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

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ABSTRACT

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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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.