

Partial Molar Volumes and Spectral Studies on Binary Mixtures of *p*-Chloroacetophenone with Aniline and *N*-Alkyl Anilines

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Ultrasonic velocities (u), viscosities (η) and densities (ρ) were measured for the binary mixtures of *p*-chloroacetophenone with aniline, *N*-methylaniline and *N,N*-dimethylaniline over the whole range of composition at different temperatures (303.15 K to 318.15 K) and at atmospheric pressure 0.1 MPa. Excess molar volume (V^E), deviation in viscosity ($\Delta\eta$) and deviation in isentropic compressibility (Δk_s) have been calculated and fitted to Redlich-Kister polynomial equation to obtain their coefficients and standard deviations. The analyzed viscosity data of binary liquid mixtures were used to test the Grunberg-Nissan, Katti-Chaudari and Hind semi-empirical equations. The FTIR spectral study supports the experimental data to explain the molecular interactions between unlike molecules. Partial molar volumes of binary mixtures were evaluated for better understanding of intermolecular interactions of the above binary mixtures.

Keywords: Excess molar volume, Partial molar volume, Redlich-Kister polynomial equation, Ultrasonic velocities.

INTRODUCTION

Thermodynamic and ultrasonic nature of binary mixtures has great importance. To know about the structural, physico-chemical behaviour, intramolecular and intermolecular nature, need of interpretation and analysis of excess parameters and along with liquid mixture theories is necessary. From the values of density (ρ), viscosity (η) and ultrasonic velocity (u) and the spectral investigation of Infra-red studies, the behaviour of intermolecular interactions between mixing molecules can be studied. The analysis of thermodynamic properties also shows the degree of deviation from ideal behaviour [1,2].

Previous investigations have been carried out on *p*-chloroacetophenone [3-5] and anilines [6-9] and amines [10,11] have been reported. Literature survey shown that no work has been executed on *p*-chloroacetophenone and aniline, *N*-methylaniline and *N,N*-dimethylaniline at 303.15 to 318.15 K. The effect of molecular size, chain length, shape and extent of molecular association of aromatic and aliphatic amines on volumetric, viscometric and acoustic properties of binary liquid mixtures containing hydrocarbons, esters and alcohols have been studied earlier [12-18].

p-Chloroacetophenone as main component with aniline, *N*-methyl aniline and *N,N*-dimethyl aniline are selected for the present investigation of the work. The selected chemicals have wide range of useful applications. *p*-Chloroacetophenone (PCAP) is a molecule having a wide range of application in the manufacture of cosmetics, drugs and perfumes, respectively. Aromatic anilines are used in rubber processing chemicals, herbicides, and dyes & pigments. A partial molar property is a thermodynamic quantity which indicates how an extensive property of a solution or mixture varies with changes in the molar composition of the mixture at constant temperature and pressure. Partial molar volumes of above mixtures have been calculated at four different temperatures.

EXPERIMENTAL

p-Chloroacetophenone, aniline, *N*-methylaniline, *N,N*-dimethylaniline are used in the present work were purchased from S.D. Fine Chemicals Ltd., India. All the chemicals selected were purified by the method described in the literature [41] and represented in Table-1. Experimental and literature values of density, viscosity and speed of sound of pure liquids *viz.*, *p*-

TABLE-1
MATERIALS DESCRIPTION

Component	CAS number	Source	Mass fraction purity	Water content (%)
<i>p</i> -Chloroacetophenone	99-91-2	SD-fine	0.980	0.042
Aniline	71-23-8	SD-fine	0.990	0.034
<i>N</i> -Methylaniline	71-36-3	SD-fine	0.990	0.033
<i>N,N</i> -Dimethylaniline	71-41-0	SD-fine	0.990	0.041

chloroacetophenone, aniline (AN), *N*-methylaniline (NMA), *N,N*-dimethylaniline (NNDMA) at four different temperatures (303.15, 308.15, 313.15, 318.15 K) are listed in Table-2.

Densities and velocities of pure liquids and mixtures were measured with an Anton-Paar Model DSA-5000M with accuracy in measurements of $\pm 0.0001 \text{ g/cm}^3$. A thermostatically controlled water bath was used. Viscosity measurements at various temperatures were calculated using Ubbelohde viscometer.

TABLE-2
COMPARISON OF EXPERIMENTAL VALUES OF DENSITIES, ULTRASONIC VELOCITY AND VISCOSITIES OF PURE COMPONENTS WITH THE CORRESPONDING LITERATURE VALUES AT TEMPERATURES (303.15, 308.15, 313.5 AND 318.15) K

Compound	T (K)	Density (ρ) (g cm^{-3})		Ultrasonic speed (u) (m s^{-1})		Viscosity (η) (mPa s)			
		Experimental	Literature	Experimental	Literature	Experimental	Literature		
<i>p</i> -Chloroacetophenone	303.15	1.1859	1.1856 ^a	1412.80	1412.00 ^a	2.3538	2.353 ^a		
	308.15	1.1806	1.1812 ^a	1389.64	1389.00 ^a	2.2924	2.292 ^a		
			1.1813 ^b	1390.00 ^b	2.293 ^c				
			1395.00 ^b	1389.98 ^d					
	313.15	1.1755	1366.12	2.2314					
318.15	1.1704	1343.04	2.1704						
Aniline	303.15	1.0150	1.01330 ^e	1625.40	1623.40 ^f	2.9890	3.097 ^e		
			1.01305 ^g		1615.18 ^t		3.027 ⁱ		
			1.01284 ^h		1619.20 ^g		3.250 ⁿ		
			1.01280 ^k		1614.50 ⁱ				
			1.01350 ^m		1615.20 ^k				
			1.01290 ^m		1615.20 ^m				
			1.01300 ⁿ		1619.30 ⁿ				
			1.01290 ⁿ		1614.50 ^o				
			1.01280 ^o		1614.00 ^s				
			1.01390 ^p		1615.00 ^s				
			1.01310 ^p						
			1.01318 ^s						
			1.01317 ^s						
			1.00890 ^e		1605.00		1601.88 ^t	2.6430	2.663 ^e
			1.00870 ⁿ				1602.95 ^r		2.800 ⁿ
1.00860 ⁿ	2.635 ⁱ								
1.00867 ^r	1585.30	1588.29 ^t	2.2970	2.329 ^e					
1.00890 ^t									
1.00460 ^e					1582.6 ^m	2.420 ⁿ			
1.00490 ^k					1580.05 ^m	2.304 ⁱ			
1.00436 ^m									
1.00463 ^m									
1.00450 ^m									
1.00490 ^m	1565.4	1574.41 ^t	1.951	2.057 ^e					
1.00440 ⁿ				2.047 ⁱ					
1.00420 ⁿ									
1.00090 ^t	303.15	0.9806	0.97770 ^e	1538.9	1545.50 ^g	1.722	1.734 ^e		
0.97801 ^g			1551.00 ^j		1.965 ^j				
0.98172 ^j			1548.30 ^k		1.963 ^e				
0.98170 ^e			1546.00 ^o						
0.97820 ^k			1546.90 ^r						
0.97828 ^o			1545.61 ^t						
0.97823 ^r									
0.97830 ^t			1518		1528.59 ^t		1.567	1.547 ^e	
0.97360 ^e									1528.15 ^r
0.97424 ^r									
0.97400 ^t			1498.5		1511.63 ^t		1.412	1.402 ^e	
0.96960 ^e									1512.40 ^k
0.96980 ^k									
0.96990 ^k									
0.96960 ^k			1478.02		1494.38 ^t		1.257	1.269 ^e	
0.96580 ^e									
0.96520 ^t									

<i>N,N</i> -Dimethylaniline	303.15	0.9481	0.94800 ^e	1462.8	1479.00 ^a	1.176	1.180 ^e
			0.94770 ^b		1468.00 ^q		1.174 ^u
			0.94800 ⁿ		1468.00 ^t		1.172 ^v
			0.94767 ⁿ				1.180 ⁿ
			0.94840 ^q				
			0.94800 ^q				
	308.15	0.9435	0.94390 ^e	1442.3	1462 ^c	1.106	1.096 ^e
			0.95173 ^a		1449.74 ^t		1.111 ^v
			0.94360 ^t				
			0.95177 ^l				
			0.94355 ⁿ				
			0.94390 ^e				
	313.15	0.9394	0.93980 ^e	1422.9	1431.27 ^t	1.036	1.020 ^e
			0.93930 ^t		1431.00 ^q		0.982 ^u
			0.93940 ⁿ				1.01 ⁿ
			0.93850 ⁿ				
0.93970 ^q							
0.93570 ^e							
318.15	0.9353	0.93570 ^e	1402.1	1412.74 ^t	0.966	0.968 ^e	
		0.93510 ^t					

^a[Ref. 19], ^b[Ref. 20], ^c[Ref. 21], ^d[Ref. 22], ^e[Ref. 3], ^f[Ref. 24], ^g[Ref. 25], ^h[Ref. 26], ⁱ[Ref. 27], ^j[Ref. 28], ^k[Ref. 29], ^l[Ref. 30], ^m[Ref. 31], ⁿ[Ref. 2], ^o[Ref. 33], ^p[Ref. 34], ^q[Ref. 35], ^r[Ref. 36], ^s[Ref. 37], ^t[Ref. 38], ^u[Ref. 39], ^v[Ref. 40]

RESULTS AND DISCUSSION

Fourier transform Infrared spectroscopy used to determine the position and absorption of peaks in the infrared region from 4000 to 400 cm⁻¹. Excess parameters in terms of thermodynamic studies are necessary to estimate the nature, extent and type of interactions/intermolecular forces between the liquid components in binary mixtures. Deviation from ideal behaviour arises due to the interactions of one component with the other component in the liquid mixtures.

p-Chloroacetophenone is a protic solvent with dipole moment 1.5549 μ and amines are strongly polar as they have large dipole moments. Primary and secondary amines form hydrogen bonding but tertiary amines do not, because they have no N-H bonds. Experimental values of density, viscosity and speed of sound at all mole fraction range and at temperatures of 303.15, 308.15, 313.15, 318.15 K of binary mixtures (PCAP+AN), (PCAP+NMA), (PCAP+NNDMA) is presented in Table-3.

Experimental values of excess molar volumes (V^E), deviation in viscosity (Δη), deviation in isentropic compressibility

TABLE-3
DENSITIES (ρ, g cm⁻³), ULTRASONIC VELOCITIES (u, m s⁻¹) AND VISCOSITIES (η, mPa s) OF
BINARY MIXTURES OF *p*-CHLOROACETOPHENONE WITH ANILINES AND *N*-ALKYL
ANILINES AT DIFFERENT TEMPERATURES (303.15, 308.15, 313.15 AND 318.15 K)

x ₁	303.15 K			308.15 K			313.15 K			318.15 K		
	ρ	u	η	ρ	u	η	ρ	u	η	ρ	u	η
PCAP + Aniline												
0.0000	1.0150	1625.40	2.9890	1.0106	1605.00	2.6430	1.0062	1585.30	2.2970	1.0018	1565.40	1.9510
0.0705	1.0349	1612.83	2.8989	1.0308	1595.97	2.5624	1.0271	1575.26	2.2258	1.0226	1602.84	1.8869
0.1462	1.0538	1596.69	2.8224	1.0497	1580.41	2.5012	1.0460	1561.40	2.1798	1.0413	1599.37	1.8565
0.2271	1.0723	1579.35	2.7494	1.0680	1563.16	2.4486	1.0643	1544.41	2.1486	1.0595	1580.44	1.8442
0.3880	1.1042	1544.47	2.6273	1.0995	1527.16	2.3738	1.0957	1507.93	2.1168	1.0906	1529.58	1.8577
0.4875	1.1215	1523.20	2.5606	1.1166	1505.40	2.3367	1.1127	1485.92	2.1069	1.1075	1496.59	1.8783
0.5879	1.1374	1502.28	2.4982	1.1324	1484.37	2.3019	1.1285	1464.13	2.1021	1.1232	1464.24	1.9020
0.6894	1.1521	1481.94	2.4384	1.1471	1463.40	2.2716	1.1429	1442.99	2.1026	1.1376	1432.82	1.9319
0.7919	1.1653	1461.49	2.3877	1.1603	1442.08	2.2523	1.1561	1421.30	2.1149	1.1507	1402.40	1.9746
0.8954	1.1770	1439.77	2.3520	1.1719	1418.35	2.2518	1.1672	1397.14	2.1483	1.1621	1372.75	2.0415
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 + <i>N</i> -Methylaniline												
0.0000	0.9806	1538.90	1.7220	0.9765	1518.00	1.5670	0.9724	1498.50	1.4120	0.9683	1478.02	1.2570
0.0827	1.0030	1530.42	1.7316	0.9991	1512.33	1.5756	0.9952	1493.06	1.4178	0.9910	1511.49	1.2597
0.1690	1.0250	1521.05	1.7602	1.0210	1502.87	1.6064	1.0171	1483.67	1.4555	1.0130	1511.82	1.2993
0.2645	1.0480	1509.63	1.7987	1.0438	1491.03	1.6530	1.0399	1471.47	1.5070	1.0355	1498.95	1.3591
0.4296	1.0847	1489.18	1.8874	1.0801	1470.00	1.7587	1.0761	1449.63	1.6247	1.0715	1466.01	1.4930
0.5305	1.1054	1476.49	1.9486	1.1006	1457.08	1.8304	1.0966	1436.46	1.7056	1.0919	1444.02	1.5837
0.6289	1.1246	1464.38	2.0126	1.1198	1444.99	1.9040	1.1156	1423.82	1.7906	1.1107	1422.44	1.6782
0.7250	1.1424	1452.59	2.0808	1.1375	1432.83	1.9824	1.1331	1411.52	1.8791	1.1282	1401.69	1.7742
0.8188	1.1587	1500.66	2.1567	1.1538	1420.43	2.0664	1.0490	1462.32	1.9746	1.1443	1489.52	1.4169
0.9104	1.1734	1427.89	2.2432	1.1684	1406.84	2.1660	1.1636	1384.35	2.0862	1.1587	1362.32	2.0049
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 + Aniline (313.15 K)							PCAP + Aniline (318.15 K)					
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	
0.0705	-0.4096	-0.7317	-0.0665	-0.1950	-0.1933	1.7566	-0.4146	-0.9123	-0.0795	-0.3014	-0.3221	1.1898
0.1462	-0.6284	-1.2106	-0.1076	-0.1675	-0.1602	1.8331	-0.6177	-1.4180	-0.1265	-0.2207	-0.2362	1.2898
0.2271	-0.7856	-1.5191	-0.1335	-0.1490	-0.1392	1.8839	-0.7745	-1.7730	-0.1566	-0.1693	-0.1828	1.3504
0.3880	-0.9126	-1.7450	-0.1548	-0.1289	-0.1165	1.9384	-0.8808	-2.0823	-0.1784	-0.1079	-0.1188	1.4209
0.4875	-0.9249	-1.7801	-0.1582	-0.1257	-0.1129	1.9477	-0.8913	-2.1111	-0.1797	-0.0900	-0.1002	1.4370
0.5879	-0.9111	-1.7512	-0.1564	-0.1284	-0.1160	1.9415	-0.8751	-2.1039	-0.1780	-0.0857	-0.0960	1.4293
0.6894	-0.8516	-1.6821	-0.1492	-0.1388	-0.1273	1.9159	-0.8246	-2.0348	-0.1703	-0.0920	-0.1030	1.3989
0.7919	-0.7498	-1.5046	-0.1302	-0.1572	-0.1478	1.8693	-0.7127	-1.8306	-0.1501	-0.1085	-0.1210	1.3412
0.8954	-0.5002	-1.0590	-0.0899	-0.1900	-0.1833	1.7841	-0.4987	-1.3327	-0.1059	-0.1427	-0.1584	1.2311
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
PCAP + <i>N</i> -Methylaniline (313.15 K)							PCAP + <i>N</i> -Methylaniline (318.15 K)					
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0827	-0.3406	-0.7028	-0.0620	-0.1932	-0.2018	1.4133	-0.3507	-0.8432	-0.0728	-0.2165	-0.2273	1.5492
0.1690	-0.5631	-1.0964	-0.0950	-0.1453	-0.1518	1.4836	-0.5893	-1.3139	-0.1121	-0.1713	-0.1803	1.6301
0.2645	-0.7231	-1.3270	-0.1218	-0.1249	-0.1301	1.5088	-0.7351	-1.6162	-0.1395	-0.1467	-0.1539	1.6706
0.4296	-0.8396	-1.4840	-0.1393	-0.0998	-0.1037	1.5374	-0.8387	-1.8204	-0.1564	-0.1201	-0.1258	1.7100
0.5305	-0.8423	-1.4900	-0.1411	-0.0939	-0.0975	1.5384	-0.8414	-1.8357	-0.1578	-0.1146	-0.1200	1.7123
0.6289	-0.8114	-1.4474	-0.1368	-0.0935	-0.0974	1.5287	-0.8072	-1.7843	-0.1533	-0.1152	-0.1208	1.7008
0.7250	-0.7336	-1.3475	-0.1270	-0.1002	-0.1046	1.5032	-0.7393	-1.6937	-0.1450	-0.1256	-0.1319	1.6656
0.8188	-0.6072	-1.1505	-0.1083	-0.1152	-0.1208	1.4566	-0.6240	-1.4884	-0.1243	-0.1429	-0.1508	1.6102
0.9104	-0.4037	-0.7600	-0.0718	-0.1399	-0.1483	1.3817	-0.4171	-1.0182	-0.0837	-0.1732	-0.1840	1.5161
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
PCAP + <i>N,N</i> -Dimethylaniline (313.15 K)							PCAP + <i>N,N</i> -Dimethylaniline (318.15 K)					
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0955	-0.3105	-0.6438	-0.0565	-0.0961	-0.1081	1.3066	-0.3508	-0.7662	-0.0655	-0.1371	-0.1506	1.1893
0.1924	-0.5172	-0.9994	-0.0866	-0.0503	-0.0614	1.3550	-0.5576	-1.2113	-0.1015	-0.0818	-0.0938	1.2416
0.2901	-0.6701	-1.2136	-0.1060	-0.0286	-0.0395	1.3764	-0.7104	-1.4279	-0.1217	-0.0490	-0.0604	1.2726
0.4685	-0.7679	-1.3403	-0.1173	-0.0064	-0.0166	1.3981	-0.7913	-1.5733	-0.1345	-0.0196	-0.0301	1.2981
0.5695	-0.7570	-1.3243	-0.1184	-0.0059	-0.0162	1.3922	-0.7838	-1.5480	-0.1345	-0.0166	-0.0272	1.2940
0.6650	-0.7059	-1.2662	-0.1128	-0.0085	-0.0190	1.3805	-0.7428	-1.4990	-0.1306	-0.0219	-0.0329	1.2751
0.7552	-0.6172	-1.1679	-0.1041	-0.0187	-0.0297	1.3520	-0.6642	-1.3974	-0.1202	-0.0331	-0.0449	1.2430
0.8411	-0.4985	-0.9472	-0.0850	-0.0311	-0.0434	1.3158	-0.5389	-1.1538	-0.1005	-0.0513	-0.0646	1.1922
0.9226	-0.3094	-0.6498	-0.0564	-0.0588	-0.0731	1.2390	-0.3498	-0.7723	-0.0644	-0.0774	-0.0935	1.1173
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

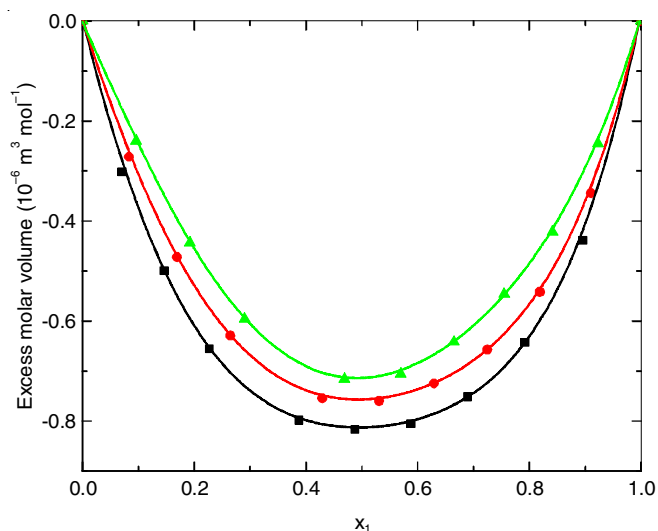


Fig. 1. Variation of excess molar volume (V^E) of the binary liquid mixtures of *p*-chloroacetophenone with aniline (■), *N*-methylaniline (●), *N,N*-dimethylaniline (▲) at 303.15 K

(b) Association through weaker physical forces like dipole-dipole interaction and,

(c) Accommodation of molecular of one component into the interstitial positions of the structural network of molecules of another component.

Similar kind of trend is also noticed for *N,N*-dimethylformamide with ketones [44]. Nitrogen atoms in anilines are good donors due to the lone pair of electrons on it. The strength of interaction order as follows:

Aniline > *N*-Methylaniline > *N,N*-dimethylaniline

$$V^E = \frac{[x_1 M_1 + x_2 M_2]}{\rho_m - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2} \right)} \quad (1)$$

where, x_1 , x_2 , M_1 , M_2 , ρ_1 , ρ_2 and ρ_m represent mole fraction, molecular mass, density of component 1 and 2 and the mixture, respectively.

Excess partial molar volumes: The partial molar volumes, $V_{m,1}^o$ of component 1 (*p*-chloroacetophenone (X_1)) and $V_{m,2}^o$ of component 2 (aniline, *N*-methylaniline and *N,N*-dimethylaniline (X_2)) in the mixture over the entire composition range are calculated using the following relations:

$$V_{m,1}^{oE} = V_m^E + V_{m,1}^* + x_2 \left(\frac{\partial V_m^E}{\partial x_1} \right)_{T,P} \quad (2)$$

$$V_{m,2}^{oE} = V_m^E + V_{m,2}^* + x_1 \left(\frac{\partial V_m^E}{\partial x_1} \right)_{T,P} \quad (3)$$

where $V_{m,1}^o$ and $V_{m,2}^o$ are the molar volumes of pure components, *p*-chloroacetophenone + aniline and substituted anilines. The $(\partial V_m^E/\partial x_1)_{T,P}$ value in eqns. 1 and 2 was calculated differentiating Redlich-Kister polynomial fitting. The eqns. 1 and 2 partial molar volumes used to calculate the excess partial molar volumes using the following equations:

$$V_{m,1}^{o,E} = V_{m,1}^o - V_{m,1}^* \quad (4)$$

$$V_{m,2}^{o,E} = V_{m,2}^o - V_{m,2}^* \quad (5)$$

where $V_{m,1}^{o,E}$ and $V_{m,2}^{o,E}$ are the excess partial molar volumes listed in Table-5 and Fig. 2. $V_{m,1}^{o,E,\infty}$ and $V_{m,2}^{o,E,\infty}$ are the excess partial molar volumes at infinite dilution were calculated by the following equations:

$$V_{m,2}^{o,E,\infty} = V_{m,2}^* + \sum_{i=0}^n A_i \quad (6)$$

$$V_{m,1}^{o,E,\infty} = V_{m,1}^* + \sum_{i=0}^n A_i \quad (7)$$

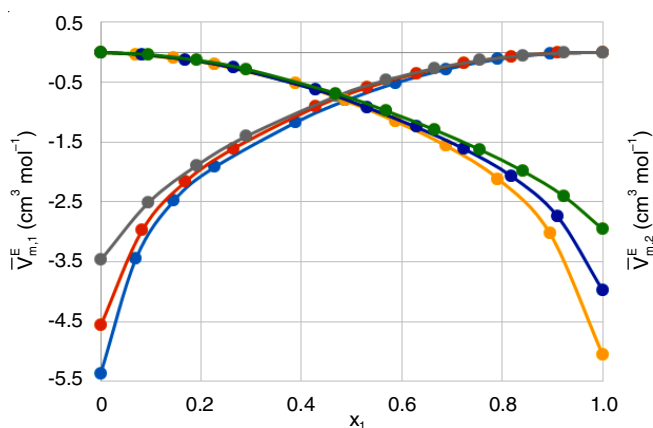


Fig. 2. Excess partial molar volumes of *p*-chloroacetophenone with aniline, *N*-methylaniline and *N,N*-dimethylaniline at 303.15 K

The negative excess partial molar volumes may be indicative of solute-solvent [45,46] interactions between unlike molecules, whereas positive values indicate the presence of strong self-association between like molecules. The observed excess partial molar volume value indicates cross-associations are strong compared to self-associations in *p*-chloroacetophenone

+ aniline and substituted anilines. Most negative values of $V_{m,1}^{o,E,\infty}$, $V_{m,2}^{o,E,\infty}$ of *p*-chloroacetophenone + aniline and substituted anilines shows stronger solute-solvent interactions at infinite dilution.

Deviation in isentropic compressibility (Δk_s): Fig. 3 shows that Δk_s for *p*-chloroacetophenone with aniline, *N*-methylaniline and *N,N*-dimethylaniline are negative over the entire composition range. The deviation in isentropic compressibility shown negative due to tightly packed molecules, which in turn proves the existence of strong intermolecular interaction between the unlike molecules [47]. Δk_s plays a key role in evaluating the compactness in liquid mixtures through hydrogen bonding, charge-transfer complex formation, dipole-dipole interactions, dipole induced dipole interactions [48].

$$k_s = \frac{1}{\rho U^2} \quad (8)$$

$$\Delta k_s = k_s - [x_1 k_{s1} + x_2 k_{s2}] \quad (9)$$

where, x_1 , x_2 , k_{s1} , k_{s2} , k_s represent mole fraction, isentropic compressibility of component 1 and 2 and the mixture, respectively.

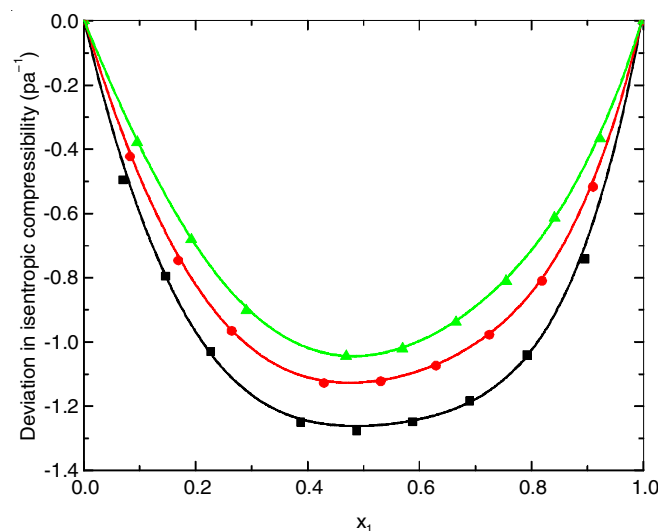


Fig. 3. Variation of deviation in isentropic compressibility (Δk_s) of the binary liquid mixtures of *p*-chloroacetophenone with aniline (■), *N*-methylaniline (●), *N,N*-dimethylaniline (▲) at 303.15 K

TABLE-5
VALUES OF $V_{m,1}^{o,\infty}$, $V_{m,1}^*$, $V_{m,1}^{o,E,\infty}$, $V_{m,2}^{o,\infty}$, $V_{m,2}^*$, $V_{m,2}^{o,E,\infty}$ OF THE COMPONENTS FOR
PCAP + ANILINE BINARY SOLUTIONS AT 303.15-318.15 K

Temp. (K)	$V_{m,1}^{o,\infty}$ (cm ³ mol ⁻¹)	$V_{m,1}^*$ (cm ³ mol ⁻¹)	$V_{m,1}^{o,E,\infty}$ (cm ³ mol ⁻¹)	$V_{m,2}^{o,\infty}$ (cm ³ mol ⁻¹)	$V_{m,2}^*$ (cm ³ mol ⁻¹)	$V_{m,2}^{o,E,\infty}$ (cm ³ mol ⁻¹)
PCAP + Aniline						
303.15	124.983	130.358	-5.375	86.700	91.754	-5.053
308.15	125.227	130.943	-5.716	86.449	92.153	-5.704
313.15	125.035	131.512	-6.477	85.729	92.556	-6.827
318.15	125.612	132.086	-6.475	86.037	92.963	-6.926
PCAP + <i>N</i> -Methylaniline						
303.15	125.789	130.358	-4.569	105.298	109.276	-3.978
308.15	125.889	130.943	-5.054	105.125	109.735	-4.609
313.15	126.458	131.512	-5.055	105.251	110.197	-4.947
318.15	126.384	132.086	-5.703	105.314	110.664	-5.350
PCAP + <i>N,N</i> -Dimethylaniline						
303.15	126.885	130.358	-3.472	124.861	127.817	-2.956
308.15	126.914	130.943	-4.029	124.932	128.440	-3.508
313.15	126.918	131.512	-4.595	124.927	129.000	-4.073
318.15	130.623	132.086	-1.464	128.664	129.566	-0.902

Deviation in viscosity ($\Delta\eta$): Fig. 4 shows that $\Delta\eta$ for *p*-chloroacetophenone with aniline, *N*-methylaniline and *N,N*-dimethylaniline are negative over the entire composition range. The negative deviation indicates that there are specific interactions in unlike molecules dominates over the mutual loss of specific interactions between the like molecules [49].

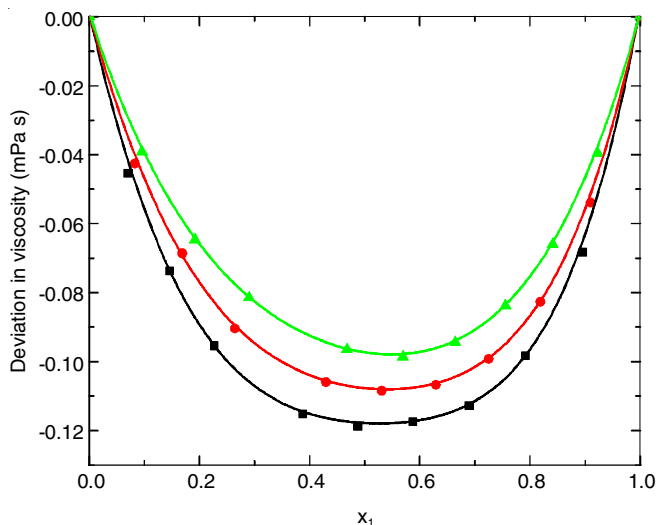


Fig. 4. Variation of deviation in viscosity ($\Delta\eta$) of the binary liquid mixtures of *p*-chloroacetophenone with aniline (■), *N*-methylaniline (●), *N,N*-dimethylaniline (▲) at 303.15 K

The strength of interaction fall in the order:

Aniline > *N*-Methylaniline > *N,N*-dimethylaniline

Figs. 1 and 4 show that V^E and $\Delta\eta$ are in the same trend and do not obey the general rule [21].

$$\Delta\eta = \eta - [x_1\eta_1 + x_2\eta_2] \quad (10)$$

Redlich-Kister equation (Y^E) [50]: This equation can be expressed as follows:

$$Y^E = x_1x_2[a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2] \quad (11)$$

$$\sigma(Y^E) = \left(\frac{\sum (Y_{obs}^E - Y_{cal}^E)^2}{(n - m)} \right)^{1/2} \quad (12)$$

where n is the total no. of experimental points and m is the no. of coefficients. The values of a_0 , a_1 , a_2 are the coefficients are

the standard deviation. From Table-6, we can say that the experimental data measured show good results by observing the values of standard deviation.

Grunberg and Nissan equation: Grunberg and Nissan [51] proposed the following equation for the viscosity measurements in binary mixtures:

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1x_2d \quad (13)$$

where, “ d ” is Grunberg-Nissan interaction parameter, shows the non-ideality of system by identifying the presence of interactions between the components.

Katti and Chaudhri equation: This equation [52] can be expressed as follows:

$$\ln \eta V = x_1 \ln V_1\eta_1 + x_2 \ln V_2\eta_2 + \frac{x_1x_2W_{vis}}{RT} \quad (14)$$

where, “ W_{vis} ” is Katti and Chaudari interaction parameter.

Similarly Hind equation [53] can be expressed as follows:

$$\eta = x_1^2\eta_1 + x_2^2\eta_2 + 2x_1x_2H_{12} \quad (15)$$

where, “ H_{12} ” is Hind interaction parameter.

FT-IR studies: The hydrogen bonding between the proton donor N-H of aniline and carbonyl group (C=O) of *p*-chloroacetophenone using FTIR spectroscopy is clearly observed. Generally, the intermolecular hydrogen bonding shows sharp peaks, whereas intramolecular hydrogen bonding shows broad peaks. Pure components show only broad bands. The characteristic absorption at 3425 and 3359 cm^{-1} N-H stretching frequency of aniline. There will be two bands for primary aniline. Only one band for *N*-methylaniline which is observed at 3408 cm^{-1} , while *N,N*-dimethylaniline does not show any N-H stretching.

Conclusion

The experimental values of density, viscosity and ultrasonic sound for the binary liquid mixtures of *p*-chloroacetophenone with aniline, *N*-methylaniline and *N,N*-dimethylaniline at four different temperatures (303.15, 308.15, 313.15, 318.15 K). From these values, excess parameters are calculated and correlated using Redlich-Kister type polynomial equation to derive the coefficients and standard deviation. The observed negative values of V^E , $\Delta\eta$ and positive values of Δk_s clearly shows that there are strong interactions between the mixing components. The order of interaction among the molecules in binary liquid

TABLE-6
COEFFICIENTS OF REDLICH-KISTER EQUATION AND STANDARD DEVIATION
VALUES OF TEMPERATURES FROM 303.15 TO 318.15 K

T (K)	PCAP + Aniline				PCAP + <i>N</i> -Methylaniline				PCAP + <i>N,N</i> -Dimethylaniline				
	A_0	A_1	A_2	σ	A_0	A_1	A_2	σ	A_0	A_1	A_2	σ	
V^E	303.15	-3.2276	-0.1608	-1.9866	0.01	-3.0113	-0.2952	-1.262	0.01	-2.8327	-0.2548	-0.3812	0.01
	308.15	-3.2503	-0.0060	-2.4601	0.01	-3.029	-0.2222	-1.8026	0.01	-2.8922	-0.2608	-0.8762	0.01
	313.15	-3.6212	0.1747	-3.0300	0.00	-3.3138	-0.1765	-2.2126	0.01	-3.0082	-0.2607	-1.3256	0.01
	318.15	-3.4590	0.2256	-3.2413	0.02	-3.3137	-0.1761	-2.2134	0.01	-3.0938	-0.2811	-1.912	0.02
Δk_s	303.15	-4.9762	-0.4261	-0.0447	0.03	-4.4888	-0.2915	-2.1362	0.02	-4.1430	-0.2245	-0.8754	0.02
	308.15	-6.0684	0.2032	-5.5800	0.03	-5.2805	0.0025	-4.1849	0.02	-4.5398	-0.2195	-2.8442	0.02
	313.15	-7.0064	-0.3791	-6.0925	0.02	-5.8521	-0.0799	-4.8668	0.02	-5.1757	-0.4957	-4.2674	0.04
	318.15	-8.2408	-0.7620	-8.1704	0.05	-7.1332	-0.7292	-6.5752	0.04	-6.1024	-0.6086	-5.2774	0.04
$\Delta\eta$	303.15	-0.4671	-0.0447	-0.3442	0.00	-0.4274	-0.0581	-0.2574	0.00	-0.3887	-0.0514	-0.162	0.00
	308.15	-0.5380	-0.0171	-0.4303	0.00	-0.4804	-0.042	-0.3358	0.00	-0.4311	-0.0455	-0.2514	0.00
	313.15	-0.6224	-0.0074	-0.5191	0.00	-0.5503	-0.0417	-0.4138	0.00	-0.4594	-0.0490	-0.3635	0.00
	318.15	-0.7072	-0.0005	-0.6580	0.00	-0.6164	-0.041	-0.5281	0.00	-0.5287	-0.0548	-0.4277	0.00

mixtures is as follows: (PCAP+AN) > (PCAP+NMA) > (PCAP+NNDMA). The increasing order of strength with respect to temperature is as follows: 318.15 K > 313.15 K > 308.15 K > 303.15 K.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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