Studies on associated solutions: Evaluation of thermodynamic parameters of blends of N-methyl formamide and o- substituted aniline at various temperatures

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Abstract

For binary mixtures of N-methylformamide and ortho-substituted anilines (2-chloroaniline, 2-methylaniline, and 2-methoxyaniline) spanning the complete composition range from 303.15 K to 318.15 K and at atmospheric pressure 0.1 MPa, the densities (ρ) and velocity of sound (u) are provided. The densities and sound velocity at experimental temperatures are used to determine the excess functions (VE and κsE). The Redlich–Kister equation correlates excess functions. For all the binary systems at infinity dilutions, the excess partial molar isentropic compressibilities are determined. The Prigogine-Flory-Patterson theory is used to interpret the VE data.

Keywords: Density, speed of sound, N-methylformamide, ortho-substituentanilines,charge-transfer complexes, PFP theory

1. Introduction

The molecular interactions at microscopic levels will reflect and alter the bulk properties. Hence, a thorough understanding of the nature and strength of molecular forces existing between molecule to molecule in pure liquids and in their blends and their variations with respect to various physicochemical parameters, is essential because the organic solvents are indispensable components of any industry.

The binding forces envisioned in and/or by the clusters of molecules at micro levels are the root cause of the success or failure of quantifying industrial chemicals. Thermodynamics is the sole method available to peek into the forces at work at the molecular level. Scientists and engineers will be greatly assisted in optimizing the design parameters for the product's manufacturing by the determination of various thermodynamic parameters and their variations with regard to organic solvents and their blends, as well as by correlating the observed data from the perspective of the structure of the molecules.

With regard to binary liquid mixes, our research team is looking into these areas of study, and some of the novel findings are presented to the reader [1]. Binary mixtures of N-methylformamide with different ortho-substituted anilines, including 2-chloroaniline, 2-methylaniline, and 2-methoxyaniline, have been explored in the current work. These chemical compounds are widely utilised as solvents and as building blocks for the synthesis of many different organic molecules in both industry and several branches of fundamental science. The amide group in N-methylformamide makes it a very polar solvent, but the amine group in o-substituted anilines allows molecules to self-associate by hydrogen bonding.

The goal of the current work is to determine the fundamental strength of the o-substituted group in the aniline molecule that, when combined with N-methylformamide, can influence both the sign and amplitude of several thermodynamic functions.

With regard to the correlation of thermodynamic data from the perspective of molecular forces, a review of the literature pertaining to the compounds chosen, or related/similar such compounds, reveals two weak attempts: one with the mixture of o-toluidine and tetrahydropyran [2] and the other with N-methylformamide and aromatic hydrocarbons [3]. The current work is a thorough and methodical investigation of the excess volume and excess isentropic compressibility of o-substituted anilines in N-methylformamide over the full range of compositions at temperature (T) of 303.15 - 318.15 K.

2 Experimental

2.1 Materials

None of the chemicals were further purified before use. Source and purity of the compounds were listed in Table 1, and physical characteristics, densities (ρ), and sound speeds (u) were listed in Table 2. The numbers in Table 2 accord well with the information found in the literature [4–14].

TABLE 1:-Provenance and purity of the materials used

Chemicals	CAS Number	Source	water content in mass fraction	purity in mass fraction (after purification)
N-methylformamide	123-39-7	Sigma Aldrich, India	0.049	0.997
2-chloroaniline	95-51-2	Sigma Aldrich, India	0.042	0.996
2-methylaniline	95-53-4	Sigma Aldrich, India	0.042	0.995
2-methoxyaniline	90-04-0	Sigma Aldrich, India	0.042	0.995

Table 2:- Densities, speed of sounds and speed of sounds of pure components at different temperatures and p= 0.1MPa

Component	density (ρ /g·cm^{-3})		Speed of sound (u / m·s^{-1})		
(in K)	Experimental	Literature	Experimental	Literature	C_P (J· K^{-1} · mol^{-1})
N-methylformamide					
303.15	0.99464	0.9946[9]	1408.5	----	124.95[11]
308.15	0.99033	0.9903[9]	1398.2	1400.6[10]	126.05[11]
313.15	0.98614	0.9861[9]	1382.5	---	128.04[13]
318.15	0.98204	0.9820[9]	1365.8	1369.0[10]	129.95[13]
2-chloroaniline					
303.15	1.20269	1.20270[5]	1469.6	1471.0[6]	208.00[13]
308.15	1.19802		1453.3		209.02[13]
313.15	1.19302		1435.2		210.02[13]
318.15	1.18849		1418.9		211.05[13]
2-methylaniline					
303.15	0.99019	0.9902[12]	1578.5	1579.0[4]	218.43[13]
308.15	0.98599	0.9860[14]	1558.2	1558.38[14]	219.09[13]
313.15	0.98169	0.9817[4]	1538.5	1539.0[4]	220.52[13]
318.15	0.97759	-	1520.5	-	221.12[13]
2-methoxyaniline					
303.15	1.09175	1.0917[8]	1595.4		190.52[13]
308.15	1.08735	-	1579.2		192.05[13]
313.15	1.08378	-	1566.3		193.62[13]
318.15	1.08080	-	1554.8		195.25[13]

2.2 Apparatus and procedure

To reduce evaporation losses, all the binary liquid combinations were made by syringing each component into airtight stopper bottles after weighing the necessary amounts of pure liquids in an electric balance (ER-120A, Afoset, or India) with a precision of ± 0.1 mg. The mole fraction's level of uncertainty was ± 1 × 10^{-4}. The measurement error for liquid combinations' densities was ±1×10^{-2} g·cm^3 and the error for temperatures was + 0.01K. The measurement error for sound

speed was ± 0.3%and the measurement error for temperature was ± 0.1K. There are several descriptions of the methodologies and measurement procedures [15].

3.0 Results and discussion:

Excess molar volumes (VE) values are derived using the following equation:

$$V^E/cm^3.mol^{-1} = [x_1M_1 + x_2M_2]/\rho_m - [x_1M_1/\rho_1 + x_2M_2/\rho_2] \quad (1)$$

Where m is the binary mixture's density and x1, M1, x2, M2, and 1 and 2 are the mole fraction, molar mass, and densities of the two pure components, 1 and 2, respectively. The experimental data is used to compute isentropic compressibility (κ_s) by using the following relation:

$$\kappa_s = (u^2\rho)^{-1} \quad (2)$$

The method used for calculating κ_s^E (Benson -Kiyohara approach) has been outlined previously [16].

. V^E and κ_s^E values are fitted to a Redlich - Kister[17] polynomial equation,

$$Y^E = x_1x_2\sum_{i=0}^{j} A_i\left(1-2x_1\right)^i \quad (3)$$

WhereY^Eisthe $V^E$and κ_s^E .Values of thecoefficients A_i aredetermined by using the method of least - squares. The standard deviation σ (Y^E) are calculated by the formula

$$\sigma(Y^E) = [\Sigma(Y^E_{exp} - Y^E_{cal})^2/(m-n)]^{1/2} \quad (4)$$

Where n is the number of parameters and m is the total number of experimental points. Table 3 displays the coefficients, Ai, and accompanying standard deviation values (σ).

Table 4 lists the densities and sound velocities for mixes of different mole fractions of N-methylformamide together with the surplus molar volumes and isentropic compressibility. Figs. 1 and 2, respectively, show a visual representation of them.

Analyzing the data reveals that for all systems across the whole composition range and at all experimental temperatures investigated, negative deviations in V^E and $\kappa_s^E$are present. Mesomeric

effect/orthopaedic effect (steric effect) and Basicity constants (K_b)of o-substituted aniline are blamed for negative deviations. The o-substituted aniline's basic strengths are as follows:

2-methoxyaniline > 2-methylaniline > 2-chloroaniline

According to Table 3, the negative V^E and κ_s^Evalues indicate that the binary liquid mixtures' component molecules interact heteromolecularly, favouring the formation of structures over those that break them.

The sequence is as follows, as indicated by the magnitude of V^E and κ_s^E

2-methoxyaniline > 2-methylaniline > 2-chloroaniline

The binary systems N-methylformamide + 2-methoxyaniline are seen in Figs. 1 and 2 to have greater negative excess functions (V^E and κ_s^E), indicating a more basic character. High basicity constant values (Kb) and/or the mesomeric effect are thought to be responsible for the strong molecular interactions between N-methylformamide and nitrogen atoms in binary liquid mixtures [18].

Table 3 -Coefficients of Redlich – Kister equation and standard deviation (σ) values

Binary mixtures	functions	A_1	A_2	A_3	σ
303.15 K					
N-methylformamide+ 2-chloroaniline	V^E/ $cm^3 \cdot mol^{-1}$	-0.435	0.059	0.064	0.001
	κ_s^E / TPa^{-1}	-10.24	-7.543	-4.441	0.080
N-methylformamide+ 2-methylaniline	V^E/ $cm^3 \cdot mol^{-1}$	-0.456	0.071	0.006	0.001
	κ_s^E / TPa^{-1}	-11.29	-7.995	-4.941	0.053
N-methylformamide+ 2-methoxyaniline	V^E/ $cm^3 \cdot mol^{-1}$	-0.468	0.083	-0.088	0.001
	κ_s^E / TPa^{-1}	-12.07	-8.366	-6.765	0.051
308.15 K					
N-methylformamide+ 2-chloroaniline	V^E/ $cm^3 \cdot mol^{-1}$	-0.449	0.054	0.009	0.001
	κ_s^E / TPa^{-1}	-11.19	-7.436	-5.310	0.019
N-methylformamide+ 2-methylaniline	V^E/ $cm^3 \cdot mol^{-1}$	-0.467	0.056	-0.055	0.001
	κ_s^E / TPa^{-1}	-12.15	-7.306	-6.897	0.001
N-methylformamide+ 2-methoxyaniline	V^E/ $cm^3 \cdot mol^{-1}$	-0.481	0.057	-0.135	0.001
	κ_s^E / TPa^{-1}	-13.04	-8.043	-7.559	0.025
313.15 K					
N-methylformamide+ 2-chloroaniline	V^E/ $cm^3 \cdot mol^{-1}$	-0.463	0.059	-0.049	0.001
	κ_s^E / TPa^{-1}	-11.79	-7.544	-7.481	0.047

N-methylformamide+ 2-methylaniline	V^E/ $cm^3 \cdot mol^{-1}$	-0.487	0.059	-0.113	0.001
	κ_s^E / TPa^{-1}	-13.24	-7.588	-8.124	0.018
N-methylformamide+ 2-methoxyaniline	V^E/ $cm^3 \cdot mol^{-1}$	-0.505	0.061	-0.226	0.001
	κ_s^E / TPa^{-1}	-13.82	-7.875	-8.545	0.047
318.15 K					
N-methylformamide+ 2-chloroaniline	V^E/ $cm^3 \cdot mol^{-1}$	-0.473	0.065	-0.126	0.001
	κ_s^E / TPa^{-1}	-12.58	-7.786	-8.963	0.057
N-methylformamide+ 2-methylaniline	V^E/ $cm^3 \cdot mol^{-1}$	-0.499	0.065	-0.1958	0.001
	κ_s^E / TPa^{-1}	-15.02	-1.522	-7.947	0.084
N-methylformamide+ 2-methoxyaniline	V^E/ $cm^3 \cdot mol^{-1}$	-0.523	0.068	-0.264	0.001
	κ_s^E / TPa^{-1}	-15.27	-8.860	-9.134	0.053

Table 4**:** Density (ρ), excess molar volumes (V^E), speed of sound (u) and excess isentropic compressibility (κ_s^E) of binary liquid mixtures of N-methylformamide with ortho-substituted anilines (2-chloroaniline, 2-methylaniline and 2-methoxyaniline) at T= (303.15 to 318.15) K and 0.1MPa pressure

	density (ρ /g·cm^{-3})				**V^E (cm^3·mol^{-1})**			
x_1	303.15K	308.15K	313.15K	318.15K	303.15K	308.15K	313.15K	318.15K
	N-methylformamide+ 2-chloroaniline							
0.0000	1.20269	1.19802	1.19302	1.18849	0.0000	0.0000	0.0000	0.0000
0.0815	1.19322	1.18861	1.18370	1.17924	-0.0327	-0.0365	-0.0414	-0.0467
0.1725	1.18172	1.17712	1.17227	1.16785	-0.0638	-0.0683	-0.0742	-0.0806
0.2634	1.16908	1.16450	1.15968	1.15527	-0.0876	-0.0921	-0.0963	-0.1017
0.3674	1.15300	1.14843	1.14367	1.13927	-0.1048	-0.1082	-0.1125	-0.1163
0.4756	1.13411	1.12958	1.12488	1.12051	-0.1098	-0.1138	-0.1170	-0.1202
0.5689	1.11575	1.11125	1.10663	1.10230	-0.1042	-0.1076	-0.1114	-0.1151
0.6623	1.09512	1.09068	1.08616	1.08188	-0.0905	-0.0958	-0.1006	-0.1043
0.7712	1.06771	1.06336	1.05896	1.05475	-0.0663	-0.0735	-0.0794	-0.0837
0.8895	1.03298	1.02866	1.02438	1.02027	-0.0351	-0.0398	-0.0435	-0.0489
1.0000	0.99464	0.99033	0.98614	0.98204	0.0000	0.0000	0.0000	0.0000
N-methylformamide+ 2-methylaniline								
0.0000	0.93942	0.93394	0.92992	0.92422	0.0000	0.0000	0.0000	0.0000
0.0896	0.94247	0.93707	0.93307	0.92750	-0.0413	-0.0451	-0.0494	-0.0567
0.1601	0.94501	0.93965	0.93568	0.93015	-0.0674	-0.0706	-0.0788	-0.0840
0.2501	0.94846	0.94316	0.93917	0.93373	-0.0925	-0.0951	-0.1022	-0.1076
0.3425	0.95228	0.94706	0.94305	0.93770	-0.1081	-0.1115	-0.1171	-0.1221
0.4328	0.95632	0.95118	0.94715	0.94191	-0.1138	-0.1170	-0.1216	-0.1263
0.5424	0.96176	0.95673	0.95269	0.94760	-0.1117	-0.1149	-0.1196	-0.1238
0.6554	0.96809	0.96323	0.95917	0.95429	-0.0969	-0.1023	-0.1075	-0.1126
0.7342	0.97307	0.96832	0.96428	0.95956	-0.0817	-0.0876	-0.0944	-0.1004
0.8414	0.98075	0.97620	0.97213	0.96765	-0.0545	-0.0611	-0.0669	-0.0726
1.0000	0.99464	0.99033	0.98614	0.98204	0.0000	0.0000	0.0000	0.0000
N-methylformamide+ 2-methoxyaniline								

0.0000	1.09157	1.08735	1.08378	1.08080	0.0000	0.0000	0.0000	0.0000
0.0714	1.08821	1.08399	1.08045	1.07745	-0.0408	-0.0422	-0.0484	-0.0517
0.1715	1.08286	1.07865	1.07511	1.07206	-0.0777	-0.0809	-0.0904	-0.0969
0.2636	1.07731	1.07309	1.06949	1.06637	-0.1016	-0.1040	-0.1123	-0.1187
0.3576	1.07092	1.06668	1.06303	1.05982	-0.1147	-0.1170	-0.1244	-0.1298
0.4701	1.06215	1.05791	1.05420	1.05087	-0.1182	-0.1212	-0.1281	-0.1321
0.5625	1.05391	1.04967	1.04589	1.04249	-0.1144	-0.1179	-0.1237	-0.1296
0.6556	1.04443	1.04022	1.03640	1.03289	-0.1022	-0.1081	-0.1150	-0.1208
0.7454	1.03400	1.02979	1.02593	1.02229	-0.0857	-0.0919	-0.1003	-0.1047
0.8325	1.02238	1.01819	1.01427	1.01051	-0.0622	-0.0699	-0.0786	-0.0831
1.0000	0.99464	0.99033	0.98614	0.98204	0.0000	0.0000	0.0000	0.0000
speed of sound (u / m·s^{-1})					**κ_s^E / (TPa^{-1})**			
N-methylformamide+ 2-chloroaniline								
0.0000	1469.6	1453.3	1435.2	1418.9	0.000	0.000	0.000	0.000
0.0815	1465.4	1449.7	1432.0	1415.8	-0.494	-0.638	-0.804	-0.921
0.1725	1460.8	1445.4	1427.8	1411.6	-1.135	-1.251	-1.417	-1.596
0.2634	1455.3	1440.7	1423.3	1407.2	-1.418	-1.725	-1.910	-2.118
0.3674	1449.4	1435.2	1418.0	1401.8	-2.023	-2.253	-2.431	-2.644
0.4756	1442.9	1429.3	1412.4	1396.1	-2.472	-2.698	-2.922	-3.116
0.5689	1437.3	1424.0	1407.3	1390.9	-2.864	-2.997	-3.196	-3.395
0.6623	1431.0	1418.7	1402.1	1385.7	-2.834	-3.159	-3.298	-3.516
0.7712	1424.0	1412.2	1395.9	1379.5	-2.722	-2.951	-3.140	-3.360
0.8895	1416.0	1405.0	1389.1	1372.6	-1.877	-1.995	-2.208	-2.402
1.0000	1408.5	1398.2	1382.5	1365.8	0.000	0.000	0.000	0.000
N-methylformamide+ 2-methylaniline								
0.0000	1578.5	1558.2	1538.5	1520.5	0.000	0.000	0.000	0.000
0.0896	1570.0	1550.7	1531.4	1513.6	-0.638	-0.881	-1.018	-1.215
0.1601	1562.7	1544.0	1524.9	1507.2	-1.098	-1.394	-1.588	-1.802
0.2501	1552.6	1534.6	1515.7	1498.2	-1.633	-1.917	-2.145	-2.393
0.3425	1541.3	1523.8	1505.4	1487.8	-2.146	-2.372	-2.651	-2.867
0.4328	1529.0	1512.3	1494.1	1476.8	-2.544	-2.772	-3.044	-3.353
0.5424	1512.3	1496.7	1478.9	1461.7	-2.967	-3.182	-3.469	-3.817
0.6554	1492.6	1478.2	1460.8	1443.7	-3.159	-3.408	-3.678	-4.010
0.7342	1477.0	1463.5	1446.4	1429.5	-3.074	-3.335	-3.605	-3.919
0.8414	1452.9	1440.5	1424.0	1407.1	-2.594	-2.717	-2.978	-3.198
1.0000	1408.5	1398.2	1382.5	1365.8	0.000	0.000	0.000	0.000
N-methylformamide+ 2-methoxyaniline								
0.0000	1595.4	1579.2	1566.3	1554.8	0.000	0.000	0.000	0.000
0.0714	1586.7	1571.1	1558.2	1546.3	-0.645	-0.784	-0.913	-0.946
0.1715	1573.5	1558.4	1545.1	1533.0	-1.357	-1.541	-1.683	-1.902
0.2636	1560.2	1545.6	1532.2	1519.6	-1.886	-2.125	-2.282	-2.562
0.3576	1545.7	1531.6	1517.9	1504.8	-2.361	-2.596	-2.816	-3.124
0.4701	1527.1	1513.5	1499.5	1485.8	-2.936	-3.138	-3.398	-3.737
0.5625	1510.4	1497.4	1483.0	1468.8	-3.245	-3.534	-3.691	-4.058
0.6556	1492.2	1479.7	1465.1	1450.3	-3.428	-3.651	-3.871	-4.190
0.7454	1473.1	1461.2	1446.3	1431.0	-3.285	-3.575	-3.765	-4.081
0.8325	1453.1	1441.5	1426.2	1410.7	-2.934	-3.026	-3.157	-3.566
1.0000	1408.5	1398.2	1382.5	1365.8	0.000	0.000	0.000	0.000

The standard uncertainties are u (X_1) = 1×10^{-4}, u (ρ) = 1×10^{-2} g.cm^{-3}, u (u) = 0.3%, u (T) = 0.01 K for density, u (T) = 0.1 K for speed of sound and u (p) = 1 kPa.

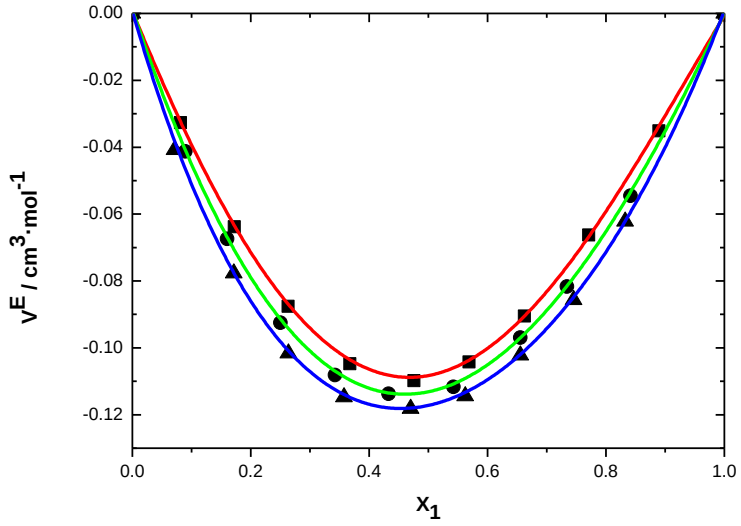

Figure-1

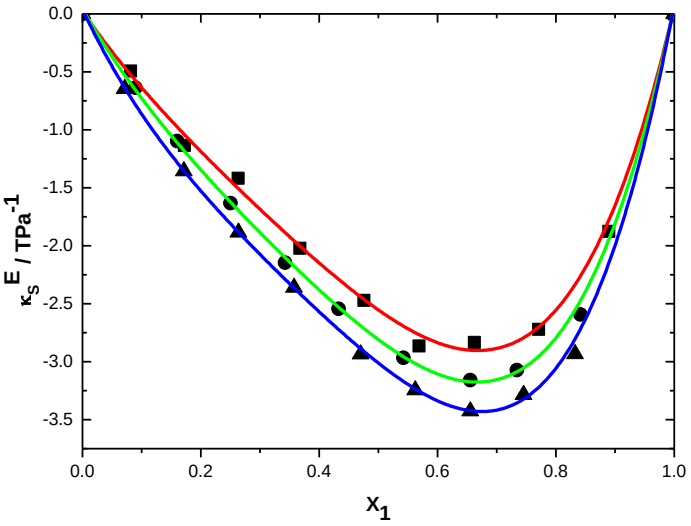

Figure-2

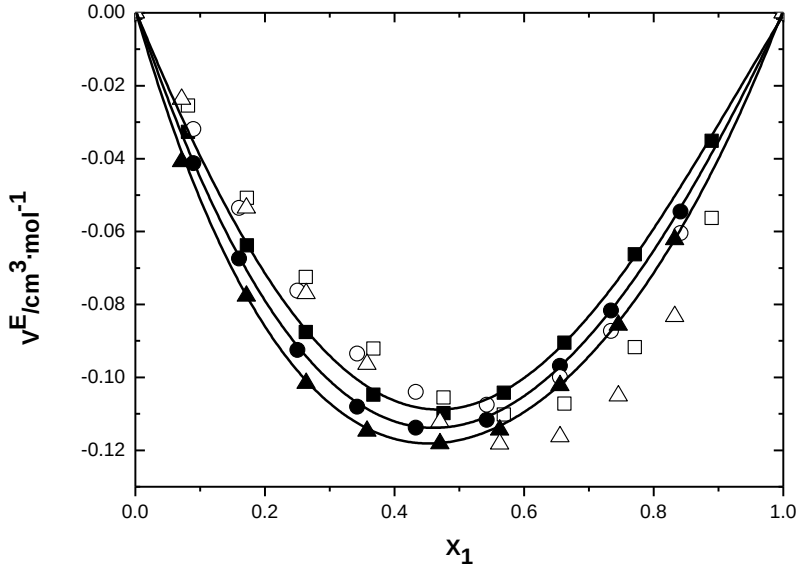

Figure 3

3.1Prigogine-Flory-Patterson theory

Patterson and Delmas[19] used the Prigogine-Flory-Patterson theory to interpret the excess volume for a number of binary systems [20, 21]. The expression for the excess molar volume that manifest into three contributions is given as:

$$\frac{V^E}{x_1V_1^* + x_2V_2^*} = \frac{(\tilde{V}^{1/3}-1)\tilde{V}^{2/3}}{[(4/3)\tilde{V}^{-1/3}-1]}\Psi_1\theta_2\left(\frac{\chi_{12}}{P_1^*}\right) \text{(int.contribution)} - \frac{(V_1-V_2)^2[(14/9)\tilde{V}^{-1/3}-1]\Psi_1\Psi_2}{[(4/3)\tilde{V}^{-1/3}-1)\tilde{V}}$$

$$\text{(fv.contribution)} + \frac{(\tilde{V}_1-\tilde{V}_2)(P_1^*-P_2^*)}{P_1^*\Psi_2 + P_2^*\Psi_1}\Psi_1\Psi_2 \ (P^*\text{contribution}) \qquad (5)$$

Reduced volume $\tilde{V}$ is calculated from thermal expansion coefficient,

$$\tilde{V} = \left[\frac{1+(4/3)\alpha T}{1+\alpha T}\right]^3 \qquad (6)$$

Where θ, ψ and P^* are the molecular contact energy fraction, molecular surface fraction and characteristic pressure respectively,which are calculated by using the following relations

$$\theta_2 = 1-\theta_1 = \frac{\phi_2}{\phi_2 + \phi_1(V_2^*/V_1^*)} \qquad (7)$$

$$\psi_2 = 1-\psi_2 = \frac{\phi_2 P_1^*}{\phi_1 P_1^* + \phi_2 P_2^*} \qquad (8)$$

$$P^* = \frac{T\tilde{V}^2\alpha}{\kappa_T} \qquad (9)$$

Equations (5) through (9) employ the same notations and concepts as those described in the literature [22–25]. The values of χ_{12}, θ_2, three PFP contributions [V_m^E (int.), V_m^E (fv.) and V_m^E (P^*)], along with the experimental and calculated V_m^E values using PFP theory, are shown in Table 5. The remaining parameters relevant to pure liquids and mixtures are found using the equations provided in the literature [22–25]. Fig. 3 displays graphically the contrast between experimental V_m^E data and those computed using PFP.

Table 5 makes it evident that the primary factor determining the direction and size of surplus molar volumes for N-methylformamide + o-substituted aniline is the excess free volume contribution.

Table 5:

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			$V^E(x=0.5)$		
		Interactional (10^{-9})	Free volume	P* effect	EXP	PFP	δ / $cm^3.mol^{-1}$
N-methylformamide+ 2-chloroaniline	-1.146	6.377	-0.0049	-0.0308	-0.1089	-0.1088	-0.0001
N-methylformamide+ 2-methylaniline	-2.851	7.401	-0.0212	0.1183	-0.1138	-0.1139	0.0001
N-methylformamide+ 2-methoxyaniline	-1.309	6.430	-0.0029	-0.0299	-0.1178	-0.1171	-0.0007

3.2 Partial molar properties

The interpretation of excess partial molar properties ($\overline{K}^{E}_{s,m,1}$ and $\overline{K}^{E}_{s,m,2}$) and excess partial molar properties at infinite dilution ($\overline{K}^{\circ E}_{s,m,1}$ and $\overline{K}^{\circ E}_{s,m,2}$) of components 2 are described else ware [15].Tables 6 and 7 show that the values of $\overline{K}^{E}_{s,m,1}$, $\overline{K}^{E}_{s,m,2}$, $\overline{K}^{\circ E}_{s,m,1}$ and $\overline{K}^{\circ E}_{s,m,2}$ are negative over the whole range at experimental temperatures. The negative values found, suggest that the hetero molecular association interactions is stronger than the self-association of inter molecular interactions of like molecules in the mixtures[26.27]

Table 6: The values $\bar{K}^{E}_{s,m,1}$, $\bar{K}^{E}_{s,m,2}$ of liquid mixtures of N-methylformamide with o-substituted aniline at T= (303.15 - 318.15) K

	303.15 K		308.15 K		313.15 K		318.15 K	
x1	$\bar{K}^{E}_{s,m,1}$	$\bar{K}^{E}_{s,m,2}$	$\bar{K}^{E}_{s,m,1}$	$\bar{K}^{E}_{s,m,2}$	$\bar{K}^{E}_{s,m,1}$	$\bar{K}^{E}_{s,m,2}$	$\bar{K}^{E}_{s,m,1}$	$\bar{K}^{E}_{s,m,2}$
N-methylformamide+ 2-chloroaniline								
0.0000	-15.34	0.000	-16.97	0.000	-19.48	0.000	-21.78	0.000

0.0815	-11.22	-0.170	-12.17	-0.196	-14.84	-0.249	-14.57	-0.292
0.1725	-7.755	-0.666	-8.292	-0.751	-10.81	-0.915	-9.209	-1.053
0.2634	-5.259	-1.355	-5.610	-1.490	-7.764	-1.736	-5.913	-1.955
0.3674	-3.297	-2.249	-3.593	-2.407	-5.205	-2.654	-3.818	-2.901
0.4756	-1.978	-3.201	-2.288	-3.348	-3.326	-3.487	-2.721	-3.686
0.5689	-1.240	-4.003	-1.556	-4.144	-2.169	-4.157	-2.164	-4.291
0.6623	-0.742	-4.797	-1.026	-4.992	-1.321	-4.950	-1.681	-5.072
0.7712	-0.354	-5.777	-0.547	-6.212	-0.624	-6.391	-1.049	-6.710
0.8895	-0.093	-7.066	-0.158	-8.159	-0.156	-9.273	-0.340	-10.32
1.0000	0.000	-8.714	0.000	-11.02	0.000	-14.10	0.000	-16.64
N-methylformamide+ 2-methylaniline								
0.0000	-17.33	0.000	-19.72	0.000	-21.95	0.000	-24.66	0.000
0.0896	-12.25	-0.229	-13.26	-0.288	-16.26	-0.332	-15.90	-0.388
0.1601	-9.236	-0.656	-9.676	-0.793	-12.73	-0.903	-11.25	-1.041
0.2501	-6.370	-1.387	-6.533	-1.592	-9.227	-1.781	-7.424	-2.010
0.3425	-4.314	-2.246	-4.503	-2.436	-6.540	-2.669	-5.182	-2.938
0.4328	-2.932	-3.114	-3.275	-3.206	-4.594	-3.442	-3.980	-3.688
0.5424	-1.814	-4.170	-2.331	-4.097	-2.885	-4.310	-3.126	-4.495
0.6554	-1.055	-5.297	-1.608	-5.182	-1.648	-5.429	-2.371	-5.640
0.7342	-0.668	-6.179	-1.136	-6.265	-1.011	-6.651	-1.760	-7.047
0.8414	-0.271	-7.665	-0.520	-8.603	-0.387	-9.472	-0.844	-10.55
1.0000	0.000	-11.04	0.000	-15.33	0.000	-17.99	0.000	-21.61
N-methylformamide+ 2-methoxyaniline								
0.0000	-19.94	0.000	-21.58	0.000	-23.75	0.000	-25.7	0.000
0.0714	-14.45	-0.196	-15.46	-0.218	-18.55	-0.248	-18.25	-0.266
0.1715	-9.068	-0.921	-9.584	-1.007	-12.95	-1.129	-11.18	-1.215
0.2636	-5.903	-1.788	-6.239	-1.922	-9.190	-2.114	-7.246	-2.288
0.3576	-3.895	-2.680	-4.199	-2.828	-6.387	-3.044	-4.925	-3.317
0.4701	-2.510	-3.643	-2.849	-3.765	-4.037	-3.947	-3.450	-4.339
0.5625	-1.825	-4.370	-2.182	-4.474	-2.682	-4.617	-2.729	-5.106
0.6556	-1.310	-5.173	-1.639	-5.323	-1.677	-5.489	-2.109	-6.080
0.7454	-0.867	-6.218	-1.119	-6.555	-0.954	-6.896	-1.467	-7.603
0.8325	-0.462	-7.756	-0.607	-8.501	-0.441	-9.272	-0.805	-10.12
1.0000	0.000	-13.45	0.000	-16.04	0.000	-18.87	0.000	-20.20

Table 7: 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 N-methylformamide + o-substituted aniline binary mixtures at T= (303.15 - 318.15) K

T/K	$\overline{K}^{\circ}_{s,m,1}$	$K^{*}_{s,m,1}$	$\overline{K}^{\circ E}_{s,m,1}$	$\overline{K}^{\circ}_{s,m,2}$	$K^{*}_{s,m,2}$	$\overline{K}^{\circ E}_{s,m,2}$
			(TPa^{-1})			
N-methylformamide+ 2-chloroaniline						
303.15	-12.33	3.010	-15.34	-4.630	4.084	-8.71
308.15	-13.88	3.081	-16.97	-6.813	4.208	-11.02
313.15	-16.31	3.178	-19.48	-9.747	4.351	-14.10

318.15	-18.50	3.283	-21.78	-12.15	4.486	-16.64
			N-methylformamide+ 2-methylaniline			
303.15	-14.32	3.010	-17.33	-6.170	4.873	-11.04
308.15	-16.64	3.081	-19.72	-10.27	5.060	-15.33
313.15	-18.77	3.178	-21.95	-12.75	5.235	-17.99
318.15	-21.37	3.283	-24.66	-16.19	5.426	-21.61
			N-methylformamide+ 2-methoxyaniline			
303.15	-16.93	3.010	-19.94	-9.39	4.061	-13.45
308.15	-18.50	3.081	-21.58	-11.86	4.177	-16.04
313.15	-20.57	3.178	-23.75	-14.60	4.274	-18.87
318.15	-22.45	3.283	-25.73	-15.79	4.361	-20.16

4. Conclusions:

Binary mixes of N-methylformamide and the o-substituted anilines (2-chloroaniline, 2-methylaniline, and 2-methoxyaniline) have had their densities and sound speeds evaluated at various temperatures, and the derived parameters, as well as their excess values, are calculated. The outcomes are examined in terms of the precise interactions created by the heteromolecular association of the mixture's constituent parts, which leads to the development of complexes. The excess free volume contribution is the primary parameter for the negative values of excess molar volumes, according to an analysis of the VE values using the Prigogine- Flory-Patterson theory.

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Figure captions:

Fig.1: Variation of excess volume (V^E) of the binary liquid mixture of N-methylfromamide with 2-chloroaniline (■);2-methylaniline (●) and 2-methoxyaniline (▼)at 303.15 K.

Fig. 2 Variation of excess isentropic compressibility of the binary mixture of N-methylfromamidewith 2-chloroaniline (■);2-methylaniline (●) and 2-methoxyaniline (▼) at 303.15 K.

Fig. 3 Excessmolar volumes of the binary mixtures against mole fraction x_1 at T = 303.15 K forN-methylformamide with 2-chloroaniline (■);2-methylaniline (●) and 2-methoxyaniline (▼) and (---) calculated with PFP theory usingParametersat 303.15 K.