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RESEARCH ARTICLE

Acoustic, Volumetric and Viscometric Studies of Binary Liquid Mixtures of p-Chloroacetophenone with *n*-Alkanols at Different Temperatures

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Abstract: Density (ρ), speed of sound (u) and viscosity (η) have been measured for the binary liquid mixtures of p-chloroacetophenone with *n*-propanol, *n*-butanol, *n*-pentanol at all temperature range from 303.15 K to 318.15 K. From this experimental data, excess molar volume (v^E), deviation in viscosity (Δη), deviation in isentropic compressibility (Δks) and excess Gibbs energy of activation of viscous flow (G^{*E}) have been calculated and fitted to Redlich-Kister polynomial equation. These excess parameters, reveals that there is a strong interaction between the unlike molecules. The analyzed viscosity data of binary liquid mixtures were used to test the Grunberg-Nissan, Katti chaudari and Hind semi-empirical equations.

Keywords: Density, viscosity, speed of sound, para-chloroacetophenone, excess thermodynamic parameters

Introduction

Ultrasonic and thermodynamic properties of liquid mixtures are of great significance to know about inter and intra-molecular interactions, structural and physiochemical behaviour and also in finding various liquid state theories by which measuring the properties of liquid mixtures is possible. Thermodynamic properties of solutions studies with an ultrasonic interferometer can be done for accurate measurement of the velocity of sound in liquids. The analysis in the change of thermodynamic properties of mixtures and their degree of deviation from ideality shows an excellent significant way to obtain information about molecular structure and intermolecular forces in liquid mixtures[1].

Thermodynamic properties derive from the measurement of densities (ρ), viscosities (η) and speed of sound (u) are being increasingly used as tools for the investigation of nature

and type of intermolecular interactions between the component molecules present in the binary liquid mixtures. The components selected in this work have a wide range of useful applications. p-chloroacetophenone (PCAP) is a molecule having a wide range of application in the manufacture of drugs, perfumes and cosmetics respectively. Alkanols are protic, highly associated through hydrogen bonding and this association decreases as alkyl chain length in *n*-alkanols. The literature survey indicates that no studies on these systems have been reported.

Experimental

p-Chloroacetophenone (PCAP), is taken as the main component and *n*-alcohols (*n*-propanol, *n*-butanol, *n*-pentanol) are taken as secondary components as three binary systems. These chemicals purchased from S.D. Fine chemicals Ltd, India were used in the present work. The Mass purity of chemicals was checked as shown in Table 1. The mixtures were prepared by mixing weighed amounts of the pure liquids by adopting the method of a closed system by using Mettler Toledo (ME204) balance with the precision of ±0.1 mg. Mixtures were allowed to stand for some time before every measurement so as to avoid air bubbles[2].

Table 1. Materials description

Component	Cas number	Source	Mass fraction purity	Water content, %
p-Chloro acetophenone	99-91-2	SD-fine	0.980	0.042
n-Propanol	71-23-8	SD-fine	0.990	0.034
n-Butanol	71-36-3	SD-fine	0.990	0.033
n-Pentanol	71-41-0	SD-fine	0.990	0.041

p-Chloroacetophenone as a common component with *n*-propanol, *n*-butanol and *n*-pentanol measured densities (ρ), viscosities (η) and speed of sound (u) at 303.15 K, 308.15 K, 313.15 K and 318.15 K. From this data, the various excess thermodynamic parameters like excess volumes (v^E), deviation in viscosity (Δη), deviation in isentropic compressibility (Δks) and excess Gibbs energy of activation of viscous flow (G^{*E}) have been evaluated. The variation in these parameters with the composition of binary mixtures reveals the qualitative nature and extent of intermolecular interactions between the component molecules. This study will also provide an attest of various interaction parameters. The components at different mole fractions show deviations in the parameters indicate the nature and extent of intermolecular interactions between the selected binary liquid mixtures.

Table 2. Physical properties of pure components comparison of experimental values of densities, ultrasonic velocity and viscosities of pure liquids with the corresponding literature values at 303.15 K, 308.15 K, 313.5 K and 318.15 K

Compound	T, K	Density (ρ)		Ultrasonic speed(u)		Viscosity(η)	
		Expt. g/cm^{-3}	Lit. g/cm^{-3}	Expt. m. s^{-1}	Lit. m. s^{-1}	Expt. mPa.s	Lit. mPa.s
p-Chloroacetophenone	303.15	1.18589	1.18565[c]	1412.8	1412[c]	2.3538	2.353[c]
	308.15	1.18059	1.18125[c]	1389.64	1389[c]	2.2924	2.292[c]
	313.15	0.17548		1366.12		2.2314	
	318.15	0.17037		1343.04		2.1704	
n-Propanol	303.15	0.7954	0.7956[a]	1187.64	1188.64[d]	1.8746	1.8742[a]

Contd…

	308.15	0.7914	0.7915[a]	1170.88	1171.81[d]	1.6962	1.6709[a]
	313.15	0.7874	0.7874[a]	1154.02		1.53015	1.5237[a]
	318.15	0.7834	0.7833[a]	1137.89		1.3837	1.3833[a]
n-Butanol	303.15	0.80208	0.8021[a]	1222.51	1223.41[d]	2.3146	2.3147[a]
	308.15	0.79821	0.7982[a]	1205.13	1206.83[d]	2.07756	2.0655[a]
	313.15	0.79434	0.7943[a]	1188.17		1.8599	1.8476[a]
	318.15	0.79047	0.7904[a]	1172.36		1.6593	1.6597[a]
n-Pentanol	303.15	0.8078		1258.63	1259.46[d]	2.9252	
	308.15	0.80408	0.80345[b]	1248.12	1248.06[d]	2.62703	2.6387[b]
	313.15	0.8004		1237.48		2.3444	
	318.15	0.79664	0.79619[b]	1226.53		2.0661	2.0661[b]

a=Ref:[3], b= Ref:[4], c= Ref:[5], d= Ref:[6]

Apparatus and procedure

Proper care was taken to avoid any evaporation loss while doing the experiment. Densities were measure by using Gay-Lussac Pycnometers and are calibrated by using double distilled water. Viscosities were measured by using ubbelhode viscometer and electronic stopwatch with precision ±0.01s. Desired temperatures were kept constant using a thermostat. Speed of sound (u) was determined by using an Ultrasonic Interferometer Model F-05, exact frequency 1.9896 MHz Error ±0.0001%, from Mittal Enterprises, New Delhi.

Theory

Using the measured data, the following acoustical parameters have been calculated

Excess molar volume (V^E)

$$V^E = \frac{x_1M_1 + x_2M_2}{\rho_m} - \left\{\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2}\right\} \quad (1)$$

x_1 and x_2 = Mole fractions of pure components 1 and 2.
P_m = density mixture

M_1 and M_2 = Molecular weights of pure components 1 and 2

ρ1 and ρ2 = density of pure components 1 and 2

Deviation in isentropic compressibility (Δks)

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

The excess isentropic compressibilities are calculated from

$$K_S^E = K_S - K_S^{iD} \quad (3)$$

$$K_S^{iD} = \sum_{i=1}^{2}\phi_i\left\{K_{si} + \frac{TV_i(a_i^2)}{c_{pi}}\right\} - \left\{T(\sum_{i=1}^{2}x_iV_i)(\sum_{i=1}^{2}\phi_i a_i)\text{^}2/(\sum_{i=1}^{2}x_iC_{pi})\right\} \quad (4)$$

Deviation in viscosity (Δη)

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \quad (5)$$

*Excess Gibbs free energy of activation of viscous flow (G*E)*

$$G^{*E} = RT[1n\,\eta m\,Vm - (x_1 \ln \eta 1 V_1 + x_2 \ln \eta 2 V_2)] \quad (6)$$

Where Vm = molar volume of the mixture, R= Real gas constant, T=Temperature. The excess parameters (Y^E) was fitted by a Redlich-Kister type polynomial

$$Y^E = \sum_{i=0}^{n} a_1 (x_1 - x_2) \quad (7)$$

Where $y^E = V^E$ or Δks or $\Delta\eta$ or G^{*E}

x_1 and x_2 = mole fractions of pure components 1 and 2, respectively. The excess parameters have been calculated by using the relation

$$Y^E = Y_{\exp} - Y_{ideal} \quad (8)$$

The standard deviations (σ) for the excess properties were computed using the relation[7].

$$\sigma Y^E = \frac{\left[\frac{\sum (Y^E{}_{obs} - Y^E{}_{cal})}{m-n}\right]}{2} 1/2 \quad (9)$$

Where $Y^E = V^E$ or Δks or $\Delta\eta$ or G^{*E}

x_1 and x_2 are the mole fractions of components 1 and 2.

M = No. of parameters

N = No. of experimental values

Results and Discussion

Para-chloroacetophenone is a protic solvent with dipole moment 1.5549 μ and alcohols are polar and self-associated molecules through hydrogen bonding in its pure state, they can easily form hydrogen bonds with other components due to some polar attractions. Deviation from ideal behaviour arises due to the interactions of one component with the other component in the liquid mixtures.

Table 3. Densities (ρ/g·cm^{-3}), ultrasonic velocities (u/m·s^{-1}) and viscosities (η/mPa.s) of binary mixtures of propiophenone with 2-alkoxy ethanols at different temperatures (303.15, 308.15, 313.15 and 318.15 K)

X1	303.15 K			308.15 K			313.15 K			318.15 K		
	ρ g cm^{-3}	U m.s^{-1}	η mPa.s	ρ g cm^{-3}	U m.s^{-1}	η mPa.s	ρ g cm^{-3}	U m.s^{-1}	η mPa.s	ρ g cm^{-3}	U m.s^{-1}	η mPa.s
PCAP + *n*-Propanol												
0.0000	0.7954	1187.64	1.8746	0.7914	1170.88	1.6962	0.7874	1154.02	1.5302	0.7834	1137.89	1.3837
0.0587	0.8337	1181.80	1.9490	0.8296	1166.29	1.7814	0.8255	1149.31	1.6447	0.8214	1134.02	1.5096
0.1233	0.8722	1178.44	2.0120	0.8680	1163.22	1.8547	0.8639	1146.82	1.7302	0.8597	1131.51	1.6070
0.1943	0.9109	1178.87	2.0729	0.9066	1163.71	1.9297	0.9023	1147.45	1.8121	0.8980	1132.24	1.6964
0.3423	0.9811	1191.16	2.1829	0.9766	1175.53	2.0556	0.9720	1159.04	1.9457	0.9676	1143.99	1.8425
0.4384	1.0205	1206.64	2.2413	1.0158	1190.68	2.1227	1.0112	1173.94	2.0187	1.0066	1158.51	1.9225
0.5395	1.0576	1229.10	2.2898	1.0528	1212.90	2.1818	1.0481	1195.53	2.0906	1.0434	1179.86	2.0019
0.6457	1.0925	1259.77	2.3258	1.0876	1242.94	2.2350	1.0828	1225.04	2.1576	1.0780	1208.84	2.0805
0.7576	1.1255	1300.03	2.3493	1.1204	1282.21	2.2793	1.1156	1263.55	2.2139	1.1107	1246.39	2.1497
0.8756	1.1566	1351.47	2.3624	1.1515	1331.34	2.3047	1.1465	1311.41	2.2482	1.1415	1292.88	2.1899
1.0000	1.1859	1412.80	2.3538	1.1806	1389.64	2.2924	1.1755	1366.12	2.2314	1.1704	1343.04	2.1704
PCAP + *n*-Butanol												
0.0000	0.8021	1222.51	2.3146	0.7982	1205.13	2.0776	0.7943	1188.17	1.8599	0.7905	1172.36	1.6593
0.0708	0.8396	1219.57	2.3536	0.8356	1203.47	2.1430	0.8317	1186.70	1.9539	0.8277	1171.47	1.7722
0.1467	0.8775	1219.54	2.3911	0.8733	1203.43	2.1941	0.8693	1186.74	2.0230	0.8652	1171.79	1.8539
0.2278	0.9155	1222.67	2.4256	0.9112	1206.35	2.2442	0.9070	1189.52	2.0838	0.9028	1174.82	1.9274
0.3889	0.9845	1238.06	2.4716	0.9799	1221.20	2.3145	0.9755	1203.82	2.1714	0.9710	1188.96	2.0356
0.4884	1.0232	1253.73	2.4840	1.0185	1236.53	2.3416	1.0139	1218.79	2.2112	1.0094	1203.60	2.0894

Contd...

0.5888	1.0596	1274.57	2.4805	1.0548	1257.12	2.3573	1.0501	1238.72	2.2438	1.0454	1222.96	2.1369
0.6902	1.0939	1300.89	2.4632	1.0890	1282.86	2.3603	1.0843	1263.85	2.2662	1.0795	1247.61	2.1778
0.7926	1.1264	1332.91	2.4326	1.1213	1314.06	2.3524	1.1165	1294.20	2.2807	1.1116	1277.20	2.2061
0.8959	1.1570	1370.56	2.3939	1.1518	1350.46	2.3337	1.1469	1329.07	2.2742	1.1419	1310.35	2.2115
1.0000	1.1859	1412.80	2.3538	1.1806	1389.64	2.2924	1.1755	1366.12	2.2314	1.1704	1343.04	2.1704
PPH+2-BOE												
0.0000	0.8078	1258.63	2.9252	0.8041	1248.12	2.6270	0.8004	1237.48	2.3444	0.7966	1226.53	2.0661
0.0830	0.8449	1258.04	2.9026	0.8410	1248.16	2.6396	0.8372	1237.80	2.3893	0.8334	1227.14	2.1444
0.1696	0.8823	1260.12	2.8880	0.8783	1249.86	2.6467	0.8744	1239.14	2.4231	0.8704	1228.59	2.1971
0.2594	0.9199	1265.05	2.8730	0.9157	1253.88	2.6505	0.9116	1242.67	2.4450	0.9075	1231.50	2.2378
0.4305	0.9879	1281.41	2.8197	0.9835	1268.61	2.6313	0.9791	1255.94	2.4548	0.9747	1243.57	2.2794
0.5314	1.0260	1295.78	2.7635	1.0214	1281.90	2.5989	1.0169	1268.30	2.4435	1.0124	1254.87	2.2907
0.6297	1.0618	1313.33	2.6897	1.0571	1298.44	2.5512	1.0525	1283.80	2.4203	1.0478	1269.38	2.2943
0.7257	1.0955	1334.13	2.6044	1.0907	1318.26	2.4950	1.0860	1302.35	2.3895	1.0812	1286.67	2.2870
0.8193	1.1273	1357.72	2.5115	1.1224	1340.38	2.4319	1.1175	1322.76	2.3480	1.1127	1305.47	2.2678
0.9107	1.1574	1384.32	2.4290	1.1523	1365.08	2.3656	1.1473	1345.43	2.2989	1.1424	1325.56	2.2285
1.0000	1.1859	1412.80	2.3538	1.1806	1389.64	2.2924	1.1755	1366.12	2.2314	1.1704	1343.04	2.1704

Table 4. Experimental values of excess molar volumes (V^E), deviation in viscosity ($\Delta\eta$) deviation in isentropic compressibility (ks^E) and excess Gibbs free energy of activation of viscous flow(G^{*E}), Grunberg-Nissan interaction parameters (d), Katti-Chaudari interaction parameters (W_{vis}) and hind interaction parameters (H_{12}) at 303.15 K

x_1	V^E $cm^3.mol^{-1}$	Δks pa^{-1}	$\Delta\eta$ mPa.s	G^{*E} $J.mol^{-1}$	d	W_{vis}	H_{12}
PCAP+*n*-Propanol	303.15 K						
0.0000	0.0000	0.0000	0.0000	0.0000			
0.0587	-0.0310	-0.4954	0.0463	0.3759	0.2011	0.2741	2.5334
0.1233	-0.0539	-0.7953	0.0783	0.6532	0.1714	0.2428	2.4765
0.1943	-0.0726	-1.0303	0.1052	0.8797	0.1563	0.2258	2.4503
0.3423	-0.0944	-1.2500	0.1443	1.1718	0.1434	0.2091	2.4346
0.4384	-0.0978	-1.2762	0.1566	1.2418	0.1391	0.2026	2.4323
0.5395	-0.0953	-1.2492	0.1567	1.2147	0.1351	0.1964	2.4296
0.6457	-0.0862	-1.1836	0.1418	1.0795	0.1304	0.1896	2.4241
0.7576	-0.0707	-1.0406	0.1116	0.8364	0.1259	0.1830	2.4181
0.8756	-0.0445	-0.7421	0.0683	0.4947	0.1275	0.1825	2.4275
1.0000	0.0000	0.0000	0.0000	0.0000			
PCAP+*n*-Butanol							
0.0000	0.0000	0.0000	0.0000	0.0000			
0.0708	-0.0281	-0.4262	0.0362	0.2109	0.1024	0.1288	2.6093
0.1467	-0.0515	-0.7538	0.0707	0.4059	0.1043	0.1303	2.6168
0.2278	-0.0702	-0.9749	0.1021	0.5770	0.1062	0.1318	2.6244
0.3889	-0.0899	-1.1391	0.1417	0.7848	0.1080	0.1327	2.6324
0.4884	-0.0909	-1.1332	0.1503	0.8256	0.1085	0.1328	2.6349
0.5888	-0.0854	-1.0830	0.1428	0.7843	0.1064	0.1302	2.6291
0.6902	-0.0735	-0.9851	0.1215	0.6711	0.1028	0.1261	2.6184
0.7926	-0.0564	-0.8144	0.0869	0.4869	0.0962	0.1190	2.5987
0.8959	-0.0339	-0.5206	0.0442	0.2533	0.0869	0.1091	2.5713
1.0000	0.0000	0.0000	0.0000	0.0000			
PCAP+*n*-Pentanol							
0.0000	0.0000	0.0000	0.0000	0.0000			
0.0830	-0.0240	-0.3794	0.0249	0.1226	0.0587	0.0647	2.8028
0.1696	-0.0470	-0.6814	0.0597	0.2806	0.0299	0.0800	2.8514
0.2594	-0.0661	-0.9025	0.0960	0.4423	0.0582	0.0925	2.8895
0.4305	-0.0846	-1.0453	0.1405	0.6489	0.0444	0.1063	2.9261
0.5314	-0.0835	-1.0225	0.1419	0.6685	0.0650	0.1079	2.9245
0.6297	-0.0744	-0.9382	0.1243	0.6047	0.0550	0.1042	2.9061
0.7257	-0.0604	-0.8104	0.0939	0.4770	0.0385	0.0963	2.8753
0.8193	-0.0433	-0.6143	0.0544	0.2969	0.0114	0.0806	2.8232
0.9107	-0.0232	-0.3673	0.0241	0.1412	-0.0230	0.0698	2.7879
1.0000	0.0000	0.0000	0.0000	0.0000			

Table 5. Experimental values of excess molar volumes (V^E), deviation in viscosity($\Delta\eta$) deviation in isentropic compressibility (ks^E) and excess gibbs free energy of activation of viscous flow (G^{*E}), Grunberg-Nissan interaction parameters(d), Katti-Chaudari interaction parameters (W_{vis}) and hind interaction parameters (H_{12}) at 308.15 K

x_1	V^E $cm^3.mol^{-1}$	Δks pa^{-1}	$\Delta\eta$ mPa.s	G^{*E} $J.mol^{-1}$	d	W_{vis}	H_{12}
PCAP + *n*-Propanol 308.15 K							
0.0000	0.0000	0.0000	0.0000	0.0000			
0.0587	-0.0352	-0.7101	0.0502	0.4383	0.2463	0.3187	2.4487
0.1233	-0.0612	-1.0680	0.0850	0.7548	0.2097	0.2805	2.3875
0.1943	-0.0822	-1.3292	0.1177	1.0303	0.1954	0.2644	2.3701
0.3423	-0.1040	-1.5301	0.1554	1.3296	0.1719	0.2373	2.3394
0.4384	-0.1071	-1.5515	0.1652	1.3849	0.1628	0.2260	2.3297
0.5395	-0.1036	-1.5388	0.1639	1.3425	0.1560	0.2171	2.3242
0.6457	-0.0958	-1.4607	0.1539	1.2152	0.1545	0.2134	2.3306
0.7576	-0.0800	-1.2855	0.1314	0.9865	0.1591	0.2158	2.3520
0.8756	-0.0524	-0.8743	0.0865	0.6108	0.1707	0.2253	2.3911
1.0000	0.0000	0.0000	0.0000	0.0000			
PCAP + *n*-Butanol							
0.0000	0.0000	0.0000	0.0000	0.0000			
0.0708	-0.0336	-0.6302	0.0502	0.3024	0.1587	0.1847	2.5666
0.1467	-0.0576	-0.9775	0.0850	0.5140	0.1392	0.1650	2.5245
0.2278	-0.0776	-1.1941	0.1177	0.7024	0.1351	0.1604	2.5194
0.3889	-0.0977	-1.3464	0.1534	0.8987	0.1274	0.1519	2.5076
0.4884	-0.0986	-1.3403	0.1592	0.9235	0.1244	0.1485	2.5035
0.5888	-0.0927	-1.3069	0.1532	0.8811	0.1226	0.1462	2.5014
0.6902	-0.0807	-1.2006	0.1344	0.7679	0.1212	0.1443	2.4993
0.7926	-0.0633	-1.0098	0.1046	0.5923	0.1222	0.1448	2.5030
0.8959	-0.0388	-0.6720	0.0637	0.3550	0.1309	0.1529	2.5264
1.0000	0.0000	0.0000	0.0000	0.0000			
PCAP + *n*-Pentanol							
0.0000	0.0000	0.0000	0.0000	0.0000			
0.0830	-0.0313	-0.5284	0.0403	0.1844	0.0918	0.0974	2.7247
0.1696	-0.0543	-0.8518	0.0764	0.3500	0.0942	0.0999	2.7309
0.2594	-0.0736	-1.0448	0.1103	0.5051	0.1000	0.1056	2.7468
0.4305	-0.0908	-1.1683	0.1483	0.6853	0.1068	0.1123	2.7621
0.5314	-0.0901	-1.1417	0.1497	0.7003	0.1075	0.1130	2.7602
0.6297	-0.0819	-0.0721	0.1349	0.6427	0.1052	0.1107	2.7489
0.7257	-0.0692	-0.9709	0.1108	0.5383	0.1032	0.1087	2.7379
0.8193	-0.0519	-0.7705	0.0790	0.3922	0.1010	0.1064	2.7266
0.9107	-0.0302	-0.5036	0.0433	0.2190	0.1029	0.1082	2.7262
1.0000	0.0000	0.0000	0.0000	0.0000			

Table 6. Experimental values of excess molar volumes (V^E), deviation in viscosity($\Delta\eta$) deviation in isentropic compressibility (ks^E) and excess Gibbs free energy of activation of viscous flow (G^{*E}), Grunberg-Nissan interaction parameters (d), Katti-Chaudari interaction parameters (W_{vis}) and hind interaction parameters (H_{12}) at 313.15 K

x_1	V^E $cm^3.mol^{-1}$	Δks pa^{-1}	$\Delta\eta$ mPa.s	G^{*E} $J.mol^{-1}$	d	W_{vis}	H_{12}
PCAP + n-Propanol	313.15 K						
0.0000	0.0000	0.0000	0.0000	0.0000			
0.0587	-0.0419	-0.7308	0.0734	0.6392	0.3932	0.4648	2.5446
0.1233	-0.0737	-1.2091	0.1135	0.0135	0.3067	0.3767	2.4060
0.1943	-0.0955	-1.5172	0.1457	0.3021	0.2658	0.3342	2.3461
0.3423	-0.1129	-1.7428	0.1755	1.5658	0.2144	0.2794	2.2706
0.4384	-0.1157	-1.7781	0.1811	1.5931	0.1970	0.2600	2.2486
0.5395	-0.1140	-1.7496	0.1821	1.5491	0.1898	0.2505	2.2473
0.6457	-0.1082	-1.6811	0.1746	1.4146	0.1899	0.2484	2.2624
0.7576	-0.0929	-1.5042	0.1525	0.1610	0.1976	0.2540	2.2959
0.8756	-0.0628	-0.0592	0.1041	0.7353	0.2171	0.2712	2.3585
1.0000	0.0000	0.0000	0.0000	0.0000			
PCAP + n-Butanol							
0.0000	0.0000	0.0000	0.0000	0.0000			
0.0708	-0.0404	-0.7028	0.0677	0.4352	0.2403	0.2658	2.5601
0.1467	-0.0676	-1.0964	0.1086	0.6988	0.1989	0.2243	2.4794
0.2278	-0.0870	-1.3270	0.1393	0.8901	0.1783	0.2033	2.4416
0.3889	-0.1040	-1.4840	0.1671	1.0526	0.1536	0.1779	2.3971
0.4884	-0.1054	-1.4900	0.1699	1.0572	0.1461	0.1700	2.3855
0.5888	-0.1018	-1.4474	0.1652	1.0102	0.1443	0.1676	2.3867
0.6902	-0.0927	-1.3475	0.1499	0.8985	0.1460	0.1688	2.3961
0.7926	-0.0769	-1.1505	0.1263	0.7353	0.0575	0.1797	2.4299
0.8959	-0.0483	-0.7600	0.0814	0.4603	0.0767	0.1983	2.4823
1.0000	0.0000	0.0000	0.0000	0.0000			
PCAP + n-Pentanol							
0.0000	0.0000	0.0000	0.0000	0.0000			
0.0830	-0.0360	-0.6440	0.0543	0.2594	0.1316	0.1369	2.6443
0.1696	-0.0617	-0.9998	0.0979	0.4666	0.1277	0.1331	2.6354
0.2594	-0.0801	-1.2142	0.1299	0.6188	0.1239	0.1294	2.6260
0.4305	-0.0959	-1.3409	0.1591	0.7606	0.1192	0.1246	2.6123
0.5314	-0.0959	-1.3249	0.1592	0.7649	0.1180	0.1234	2.6075
0.6297	-0.0886	-1.2667	0.1471	0.7120	0.1173	0.1227	2.6033
0.7257	-0.0777	-1.1684	0.1271	0.6197	0.1198	0.1251	2.6071
0.8193	-0.0598	-0.9475	0.0962	0.4733	0.1232	0.1284	2.6128
0.9107	-0.0358	-0.6499	0.0574	0.2844	0.1355	0.1405	2.6406
1.0000	0.0000	0.0000	0.0000	0.0000			

Table 7. Experimental values of excess molar volumes (V^E), deviation in viscosity($\Delta\eta$) deviation in isentropic compressibility (ks^E) and excess Gibbs free energy of activation of viscous flow (G^{*E}), Grunberg-Nissan interaction parameters(d), Katti-Chaudari interaction parameters (W_{vis}) and hind interaction parameters (H_{12}) at 318.15 K

X1	V^E $cm^3.mol^{-1}$	Δks pa^{-1}	$\Delta\eta$ mPa.s	G^{*E} $J.mol^{-1}$	d	W_{vis}	H_{12}
PCAP + *n*-Propanol	318.15 K						
0.0000	0.0000	0.0000	0.0000	0.0000			
0.0587	-0.0474	-0.9123	0.0797	0.7528	0.4766	0.5474	2.4981
0.1233	-0.0830	-1.4180	0.1263	1.2041	0.3782	0.4475	2.3614
0.1943	-0.1071	-1.7730	0.1599	1.5214	0.3226	0.3905	2.2877
0.3423	-0.1255	-2.0823	0.1895	1.7917	0.2551	0.3197	2.1978
0.4384	-0.1282	-2.1111	0.1939	1.8047	0.2320	0.2945	2.1708
0.5395	-0.1265	-2.1039	0.1938	1.7406	0.2211	0.2815	2.1670
0.6457	-0.1199	-2.0348	0.1888	1.5980	0.2224	0.2806	2.1896
0.7576	-0.1066	-1.8306	0.1700	0.3317	0.2354	0.2914	2.2399
0.8756	-0.0712	-1.3327	0.1173	0.8475	0.2589	0.3126	2.3157
1.0000	0.0000	0.0000	0.0000	0.0000			
PCAP + *n*-Butanol							
0.0000	0.0000	0.0000	0.0000	0.0000			
0.0708	-0.0470	-0.8432	0.0767	0.5470	0.3091	0.3340	2.4980
0.1467	-0.0761	-1.3139	0.1196	0.8507	0.2481	0.2730	2.3927
0.2278	-0.0956	-1.6162	0.1517	1.0665	0.2188	0.2436	2.3461
0.3889	-0.1115	-1.8204	0.1776	1.2236	0.1827	0.2069	2.2884
0.4884	-0.1132	-1.8357	0.1805	1.2211	0.1727	0.1963	2.2760
0.5888	-0.1096	-1.7843	0.1766	1.1648	0.1701	0.1933	2.2796
0.6902	-0.1006	-0.6937	0.1657	1.0562	0.1758	0.1985	2.3023
0.7926	-0.0869	-0.4884	0.1417	0.8682	0.1902	0.2122	2.3459
0.8959	-0.0573	-0.0182	0.0943	0.5541	0.2175	0.2387	2.4204
1.0000	0.0000	0.0000	0.0000	0.0000			
PCAP + *n*-Pentanol							
0.0000	0.0000	0.0000	0.0000	0.0000			
0.0830	-0.0427	-0.7662	0.0697	0.3674	0.1889	0.1939	2.5758
0.1696	-0.0694	-0.2113	0.1133	0.5924	0.1638	0.1690	2.5205
0.2594	-0.0879	-0.4279	0.1447	0.7502	0.1516	0.1569	2.4947
0.4305	-0.1024	-1.5733	0.1684	0.8653	0.1365	0.1418	2.4616
0.5314	-0.1016	-1.5480	0.1692	0.8656	0.1343	0.1397	2.4579
0.6297	-0.0961	-0.4990	0.1625	0.8275	0.1373	0.1426	2.4667
0.7257	-0.0857	-0.3974	0.1452	0.7370	0.1436	0.1487	2.4829
0.8193	-0.0704	-0.1538	0.1163	0.5890	0.1549	0.1599	2.5109
0.9107	-0.0442	-0.7723	0.0674	0.3426	0.1646	0.1693	2.5328
1.0000	0.0000	0.0000	0.0000	0.0000			

The non-linear behaviour with the mole fraction of PCAP and the density, viscosity and velocity mixtures shows that the existence of intermolecular interactions between the unlike molecules[8].

Excess molar volumes (V^E)

From Figure 1 and Tables 4-7 V^E values show the negative excess molar volume (V^E) values increases with increase in temperature. This shows the contraction of volume which shows the presence of strong intermolecular forces between unlike molecules than the like molecules. The intermolecular interactions are formed between the oxygen atom of -OH group of alcohols and the carbonyl group of p-chloroacetophenone[9].
Excess molar volumes (V^E) depends on some important factors like[10].

(1) The disruption of dipolar molecules due to the addition of the second type of molecule
(2) Formation of charge transfer complex or dipole-dipole interactions or hydrogen bonding
(3) Chemical association between unlike molecules through the formation of hydrogen bond, which is a strong specific interaction
(4) Association through weaker physical forces like dipole-dipole interaction and
(5) Accommodation of molecular of one component into the interstitial positions of the structural network of molecules of another component

The first factor shows about positive excess molar volumes (V^E) due to the expansion of volume. And the three other factors[11] show about negative excess molar volumes (V^E) due to the contraction of volume.

Strength of interaction between –C=O and –OH order as follows:

PCAP + *n*-Propanol > PCAP + *n*-Butanol > PCAP + *n*-Pentanol

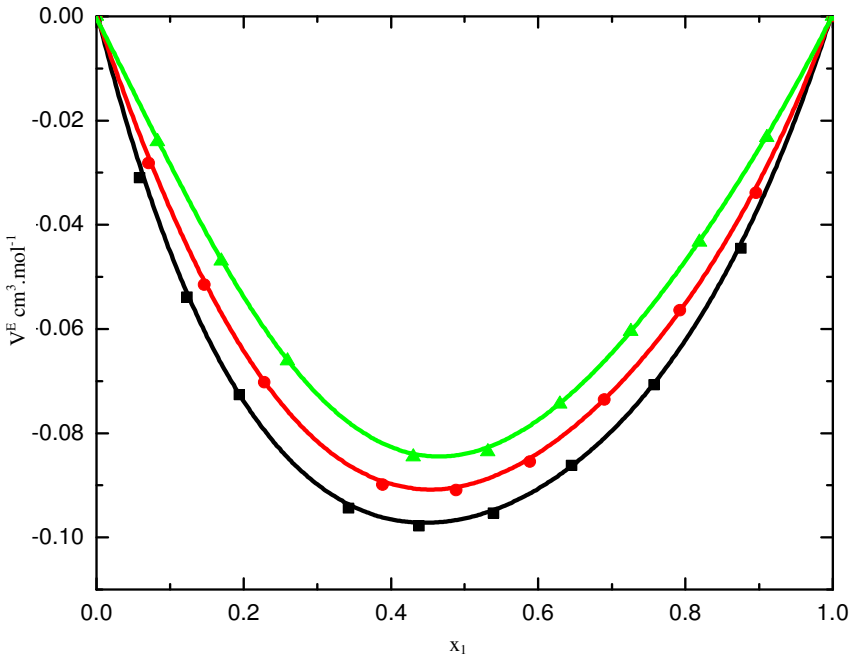

Figure 1. Variation of V^E of the binary liquid mixtures of PCAP with *n*-Propanol(▪), *n*-Butanol(●) and *n*-Pentanol(▲) at 303.15 K

Deviation in isentropic compressibility

Kiyohara and Benson[12] have discussed that variation of isentropic compressibility (Δks) is due to few factors like dipole-dipole, charge transfer, hydrogen bond and dipole- induced dipole interactions. The negative deviation in isentropic compressibility for all the three systems at all temperatures as shown in Figure 2 and Table 4-7 Δks values indicates the packing is highly efficient than in the pure components and the presence of strong intermolecular bonding between the components in the binary mixture[13]. There are stronger interactions for the PCAP + *n*-Propanol system. Fort and moore[14] have reported that Δks becomes increasingly negative and becomes weaker as the chain length of alcohol increases. The interaction follows the order: *n*-Propanol > *n*-Butanol > *n*-Pentanol.

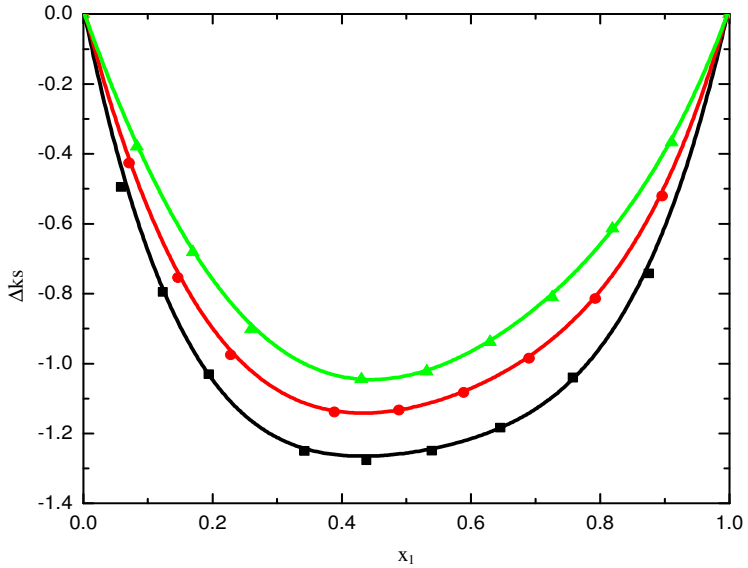

Figure 2. Variation of Δks of the binary liquid mixtures of PCAP with *n*-propanol(▪), *n*- butanol(●) and *n*-pentanol(▲) at 303.15 K

Deviation in viscosity

The positive deviation in viscosity increases with increase in temperature and decreases with increasing chain length, as shown in Figure 3 and Table 4-7 Δη shows the strong intermolecular interaction leads to a compact structure and makes more negative deviation of isentropic compressibility. The positive values of Δη indicates the specific interactions of unlike molecules.

Gibbs energy of activation of viscous flow (G^{*E})

The positive values of Gibbs energy of activation of viscous flow as shown in Figure 4 increases with increasing temperature and decreases with increasing chain length. This trend may suggest that there is a thermal agitation of liquid systems in high temperatures[15]. Large positive values of G^{*E} are attributed to the considerable size and cohesive energy difference between the two unlike molecules[16]. G^{*E} and d values also decide the type of interaction between the unlike molecules[17]. The positive values of G^{*E} and Grunberg-Nissan (d) indicate the strong specific interactions, while negative values of G^{*E} and Grunberg-Nissan(d) point out the dominance of dispersion forces between unlike molecules[16].

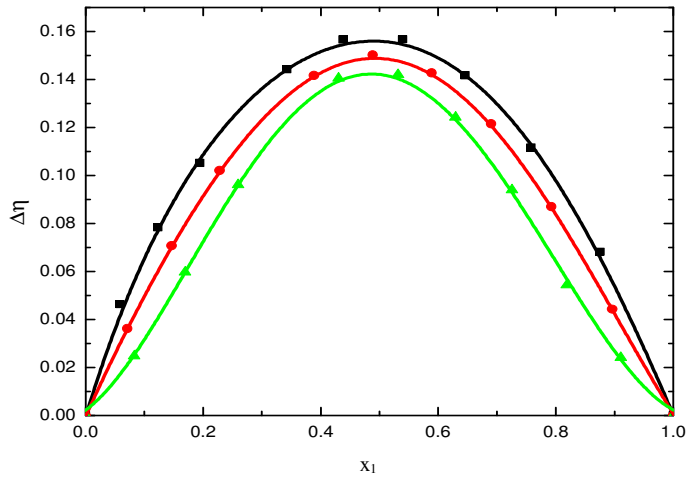

Figure 3. Variation of Δη of the binary liquid mixtures of PCAP with *n*-propanol (▪), *n*-butanol (●) and *n*-pentanol (▲) at 303.15 K

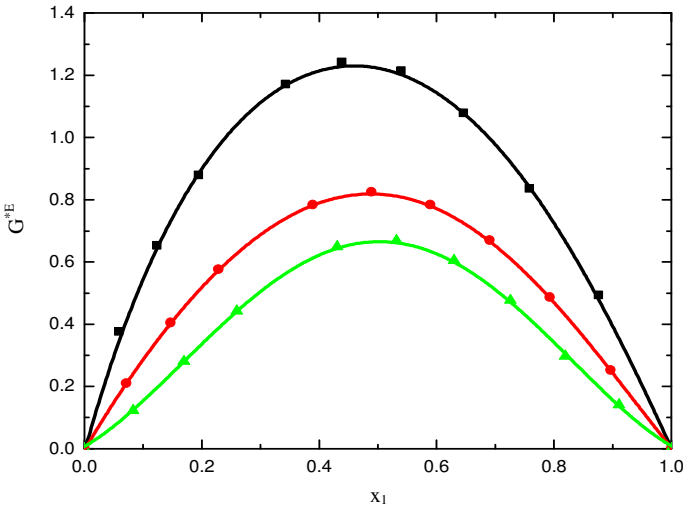

Figure 4. Variation of G^{*E} of the binary liquid mixtures of PCAP with *n*-propanol (▪), *n*-butanol (●) and *n*-pentanol (▲) at 303.15 K

Spectral investigation

Infra-red spectroscopy is applied to the qualitative and quantitative determination of molecular species of all types. The IR also shows the difference between inter and intramolecular hydrogen bonding by intensity and sharpness of bands. The IR region lies between 4000-650 cm^{-1}. IR studies have been carried out for binary mixtures of *n*-propanol, *n*-butanol and *n*-pentanol with PCAP with equal proportions. The frequency of –CO band in PCAP is observed at 1678.14 cm^{-1}. The broadening of –OH peaks indicates that there is strong intermolecular hydrogen bonding between the binary liquid components.The –OH stretching of 1:1 ratio of PCAP+*n*-propanol, PCAP+*n*-butanol, PCAP+*n*-pentanol are 3338.78 cm^{-1}, 3342.63 cm^{-1}, 3348.42 cm^{-1} as shown in Figure 5 and Table 8. As the chain length of alcohols increases, -OH stretching frequency increases.

Table 8. Experimental FT-IR frequencies of –OH Stretching for the binary liquid mixtures of PCAP + *n*-Propanol, PCAP + *n*-Butanol, PCAP + *n*-Pentanol at equal proportions

Mixtures	-OH, cm^{-1}	-CO, cm^{-1}
PCAP + *n*-Propanol	3338.78	1679.99
PCAP + *n*-Butanol	3342.63	1679.99
PCAP + *n*-Pentanol	3348.42	1679.99

Table 9. Coefficients of Redlich-Kister polynomial equation

Property	Temp, K	A_0	A_1	A_2	σ	A_0	A_1	A_2	σ	A_0	A_1	A_2	σ
PCAP+*n*-propanol						PCAP+*n*-butanol				PCAP+*n*-pentanol			
V^E	303.15	-0.3837	0.0655	-0.1345	0.001	-0.3600	0.0427	-0.0443	0.0010	-0.3358	0.0283	0.0534	0.0012
	308.15	-0.4201	0.0638	-0.1922	0.0008	-0.3876	0.0497	-0.0983	0.0013	-0.3584	0.0266	-0.0393	0.0012
	313.15	-0.4586	0.0663	-0.3046	0.001	-0.4175	0.0376	-0.2084	0.0007	-0.3818	0.0220	-0.1032	0.0008
	318.15	-0.5089	0.0685	-0.3637	0.001	-0.4435	0.0322	-0.3109	0.0015	-0.4027	0.0109	-0.2094	0.0015
Δks	303.15	-4.9497	0.5488	-4.0594	0.0267	-4.5335	0.4981	-2.1896	0.0109	-4.1442	0.4190	-0.8757	0.0170
	308.15	-5.9603	1.3882	-6.1057	0.0718	-5.2603	0.9090	-4.3400	0.0314	-4.5542	0.4923	-2.8167	0.0165
	313.15	-6.9353	0.9864	-6.5021	0.0338	-5.8370	0.9253	-5.0209	0.0328	-5.2221	0.3215	-4.1598	0.0279
	318.15	-8.1917	0.8539	-8.6074	0.0649	-7.1683	0.5031	-6.6128	0.0317	-6.1583	0.3548	-5.1406	0.0211
Δη	303.15	0.6144	-0.0747	0.1407	0.0043	0.5986	-0.0471	-0.1300	0.0010	0.5695	-0.0355	-0.3871	0.0016
	308.15	0.6547	-0.0149	0.2691	0.0021	0.6262	-0.0305	0.1180	0.0024	0.5926	-0.0070	-0.1029	0.0022
	313.15	0.7090	-0.0830	0.5944	0.0062	0.6672	-0.0487	0.3911	0.0027	0.6356	-0.0193	0.0999	0.0018
	318.15	0.7621	-0.0715	0.7020	0.0053	0.7082	-0.0334	0.5280	0.0032	0.6800	-0.0297	0.2768	0.0016
G^{*E}	303.15	4.8458	-1.0476	0.9877	0.0249	3.2925	-0.2947	-0.5015	0.0049	2.6735	0.0328	-1.4959	0.0055
	308.15	5.4199	-1.0160	1.7679	0.0156	3.6390	-0.3687	0.6984	0.0120	2.7685	0.1277	-0.3595	0.0090
	313.15	6.1289	-1.8580	4.0146	0.0540	4.1487	-0.7200	2.2201	0.0182	3.0498	-0.0135	0.5569	0.0088
	318.15	6.9246	-2.2853	5.1059	0.0599	4.7784	-0.9809	3.2114	0.0268	3.4798	-0.2509	1.4936	0.0090

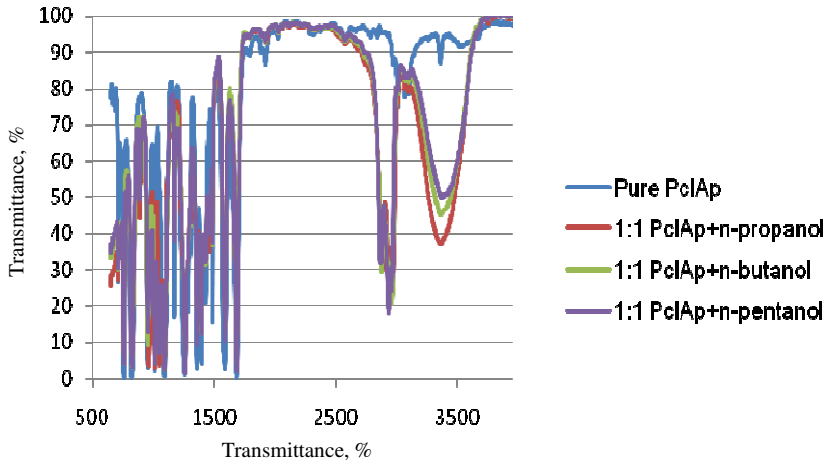

Figure 5. Observed –CO and –OH stretching bands in IR spectra

Correlation of viscosity data with semi-empirical relations

Grunberg-Nissan relation

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln 2 + x_1 x_2 d_{12} \quad (10)$$

d_{12} is a Grunberg–Nissan interaction parameter[18]. Fort and Moore[14] suggested that for any binary mixtures, a positive value of d_{12} indicates the presence of specific interactions while a negative value of d_{12} indicates the presence of weak interactions between unlike molecules.

Katti-Chaudari[19] relation

$$\ln V\eta = x_1 \ln V_1\eta_1 + x_2 \ln v_2\eta_2 + x_1x_2\, Wvis/RT \quad (11)$$

W_{Vis}/RT = interaction term

Hind *et al.*,[20] relation

$$H = x_{12}\eta_1 + x_2\eta_2 + 2x_1x_2\, H_{12} \quad (12)$$

H_{12}= Hind's interaction parameter

These relations has been considered as valid measure for detecting the presence of interactions between the components as shown in Table 4-7. The Excess parameters are well fitted in the Redlich-kister equation by least square method as shown in Table 9.

Conclusion

The experimental data of density, viscosity and speed of sound for the binary liquid mixtures of p-chloroacetophenone with *n*-propanol, *n*-butanol and *n*-pentanol have been measured. The negative V^E, Δks and the positive Δη, G^{*E} for all the systems at all temperatures shows that there is a strong intermolecular interaction between unlike molecules. The FT-IR studies also support the experimental intermolecular interactions.

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