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Temperature Dependence of Acoustical and Excess Acoustical Parameters in Propylene Glycol and Ethanol Binary Liquid Mixtures

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ABSTRACT

Speeds of sound, densities and viscosities have been measured in the binary liquid mixtures containing propylene glycol and ethanol at temperatures T=(298.15, 303.15, 308.15, 313.15 and 318.15)K for the entire molefraction range. of propylene glycol. From the experimentally measured data, acoustical parameters such as intermolecular freelength (L_f), adiabatic compressibility (β), free volume (V_f), internal pressure (π), enthalpy (H) and their corresponding excess acoustical parameters like excess intermolecular freelength (L_f^E), excess adiabatic compressibility (β^E), excess free volume (V_f^E), excess internal pressure (π^E), excess enthalpy (H^E) and excess Gibb's free energy (G^{*E}) have been calculated. These results have been explained on the basis of molecular interactions present between the component molecules of the liquid mixtures.

Keywords:— *Acoustical parameters, density, ethanol, excess acoustical parameters; propylene glycol, speed of sound.*

I. INTRODUCTION

Study of acoustical parameters and excess acoustical parameters is most important data in explaining the strength of molecular interactions in binary liquid mixtures [1-3]. Molecular interactions in the liquid mixtures is of considerable elucidation of the structural properties of the molecules. The temperature dependence of these parameters gives important information about the molecular interactions between the component molecules of liquid mixtures. Propylene glycol is an organic compoun with the chemical formula $C_3H_8O_2$. Propylene glycol is a viscous and colourless liquid with faintly sweet taste. Propylene glycol is very much useful in pharmaceutical industry. It is also useful in edible items such as coffee-based drinks, liquid sweeteners, ice cream, whipped dairy products and soda. Ethanol is an organic compound with chemical formula C_2H_6O. Ethanol is also known as ethyl alcohol or drinking alcohol and it is a colourless liquid with slight chemical odour. Ethanol is very much useful as

antiseptic and as a solvent in fuels. As a part of ongoing research work [4-6], the authors are reporting here thermo-acoustical and their excess parameters in binary liquid mixtures of propylene glycol with ethanol at temperatures T = (298.15, 303.15, 308.15, 313.15 and 318.15)K over entire molefraction range of propylene glycol. The results are discussed with help of molecular interactions present between the components of liquid mixtures.

II. Experimental

The chemicals propylene glycol and ethanol used in the present investigation are of analytical reagent grade which are obtained from M/s Merck company, Germany. Further, they are purified by standard procedure. The different concentrations of the liquid mixture are prepared by varying molefractions with respect to Job's method of continuous variation. Stoppard conical flasks are used for preserving the prepared mixtures and the flasks are left undisturbed to attain thermal equilibrium. Ultrasonic pulse echo interferometer (Mittal enterprises, India) is used for speed of sound measurements and all these measurements are done at a fixed frequency of 3MHz. The temperature variations of pure liquids and liquid mixtures are done by using temperature controlled water bath by circulating water around the liquid cell which is present in interferometer. Specific gravity bottle is used for the measurement of densities of pure liquids and liquid mixtures with an accuracy of + or - 0.5%. An electronic weighing balance (Shimadzu AUY220, Japan) with a precision of + or - 0.1 mg is used for the measurements of mass of pure liquids or liquid mixtures. Average of 4 to 5 measurements is taken for each sample. Ostwald's viscometer is used for the measurement of viscosity of pure liquids and liquid mixtures. The time of flow of liquid in the viscometer is measured with an electronic stopwatch with a precision of 0.01s.

III. Theory

Acoustical parameters are evaluated from the experimentally measured values of ultrasonic velocity (u), viscosity (η) and density (ρ) by using the following equations which are given in our earlier papers [4,5].

$$\beta = 1/\rho u^2 \ m^2N\text{-}^1 \quad \text{.....(1)}$$

$$L_f = K.\ \beta^{1/2}\ \text{Å} \quad \text{.....(2)}$$

$$V_f = (M_{eff}\, u)^{3/2} / (K . \eta)^{3/2}\ m^3mol^{-1} \quad \text{.....(3)}$$

$$\pi = bRT\ ((K\eta)^{1/2}/(u)^{1/2}).\ ((\rho^{2/3}) / (M_{eff})^{7/6})\ \text{atm} \quad \text{.....(4)}$$

$$H = \pi . V_m J\ mol^{-1} \quad \text{.....(5)}$$

The corresponding excess acoustical parameters have been calculated by using the following equations,

$$\beta^E = \beta_{exp} - (X_1\beta_1 + X_2\beta_2)\ m^2N^{-1} \quad \text{.....(6)}$$

$$L_f^E = L_f(exp) - (X_1L_{f1} + X_2L_{f2})\ \text{Å} \quad \text{.....(7)}$$

$$V_f^E = V_{f(exp)} - (X_1V_{f1} + X_2V_{f2})\ m^3\ mol^{-1} \quad \text{.....(8)}$$

$$\pi^E = \pi_{exp} - (X_1\pi_1 + X_2\pi_2)\ \text{atm} \quad \text{.....(9)}$$

$$H^E = H_{exp} - (X_1H_1 + X_2H_2)\ J\ mol^{-1} \quad \text{.....(10)}$$

$$G^{*E} = RT\left[\ln\left(\frac{\eta V_m}{\eta_2 V_{m2}}\right) - x_1 \ln\left(\frac{\eta_1 V_{m1}}{\eta_2 V_{m2}}\right)\right]\ \text{Calmol}^1 \quad \text{.....11)}$$

IV. Results and Discussion

Generally acoustical and excess acoustical parameters are important in studying the nature of molecular interactions in liquid mixtures [7-9]. The excess acoustical

parameters are defined as the difference between the experimental values and ideal mixture values. They are a measure of non-ideality of the system as a consequence of associative or of other interactions [10]. Comparison of experimentally measured values of densities, ultrasonic velocities and viscosities of pure liquids together with the literature values is given in Table 1.

Table 1: The Values of Densities (r), Speeds of Sound (u) and Viscosities (η) of Pure Liquids Together with Literature Values at Temperature T=298.15K

Liquid	Density r(Kg . m^{-3})		Speed of sound u($m.s^{-1}$)		Viscosity η (m.Pa.S)	
	Exp	Lit	Exp	Lit	Exp	Lit
Propylene glycol	997.53	997.63 [11]	1544.77	1542.40 [11]	0.7654	0.762 [12]
Ethanol	789.46	789.00 [13]	1174.76	1176.00[13]	1.1198	1.1000 [13]

Table 2: The Values of Thermo-Acoustical Parameter– Intermolecular Free Length (L_f) in Binary Liquid Mixtures Containing Propylene Glycol and Ethanol at Temperatures T=(298.15, 303.15, 308.15, 313.15 and 318.15)K

(Propylene glycol + Ethanol)					
Mole Fraction of Propylene Glycol (X)	Intermolecular freelength L_f(Å)				
	298.15K	303.15K	308.15K	313.15K	318.15K
0.0000	0.1900	0.1965	0.2047	0.2140	0.2225
0.0811	0.1764	0.1819	0.1890	0.1972	0.2048
0.1658	0.1654	0.1705	0.1769	0.1844	0.1911
0.2541	0.1582	0.1629	0.1689	0.1756	0.1820
0.3463	0.1527	0.1569	0.1626	0.1690	0.1750
0.4428	0.1481	0.1523	0.1578	0.1639	0.1694
0.5438	0.1441	0.1481	0.1532	0.1590	0.1643
0.6497	0.1398	0.1437	0.1486	0.1542	0.1593
0.7607	0.1361	0.1398	0.1446	0.1499	0.1548
0.8773	0.1321	0.1356	0.1401	0.1452	0.1500
1.0000	0.1285	0.1319	0.1362	0.1411	0.1456

Table 3: The Values of Thermo-Acoustical Parameter– Adiabatic Compressibility (b) in Binary Liquid Mixtures Containing Propylene Glycol and Ethanol at Temperatures T=(298.15, 303.15, 308.15, 313.15 and 318.15)K

(Propylene glycol + Ethanol)					
Mole fraction of Propylene glycol (X)	Adiabatic compressibility b(10^{-11} $m^2.N^{-1}$)				
	298.15K	303.15K	308.15K	313.15K	318.15K
0.0000	91.78	98.19	105.05	113.18	120.65
0.0811	79.11	84.19	89.61	96.18	102.25
0.1658	69.56	73.95	78.50	84.04	89.03
0.2541	63.64	67.49	71.54	76.25	80.74
0.3463	59.32	62.63	66.30	70.58	74.67
0.4428	55.77	58.99	62.40	66.38	69.97
0.5438	52.79	55.78	58.85	62.52	65.83
0.6497	49.74	52.50	55.40	58.79	61.84
0.7607	47.10	49.71	52.44	55.57	58.42
0.8773	44.40	46.74	49.21	52.14	54.82
1.0000	42.01	44.22	46.54	49.23	51.67

Table 4: The Values of Thermo-Acoustical Parameter– Intermolecular Free Volume (V_f)) in Binary Liquid Mixtures Containing Propylene Glycol and Ethanol at Temperatures T=(298.15,303.15,308.15,313.15 and 318.15)K

(Propylene glycol + Ethanol)					
Mole fraction of Propylene glycol (X)	Free volume V_f($10^{-7}$$m^3$.$mol^{-1}$)				
	298.15K	303.15K	308.15K	313.15K	318.15K
0.0000	1.1972	1.1761	1.1615	1.1523	1.1400
0.0811	1.4444	1.4249	1.4121	1.4067	1.3960
0.1658	1.7396	1.7170	1.7058	1.7062	1.6995
0.2541	2.0353	2.0138	2.0041	2.0133	2.0054
0.3463	2.3820	2.3674	2.3614	2.3731	2.3679
0.4428	2.8195	2.8017	2.8000	2.8220	2.8269
0.5438	3.3265	3.3122	3.3232	3.3573	3.3752
0.6497	3.8859	3.8724	3.8809	3.9299	3.9604
0.7607	4.6199	4.6168	4.6451	4.7202	4.7597
0.8773	5.5212	5.5352	5.6019	5.7196	5.7826
1.0000	6.7845	6.8227	6.9095	7.0876	7.1961

Table 5: The Values of Thermo-Acoustical Parameter– Internal Pressure (π) in Binary Liquid Mixtures Containing Propylene Glycol and Ethanol at Temperatures T = (298.15, 303.15, 308.15, 313.15 and 318.15)K

(Propylene Glycol + Ethanol)					
Mole Fraction of Propylene Glycol (X)	Internal pressure $\pi(10^6 N.m^{-2})$				
	298.15K	303.15K	308.15K	313.15K	318.15K
0.0000	310.65	310.89	309.97	308.88	308.26
0.0811	286.67	286.46	285.28	283.91	283.07
0.1658	264.78	264.66	263.42	261.68	260.50
0.2541	246.82	246.35	245.20	243.38	242.33
0.3463	230.21	229.61	228.38	226.61	225.62
0.4428	213.67	213.14	211.83	210.08	208.92
0.5438	198.66	198.07	196.67	194.95	193.67
0.6497	185.32	184.74	183.54	181.81	180.47
0.7607	171.51	170.80	169.42	167.68	166.39
0.8773	158.73	157.92	156.43	154.56	153.24
1.0000	145.72	144.85	143.44	141.54	140.15

Table 6: The Values of Thermo-Acoustical Parameter– Enthalpy (H) in Binary Liquid Mixtures Containing Propylene Glycol and Ethanol at Temperatures T = (298.15, 303.15, 308.15, 313.15 and 318.15)K

(Propylene Glycol + Ethanol)					
Mole Fraction of Pro-pylene Glycol (X)	Enthalpy $H(10^2 J.mol^{-1})$				
	298.15K	303.15K	308.15K	313.15K	318.15K
0.0000	0.1900	0.1965	0.2047	0.2140	0.2225
0.0811	0.1764	0.1819	0.1890	0.1972	0.2048
0.1658	0.1654	0.1705	0.1769	0.1844	0.1911
0.2541	0.1582	0.1629	0.1689	0.1756	0.1820
0.3463	0.1527	0.1569	0.1626	0.1690	0.1750
0.4428	0.1481	0.1523	0.1578	0.1639	0.1694
0.5438	0.1441	0.1481	0.1532	0.1590	0.1643
0.6497	0.1398	0.1437	0.1486	0.1542	0.1593
0.7607	0.1361	0.1398	0.1446	0.1499	0.1548
0.8773	0.1321	0.1356	0.1401	0.1452	0.1500
1.0000	0.1285	0.1319	0.1362	0.1411	0.1456

The values of acoustical parameters such as intermolecular freelength (L_f), adiabatic compressibility (b), free volume (V_f), internal pressure (π) and enthalpy (H) at temperatures T=(298.15, 303.15, 308.15, 313.15 and 318.15)K are given in Table 2 to Table 6 respectively and the values of excess acoustical parameters such as excess intermolecular freelength (L_f^E), excess adiabatic compressibility (b^E), excess free volume (V_f^E), excess internal pressure (π^E), and excess enthalpy (H^E) at temperatures T=(298.15, 303.15, 308.15, 313.15 and 318.15) K are calculated and their variations with temperatures T= (298.15, 303.15, 308.15, 313.15 and 318.15)K and molefractions of propylene glycol are represented in the figures from Figure 1 to Figure 6.

The variations of excess intermolecular freelength ($\mathbf{L_f^E}$) with the molefraction of propylene glycol ranging from 0 to 1 at temperatures T=(298.15, 303.15, 308.15, 313.15 and 318.15)K in the binary liquid mixtures containing propylene glycol and ethanol is as shown in Figure 1. From Figure 1, it is observed that the excess intermolecular free length values are negative for the entire mole fraction range.

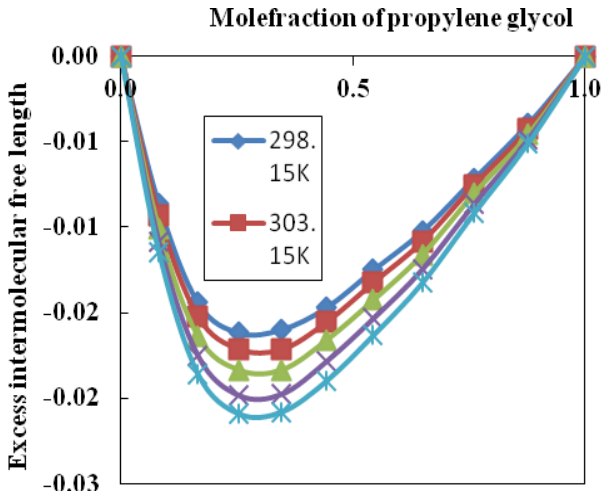

Figure 1: Temperature dependence of excess intermolecular freelength (L_f^E)

The negative values of excess intermolecular freelength suggest that there exist strong interactions between the components of liquid mixture [14].

Figure 2 represents the variations of excess adiabatic compressibility (β^E) in binary liquid mixtures containing propylene glycol and ethanol over the entire molefraction range of propylene glycol at temperatures T=(298.15, 303.15, 308.15, 313.15 and 318.15)K From Figure 2, it is observed that the excess adiabatic compressibility (β^E) values are negative. This indicates that the attractive forces between the molecules of components are stronger [15] than the intramolecular attractions in each component.

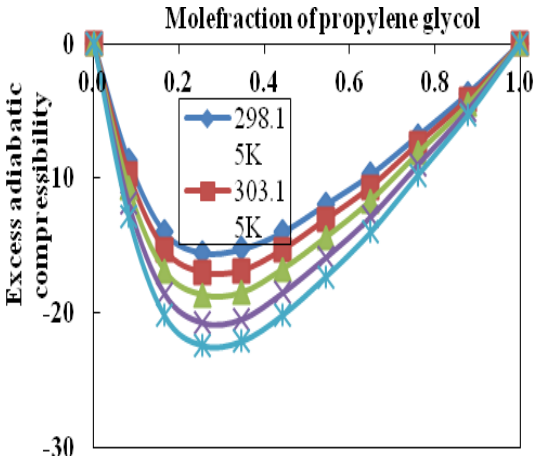

Figure 2: Temperature dependence of excess adiabatic compressibility (β^E)

According to Fort and Moore [16] a negative excess compressibility is an indication of strong hetromolecular interaction in the liquid mixtures which is attributable to charge transfer, dipole-dipole, dipole-induced dipole interactions, and hydrogen bonding between unlike components. In the present study, the excess compressibility is negative and it suggests the existence of strong intermolecular interactions in the binary liquid mixture.

The variation of excess free volume (V_f^E) with the molefraction of propylene glycol is represented in Figure 3. It is observed from Figure 3 is that, V_f^E values are negative over the entire composition range.

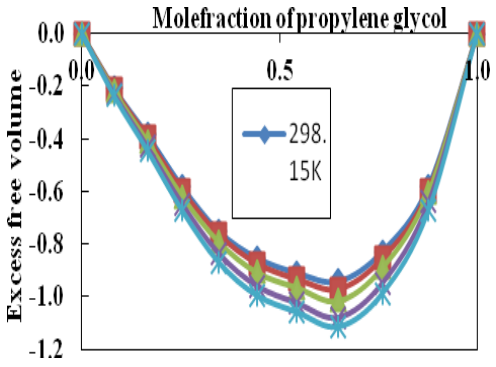

Figure 3: Temperature dependence of excess free volume (V_f^E)

This suggests that the component molecules are more close together in the liquid mixture than in pure liquids forming the mixture, indicating that strong attractive interactions [17-18].

Figure 4 represents the variations of excess internal pressure (π^E). It is observed from Figure 4 is that π^E values are negative over the entire composition range of propylene glycol.

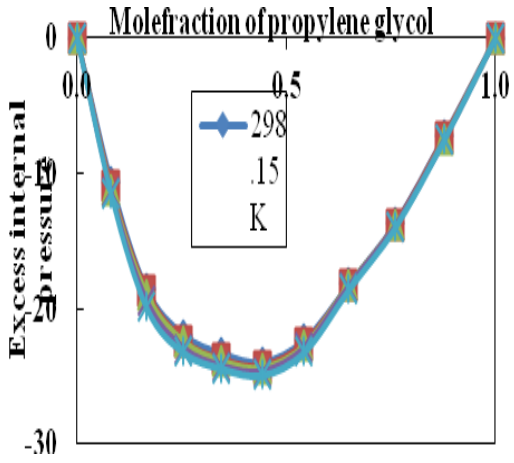

Figure 4: Temperature Dependence of Excess Internal Pressure (π^E).

According to Rama Rao et al.[19] and Misra et al. [20] if the excess internal pressure values are negative, the interactions are strong. Excess enthalpy (H^E) is an important solution thermodynamic property. This solution property can provide information about the molecular interactions and macroscopic behaviour of liquid mixtures.

The variations of excess enthalpy in the present binary system are as shown in Figure 5. From Figure 5, it is observed that H^E values are negative over the entire composition range of propylene glycol. The negative values of H^E suggest strong interactions [20-21].

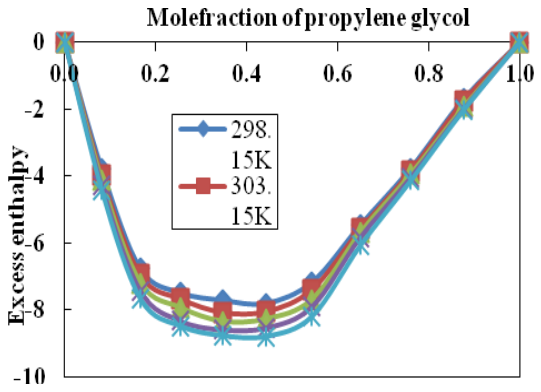

Figure 5: Temperature Dependence of Excess Enthalpy H^E

The excess Gibb's free energy of activation (G^{*E}) is evaluated from viscosity data. According to Oswal *et al.*[22] and Reed *et al.*[23] the positive G^{*E} may be attributed to specific interactions. The variations of excess Gibb's free energy of activation (G^{*E}) in the binary liquid mixture containing propylene glycol and ethanol over the entire molefraction range of propylene glycol at temperatures T= (298.15, 303.15, 308.15, 313.15 and 318.15)K is as shown in Figure 6. It is observed from Figure 6 is that G^{*E} values are positive. According to Rathnam et al. [24] and Chorazewski [25], the positive values of G^{*E} show strong interactions.

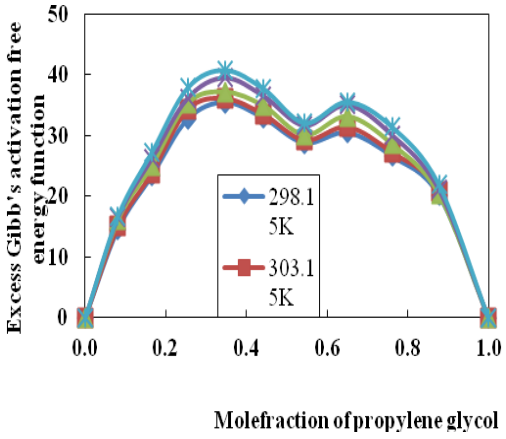

Figure 6: Temperature dependence of excess Gibb's free energy G^{*E}

V. CONCLUSIONS

Speed of sound, density and viscosity values are measured in the binary liquid mixtures containing propylene glycol and ethanol at temperatures T = (298.15, 303.15, 308.15, 313.15 and 318.15)K. By using these values, acoustical and excess acoustical parameters have been calculated over the entire molefraction range of propylene glycol. An analysis of these results suggests the presence of strong intermolecular interactions in the binary liquid mixtures. Also the strength of intermolecular interactions is observed to be decreased in the present binary system with temperature. The anomalous relationship is observed in various excess parameters may be attributed to the characteristic property of strong dipolar interactions between component molecules.

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