Thermodynamic and Spectroscopic properties of binary liquid mixtures of p-chloroacetophenone and isomeric xylenes at various temperatures

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Abstract

Experimental values of the density(ρ), speed of sound(u), and viscosity(η) have been measured for binary mixtures of p-chloroacetophenone with isomeric xylenes (o-xylene, m-xylene, and p-xylene) at temperatures of 303.15 K, 308.15 K, 313.15 K and 318.15K over the entire composition range and at atmospheric pressure 0.1 MPa. By using this data, the excess parameters (excess volume (V^E), excess isentropic compressibility (κ_s^E), deviation in viscosity ($\Delta\eta$) and excess Gibbs free energy of activation of viscous flow (G^{*E})) for the binary systems at the above mentioned temperatures were calculated and fitted to Redlich-Kister equation to determine the fitting parameters and the root-mean-square deviations. FT-IR spectral data have been analyzed to study the n-π interactions and dipole-induced dipole interaction between unlike molecules.

Keywords: *Viscosity, excess molar volume, p-chloroacetophenone, isomeric xylenes, FT-IR Spectra*

1. Introduction

Thermodynamic and thermophysical properties of binary liquid mixtures are useful to study and understand the nature and extent of molecular interactions of the liquid state. p-chloroacetophenone is an aromatic ketone having a wide range of application in the manufacture of drugs, perfumes and cosmetics respectively. Isomeric xylenes are used as solvents and in printing, rubber and leather industries. *o-xylene* is used in medicines and dyes. *m-xylene* is used in industry, and used in paints and coatings. *p-xylene* is used as raw material for terephthalic acid, a key component in polyethylene terephthalate (PET) resins. Hence, thermodynamics properties are also important in designing industrial equipment, pharmacological applications [1-7]

The present research paper presents the data on densities, viscosity and velocity of binary liquid mixtures of p-chloroacetophenone with Isomeric xylenes (*o-xylene, m-xylene, and p-xylene*) at temperatures 303.15, 308.15, 313.15, and 318.15K. By using this data, various acoustical parameters like excess volumes, excess isentropic compressibility, deviation in viscosity and Gibbs free energy were calculated and fitted to the redlich-kister equation to estimate the standard deviations. The results obtained are used to explain the nature and extent of intermolecular interactions between the binary liquid components.

A literature review has shown that the thermodynamic properties of a binary mixture N, N-dimethylformamide with aromatic hydrocarbons [8], 1,2-dibromoethane plus aromatic hydrocarbon [9] ethyl iodide plus aromatic hydrocarbon [10] were already discussed.

However, there is no systematic study on thermodynamic and spectral studies of P-chloroacetophenone and Isomeric xylenes over the entire composition range and at temperature range 303.15K to 318.15K.

2. Experimental

2.1. Materials

Table 1 contains information regarding their source, purification method, purity, and analysis method of P-chloroacetophenone and Isomeric xylenes. Experimental values of density, speed of sound, and viscosity are presented in Table 2. These values are a good agreement with the data available in the literature [11-29].

2.2 Apparatus and procedure

All the binary liquid mixtures were prepared by weighing required amounts of pure liquids by using electric balance Mettler Toledo (ME204) with a precision of ± 0.01 mg by syringing each component into air-tight stopper bottles to minimize evaporation losses. The uncertainty of the mole fraction was ± 1×10^{-4}

After mixing the sample, the bubble free homogenous sample is transferred into the U-tube of the densimeter through a syringe. The density measurements were performed with a Rudolph Research Analytical digital densimeter (DDH-2911 Model), equipped with a built-in solid-state thermostat and a resident program with accuracy of temperature of (303.15 + ±0.03) K. The uncertainty of density measurement for liquid mixtures is $\pm 0.2 \times 10^{-4}$ g·cm^3 and the

uncertainty of temperature ±0.01K, Proper calibrations at each temperature were achieved with triply distilled, deionized water and with air as standards.

The speed of sound in pure liquids and in their mixtures was measured by using a multi frequency ultrasonic interferometer (M-82 Model, Mittal Enterprise, New Delhi, India) single-crystal variable path, operated at 2 MHz by using a digital constant temperature water bath. The uncertainty in the measurement of the speed of sound is ± 0.5% and uncertainty of temperature is ±0.02 K. Viscosities of all pure and liquid mixtures were measured using Ubbelohde viscometer of 10ml capacity. Efflux time was determined by using a digital chronometer to within ± 0.001s. The uncertainty in viscosity measurements was within ± 1.03% and the uncertainty of temperature ± 0.02 K.

3. Results and discussion

The excess thermodynamic / deviation functions were calculated by using the following equations

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

$$\Delta\eta = \eta - [x_1\eta_1 + x_2\eta_2] \quad (2)$$

$$G^{*E} = RT[ln\eta V - (X_1 ln\eta_1 V_1 + X_2 ln\eta_2 V_2) \quad (3)$$

where η, η_1, η_2, V, V_1 and V_2 are viscosities and mixture molar volumes and pure components respectively.

The isentropic compressibilities were calculated from the relation

$$k_s = 1/\rho\, U^2 \quad (4)$$

where ρ is the density and u is the speed of sound of the binary mixture.

Further, the excess isentropic compressibilities (Ks^E) are calculated from the following relations recommended by Benson and Kiyohara [30]

$$K_s^E = K_s - K_s^{id} \quad (5)$$

$$K_s^{iD} = \sum_{i=1}^{2} \emptyset_i \left\{K_{si} + \frac{TV_i(\alpha_i^2)}{C_{pi}}\right\} - \{T(\sum_{i=1}^{2} x_iV_i)(\sum_{i=1}^{2} \emptyset_i\alpha_i)\text{^}2\ /(\sum_{i=1}^{2} x_iC_{pi})\} \quad (6)$$

where φ_i, $C_{p,i}$, V_i, $\kappa_{s,i}$ and α_i are the volume fraction, molar heat capacity, molar volume, isentropic compressibility and coefficient of isobaric thermal expansion of pure components respectively.

Calculated Excess values (V^E, $\Delta\eta$, G^{*E}, K_S^E) and Experimental values (ρ, η, u) are given in Table 3 at temperatures from T= (303.15- 318.15) K for the binary mixtures of p-chloroacetophenone with *o-xylene*, *m-xylene* and *p*-xylene.

Excess molar volumes: (V^E)

Fig 1 shows that the values of Excess molar volume are negative for the binary liquid mixtures of p-chloroacetophenone with *o-xylene, m-xylene and p-xylene* over the entire composition range at T = 303.15K to 318.15K. Excess molar volume values are decreasing with increase in temperature from 303.15K to 318.15K. More negative values are observed for PCAP+p-xylene than the other two binary mixtures. Negative values of V^E suggest that there is presence of specific charge transfer interactions between the two component molecules.

There is comparatively weak interaction for ortho & meta isomers is due to the presence of steric hindrance. This is also supported by Nain et.al [31,32] and N. Gayatri et al [33]. The order of interactions for studied systems

PCAP+ *p-xylene* > PCAP+ *m-xylene* > PCAP+ *o-xylene*.

From the Table 5, it can be seen that the values of $\overline{V}^{\circ E}_{m,1}$, and $\overline{V}^{\circ E}_{m,2}$ are negative for all the binary liquid mixtures. Negative values may be attributed to the hydrogen bonding and dipole-dipole interactions between unlike molecules are dominant over the breaking up of self-associated structures of the components of the binary liquid mixtures.

Deviation in viscosity: ($\Delta\eta$)

Deviation in Viscosity shows the strength of intermolecular interactions. Fig 2 and Table 3 shows the values of deviation in viscosity are negative for all the binary mixtures and at whole temperature range (303.15K to 318.15K). The negative values are decreasing with increase in temperature.

This is due to the difference in size and shape of the component molecules and the loss of dipolar association in pure component, which is in agreement with Fort and Moore [34] and Pikkarainen [35]

It is generally explained that deviation in viscosity tends to become more negative where dispersion and dipolar interactions are operating and positive deviation in viscosity ($\Delta\eta$) tends to increase as the specific interactions and charge transfer complexes increases. The order of interactions

PCAP+ *p-xylene* > PCAP+ *m-xylene* > PCAP+ *o-xylene*.

Gibb's free energy: (G^{*E})

Fig 3 and Table 3 shows that Positive G^{*E} values were observed for all the three studied binary mixtures, at whole temperature range (303.15K to 318.15K) indicating specific interactions (like dipole-dipole inter-actions and hydrogen bonding) between unlike molecules, which is in agreement with Reed and Taylor [36], where it is explained that the positive deviations in Gibbs free energy activation G^{*E} may be due to specific interactions like hydrogen bonding and charge transfer, whereas the negative deviations may be due to dispersion forces within the systems.

Excess Isentropic compressibility:(κ_s^E)

Excess isentropic compressibility is evident from Fig 4 and Table 3 that the Ks^E values are negative over the entire mole fraction range and become more negative with increasing all three binary mixtures. Thus, the mixtures are less compressible than the pure components, i.e. the greater resistance to compression (enhanced rigidity) is observed. In present investigation, the negative values of Ks^E may be attributed to the attractive interactions (which are responsible for structure-making effects) to be the driving forces in the liquid structures of these mixed non-electrolytic solutions [37,38].

Excess / deviation functions (V^E, $\Delta\eta$ and κ_s^E) values are fitted to a Redlich-Kister polynomial equation [39]

$$Y^E = x_1x_2[a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2] \qquad (7)$$

Where Y^E is the V^E, $\Delta\eta$ and κ_s^E coefficients values A_i are determined by using the method of least-squares. The standard deviations σ (Y^E) were calculated by the formula as follows

$$\sigma(Y^E) = [\sum(Y_{obs}^E - Y_{cal}^E)^2 / (n-m)]^{1/2} \quad (8)$$

Where *m* is the total number of experimental points and *n* is the number of parameters. The coefficients, A_i and corresponding standard deviation values (σ) are presented in Table 4.

3.1 Partial molar volumes

The interpretations of excess partial molar volumes ($\bar{V}_{m,1}^E$,$\bar{V}_{m,2}^E$) and excess partial molar properties at infinite dilution ($\bar{V}_{m,1}^{\circ E}$, $\bar{V}_{m,2}^{\circ E}$) of components 2 have previously been described [40].

Tables 5 shows that the values of $\bar{V}_{m,1}^{\circ E}$, $\bar{V}_{m,2}^{\circ E}$ are negative over the whole composition range at experimental temperatures. The negative values found to suggest that the hetero molecular association interactions are more reliable than the self-association of molecular interactions of like molecules in the mixtures [41,42].

4. FT-IR Studies

FT-IR spectroscopy has been extensively used to study an intermolecular hydrogen bonding interactions between component molecules. In the present investigation FT-IR spectrum considered at room temperature and equimolar concentration, the resultant absorption bands of PCAP + *o-xylene*, PCAP + *m-xylene* and PCAP + *p-xylene* are 3739.47 cm^{-1}, 3615.51 cm^{-1} and 3616.34 cm^{-1} respectively, that indicates intermolecular interactions between component molecules like hydrogen bonding between the hydrogen in the methyl group of Isomeric xylenes with carbonyl oxygen in p-chloroacetophenone, it shows in Figs 5-7

5. Conclusions

This paper reports experimental data of densities, speeds of sound and viscosities of binary blends of p-chloroacetophenone with aromatic hydrocarbon (*o-xylene*, *m-xylene*, *and p-xylene*) binary mixtures over the entire composition range at T= (303.15 - 313.15) K with 5 K intervals. From the experimental data, various physicochemical parameters, *viz.*, V^E, κ_s^E ,$\Delta\eta$ and G^{*E} of the mixtures of components were calculated. The results are analyzed in terms of structural effects and stretching or breaking of the hydrogen bonds in p-chloroacetophenone structures, a steric hindrance to the molecular interaction by two methyl groups and weak physical forces in the binary mixture.

Acknowledgments

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Table captions

Table 1: List of chemicals with details of source, CAS number, Purity and water content

Table 2: Densities, viscosity and speeds of sounds data of pure components at different temperatures and 0.1MPa pressure

Table 3**:** Density (ρ), excess molar volumes (V^E), speed of sound (u), Deviation in isentropic compressibility (ΔKs), viscosity (η), deviation in viscosity ($\Delta\eta$) and excess Gibbs energy of activation of viscous flow (G^{*E}) of binary liquid mixtures of p-chloroacetophenone with Alkoxy ethanols at T= (303.15 to 318.15) K

Table 4: Coefficients of Redlich – Kister equation and standard deviation (σ) values for liquid mixtures of p-chloroacetophenone with Alkoxy ethanols at T= (303.15 - 318.15) K

Table 5**:**The values of $\overline{V}^{\circ}_{m,1}, V^{*}_{m,1}, \overline{V}^{\circ E}_{m,1}, \overline{V}^{\circ}_{m,2}$, $V^{*}_{m,2}$ and $\overline{V}^{\circ E}_{m,2}$ of the components for p-chloroacetophenone with 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol of binary mixtures at T= (303.15 - 318.15) K

Figure captions

Fig 1: Plot of excess molar volume (V^E) values against mole fraction (X_1) of the binary liquid mixtures PCAP+*o-xylene* (♦), PCAP+*m-xylene* (▲) and PCAP+*p-xylene* (∗)at temperature T = 303.15 K.

Fig 2: Plot of deviation in viscosity (Δη) against mole fraction of (X_1) for PCAP + *o-xylene* (♦),PCAP + *m-xylene* (■), and PCAP + *p-xylene* (▲) binary systems at T = 303.15K.

Fig 3: Plot of deviation in Gibbs free energy (G^{*E}) against mole fraction of (X_1) for PCAP +o-*xylene* (♦), PCAP + *m-xylene* (■), and PCAP + *p-xylene* (▲) binary Systems at T = 303.15 K.

Fig 4: Plot of deviation isentropic compressibility (ΔKs) against mole fraction of (X_1) for PCAP + *o-xylene* (♦), PCAP + *m-xylene* (■), and PCAP + *p-xylene* (▲) binary systems at T = 303.15 K.

Images

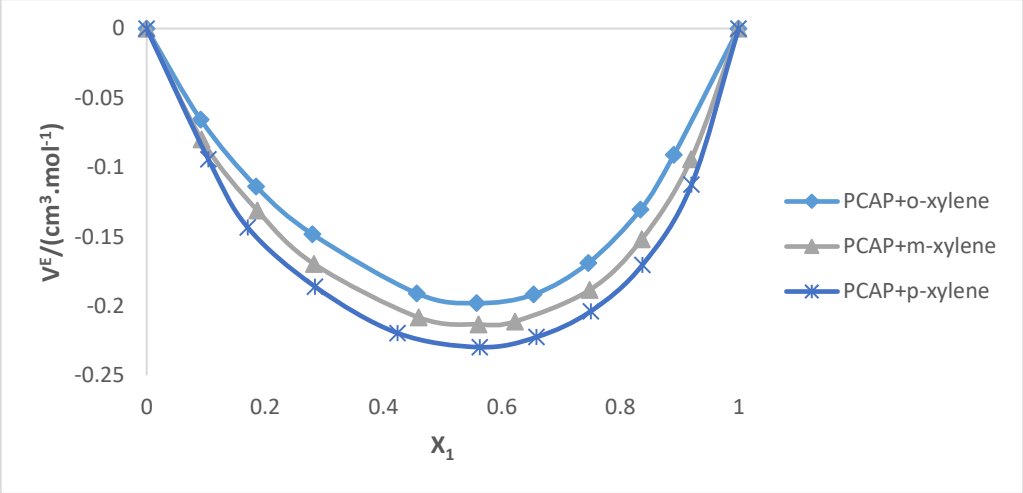

Fig 1: Plot of excess molar volume (V^E) values against mole fraction (X_1) of the binary liquid mixtures PCAP+*o-xylene* (♦), PCAP+*m-xylene* (▲) and PCAP+*p-xylene* (❋)at temperature T = 303.15 K.

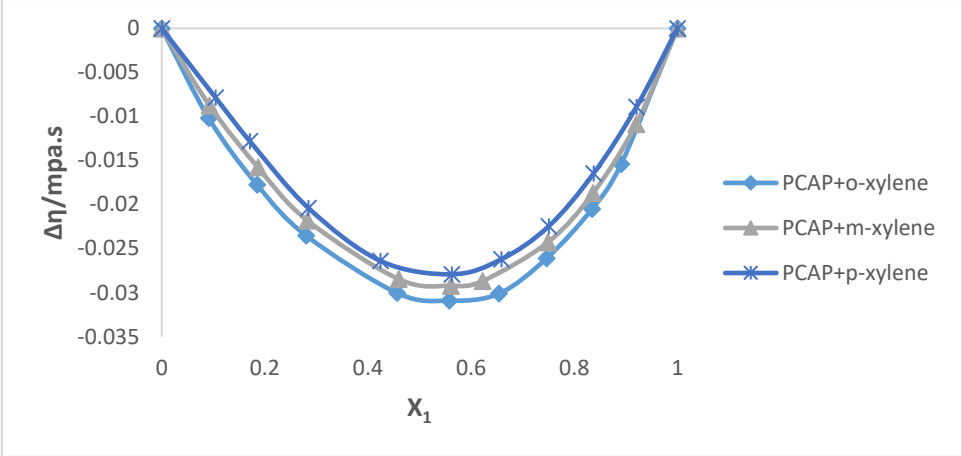

Fig 2: Plot of deviation in viscosity (Δη) against mole fraction of (X_1) for PCAP + *o-xylene* (♦),PCAP + *m-xylene* (■), and PCAP + *p-xylene* (▲) binary systems at *T* = 303.15K.

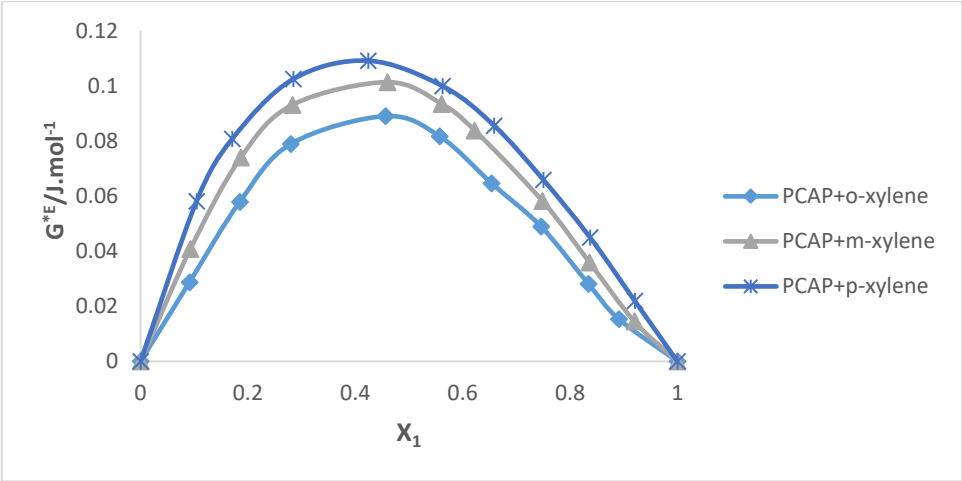

Fig 3: Plot of deviation in Gibbs free energy (G^{*E}) against mole fraction of (X_1) for PCAP +o-*xylene* (♦), PCAP + *m-xylene* (■), and PCAP + *p-xylene* (▲) binary Systems at *T* = 303.15 K.

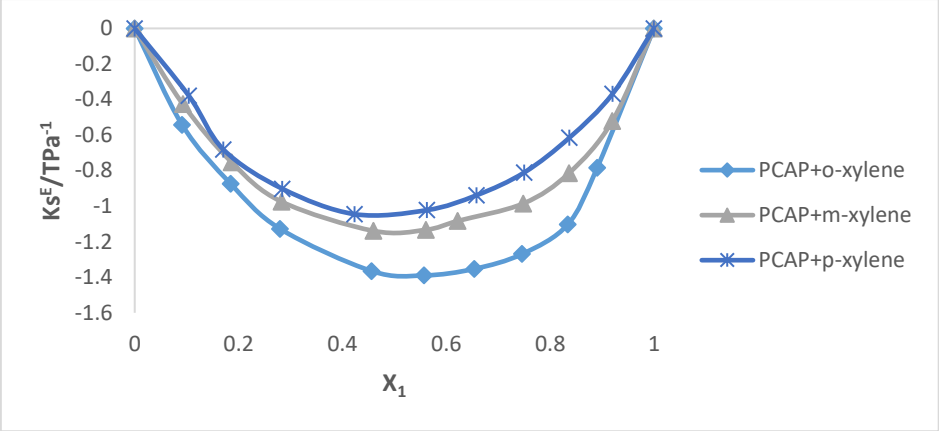

Fig 4: Plot of Excess isentropic compressibility (Ks^E) against mole fraction of (X_1) for PCAP + *o-xylene* (♦), PCAP + *m-xylene* (■), and PCAP + *p-xylene* (▲) binary systems at T = 303.15 K.

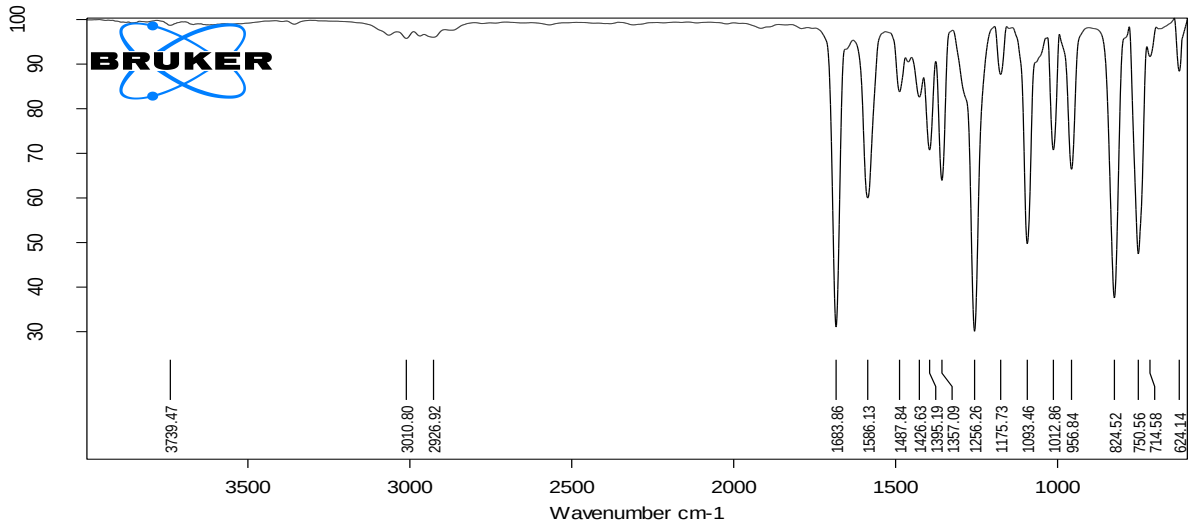

Fig 5: Infra-red spectra of P-chloroacetophenone and 1:1 ratio of o-xylene

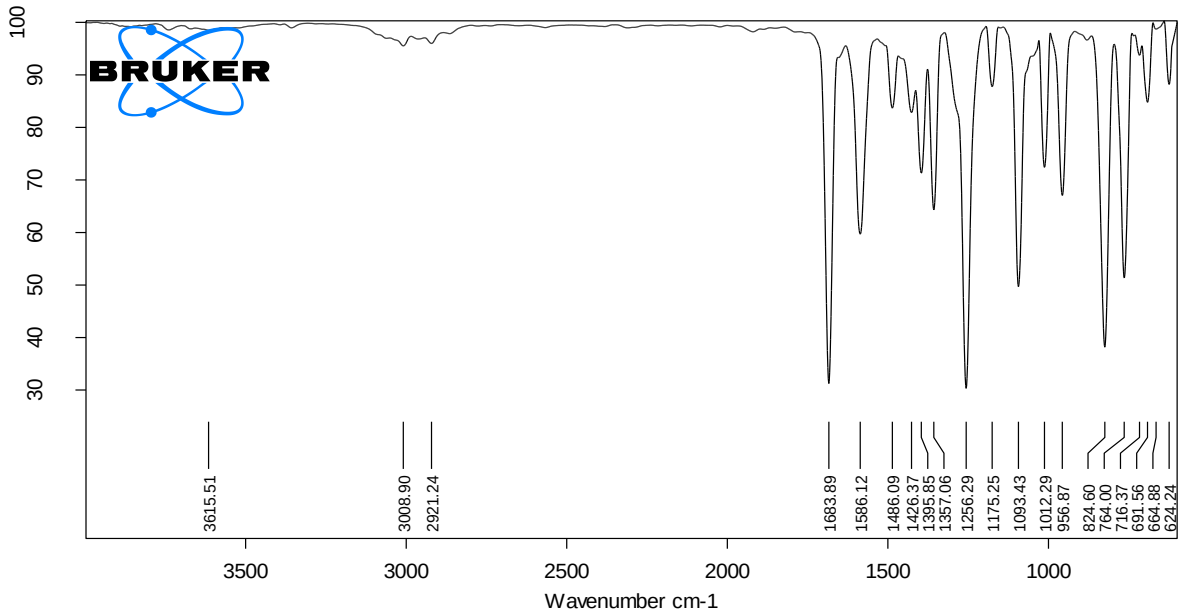

Fig 6: Infra-red spectra of P-chloroacetophenone and 1:1 ratio of m-xylene

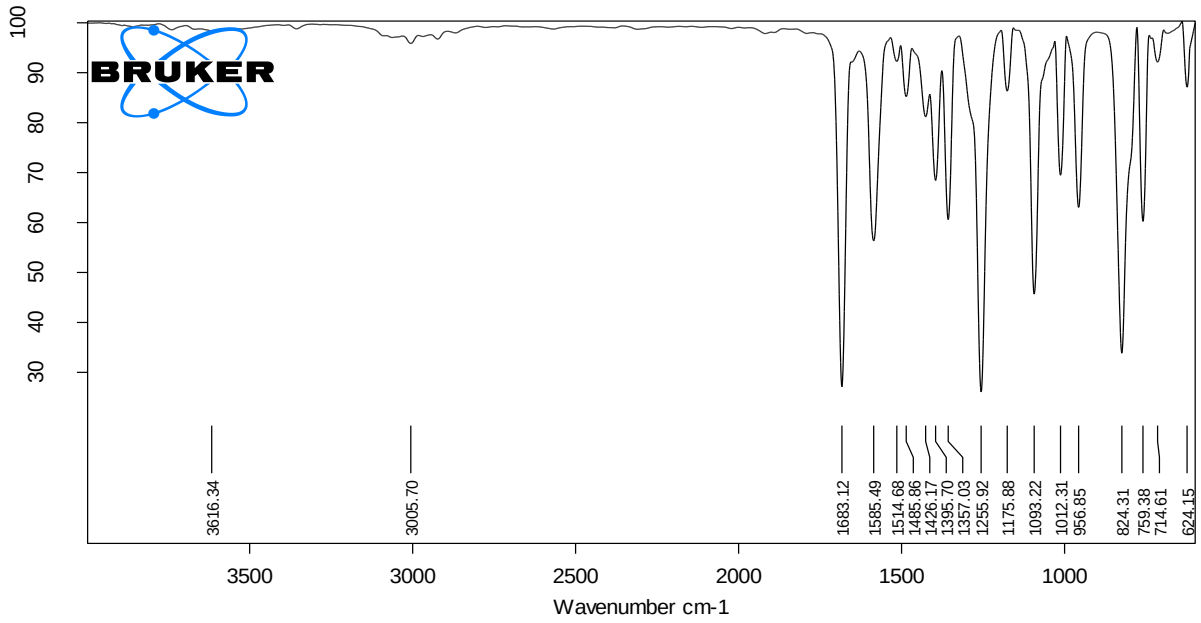

Fig 7: Infra-red spectra of P-chloroacetophenone and 1:1 ratio of p-xylene

Table 1: List of chemicals with details of source, CAS number, Purity and water content

Name of the chemical	Source	CAS number	mass purity	**water content mass fraction
p-chloroacetophenone	SD Fine chemicals, India	99-91-2	99.5	0.00039
o-xylene	SD Fine chemicals, India	95-47-6	99.6	0.00039
m-xylene	SD Fine chemicals, India	108-33-3	99.5	0.00042
p-xylene	SD Fine chemicals, India	106-42-3	99.5	0.00040

** Karl-Fischer method.

Table 2: Densities, viscosity and speeds of sounds data of pure components at different temperatures and 0.1MPa pressure

Compound	T(K)	Density (ρ)		Ultrasonic speed (u)		Viscosity(η)	
		Experimental	literature	Experimental	literature	Experimental	literature
		gm/cm^{-3}	gm/cm^{-3}	$m.\ s^{-1}$	$m.\ s^{-1}$	mPa.s	mPa.s
p-chloroacetophenone	303.15	1.1859	1.1857[a]	1412.80	1412.00[a]	2.3538	2.3530[a]
	308.15	1.1806	1.1812[a]	1389.60	1389.00[a]	2.2924	2.2920[a]
			1.1813[b]		1390.00[b]		2.2930[c]
					1395.00[b]		
					1389.98[d]		
	313.15	1.1755		1366.10		2.2314	
	318.15	1.1704		1343.00		2.1704	
o-xylene	303.15	0.8713	0.8714[e]	1325.40	1328.30[g]	1.5014	1.5002[f]
			0.8713[f]		1326.20[q]		
			0.8721[i]		1329.33[k]		
			0.8717[j]				
			0.8718[k]				
	308.15	0.8661	0.8670f	1318.80	1323.00[h]	1.4987	1.4975[f]
			0.8677[i]		1306.10[q]		
			0.8674[l]		1309.19[k]		
			0.8675[k]				

	313.15	0.8614	0.8628[f] 0.8640[i] 0.8633[k]	1312.40		1.4954	1.4948[f]
	318.15	0.8568	0.8585[f] 0.8597[i] 0.8590[k]	1305.40		1.4916	1.4921[f]
m-xylene	303.15	0.8533	0.8559[e] 0.8557[f] 0.8555[k] 0.8556[i] 0.8558[j] 0.8558[m]	1300.00	1300.34[g] 1307.00[s] 1299.20[k]	1.4917	1.4922[f]
	308.15	0.8502	0.8514[f] 0.8512[k] 0.8511[i] 0.8516[l] 0.8514[n]	1281.20	1286.00[h] 1279.00[t] 1280.00[s] 1278.67[k]	1.4890	1.4896[f]
	313.15	0.8461	0.8472[f] 0.8469[k] 0.8469[i]	1262.90	1258.32[k] 1255.00[s]	1.4859	1.4870[f]
	318.15	0.8413	0.8429[f] 0.8424[i] 0.8426[k]	1245.40	1238.11[k]	1.4829	1.4844[f]
p-xylene	303.15	0.8504	0.8524[e] 0.8525[f] 0.8523[k] 0.8520[i] 0.8523[o] 0.8523[j]	1286.50	1289.68[g] 1289.40[r] 1288.97[k]	1.4900	1.4907[f]
	308.15	0.8482	0.8481[f] 0.8478[k]	1263.50	1272.00[h] 1269.00[t]	1.4877	1.4881[f]

		0.8477[i]		1268.49[k]		
		0.8479[l]				
		0.8479[p]				
313.15	0.8435	0.8438[f]	1240.70	1248.16[k]	1.4850	1.4855[f]
		0.8434[k]				
		0.8432[i]				
318.15	0.8395	0.8394[f]	1215.40	1227.69[k]	1.4817	1.4830[f]
		0.8387[i]				
		0.8390[k]				

a[11], b[12] ,c[13] ,d[14] ,e[15] ,f[16] ,g[17] ,h[18] ,i[19] ,j[20] ,k[21] ,l[22] ,m[23] ,n[4] ,o[24] ,p[25] ,q[26] ,r[27] ,s[28] ,t[29]

The standard uncertainties are (x_1) = 1×10^{-4}, u (ρ) ± 0.2×10^{-4} g·cm^{-3}, u (u) = 0.5%, u (η) = 1.03%, u (T) = 0.01 K for density, viscosity and speed of sound, u (T) = 0.02 K for viscosity and u (p) = 1 kPa

Table 3**:** Density (ρ), excess molar volumes (V^E), speed of sound (u), Deviation in isentropic compressibility (ΔKs), viscosity (η), deviation in viscosity ($\Delta\eta$) and excess Gibbs energy of activation of viscous flow (G^{*E}) of binary liquid mixtures of p-chloroacetophenone with Isomeric xylenes at T= (303.15 to 318.15) K

X1	density(ρ) g·cm^{-3}	V^E cm^3·mol^{-1}	u m.s^{-1}	ΔKs TPa^{-1}	viscosity (η / mPa·s)	$\Delta\eta$ / mPa·s	G*^{E} / J·mol^{-1}
p-chloroacetophenone (1) + o-xylene (2)							
			303.15K				
0.0000	0.8713	0.0000	1325.4	0.000	1.501	0.000	0.000
0.0913	0.9016	-0.0656	1329.7	-0.543	1.617	-0.010	0.029
0.1848	0.9323	-0.1137	1334.0	-0.874	1.726	-0.018	0.058
0.2800	0.9632	-0.1482	1339.7	-1.128	1.837	-0.024	0.079
0.4564	1.0195	-0.1909	1353.4	-1.365	2.023	-0.030	0.089
0.5573	1.0511	-0.1979	1363.2	-1.390	2.117	-0.031	0.082

0.6538	1.0811	-0.1917	1374.1	-1.353	2.193	-0.030	0.065
0.7462	1.1094	-0.1690	1386.0	-1.269	2.248	-0.026	0.049
0.8343	1.1362	-0.1306	1398.0	-1.102	2.290	-0.021	0.028
0.8907	1.1532	-0.0911	1403.4	-0.784	2.311	-0.015	0.015
1.0000	1.1859	0.0000	1412.8	0.000	2.354	0.000	0.000
			308.15K				
0.0000	0.8661	0.0000	1318.8	0.000	1.499	0.000	0.000
0.0913	0.8964	-0.0787	1323.6	-0.710	1.613	-0.008	0.030
0.1848	0.9270	-0.1289	1327.2	-1.068	1.726	-0.016	0.049
0.2800	0.9579	-0.1613	1331.8	-1.329	1.832	-0.022	0.062
0.4564	1.0141	-0.2029	1342.6	-1.530	2.009	-0.028	0.067
0.5573	1.0457	-0.2120	1350.8	-1.552	2.095	-0.029	0.059
0.6538	1.0757	-0.2048	1360.4	-1.539	2.162	-0.028	0.049
0.7462	1.1040	-0.1839	1370.6	-1.461	2.209	-0.024	0.037
0.8343	1.1308	-0.1447	1380.8	-1.286	2.243	-0.018	0.025
0.8907	1.1478	-0.1070	1383.5	-0.861	2.279	-0.012	0.013
1.0000	1.1806	0.0000	1389.6	0.000	2.292	0.000	0.000
			313.15K				
0.0000	0.8614	0.0000	1312.4	0.000	1.495	0.000	0.000
0.0913	0.8915	-0.0920	1316.2	-0.731	1.612	-0.006	0.031
0.1848	0.9221	-0.1442	1319.8	-1.209	1.725	-0.014	0.041
0.2800	0.9529	-0.1787	1323.7	-1.517	1.828	-0.020	0.048
0.4564	1.0091	-0.2173	1332.2	-1.743	1.992	-0.026	0.046
0.5573	1.0407	-0.2243	1339.0	-1.778	2.072	-0.027	0.040
0.6538	1.0705	-0.2222	1346.6	-1.750	2.135	-0.026	0.033
0.7462	1.0989	-0.2023	1355.2	-1.681	2.178	-0.022	0.025
0.8343	1.1256	-0.1631	1363.6	-1.504	2.205	-0.016	0.019
0.8907	1.1426	-0.1244	1364.0	-0.995	2.231	-0.010	0.012
1.0000	1.1755	0.0000	1366.1	0.000	2.232	0.000	0.000
			318.15K				
0.0000	0.8568	0.0000	1305.4	0.000	1.492	0.000	0.000
0.0913	0.8868	-0.1043	1309.8	-0.912	1.614	-0.005	0.031

0.1848	0.9173	-0.1606	1312.5	-1.418	1.731	-0.012	0.035
0.2800	0.9481	-0.1971	1315.6	-1.773	1.832	-0.018	0.037
0.4564	1.0041	-0.2316	1322.8	-2.082	1.988	-0.025	0.029
0.5573	1.0357	-0.2376	1328.0	-2.111	2.060	-0.026	0.022
0.6538	1.0655	-0.2376	1334.3	-2.104	2.117	-0.024	0.019
0.7462	1.0937	-0.2228	1339.3	-1.883	2.158	-0.019	0.018
0.8343	1.1205	-0.1846	1341.7	-1.391	2.185	-0.013	0.015
0.8907	1.1375	-0.1438	1342.8	-1.001	2.210	-0.008	0.012
1.0000	1.1704	0.0000	1343.0	0.000	2.174	0.000	0.000
p-chloroacetophenone(1) + m-xylene (2)							
			303.15K				
0.0000	0.8533	0.0000	1300.0	0.000	1.492	0.000	0.000
0.0928	0.8853	-0.0799	1304.3	-0.426	1.619	-0.009	0.041
0.1869	0.9175	-0.1311	1309.9	-0.754	1.735	-0.016	0.074
0.2827	0.9500	-0.1697	1316.8	-0.975	1.844	-0.022	0.093
0.4596	1.0093	-0.2083	1333.1	-1.139	2.032	-0.029	0.101
0.5607	1.0429	-0.2133	1344.9	-1.133	2.125	-0.029	0.094
0.6223	1.0632	-0.2112	1352.8	-1.083	2.176	-0.029	0.084
0.7485	1.1045	-0.1884	1372.3	-0.985	2.260	-0.024	0.058
0.8363	1.1330	-0.1520	1387.2	-0.814	2.303	-0.019	0.036
0.9199	1.1601	-0.0941	1401.3	-0.521	2.335	-0.011	0.015
1.0000	1.1859	0.0000	1412.8	0.000	2.354	0.000	0.000
			308.15K				
0.0000	0.8502	0.0000	1281.2	0.000	1.489	0.000	0.000
0.0928	0.8819	-0.0953	1288.7	-0.630	1.625	-0.007	0.041
0.1869	0.9139	-0.1475	1296.1	-0.978	1.740	-0.014	0.067
0.2827	0.9462	-0.1899	1304.9	-1.194	1.848	-0.019	0.080
0.4596	1.0052	-0.2264	1325.0	-1.346	2.019	-0.027	0.079
0.5607	1.0385	-0.2315	1339.4	-1.340	2.105	-0.028	0.070
0.6223	1.0587	-0.2293	1349.4	-1.307	2.153	-0.027	0.063
0.7485	1.0997	-0.2084	1373.0	-1.201	2.233	-0.022	0.046
0.8363	1.1280	-0.1684	1391.0	-1.010	2.272	-0.016	0.032

0.9199	1.1549	-0.1085	1408.0	-0.672	2.294	-0.008	0.017
1.0000	1.1806	0.0000	1420.6	0.000	2.292	0.000	0.000
			313.15K				
0.0000	0.8461	0.0000	1262.9	0.000	1.486	0.000	0.000
0.0928	0.8777	-0.1096	1271.7	-0.703	1.630	-0.005	0.039
0.1869	0.9095	-0.1699	1280.3	-1.096	1.745	-0.012	0.057
0.2827	0.9417	-0.2111	1290.1	-1.327	1.846	-0.017	0.065
0.4596	1.0005	-0.2455	1312.4	-1.484	2.005	-0.025	0.057
0.5607	1.0337	-0.2491	1328.4	-1.490	2.085	-0.026	0.050
0.6223	1.0538	-0.2491	1339.3	-1.447	2.130	-0.025	0.046
0.7485	1.0947	-0.2271	1365.4	-1.348	2.206	-0.019	0.037
0.8363	1.1230	-0.1881	1385.2	-1.151	2.241	-0.013	0.030
0.9199	1.1498	-0.1248	1403.7	-0.760	2.254	-0.007	0.017
1.0000	1.1755	0.0000	1417.1	0.000	2.232	0.000	0.000
			318.15K				
0.0000	0.8413	0.0000	1245.4	0.000	1.483	0.000	0.000
0.0928	0.8728	-0.1242	1255.9	-0.843	1.630	-0.004	0.037
0.1869	0.9046	-0.1922	1265.9	-1.314	1.749	-0.010	0.049
0.2827	0.9367	-0.2346	1277.3	-1.616	1.851	-0.016	0.050
0.4596	0.9954	-0.2637	1302.3	-1.820	2.001	-0.023	0.036
0.5607	1.0286	-0.2669	1320.1	-1.836	2.075	-0.024	0.030
0.6223	1.0487	-0.2658	1331.9	-1.784	2.114	-0.023	0.030
0.7485	1.0895	-0.2448	1360.8	-1.694	2.179	-0.017	0.029
0.8363	1.1178	-0.2063	1382.7	-1.488	2.209	-0.011	0.027
0.9199	1.1445	-0.1382	1402.3	-1.018	2.215	-0.005	0.019
1.0000	1.1704	0.0000	1414.0	0.000	2.174	0.000	0.000
p-chloroacetophenone(1) + p-xylene (2)							
			303.15K				
0.0000	0.8504	0.0000	1286.45	0.000	1.490	0.000	0.000
0.1043	0.8866	-0.0943	1291.02	-0.379	1.609	-0.008	0.058
0.1708	0.9095	-0.1434	1296.07	-0.681	1.687	-0.013	0.081
0.2845	0.9485	-0.1861	1304.52	-0.903	1.820	-0.020	0.102

0.4238	0.9957	-0.2195	1318.15	-1.045	1.973	-0.026	0.109
0.5627	1.0425	-0.2297	1335.03	-1.023	2.104	-0.028	0.100
0.6587	1.0745	-0.2224	1348.98	-0.938	2.177	-0.026	0.086
0.7503	1.1049	-0.2038	1364.22	-0.810	2.232	-0.023	0.066
0.8374	1.1335	-0.1705	1380.11	-0.614	2.274	-0.017	0.045
0.9205	1.1605	-0.1126	1396.73	-0.367	2.313	-0.009	0.022
1.0000	1.1859	0.0000	1412.8	0.000	2.354	0.000	0.000
			308.15K				
0.0000	0.8482	0.0000	1263.42	0.000	1.488	0.000	0.000
0.1043	0.8841	-0.1076	1271.13	-0.528	1.599	-0.006	0.055
0.1708	0.9069	-0.1567	1277.59	-0.852	1.677	-0.011	0.072
0.2845	0.9455	-0.2104	1288.17	-1.045	1.810	-0.019	0.084
0.4238	0.9923	-0.2440	1305	-1.168	1.958	-0.025	0.084
0.5627	1.0386	-0.2550	1325.86	-1.142	2.079	-0.027	0.074
0.6587	1.0704	-0.2479	1343.24	-1.072	2.144	-0.025	0.065
0.7503	1.1004	-0.2311	1362.36	-0.971	2.188	-0.020	0.054
0.8374	1.1288	-0.1941	1381.99	-0.771	2.223	-0.014	0.038
0.9205	1.1555	-0.1289	1402.43	-0.504	2.257	-0.007	0.022
1.0000	1.1806	0.0000	1420.64	0.000	2.292	0.000	0.000
			313.15K				
0.0000	0.8435	0.0000	1240.67	0.000	1.485	0.000	0.000
0.1043	0.8793	-0.1199	1250.24	-0.644	1.597	-0.005	0.052
0.1708	0.9020	-0.1679	1257.62	-0.999	1.675	-0.010	0.062
0.2845	0.9405	-0.2310	1269.78	-1.214	1.801	-0.017	0.067
0.4238	0.9873	-0.2680	1288.69	-1.340	1.942	-0.024	0.060
0.5627	1.0335	-0.2790	1312.22	-1.324	2.054	-0.025	0.051
0.6587	1.0652	-0.2734	1331.84	-1.266	2.111	-0.023	0.046
0.7503	1.0953	-0.2563	1353.34	-1.168	2.148	-0.018	0.040
0.8374	1.1237	-0.2147	1375.28	-0.947	2.178	-0.012	0.031
0.9205	1.1504	-0.1468	1398.14	-0.650	2.202	-0.005	0.020
1.0000	1.1755	0.0000	1417.12	0.000	2.232	0.000	0.000
			318.15K				

0.0000	0.8395	0.0000	1215.42	0.000	1.482	0.000	0.000
0.1043	0.8751	-0.1343	1226.9	-0.766	1.601	-0.003	0.048
0.1708	0.8977	-0.1848	1235.73	-1.211	1.681	-0.008	0.053
0.2845	0.9361	-0.2538	1249.49	-1.428	1.812	-0.015	0.052
0.4238	0.9827	-0.2934	1270.93	-1.573	1.942	-0.022	0.038
0.5627	1.0288	-0.3030	1297.28	-1.548	2.041	-0.024	0.029
0.6587	1.0604	-0.2973	1319.44	-1.499	2.096	-0.021	0.029
0.7503	1.0904	-0.2802	1343.61	-1.397	2.136	-0.017	0.028
0.8374	1.1188	-0.2404	1368.3	-1.154	2.167	-0.011	0.025
0.9205	1.1454	-0.1625	1393.28	-0.772	2.181	-0.004	0.019
1.0000	1.1704	0.0000	1414.04	0.000	2.174	0.000	0.000

Table 4: Coefficients of Redlich – Kister equation and standard deviation (σ) values for liquid mixtures of p-chloroacetophenone with Isomeric xylenes at T= (303.15 - 318.15) K

T/K	A_0	A_1	A_2	σ
p-chloroacetophenone(1) + o-xylene (2)				
V^E/ $cm^3 \cdot mol^{-1}$				
303.15	-0.7848	-0.1235	-0.1344	0.0
308.15	-0.8268	-0.1271	-0.3035	0.0
313.15	-0.8785	-0.1421	-0.4796	0.0
318.15	-0.9309	-0.1706	-0.6695	0.0
ΔKs/ Tpa^{-1}				
303.15	-5.4774	-1.1959	-2.9946	0.0
308.15	-6.1930	-0.8376	-4.2219	0.0
313.15	-7.1420	-1.3778	-4.2949	0.1
318.15	-8.5624	-0.1873	-3.2173	0.1
$\Delta\eta$/ mPa· s				
303.15	-0.1218	-0.0227	-0.0280	0.0
308.15	-0.1167	-0.0182	0.0050	0.0
313.15	-0.1104	-0.0162	0.0297	0.0

318.15	-0.1035	-0.0156	0.0494	0.0
p-chloroacetophenone(1) + m-xylene (2)				
V^E/ $cm^3 \cdot mol^{-1}$				
303.15	-0.8342	-0.1766	-0.3873	0.0
308.15	-0.8997	-0.1783	-0.5504	0.0
313.15	-0.9689	-0.1855	-0.7313	0.0
318.15	-1.0390	-0.1744	-0.8903	0.0
ΔKs/ Tpa^{-1}				
303.15	-4.4754	-0.8322	-2.2872	0.0
308.15	-3.9471	-2.0149	-10.0877	0.2
313.15	-4.4220	-2.2496	-11.1935	0.2
318.15	-5.7131	-2.7455	-12.8531	0.3
$\Delta\eta$/ mPa· s				
303.15	-0.1150	-0.0247	-0.0142	0.0
308.15	-0.1095	-0.0213	0.0174	0.0
313.15	-0.1028	-0.0173	0.0404	0.0
318.15	-0.0972	-0.0131	0.0640	0.0
p-chloroacetophenone(1) + p-xylene (2)				
V^E/ $cm^3 \cdot mol^{-1}$				
303.15	-0.8848	-0.2252	-0.5635	0.0
308.15	-0.9821	-0.2684	-0.6779	0.0
313.15	-1.0691	-0.3209	-0.8013	0.0
318.15	-1.1618	-0.3520	-0.3520	0.0
ΔKs/ Tpa^{-1}				
303.15	-4.2050	-0.1462	-0.6658	0.0
308.15	-4.6066	-0.1608	-2.5695	0.0
313.15	-5.2596	-0.4386	-3.9160	0.1
318.15	-6.1969	-0.5379	-4.8792	0.1
$\Delta\eta$/ mPa· s				
303.15	-0.1115	-0.0233	0.0138	0.0
308.15	-0.1067	-0.0202	0.0379	0.0
313.15	-0.1018	-0.0185	0.0581	0.0
318.15	-0.0970	-0.0160	0.0745	0.0

Table 5: The values of $\overline{V}^{\circ}_{m,1}, V^{*}_{m,1}, \overline{V}^{\circ E}_{m,1}, \overline{V}^{\circ}_{m,2}$, $V^{*}_{m,2}$ and $\overline{V}^{\circ E}_{m,2}$ of the components for p-chloroacetophenone with *o-xylene, m-xylene* and *p-xylene* of binary mixtures at T= (303.15 - 318.15) K

T/K	$\overline{V}^{\circ}_{m,1}$	$V^{*}_{m,1}$	$\overline{V}^{\circ E}_{m,1}$	$\overline{V}^{\circ}_{m,2}$	$V^{*}_{m,2}$	$\overline{V}^{\circ E}_{m,2}$
	$cm^3.mol^{-1}$					
			PCAP+ o-xylene			
303.15	129.3151	130.3578	-1.0427	121.0508	121.8465	-0.7957
308.15	129.6856	130.9430	-1.2574	121.5678	122.5710	-1.0032
313.15	130.0120	131.5122	-1.5002	122.0295	123.2455	-1.2160
318.15	130.3154	132.0864	-1.7710	122.4731	123.9029	-1.4298
			PCAP+ m-xylene			
303.15	128.9597	130.3578	-1.3981	123.3662	124.4111	-1.0449
308.15	129.3146	130.9430	-1.6284	123.5988	124.8706	-1.2718
313.15	129.6265	131.5122	-1.8857	123.9566	125.4713	-1.5147
318.15	129.9827	132.0864	-2.1037	124.4308	126.1857	-1.7549
			PCAP+ p-xylene			
303.15	128.6843	130.3578	-1.6735	123.6123	124.8354	-1.2231
308.15	129.0146	130.9430	-1.9284	123.7617	125.1533	-1.3916
313.15	129.3209	131.5122	-2.1913	124.3041	125.8536	-1.5495
318.15	130.2206	132.0864	-1.8658	125.2944	126.4562	-1.1618