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### Speed of Sound and Viscosities of Butyl Acetate and Substituted Alcohols at 303.15 K

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## SPEED OF SOUND AND VISCOSITIES OF BUTYL ACETATE AND SUBSTITUTED ALCOHOLS AT 303.15 K

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Speed of sound and viscosities at 303.15 K and atmospheric pressure are reported for six binary liquid mixtures containing butylacetate as common component and propan-1-ol, butan-1-ol, pentan-1-ol, propan-2-ol, 2 methyl propan-1-ol and 3 methyl butan-1-ol as non common components. The speed of sound have been analysed in terms of free length theory (FLT) and collision factor theory (CFT). The speed of sound data were also used along with densities to compute isentropic compressibilities ( $K_s$ ) and the deviations in isentropic compressibility ( $\Delta K_s$ ).

On the other hand, the viscosity values have been discussed in terms of viscosity-composition relations developed for binary solutions by Greenberg and Nissan and Katti and Chaudhari. Further, the study has been extended to investigate intermolecular interactions in terms of excess free energy for activation of flow ( $G^E$ ), interaction parameter ( $d$ ) and interaction energy ( $W_{A...}$ ) for the mixtures mentioned. The extent and nature of interaction among the component liquids are discussed.

*Keywords:* Butylacetate; hydrogenbonding; alcohols; CFT; FLT; Gibbs free energy

### INTRODUCTION

Speed of sound methods find extensive applications owing to their ability of characterizing the physico chemical behaviour of liquid systems from absorption and speed of sound data. The measurement of the speed of sound in solutions formed by liquid components reveals their degree of deviation from ideality, eventual molecular associations in solutions as well as important correlations with various parameters, such as adiabatic and isothermal compressibilities, ratio

of heat capacities, free volume and internal pressure. The study of transport properties of liquid mixtures, on the other hand, is also informative as it gives an insight into the intermolecular forces and the macroscopic structure of liquids [1]. Alcohols are strongly associated [2–3] and for binary solutions rich in alcohol a three dimensional network of hydrogen bonded alcohol molecules is believed to be present [4, 5] viscosities for the binary mixtures of butyl acetate with butanol [6], 2-hexanone [6], amylacetate [6], carbon-tetrachloride [7], alkanes [8] have been reported earlier. But no attempt has been made on the title systems. Hence, we report here speed of sound, viscosities for the binary mixtures butyl-acetate with propan-1-ol, butan-1-ol, pentan-1-ol, propan-2-ol, 2-methyl propan-1-ol, and 3-methyl butan-1-ol at 303.15 K. Speed of sound data have been analysed in terms of free length theory (FLT) due to Jacobson [9] and Collision factor theory (CFT) developed by Schaafs [10], viscosity data have been analysed in terms of excess viscosities ( $\eta^E$ ) of the mixtures were calculated by the relation suggested by Fort and More [11].

The theoretical aspects of FLT and CFT have been described in detail by Chaudary and Naidu [15] and excess viscosity relation, Eyring relation, Kendall relation and Katti and Chaudhari relation have been described in detail by Rambabu [16] and Raman [16]. The results have been evaluated and the interaction between unlike molecules have been discussed in terms of these parameters.

## EXPERIMENTAL

*Materials* The method of purifying the various components and checking their purity have been described earlier [17].

Speed of sound was measured with a single-crystal interferometer [18] at a frequency of 3 MHz and was accurate to  $\pm 0.15\%$ . All measurements were made at constant temperature by circulating water around the cell from a U-10 thermostat, maintained at  $303.15 \pm 0.01\text{K}$ . Densities of the mixtures were computed from the measured excess volume data [17] using the relation.

$$\rho = \frac{XM_1 + (1 - X)M_2}{V^0 \pm V^E} \quad (1)$$

where  $X$  denotes the molefractions of butyl acetate.  $V^0$  and  $V^E$  stand for ideal molar volume and excess molar volume respectively.  $M_1$  and  $M_2$  represent molecular weights.

Viscosities were measured using a suspended level ubbelohde viscometer. The viscometer was calibrated at 303.15 K using distilled water. The viscometer constant  $K$  was calculated from viscosity,  $\eta_w$ , density,  $\rho_w$  and flow time,  $t_w$  of water using the relation  $K = \eta_w / \rho_w \cdot t_w$ . The average of these measurements which do not differ more than  $0.0005 \text{ cm}^2/\text{S}^2$  was taken as  $K$  value. An electronic stop watch capable of measuring time to  $\pm 0.015 \text{ S}$  was used for time measurement. Kinetic energy corrections are applied and found to be negligible. The estimated error in viscosity is  $\pm 5 \times 10^{-4}$  mpa.s. The performable of the viscometer was assessed by measuring and comparing the viscosities of the pure components with the values reported in the literature [19].

## RESULTS AND DISCUSSION

The surface area ( $\gamma$ ) and collision factor ( $s$ ) of the pure components used in FLT and CFT were calculated using the experimental sound velocities and densities, critical temperature, surface tension and the ratio of specific heats which were used in the calculation of molar volume at absolute zero ( $V_0$ ) and the average molecular radius ( $\gamma_m$ ) were taken from the literature [20–23]. The values of molar volume ( $V_m$ ), available volume ( $V_a$ ), free length ( $L_f$ ), surface area ( $\gamma$ ), collision factor ( $s$ ) and the average radius of the molecular ( $r_m$ ) of the pure components are given in Table I.

Speed of sound ( $u$ ) along with the density ( $\rho$ ) data are used to calculate isentropic compressibilities ( $K_S$ ) and deviation in isentropic compressibility ( $\Delta K_S$ )

$$K_S = \frac{1}{\mu^2 \rho} \quad (2)$$

$$\Delta K_S = K_S - \phi_1 K_{S1} - \phi_2 K_{S2} \quad (3)$$

where  $\phi_1$  and  $\phi_2$  are the ideal volume fractions of components 1 and 2 respectively and  $K_S$ ,  $K_{S1}$ ,  $K_{S2}$ , are the isentropic compressibilities of the mixture and components 1 and 2 respectively. The values of  $K_S$  are

TABLE I Molar Volume,  $V$ , Molar Volume at absolute zero,  $V_0$ , available Volume,  $V_a$ , Free length,  $L_f$ , Surface area,  $Y$ , Collision Factor,  $S$  and average Molecular radius,  $r_m$ , of the Pure liquid Components of 303.15 K

Component	$V_m$	$V_0$	$V_a$	$L_f$	$Y$	$S$	$r_m$
	$\text{Cm}^3, \text{mol}^{-1}$			$\text{\AA}$			$\text{\AA}$
butyl acetate	133.323	106.743	26.579	0.5753	92.277	1.5365	2.934
Propan-1-ol	75.503	58.825	16.678	0.5938	56.174	1.7304	2.438
butan-1-ol	92.412	73.278	19.134	0.5752	66.529	1.7149	2.539
Pentan-1-ol	109.145	87.679	21.466	0.5586	76.855	1.7014	2.714
Propan-2-ol	77.353	58.921	18.432	0.6352	58.035	1.6462	2.359
2 methyl propan-1-ol	93.304	73.259	20.046	0.6041	66.366	1.6595	2.537
3 methyl butan-1-ol	109.937	88.069	21.868	0.5776	75.719	1.6712	2.709

TABLE II Volume Fraction, ( $\phi_1$ ), Density, ( $\rho$ ), experimental Speed of sound  $U_{\text{exp}}$ , predicted Speed of sounds,  $U_{\text{FLT}}$ ,  $U_{\text{CFT}}$ , isentropic Compressibility,  $K_S$  and deviation in isentropic Compressibility,  $\Delta K_S$ , for binary mixtures at 303.15 K

$\phi_1$	$\rho$	$U^{\text{exp}}$	$U_{\text{FLT}}$	$U_{\text{CFT}}$	$K_S$	$\Delta K_S$
	$\text{g.cm}^{-3}$	$\text{m.s.}^{-1}$			$\text{TPa}^{-1}$	
butyl acetate + propan-1-ol						
0.0000	0.79600	1191	1191	1191	886	0
0.1671	0.80813	1180	1188	1190	881	12
0.2058	0.81096	1178	1187	1189	889	14
0.4923	0.83194	1168	1182	1186	881	22
0.5459	0.83589	1168	1181	1185	877	21
0.6554	0.84406	1168	1179	1183	868	18
0.7338	0.84999	1169	1178	1182	861	15
0.8339	0.85769	1172	1176	1180	849	9
0.8930	0.86238	1173	1175	1178	843	6
0.9354	0.86584	1173	1175	1177	839	4
1.0000	0.87127	1175	1175	1175	831	0
butyl acetate + butan-1-ol						
0.0000	0.80201	1225	1225	1225	831	0
0.1554	0.81205	1212	1217	1238	838	17
0.1929	0.81449	1209	1219	1245	839	18
0.3695	0.82634	1197	1206	1247	845	14
0.5203	0.83681	1188	1198	1244	847	16
0.5702	0.84030	1186	1195	1242	846	15
0.7172	0.85084	1181	1186	1229	843	12
0.7655	0.85434	1178	1183	1222	843	12
0.8125	0.85773	1179	1183	1215	839	8
0.9089	0.86473	1177	1178	1197	835	4
1.0000	0.87127	1175	1175	1175	831	0

TABLE 2 (Continued)

butyl acetate – propan-1-ol						
0.0000	0.80759	1257	1257	1257	784	0
0.1217	0.81476	1240	1247	1280	798	8
0.1804	0.81829	1234	1242	1289	803	11
0.3666	0.82965	1215	1226	1302	816	15
0.4123	0.83251	1213	1223	1303	816	13
0.5881	0.84368	1202	1208	1291	820	8
0.6673	0.84888	1197	1201	1279	822	7
0.7406	0.85369	1188	1195	1264	830	5
0.8219	0.85912	1187	1188	1242	826	3
0.8832	0.86326	1184	1183	1222	826	0
1.0000	0.87127	1175	1175	1175	831	0
butyl acetate + propan-1-ol						
0.0000	0.77691	1127	1127	1127	1013	0
0.1388	0.78824	1129	1133	1136	995	7
0.1926	0.79283	1129	1135	1140	990	12
0.4696	0.81770	1136	1147	1156	948	20
0.5866	0.82900	1143	1141	1162	923	17
0.6459	0.83489	1147	1142	1164	910	15
0.6940	0.83975	1150	1144	1166	900	13
0.8469	0.85555	1162	1148	1172	866	7
0.8888	0.85993	1166	1149	1173	855	4
0.9318	0.86437	1169	1169	1174	847	4
1.0000	0.87127	1175	1175	1175	831	0
butyl acetate + 2 methyl propan-1-ol						
0.0000	0.79439	1172	1172	1172	916	0
0.2001	0.80874	1170	1172	1199	903	4
0.2929	0.81557	1168	1172	1209	899	8
0.3271	0.81810	1167	1172	1211	898	10
0.4599	0.82801	1165	1173	1219	890	13
0.5792	0.83716	1166	1173	1220	879	12
0.6881	0.84562	1167	1173	1217	868	10
0.7879	0.85357	1169	1173	1209	857	8
0.8644	0.85929	1171	1174	1200	848	5
0.9069	0.86327	1173	1173	1193	842	3
1.0000	0.87127	1175	1175	1175	831	0
butyl acetate + 3 methyl butan-1-ol						
0.0000	0.80177	1220	1220	1220	838	0
0.1220	0.80981	1210	1214	1248	843	6
0.2336	0.81718	1203	1209	1267	846	10
0.3409	0.82443	1197	1204	1278	847	11
0.3925	0.82795	1194	1202	1281	847	12
0.5321	0.83760	1190	1195	1280	843	9
0.6414	0.84533	1187	1190	1271	840	6
0.6814	0.84815	1186	1188	1265	838	5
0.8362	0.85930	1181	1181	1232	834	2
0.8887	0.86308	1179	1179	1216	834	2
1.0000	0.87127	1175	1175	1175	831	0

accurate to  $\pm 2 \text{ Tpa}^{-1}$ . Experimental speed of sound ( $u$ ) and predicted speed of sound in terms of FLT and CFT along with volume fraction ( $\phi$ ), isentropic compressibility and deviation in isentropic compressibility for the title systems at 303.15 K are given in Table II. Variation of  $\Delta K_s$  with volume fraction are graphically represented in Figure 1 and 2 respectively. The results in Table II shows that the FLT speed of sound are in excellent agreement with experimental results in all the

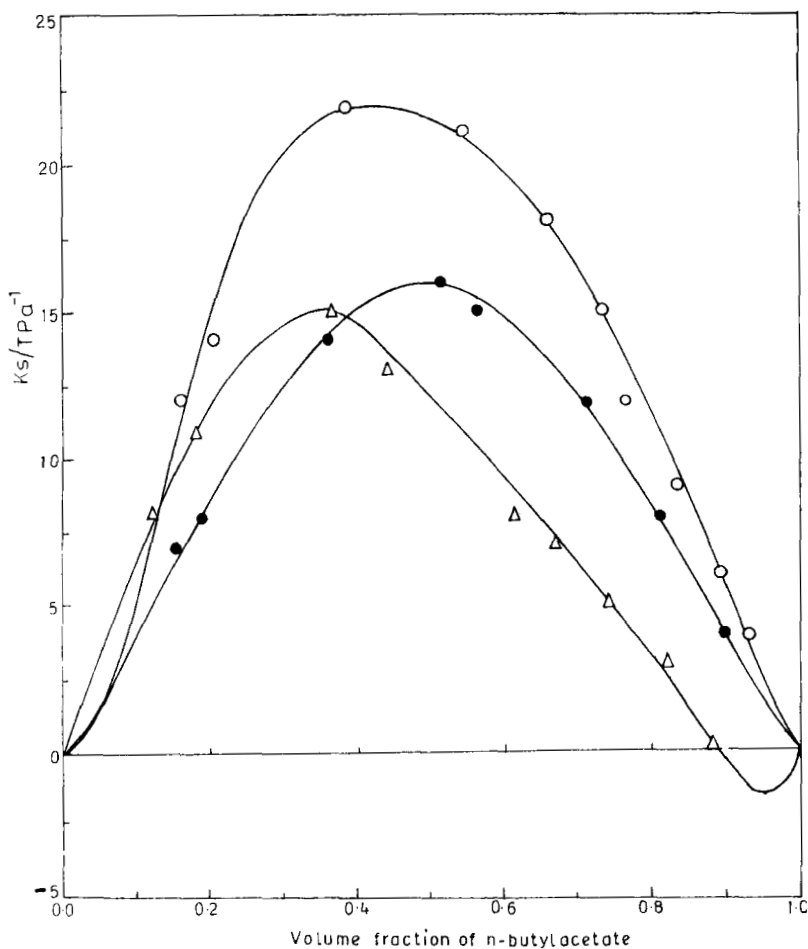


FIGURE 1 Deviation in isentropic compressibilities ( $K_s$ ) for *n*-butylacetate + propan-1-ol (○), +butan-1-ol (●), +pentan-1-ol (△) at 303.15 K.

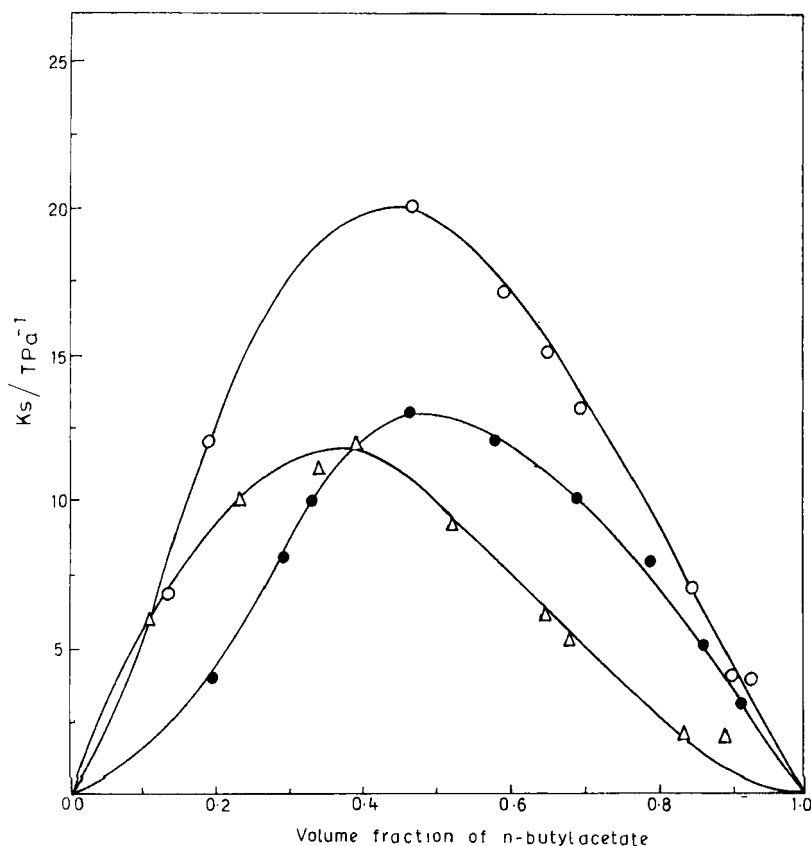


FIGURE 2 Deviation in isentropic compressibilities ( $K_s$ ) for *n*-butylacetate + propan-2-ol (○), + 2-methylpropan-1-ol (●), + 3-methylbutan-1-ol (△) at 303.15 K.

systems. However the speed of sound estimated in CFT are not in good agreement with experimental results which is shown clearly in Figures 3 and 4 respectively.

Excess viscosity ( $\eta^E$ ) was estimated using the relations

$$\eta^E = \eta_m - x_1 \eta_1 - x_2 \eta_2 \quad (4)$$

where  $\eta_m, \eta_1$  and  $\eta_2$  are the viscosities of the mixture, pure components 1 and 2 respectively. The values of mole fraction ( $X_1$ ), density ( $\rho$ ), viscosity ( $\eta_m$ ), excess viscosity ( $\eta^E$ ), excess free energy of mixing ( $G^E$ ),



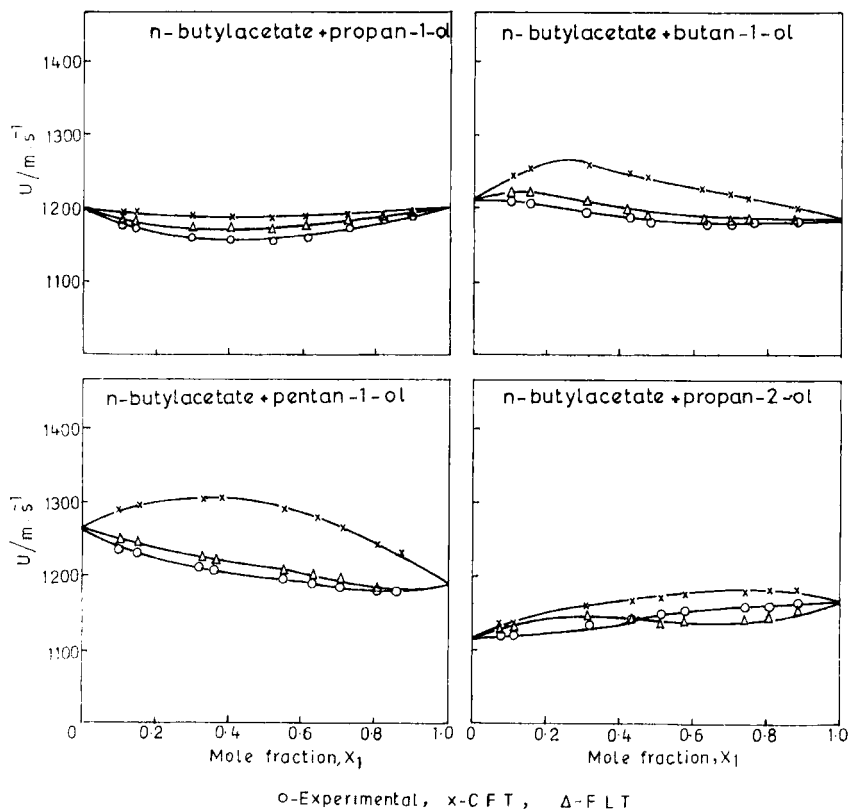


FIGURE 3

strength of interaction parameter ( $d$ ) and interaction energy ( $W_{\text{visc}}$ ) between the components for the systems of butylacetate with normal and substituted alcohols are given in Table III. Variation of  $\eta^E$  with molefraction are illustrated in Figure 5 and 6 respectively.

The composition dependence of deviation in isentropic compressibility and excess viscosity are correlated by Redlich-kister Polynomial

$$X = X_1 X_2 \sum_{i=0}^2 a_i (X_1 - X_2)^i \quad (5)$$

where  $X$  is excess viscosity, the composition is molefraction and if  $X$  is deviation in compressibility, volume fraction should be taken as

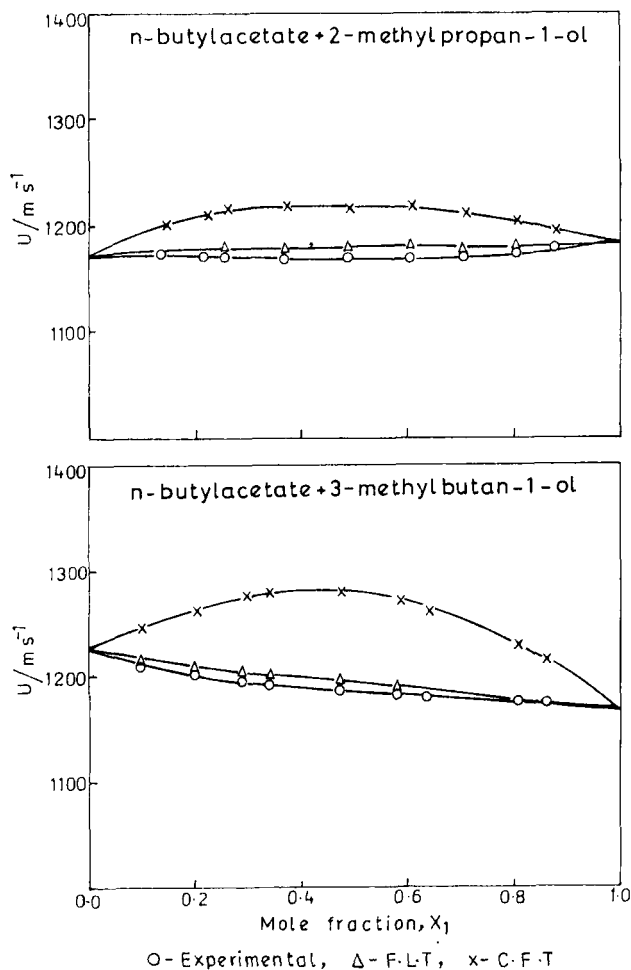


FIGURE 4

composition variable  $a_i$ 's are the adjustable parameters and are evaluated by a least square method. The values of the parameters along with the standard deviation are given in Table IV. Values of  $\sigma$  are obtained from the equation

$$\sigma = \sqrt{\frac{\sum (X_{\text{expt}} - X_{\text{calc}})^2}{n - p}} \quad (6)$$

TABLE III Molefraction ( $X_1$ ), density, ( $\rho$ ), Viscosity ( $\eta_m$ ), excess viscosity ( $\eta^E$ ), log of kinematic viscosity ( $\ln\eta v$ ), strength of interaction parameter ( $d$ ), interaction energy, ( $W_{visc}$ ) and excess Gibbs free energy for activation of flow ( $G^{*E}$ ) for the binary mixtures at 303.15 K.

$X_1$	$\rho$ <i>g.cm<sup>-3</sup></i>	$\eta^E$ <i>mpa.s</i>	$\eta^E$ <i>mpa.s</i>	$\ln\eta v$	$d$	$\frac{W_{visc}}{cal\ mol^{-1}} - 1$	$\frac{G^E}{cal\ mol} - 1$
butyl acetate + propan-1-ol							
0.0000	0.79600	1.722	-	4.8677	-	-	-
0.1020	0.80813	1.354	-0.334	4.7024	-2.382	-1321.636	-121.062
0.1280	0.81096	1.267	-0.412	4.6543	-2.498	-1393.492	-155.514
0.3545	0.83194	0.760	-0.842	4.2899	-3.236	-1847.632	-422.738
0.4050	0.83589	0.693	-0.892	4.2276	-3.409	-1953.965	-470.906
0.5185	0.84406	0.622	-0.925	4.1837	-3.624	-2087.562	-521.264
0.6095	0.84999	0.627	-0.889	4.2404	-3.685	-2127.247	-506.285
0.7398	0.85769	0.753	-0.719	4.4893	-3.457	-1993.831	-383.812
0.8254	0.86238	0.908	-0.535	4.7175	-3.189	-1834.770	-264.390
0.8913	0.86584	1.054	-0.362	4.9018	-3.006	-1726.121	-167.261
1.0000	0.87127	0.628	-	5.2175	-	-	-
butyl acetate + butan-ol							
0.0000	0.80201	2.271	-	5.3465	-	-	-
0.1131	0.81205	1.605	-0.566	5.0482	-2.903	-1703.842	-170.895
0.1421	0.81449	1.451	-0.694	4.9595	-3.099	-1821.749	-222.071
0.2889	0.82634	0.848	-1.167	4.4817	-4.100	-2426.832	-498.471
0.4292	0.83681	0.493	-1.397	3.9930	-5.366	-3191.601	-781.942
0.4791	0.84030	0.422	-1.424	3.8559	-5.793	-3448.110	-860.065
0.6374	0.85084	0.380	-1.325	3.8072	-6.371	-3797.848	-877.683
0.6935	0.85434	0.437	-1.219	3.9662	-6.137	-3657.330	-777.548
0.7502	0.85773	0.535	-1.070	4.1875	-5.729	-3414.303	-639.840
0.8737	0.86473	0.863	-0.633	4.7059	-4.845	-2882.874	-317.981
1.0000	0.87127	0.628	-	5.2175	-	-	-
butyl acetate + pentan-1-ol							
0.0000	0.80759	2.987	-	5.7871	-	-	-
0.1019	0.81476	2.125	-0.699	5.4688	-2.863	-1713.318	-156.769
0.1527	0.81829	1.747	-0.996	5.2838	-3.237	-1937.986	-250.775
0.3215	0.82965	0.797	-1.675	4.5346	-4.924	-2953.448	-644.147
0.3648	0.83251	0.618	-1.784	4.2891	-5.588	-3354.207	-777.170
0.5389	0.84368	0.209	-1.914	3.2400	-9.033	-5430.061	-1349.370
0.6215	0.84888	0.171	-1.820	3.0556	-10.128	-6088.881	-1432.105
0.7004	0.85369	0.241	-1.623	3.4140	-9.430	-5668.010	-1189.149
0.7907	0.88912	0.442	-1.277	4.0376	-7.866	-4728.309	-782.535
0.8609	0.86326	0.680	-0.927	4.4816	-6.827	-4098.513	-491.002
1.0000	0.87127	0.628	-	5.2175	-	-	-

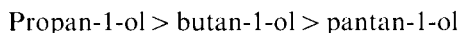
Table III Continued.

butyl acetate + propan-2-ol							
0.0000	0.77691	1.767	-	4.9177	-	-	-
0.0885	0.78824	1.371	-0.363	4.7239	-2.972	-1690.248	-132.177
0.1216	0.79283	1.219	-0.501	4.6307	-3.198	-1824.312	-194.836
0.3394	0.81770	0.588	-1.049	4.0369	-4.538	-2639.827	-591.849
0.4515	0.82900	0.430	-1.164	3.2871	-5.262	-3079.816	-762.562
0.5142	0.83489	0.395	-1.175	3.7358	-5.495	-3221.722	-804.786
0.5682	0.83975	0.387	-1.162	3.7434	-5.623	-3301.916	-809.960
0.7624	0.85555	0.618	-0.857	4.3064	-4.770	-2793.494	-505.902
0.8226	0.85993	0.764	-0.688	4.5462	-4.367	-2551.936	-372.327
0.8880	0.86437	0.956	-0.471	4.7996	-3.992	-2326.634	-231.500
1.0000	0.87127	0.628	-	5.2175	-	-	-
butyl acetate + 2 methyl propan-1-ol							
0.0000	0.79439	2.874	-	5.5916	-	-	-
0.1490	0.80874	1.810	-0.842	5.1911	-2.790	-1637.766	-207.669
0.2247	0.81557	1.373	-1.166	4.9449	-2.298	-1945.529	-338.911
0.2538	0.81810	1.231	-1.265	4.8470	-3.496	-2066.128	-391.325
0.3734	0.81801	0.750	-1.568	4.3967	-4.576	-2716.308	-635.616
0.4906	0.83716	0.468	-1.675	3.9674	-5.827	-3472.342	-867.738
0.6009	0.84562	0.362	-1.608	3.7511	-6.824	-4073.267	-971.882
0.7222	0.85357	0.447	-1.351	4.0005	-6.644	-3966.457	-795.671
0.8169	0.85979	0.652	-1.005	4.4085	-5.927	-3533.213	-528.569
0.8721	0.86327	0.823	-0.751	4.6588	-5.500	-3276.765	-365.359
1.0000	0.87127	0.628	-	5.2175	-	-	-
butyl acetate + 3 methyl butan-1-ol							
0.0000	0.80177	2.959	-	5.7848	-	-	-
0.1028	0.80981	2.093	-0.704	5.4601	-2.904	-1740.318	-160.457
0.2009	0.81718	1.408	-1.235	5.0839	-3.677	-2202.756	-353.542
0.2990	0.82443	0.878	-1.610	4.6315	-4.712	-2828.946	-592.527
0.3476	0.82795	0.665	-1.746	4.3633	-5.418	-3251.641	-737.472
0.4839	0.83760	0.274	-1.923	3.5033	-8.058	-4841.509	-1208.925
0.5959	0.84533	0.157	-1.863	2.9677	-10.315	-6201.312	-1493.276
0.6381	0.84815	0.168	-1.786	3.0434	-10.324	-6207.262	-1433.257
0.8081	0.85930	0.489	-1.197	4.1431	-7.645	-4595.425	-712.750
0.8681	0.86308	0.706	-0.886	4.5212	-6.752	-4056.727	-646.495
1.0000	0.87127	0.628	-	5.2175	-	-	-

where  $n$  is the number of experimental points and  $p$  is the number of parameters in Equation 5.

The data included in Table II and Figures 1 and 2 indicate that the deviation in isentropic compressibility are positive in all the systems over the entire range of composition except for the system of butyl acetate with pentan-1-ol in which an inversion in sign is observed. The data may be interpreted in terms of the two effects. (1) break-up of

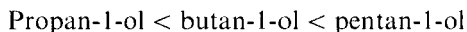
hydrogen bonds present in alcohol aggregates and (2) weak interactions between unlike molecules. The first effect contributes to an increase in free lengths described by Jacobson [24]. This leads to negative deviation in speed of sound and positive deviation in  $\Delta K_s$ . The second effect on the other hand, contributes to decrease in free length which leads to positive deviation in sound speed and negative deviation in  $\Delta K_s$ . The actual deviation would be the resultant of the two afore-said effects. The experimental values of  $\Delta K_s$ , which are positive point out that the former effect is stronger than the later. The values of  $\Delta K_s$  for normal and substituted alcohols fall in the order:



and propan-2-ol > 2 methylpropan-1-ol > 3 methyl butan-1-ol.

The higher positive values of  $\Delta K_s$  for the normal alcohols than substituted alcohols indicates that normal alcohols interacts more strongly than substituted alcohols. This may be attributed to the steric hindrance of the methyl group in substituted alcohols. The results may also be explained in terms of the structure breaking and structure making effects on free length, defined by Jacobson [24]. The results shows that structure breaking is dominant in all the mixtures.

Figures 5 and 6 indicate excess viscosity are negative over the entire range of composition in all the systems. The negative values of  $\eta^E$  for the systems butyl acetate with normal and substituted alcohols may be due to the mutual loss of dipolar association and difference in size and shape of unlike molecules. The  $\eta^E$  versus  $X_1$  graphical curves are showed with maxima at 0.50 mole fraction of butyl acetate. The algebraic values of the negative excess viscosities for the systems of butylacetate with normal and substituted alcohols of all in the order:



and propan-2-ol < ethyl propan-1-ol < 3 methyl butan-1-ol.

This indicates that increase in chain length of alcohol leads to decrease in hydrogen bonding interactions between butyl acetate and alcohol. The negative values of  $\eta^E$  are greater in mixtures containing substituted alcohols than that of normal alcohols which may be due to steric hindrance.

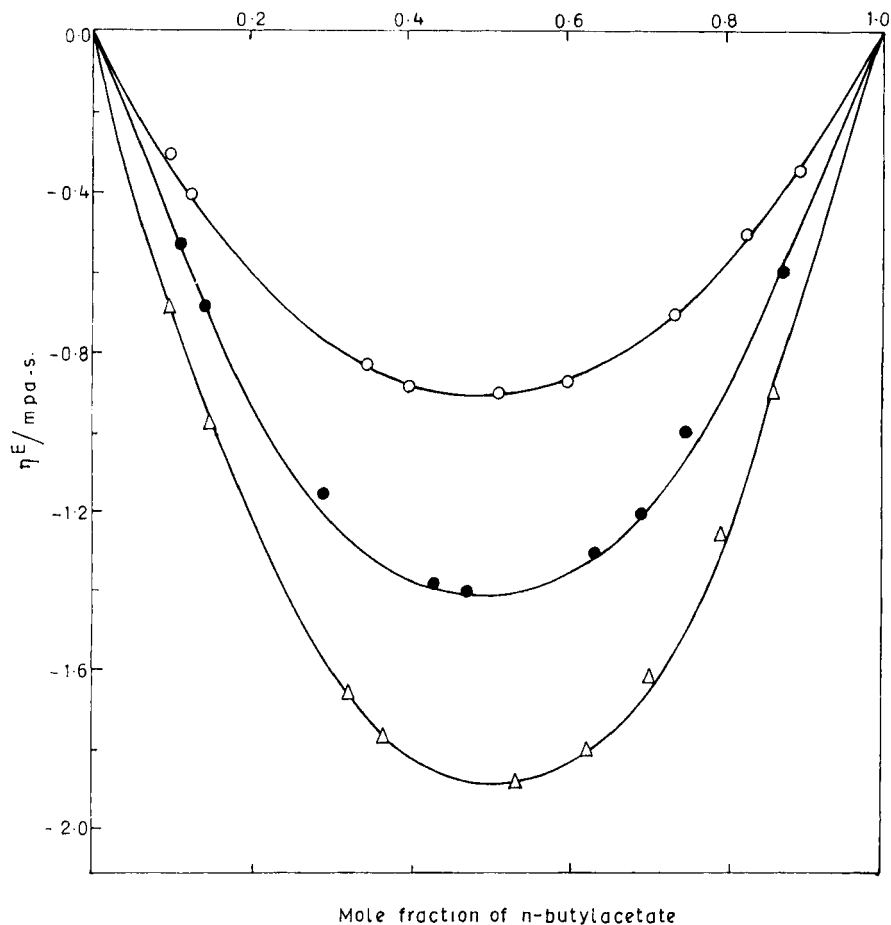


FIGURE 5 Excess Viscosities ( $\eta^E$ ) for  $n$ -butylacetate + propan-1-ol(○), + butan-1-ol(●), + pentan-1-ol(△) at 303.15 K.

In general positive values of excess viscosity ( $\eta^E$ ) would be expected to be associated with negative excess volumes ( $V^E$ ) and negative deviations in isentropic compressibility ( $\Delta K_S$ ) and negative ( $\eta^E$ ) with positive  $V^E$  and  $\Delta K_S$ . As expected, the values of  $\eta^E$  run anti parallel with the excess volume ( $V^E$ ) and deviation in isentropic compressibility ( $\Delta K_S$ ).

The thermodynamic parameter ( $d$ ) gives an idea about the quantitative estimation of the strength of interaction between unlike molecules.

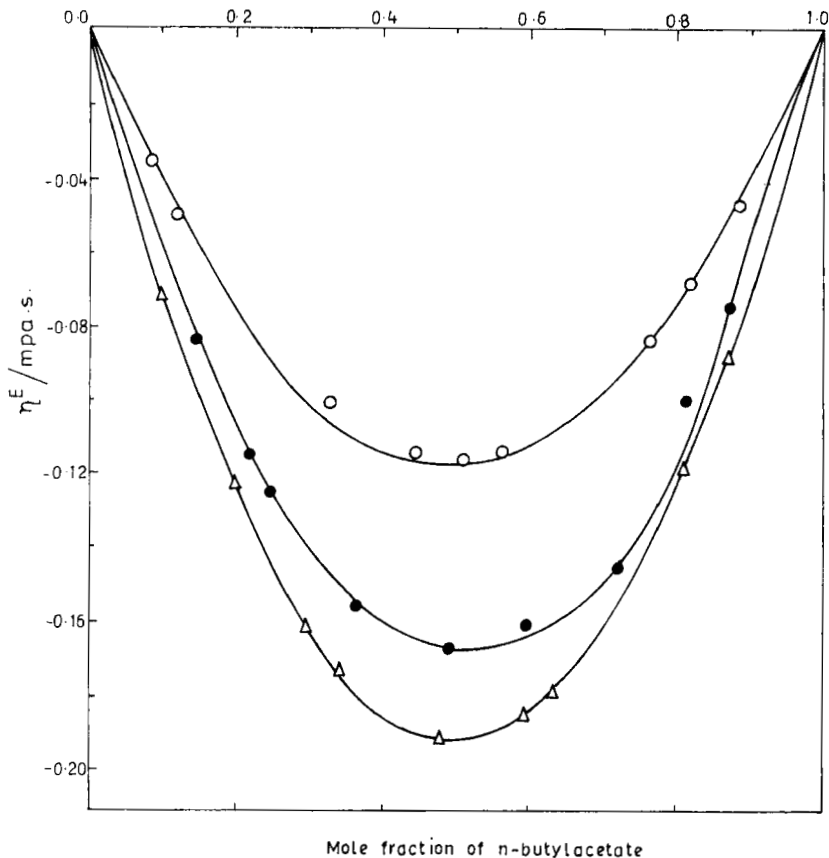


FIGURE 6 Excess Viscosities ( $\eta^E$ ) for *n*-butylacetate + propan-1-ol( $\circ$ ), + 2-methylpropan-1-ol( $\bullet$ ), + 3-methylbutan-1-ol( $\triangle$ ) at 303.15 K.

According to Nigam *et al.* [25, 26] and Ramamurthy [27], the specific interactions are present if  $d > 0$  and large in magnitude: if  $d > 0$  but not large in magnitude weak specific interactions are present, if  $d < 0$  and large in magnitude there is no specific interactions. The thermodynamic quantity,  $W_{\text{visc}}$ , the interaction energy between the unlike molecules is approximately equated to  $LT.d$ . The  $d$  values are negative and small in magnitude for all the systems over the entire range of composition. This indicates that weak interactions are present between unlike molecules in all the systems. An examination of  $d$  and  $W_{\text{visc}}$  values, reveals that the values of  $W_{\text{visc}}$  run parallel with  $d$  in

TABLE IV Values of parameters of Eq. (5) and standard deviation  $\sigma(x)$  at 303.15 K

$X$	$a_0$	$a_1$	$a_2$	$\sigma(X)$
butyl acetate + propan-1-ol				
$\Delta K_S/(Tpa)^{-1}$	84.965	-9.256	-17.672	0.5
$\eta^E/MPa.s$	-3.709	-0.050	0.019	0.003
butyl acetate + butan-1-ol				
$\Delta K_S/(Tpa)^{-1}$	63.237	4.619	-23.046	1
$\eta^E/MPa.s$	-5.711	-0.057	0.020	0.003
butyl acetate + pentan-1-ol				
$\Delta K_S/(Tpa)^{-1}$	48.120	-44.385	-12.003	1
$\eta^E/MPa.s$	7.712	-0.058	0.025	0.003
butyl acetate + propan-2-ol				
$\Delta K_S/(Tpa)^{-1}$	71.663	-5.255	-21.757	1
$\eta^E/MPa.s$	-4.710	-0.053	0.022	0.003
butyl acetate + 2 methyl propan-1-ol				
$\Delta K_S/(Tpa)^{-1}$	51.768	8.738	-39.714	1
$\eta^E/MPa.s$	-6.719	-0.056	0.056	0.003
butyl acetate + 3 methyl butan-1-ol				
$\Delta K_S/(Tpa)^{-1}$	38.145	-27.779	-1.195	1
$\eta^E/MPa.s$	-7.719	-0.063	0.048	0.003

all the systems. The excess Gibbs free energy for the activation of flow gives the quantity of free flow of the mixtures. The  $G^E$  values suggest that the behaviour of the systems is in true with the observations made by Read and Tayler [28].

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