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Thermoacoustical analysis of solutions of poly(ethylene glycol) 200 through H-bond complex formation

Maimoona Yasmin, Manisha Gupta*

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

A R T I C L E I N F O

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Densities (ρ) and ultrasonic velocities (u) of binary mixtures of poly(ethylene glycol) 200, PEG, with ethanolamine, m-cresol and aniline have been measured at various concentrations at 293.15, 303.15 and 313.15 K and have been fitted by third order polynomial equations at each temperature. The calculated values of isentropic compressibility (k_s), free volume (V_f), internal pressure (π_i), relaxation time (τ) and surface tension (σ) at different mole fractions of PEG have been used to explain the hydrogen bonding and intermolecular interactions present in the mixture. Using these data, excess molar volume (V^E), excess intermolecular free length (L_f^E), excess acoustic impedance (Z^E) and excess pseudo-Grüneisen parameter (Γ^E) have been calculated and the results have been fitted to Redlich–Kister polynomial equation. All the results support each other and help in understanding the interactions in the mixture. Various models and mixing rules have been applied to evaluate the ultrasonic velocity data and have been compared with the experimental results.

1. Introduction

Poly(ethylene glycol), PEG, belongs to a class of synthetic polymers that finds several industrial applications because of their availability in a wide range of molecular masses, besides having an unusual combination of properties such as water solubility, lubricity and low toxicity. PEGs are also used as processing aid in making other products. Molten PEGs are used in heat transfer baths [1]. PEGs are frequently used in pharmaceutical and cosmetic fluids as solvents, carriers, humectants, lubricants, binders, bases and coupling agents [2] and also for extraction, separation and purification of biological materials [3,4]. Aqueous solutions of PEGs have been extensively studied but their solutions in organic solvent still needs thorough investigation.

Ethanolamine is an industrially important compound used in the manufacture of cosmetics, pharmaceuticals, surface active agents, insecticides and waxes and in scrubbing on CO_2 and H_2S from refinery streams. m-Cresol, a good solvent for dissolving polymers, has many applications such as plasticizers, gasoline, additives, explosives, pigments, disinfectants, fumigants and pharmaceutical intermediates. Aniline is used in the manufacturing of synthetic dyes, drugs and as an accelerator in vulcanization of rubber.

In the present work solutions of PEG 200 in ethanolamine, m-cresol and aniline have been thermodynamically studied. The aim of this work is to obtain information about the mixtures under study, to investigate correlations among them and to provide qualitative interpretation in terms of molecular interactions. To our knowledge no density and velocity data have previously been reported for these mixtures.

Measurements of densities and velocities have been reported as a function of temperature and mole fraction for the systems PEG + ethanolamine, PEG + m-cresol and PEG + aniline. Measurements were carried out at varying temperature and at atmospheric pressure. From the measured data thermodynamic parameters such as isentropic compressibility, free volume, internal pressure, relaxation time and surface tension values at different mole fractions of poly(ethylene glycol) 200 have been calculated for the three systems and discussed in terms of hydrogen bonding and intermolecular interaction present in the mixtures.

Most experimentalists tabulate the results of their measurements on thermodynamic properties of non-ideal mixtures in the form of excess functions. Such data are used subsequently by a variety of physical scientists, including those in the field of chemical kinetics and spectroscopy, interested in reactions occurring in solution and by chemical engineers engaged in operation or design of chemical reactors, distillation columns or other types of separation

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* Corresponding author. Tel.: +91 9415020362.
E-mail addresses: myasmin908@gmail.com (M. Yasmin), guptagm@rediffmail.com (M. Gupta).

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Table 1
Densities ρ and ultrasonic velocities u of the pure components and their comparison with literature at 293.15, 303.15 and 313.15 K.

Compound	T (K)	ρ (g cm^{-3})		u (ms^{-1})	
		Experimental	Literature	Experimental	Literature
PEG 200	293.15	1.127	1.1248[a]	1629.6	–
	303.15	1.117	1.11698[a]	1592.0	1592[b]
	313.15	1.108	1.10898[a]	1552.0	–
Ethanolamine	293.15	1.017	1.018[c]	1723.6	–
	303.15	1.009	1.0098[d]	1697.6	–
	313.15	1.001	1.0009[d]	1668.5	–
m-Cresol	293.15	1.033	1.034[e]	1500.0	1500[f]
	303.15	1.025	1.0263[e]	1464.0	–
	313.15	1.018	1.0189[e]	1440.0	–
Aniline	293.15	1.021	1.02166[g]	1664.0	–
	303.15	1.013	1.029[h]	1617.6	1617.4[i]
	313.15	1.006	1.0042[h]	1588.0	–

[a] Ref. [25].
[b] Ref. [26].
[c] Ref. [27].
[d] Ref. [28].
[e] Ref. [29].
[f] Ref. [30].
[g] Ref. [31].
[h] Ref. [32].
[i] Ref. [33].

device [5]. Excess molar volume, excess intermolecular free length, excess acoustic impedance and excess pseudo Grüneisen parameter have been calculated over the whole composition range and the results have been fitted to Redlich–Kister polynomial equation.

Different models and mixing rules like Nomoto's, Van Dael and Van Geel's, Junjie's, Schaaff's mixing rules, Eyring and Hirsehfelder's relation, Altenburg's relation, Brock and Bird theory and Flory statistical theory have been applied to the systems under study to analyze the experimental data and to verify their applicability for evaluating ultrasonic velocity for the pure liquids and their mixtures. The results have been expressed in terms of average percentage deviations.

2. Experimental

2.1. Materials

The analytical grade chemicals PEG 200 (Fluka), Ethanolamine (Aldrich, purified by redistillation, ≥99.5%), m-cresol (Fluka, puriss. p.a., ≥99.7%) and aniline (Sigma–Aldrich, ACS reagent, ≥99.5%) have been obtained from Sigma–Aldrich Chemicals Pvt. Ltd. All chemicals were purified by standard procedure discussed by Perrin and Armarego [6]. The density and ultrasonic velocity of pure liquids along with their literature data are given in Table 1 and are found to be in good agreement.

Solutions have been prepared by mass, using air tight bottles and have been measured on electronic balance OHAUS-AR 2104 (Ohaus Corp., Pine Brook, NJ, USA) with an accuracy of 1×10^{-4} g. The possible error in the estimation of mole fraction is less than ±0.0001.

2.2. Apparatus and procedure

Densities have been measured by a sensitive single capillary calibrated pyknometer, with a bulb capacity of 6.7 ml volume. The pyknometer stem contained graduation of 0.01 ml. Pyknometer was immersed vertically in a double walled cylindrical water circulated glass jacket. The liquid rise in the capillary of pyknometer was measured by travelling microscope (having a least count of 0.001 cm) for accuracy. The precision of the measured densities is of the order of $\pm 1 \times 10^{-4}$ g cm^{-3}.

The interferometric technique has been used for the determination of ultrasonic velocity. The apparatus is a variable path fixed frequency (2 MHz) interferometer (Model F-81, Mittal Enterprises, New Delhi). It consists of a high frequency generator and a double walled measuring cell. A digital micrometer (with a least count of 0.001 mm) has been used to measure the distance between the reflector plate and the crystal within the cell. Once the wavelength is known, the ultrasonic velocity (u) in the liquid can be obtained using the following relation:

$$\text{ultrasonic velocity} \quad (u) = \text{frequency} \quad (f) \times \text{wavelength} \quad (\lambda)$$

The accuracy in the measurement of ultrasonic velocity is found to be 0.1 m/s.

The viscosity data used in the evaluation of various thermodynamic parameters were measured experimentally using Brookfield LVDV-II+Pro programmable viscometer (Brookfield Engineering Laboratories, Inc., USA) with complete control by PC using Brookfield Rheocalc 32 Software.

Circulating water bath with programmable temperature controller (TC-502, Brookfield Engineering Laboratories, Inc., USA), having variable pump speeds, has been used for water circulation around liquid cell of interferometer and water jacket of pyknometer. The programmable controllers incorporate an RS232 interface to provide remote data logging and control capability. The temperature controller covers the temperature measurement range of 253–473 K, with temperature stability of ±0.01 K.

3. Results and discussion

3.1. Thermodynamic parameters

The experimentally measured values of density and ultrasonic velocity of binary mixtures PEG + ethanolamine, PEG + m-cresol and PEG + aniline are listed in Table 2, as a function of temperature. Study of these binary mixtures is of importance in chemical and industrial processes, as they provide a wide range of solutions of varying proportions which permits continuous adjustment of desired properties of the medium.

Table 2
Experimental values of densities ρ and ultrasonic velocities u for the systems PEG + ethanolamine, PEG + m-cresol and PEG + aniline at 293.15, 303.15 and 313.15 K, respectively, with respect to the mole fraction x_1 of PEG.

x_1	293.15 K		303.15 K		313.15 K	
	ρ (g cm^{-3})	u (ms^{-1})	ρ (g cm^{-3})	u (ms^{-1})	ρ (g cm^{-3})	u (ms^{-1})
PEG + ethanolamine						
0.0000	1.017	1723.6	1.009	1697.6	1.001	1668.6
0.1009	1.046	1712.5	1.039	1686.1	1.032	1656.1
0.2000	1.067	1702.4	1.060	1674.8	1.053	1643.9
0.3012	1.083	1692.4	1.076	1663.6	1.069	1631.7
0.4019	1.095	1682.8	1.088	1652.8	1.081	1619.8
0.5002	1.105	1673.5	1.097	1642.6	1.090	1608.5
0.6009	1.112	1664.4	1.104	1632.4	1.097	1597.1
0.7006	1.117	1655.4	1.110	1622.3	1.102	1585.9
0.8001	1.121	1646.6	1.113	1612.2	1.106	1574.7
0.8999	1.124	1638.1	1.115	1602.2	1.107	1563.4
1.0000	1.127	1629.6	1.117	1592.0	1.108	1552.0
PEG + m-cresol						
0.0000	1.033	1500.0	1.025	1464.0	1.018	1440.0
0.1049	1.050	1512.7	1.042	1476.3	1.035	1451.4
0.2006	1.063	1524.4	1.056	1487.5	1.048	1461.7
0.3017	1.075	1536.7	1.068	1499.3	1.061	1472.5
0.4014	1.086	1549.1	1.078	1511.0	1.071	1483.2
0.5011	1.095	1561.6	1.087	1522.8	1.080	1494.1
0.5996	1.103	1574.2	1.095	1534.7	1.088	1504.9
0.7000	1.111	1587.2	1.102	1547.0	1.095	1516.1
0.8002	1.117	1600.6	1.109	1559.7	1.100	1527.8
0.9000	1.122	1614.3	1.113	1572.9	1.105	1539.6
1.0000	1.127	1629.6	1.117	1586.4	1.108	1552.0
PEG + aniline						
0.0000	1.021	1664.0	1.013	1617.6	1.006	1588.0
0.1019	1.041	1658.1	1.032	1613.4	1.026	1583.0
0.1998	1.057	1653.8	1.048	1609.9	1.041	1578.6
0.3003	1.071	1649.8	1.062	1606.8	1.055	1574.5
0.4010	1.082	1646.0	1.074	1604.1	1.066	1570.9
0.5021	1.092	1642.7	1.084	1601.5	1.076	1567.3
0.5983	1.101	1639.7	1.092	1599.4	1.084	1564.0
0.7249	1.110	1636.0	1.101	1596.7	1.093	1560.0
0.8002	1.115	1634.0	1.106	1595.2	1.097	1557.6
0.9001	1.121	1631.6	1.111	1593.4	1.103	1554.5
1.0000	1.127	1629.6	1.117	1592.0	1.108	1552.0

For calculating isentropic compressibility (k_s), free volume (V_f) and internal pressure (π_i) following relations were used

$$k_s = \frac{1}{u^2\rho} \quad (1)$$

$$V_f = \left[\frac{Mu}{k\eta}\right]^{3/2} \quad (2)$$

$$\pi_i = \frac{\alpha T}{k_T} \quad (3)$$

where ρ is the density, u is the ultrasonic velocity, η is the viscosity, M is the effective molecular mass, k is a dimensionless temperature-independent constant having a value of 4.28×10^9, α is the coefficient of thermal expansion, k_T is the isothermal compressibility and T is the absolute temperature of the mixture.

The variation of isentropic compressibility (k_s) and free volume (V_f) with mole faction of PEG for the three systems and at mentioned temperatures is shown in Figs. 1 and 2. The graphical representation of isentropic compressibility and free volume shows that for system PEG + ethanolamine values of k_s and V_f for the mixture are lesser than that of pure components giving a minimum at around $x = 0.3$–0.4. This non-linear behavior reflects the complex formation near this concentration through hydrogen bonding between oxygen atom of PEG and hydrogen atom of –OH group of ethanolamine and also between hydrogen atom of –OH group of PEG and nitrogen atom of –NH_2 group of ethanolamine. For the systems PEG + m-cresol and PEG + aniline compressibility is more than that for corresponding ideal mixture but the extent of interaction is found to be lesser than that in PEG + ethanolamine. With the increase in mole fraction of PEG the free volume for the systems PEG + m-cresol and PEG + aniline decreases sharply due to fitting of the smaller molecules of m-cresol and aniline in the voids formed by the larger PEG molecules and then increases to the value of free volume of self associated PEG molecules. The increase in their values with increase in temperature may be because of increase in interaction with temperature. As the interaction increases with temperature, complex formation also increases, resulting in apparently larger structures, hence increasing the free volume of the mixture. Also the increase in non-linearity at higher temperature may be due to the more prominent specific intermolecular interactions.

The variation of internal pressure with mole fraction is shown in Fig. 3. The internal pressure of the mixture increases with increase in concentration of PEG, the non linear variation in the three systems under investigation suggests the presence of strong interaction in the mixtures.

Surface tension (σ) and relaxation time (τ) calculated using experimentally measured data with the help of Eqs. (4) and (5), has been given in Table 3 for the systems PEG + ethanolamine, PEG + m-cresol and PEG + aniline, at 293.15, 303.15 and 313.15 K, respectively.

$$\sigma = 6.3 \times 10^{-4}\rho u^{3/2} \quad (4)$$

$$\tau = \frac{4\eta}{3u^2\rho} \quad (5)$$

The variation of relaxation time with the mole fraction of PEG is similar to that of internal pressure as can be seen from Table 3.

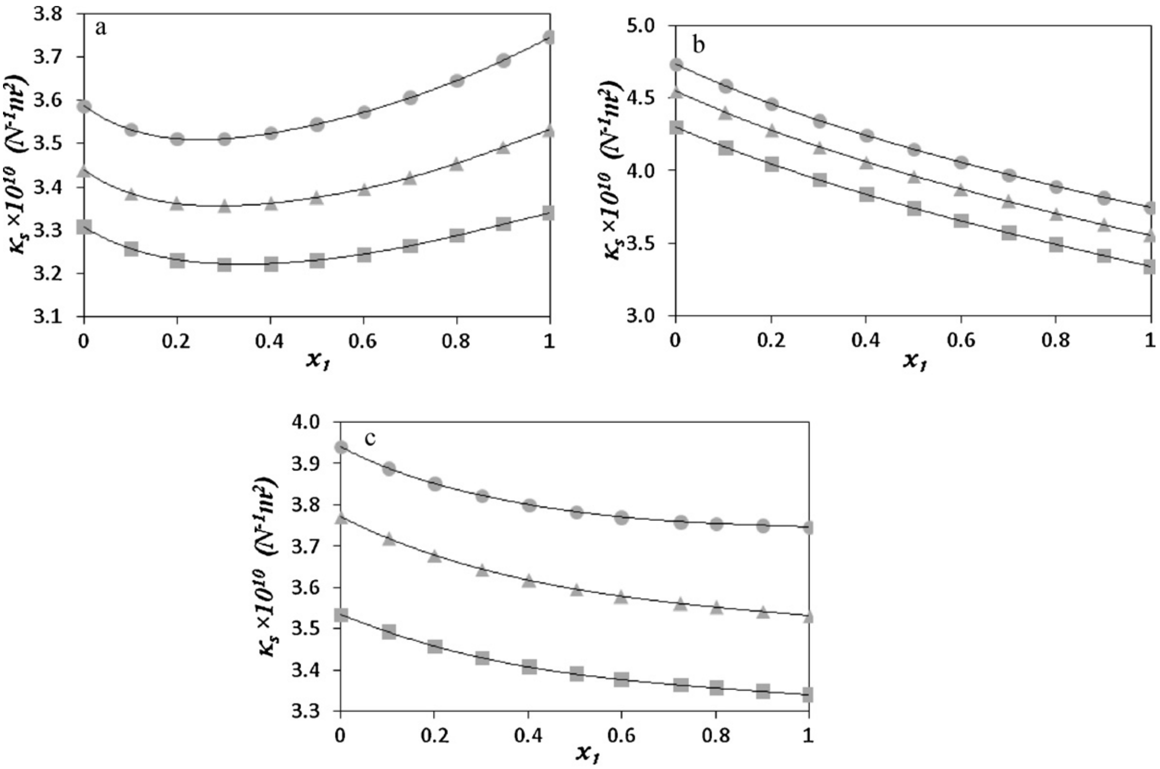

Fig. 1. Isentropic compressibilities for the systems (a) PEG + ethanolamine, (b) PEG + m-cresol and (c) PEG + aniline at (■) 293.15 K; (▲) 303.15 K; and (●) 313.15 K with respect to the mole fraction of PEG.

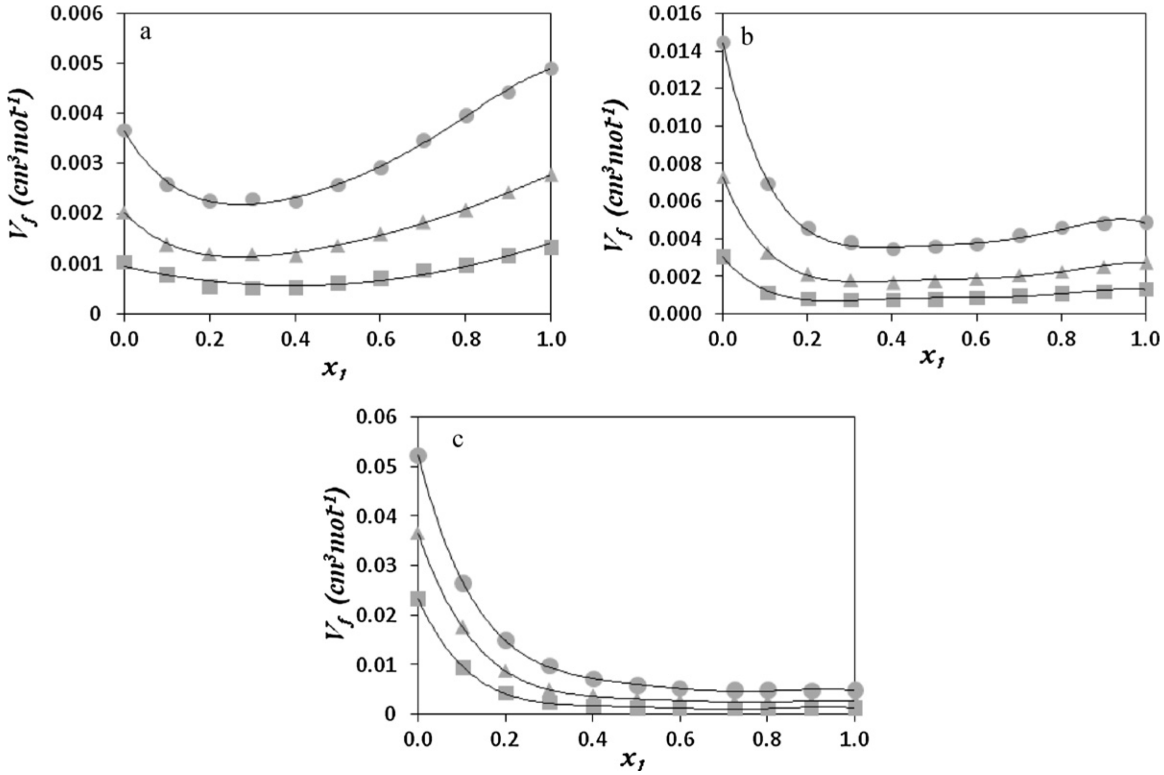

Fig. 2. Free volume for the systems (a) PEG + ethanolamine, (b) PEG + m-cresol and (c) PEG + aniline at (■) 293.15 K; (▲) 303.15 K; and (●) 313.15 K with respect to the mole fraction of PEG.

Relaxation time near $x = 0.4$ is larger than that of pure components for PEG + ethanolamine. The same is the case for PEG + m-cresol and PEG + aniline but with lesser increase in values suggesting lesser intermolecular interaction.

A close perusal of Table 3 indicates that the surface tension values increase with increase in mole fraction of PEG and reach a maximum at equimolar composition and again start decreasing for the system PEG + ethanolamine. While for the systems PEG + aniline

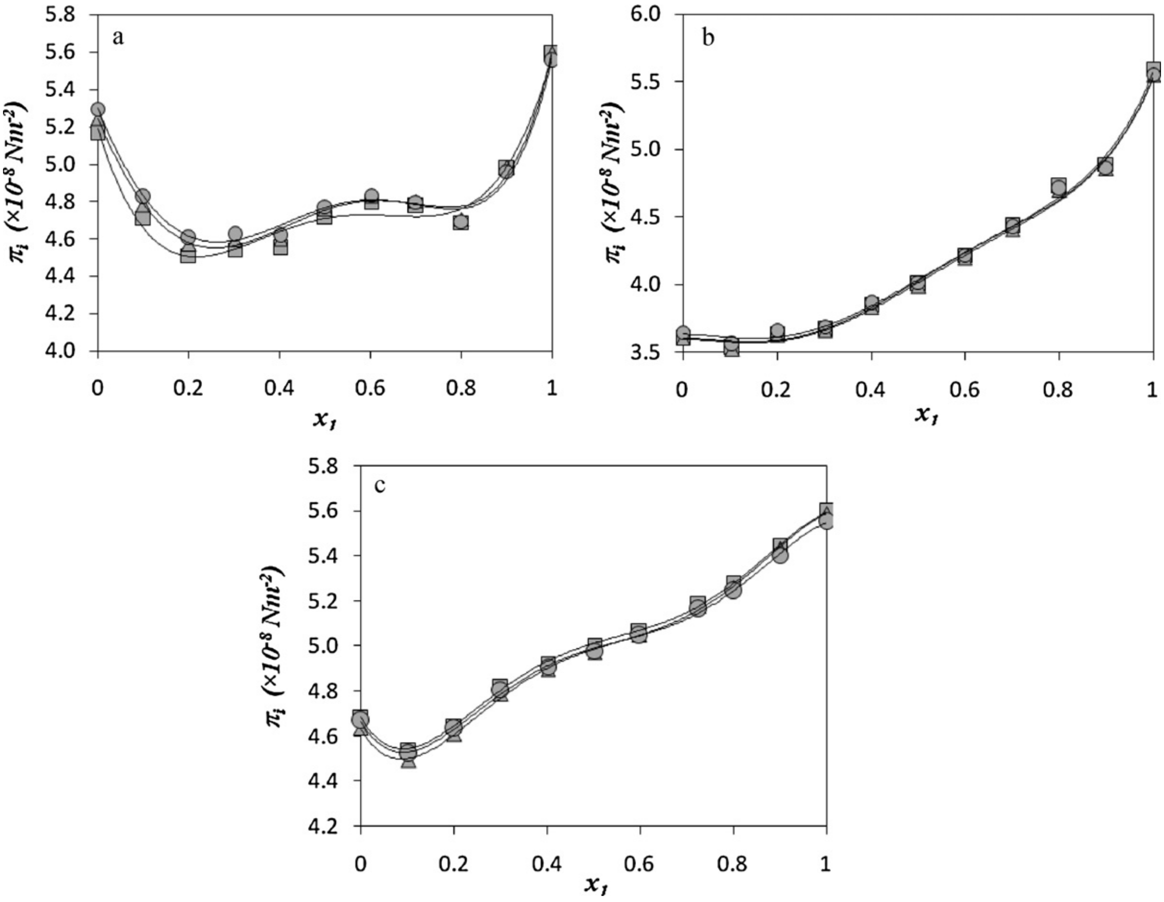

Fig. 3. Internal pressure for the systems (a) PEG + ethanolamine, (b) PEG + m-cresol and (c) PEG + aniline at (■) 293.15 K; (▲) 303.15 K; and (●) 313.15 K with respect to the mole fraction of PEG.

the change is not so prominent and for PEG + m-cresol the variation is somewhat linear. Substances which involve hydrogen bonding exist as associated molecules and have high surface tension, in contrast to those substances which involve intramolecular H-bonds exist as discrete and hence have low surface tension. The surface tension values decrease with increase in temperature for all the three systems as expected.

3.2. Data correlation

The density and ultrasonic velocity data are fitted by the following relations:

$$\rho \quad (\mathrm{g\,cm^3}) = ax_1^3 + bx_1^2 + cx_1 + d \tag{6}$$

$$u \quad (\mathrm{ms^{-1}}) = a'x_1^3 + b'x_1^2 + c'x_1 + d' \tag{7}$$

where ρ and u are the density and velocity of the solution at the measured temperature, a, b, c and d are the coefficients of the polynomial in g cm^{-3}, a', b', c' and d' are the coefficients of the polynomial in ms^{-1} and x_1 is the mole fraction of the polymer in the solution. Values of the coefficients are obtained by regression. The coefficients in Eqs. (6) and (7) along with the percentage average absolute deviations (%AAD) calculated using Eq. (8) are given in Tables 4.1 and 4.2 respectively.

$$\%\mathrm{AAD} = \frac{100}{n}\sum_{i=1}^{n}\left|\frac{A_{\mathrm{cal}} - A_{\mathrm{exp}}}{A_{\mathrm{exp}}}\right| \tag{8}$$

where A_{cal} and A_{exp} is calculated and experimental density and velocity respectively.

3.3. Excess parameters

Deviations in ultrasonic velocity, excess molar volume, excess intermolecular free length, excess acoustic impedance and excess pseudo-Grüneisen parameter have been reported in Figs. 4–8. The most common way to evaluate the excess value [7] of a given thermodynamic parameter is to use the equation

$$A^{\mathrm{E}} = A_{\mathrm{exp}} - \sum_i x_i A_i \tag{9}$$

here A_{exp}, A_i, and x_i are experimentally measured value of the parameter A, value of parameter A for ith component and mole fraction of ith component (i = 1, 2 for binary mixture) respectively. A^{E} is deviation/excess value of the respective parameter. Excess molar volume (V^{E}), excess intermolecular free length ($L_{\mathrm{f}}^{\mathrm{E}}$), excess acoustic impedance (Z^{E}) and excess pseudo-Grüneisen parameter (Γ^{E}) can thus be written as,

$$V_{\mathrm{m}}^{\mathrm{E}} = \left(\frac{x_1 m_1 + x_2 m_2}{\rho_{\mathrm{m}}}\right) - \left(\frac{x_1 m_1}{\rho_1} + \frac{x_2 m_2}{\rho_2}\right) \tag{10}$$

$$L_{\mathrm{f}}^{\mathrm{E}} = \frac{K}{(u_m{}^2 \rho_m)^{1/2}} - \left[\frac{x_1 K}{(u_1^2 \rho_1)^{1/2}} + \frac{x_2 K}{(u_2^2 \rho_2)^{1/2}}\right] \tag{11}$$

$$Z^{\mathrm{E}} = (\rho_{\mathrm{m}} u_{\mathrm{m}}) - (x_1 \rho_1 u_1 + x_2 \rho_2 u_2) \tag{12}$$

$$\Gamma^{\mathrm{E}} = \Gamma_{\mathrm{m}} - (x_1 \Gamma_1 + x_2 \Gamma_2) \tag{13}$$

These excess properties are fundamentally important in understanding the intermolecular interactions and nature of molecular agitation in dissimilar molecules. These are found to be sensitive

Table 3
Surface tension σ and relaxation time τ for the systems PEG + ethanolamine, PEG + m-cresol and PEG + aniline at 293.15, 303.15 and 313.15 K, respectively, against the mole fraction x_1 of PEG.

x_1	293.15 K		303.15 K		313.15 K	
	σ (mN m^{-1})	τ ($\times 10^{-8}$ s)	σ (mN m^{-1})	τ ($\times 10^{-8}$ s)	σ (mN m^{-1})	τ ($\times 10^{-8}$ s)
PEG + ethanolamine						
0.0000	45.869	1.064	44.466	0.692	42.996	0.479
0.1009	46.738	1.528	45.326	1.082	43.826	0.727
0.2000	47.256	2.288	45.790	1.378	44.245	0.930
0.3012	47.542	2.722	46.019	1.589	44.411	1.057
0.4019	47.661	3.034	46.085	1.824	44.415	1.215
0.5002	47.674	3.042	46.040	1.831	44.308	1.235
0.6009	47.596	3.042	45.910	1.830	44.118	1.260
0.7006	47.440	2.939	45.709	1.830	43.862	1.234
0.8001	47.216	2.949	45.428	1.843	43.545	1.231
0.8999	46.961	2.846	45.067	1.796	43.142	1.242
1.0000	46.710	2.807	44.702	1.774	42.689	1.257
PEG + m-cresol						
0.0000	37.833	1.025	36.205	0.593	35.060	0.386
0.1049	38.925	2.104	37.266	1.073	36.076	0.669
0.2006	39.879	2.737	38.171	1.517	36.930	0.930
0.3017	40.818	3.045	39.078	1.753	37.776	1.106
0.4014	41.717	3.192	39.908	1.949	38.557	1.240
0.5011	42.586	3.240	40.721	1.972	39.309	1.262
0.5996	43.427	3.166	41.500	1.965	40.022	1.288
0.7000	44.261	3.049	42.277	1.928	40.731	1.240
0.8002	45.079	2.955	43.038	1.888	41.416	1.215
0.9000	45.865	2.880	43.775	1.824	42.080	1.218
1.0000	46.710	2.807	44.467	1.786	42.689	1.257
PEG + aniline						
0.0000	43.690	0.208	41.537	0.160	40.110	0.129
0.1019	44.289	0.418	42.173	0.287	40.719	0.224
0.1998	44.794	0.769	42.688	0.491	41.162	0.356
0.3003	45.217	1.229	43.120	0.783	41.528	0.510
0.4010	45.555	1.677	43.479	1.013	41.828	0.678
0.5021	45.838	2.109	43.777	1.253	42.065	0.836
0.5983	46.059	2.353	44.018	1.417	42.245	0.955
0.7249	46.295	2.575	44.269	1.604	42.431	1.080
0.8002	46.418	2.638	44.401	1.663	42.514	1.133
0.9001	46.565	2.735	44.554	1.741	42.600	1.199
1.0000	46.710	2.807	44.702	1.774	42.689	1.257

Table 4.1
Coefficients of polynomial equation (6) for the systems PEG + ethanolamine, PEG + m-cresol and PEG + aniline at 293.15, 303.15 and 313.15 K, respectively.

T (K)	a	b	c	d	%AAD
PEG + ethanolamine					
293.15	0.119	−0.311	0.300	1.108	−0.0802
303.15	0.114	−0.311	0.303	1.010	−0.0713
313.15	0.119	−0.320	0.307	1.002	−0.0904
PEG + m-cresol					
293.15	0.020	−0.091	0.163	1.033	−0.1255
303.15	0.019	−0.093	0.165	1.026	−0.0326
313.15	0.019	−0.097	0.167	1.018	−0.1040
PEG + aniline					
293.15	0.052	−0.151	0.204	1.021	−0.0944
303.15	0.051	−0.152	0.204	1.021	−0.0753
313.15	0.053	−0.155	0.203	1.006	−0.0831

Table 4.2
Coefficients of polynomial equation (7) for the systems PEG + ethanolamine, PEG + m-cresol and PEG + aniline at 293.15, 303.15 and 313.15 K, respectively.

T (K)	a'	b'	c'	d'	%AAD
PEG + ethanolamine					
293.15	−6.86	22.25	−109.30	1723	−0.0272
303.15	−9.29	22.76	−119.10	1697	−0.0427
313.15	−7.74	18.64	−127.50	1668	−0.0415
PEG + m-cresol					
293.15	14.88	−9.18	123.70	1499	−0.0581
303.15	12.13	−8.07	118.30	1464	−0.0009
313.15	11.75	−9.30	109.50	1440	−0.0018
PEG + aniline					
293.15	−9.05	29.52	−54.78	1663	−0.0445
303.15	−7.00	23.21	−41.83	1617	−0.0311
313.15	−6.28	20.00	−49.80	1587	−0.0593

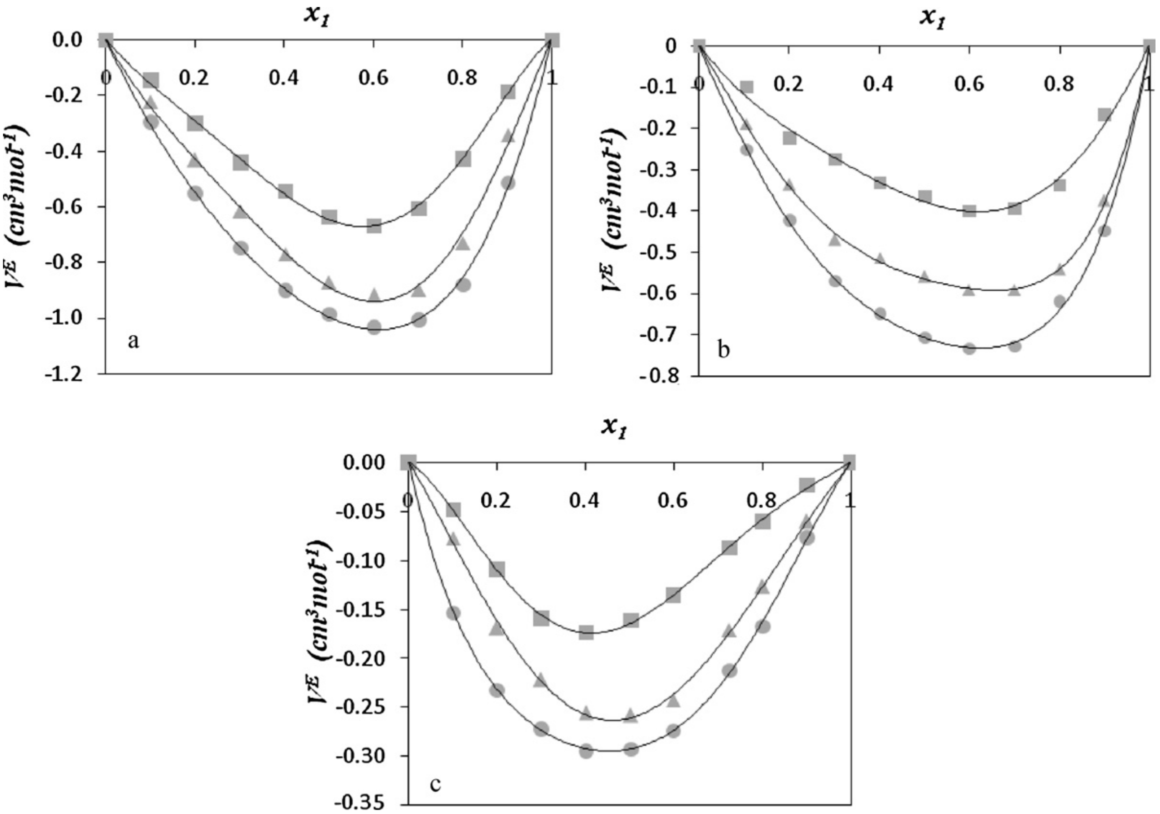

Fig. 4. Excess molar volume for the systems (a) PEG + ethanolamine, (b) PEG + m-cresol and (c) PEG + aniline at (■) 293.15 K; (▲) 303.15 K; and (●) 313.15 K with respect to the mole fraction of PEG.

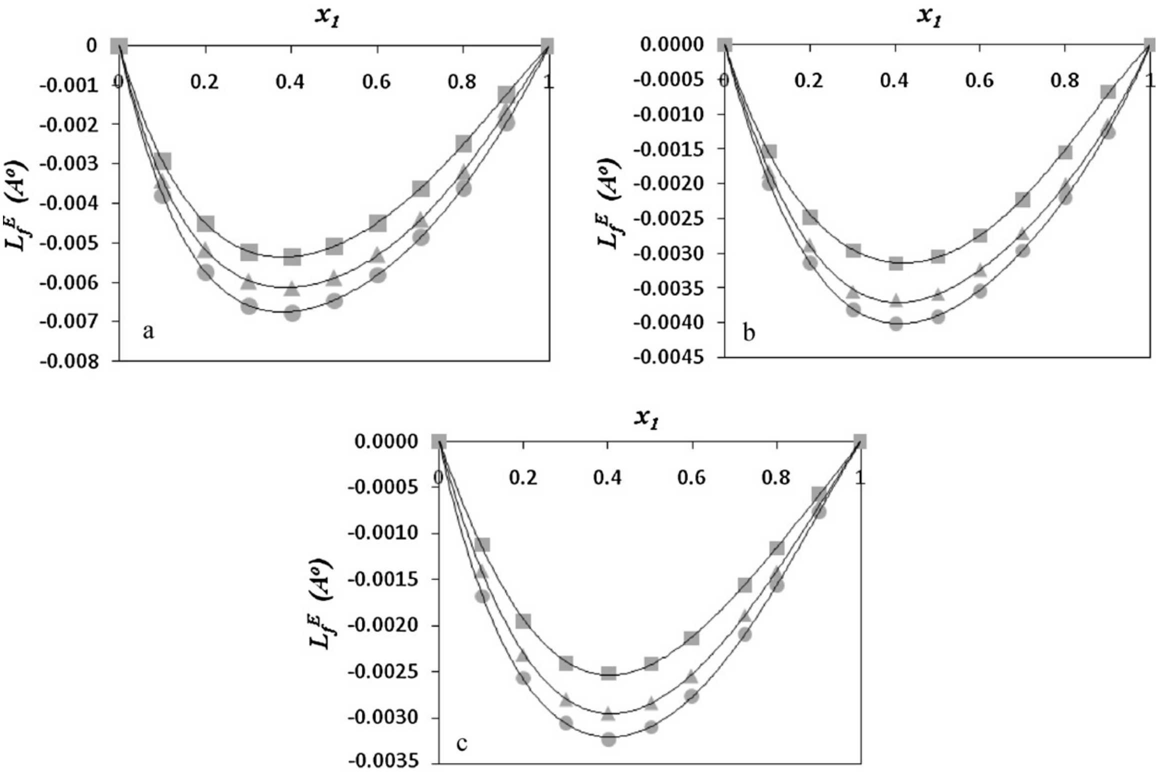

Fig. 5. Excess free length for the systems (a) PEG + ethanolamine, (b) PEG + m-cresol and (c) PEG + aniline at (■) 293.15 K; (▲) 303.15 K; and (●) 313.15 K with respect to the mole fraction of PEG.

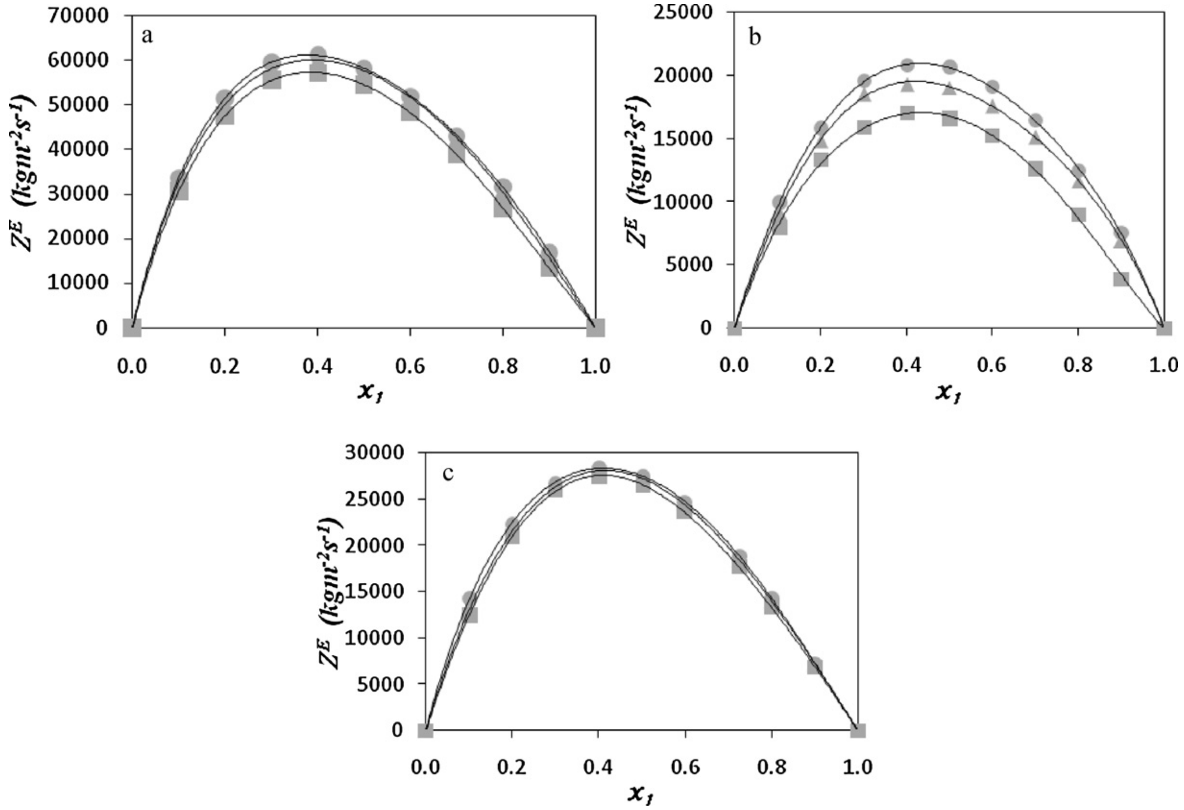

Fig. 6. Excess acoustic impedance for the systems (a) PEG + ethanolamine, (b) PEG + m-cresol and (c) PEG + aniline at (■) 293.15 K; (▲) 303.15 K; and (●) 313.15 K with respect to the mole fraction of PEG.

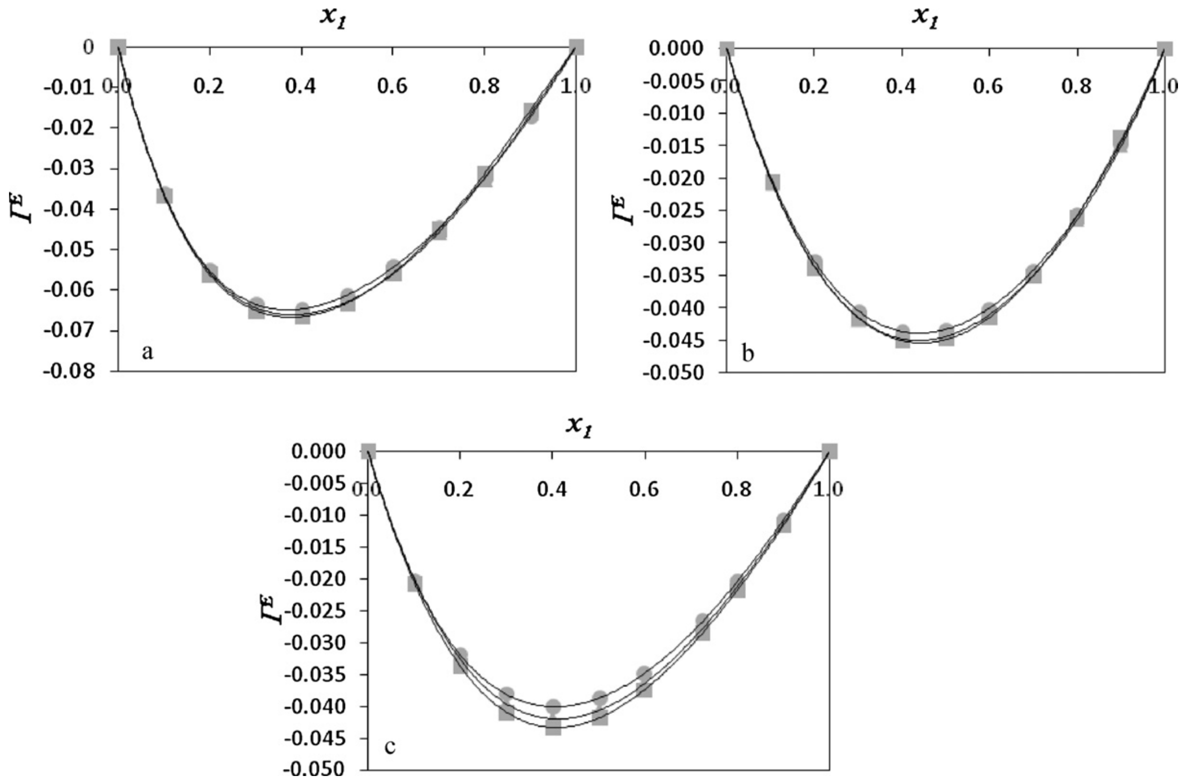

Fig. 7. Excess pseudo-Grüneisen parameter for the systems (a) PEG + ethanolamine, (b) PEG + m-cresol and (c) PEG + aniline at (■) 293.15 K; (▲) 303.15 K; and (●) 313.15 K with respect to the mole fraction of PEG.

towards difference in size and shape of the molecules [8]. These functions give an idea about the extent to which the given liquid mixtures deviate from ideality.

The excess molar volume V^E, as presented in Fig. 4, shows the values to be negative over entire composition range at all three temperatures. The large negative values for PEG + ethanolamine arise due to increased interactions between PEG and solvents or a very large difference in the molar volumes of the pure components. Treszczanowicz et al. [9] suggested that V^E is the result of contributions from several opposing effects. These may be divided arbitrarily into three types, namely, physical, chemical, and structural. Physical contributions, which are non specific interactions between the real species present in the mixture, contribute a positive term to V^E. The chemical or specific intermolecular interactions result in a volume decrease. This effect contributes negative values to V^E. The structural contributions are mostly negative and arise from several effects, especially from interstitial accommodation and changes in the free volume. In other words, structural contributions arising from the geometrical fitting (interstitial accommodation) of one component into other due to the differences in the free volumes and molar volumes between components lead to negative contribution to V^E. The actual value of V^E would depend on the relative strengths of these effects. The experimental values of V^E suggest that H-bonding and interstitial accommodation both are leading to the negative values while increase in negative values with temperature suggest that structural effect is more prominent than chemical effect in these solutions because of the large difference in molar volumes between components (molar volumes of PEG, ethanolamine, m-cresol and aniline are 177.45, 60.03, 104.614 and 91.15 $\mathrm{cm^3\,mol^{-1}}$ respectively at 293.15 K). The ethanolamine molecules exhibit strong ability of hydrogen bond formation, as the molecules posses hydrogen bond donors on the –OH group and acceptors on the oxygen or nitrogen atom.

The values of excess intermolecular free length are negative as shown in Fig. 5. The decrease in excess intermolecular free length with increasing mole fraction of PEG is indicating a formation of more tightly bonded structure of molecules. The closer packing of molecules caused by the hydrogen bonds between the solute and the solvent molecules reduces the free length of the system. The minimum at around $x = 0.4$ for the system PEG + ethanolamine shows the formation of complex structures as suggested below. There may be clustering due to the dipole–dipole interaction and primarily due to the formation of H-bonds at both the end of large PEG and the ethanolamine molecules, resulting in more compact structure. While for systems PEG + m-cresol and PEG + aniline lesser negative values of excess intermolecular free length show H-bond formation to a lesser extent. PEG is linear chain oligomer bearing an –OH group at end that can strongly interact via H-bonds, hence formation of H-bond results at both the ends of large sized molecule of PEG and the mixture with ethanolamine molecules producing a more compact structure.

Acoustic impedance is almost the opposite of isentropic compressibility. The variation of excess acoustic impedance is given in Fig. 6. The values are found to be positive for all the three systems under investigation and at all the temperatures studied suggesting the presence of strong interaction in all these systems. From the more positive values the interaction is inferred to be stronger in PEG + ethanolamine than in other systems. The maximum value at around $x = 0.4$ for Z^E indicates the enhancement of bond strength at this concentration.

It can be seen from Fig. 7 that the values of excess pseudo-Grüneisen parameter (Γ^E) are negative for all the three mixtures which indicate the presence of specific intermolecular interaction through hydrogen bonding between the unlike species. The effect of temperature on Γ^E is not very prominent in all the mixtures. The values are more negative for PEG + ethanolamine as compared to PEG + m-cresol and PEG + aniline.

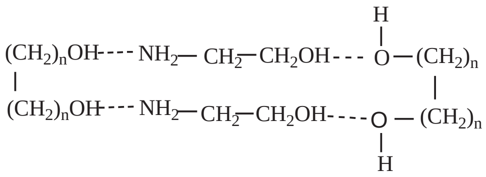

Fig. 8. Complex structure formed by mixing ethanolamine in PEG 200.

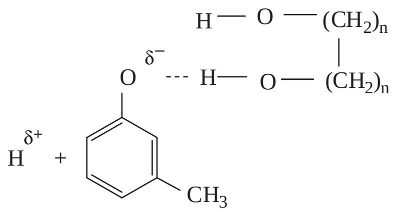

Fig. 9. Hydrogen bonding in molecules of m-cresol and PEG 200.

The above results support each other and infer that because of the presence of two electronegative elements viz. nitrogen and oxygen in its molecular architecture ethanolamine has greater extent of interaction with PEG. Both atoms may be involved in a complex type of network of hydrogen bonding near mole fraction of $x = 0.4$ as shown in Fig. 8.

Ethanolamine being an aliphatic amine gives its unshared electron pair more effectively i.e. the electron pair is more available for taking the alcoholic proton of polyethylene glycol. Thus intermolecular interaction between ethanolamine and PEG molecule is strong.

m-Cresol is an acidic compound. Here the oxygen of m-cresol is less likely to be protonated. In this case a hydrogen bond formation may take place between the m-methylphenoxide ion and one of the hydrogen atoms of the PEG as proposed in Fig. 9.

Since m-cresol is a very weak acid, formation of m-methylphenoxide ion may take place in less magnitude.

Aniline, which is a primary amine, shows property of both benzene nucleus and amine group ($-NH_2$). Aniline is a weak base as compared to ethanolamine, an aliphatic amine. In aliphatic amines, the non-bonding electron pair of nitrogen is localized and is fully available for coordination with proton. On the other hand, in aniline, the non-bonding electron pair of nitrogen is delocalized into benzene ring by resonance. Thus, electron density is less on nitrogen atom of aniline and the unshared electron pair is less available resulting in least interaction in the system PEG + aniline.

3.4. Redlich–Kister polynomial equation

The composition dependences of the excess properties are correlated by the Redlich–Kister polynomial equation [10]

$$Y^E = x_1(1 - x_1)\sum_{i=1}^{5} a_i(2x_1 - 1)^{i-1} \qquad (14)$$

The values of the coefficient a_i were calculated by method of least squares along with the standard deviation $\sigma(Y^E)$. The coefficient a_i is adjustable parameters for a better fit of the excess functions.

The standard deviation values were obtained from relation

$$\sigma(Y^E) = \left[\frac{\sum_{i=1}^{n}(Y^E_{\mathrm{expt}} - Y^E_{\mathrm{cal}})^2}{n - p}\right]^{1/2} \qquad (15)$$

Table 5.1
Coefficients of the Redlich–Kister equation for excess parameters and their standard deviation for the system PEG + ethanolamine.

Parameters	T (K)	a_1	a_2	a_3	a_4	a_5	$\sigma(Y^E)$
V_m^E (cm^3 mol^{-1})	293.15	−2.4592	3.2282	−1.0010	−4.1593	4.1318	0.1877
	303.15	−2.2510	23.1849	−22.0574	−30.3352	43.8896	2.1133
	313.15	−5.4361	−28.1117	22.0580	40.0582	−47.9283	2.8985
L_f^E (Å)	293.15	−0.0450	−0.4767	0.4017	0.6272	−0.8242	0.0460
	303.15	−0.0358	−0.2425	0.1936	0.3100	−0.4085	0.0230
	313.15	0.0577	1.2290	−0.7633	−1.7153	1.5441	0.1047
Z^E ($\times 10^{-3}$ kg m^{-2} s^{-1})	293.15	218.3860	91.8607	45.5083	41.4365	−9.5952	0.0765
	303.15	228.5132	88.9134	88.9622	45.3268	−50.9390	0.0813
	313.15	232.4622	93.5238	78.5990	34.2705	−8.7586	0.1159
Γ^E	293.15	−0.3763	−2.4373	1.9683	3.0894	−4.1119	0.2286
	303.15	−0.3838	−2.6164	2.0830	3.3379	−4.3786	0.2467
	313.15	−0.4024	−3.1029	2.4994	4.0059	−5.2521	0.2944

Table 5.2
Coefficients of the Redlich–Kister equation for excess parameters and their standard deviation for the system PEG + m-cresol.

Parameters	T (K)	a_1	a_2	a_3	a_4	a_5	$\sigma(Y^E)$
V_m^E (cm^3 mol^{-1})	293.15	−1.4639	0.5331	−2.1369	−0.0502	3.3784	0.0067
	303.15	−2.2392	0.8213	−1.2600	0.8477	−0.0873	0.0092
	313.15	−2.8265	0.6892	−0.5435	1.1582	−1.5772	0.0057
L_f^E (Å)	293.15	−0.0122	−0.0039	−0.0027	−0.0026	0.0048	0.0000
	303.15	−0.0140	−0.0025	0.0000	−0.0028	−0.0051	0.0000
	313.15	−0.0159	−0.0051	−0.0011	0.0004	−0.0029	0.0000
Z^E ($\times 10^{-3}$ kg m^{-2} s^{-1})	293.15	66.5433	16.5399	22.3674	15.4914	−40.1572	0.1084
	303.15	76.0286	18.6851	16.8675	−8.3163	1.6468	0.1467
	313.15	82.6257	18.8618	15.9392	−7.3246	6.2550	0.0685
Γ^E	293.15	−0.1784	−0.0377	−0.0312	−0.0065	0.0306	0.0001
	303.15	−0.1768	−0.0404	−0.0294	0.0080	0.0043	0.0001
	313.15	−0.1687	−0.0021	0.0211	−0.0550	−0.0900	0.0000

Table 5.3
Coefficients of the Redlich–Kister equation for excess parameters and their standard deviation for the system PEG + aniline.

Parameters	T (K)	a_1	a_2	a_3	a_4	a_5	$\sigma(Y^E)$
V_m^E (cm^3 mol^{-1})	293.15	−0.6487	−0.3842	0.2359	0.3442	0.2654	0.0013
	303.15	−1.0049	0.2517	0.1959	0.2370	0.3230	0.0031
	313.15	−1.0139	−0.2247	−1.1993	−0.4496	1.2854	0.0020
L_f^E (Å)	293.15	−0.0099	−0.0047	0.0048	0.0166	0.0127	0.0000
	303.15	−0.0121	−0.0091	−0.0060	0.0069	0.0108	0.0000
	313.15	−0.0124	−0.0041	−0.0017	−0.0032	0.0002	0.0000
Z^E ($\times 10^{-3}$ kg m^{-2} s^{-1})	293.15	105.9722	40.2158	14.6745	−4.0726	−22.3439	0.0702
	303.15	115.7349	81.0197	51.5957	−66.4098	−93.1234	0.1849
	313.15	109.3023	34.7409	19.0143	19.4933	−8.2251	0.1401
Γ^E	293.15	−0.1668	−0.0603	−0.0173	−0.0010	0.0033	0.0001
	303.15	−0.1620	−0.0551	−0.0161	−0.0059	0.0046	0.0002
	313.15	−0.1541	−0.0526	−0.0243	−0.0165	0.0006	0.0001

where n is the no. of experimental points, p is the no. of parameters, Y_{expt} and Y_{cal} are the experimental and calculated parameters respectively.

The values of co-efficient a_i evaluated using the method of least squares for the mixtures are given in Tables 5.1–5.3 along with the standard deviations $\sigma(Y^E)$.

3.5. Velocity modeling

Ultrasonic velocity data furnish wealth of information about the interaction between ions, dipoles, hydrogen bonding, multipolar and dispersive forces [11,12]. Mixing rules for velocity and other theories have been used to evaluate ultrasonic velocity data. The average percentage deviation in the calculated values from the experimental values is given in Table 6. Nomoto [13] assuming the linearity of the molar sound velocity and the additivity of the molar volumes in liquid solutions, gave the following relation

$$u_m = \left(\frac{R_m}{V_m}\right)^3 = \left(\frac{x_1R_1 + x_2R_2}{x_1V_1 + x_2V_2}\right)^3 \tag{16}$$

Van Dael and Van Geel [14] proposed the following ideal mixing relation for predicting speed of sound of a binary liquid mixture

$$\left(\frac{1}{x_1M_1 + x_2M_2}\right)\frac{1}{u_m^2} = \left(\frac{x_1}{M_1u_1^2} + \frac{x_2}{M_2u_2^2}\right) \tag{17}$$

Junjie [15] gave following relation for the ultrasonic velocity in a binary mixture

$$u_m = \frac{x_1V_1 + x_2V_2}{\sqrt{(x_1M_1 + x_2M_2)((x_1V_1/\rho_1u_1^2) + (x_2V_2/\rho_2u_2^2))}} \tag{18}$$

Schaaffs' relation [16], which is based on the Collision Factor Theory (CFT), for predicting ultrasonic velocity in pure liquids, has been extended to the binary liquid mixtures by Nutsch–Kuhnkies and is given as

$$u_m = u_\infty(x_1S_1 + x_2S_2)\frac{x_1B_1 + x_2B_2}{V_m} \tag{19}$$

where M, ρ, u_m and x represent molecular weight, density, ultrasonic velocity, and mole fraction of mixtures respectively. Symbols 1, 2 and m, in suffix represent pure components and mixtures respectively.

Table 6
Average percentage deviations of the values of ultrasonic velocity calculated using different theories.

T (K)	Schaaff	Nomoto	Van Deal and Van Geel	Junjie	Eyring and Hirschfelder	Altenburg	Brock and Bird	Flory
PEG + ethanolamine								
293.15	3.49	−0.03	−3.90	−0.08	−3.56	−8.50	−12.50	−3.12
303.15	4.56	−0.94	−8.68	−0.99	−9.46	−6.55	−12.20	−4.33
313.15	3.95	−1.09	−8.59	−1.14	−10.26	−6.17	−11.91	−2.71
PEG + m-cresol								
293.15	6.13	0.76	−3.52	0.48	−0.46	−8.63	−9.50	−3.88
303.15	5.86	0.70	−3.52	0.44	0.18	−8.16	−8.49	−2.11
313.15	5.52	0.65	−3.48	0.41	−0.76	−7.83	−8.10	−0.43
PEG + aniline								
293.15	3.51	−0.05	−3.82	−0.10	−4.22	−8.96	−13.55	−4.94
303.15	3.49	−0.03	−3.90	−0.08	−3.56	−8.50	−12.50	−3.12
313.15	3.08	−0.12	−3.85	−0.16	−4.21	−8.12	−11.89	−1.41

In Eq. (15), S and B respectively are 'collision factor' and 'actual volume' of the molecules per mole and are given as

$$S = \frac{uV}{u_\infty B} \quad \text{and} \quad B = \left(\frac{4}{3\pi r^3}\right) N_A$$

where $u_\infty = 1600$ m/s, an empirical constant, N_A = Avogadro number, $r = \sqrt[3]{(3/16\pi N)V\left[1-(RT/Mu^2)\left\{\left(\sqrt{1+(Mu^2/RT)}\right)-1\right\}\right]}$, the molecular radius of the given component.

The concept of intermolecular free length L_f given by Eyring and Hirschfelder [17] is directly related to available volume per mole V_a and is given as

$$L_f = \frac{2V_a}{Y} = \frac{K}{u\rho^{1/2}} \tag{20}$$

where $V_a = V_T - V_0$,

$$Y = (36\pi N_A V_0{}^2)^{1/3} \tag{21}$$

$$V_0 = V_T\left(1 - \frac{T}{T_c}\right)^{0.3} \tag{22}$$

V_0, V_T, T_c, N_A, and K are molar volume at absolute zero temperature, molar volume at absolute temperature T, critical temperature of the liquid, Avogadro's number, and temperature dependent empirical constant, proposed by Jacobson [18]. Using this relation we can evaluate velocity as

$$u = \frac{KY}{2V_a\rho^{1/2}} \tag{23}$$

Altenburg [19] has also proposed a relation between ultrasonic velocity, surface tension and molecular weight M.

$$\sigma = 3.69 \times 10^{-10}\rho^{2/3}M^{1/3}u^2 \tag{24}$$

This has been used with Eq. (25) to calculate the velocity of the mixture.

Another theoretical model we analyzed is due to Brock and Bird [20], which obtains the surface tension of pure components only from the values of critical parameters. Using a suggestion by Miller, Brock and Bird expression for surface tension of a binary mixture is given by

$$\sigma = P_{cm}^{2/3}T_{cm}^{1/3}Q(1 - T_r)^{11/9} \tag{25}$$

where

$$Q = 0.1196\left[1 + \frac{T_{br}\ \ln(P_{cm}/1.01325)}{1 - T_{br}}\right] - 0.279 \tag{26}$$

and P_{cm}, T_{cm}, T_{br} are the critical pressure, critical temperature and boiling temperature for the mixture. This has been used with Eq. (25) to calculate the velocity of the mixture.

Patterson and Rastogi [21] have used Flory Statistical Theory (FST) theory to calculate surface tension which in turn is used to evaluate ultrasonic velocity in liquid mixtures. The equation for reduced surface tension is given by

$$\tilde{\sigma}(\tilde{V}) = M\tilde{V}^{-5/3} - \frac{\tilde{V}^{1/3} - 1}{\tilde{V}^2}\ \ln\left[\frac{\tilde{V}^{1/3} - 0.5}{\tilde{V}^{1/3} - 1}\right] \tag{27}$$

where M is the fraction of nearest neighbours that a molecule loses on moving from the bulk of the liquid to the surface.

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

$$\sigma_m = \sigma^* \times \tilde{\sigma}(\tilde{V}), \tag{28}$$

where σ^* is characteristic surface tension.The values of surface tension obtained by Flory theory have been used to evaluate ultrasonic velocity, making use of the well known Auerbach relation [22],

$$u_m = \left(\frac{\sigma_m}{6.3 \times 10^{-4}\rho_m}\right)^{2/3} \tag{29}$$

Some of these relations have also been used previously for estimation of ultrasonic data [23,24] for other mixtures.

A close perusal of Table 6 reflects that Nomoto and Junjie's relation are the best suited for estimation of ultrasonic velocity with minimum average percentage deviation of 0.03% and 0.08% respectively, while Schaaff's, Van Deal and Van Geel relation and Flory's theory give little larger deviations for all three mixtures. However Eyring and Hirschfelder, Altenburg and Brock and Bird theory needs modification to predict the accurate values and hence should include the interactions present in the system.

4. Conclusion

It can be concluded here on the basis of the results that ethanolamine has greater extent of interaction with PEG than m-cresol and aniline particularly with least magnitude from aniline, where electron availability is least because of delocalization. The larger difference in molar volume between the components, along with the more prominent H-bonding, in the system PEG + ethanolamine than in PEG + m-cresol and PEG + aniline is also responsible for stronger interaction in PEG + ethanolamine. Specific interactions present in the system PEG + ethanolamine results in formation of complex structures. Nomoto and Junjie's relation exhibit an excellent agreement between the experimental and theoretically estimated values of ultrasonic velocity.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2011.02.011.

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