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Ultrasonic and Volumetric Investigations of γ-Butyrolactone with Aliphatic Alcohols

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Abstract
Densities (ρ) and speeds of sound (u) have been determined for the binary liquid mixtures of γ-butyrolactone (GBL) with 1-propanol (1-Pro), 2-propanol (2-Pro), 1-butanol (1-But) and 2-butanol (2-But) at 303.15, 308.15, and 313.15 K and entire composition range. From the experimental results, the excess molar volume (V^E), and deviation in isentropic compressibility ($\Delta\kappa_s$) were calculated. The computed properties have been fitted to a Redlich-Kister type polynomial equation to derive binary coefficients and standard deviations.
Key Words: γ-Butyrolactone, Aliphatic alcohols, Excess molar volume, Deviation in isentropic compressibility

I. INTRODUCTION

Studies on thermodynamic properties of binary liquid mixtures provide information on the nature of interactions in the constituent binaries. In continuation of our research program to determine the thermodynamic properties of binary liquid mixtures [1-7], we report here in the excess molar volume (V^E) and deviation in isentropic compressibility ($\Delta\kappa_s$) of the binary systems: γ-butyrolactone (GBL) with homologous series of aliphatic alcohols (1-propanol, 2-propanol, 1-butanol and 2-butanol).

γ–butyrolactone is an important solvent having several advantageous physico-chemical properties such as a broad liquid range (–45 ^{0}C to 205 ^{0}C) and medium relative permittivity (41.65 at 25 ^{0}C). It is an excellent electrolytic solvent having wide applications as a medium for any chemical and electrochemical reactions. The usefulness of GBL as a solvent in lithium batteries is broadly known [8-10]. Alcohols are used as hydraulic fluids, in medications for animals, as an antiseptic agent in manufacturing of perfumes, flavors, dyestuffs and paints removers.

A survey of literature reveals that these properties are not yet reported for the selected γ-butyrolactone and alcohol systems. Reddy and Naidu [11-12] have studied the molecular interactions of methyl ethyl ketone and isobutyl ketone with same alcohols. Dharmaraju *et.al.* [13] have reported the excess volumes and isentropic compressibilities of acetonitrile with alcohols. However, no attempt has been made to study the interactions between GBL and n-alkanols.

The results have been fitted to Redlich-Kister type polynomial equation using multiparametric nonlinear regression analysis [14] to derive the binary coefficients and to estimate the standard deviation between experimental and calculated data.

II. EXPERIMENTAL SECTION

2.1 MATERIALS

γ-butyrolactone (Aldrich, >99 mol %) was purified by fractional distillation under reduced pressure as reported in the literature [15]. 1-propanol, 2-propanol, 1-butanol and 2-butanol were obtained from Merck (>99%) India. All solvents were used after single distillation and the isomeric alcohols were stored over 3A x 1.5 nm molecular sieves. The purity of the samples was tested by measuring their physical properties; density and speed of sound. The experimental densities and speeds of sound of pure substances and their comparison with literature values are listed in Table 1.

TABLE 1 – Experimental Densities (ρ) and Speeds of Sound (u) of Pure Liquids at T = 303.15 K.

	$10^{-3}.\rho$/(kg·m^{-3})		u/(m·s^{-1})	
Component	exptl.	lit.	exptl.	lit.
γ-Butyrolactone	1.12032	1.11883[21]	1498.8	1500.0[22]
1-Propanol	0.80801[#]	0.79959[23]	1227.5[#]	1212.0[24]
2-Propanol	0.79560[#]	0.78100[25]	1154.7[*]	
1-Butanol	0.80654[#]	0.8060[26]	1252[#]	1239[26]
2-Butanol	0.79883	0.79891[27]	1182.6[*]	1174[24]

values at T=298.15K and * values at T=308.15K

2.2 APPARATUS AND PROCEDURE

Binary mixtures were prepared by mass in air tight bottles. The mass measurements were performed on a Dhona 100 DS, India, single pan analytical balance with a resolution of ± 0.01·10^{-6} kg. The required properties of the mixture were measured on the same day. The uncertainty in mole fraction was estimated to be less than ± 1·10^{-4}.

Density of pure liquids and their mixtures were determined by using $1{\cdot}10^{-5}$ m^3 double arm pycnometer [7]. The uncertainties in density and excess molar volume values were found to be $\pm\ 4{\cdot}10^{-5}$ $g{\cdot}cm^{-3}$ and $1{\cdot}10^{-3}$ $cm^3{\cdot}mol^{-1}$.

Speeds of sound were determined by using an ultrasonic interferometer (Model M-82, Mittal Enterprises, India) operating at 2 MHz frequency. The working principle used in the measurement of the speed of sound through a medium was based on the accurate determination of the wavelength of ultrasonic waves of known frequency produced by a quartz crystal in the measuring cell [4-7] The temperature of the solution was controlled by circulating water at a desired temperature through the jacket of the double-walled cell. The speed of sound was measured with relative uncertainty of 0.3%.

In all the property measurements the temperature was controlled within ± 0.01 K using a constant temperature bath (INSREF model IRI-016 C, India), and the temperature was monitored with a platinum resistance thermometer with an accuracy of ± 0.001 K and an uncertainty of ± 0.004 K.

III. RESULTS AND DISCUSSION

The values of density (ρ) and speed of sound (u) for the binary mixtures of γ-butyrolactone (1) with 1-propanol (2), 2-propanol (2), 1-butanol (2) and 2-butanol (2) at the temperatures of T= 303.15, 308.15, and 313.15 K along with the mole fraction are listed in Table 2.

The density values have been used to calculate excess molar volumes (V^E) using the following equation:

$$V^E = (x_1M_1 + x_2M_2) / \rho_m - (x_1M_1/\rho_1 + x_2M_2/\rho_2) \quad \ldots.(1)$$

where ρ_m is the density of the mixture; x_1, M_1, ρ_1 and x_2, M_2 and ρ_2 are the mole fraction, molar mass and density of pure components respectively.

The speed of sound 'u' is used to calculate the isentropic compressibility (κ_s) using the equation

$$\kappa_s = 1/(u^2.\rho) \quad \ldots.(2)$$

The deviation from isentropic compressibility ($\Delta\kappa_s$) have been evaluated using the equation

$$\Delta\kappa_s = \kappa_s - (\Phi_1\kappa_{s1} + \Phi_2\kappa_{S2}) \quad \ldots.(3)$$

where κ_{s1}, κ_{s2} and κ_s are the isentropic compressibility of the pure components and observed isentropic compressibility of liquid mixture respectively. Φ_i is the volume fraction of pure components and is calculated from the individual pure molar volumes, V_i, with the relation:

$$\Phi_i = x_iV_i/(\Sigma x_iV_i) \quad \ldots.(4)$$

The excess properties ΔY were fitted by the method of non linear least squares to a Redlich-Kister type polynomial [11]

$$\Delta Y = x_1x_2\,\Sigma A_i\,(x_1\text{-}x_2)^i \quad \ldots.(5)$$

In each case, the optimum number of coefficients A_i was determined from an examination of the variation of standard deviation (σ)as calculated by:

$$\sigma(\Delta Y) = [\Sigma(\Delta Y_{obs} - \Delta Y_{cal}) / (n - m)]^{1/2} \quad \ldots.(6)$$

where 'n' represents the number of experimental points and 'm' is the number of coefficients. It is found that for the solution of the fifth degree polynomial, the agreement between the experimental values and the calculated ones is satisfactory. The derived parameters (A_i) and the estimated standard deviation (σ) for V^E and $\Delta\kappa_s$ are given in Table 3.

3.1 MOLAR VOLUME

The excess molar volumes (V^E) for GBL+1-pro, +2-pro, +1-but and +2-but are observed to be negative over the entire range of composition at temperatures 303.15, 308.15 and 313.15 K indicating negative deviations from ideal behavior. The largest deviations for all systems are located at $x_1 \approx 0.5\text{-}0.6$ which can be observed from figure 1. The negative V^E values for aliphatic alcohols at 303.15 K fall in the sequence:

1-But > 1-Pro> 2-Pro > 2-But > 0

TABLE 2- The Values of Density (ρ) and Speed of Sound (u) for the Binary Liquid Mixtures at Various Temperatures (K)

x_1	$10^{-3}{\cdot}\rho$/(kg·m^{-3})			u/(m·s^{-1})		
	303.15	**308.15**	**313.15**	**303.15**	**308.15**	**313.15**
	γ-Butyrolactone (1) + 1-Propanol (2)					
0.0000	0.8233	0.8180	0.8144	1226.3	1227.5	1219.7
0.0207	0.8309	0.8253	0.8226	1231.4	1234.6	1225.9
0.1409	0.8705	0.8654	0.8628	1264.0	1266.5	1261.2
0.2623	0.9094	0.9041	0.9015	1300.4	1300.6	1296.4
0.3852	0.9474	0.9424	0.9395	1337.8	1338.1	1333.9
0.4913	0.9794	0.9746	0.9715	1368.4	1369.3	1363.1
0.6003	1.0112	1.0064	1.0033	1391.4	1394.5	1386.4
0.7242	1.0462	1.0418	1.0383	1423.2	1420.3	1409.3
0.8512	1.0811	1.0766	1.0727	1457.1	1445.1	1433.9
0.9776	1.1149	1.1095	1.1054	1497.5	1472.9	1466.0
1.0000	1.1203	1.1141	1.1096	1498.8	1480.9	1469.0
	γ-Butyrolactone (1) + 1-Butanol (2)					
0.0000	0.8038	0.7991	0.7959	1203.0	1201.7	1205.2
0.0214	0.8111	0.8070	0.8026	1212.5	1216.3	1212.5
0.1441	0.8509	0.8464	0.8420	1238.3	1250.8	1242.5
0.2658	0.8914	0.8866	0.8837	1265.7	1281.2	1272.6
0.3914	0.9326	0.9276	0.9256	1303.4	1313.8	1312.5
0.4966	0.9670	0.9622	0.9596	1336.7	1343.5	1348.3
0.6264	1.0085	1.0026	0.9984	1378.2	1377.0	1382.5
0.7621	1.0522	1.0455	1.0364	1424.4	1410.5	1415.4
0.8728	1.0865	1.0785	1.0699	1456.3	1441.8	1440.8
0.9824	1.1152	1.1095	1.1043	1495.3	1478.6	1464.4
1.0000	1.1203	1.1141	1.1096	1498.8	1480.9	1469.0
	γ-Butyrolactone (1) + 2-Propanol (2)					
0.0000	0.7913	0.7857	0.7817	1151.8	1154.7	1144.5
0.0222	0.7988	0.7934	0.7893	1164.0	1161.2	1154.6
0.1463	0.8412	0.8359	0.8316	1204.1	1203.2	1194.1
0.2695	0.8829	0.8775	0.8734	1243.9	1243.5	1234.8
0.3947	0.9251	0.9194	0.9155	1286.3	1284.9	1276.5
0.4999	0.9600	0.9541	0.9504	1326.2	1323.9	1313.6
0.6003	0.9930	0.9867	0.9834	1362.4	1360.4	1346.2
0.7253	1.0335	1.0270	1.0239	1399.4	1398.7	1388.1
0.8510	1.0735	1.0672	1.0635	1438.3	1436.3	1430.5
0.9758	1.1128	1.1066	1.1024	1486.3	1478.0	1472.7
1.0000	1.1203	1.1141	1.1096	1498.8	1480.9	1469.0
	γ-Butyrolactone (1) + 2-Butanol (2)					
0.0000	0.7988	0.7936	0.7899	1180.1	1182.6	1180.7
0.0279	0.8067	0.8015	0.7981	1187.3	1187.6	1186.8
0.1719	0.8466	0.8417	0.8383	1218.3	1216.3	1217.1
0.3115	0.8872	0.8824	0.8791	1252.1	1250.5	1251.2
0.4437	0.9275	0.9228	0.9196	1290.3	1289.4	1289.6
0.5500	0.9615	0.9567	0.9535	1326.1	1324.9	1324.2
0.6486	0.9941	0.9891	0.9856	1357.5	1358.7	1355.2
0.7642	1.0340	1.0286	1.0247	1397.0	1397.1	1393.1
0.8748	1.0737	1.0681	1.0639	1439.2	1436.5	1433.2
0.9814	1.1135	1.1073	1.1029	1489.3	1477.5	1470.2
1.0000	1.1203	1.1141	1.1096	1498.8	1480.9	1469.0

The same trend is also observed at other temperatures (i.e., 308.15 and 313.15 K). The negative V^E values are increasing with increasing chain length of the alcohol molecules.

The negative V^E values suggests that specific interactions [16] are acting between the unlike molecules and these interactions are due to inter-molecular H-bonding. It is well known that alkanols are strongly self associated with degree of association depending on chain length, the position of the –OH group and temperature. GBL structure is stabilized by dipolar-dipole interactions. Thus, both GBL and alkanols are self-associated liquids [17].

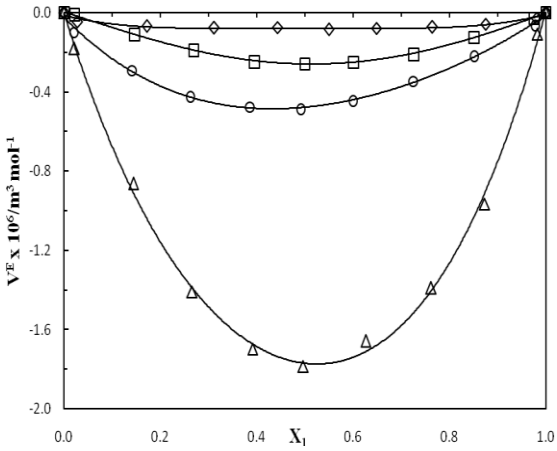

***Fig. 1** Variation of excess molar volumes (V^E) versus mole fraction (x_1) of the binary mixtures of γ-butyrolactone (1) with ○; 1-propanol (2), Δ; 1-butanol (2), □; 2-propanol (2) and ◊; 2-butanol (2) at 303.15 K.*

The negative V^E values for all the systems may also be discussed in terms of several effects which may be arbitrarily divided into physical, chemical and geometrical contributions [18]. The physical interactions involve mainly dispersion forces giving a positive contribution to V^E (Aminabhavi et al., 1993). The chemical or specific interactions between constituent molecules of the mixture results decrease in volume. In the present investigation, specific interaction between alkanol and GBL molecules takes place through dipole-dipole interactions, forming the complex through hydrogen bond formation. The structural contributions arising from the geometrical fitting of one component into the other, due to differences in the molar volumes and free volumes between components, lead to negative contributions. The effect of temperature on V^E is noteworthy. There is a gradual decrease, followed by an increase in V^E with a rise in temperature for all mixtures.

3.2 ISENTROPIC COMPRESSIBILITY

The isotherm of $\Delta\kappa_s$ for the systems of GBL +1-pro, +2-pro, +1-but and +2-but shows negative deviations over the entire range of volume fraction and become more negative at higher temperatures except in the case of 2-propanol. The negative $\Delta\kappa_s$ values for aliphatic alcohols at 313.15 K fall in the sequence:

1-But > 2-Pro> 1-Pro > 2-But > 0

The observed trend for both V^E and $\Delta\kappa_s$ has negative values. This similar trend in both the properties lends support to the existence of specific interactions between GBL and alcohols which leads to volume reduction of the system.

TABLE-3 Binary Coefficients A_i and Corresponding Standard Deviation (σ) of Equation (6)

Temp	A_0	A_1	A_2	A_3	A_4	σ
	γ-Butyrolactone (1) + 1-Propanol (2)					
	$10^6 \cdot V^E/(m^3 \cdot mol^{-1})$					
303.15	-1.96	0.39	0.75	0.26	-2.25	0.014
308.15	-2.29	0.12	0.5	-0.37	-2.86	0.014
313.15	-2.66	0.16	0.96	0.41	-4.9	0.025
	$10^{11} \cdot \Delta\kappa_s/(m^2 \cdot N^{-1})$					
303.15	-21.97	8.16	12.46	-8.702	-16.27	0.094
308.15	-24.44	2.6942	12.17	5.91	-13.04	0.073
313.15	-26.42	6.85	14.55	1.046	-19.36	0.048
	γ-Butyrolactone (1) + 1-Butanol (2)					
	$10^6 \cdot V^E/(m^3 \cdot mol^{-1})$					
303.15	-7.08	0.046	-1.192	-1.74	-0.21	0.035
308.15	-7.34	0.19	1.23	-0.05	-3.43	0.042
313.15	-7.88	2.5	6.16	-2.15	-3.64	0.024
	$10^{11} \cdot \Delta\kappa_s/(m^2 \cdot N^{-1})$					
303.15	-29.2	0.53	11.23	9.23	-23.88	0.224
308.15	-33.199	10.54	13.61	14.102	-44.25	0.303
313.15	-35.33	7.09	20.02	0.61	-25.34	0.124
	γ-Butyrolactone (1) + 2-Propanol (2)					
	$10^6 \cdot V^E/(m^3 \cdot mol^{-1})$					
303.15	-1.04	-0.036	0.14	-0.13	0.12	0.004
308.15	-1.08	0.33	0.36	-0.15	-0.73	0.003
313.15	-1.33	-0.18	0.12	-0.02	-0.13	0.007
	$10^{11} \cdot \Delta\kappa_s/(m^2 \cdot N^{-1})$					
303.15	-32.63	3.25	12.68	20.51	-23.76	0.153
308.15	-33.03	3.59	2.99	4.81	-6.6	0.151
313.15	-34.59	6.21	9.25	-1.37	-30.46	0.152
	γ-Butyrolactone (1) + 2-Butanol (2)					
	$10^6 \cdot V^E/(m^3 \cdot mol^{-1})$					
303.15	-0.34	-0.008	0.25	0.29	-1.41	0.008
308.15	-0.7	-0.03	0.41	0.32	-1.56	0.005
313.15	-1.05	-0.02	1.17	0.67	-2.84	0.008
	$10^{11} \cdot \Delta\kappa_s/(m^2 \cdot N^{-1})$					
303.15	-21.85	1.41	10.36	6.69	-15.36	0.049
308.15	-23.35	-1.73	9.47	0.54	-12.13	0.055
313.15	-25.34	0.503	11.08	-3.16	-23.195	0.063

Kiyohara and Benson [19] suggested that $\Delta\kappa_s$ is the resultant of several opposing effects. A strong molecular interaction through H-bonding, charge transfer, dipole-induced dipole and dipole-dipole interactions [20] and orientation order of molecules which leads to a more compact structure contributes negative $\Delta\kappa_s$. The magnitude of the various contributions depends mainly on the relative molecular size of the components.

IV. CONCLUSIONS

This paper reports experimental data for density and speed of sound at T = 303.15, 308.15 and 313.15 K for four binary systems of GBL+1-pro, +2-pro, +1-but and +2-but. The results are analyzed to explain the intermolecular interactions between mixing components.

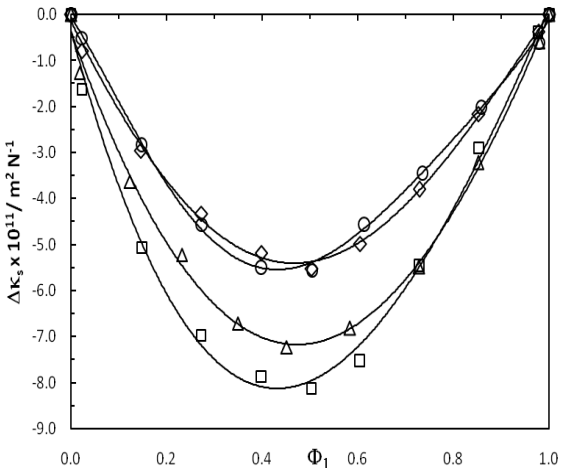

Fig. 2 *Variation of deviation in isentropic compressibility ($\Delta\kappa_s$) versus volume fraction (Φ_1) of the binary mixtures of γ-butyrolactone (1) with ○; 1-propanol (2), Δ; 1-butanol (2), □; 2-propanol (2) and ◊; 2-butanol (2) at 303.15 K.*

Position of hydroxyl group with alkyl chain length has shown significant effects on thermodynamic properties of the investigated systems. The computed excess molar volume (V^E) and deviation in isentropic compressibility ($\Delta\kappa_s$) values are fitted to Redlich-Kister type equation.

V. ACKNOWLEDGEMENT

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