VOLUMES OF MIXING AND VISCOSITIES OF LIQUID MIXTURES OF KETONE AND META-SUBSTITUTED ANILINE AT VARIOUS TEMPERATURES

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Abstract

Excess molar volume, excess isentropic compressibility, deviation in viscosity and excess Gibbs free energy for activation of viscous flow for binary mixtures of 4-hydroxy-4-methyl-2-pentanone with meta-substituted aniline (3-chloroaniline, 3-methoxyaniline and 3-methylaniline)
at selected compositions were determined from the measured values of densities (ρ), viscosities (η), and speeds of sound (u) of pure components and their mixtures at from 303.15 K to 313.15 K. The results are analyzed in terms of interactions arising due to electron donor-acceptor in the binary mixtures. Finally, the Prigogine-Flory-Patterson (PFP) Theory is applied to identify the most predominant molecular interaction.

Keywords: Density, speed of sound, 4-hydroxy-4-methyl-2-pentanone, meta-substituent aniline

1. Introduction

Thermo-physical properties of liquid mixtures are utilized to understand various types of association, molecular packing, molecular motion and different kinds of intermolecular interactions between dissimilar molecules in mixtures. These properties are for most part helpful for interpreting solvent-solvent, solute-solvent and solute-solute interaction in solution phase. The experimental values of thermo-physical properties allow us in establishing new predicting interactions and information about the molecular level structure of the mixtures to determine the properties that are necessary for the industries in a fast reliable and economic way. Therefore, a deep knowledge of thermo-physical properties of liquid mixtures containing industrially important organic liquids is essentially required for scientific community [1-3].

4-Hydroxy- 4-methyl -2- pentanone is used as an antifungal and antibacterial coating solvent. 3-Chlorobenzenamine is used in the synthesis of pyrimidoazepine analogs as serotonin 5-HT2A and 5-HT2C receptor ligands for the treatment of obesity. 3-methylaniline is used in the production of dyes and its primary application is as a precursor to the pesticides metolachlor and acetochlor. This work is continuation of our previous research [4] on the thermodynamic properties of binary liquid mixtures. In this work, the binary mixtures of 4-hydroxy-4-methyl-2-pentanone and m-substituted aniline (3-chloroaniline, 3-methoxyaniline and 3-methylaniline) are picked as a result of their wide utility in industries besides their incessant use in different fields of science, particularly about routine works.

In the present study, binary polar liquid mixtures of aromatic bases such as m-chloroaniline (m-CA), m-methoxyaniline (m-MOA) and m-methylaniline (m-MA) with 4-hydroxy-4-methyl-2-pentanone are undertaken to probe the nature of molecular interactions in these systems. Attempts are also made to understand the role of basicity due to different substituents in donors which govern the formation and stability of molecular association or complexation.

2 Experimental

2.1 Materials

m-substituted aniline (m-SA) and 4-hydroxy-4-methyl-2-pentanone chemicals were purchased from S.D. Fine Chemical and Sigma Aldrich. Table 1 contains data with respect to their source, purity and analysis method. Density, speed of sound and viscosity values listed in Table 2 and in good agreement with the data available in the literature [5-9].

2.2 Apparatus and procedure

The densities, speeds of sound and viscosities of pure liquids as well as the binary mixtures were determined using a single-capillary pycnometer (made of Borosil glass), ultrasonic interferometer model F-82 provided by Mittal enterprises, New Delhi and an Ostwald's viscometer respectively. The uncertainty in density, speed of sound and viscosity measurement of liquid mixtures was ± 1.09 $\times 10^{-3}$ g·cm^{-3}, 0.5 m·s$^{-1,}$ and 1.13% respectively. The uncertainty of the mole fraction was ± 1 × 10^{-4}.

3.0 Results and discussion:

The excess / deviation quantities such as excess molar volume and deviation viscosity and excess Gibbs free energy for viscous flow were calculated with the following equations

$$V^E = V - (x_1 V_1 + x_2 V_2) \quad (1)$$

$$\Delta\eta = \eta - (x_1\eta_1 + x_1\eta_1) \quad (2)$$

$$\Delta G^{*E} = RT\,[\ln\eta V - (x_1 \ln\eta_1 V_1 + x_2 \ln\eta_2 V_2) \quad (3)$$

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

The isentropic compressibilities were calculated from the following equation [10]

$$k_S = \frac{1}{u^2 \rho} \quad (4)$$

where ρ is the density and u are the speed of sound of the binary mixture. Further, the excess isentropic compressibilities (κ_S^E) are calculated from Benson and Kiyohara [11] equation.

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

$$k_s^{id} = \sum_{i=1}^{2} \varphi_i \left[\kappa_{s,i} + \frac{T V_i (\alpha_i^2)}{C_{p,i}} \right] - \left\{ \frac{T \left(\sum_{i=1}^{2} x_i V_i \right) \left(\sum_{i=1}^{2} \varphi_i \alpha_i \right)^2}{\sum_{i=1}^{2} x_i C_{p,i}} \right\} \quad (6)$$

where $\varphi_i, C_{p,i}$, 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

All the experimental results are given in Table 3. The variation of V^E, κ_s^E, $\Delta\eta$ and ΔG^{*E} as functions of composition of 4-hydroxy-4-methyl-2-pentanone are graphically represented in Figs. from 1 to 4 respectively.

The excess molar volume, excess isentropic compressibility and deviation in viscosity data were fitted to a Redlich-Kister polynomial equation [12] by the least-squares method.

$$Y^E = x_1 x_2 \sum_{i=0}^{j} A_i (1 - 2x_1)^i \quad (7)$$

Where Y^E is the values of V^E, $\Delta\eta$ and κ_s^E.

The standard deviations $\sigma(Y^E)$ were calculated by

$$\sigma (Y^E) = [\Sigma (Y^E_{exp} - Y^E_{cal})^2/(m-n)]^{1/2} \quad (8)$$

where m is the total number of experimental points, and n is the number of parameters. The adjustable parameters A_i and standard deviation values (σ) for all the systems are given in Table 4

Excess /deviation parameters depends upon several factors

(i) Inductive effect

(ii) Values of p^{Kb}
(iii) Electron donor-acceptor interactions
(iv) Basic nature of m-substituted aniline
(v) n-π interactions

Lower the p^{Kb} values indicate more basic nature of amines. The p^{Kb} values of 3-chloroaniline, 3-methoxyaniline and 3-methylaniline are 10.53, 9.81 and 9.34 respectively. Thus, among the given m-substituted aniline, 3-chloroaniline is the weakest base and has maximum p^{Kb} value. 3-methylaniline is more basic than 3-methoxyaniline because in 3-methylaniline, the methyl group (electron releasing nature) increases the electron density on nitrogen atom of amino group.

The basic strength of m-substituted aniline follows in the order:

3- methylaniline > 3- methoxyaniline > 3-chloroaniline,

Fig.1 indicates that the negative excess molar volume values are obtained over the entire composition range for all these systems which indicates strong interaction between donor and acceptor molecules in binary mixtures [13, 14)

In the present case it is interactions are more probable that the donor-acceptor interaction between 4-hydroxy-4-methyl-2-pentanone and 3-methylaniline molecules may be because of a more basic nature (positive inductive effect) and lower p^{Kb} values.

It is also observed from Fig 1 (Table 3) that the negative values fall in the sequence.

3- methylaniline > 3- methoxyaniline > 3-chloroaniline

The excess isentropic compressibility values for all the binary systems are negative at all compositions. The negative values in all of the systems support the complex formation [15]. The order of values of excess isentropic compressibility is almost similar to that observed with respect to excess molar volumes.

Figs 3 and 4 shows that the values of $\Delta\eta$ and ΔG^{*E} are positive for all the binary mixtures over entire composition, which suggests that the component molecules are closer together in the liquid mixture than in the pure liquids forming the mixture, indicating strong attractive interactions between molecules [16,17].

It is also observed from Fig 3 (Table 3) that the positive values fall in the sequence

3- methylaniline > 3- methoxyaniline > 3-chloroaniline

3.1 Partial molar properties

The interpretations of excess partial molar properties ($\overline{V}^{E}_{m,1}, \overline{V}^{E}_{m,2}, \overline{K}^{E}_{s,m,1}$ and $\overline{K}^{E}_{s,m,2}$) and excess partial molar properties at infinite dilution($\overline{V}^{\circ E}_{m,1}$, $\overline{V}^{\circ E}_{m,2}$ $\overline{K}^{\circ E}_{s,m,1}$ and $\overline{K}^{\circ E}_{s,m,2}$) of components have previously been described [18].

From tables 5 and 6, excess partial molar properties at infinite dilution values are negative over the whole composition range at experimental temperatures. The negative values indicate that the interaction between electrophilic nature of carbonyl group of ketone and nucleophilic nature of m-substituted aniline leading to complex formation [19]

4. Application of Prigogine-Flory-Patterson (PFP) Theory

The Prigogine-Flory-Patterson (PFP) theory [20-24] was used in present study to correlate the excess molar volume results for the present mixtures. The details of the Prigogine-Flory-Patterson (PFP) theory and their equations were described elsewhere [18]. It is clear from Table7 that the free volume contribution is supporting factor for sign and magnitude of excess volumes for binary mixtures.

5. Conclusions:

Densities and speeds of the sound of binary mixtures of4-hydroxy-4-methyl-2-pentanone with m-substituted aniline (3-CA, 3-MA, and 3-MOA) have been measured at different temperatures and derived parameters along with their excess values and also excess partial molar properties at infinite dilution are calculated. The results are analyzed in terms of the specific interactions through electron donor-acceptor between the components of the mixtures, resulting in the formation of complexes. Moreover, the V^E values were analyzed with Prigogine- Flory-Patterson theory and shown that the free volume contribution is the supporting factor for negative values of excess molar quantities

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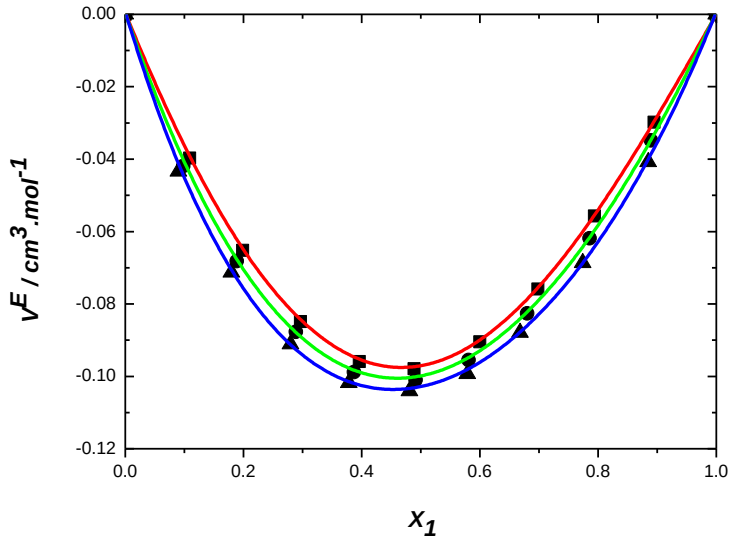

Fig 1 Variation of excess molar volume (V^E) with mole fraction (x_1) of 4-methyl-4-methoxy-2-pentanone for the binary liquid mixtures of 4-methyl-4-methoxy-2-pentanone with 3-chloroaniline (■); 3-methoxyaniline (●) and 3-methylaniline (▲) at 303.15 K

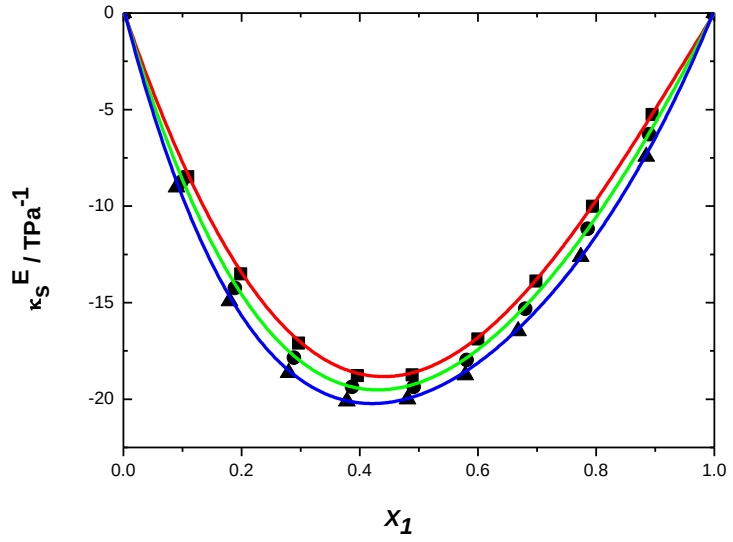

Fig 2 Variation of excess isentropic compressibility with mole fraction (x_1) of 4-methyl-4-methoxy-2-pentanone for the binary liquid mixtures of 4-methyl-4-methoxy-2-pentanone with 3-chloroaniline (■); 3-methoxyaniline (●) and 3-methylaniline (▲) at 303.15 K

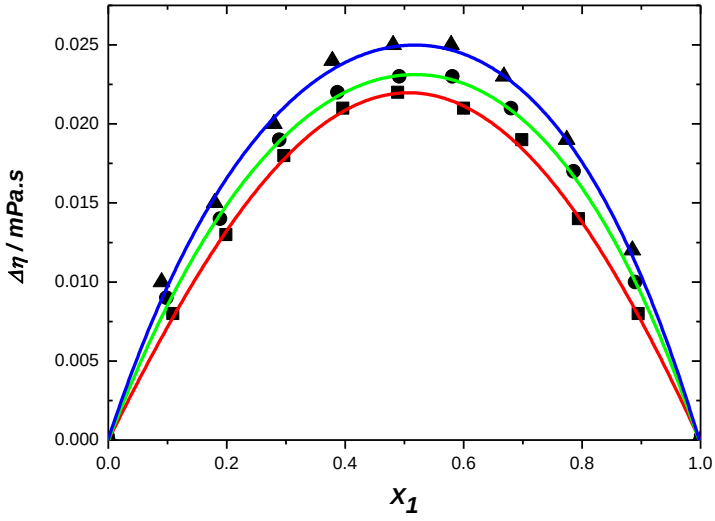

Fig 3 Variation of deviation in viscosity with mole fraction (x_1) of 4-methyl-4-methoxy-2-pentanone for the binary liquid mixtures of 4-methyl-4-methoxy-2-pentanone with 3-chloroaniline (■); 3-methoxyaniline (●) and 3-methylaniline (▲) at 303.15 K

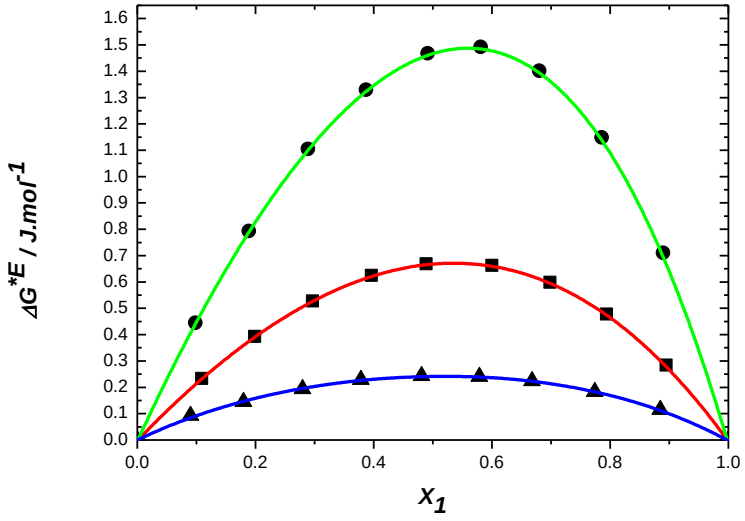

Fig 4 Excess Gibbs energy of activation of viscous flow with mole fraction (x_1) of 4-methyl-4-methoxy-2-pentanone for the binary liquid mixtures of 4-methyl-4-methoxy-2-pentanone with 3-chloroaniline (■); 3-methoxyaniline (●) and 3-methylaniline (▲) at 303.15 K

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

Name of the chemical	CAS Number	Source	**water content %	purity in mass fraction (after purification)
4-hydroxy-4-methyl-2-pentanone	123-42-2	Sigma Aldrich, India	0.049	0.997
3-chloroaniline	108-42-9	S.D. Fine chemicals	0.042	0.996
3-methylaniline	108-44-1	S.D. Fine chemicals	0.042	0.995
3-methoxyaniline	536-90-3	Sigma Aldrich, India	0.042	0.995

** Karl-Fischer method.

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

component	density		Speed of sound		viscosity	
4-hydroxy-4-methyl- 2-pentanone	experimental	Literature	experimental	Literature	experimental	Literature
303.15K	0.93590	0.9360[5]	1255	1256[5]	2.891	2.8900
308.15K	0.92398		1218.3		2.841	
313.15K	0.9121	0.9010[5]	1182	1183[5]	2.792	2.7910
3-methoxyaniline						
303.15K	1.09025		1579.9		5.593	
308.15K	1.08705		1552.0		5.160	
313.15K	1.08320		1523.4		4.733	
3-methylaniline						
303.15K	0.98032		1568.2		3.018	
308.15K	0.97611		1530.6		2.707	
313.15K	0.97186		1491.7		2.396	
3-chloroaniline						
303.15K	1.20532	1.20530[6]	1517.5	1517.0[6]	4.255	4.2556[7]
		1.2080[8]		1517.0[9]		4.2556[8]
		1.2053[9]				
308.15K	1.20075		1501.2		3.842	
313.15K	1.19602	1.19600[6]	1480.0	1484.0[6]	3.430	
		1.1960[9]		1484.0[9]		

The standard uncertainties are u (x_1) = 1×10^{-4}, u (ρ) ± 1.09×10^{-3} g·cm^{-3}, u (u) = 0.5 m·s^{-1}, u (η) = 1.11%, u (T) = 0.01 K for density, viscosity and speed of sound, and u (P) = 1 kPa

Table 3: Density (ρ), excess molar volumes (V^E), speed of sound (u), excess isentropic compressibility (κ_s^E), viscosity (η), deviation in viscosity ($\Delta\eta$) and excess Gibbs energy of activation of viscous flow (G^{*E}) of binary liquid mixtures at T = (303.15 to 313.15) K and 0.1 MPa pressure.

x_1	Density(ρ) g·cm^{-3}	V^E cm^3·mol^{-1}	u m.s^{-1}	κ_s^E TPa^{-1}	viscosity (η / mPa·s)	$\Delta\eta$ / mPa·s	G*^{E} / J·mol^{-1}
4-methoxy-4-methyl-2-pentanone (1) + 3-chloroaniline (2)							
			303.15 K				
0.0000	1.20532	0.0000	1517.5	0.000	4.255	0.000	0.000
0.1089	1.17198	-0.0397	1476.0	-8.476	4.114	0.008	0.234
0.1985	1.14536	-0.0652	1444.6	-13.51	3.998	0.013	0.393
0.2967	1.11700	-0.0849	1412.9	-17.09	3.868	0.018	0.528
0.3963	1.08905	-0.0959	1383.3	-18.78	3.735	0.021	0.625
0.4888	1.06381	-0.0979	1358.0	-18.74	3.610	0.022	0.669
0.5999	1.03438	-0.0905	1330.4	-16.89	3.458	0.021	0.663
0.6981	1.00913	-0.0759	1308.5	-13.89	3.321	0.019	0.599
0.7941	0.98514	-0.0557	1289.2	-10.00	3.186	0.014	0.478
0.8947	0.96071	-0.0298	1271.2	-5.263	3.043	0.008	0.284
1.0000	0.93590	0.0000	1255.0	0.000	2.891	0.000	0.000
			308.15 K				
0.0000	1.20075	0.0000	1501.2	0.000	3.842	0.000	0.000
0.1089	1.16624	-0.0429	1453.8	-9.266	3.742	0.009	0.191
0.1985	1.13873	-0.0687	1418.1	-14.38	3.658	0.015	0.317
0.2967	1.10946	-0.0877	1382.6	-17.79	3.564	0.019	0.422
0.3963	1.08069	-0.0988	1350.6	-19.47	3.468	0.022	0.497
0.4888	1.05474	-0.1005	1323.7	-19.37	3.376	0.023	0.528
0.5999	1.02456	-0.0940	1294.9	-17.47	3.264	0.023	0.523
0.6981	0.99872	-0.0796	1272.7	-14.71	3.163	0.020	0.471
0.7941	0.97420	-0.0599	1253.3	-11.02	3.063	0.015	0.372
0.8947	0.94928	-0.0338	1235.2	-6.17	2.955	0.009	0.220
1.0000	0.92398	0.0000	1218.3	0.000	2.841	0.000	0.000
			313.15 K				
0.0000	1.19602	0.0000	1480.0	0.000	3.430	0.000	0.000
0.1089	1.16037	-0.0474	1427.4	-10.06	3.371	0.010	0.156
0.1985	1.13197	-0.0728	1388.2	-15.24	3.319	0.016	0.257
0.2967	1.10180	-0.0911	1349.7	-18.48	3.262	0.021	0.343
0.3963	1.07221	-0.1018	1315.9	-20.16	3.201	0.024	0.397
0.4888	1.04559	-0.1031	1288.0	-20.01	3.143	0.025	0.422
0.5999	1.01468	-0.0973	1258.5	-18.04	3.072	0.025	0.413
0.6981	0.98828	-0.0839	1236.3	-15.54	3.007	0.022	0.372

0.7941	0.96326	-0.0647	1217.1	-12.04	2.941	0.017	0.296
0.8947	0.93786	-0.0378	1199.2	-7.07	2.869	0.010	0.172
1.0000	0.91210	0.0000	1182.0	0.000	2.792	0.000	0.000
4-methoxy-4-methyl-2-pentanone (1) + 3-methoxyaniline (2)							
303.15 K							
0.0000	1.09025	0.0000	1579.9	0.000	5.593	0.000	0.000
0.0981	1.07417	-0.0419	1541.2	-8.749	5.337	0.009	0.445
0.1889	1.05943	-0.0682	1505.3	-14.24	5.097	0.014	0.793
0.2887	1.04343	-0.0877	1466.7	-17.86	4.832	0.019	1.105
0.3869	1.02791	-0.0988	1430.5	-19.37	4.570	0.022	1.330
0.4912	1.01166	-0.1010	1394.7	-19.37	4.289	0.023	1.468
0.5809	0.99787	-0.0955	1365.8	-17.97	4.046	0.023	1.492
0.6799	0.98287	-0.0826	1336.2	-15.32	3.777	0.021	1.402
0.7858	0.96707	-0.0619	1306.9	-11.17	3.486	0.017	1.149
0.8898	0.95180	-0.0348	1280.6	-6.276	3.199	0.010	0.711
1.0000	0.93590	0.0000	1255.0	0.000	2.891	0.000	0.000
308.15K							
0.0000	1.08705	0.0000	1552.0	0.000	5.160	0.000	0.000
0.0981	1.06991	-0.0455	1510.1	-9.46	4.942	0.010	0.391
0.1889	1.05421	-0.0708	1471.3	-15.03	4.738	0.016	0.697
0.2887	1.03721	-0.0902	1430.5	-18.61	4.511	0.021	0.968
0.3869	1.02077	-0.1019	1393.1	-20.13	4.286	0.024	1.160
0.4912	1.00358	-0.1036	1356.5	-20.02	4.046	0.025	1.275
0.5809	0.98904	-0.0990	1327.5	-18.59	3.838	0.025	1.292
0.6799	0.97324	-0.0862	1298.2	-16.10	3.606	0.023	1.211
0.7858	0.95665	-0.0665	1269.7	-12.27	3.356	0.018	0.988
0.8898	0.94064	-0.0384	1243.9	-7.19	3.108	0.011	0.610
1.0000	0.92398	0.0000	1218.3	0.000	2.841	0.000	0.000
313.15K							
0.0000	1.08320	0.0000	1523.4	0.000	4.733	0.000	0.000
0.0981	1.06507	-0.0491	1478.3	-10.17	4.553	0.010	0.336
0.1889	1.04847	-0.0748	1436.8	-15.82	4.384	0.017	0.602
0.2887	1.03055	-0.0947	1394.0	-19.36	4.195	0.023	0.830
0.3869	1.01323	-0.1050	1355.5	-20.89	4.008	0.026	0.990
0.4912	0.99518	-0.1063	1318.3	-20.67	3.807	0.027	1.084
0.5809	0.97995	-0.1025	1289.2	-19.22	3.632	0.027	1.095
0.6799	0.96344	-0.0898	1260.4	-16.89	3.438	0.025	1.026
0.7858	0.94613	-0.0710	1232.6	-13.37	3.227	0.019	0.830
0.8898	0.92944	-0.0419	1207.3	-8.10	3.018	0.012	0.512
1.0000	0.91210	0.0000	1182.0	0.000	2.792	0.000	0.000

4-methyl-4-methoxy-2-pentanone (1) + 3-methylaniline (2)							
303.15 K							
0.0000	0.98032	0.0000	1568.2	0.000	3.018	0.000	0.000
0.0899	0.97622	-0.0434	1539.2	-9.021	3.017	0.010	0.092
0.1798	0.97209	-0.0713	1507.9	-14.92	3.011	0.015	0.145
0.2797	0.96750	-0.0911	1472.3	-18.64	3.003	0.020	0.194
0.3783	0.96302	-0.1018	1437.7	-20.11	2.994	0.024	0.229
0.4808	0.95841	-0.1041	1403.2	-20.01	2.982	0.025	0.243
0.5789	0.95405	-0.0993	1372.2	-18.76	2.969	0.025	0.240
0.6681	0.95012	-0.0879	1345.1	-16.47	2.956	0.023	0.224
0.7741	0.94552	-0.0687	1314.7	-12.63	2.938	0.019	0.183
0.8847	0.94079	-0.0408	1284.9	-7.427	2.918	0.012	0.115
1.0000	0.93590	0.0000	1255.0	0.000	2.891	0.000	0.000
308.15 K							
0.0000	0.97611	0.0000	1530.6	0.000	2.707	0.000	0.000
0.0899	0.97122	-0.0466	1500.6	-9.694	2.729	0.010	0.108
0.1798	0.96629	-0.0750	1468.2	-15.81	2.748	0.017	0.183
0.2797	0.96086	-0.0952	1431.8	-19.51	2.767	0.022	0.238
0.3783	0.95557	-0.1048	1396.9	-20.88	2.783	0.025	0.270
0.4808	0.95014	-0.1070	1362.6	-20.65	2.798	0.027	0.285
0.5789	0.94504	-0.1021	1331.9	-19.28	2.811	0.027	0.284
0.6681	0.94047	-0.0916	1305.8	-17.23	2.822	0.025	0.263
0.7741	0.93512	-0.0727	1276.6	-13.69	2.831	0.021	0.215
0.8847	0.92964	-0.0448	1247.7	-8.33	2.839	0.013	0.135
1.0000	0.92398	0.0000	1218.3	0.000	2.841	0.000	0.000
313.15 K							
0.0000	0.97186	0.0000	1491.7	0.000	2.396	0.000	0.000
0.0899	0.96617	-0.0498	1460.7	-10.37	2.442	0.011	0.150
0.1798	0.96045	-0.0788	1427.6	-16.71	2.486	0.019	0.262
0.2797	0.95418	-0.0993	1390.7	-20.38	2.532	0.025	0.350
0.3783	0.94807	-0.1078	1355.8	-21.66	2.573	0.028	0.389
0.4808	0.94185	-0.1100	1321.8	-21.29	2.615	0.029	0.403
0.5789	0.93601	-0.1050	1291.6	-19.80	2.654	0.029	0.393
0.6681	0.93080	-0.0952	1266.5	-17.98	2.687	0.027	0.359
0.7741	0.92473	-0.0767	1238.5	-14.76	2.725	0.022	0.293
0.8847	0.91852	-0.0487	1210.6	-9.23	2.761	0.014	0.178
1.0000	0.91210	0.0000	1182.0	0.000	2.792	0.000	0.000

Table 4

Coefficients of Redlich – Kister equation and standard deviation (σ) values for liquid mixtures of

4-hydroxy-4-methyl-2-pentanone with meta-substituted aniline at T = (303.15 - 313.15) K

T/K	A_0	A_1	A_2	σ
4-hydroxy-4-methyl-2-pentanone + 3-chloroaniline				
V^E/ cm^3·mol^{-1}				
303.15	-0.391	0.059	0.045	0.001
308.15	-0.401	0.054	0.002	0.001
313.15	-0.411	0.053	-0.052	0.001
κ_s^E/ TPa^{-1}				
303.15	-74.55	19.99	4.659	0.001
308.15	-76.71	19.23	-6.036	0.073
313.15	-78.86	18.46	-16.71	0.149
$\Delta\eta$/ mPa· s				
303.15	0.087	0.004	-0.004	0.001
308.15	0.093	0.003	0.001	0.001
313.15	0.102	0.003	0.005	0.001
4-hydroxy-4-methyl-2-pentanone + 3-methoxyaniline				
V^E/ cm^3·mol^{-1}				
303.15	-0.400	0.069	-0.018	0.001
308.15	-0.410	0.065	-0.061	0.001
313.15	-0.422	0.066	-0.102	0.001
κ_s^E/ TPa^{-1}				
303.15	-76.90	21.66	-6.675	0.076
308.15	-79.30	20.57	-16.53	0.061
313.15	-81.71	19.48	-26.40	0.121
$\Delta\eta$/ mPa· s				
303.15	0.093	0.003	0.010	0.001
308.15	0.100	0.004	0.015	0.001
313.15	0.109	0.005	0.015	0.001
4-hydroxy-4-methyl-2-pentanone + 3-methylaniline				
V^E/ cm^3·mol^{-1}				
303.15	-0.411	0.073	-0.078	0.001
308.15	-0.422	0.071	-0.121	0.001
313.15	-0.433	0.070	-0.164	0.001
κ_s^E/ TPa^{-1}				
303.15	-79.40	22.41	-18.14	0.092
308.15	-81.83	21.75	-27.97	0.001
313.15	-84.26	21.09	-37.80	0.092
$\Delta\eta$/ mPa· s				
303.15	0.098	0.001	0.029	0.001
308.15	0.107	0.004	0.033	0.001
313.15	0.117	0.005	0.030	0.001

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 4-hydroxy-4-methyl-2-pentanone with meta-substituted aniline of binary mixtures at T= (303.15 - 313.15) K

T/K	$\overline{V}^{\circ}_{m,1}$	$V^{*}_{m,1}$	$\cdot\overline{V}^{\circ E}_{m,1}$	$\overline{V}^{\circ}_{m,2}$	$V^{*}_{m,2}$	$\overline{V}^{\circ E}_{m,2}$
			($cm^3 \cdot mol^{-1}$)			
4-hydroxy-4-methyl-2-pentanone (1) + 3-chloroaniline (2)						
303.15	123.83	124.12	-0.287	105.43	105.84	-0.405
308.15	125.37	125.72	-0.345	105.79	106.24	-0.453
313.15	126.94	127.35	-0.410	106.14	106.66	-0.516
4-hydroxy-4-methyl-2-pentanone (1) + 3-methoxyaniline (2)						
303.15	123.77	124.12	-0.349	112.47	112.96	-0.487
308.15	125.31	125.72	-0.406	112.75	113.29	-0.536
313.15	126.90	127.35	-0.459	113.10	113.69	-0.590
4-hydroxy-4-methyl-2-pentanone (1) + 3-methylaniline (2)						
303.15	123.70	124.12	-0.416	108.74	109.30	-0.562
308.15	125.24	125.72	-0.472	109.16	109.77	-0.614
313.15	126.83	127.35	-0.527	109.59	110.25	-0.666

Table 6: The values of $\overline{K}^{\circ}_{s,m,1}$, $K^{*}_{s,m,1}$, $\overline{K}^{\circ E}_{s,m,1}$, $\overline{K}^{\circ}_{s,m,2}$, $K^{*}_{s,m,2}$ and $\overline{K}^{\circ E}_{s,m,2}$ of the components for 4-hydroxy-4-methyl-2-pentanone with meta-substituted aniline of binary mixtures at T = (303.15 - 313.15) K

T/K	$\overline{K}^{\circ}_{s,m,1}$	$K^{*}_{s,m,1}$	$\overline{K}^{\circ E}_{s,m,1}$	$\cdot\overline{K}^{\circ}_{s,m,2}$	$K^{*}_{s,m,2}$	$\overline{K}^{\circ E}_{s,m,2}$
			TPa^{-1}			
4-hydroxy-4-methyl-2-pentanone (1) + 3-chloroaniline (2)						
303.15	-62.94	8.420	-71.36	-100.01	3.813	-103.83
308.15	-81.00	9.167	-90.17	-114.58	3.926	-118.51
313.15	-99.25	9.994	-109.24	-129.36	4.071	-133.43
4-hydroxy-4-methyl-2-pentanone (1) + 3-methoxyaniline (2)						
303.15	-79.70	8.420	-88.12	-125.80	4.151	-129.95
308.15	-96.93	9.167	-106.10	-139.19	4.327	-143.52
313.15	-114.57	9.994	-124.56	-152.78	4.523	-157.30
4-hydroxy-4-methyl-2-pentanone (1) + 3-methylaniline (2)						
303.15	-94.31	8.420	-102.73	-136.78	4.534	-141.31
308.15	-111.85	9.167	-121.02	-151.23	4.800	-156.03
313.15	-129.91	9.994	-139.90	-166.04	5.098	-171.14

Table 7: PFP interaction parameter, χ_{12} and calculated values of the three contributions from the PFP theory with experimental excess molar volumes at x_1= 0.5 at 303.15K

Binary mixtures	χ_{12} ($10^{7)}$	Calculated contributions			V^E (x=0.5) $cm^3.mol^{-1}$		δ / $cm^3.mol^{-1}$
		Interactional ($10^{-8)}$	Free volume	P* effect	EXP	PFP	
4-hydroxy-4-metghyl-2-pentanone+3-chloroaniline	5.211	1.782	-2.861	1.823	-0.0978	-0.0829	0.0149
4-hydroxy-4-metghyl-2-pentanone+3-methoxyaniline	-6.255	1.971	-4.035	2.167	-0.1001	-0.1114	- 0.0113
4-hydroxy-4-metghyl-2-pentanone+3-methylaniline	4.119	1.808	-2.481	1.633	-0.1028	-0.0842	0.0186