$$\bar{V}_1 = V_1^* + (1 - x_1)^2 \sum_{i=0}^{n} a_i(2x - 1)^i + x_1(1 - x_1)^2 \sum_{i=0}^{n} 2(i)a_i(2x_1 - 1)^{i-1}, \tag{23}$$

$$\bar{V}_2 = V_2^* + (1 - x_2)^2 \sum_{i=0}^{n} a_i(1 - 2x_2)^i + x_2(1 - x_2)^2 \sum_{i=0}^{n} (-2)(i)a_i(1 - 2x_2)^{i-1}. \tag{24}$$

We are interested to evaluate the partial molar volume of polymers at infinite dilution ($x_1 = 0$) in alcohols and the partial molar volume of alcohols at infinite dilution ($x_2 = 0$) in polymers. Therefore, $\bar{V}_i^0$ is obtained by setting $x_1 = 0$ and $x_2 = 0$ in above equations which leads to

$$\bar{V}_1^0 = V_1^* + \sum_{i=0}^{n} a_i(-1)^i, \tag{25}$$

and

$$\bar{V}_2^0 = V_2^* + \sum_{i=0}^{n} a_i. \tag{26}$$

In Equations (25) and (26), $\bar{V}_1^0$ and $\bar{V}_2^0$ represent the partial molar volume of polymers at infinite dilution in alcohols and the partial molar volume of alcohols at infinite dilution in polymers, respectively.

Partial molar excess volumes at infinite dilution $\bar{V}^{\mathrm{E},\infty}$ for each component in binary liquid mixtures were evaluated with the following relations:

$$\bar{V}_1^{E,\infty} = \bar{V}_1^0 - V_1^*, \tag{27}$$

$$\bar{V}_2^{E,\infty} = \bar{V}_2^0 - V_2^*. \tag{28}$$

3. Results and discussion

The computed values for relaxation strength (R_S), relative association (R_A), molecular constant (n_M), fractional free volume (f), available volume (V_a) and Beyer's non-linearity parameter (B/A) at 298.15 K have been reported in Table 1.

The fractional free volume, which is expressed in terms of the repulsive exponent of intermolecular potential, is found to have values near about 0.2. The values of f are low in almost all the alcohols and polymers [29]. The low values of f may be assumed to reflect greater disorderness of molecules and hence irregular packing of molecules. The values are found to decrease with mole fraction of polymers due to close association between solute and solvent. The free volume reduces when the internal pressure decreases. Thus, fractional free volume is smaller in PEG than in PPG. Available volume is found to increase with increasing mole fraction of polymers. Such variation in fractional free volume and available volume may be due to the accommodation of small ethanol molecules in the voids provided by the PEG molecules. Decrease in relaxation strength, R_S, suggests predominance of solute–solute interaction over solvent–solvent molecules. PEG mixtures exhibit lower relaxation strength than PPG ones. The relative association increases non-linearly with increasing concentration of polymers. It gives largest values for the system PEG400 + ethanol system. It can be seen that PPG has properties in common with polyethylene glycol.

As the factor $B/A + 1$ is a fully defined quantity provided the ratio of the coefficients is known, it predicts the properties very well. The thermal expansivity data is the controlling factor for the evaluation of $B/A + 1$. Due to its dependence on temperature it accounts for the thermal effects also.

Table 1. Relaxation strength (R_S), relative association (R_A), molecular constant (n_M), fractional free volume (f), available volume (V_a) and Beyer's non-linearity parameter (B/A) for the systems PEG400 + methanol, PEG400 + ethanol, PPG400 + ethanol and PPG400 + 2-propanol with mole fraction of polymer at 298.15 K using thermodynamical relations.

x_1	R_S	R_A	n_M	f	V_a (cm^3 mol^{-1})	B/A
PEG400 + methanol						
0.0000	0.5200	–	1.3330	0.2175	8.8581	7.4897
0.1077	0.2821	1.1565	1.3400	0.2171	15.9890	8.0347
0.1998	0.1850	1.1980	1.3462	0.2167	22.2141	8.0696
0.2970	0.1267	1.2207	1.3529	0.2161	28.7822	7.9444
0.4143	0.0847	1.2364	1.3613	0.2154	36.6792	7.7192
0.4748	0.0691	1.2420	1.3657	0.2150	40.7233	7.5993
0.5591	0.0530	1.2481	1.3721	0.2143	46.3298	7.4443
0.7293	0.0301	1.2565	1.3854	0.2127	57.4756	7.2269
0.8173	0.0211	1.2597	1.3925	0.2117	63.1185	7.1895
0.9370	0.0120	1.2631	1.4026	0.2102	70.6487	7.2532
1.0000	0.0062	1.2643	1.4080	0.2092	74.5200	7.3501
PEG400 + ethanol						
0.0000	0.4897	–	1.3472	0.2166	12.7096	7.4468
0.1026	0.3229	1.1316	1.3528	0.2161	19.1203	7.6843
0.2129	0.2173	1.1895	1.3590	0.2156	26.1059	7.6927
0.3162	0.1555	1.2191	1.3649	0.2150	32.6380	7.5973
0.3778	0.1283	1.2309	1.3685	0.2147	36.5322	7.5216
0.5047	0.0869	1.2487	1.3760	0.2138	44.4867	7.3619
0.5669	0.0722	1.2552	1.3798	0.2134	48.3605	7.2933
0.7382	0.0401	1.2682	1.3906	0.2120	58.8940	7.1786
0.7971	0.0320	1.2719	1.3944	0.2114	62.4594	7.1744
0.9182	0.0166	1.2774	1.4025	0.2102	69.7120	7.2395
1.0000	0.0087	1.2807	1.4080	0.2092	74.5187	7.3523
PPG400 + ethanol						
0.0000	0.4897	–	1.3472	0.2166	12.7096	7.4468
0.0998	0.3979	1.0968	1.3517	0.2162	19.9077	7.5840
0.2005	0.3511	1.1371	1.3564	0.2158	27.2327	7.5871
0.3000	0.3245	1.1588	1.3610	0.2154	34.4735	7.5411
0.4391	0.3020	1.1766	1.3677	0.2148	44.5574	7.4540
0.4991	0.2963	1.1821	1.3706	0.2144	48.8923	7.4166
0.6015	0.2875	1.1890	1.3757	0.2139	56.2561	7.3611
0.6982	0.2821	1.1942	1.3806	0.2133	63.1638	7.3223
0.7996	0.2772	1.1983	1.3859	0.2126	70.3540	7.3007
0.8637	0.2749	1.2006	1.3893	0.2122	74.8636	7.2990
1.0000	0.2704	1.2048	1.3966	0.2111	84.3197	7.3314
PPG400 + 2-propanol						
0.0000	0.4933	–	1.3457	0.2167	16.6790	7.4527
0.1000	0.4164	1.0824	1.3503	0.2163	23.5482	7.5658
0.2001	0.3744	1.1252	1.3551	0.2159	30.4477	7.5714
0.3006	0.3421	1.1498	1.3599	0.2155	37.3655	7.5368
0.4003	0.3223	1.1668	1.3648	0.2150	44.2019	7.4808
0.4983	0.3079	1.1788	1.3697	0.2145	50.8890	7.4223
0.6008	0.2967	1.1882	1.3750	0.2140	57.8465	7.3673
0.7008	0.2884	1.1954	1.3802	0.2133	64.5816	7.3264
0.7991	0.2813	1.2010	1.3855	0.2127	71.1385	7.3039
0.8598	0.2759	1.2034	1.3888	0.2122	75.1649	7.2999
1.0000	0.2779	1.2120	1.3966	0.2111	84.3197	7.3370

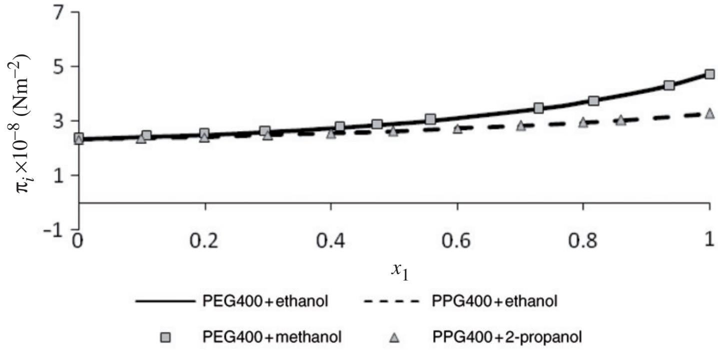

Figure 1. Internal pressure *vs.* mole fraction of polymer, for the four polymer solutions.

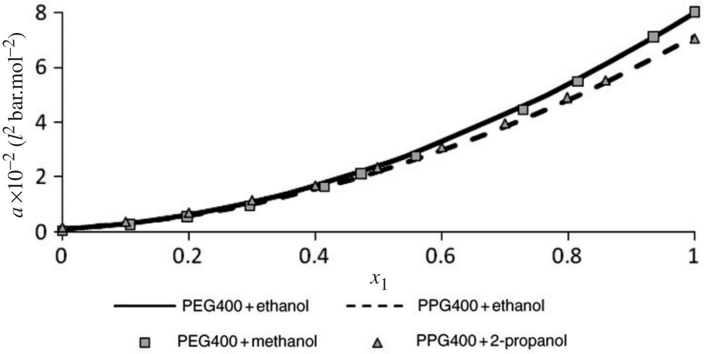

Figure 2. van der Waals' constant *a* *vs.* mole fraction of polymer, for the four polymer solutions.

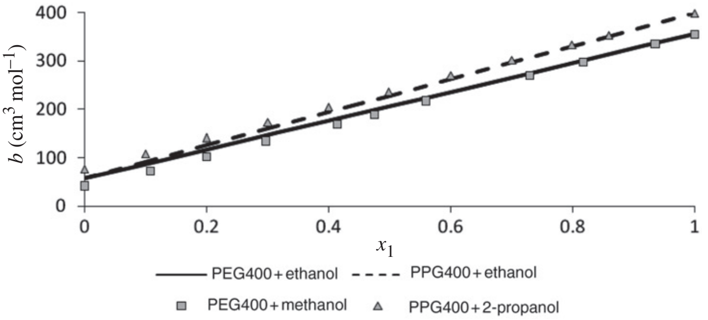

Figure 3. van der Waals' constant *b* *vs.* mole fraction of polymer, for the four polymer solutions.

Figures 1–4 represent graphically the computed values of internal pressure (π_i), van der Waals' constants *a* and *b* and molecular radius *r* with respect to the mole fraction of polymers.

Internal pressure is a fundamental liquid property, which is a resultant force of attraction and repulsion between the constituents of liquids. As degree of cohesion

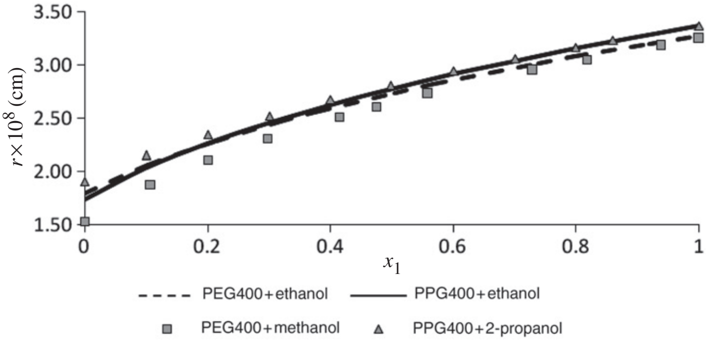

Figure 4. Molecular radius of molecules *vs*. mole fraction of polymer, for the four polymer solutions.

differs from liquid to liquid, internal pressure provides useful information about the molecular interactions in the liquid systems. The internal pressure values are comparatively smaller in alcohol-rich regions, which imply that these are much weakly held than the polymer molecules (Figure 1). The reduction in the internal pressure at lower concentrations may be attributed to breaking of intermolecular forces. The molecules are more closely packed in PEG400 molecules than in PPG400. The term internal pressure includes the physical forces that arise due to pure van der Waals interactions, the attractive forces that arise due to weak intermolecular bonds like hydrogen bonding, as well as the pressure due to thermal motion of the individual molecules [10]. It can be seen that internal pressure in PEG400 solution is greater than that in PPG400 solution.

This is further supported by the van der Waals' constant a. The larger values of van der Waals' constant (a) in polymer rich region put forward the strong force of attraction between polymer molecules (Figure 2). These values are smaller for PPG than PEG, which might be due to the reason that secondary hydroxyl groups in PPG are less reactive than primary hydroxyl groups in PEG.

It can be seen from Figure 3 that van der Waals' constant b increases linearly for all the four systems. The b values reflect the packing effect quite satisfactorily.

Figure 4 reveals that there is a considerable change in molecular radius with composition. It is large in polymer-rich region and gradually increases with increasing mole fraction of polymers. The interaction between the hydrogen atom of hydroxyl group of ethanol and the oxygen atoms of PEG, as well as packing effect may be responsible for this increase. This gives larger radius as the molecules now occupy a larger volume. The smaller entities occupying smaller volume cause a compact arrangement giving smaller values of radii at lower concentrations. Also, it can be inferred that in the case of polymers homomolecular bonding is more prominent than the heteromolecular bonding. There is not much difference in the molecular radius of PPG and PEG molecules due to their approximately equal molecular weights.

The values of characteristic parameters V^*, T^* and P^*, thermal expansion coefficient α, isothermal compressibility k_T and reduced volume $\tilde{V}$ for pure component used in evaluating excess molar volume in FST and PFP theories, along with the values of critical temperatures specific heat are listed in Table 2.

Table 2. Values of molar volume (V), reduced volume ($\tilde{V}$), thermal expansion coefficient (α), isothermal compressibility (k_T) and characteristic parameter (P^*, V^*), T_C and heat capacity for pure liquids at 298.15 K.

Liquid component	$V \times 10^6$ ($m^3 mol^{-1}$)	$\tilde{V}$	$\alpha \times 10^3$ (K^{-1})	$k_T \times 10^9$ ($N^{-1} m^2$)	$P^* \times 10^6$ ($J cm^{-3}$)	$V^* \times 10^6$ ($m^3 mol^{-1}$)	T_C (K)	C_p ($J mol^{-1} K^{-1}$)
PPG400	399.43	1.20	0.794	0.724	473.93	331.79	934.83[a]	–
PEG400	356.15	1.19	0.728	0.459	668.81	299.48	925.10[a]	772.8[c]
Methanol	40.72	1.29	1.220	1.523	398.31	31.54	512.64[b]	77.61[b]
Ethanol	58.68	1.27	1.114	1.436	373.56	46.18	513.92[b]	112.3[b]
2-Propanol	76.97	1.27	1.126	1.457	373.23	60.47	508.30[b]	–

Notes: [a]Calculated by a method given in reference [33]; [b]reference [34] and [c]reference [35].

The FST which is generally valid for non-polar liquids and their mixtures and its modified form, known as PFP theory, which is applicable to both polar and non-polar liquids and their mixtures, have been successfully employed to estimate and analyse thermodynamic functions of binary liquid mixtures by a number of workers in recent years. Some previous workers have found this theory giving good results showing minimum percentage error for theoretical estimation of isothermal compressibility [7], surface tension [30], ultrasonic velocity [31], excess molar volume [32], etc. Here, values of the parameters calculated with the help of Flory's theory are shown in Table 3. The values of excess heat capacity at constant pressure C_P^E and excess isothermal compressibility k_T^E are plotted against the mole fraction of polymers and are shown in Figures 5 and 6. The negative behaviour reflected in Figure 6 for the excess isothermal compressibility for the whole range of composition implies a great difficulty to compress the polymer solutions than the ideal behaviour at different polymer mole fractions and the working temperature. PEG solutions are less compressible than the PPGs. The observed values of C_P^E and k_T^E indicate that the molecular interactions in PEGs are stronger than in PPGs.

The experimental and predicted values of k_T using FST, Mc-Gowans equation and four hard sphere models at 298.15 K are graphically presented in Figures 7(a) and (b). Flory's theory and four hard sphere models were compared with the experimental k_T values. It is clear from the graph that out of all theories, Flory's theory and Mc-Gowans equation predict k_T values the best, followed by Guggenheim model, Carnahan–Starling model and Thiele–Lebowitz model, while Thiele model could not predict k_T values well.

Figure 8 is the graphical depiction of the excess molar volume evaluated by various theories which show the relative deviations from the experimental values. The values of V^E calculated from the recognised Flory's theory, PFP theory and the proposed new method using the ultrasonic data were found to be in good agreement with the experimental values for the mixture. As it is evident from Table 4, the partial molar volumes of alcohol at infinite dilution $\bar{V}_1^0$ in PEG or PPG and PEG or PPG at infinite dilution $\bar{V}_2^0$ in alcohol are smaller than the corresponding molar volume V_1^* and V_2^* of alcohols and PEG or PPG, respectively. This observation is consistent with an idea that the molar volume of pure

Table 3. Surface tension (σ), ultrasonic velocity (u), coefficient of thermal expansion (α) and thermal conductivity (λ) for the systems PEG400 + methanol, PEG400 + ethanol, PPG400 + ethanol and PPG400 + 2-propanol with mole fraction of polymer at 298.15 K using FST.

x_1	$\sigma\,(\mathrm{mN\,m^{-1}})$	$u\,(\mathrm{m\,s^{-1}})$	$\alpha\,(\times 10^3\,\mathrm{K})$	$\lambda\,(\mathrm{W\,mK^{-1}})$
PEG400 + methanol				
0.0000	19.288	1148.3	1.220	0.2128
0.1077	31.383	1378.7	0.865	0.0945
0.1998	35.328	1436.9	0.800	0.0865
0.2970	37.553	1466.7	0.769	0.0829
0.4143	39.069	1485.3	0.752	0.0805
0.4748	39.616	1491.9	0.746	0.0797
0.5591	40.174	1498.1	0.741	0.0788
0.7293	40.954	1506.6	0.735	0.0775
0.8173	41.260	1510.0	0.732	0.0771
0.9370	41.562	1513.1	0.730	0.0766
1.0000	41.706	1514.6	0.728	0.0764
PEG400 + ethanol				
0.0000	19.961	1176.6	1.114	0.1719
0.1026	28.831	1341.6	0.895	0.0982
0.2129	33.559	1413.1	0.819	0.0875
0.3162	36.149	1448.4	0.785	0.0835
0.3778	37.188	1461.5	0.774	0.0819
0.5047	38.800	1481.4	0.756	0.0798
0.5669	39.373	1488.2	0.750	0.0791
0.7382	40.568	1502.0	0.739	0.0777
0.7971	40.895	1505.8	0.735	0.0774
0.9182	41.407	1511.3	0.731	0.0767
1.0000	41.706	1514.6	0.728	0.0764
PPG400 + ethanol				
0.0000	19.961	1176.6	1.114	0.1719
0.0998	25.032	1263.1	0.928	0.0828
0.2005	27.303	1295.8	0.866	0.0718
0.3000	28.525	1311.6	0.838	0.0673
0.4391	29.522	1323.5	0.818	0.0641
0.4991	29.800	1326.5	0.813	0.0632
0.6015	30.165	1330.3	0.807	0.0620
0.6982	30.420	1332.8	0.803	0.0612
0.7996	30.620	1334.6	0.800	0.0605
0.8637	30.727	1335.5	0.798	0.0601
1.0000	30.958	1338.1	0.794	0.0596
PPG400 + 2-propanol				
0.0000	19.783	1173.8	1.125	0.1428
0.1000	23.894	1243.1	0.975	0.0833
0.2001	26.155	1276.7	0.908	0.0723
0.3006	27.567	1296.2	0.871	0.0676
0.4003	28.523	1308.7	0.848	0.0650
0.4983	29.201	1317.2	0.832	0.0633
0.6008	29.721	1323.5	0.821	0.0621
0.7008	30.119	1328.1	0.812	0.0612
0.7991	30.445	1332.0	0.805	0.0605
0.8598	30.600	1333.7	0.802	0.0602
1.0000	30.958	1338.1	0.794	0.0596

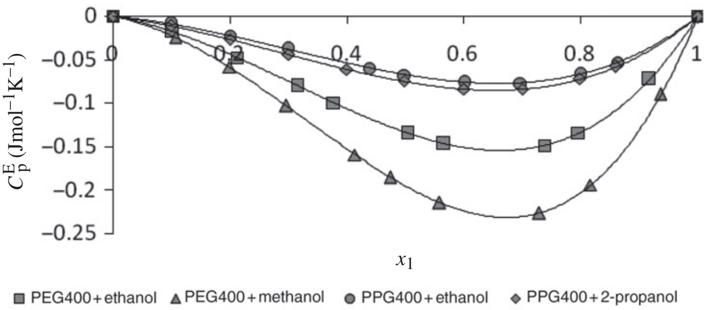

Figure 5. Excess heat capacity at constant pressure for the mixtures of polymer with alcohols with respect to the mole fraction of polymer at 298.15 K.

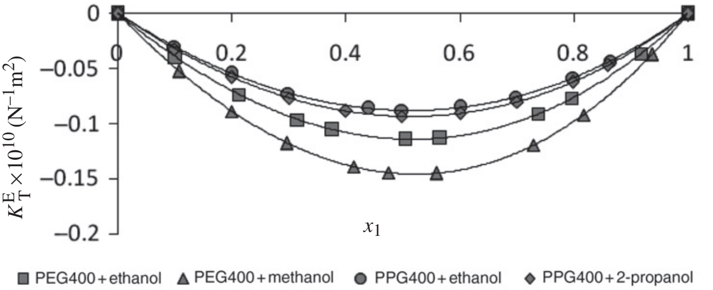

Figure 6. Excess isothermal compressibility for the mixtures of polymer with alcohols with respect to the mole fraction of polymer at 298.15 K.

components is a result of the sum of the actual molar volume plus the free or empty volume that arises from the intramolecular self association of pure molecules. The negative values of $\bar{V}^{E,\infty}$ are higher in the mixture of alcohols with PEG400. This further supports the presence of strong intermolecular interactions between unlike molecules and more pronounced interaction in the mixture of alcohols with PEG400, as also reflected from other parameters.

All the results support each other and interpret the molecular properties well.

4. Conclusion

The straightforward and precise method for determination of thermoacoustical parameters has proven to be advantageous in exact determination of intermolecular interaction and other thermodynamic properties. Flory's theory predicts the thermodynamic properties, such as excess molar volume and isothermal compressibility, quite well for polymer solutions also as compared with other theories. The negative behaviour for the excess molar volume, excess isothermal compressibility and excess heat capacity at constant pressure for these large molecule solutions implies that it has larger volume than the ideal solution at this temperature.

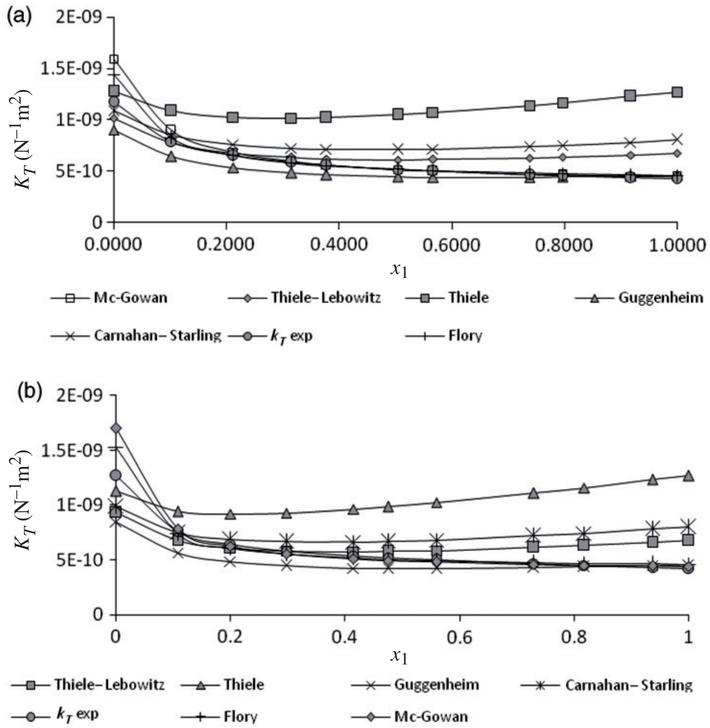

Figure 7. (a) Comparative representation of isothermal compressibility using different theories and experimental values for PEG400 + ethanol with respect to the mole fraction of polymer at 298.15 K. (b) Comparative representation of isothermal compressibility using different theories and experimental values for PEG400 + methanol with respect to the mole fraction of polymer at 298.15 K.

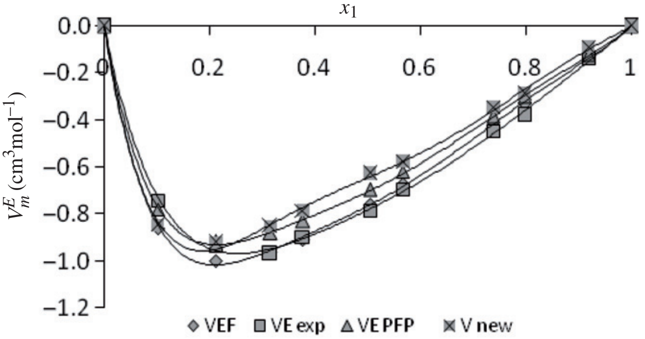

Figure 8. Comparison of the experimental and theoretically calculated values of excess molar volume for the system PEG400 + ethanol at 298.15 K.

Table 4. Molar volumes of pure liquids (V^*), partial molar volume ($\bar{V}^0$) and partial molar excess volume ($\bar{V}^{E,\infty}$) at infinite dilution of each component in PEG400 + methanol, PEG400 + ethanol, PPG400 + ethanol and PPG400 + 2-propanol mixtures at 298.15 K.

System	V_1^*	V_2^*	$\bar{V}_1^0$	$\bar{V}_2^0$	$\bar{V}_1^\infty$	$\bar{V}_2^\infty$
PEG400 + methanol	356.16	40.72	353.35	22.90	−2.81	−17.82
PEG400 + ethanol	356.16	58.68	345.17	57.19	−10.99	−1.50
PPG400 + ethanol	399.43	58.68	389.67	56.35	−9.76	−2.33
PPG400 + 2-propanol	399.43	76.97	393.47	74.84	−5.96	−2.12

The new method proposed by us for computation of excess molar volume gives an excellent agreement when compared with experimental values.

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