

Sonochemical and Infrared Spectroscopies Study of Binary Liquid Mixture of O-Chlorotoluene and P-Chlorotoluene with T-Butanol At 308.15 K and 313.15 K

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Abstract: Densities, ultrasonic velocities and Infra-red spectroscopies of binary liquid mixture of o-chlorotoluene and p-chlorotoluene with t-butanol have been measured at 308.15 and 313.15 K using these parameter the isentropic compressibilities (K_s) intermolecular free length (L_f) have been calculated. Deviation in isentropic compressibilities (ΔK_s) and Excess intermolecular free length (L_f^E) are interpreted in terms of hetroassociation. These Derived parameters have been used to study the intermolecular interaction in binary liquid mixtures. The theoretically calculated values of ultrasonic speed are derived by using free length theory. Collision factor theory, Nomoto's and Van Dael's equation were compared with those obtained experimentally.

Keywords: Densities, Ultrasonic velocities, isentropic compressibilities, free length theory, collision factor theory, Nomoto's equation and Van Dael equation and Infra red spectroscopy.

1. INTRODUCTION

Binary mixture of t-butanol, with aromatic Hydrocarbons is of a great interest due to their extremely non-ideal behaviour and practical importance to the chemical industry. A lot of work has been reported in the literatures (1-6).

The studies of density, ultrasonic velocity, and infrared spectroscopy, are being increasingly used as tools for investigation of properties of pure components and the nature of intermolecular interaction in the liquid mixture. In order to investigate this effect in the present investigation densities (ρ), Ultrasonic Velocity (v) and Infrared spectroscopy of the binary mixture of t-butanol with o-chlorotoluene and p-chloro toluene have been measured over the entire range of composition at 308.15 and 313.15K.

2. EXPERIMENTAL

t-butanol, o-chlorotoluene and p-chlorotoluene were of high grade and used after single distillation. The purity of the solvent after Purification was ascertained by comparing density, ultrasonic velocity with the corresponding literature values at 303.15 and 313.15 K (Table -1).

Table1. Comparison of experimental density (ρ) and speed of sound (u) of pure liquid with literature values at 308.15 and 313.15 K.

Liquid	Temp.	$\rho \times 10^{-3} \text{ kg} \cdot \text{m}^{-3}$		$u(\text{m} \cdot \text{s}^{-1})$	
	K	Expt.	Lit.	Expt.	Lit.
t-Butanol	308.15	0.7700	0.7702 ²⁰	1094	1093 ¹⁹
	313.15	0.7648	0.7648 ²⁰	1084	1081 ¹⁹
o-Chlorotoluene	308.15	1.0679	1.0678 ²²	1262	1259 ²³
	313.15	1.0631	1.0630 ²¹	1243	1240 ²³
p-Chlorotoluene	308.15	1.0526	1.052 ²¹	1249	-
	313.15	1.0474	1.047 ²¹	1237	-

Binary mixture was prepared by mixing known masses of each liquid in airtight stoppered glass bottle. The measurement was made on single pan electronic balance to an accuracy of 1 mole fraction and was less than 1×10^{-4} .

The density of pure liquid and its mixture was determined in 15 cm³ double arm pycnometer (7-10) and capillary bore with an internal diameter of 1 mm in a transparent glass walled water bath having a thermal stability of ± 0.01 K (11-12). The pycnometer was calibrated using water having conductivity less than $1 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$. The pycnometer filled with air bubble in free experimental liquid was kept in transparent walled water bath in which the temperature was maintained constant to ± 0.01 K for 10-15 minutes to attain thermal equilibrium.

The position of the liquid level in the two arms were recorded with travelling microscope which read correctly to ± 0.01 mm, the density values were reproducible within $5 \times 10^{-5} \text{g cm}^{-3}$

The sound speed u , was measured at a frequency of 2MHz in this solution through the interferometric method (using mettall's F-81 model). The estimated error in sound speed measurement at $\pm 1 \text{ms}^{-1}$. The other experimental details are the same as those reported earlier (5-6). FTIR spectra were recorded on a FTIR spectrometer (model SHIMADZU 8400 PC) by using KBr pellet in the Region 400-40 cm^{-1} . The averaged value of density and ultrasonic velocities for these two systems are listed in (table -2).

Table2. Densities (ρ), Ultrasonic velocities (U), isentropic compressibilities (K_s) and intermolecular free length (L_f) of *t*-butanol + *o*-chlorotoluene and *p*-chlorotoluene at various temperatures.

t-butanol + *o*-chlorotoluene

Temp K	x_1	$\rho \times 10^{-3} \text{kg m}^{-3}$	$u \text{ m s}^{-1}$	$K_s \text{ TPa}^{-1}$	$\Delta K_s \text{ TPa}^{-1}$	$L_f \text{ \AA}$	L_f^E
308.15	0.0000	1.0679	1262	588	0	0.4869	0.0000
	0.1005	1.0421	1233	632	2	0.5047	0.0002
	0.1998	1.0160	1207	676	4	0.5221	0.0003
	0.3024	0.9881	1184	722	5	0.5396	-0.0001
	0.3987	0.9611	1163	770	8	0.5572	0.0007
	0.5001	0.9318	1144	820	9	0.5751	0.0009
	0.6001	0.9018	1128	871	10	0.5927	0.0010
	0.6999	0.8707	1115	923	10	0.6102	0.0011
	0.7997	0.8386	1105	976	8	0.6274	0.0009
	0.9011	0.8045	1098	1031	5	0.6449	0.0006
	1.0000	0.7700	1094	1085	0	0.6615	0.0000
313.15	0.0000	1.0631	1243	609	0	0.5009	0.0000
	0.1005	1.0375	1215	653	2	0.5188	0.0001
	0.1998	1.0116	1190	698	4	0.5363	0.0002
	0.3024	0.9841	1168	744	4	0.5539	-0.0004
	0.3987	0.9574	1148	792	7	0.5715	0.0002
	0.5001	0.9284	1131	843	8	0.5893	0.0002
	0.6001	0.8987	1116	894	8	0.6069	0.0002
	0.6999	0.8681	1104	946	7	0.6244	0.0001
	0.7997	0.8362	1094	999	5	0.6416	-0.0003
	0.9011	0.8025	1087	1054	1	0.6591	-0.0007
	1.0000	0.7648	1084	1113	0	0.6772	0.0000

t-butanol + *p*-chlorotoluene

Temp K	x_1	$\rho \times 10^{-3} \text{kg m}^{-3}$	$u \text{ m s}^{-1}$	$K_s \text{ TPa}^{-1}$	$\Delta K_s \text{ TPa}^{-1}$	$L_f \text{ \AA}$	L_f^E
308.15	0.0000	1.0526	1249	609	0	0.4955	0.0000
	0.0953	1.0295	1224	649	3	0.5114	0.0001
	0.1989	1.0038	1199	693	5	0.5285	0.0000
	0.2901	0.9805	1179	733	7	0.5438	0.0001
	0.3943	0.9531	1159	781	9	0.5612	0.0002
	0.4902	0.9269	1143	826	10	0.5772	0.0003
	0.5922	0.8980	1128	876	11	0.5943	0.0005
	0.6981	0.8668	1115	929	11	0.6119	0.0006
	0.7988	0.8359	1105	980	9	0.6287	0.0006

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	0.8997	0.8035	1098	1033	6	0.6453	0.0005
	1.0000	0.7700	1094	1085	0	0.6615	0.0000
313.15	0.0000	1.0474	1237	624	0	0.5071	0.0000
	0.0953	1.0245	1212	665	3	0.5233	0.0000
	0.1989	0.9992	1187	710	5	0.5409	0.0000
	0.2901	0.9762	1168	751	7	0.5564	0.0000
	0.3943	0.9490	1148	800	8	0.5741	-0.0001
	0.4902	0.9232	1132	846	9	0.5903	-0.0002
	0.5922	0.8947	1117	896	9	0.6076	-0.0002
	0.6981	0.8639	1104	950	8	0.6256	-0.0003
	0.7988	0.8334	1095	1001	6	0.6425	-0.0005
	0.8997	0.8014	1088	1055	2	0.6593	-0.0009
	1.0000	0.7648	1084	1113	0	0.6772	0.0000

3. RESULT AND DISCUSSION

Experimental values of density (ρ) and sound velocity (v) of binary liquid system are recorded respectively at 308.15 and 313.15 K. the isentropic compressibility (K_S). Inter-molecular free length (L_f). Deviation in isentropic compressibility (ΔK_S) and Excess intermolecular free length (L_f^E) have been calculated using the following:

$$K_S = 1/\rho U^2 \quad (1)$$

$$L_f = K/U_p \frac{1}{2} \quad (2)$$

$$\Delta K_S = K_{S12} - \phi_2 K_{S2} \quad (3)$$

$$L_f^E = L_{F12} - \phi L_{F1} - \phi L_{F2} \quad (4)$$

Where K_{S1} , L_{F1} , ϕ_1 and K_{S2} , L_{F2} and ϕ_2 are isentropic compressibility intermolecular free length and volume fraction of components. 1 and 2 respectively. K_{S12} and L_{F12} are isentropic compressibility and inter molecular free length of binary mixture.

Figures 1 and 2 show respective plots of variation of ΔK_S and L_f^E with volume fraction at 308.15 and 313.15 K. The variation of ultrasonic velocity in a solution depends upon the increase or decrease of intermolecular free length after mixing the components. On the basis of model proposed by Eyring Kincaid (13) ultrasonic Velocity should increase if the intermolecular free length increases as a result observed in the present investigation.

For the mixture of t-butanol with o-chlorotoluene and p-chlorotoluene, ΔK_S values are positive over the entire composition range of binary mixture. It has been suggested by Kiyoha and Benson (14) that ΔK_S result from several contribution effect. Which are characterized as physical, chemical and structural effect mixing of hydrocarbons leads to breaking self association leading to decreases in the molecular order resulting in volume expansion there by giving positive values of ΔK_S which means that the binary mixture is more compressible there by the pure compound. The L_f^E values are also positive over the entire composition range, and L_f^E arises due to breaking of H-bond in self associated alcohol and steric hindrance due to bulky methyl group in t-butanol.

The theoretical values of sound velocities through binaries at all temperatures have been evaluated using Nomoto, (15) Van Deal ideal mixing, (16) Jacobson's, (17), free length and schoff's, (18) collision factor theories. A comparison has been given in (Table 3).

From calculated speed of sound, along with average percent error for both the binary system are summarized in table (Table – 3) on the basis of the table following observations can be made.

- 1) Nomoto's empirical equation-seems to fit the data very well.
- 2) Schaff's collision factor theory succeeds in making accurate prediction of speed of sound.
- 3) Van deal ideal mixing law does not predict the speed of sound of binary mixture as Nomoto's and schaff's equation does.
- 4) Jacobson's free length fails to predict accurately the speed of sound of binary mixture.

IR measurement for mixture of *t*-butanol with chlorotolues over the entire range has been carried out in (Table-4).

It is seen that Δv values are changed when change in mole fraction occurs these values are positive and conclude that there is a variable degree of intermolecular H-bonding between the components of mixture.

Table3. Comparison of Experimental Speed of Sound with Various Theories for the *t*-Butanol + *o*-Chlorotoluene

Temp. K	x_1	Ultrasonic Velocity $m.s^{-1}$					% Errors			
		Expt.	NOMOTO	Van	CFT	FLT	NOMOTO	Van	CFT	FLT
308.15	0.0000	1258	1258	1258	1258	1052	1.73	1.33	1.47	9.73
	0.0923	1230	1241	1239	1239	1044				
	0.2003	1201	1222	1217	1218	1042				
	0.3009	1179	1205	1199	1200	1043				
	0.4005	1160	1188	1181	1183	1046				
	0.5011	1144	1172	1165	1167	1051				
	0.6007	1129	1155	1149	1152	1057				
	0.7011	1117	1140	1134	1137	1065				
	0.8005	1107	1124	1120	1122	1072				
	0.9008	1099	1109	1107	1108	1080				
1.0000	1094	1095	1094	1094	1089					
313.15	0.0000	1232	1233	1232	1232	1035	1.67	1.22	1.15	10.00
	0.0923	1206	1218	1215	1213	1026				
	0.2003	1180	1201	1196	1194	1023				
	0.3009	1160	1186	1179	1178	1023				
	0.4005	1143	1170	1164	1162	1025				
	0.5011	1129	1155	1149	1148	1029				
	0.6007	1116	1141	1134	1134	1034				
	0.7011	1107	1127	1121	1120	1040				
	0.8005	1098	1113	1108	1107	1048				
	0.9008	1091	1099	1096	1095	1058				
1.0000	1084	1086	1084	1084	1072					

t-Butanol + *p*-Chlorotoluene

Temp. K	x_1	Ultrasonic Velocity $m.s^{-1}$					% Errors			
		Expt.	NOMOTO	Van	CFT	FLT	NOMOTO	Van	CFT	FLT
308.15	0.0000	1249	1249	1249	1249	866	2.28	2.28	2.66	19.26
	0.0953	1224	1236	1206	1238	877				
	0.1989	1199	1222	1169	1226	891				
	0.2901	1179	1209	1144	1214	905				
	0.3943	1159	1194	1121	1200	923				
	0.4902	1143	1180	1106	1186	942				
	0.5922	1128	1164	1094	1170	964				
	0.6981	1115	1147	1088	1153	990				
	0.7988	1105	1130	1085	1134	1019				
	0.8997	1098	1113	1088	1115	1051				
	1.0000	1094	1095	1094	1094	1089				
313.15	0.0000	1237	1236	1237	1237	852	2.29	2.26	2.83	19.43
	0.0953	1212	1224	1194	1227	863				
	0.1989	1187	1210	1158	1215	879				
	0.2901	1168	1198	1133	1204	893				
	0.3943	1148	1183	1111	1190	912				
	0.4902	1132	1169	1096	1177	932				
	0.5922	1117	1153	1084	1162	956				
	0.6981	1104	1137	1078	1145	984				
	0.7988	1095	1120	1076	1128	1015				
	0.8997	1088	1103	1078	1109	1049				
	1.0000	1084	1086	1084	1084	1072				

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Table4. IR Frequencies ($\nu \text{ cm}^{-1}$) for *t*-Butanol with *o*-Chlorotoluene

Mole fraction of <i>t</i> -Butanol	ν (O-H)	ν (Ar-Cl)
<i>o</i> -Chlorotoluene	-	746.81
0.2	3373.61	748.41
0.4	3377.47	748.41
0.5	3373.61	748.41
0.6	3373.47	748.41
0.8	3371.68	746.48
<i>t</i> -Butanol	3377.47	-

t-Butanol with *p*-Chlorotoluene

Mole fraction of <i>t</i> -Butanol	ν (O-H)	ν (Ar-Cl)
<i>p</i> -Chlorotoluene	-	806.27
0.2	3379.40	806.27
0.4	3379.40	806.27
0.5	3379.40	806.27
0.6	3389.33	806.27
0.8	3367.82	806.27
<i>t</i> -Butanol	3377.47	-

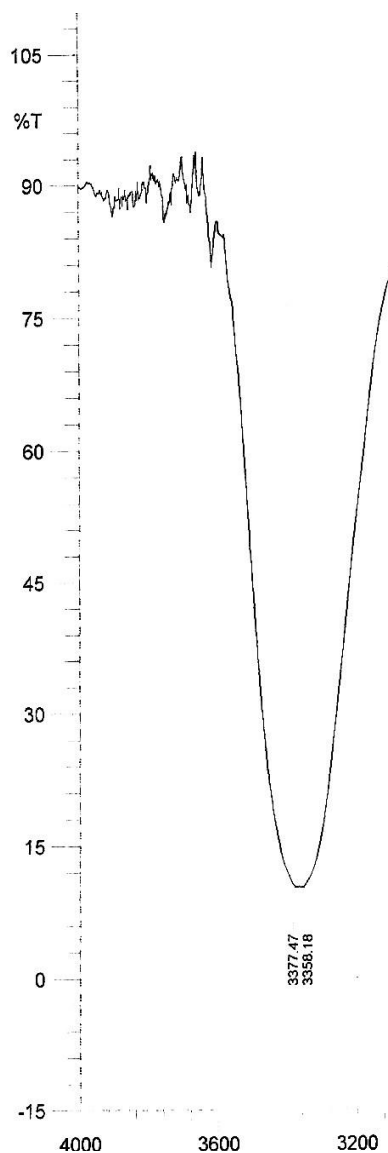


Figure1. Neat FTIR -OH Frequency (cm^{-1}) Cut Section (Spectrum) of *t*-Butanol

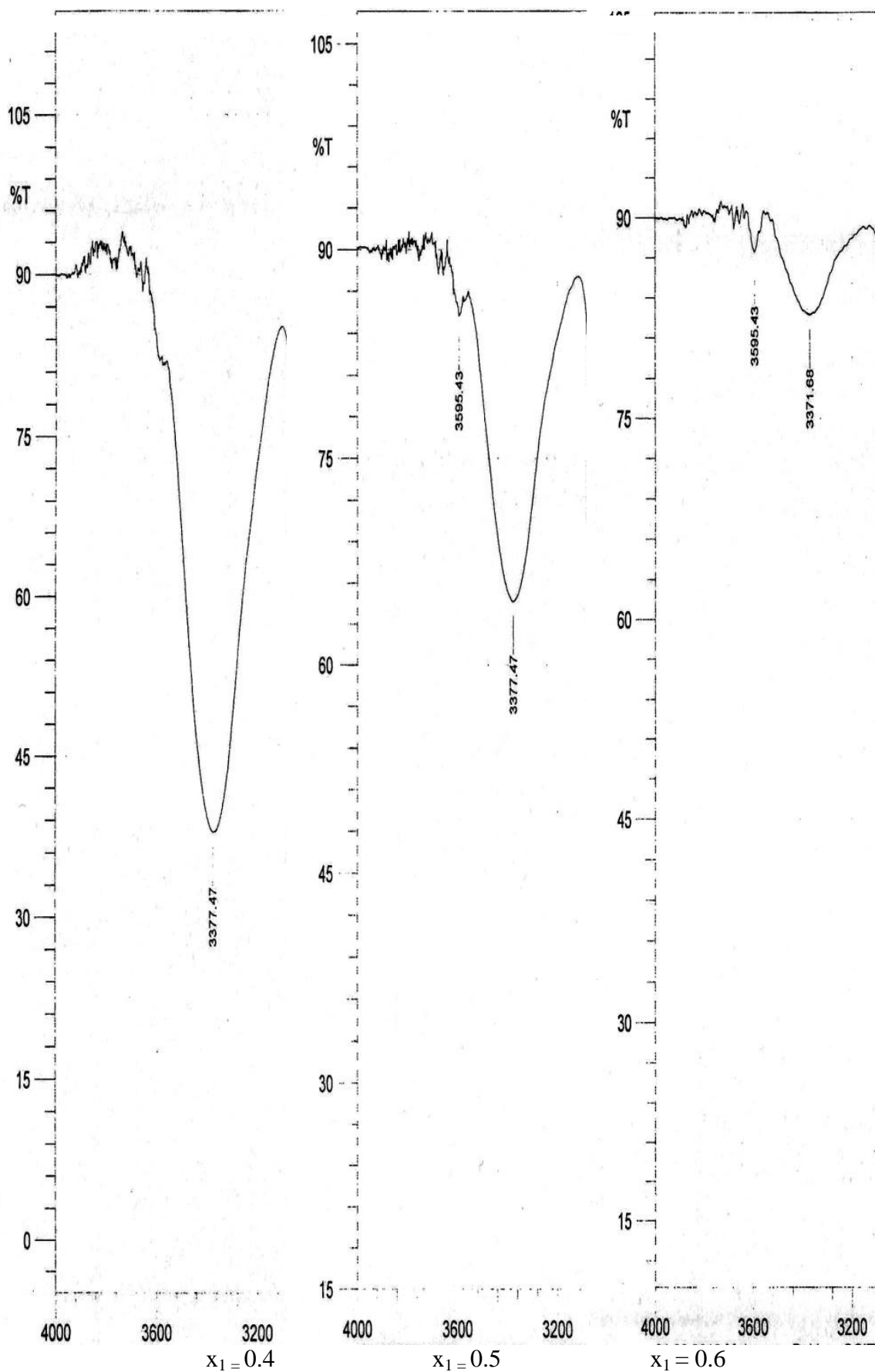


Figure2. Neat FTIR -OH Frequency (cm⁻¹) Cut Section (Spectrum) of t-Butanol + o-Chlorotoluene.

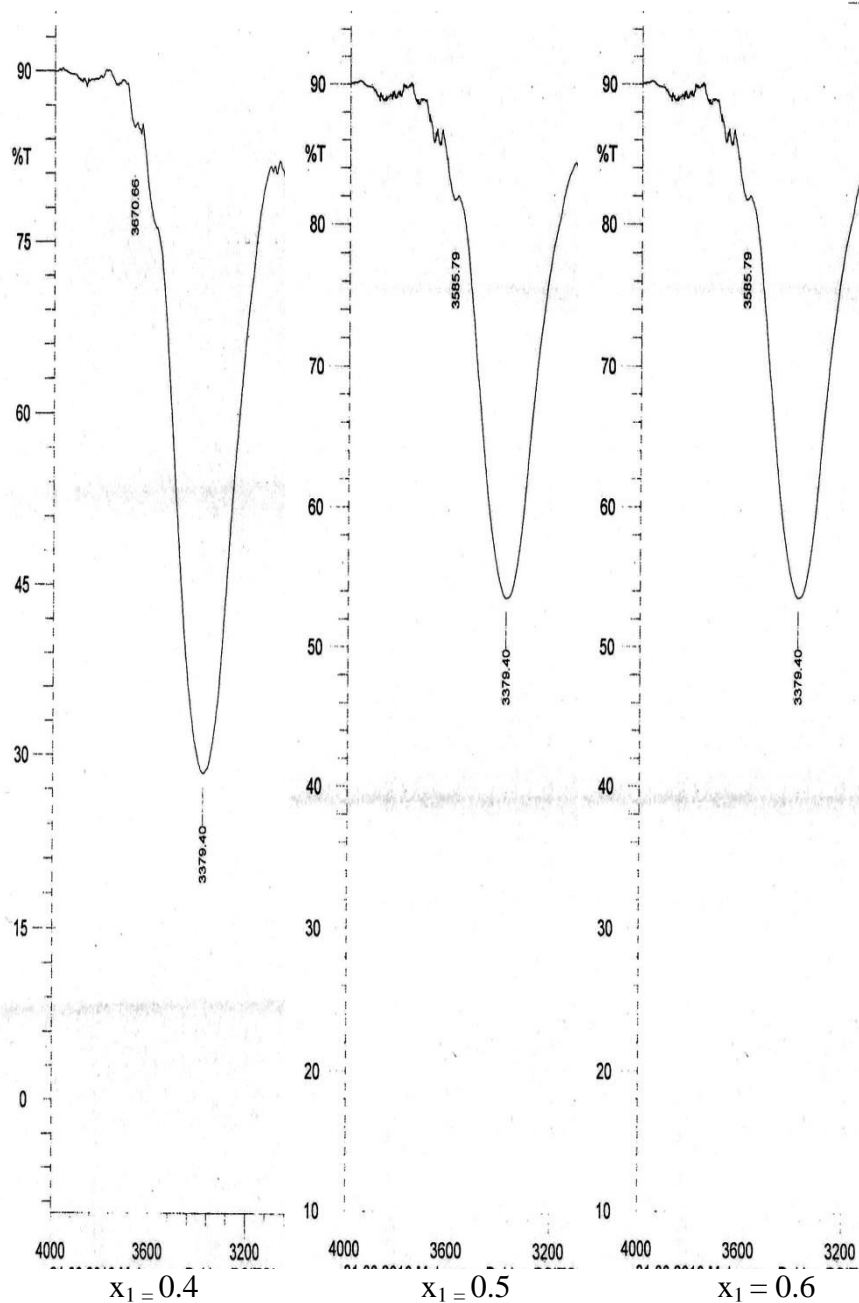


Figure3. Neat FTIR -OH Frequency (cm^{-1}) Cut Section (Spectrum) of *t*-Butanol + *p*-Chlorotoluene.

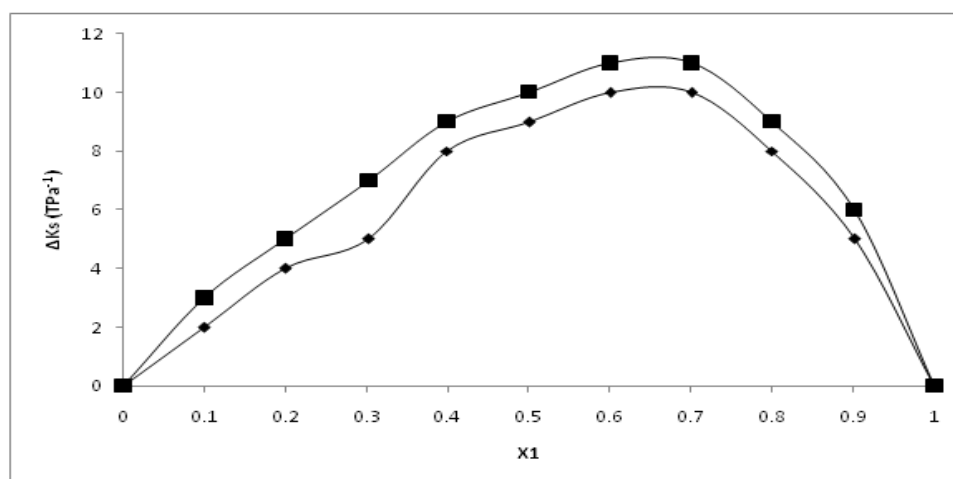


Figure1. ΔK_s value at 308.15 K for (X_1) *t*-butanol + ($1 - x$) *o*-chlorotoluene (♦), *p*-chlorotoluene (■).

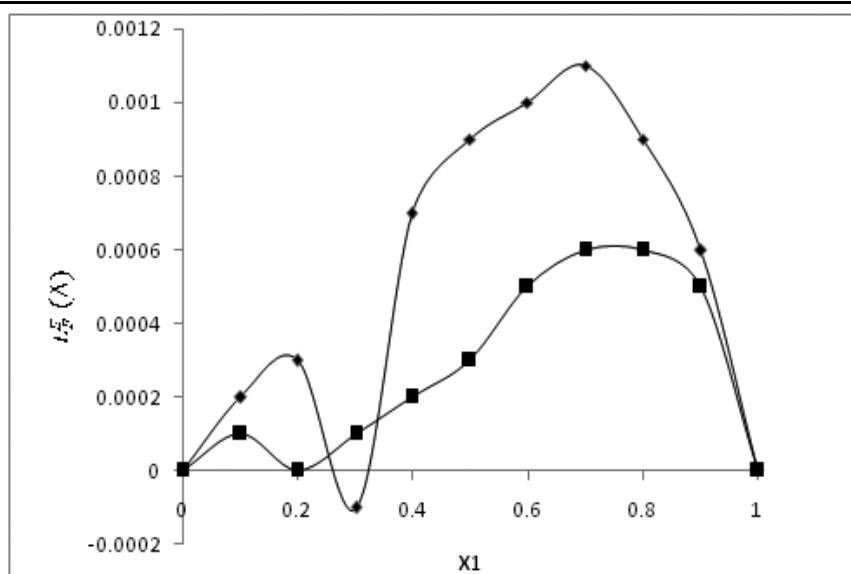


Figure 2. L_F^E (Å) value at 308.15 K for (X_1) *t*-butanol + $(1 - x)$ *o*-chlorotoluene (♦), *p*-chlorotoluene (■).

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