Chemical Data Collections 22 (2019) 100241

Contents lists available at ScienceDirect

Chemical Data Collections

journal homepage: www.elsevier.com/locate/cdc

Data Article

Thermodynamic, DFT and molecular dynamics studies of intermolecular interactions between 2-methoxyaniline and N-substituted amide mixtures

B. Mukesh[a,*], M. Chandra Sekhar[a,**], K. Chandra Sekhar Reddy[b], T. Sreekanth[c]

[a] *Department of Physics, Department of Physics, Vignan Institute of Technology and Science, Telangana State, India*
[b] *Department of Physics, SSBN College, Anantapur, Andhra Pradesh, India*
[c] *Department of Physics, J.N.T. University, Jagitial 505327, Telangana State, India*

ARTICLE INFO

Article history:
Received 15 December 2018
Revised 18 May 2019
Accepted 7 June 2019
Available online 11 June 2019

Keywords:
2-methoxyaniline
N-alkylamides
DFT
QTAIM
NBO
RDF

ABSTRACT

The experimental data of density(ρ) and speed of the sound(u) of 2-methoxyaniline and N-alkyl amides binary liquid mixtures have been evaluated at temperatures $T = (303.15$ to $318.15)$ K. Values of excess molar volume (V_m^E), excess isentropic compressibility (k_s^E), excess partial molar volumes ($\overline{V}^E_{m,1}, \overline{V}^E_{m,2}$), and excess partial molar volumes at infinite dilution($\overline{V}^{E,\infty}_{m,1}, \overline{V}^{E,\infty}_{m,2}$) over the whole composition range have been calculated by using the density and the speed of sound measurements. The calculated excess parameters were used to discuss the intermolecular interactions. A quantum mechanical approach was performed in gas phase and classical molecular dynamic simulations were done in liquid phase to study the intermolecular interactions in self and cross-associated complexes. The details of experimental, quantum mechanical and classical molecular dynamic methods are used to investigate the formation of a hydrogen-bonded network between 2-methoxyaniline and N-alkyl amide mixtures.

Specifications table

Subject area	Organic chemistry, charge transfer, Chemical Engineering, Chemical Thermodynamics Guassian09, NBO, DFT, Molecular Dynamics
Compounds	2-methoxyaniline with three N-alkylamides (N-methylformamide (NMF), N-methylacetamide (NMA) and N-ethylacetamide (NEA))
Data category	Density, speed of sound, Hydrogen bond lengths, Interaction energies, Radial distribution function
Data acquisition format	Thermodynamic, DFT and Molecular Dynamics
Data type	Raw, Analyzed and simulated
Procedure	The density and speed of sound are measured with an Anton Paar (DSA 5000 M) nstrument which employs the well-known oscillating U-tube principle (for density measurement). Geometrical optimizations, determination of interactive energy and non-covalent interaction plots (NCI) analysis have been carried out using density functional theory (DFT) with the popular hybrid method (B3LYP) with basis set 6-311++G(d,p) by using Gaussian 09 software.
Data accessibility	Data analyzed by in this article

---

[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: bmkchandra48@gmail.com (B. Mukesh), sekharchandra6@gmail.com (M.C. Sekhar).

https://doi.org/10.1016/j.cdc.2019.100241
2405-8300/

1. Rationale

Hydrogen bond plays a significant role in many prominent chemical and biological processes in relation to retrieve the chemical dynamics of molecules [1–5]. Subsequently, the investigation of hydrogen bonding interactions in the liquid state offers a promising method in developing statistical thermodynamic models to describe the pronounced features of liquid state systems [6–8]. Owing to the complex nature of intermolecular interactions in liquid state, it is necessary to carry out studies on the effect of functional groups. A clear understanding of intermolecular interactions in liquid state is quite essential to investigate the structural features as well as macroscopic properties of liquids. Thus a comprehensive microscopic view of intermolecular interactions in liquid systems could be retrieved by experimental and theoretical methods.

In recent years, considerable amount of interest has been reported to explain the intermolecular hydrogen bonding in liquid mixtures with the aid of experimental results supplemented by theoretical methods [9–14]. In the liquid mixtures, density and speed of sound are considered to be the vital parameters to explore the theoretical calculations. Further, excess thermodynamic properties associated with the liquid mixtures play a vital role to analyze the structures, molecular interactions, and thermal motion of molecules [15–17]. Density functional theory (DFT) incorporating quantum mechanical approach is a promising method to estimate the binary interaction parameters of molecular complexes with much precision. Quantum mechanical approaches such as Density Function Theory (DFT) can be successfully used to estimate the binary interaction parameters among the liquid mixtures.

The liquids which are chosen in the present investigation have many potential applications towards the chemical industries. 2-Methoxyaniline is a polar solvent that is self-associated through hydrogen bonding of the Amine group. 2-Methoxyaniline is used in the manufacturing of dyes and hair dyes. 2-Methoxyaniline is also used as an intermediate chemical in the production of Synthetic Guaiacol. N-Substituted amides are the simplest model molecules which has peptide group, and subsequently, many studies have been proved to understand that the intermolecular interactions of N-substituted amides. This paper gives us most prominent part of our continuing and systematic study of the secondary amides in chosen solutions from thermodynamic, densitometric and density functional theory aspects. In the current work we have studied the influence of an additional alkyl group on the volumetric properties of the mixtures. Especially in the case of Hydrogen bond and intermolecular forces of -NH group, it plays vital role in N-substituted amides and in Biology gives as proper model systems.

The current research was undertaken to determine the characteristics like speed of sound and density of N-Methylformamide(NMF), N-Methylacetamide(NMA) and N-Ethylacetamide(NEA) and their binary mixtures with 2-Methoxyaniline at a temperature (T) of 303.15–318.15 K. In theoretical study, monomer's and all possible hydrogen-bonded dimer's geometrical structures are completely optimized with the help of Density Functional Theory (DFT) with the Lee–Yang–Parr (LYP) correlation function (B3LYP) and the 6-311++G(d,p) basis set. An extensive examination of the computational results is carried out to confirm the complex formation of the Hydrogen-Bond and also its interacting nature.

2. Procedure

2.1. Materials

The 2-methoxyaniline and N-alkylamides (N-methylformamide (NMF), N-methylacetamide (NMA) and N-ethylacetamide (NEA)) are obtained from Sigma Aldrich Corporation, India and are used without further purification. All the binary liquid combinations are made by weighing suitable quantities of pure liquids on a digital weighing balance (Mettler Toledo AB 135, Switzerland) with an uncertainty of ±0.00001 g, by injecting each liquid component into an airtight sample bottles to decrease the loss of evaporation. The uncertainty in the approximation of mole fraction is $\pm 1 \times 10^{-4}$. The structure of observed chemicals, CAS number, their organic liquid sources, and also their final purities are mentioned in the Table S1.

2.2. Measurements

Binary liquid mixtures of 2-methoxyaniline(**MOA**) and N-alkylamides (N-Methylformamide (**NMF**), N-methylacetamide(**NMA**), N-ethylacetamide(**NEA**)) were prepared in different composition by weighing appropriate amounts of pure liquids on a digital electronic balance (Mettler Toledo AB 135, Switzerland) with an uncertainty of ±0.00001 g. To minimize the evaporation or absorption losses, samples were kept in airtight stoppered bottles.

The values of density, ρ and speed of sound, u at temperatures range from 303.15 K to 318.15 K, were measured with an Anton Paar (DSA 5000 M) vibrating u-tube densitometer, which is calibrated by using ultra pure distilled water and dry air at different temperatures and atmospheric pressure. The built in thermostat controls the temperature in the vibrating U-tube with a precision of ±0.01 K. The estimated uncertainties of measured density and speed of sound were, $\pm 0.0005\ \mathrm{g\ cm^{-3}}$and $\pm 0.5\ \mathrm{m\ s^{-1}}$ and for V_m^E, k_s^E with uncertainties $\pm 0.005\ \mathrm{cm^3\ mol^{-1}}$, $\pm 0.05\ \mathrm{TPa^{-1}}$, respectively. The ρ and u values of selected organic liquids are mentioned in Table 1 and were also compared with their respective literature values [18–24].

Table 1

Comparison of densities, ρ, speeds of sound, u pure chemicals with their corresponding literature values at $T = 303.15$, 308.15 K, 313.15 K and 318.15 K andatmospheric pressure 0.1 MPa.

Compound	Density		Speed of sound	
	Experimental	Literature	Experimental	Literature
2-methoxyaniline				
303.15 K	1.09180	1.09175[a]	1595.2	1595.4[a]
308.15 K	1.08740	1.08735[a]	1579.5	1579.2[a]
313.15 K	1.08383	1.08378[a]	1566.8	–
318.15 K	1.08085	1.08080[a]	1554.2	–
N-methylformamide				
303.15 K	0.99464	0.9946[b] 0.9949[c]	1409.5	1408.5[g]
308.15 K	0.99033	0.9903[b] 0.9905[c]	1397.6	1398.2[g]
313.15 K	0.98614	0.9861[b]	1383.1	1382.5[g]
318.15 K	0.98204	0.9820[b]	1366.6	1365.8[g]
N-methylacetamide				
303.15 K	0.95132	0.9512[d]	1367.1	1367[f]
308.15 K	0.94590	0.9470[d]	1362.2	1354.2[e] 1362[f]
313.15 K	0.94363	0.9429[d]	1334.4	1339.4[e] 1334[f]
318.15 K	0.93992	0.9402[d]	1319.8	1324.8[e]
N-ethylacetamide				
303.15 K	0.92655	0.9266[c]	1450.8	–
308.15 K	0.92265	0.9226[c]	1437.9	–
313.15 K	0.91890	–	1426.4	–
318.15 K	0.91525	–	1413.9	–

[a] Ref. [26].
[b] Ref. [27].
[c] Ref. [28].
[d] Ref. [29].
[e] Ref. [30].
[f] Ref. [31].
[g] Ref. [32].

2.3. *Computational methods*

2.3.1. *DFT calculations*

Quantum mechanical electronic structure calculations are used to evaluate the intermolecular hydrogen bonding between 2-methoxyaniline and N-alkylamide complexes. The geometrical parameters, interactions energies, second-order perturbation stabilization energies and electron densities were calculated by using B3LYP method [25,26] using basis set $6 - 311 + +G(d, p)$. All these simulations in the gas phase were carried out by using Gaussian 09 software [27]. The interaction energies of all dimers are determined from the energy difference between the dimer and monomers in their optimized position. The Basis Set Superposition Error (BSSE) is eliminated by using the method of Boys and Bernard's counterpoise [28]. Charge densities, Laplacian charge densities and total electron energy densities were computed by using Multiwfn program [29] at bonding critical point (BCP). The non-covalent interactions (NCI) plots are employed for real-space visualization of attractive interactions between 2-methoxyaniline and N-alkylamides.

2.3.2. *Molecular dynamics simulations*

Classical molecular dynamics (MD) analysis of the mixture of 2-methoxyaniline (MOA) and N-alkylamides (N-methylformamide (NMF), N-methylacetamide (NMA), N-ethylacetamide (NEA) were performed using the Gromacs5.0.4 software package [30]. The simulations were carried out in a cubic box with 200 molecules. In order to make simulations more sensible, the structures of components were optimized at the B3LYP/6-31++G (d, p) level using Gaussian 09. To investigate the interactions between the selected liquid mixtures, 'Optimized Potentials for Liquid Simulation' (OPLS) force field were used [31].

All MD simulations were performed in three phases: pre-equilibration, equilibration and production. In the pre-equilibration stage the energy was minimized with steepest descent and conjugate gradient algorithms followed by equilibration in the NVT ensemble. After energy minimization equilibration was performed, then the system was switched to a NPT ensemble at 303.15 K and then the system was equilibrated for 1 ns. The pressure and temperatures were monitored by Nosé–Hoover barostat and thermostat with a relaxation time of 0.5 ps. The bond length and angles were constrained by using LINCS algorithm [32]. The particle-mesh Ewald method was used to control the cut-off radius for both electrostatic

Table 2
Density (ρ) and speed of sound (u) of binary liquid mixtures of 2-methoxyaniline with N-alkylamides at temperatures $T = (303.15–318.15)$ K.

x_1	ρ/kg m^{-3}				u/m s^{-1}			
	303.15 K	308.15 K	313.15 K	318.15 K	303.15 K	308.15 K	313.15 K	318.15 K
2-methoxyaniline+ N-methylformamide								
0.0000	994.6	990.3	986.1	982.0	1409.5	1397.6	1383.1	1366.6
0.1743	1023.8	1018.8	1015.6	1011.9	1454.4	1443.4	1428.3	1412.4
0.3220	1042.6	1037.2	1034.5	1031.1	1490.2	1478.5	1463.6	1448.5
0.4488	1055.7	1050.1	1047.7	1044.4	1518.7	1506.1	1491.5	1477.0
0.5588	1065.3	1059.6	1057.3	1054.1	1541.2	1527.8	1513.5	1499.4
0.6551	1072.6	1066.9	1064.6	1061.5	1558.9	1544.9	1530.8	1517.2
0.7402	1078.3	1072.7	1070.4	1067.3	1572.6	1558.1	1544.3	1531.2
0.8159	1082.9	1077.4	1075.0	1071.9	1582.7	1568.1	1554.7	1542.0
0.8837	1086.5	1081.3	1078.6	1075.7	1589.7	1574.9	1562.0	1549.8
0.9447	1089.4	1084.6	1081.6	1078.6	1593.9	1578.6	1566.1	1554.3
1.0000	1091.8	1087.4	1083.8	1080.9	1595.2	1579.5	1566.8	1554.2
2-methoxyaniline+ N-methylacetamide								
0.0000	951.3	945.9	943.6	939.9	1367.1	1362.2	1334.4	1319.8
0.1403	980.4	975.4	973.1	969.8	1400.6	1396.4	1368.7	1354.2
0.2685	1003.8	998.9	996.3	993.0	1432.7	1428.6	1401.6	1387.7
0.3862	1022.6	1017.8	1015.1	1011.8	1462.8	1457.9	1432.3	1418.7
0.4946	1038.1	1033.4	1030.5	1027.3	1490.3	1484.3	1460.3	1447.1
0.5948	1050.9	1046.3	1043.3	1040.1	1515.0	1507.6	1485.5	1472.6
0.6877	1061.6	1057.1	1054.0	1051.0	1536.6	1527.9	1507.9	1495.5
0.7740	1070.8	1066.3	1063.2	1060.2	1555.3	1545.0	1527.3	1515.5
0.8545	1078.7	1074.4	1071.1	1068.2	1571.0	1559.3	1543.6	1532.5
0.9296	1085.6	1081.3	1078.0	1075.1	1584.3	1570.6	1556.8	1545.9
1.0000	1091.8	1087.4	1083.8	1080.9	1595.2	1579.5	1566.8	1554.2
2-methoxyaniline+ N-ethylacetamide								
0.0000	926.6	922.6	918.8	915.3	1450.8	1437.9	1426.4	1413.9
0.1176	951.5	947.6	944.0	940.8	1467.9	1455.0	1444.0	1431.9
0.2307	973.8	969.9	966.3	963.0	1485.6	1472.6	1461.9	1450.0
0.3396	993.9	989.8	986.2	983.0	1503.4	1489.9	1479.3	1467.5
0.4444	1012.0	1007.9	1004.3	1001.2	1520.5	1506.7	1496.1	1484.3
0.5454	1028.5	1024.3	1020.8	1017.7	1536.7	1522.5	1511.8	1500.1
0.6428	1043.5	1039.3	1035.8	1032.8	1551.4	1537.2	1526.4	1514.9
0.7368	1057.2	1053.1	1049.6	1046.7	1564.8	1550.2	1539.4	1528.4
0.8276	1069.7	1065.6	1062.2	1059.4	1576.4	1561.8	1550.8	1540.0
0.9152	1081.2	1077.0	1073.6	1070.8	1586.6	1571.5	1560.0	1549.2
1.0000	1091.8	1087.4	1083.8	1080.9	1595.2	1579.5	1566.8	1554.2

Standard uncertainties u are u (T) = 0.01 K, u (ρ) = ±0.5 kg·m^{-3}, u (u) = ± 0.7 m s^{-1}, u(p) = ± 1.0 kPa.

and Vander Waals interactions. The production simulations were executed at 10 ns at constant pressure and temperature (NPT ensemble).

3. Data, value and validation

3.1. Excess molar volume and excess isentropic compressibility

The measured density, speed of sound and their calculated excess parameters (V_m^E, k_s^E) for a mixture of 2-methoxyaniline and N-alkylamides at a temperature range 303.15–318.15 K and as a function of composition are listed in Tables 2 and 3 respectively.

The values of excess molar volume of 2-methoxyaniline + N-alkylamides liquid mixtures were determined by using the following equation:

$$V_m^E = \sum_{i=1}^{2} x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i} \right) \tag{1}$$

where x_i, M_i and ρ_i are the mole fraction, molar weight and density of ith component of mixtures and ρ is the density of the mixtures.

The isentropic compressibility (κ_s) as follows:

$$\kappa_s = \frac{1}{\rho \cdot \mathrm{U}^2} \tag{2}$$

Table 3
Excess molar volume (V_m^E) and deviation in viscosity ($\Delta\eta$) of binary liquid mixtures of 2-methoxyaniline with N-alkylamides at temperatures T= (303.15–318.15) K.

x_1	V_m^E / 10^6 cm^3 mol^{-1}				k_s^E / TPa^{-1}			
	303.15 K	308.15 K	313.15 K	318.15 K	303.15 K	308.15 K	313.15 K	318.15 K
2-methoxyaniline + N-methylformamide								
0.000	0.000	0.000	0.000	0.000	0.00	0.00	0.00	0.00
0.174	−0.045	−0.051	−0.058	−0.065	−2.66	−3.16	−3.42	−3.55
0.322	−0.079	−0.086	−0.094	−0.106	−4.87	−5.55	−5.78	−6.03
0.449	−0.103	−0.109	−0.115	−0.129	−6.56	−7.19	−7.45	−7.67
0.559	−0.116	−0.122	−0.127	−0.140	−7.60	−8.16	−8.33	−8.50
0.655	−0.121	−0.126	−0.131	−0.142	−7.95	−8.46	−8.64	−8.77
0.740	−0.117	−0.122	−0.128	−0.138	−7.67	−8.16	−8.35	−8.48
0.816	−0.104	−0.111	−0.118	−0.127	−6.72	−7.28	−7.54	−7.65
0.884	−0.081	−0.089	−0.097	−0.106	−5.13	−5.75	−6.09	−6.25
0.945	−0.047	−0.054	−0.061	−0.068	−2.93	−3.37	−3.72	−3.85
1.000	0.000	0.000	0.000	0.000	0.00	0.00	0.00	0.00
2-methoxyaniline + N-methylacetamide								
0.000	0.000	0.000	0.000	0.000	0.00	0.00	0.00	0.00
0.140	−0.100	−0.122	−0.140	−0.160	−3.04	−3.51	−4.15	−4.65
0.269	−0.186	−0.207	−0.223	−0.239	−5.72	−6.35	−7.30	−8.01
0.386	−0.234	−0.254	−0.265	−0.279	−7.70	−8.31	−9.44	−10.20
0.495	−0.254	−0.271	−0.287	−0.299	−8.85	−9.45	−10.64	−11.38
0.595	−0.241	−0.261	−0.274	−0.288	−9.13	−9.72	−10.91	−11.61
0.688	−0.210	−0.227	−0.241	−0.259	−8.51	−9.20	−10.38	−11.12
0.774	−0.162	−0.179	−0.200	−0.217	−7.20	−7.84	−9.06	−9.89
0.855	−0.108	−0.130	−0.148	−0.167	−5.19	−5.93	−6.97	−7.82
0.930	−0.053	−0.070	−0.086	−0.105	−2.76	−3.29	−4.06	−4.71
1.000	0.000	0.000	0.000	0.000	0.00	0.00	0.00	0.00
2-methoxyaniline + N-ethylacetamide								
0.000	0.000	0.000	0.000	0.000	0.00	0.00	0.00	0.00
0.118	−0.145	−0.159	−0.184	−0.208	−3.58	−4.00	−4.71	−5.22
0.231	−0.243	−0.259	−0.279	−0.299	−6.52	−7.12	−8.12	−8.81
0.340	−0.294	−0.309	−0.327	−0.343	−8.66	−9.25	−10.45	−11.16
0.444	−0.313	−0.328	−0.344	−0.360	−9.90	−10.50	−11.73	−12.42
0.545	−0.308	−0.323	−0.339	−0.356	−10.27	−10.84	−12.09	−12.73
0.643	−0.284	−0.300	−0.317	−0.335	−9.66	−10.35	−11.59	−12.27
0.737	−0.244	−0.263	−0.286	−0.308	−8.29	−8.95	−10.23	−11.01
0.828	−0.175	−0.198	−0.224	−0.249	−6.05	−6.81	−7.92	−8.75
0.915	−0.090	−0.109	−0.133	−0.156	−3.26	−3.80	−4.62	−5.26
1.000	0.000	0.000	0.000	0.000	0.00	0.00	0.00	0.00

Standard uncertainties u are u (T) = 0.01 K, u (V_m^E) = ± 0.05·10^6 m^3 mol^{-1}, u (k_s^E) = 0.04 TPa^{-1}, u(p) = ± 1.0 kPa.

The comparable excess isentropic compressibilities (κ_s^E) have been calculated from the subsequent equation:

$$\kappa_s^E = \kappa_s - \kappa_s^{id} \tag{3}$$

where κ_s^{id} is the ideal value of the isentropic compressibility and calculated by using Benson and Kiyohara [33–37] expression was given below:

$$\kappa_s^{id} = \phi_1\kappa_{s,1} + \phi_2\kappa_{s,2} + T\left[\frac{\phi_1 V_{m,1}\left(\alpha_{p,1}\right)^2}{C_{p,1}} + \frac{\phi_2 V_{m,2}\left(\alpha_{p,2}\right)^2}{C_{p,2}} + \frac{V_m^{id}\left(\alpha_p^{id}\right)^2}{C_p^{id}}\right] \tag{4}$$

where, C_{pi} and α_i are the molar heat capacity and the thermal expansion coefficient of the ith component respectively. The value of C_{pi} was obtained by group contribution method [38].

The thermal expansion coefficient α_i was calculated by following equation.

$$\alpha = -\frac{1}{\rho}\left(\frac{\partial\rho}{\partial T}\right)_P \tag{5}$$

All the excess values are adapted by the method of nonlinear least-squares to a Redlich–Kister [39] polynomial equation of the category,

$$V_m^E(or\kappa_s^E) = x_1x_2\sum_{i=0}^{n} A_i(x_1 - x_2)^i \tag{6}$$

In which x_1 represents the mole fraction of 2-Methoxyaniline and x_2 is the mole fraction of N-alkylamides and the subscription 'i' in the equation takes the values from 0 to 2. By using the Least square method we can attain the values of A_i which are the binary coefficients. The standard deviation (σ) is calculated by using the below relation

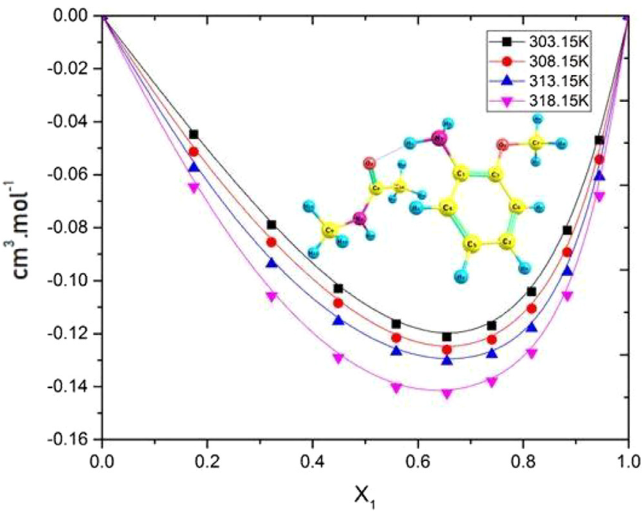


Fig. 1. Variation of excess molar volume (V_m^E) with mole fraction (x_1) of 2-methoxyaniline+ N-methylformamide at 303.15 K (■), 308.15 K (●), 313.15(▲), 318.15 K (??▼).

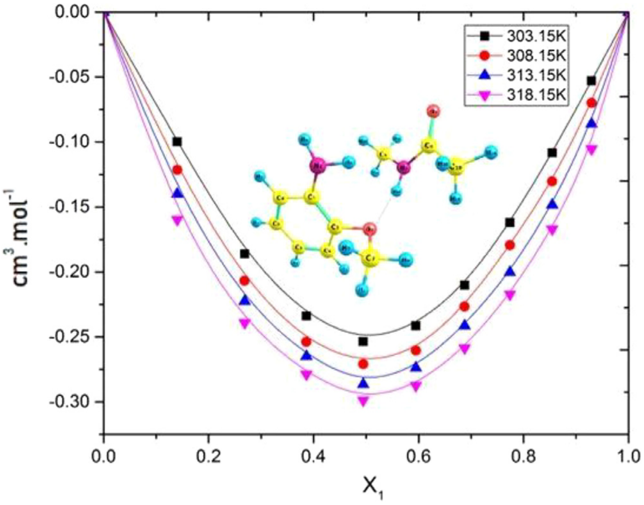


Fig. 2. Variation of excess molar volume (V_m^E) with mole fraction (x_1) of 2-methoxyaniline+ N-methylacetamide at 303.15 K (■), 308.15 K (●), 313.15(▲), 318.15 K (??▼).

The values of A_i are the binary coefficients attained by the method of least squares. The standard deviation (σ) is calculated using the relation,

$$\sigma = \left[\frac{\sum \left(Y_{\exp}^E - Y_{cal}^E \right)^2}{N - n} \right]^{\frac{1}{2}} \tag{7}$$

where N and n are the number of experimental points and number of coefficients. The values of adjustable parameters and standard deviations are presented in Table S3. The standard deviations values are found to be the highest level of confidence which gives the satisfactory results. Table S3 shows the values of adjustable parameters and standard deviations of Redlich–Kister polynomial equations. The values of standard deviations are gives valid results for the experimental values. The values of excess molar volume (V_m^E) and excess isentropic compressibility (κ_s^E) for the considered binary mixture are plotted against the mole fraction of N-alkylamides and showed in Figs. 1–3 and Figs. S1–S3.

The determined excess molar volume (V_m^E) of binary combinations with mole fraction (x_1) are mentioned in Table 3 and Figs. 1–3. A perusal of Figs. 1–3 show that the V_m^E values are negative over the entire mole fraction range and at all temperatures investigated. The uncertainty in average of the excess molar volume is estimated to be ±0.006 cm^3 mol^{-1}.

The negative excess molar volumes are associated to the dominance of the following effects: (a) dissociation of self-supported 2-methoxyaniline and N-alkylamides (b) interstitial accommodation of N-alkylamides in 2-methoxyaniline ag-

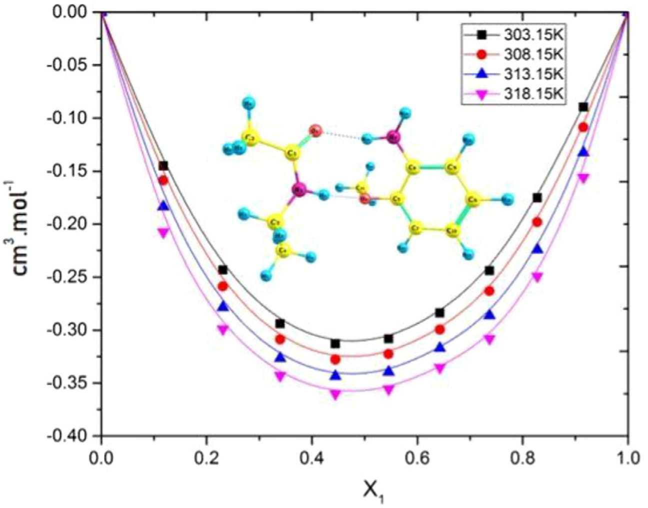


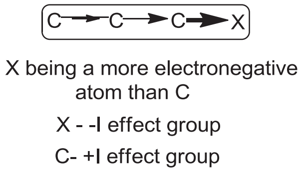
Fig. 3. Variation of excess molar volume (V_m^E) with mole fraction (x_1) of 2-methoxyaniline+ N-ethylacetamide at 303.15 K (■), 308.15 K (●), 313.15(▲), 318.15 K (??▼).

gregates (c) Hydrogen-Bond interaction between dissimilar molecules. However, the first factor contributes an increase in excess molar volume and the last two factors contribute the decrease in excess volumes; an interstitial accommodation of N-alkylamides in 2-methoxyaniline aggregates makes a negative contribution to V_m^E. The magnitude of V_m^E as follows the sequence:

$$(\mathbf{MOA + NMF}) < (\mathbf{MOA + NMA}) < (\mathbf{MOA + NEA})$$

The negative excess molar volume more will be the interactions in between the complexive partners due to hydrogen bond between the oxygen of amide and 2-methoxyaniline. By above conclusion it could be explained in terms of electronic factors of organic molecules. The Electronic factors which influence the organic molecules and in turn organic reactions are Inductive, Electrometric, Resonance effects and also hyper conjugation.

The density of electrons is distributed evenly between the two atoms in a non-polar bond like C–C or C–H bond where the two ends of the bond have same electro negativity. In contrast, a covalent bond between atoms with different electro negativities would be polarized partially or completely towards the more electronegative atom among the two, which is nothing but Inductive effect. Inductive effect categorized into two groups viz, +I effect containing electron donating groups like alkyl groups, while –I effect containing electron withdrawing groups.



Applying the above concept to our study in NEA, NMA and NMF, ethyl being the stronger +I group compared to methyl in NMA and NMF, the former pushes the electrons strongly towards N atom in NEA compared to that of latter components. More the electron density at N atom more would be the interaction with 2-methoxyaniline. This attributes to the strong interactions between the NEA and 2- methoxyaniline. Moreover, The more steric hindrance in NEA binary mixtures due to availability of -CH_3 group of +I effect near the group which is involving in H-bonding association with electron density of aromatic ring of 2-methoxyaniline.

For all the analyzed binary mixtures, a decrease in V_m^E over the entire composition range can observed with a change in temperature range from 303.15 K to 318.15 K. The increase of temperature leads to an increase in the kinetic energy of the self-supported molecules of N-substituted amides and also promotes their dissociation. However the temperature has the same impact on the complex between the components of the mixture. By the gained result we can observe that the increment in temperature will show a greater effect on the characteristics of self – supported reactions of amides and 2-methoxyanelene than the complex formations between amides and 2-methoxyanelene.

The values of the speed of the sound (u) and its derived excess isentropic compressibility (k_s^E) for the binary mixtures of 2-methoxyaniline and N-alkyl amides are given in the Table 3 and the respective graphical representation also illustrated in Figs S1–S3.

It is familiar that the values of k_s^E could be influenced by the relative strengths of several resisted effects that comprised of Structural, Physical and Chemical contributions. In which the Physical contribution gives us the positive value of

k_s^E whereas both Chemical and Structural contribution provides the negative value for k_s^E. Because of dispersion forces or weak dipole–dipole interactions the physical contribution leads to positive value of k_s^E, the specific interactions such as the origination of hydrogen bonds, charge transfer between complexes and their forming interactions including strong dipole–dipole interactions among the component molecules the Chemical contribution leads to negative result in k_s^E and structural contribution influence a change in geometrical structure and also allows the fitting of molecules belongs to two different sizes in each other's structure that results in negative contribution to k_s^E. The Figs. S1–S3 represents the gained values for k_s^E for all three binary combinations, which shows the mixture has less compressibility than the respective ideal combination. These results suggest noticeable interactions between cross associated molecules and the optimised structure of 2-methoxyaniline (MOA) gets disorder by the adding N-alkylamides.

The gained k_s^E values (Figs. S1–S3) for all the three binary combinations under study, indicate that the mixture is less compressible than the corresponding ideal mixture, suggesting significant interactions between the unlike component molecules, i.e., the compact structure of polar component (MOA), due to dipolar association, has been disrupted by the addition of N-alkylamides. With the help of present analysis we can conclude that there will be an increase in speed of sound and decrease of isentropic compressibility of the taken dipole–dipole interactions and geometrical contribution between cross associated molecules which can be known by the gained values of k_s^E and also there is a parallel relation between V_m^E and κ_s^E. In another way it can be explained as if the volume decreases at the time of mixing then the entire system becomes rigid. In the present system k_s^E becomes negative along with a raise in temperature. Breaking of associations that present in the pure liquids are supported by the raise in temperature by releasing more and more free dipoles of unlike molecules in the mixture which interact with each other.

The gained values of k_s^E can be explained in terms of dipole–dipole interactions and geometrical contribution between cross associated molecules which leads to an increase in speed of sound and decrease of isentropic compressibility as observed in the present investigation. There is a parallel relation between V_m^E and κ_s^E. In other words, during mixing the volume decreases and the whole system becomes more rigid. When temperature increases (k_s^E) becomes more and more negative in the present system. Increase in temperature promotes the breaking of associations present in the pure liquids releasing more and more free dipoles of unlike molecules in the mixture which interact with each other.

3.2. Excess partial molar volumes

To study the intermolecular interactions between various solute and solvent molecules the partial and excess partial molar volumes are used. By using the following relations we can find out the excess partial molar volumes of cross associated combinations of 2-methoxyaniline with N-alkyl amides.

The partial and excess partial molar volumes have been used to understand the intermolecular interactions between different solute–solvent molecules. The excess partial molar volumes of 2-methoxyaniline and N-alkylamides of their binary mixtures have been calculated by using the following equations:

$$\overline{V}_1^E = \overline{V}_1 - V_1^0 \tag{8}$$

$$\overline{V}_2^E = \overline{V}_2 - V_2^0 \tag{9}$$

where the elements described as V_1^0 and V_2^0– molar volumes 2-Methoxyaniline and N-Alkyl amides respectively, $\overline{V}_1$ and $\overline{V}_2$– partial molar volumes of 2-Methoxyaniline and N-Alkyl amides respectively. The partial molar volume of 2-Methoxyaniline is calculated by using the following relation which is described by Wood et al. and Cipiani et al. [40,41]:

$$\overline{V}_1 = V^E + V_1^0 - x_2\left(\frac{\partial V^E}{\partial x_2}\right)_{T,P} \tag{10}$$

And for N- Alkylamides:

$$\overline{V_2} = V^E + V_2^0 + (1 - x_2)\left(\frac{\partial V^E}{\partial x_2}\right)_{T,P} \tag{11}$$

The derived value of V^E with respect to x_2, is given in Eqs. (10) and (11), can be computed by using differentiation of the Redlich–Kister relation and combination of the results of differentiation with Eqs. (10) and (11). The results can be found by using the following relations for the partial molar volumes of 2-methoxyaniline and N-Alkylamides, respectively:

$$\overline{V_1} = V_1^0 + x_2^2\sum_{i=0}^{n} A_i(1 - 2x_2)^i + 2(1 - x_2)x_2^2\sum_{i=0}^{n} A_i(i)(1 - 2x_2)^{i-1} \tag{12}$$

$$\overline{V_2} = V_2^0 + (1 - x_2)^2\sum_{i=0}^{n} A_i(1 - 2x_2)^i - 2(1 - x_2)x_2^2\sum_{i=0}^{n} A_i(i)(1 - 2x_2)^{i-1} \tag{13}$$

The excess partial molar volume data of 2-methoxyaniline and N-alkylamides in their mixtures were depicted graphically in the Figs. 4–6 at T=(303.15–318.15) K. Further, the partial molar volumes and excess partial molar volumes of

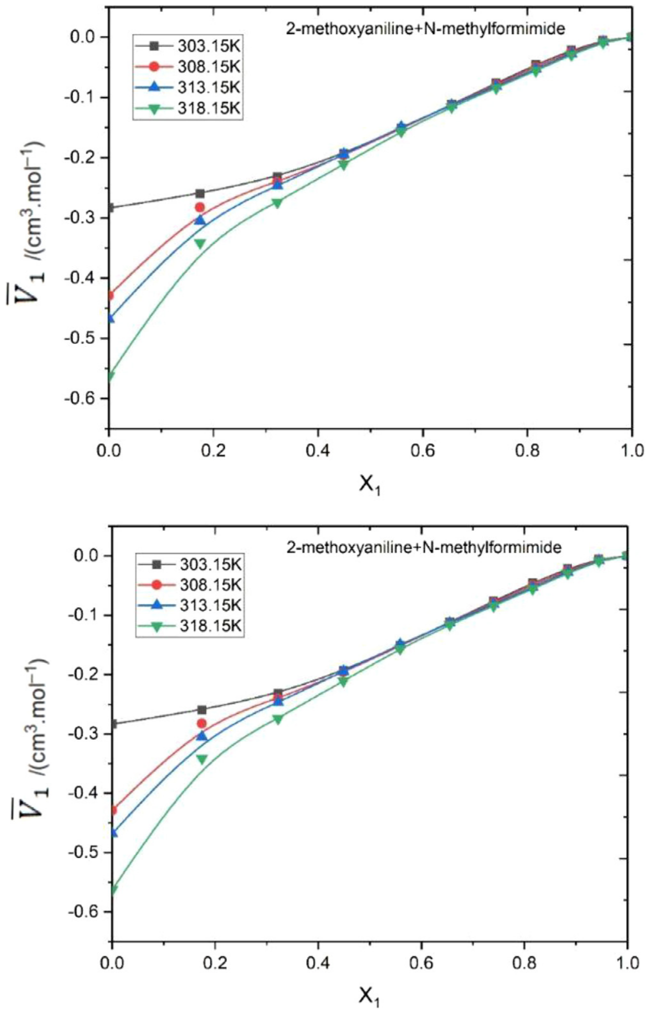


Fig. 4. Variation of the partial molar volume, $\overline{V}_1$, $\overline{V}_2$ of (a) 2-methoxyaniline and (b) N-methylformamide respectively, against mole fraction, x_1 of 2-methoxyaniline for the binary mixtures at 303.15 K (■), 308.15 K (●), 313.15(▲), 318.15 K (??▼).

2-methoxyaniline and N-alkylamides in the binary mixtures were given Table S2. It has been seen that partial molar volume data was negative over the entire composition range in the mixture containing 2-methoxyaniline and N-alkylamides. The negative excess partial molar volume values of the mixture suggest that their partial molar volumes were less than their respective molar volumes in the pure state. The overall magnitude of excess partial molar volumes ($\overline{V}_i^E$) also follows the order:

$$(\mathbf{MOA+NMF}) < (\mathbf{MOA+NMA}) < (\mathbf{MOA+NEA})$$

With the above result, the partial molar volumes at finite dilutions will give the information about intermolecular interactions between solute and solvent molecules. At infinite dilution, as the solute and solvent interactions are very small, so they can be neglected. By using the following relation the partial molar volumes of 2-methoxyaniline at infinite dilution ($x_1 = 0$) in N-alkylamides ($\overline{V}_1^{\infty}$) and the partial molar volumes of N-Alkyl amides at infinite dilution ($x_2 = 0$) in 2-methoxyaniline ($\overline{V}_2^{\infty}$) can be computed by the following relations [42] and the respective values are mentioned in Table 4.

$$\overline{V}_1^{\infty} = V_1^0 + \sum_{i=0}^{n} A_i(-1)^i \tag{14}$$

$$\overline{V}_2^{\infty} = V_2^0 + \sum_{i=0}^{n} A_i \tag{15}$$

The partial molar volumes of 2-methoxyaniline at infinite dilution ($x_1 = 0$) in N-alkylamides ($\overline{V}_1^{\infty}$) and the partial molar volumes of N-alkylamides at infinite dilution ($x_2 = 0$) in 2-methoxyaniline ($\overline{V}_2^{\infty}$) were given Table 4. The partial molar

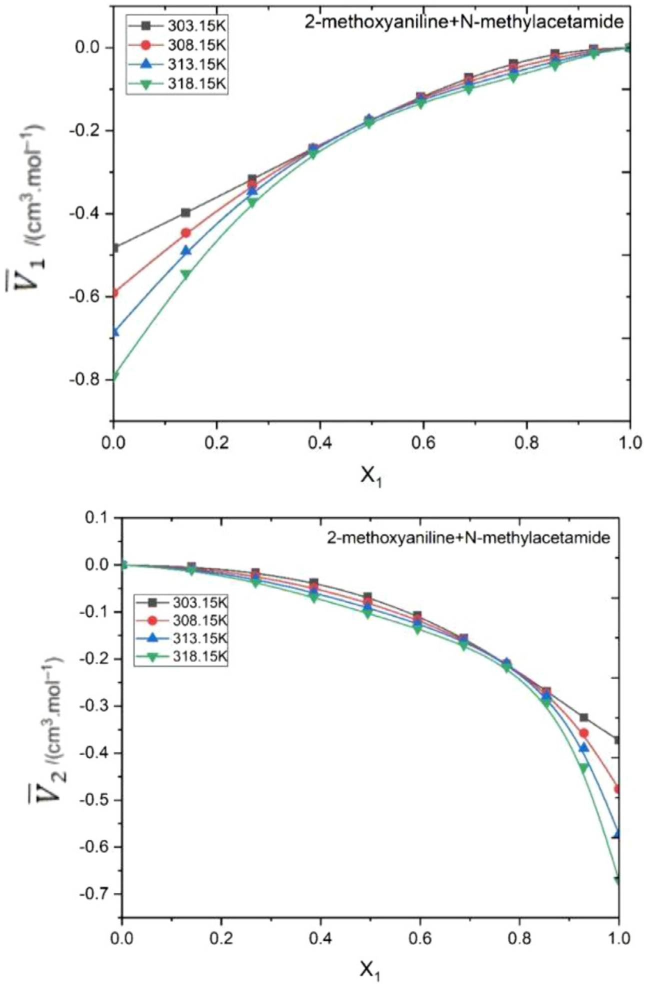


Fig. 5. Variation of the partial molar volume, $\overline{V}_1$,$\overline{V}_2$of (a) 2-methoxyaniline and (b) N-methylacetamide respectively, against mole fraction, x_1 of 2-methoxyaniline for the binary mixtures of at 303.15 K (■), 308.15 K (●), 313.15(▲), 318.15 K (??▼).

Table 4
Partial molar volumes of 2-methoxyaniline(1) at infinite dilution ($X_1 = 0$) in N-methylformamide,N-methylacetamide and N-ethylacetamide(2) ($\overline{V}_1^{\infty}$) and Partial molar volumes of N-methylformamide,N-methylacetamide and N-ethylacetamide(1) at infinite dilution ($X_2 = 0$) in 2-methoxyaniline(2) ($\overline{V}_2^{\infty}$).

System	T/K	V_1^0	$\overline{V}_1^{\infty}$	$\overline{V}_1^{E,\infty}$	V_2^0	$\overline{V}_2^{\infty}$	$\overline{V}_2^{E,\infty}$
$cm^3 mol^{-1}$							
2-methoxyaniline(1)+ N-methylformamide (2)	303.15	116.8437	116.560	−0.284	59.3782	58.361	−1.017
	308.15	117.3165	116.888	−0.429	59.6366	58.418	−1.218
	313.15	117.703	117.235	−0.468	59.8900	58.508	−1.382
	318.15	118.0275	117.465	−0.563	60.1401	58.574	−1.566
2-methoxyaniline (1)+ N-methylacetamide (2)	303.15	116.8437	116.2099	−0.6338	76.8300	76.1161	−0.713
	308.15	117.3165	116.2777	−1.0388	77.2703	76.1301	−1.140
	313.15	118.0275	116.6222	−1.4052	77.7619	76.261	−1.500
	318.15	118.0275	116.2124	−1.8150	77.76194	75.8477	−1.914
2-methoxyaniline (1)+ N-ethylacetamide (2)	303.15	116.8437	115.5438	−1.300	94.0211	93.0368	−0.984
	308.15	117.3165	115.7988	−1.518	94.4287	93.0475	−1.381
	313.15	118.0275	116.0131	−2.014	95.1819	93.2813	−1.901
	318.15	118.0275	115.5174	−2.510	95.1819	92.7759	−2.406

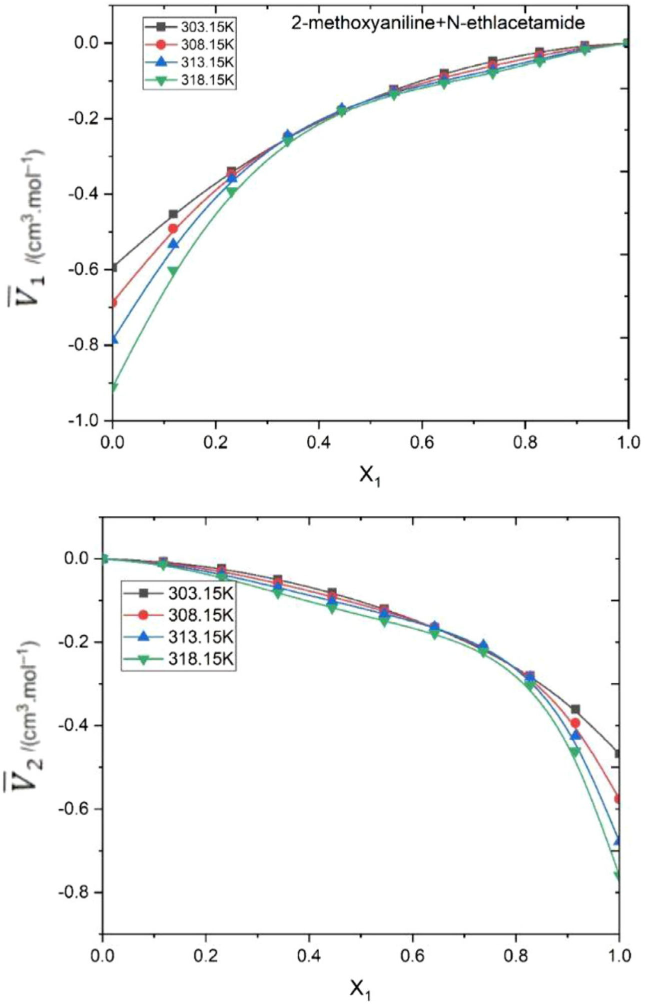


Fig. 6. Variation of the partial molar volume, $\overline{V}_1$,$\overline{V}_2$of (a) 2-methoxyaniline and (b) N-ethylacetamide respectively, against mole fraction, x_1 of 2-methoxyaniline for the binary mixtures of at 303.15 K (■), 308.15 K (●), 313.15(▲), 318.15 K (??▼).

volume values ($\overline{V}_1^{\infty}$ and $\overline{V}_2^{\infty}$) were algebraically lesser than the molar volume of pure components (V_1^0 and V_2^0). When the mixing process was over the molar volumes of two liquids in the mixture were relatively smaller when compared to molar volumes of pure liquids 1 and 2, which indicates a contraction in volume and better packing efficiency in the mixture than in the pure liquids [43].

The excess partial molar volumes at infinite dilution ($\overline{V}_1^{E,\infty}$and $\overline{V}_2^{E,\infty}$) were calculated from the Redlich–Kister coefficients by using the following equations:

$$\overline{V}_1^{E,\infty} = \overline{V}_1^{\infty} - V_1^0 = \sum_{i=0}^{n} A_i(-1)^i \tag{16}$$

$$\overline{V}_2^{E,\infty} = \overline{V}_2^{\infty} - V_2^0 = \sum_{i=0}^{n} A_i \tag{17}$$

The excess partial molar volume at infinite dilution ($\overline{V}_1^{E,\infty}$,$\overline{V}_2^{E,\infty}$) for the studied binary systems over the temperature range T= (303.15, 308.15, 313.15 and 318.15) K were reported in Table 4. The values of $\overline{V}_1^{E,\infty}$ and $\overline{V}_2^{E,\infty}$ for 2-methoxyaniline and N-alkylamides at different temperatures are observed to be negative. More negative values of 2-methoxyaniline + N-Ethylacetamide (NEA) suggest that intermolecular hydrogen bond formed between –NH_2 group of 2-methoxyaniline and –NH and C=O groups of N-Ethylacetamide were stronger than the other two isomers at infinite dilution. This also suggests that the hydrogen bonds between 2-methoxyaniline with N-Alkyl amides are not broken at infinite dilute regions. This also means that intermolecular hydrogen bonds between 2-methoxyaniline and N-alkylamides were not broken in dilute regions.

Table 5
Distances (A^0) and angles (^{0}) of the hydrogen bonds for all hydrogen bond associations at B3LYP/6-311++G (d, p).

Complexes	X–H···Y	R(X–H)	ΔR (X–H)	R(H···Y)	ΔR(H···Y)	R(X···Y)	(XHY)
COM 1	N2–H15···N1	1.01481	0.00611	2.26346	0.49840	3.26090	172.813
COM 2	N2–H7···O1	1.02852	0.02019	1.87179	0.84821	2.89730	174.549
	N1–H2···O2	1.02852	0.02019	1.87182	0.84818	2.89734	174.551
COM 3	N2–H5···O1	1.02698	0.0172	1.86707	0.85293	2.89399	179.209
	N1–H1···O2	1.02698	0.0172	1.86709	0.85291	2.89401	179.210
COM 4	N1–H1···O2	1.02775	0.02027	1.88639	0.83361	2.91353	177.562
	N2–H10···O1	1.02775	0.02027	1.88640	0.83360	2.91355	177.561
COM 5	N1–H5···O2	1.01541	0.00594	2.08521	0.63479	3.05026	157.949
COM 6	N2–H11···N1	1.01735	0.00902	2.16185	0.58815	3.17626	174.713
COM 7	N2–H11···O1	1.01566	0.00588	2.04340	0.67660	3.05025	167.453
COM 8	N1–H6···O2	1.01217	0.01239	2.08367	0.63633	3.09098	173.156
COM 9	N2–H10···N1	1.01459	0.00481	2.19828	0.55172	3.20802	173.224
COM 10	N2–H10···O1	1.01434	0.01307	1.98766	0.73234	2.98591	170.761
COM 11	N3–H4···O2	1.01813	0.00601	2.08495	0.66505	3.09501	171.196
COM 12	N1–H1···N2	1.01552	0.00804	2.21113	0.53887	3.21644	170.182
COM 13	N1–H2···O2	1.02055	0.01333	1.97610	0.7739	2.46000	172.772
	N2–H14···O1	1.01964	0.01216	2.00020	0.7498	2.99436	164.244

3.3. Experimental details of FT-IR studies

Experimental FTIR spectra of pure 2-methoxyaniline, N-alkylamides (N-methylformamide (NMF), N-methylacetamide (NMA) and N-ethylacetamide (NEA)), and the systems 2-methoxyaniline (1) + N-alkyl amides (2) with the equimolar binary mixture are as shown in Figs. S9–S11.

In the pure spectrum of N-methylformamide (NMF) the stretching frequency of –C=O group is 3291 cm^{-1} where as in the 2-methoxyaniline + N-methylformamide (Fig. S9) complex shift in the stretching vibrational frequency of –C=O group is 4 cm^{-1}. Where as in 2-methoxyaniline + N-methylacetamide (Fig. S10) shift in the stretching vibrational frequency of bonded –C=O is 8 cm^{-1}. Similarly the shift in the stretching frequencies of hydroxylgroups in 2-methoxyaniline + N-ethylacetamide (Fig. S11) complexes is 20 cm^{-1}. This indicates the formation of new hydrogen bonding interaction between 2-methoxyaniline and N-alkylamides. They also showed that in all the cases, the red-shifting of hydrogen bonds are observed.

3.4. Computational results

3.4.1. Geometrical structure

To analyse the inter molecular interactions, we found 13 possibilities of intermolecular hydrogen bond associations based on the nature and optimised structures of 2-Methoxyaniline and N-Alkylamides. All possible dimer structures are successfully optimized at the B3LYP/6-311++G (d, p) level. Harmonic vibrational frequencies and zero Point Energy Corrections (ZPE) are calculated for the optimized complexes and also for the non-bonded molecules. No imaginary frequencies are found in any of the fully optimized complexes.

The respective hydrogen bond computative framework and molecular graphs of the observed thirteen associations are mentioned in Table 5 and Figs. S5.1–S5.13 and the intermolecular hydrogen bonds have been formed in all these 13 complexes. And also it is observed that all these bonds have formed as conventional (N–H···O, O–H···O, N–H···N) hydrogen bonds.

In all of these complexes intermolecular hydrogen bonds are formed. It also observed that in all the 13 complexes, intermolecular hydrogen bonds are formed as conventional (N–H···O, O–H···O, N–H···N) hydrogen bonds. While the bond formation takes place as X–H···Y hydrogen bond, electrons transfer between X–H group and Y group which results in the compress of H···Y bond length. The compressed H···Y bond and the stronger X–H bond has the stronger interaction, and vice versa [44].

The value of shortest hydrogen bond length (H···Y) (1.97610 Å) and largest ΔR(X–H) are found in N1–H2···O2 (0.01333 Å) cross-associated hydrogen bond of **COM 13**. This shows that N–H…O hydrogen bond in **COM 13** (2-Methoxyaniline- N-Ethylacetamide) is the strongest hydrogen bond among all cross associations between 2-methoxyaniline and N-Alkyl amides complexes. The second shortest Hydrogen bond length is observed in **COM 11** as (1.98766 Å) and the largest as (0.01307 Å) of ΔR(X–H). This suggest that the second strongest Hydrogen bond is possible in **COM 11.** The hydrogen bond in **COM 11** involves in the second shortest hydrogen bond length (1.98766 Å) and the largest second largest value (0.01307 Å) of ΔR(X–H) should be the second strongest hydrogen bond present in 2-methoxyaniline and N-methylacetamide complex. Similarly the N–H···O hydrogen bond present in **COM 9** is the third strongest hydrogen bond with a hydrogen bond length (2.08367 Å) and largest value (0.01239 Å) of ΔR(X–H) present in N-Methylformamide. As shown in Table 5, all the values of hydrogen bonds are positive; these values indicate that they are all red shifting hydrogen bonds [45].

Table 6
Second order perturbation theory analysis of the Fock matrix in the NBO basis for the intermolecular interactions for Dimers.

Complex	Donor NBO(i)	Acceptor NBO(j)	E(2)(kcal/mol)	E(j)-E(i) (a.u)	F(i,J) (a.u)
COM 1	LP (1) N11	BD*(1)N29–H31	5.01	0.78	0.058
COM 2	LP (1) O3	BD*(1)N13–H14	5.32	1.11	0.069
	LP (2) O3	BD*(1)N13–H14	10.00	0.69	0.076
COM 3	LP (1) O2	BD*(1)N11–H12	4.69	1.11	0.065
	LP (1) O2	BD*(1)N11–H12	11.23	0.70	0.081
COM 4	LP(1)O17	BD*(1)N3–H4	4.73	1.10	0.065
	LP(2)O17	BD*(1)N3–H4	10.54	0.70	0.078
COM 5	LP(1)O21	BD*(1)N11–H12	2.89	1.17	0.052
	LP(2)O21	BD*(1)N11–H12	1.76	0.74	0.033
COM 6	LP(1)N11	BD*(1)N21–H22	2.46	0.95	0.044
COM 7	LP(1)O14	BD*(1)N22–H23	6.16	0.77	0.066
	LP(2)O14	BD*(1)N22–H23	2.10	0.77	0.037
COM 8	LP(1)O20	BD*(1)N11–H13	2.71	1.17	0.050
	LP(2)O20	BD*(1)N11–H13	3.87	0.74	0.049
COM 9	LP(1)N11	BD*(1)N21–H22	4.39	1.01	0.059
COM 10	LP(1)O14	BD*(1) N21–H22	6.47	0.77	0.065
	LP(2)O14	BD*(1) N21–H22	3.00	0.85	0.045
COM 11	LP(1)O29	BD*(1) N3–H4	0.50	0.93	0.019
	LP(2)O29	BD*(1) N3–H4	5.30	0.80	0.059
COM 12	LP(1)N26	BD*(1) N3–H4	3.47	0.77	0.065
COM 13	LP(1)O29	BD*(1) N3–H4	2.47	0.88	0.042
	LP(2)O29	BD*(1) N3–H4	7.41	0.85	0.065
	LP(1)O2	BD*(1) N26–H27	2.75	1.15	0.056
	LP(2)O2	BD*(1) N26–H27	4.98	0.72	0.055

In addition, a hydrogen bond parameter ΔR(H…Y) [46], is described as ΔR (H···Y) = R $(H)_{vwr}$+ $R(Y)_{vwr}$–R (H···Y) Where $R(Y)_{vwr}$ and $R(H)_{vwr}$ are the Vander Waals radii of H and Y acceptor atoms and these can be obtained by Bondi [47] respectively, R(X···Y) is the distance between the hydrogen-donor and hydrogen- acceptor. Table 5 concludes that there is possibility for the largest value of ΔR (H···Y) is 0.7739 of the intermolecular NH···O hydrogen bond in the cross association complex **COM 13** which represents the strongest bond. This shows the strongest interaction possibility between in 2-methoxyaniline and N-Ethylacetamide cross-associated dimer (**COM13**) by -NH2 group of 2-methoxyaniline and -C=O groups of N-Ethylacetamide. This shows that the 2-methoxyaniline + N-Ethylacetamide cross-associated dimer (**COM13**) and its strong interaction by hydrogen bonding between $–NH_2$ group of 2-methoxyaniline and -C=O groups of N-Ethylacetamide.

3.4.2. Natural bonding orbital (NBO) studies

The interaction among occupied Lewis type (donor) NBO's and unoccupied non-Lewis type (acceptor) NBO's can be explained in terms of hyper conjugative electron movement process from the donor orbital to acceptor orbital. The second-order perturbated stabilization energy for the interaction between proton donor and acceptors relevant to the hydrogen bond formation between the cross associations of 2-methoxyaniline with N-alkylamides from NBO analysis at B3LYP/6-311G++(d, p) level of theory are mentioned in Table 6.

The Natural Bonding Orbital data is reliable method for the confirmation of H-bonds which inter relates the changes in bond length between component molecules. This also provides relevant statistics about the deviations in charge densities between proton donor and proton acceptors and also in the bonding and anti-bonding orbitals. For each donor and acceptor, the stabilization energy E(2) associated with hydrogen bonding between sites *i* and j are given below

$$E(2) = q_i \frac{F^2(i,j)}{\varepsilon_i - \varepsilon_j} \tag{18}$$

where q_i is the *i*th donor orbital frequency, ε_i and ε_j are the diagonal elements in connection with NBO Fock matrix.

The computed and compared stabilization energies between lone pair of electrons (n) of proton acceptor and anti bonding orbitals (σ^*) of the proton donor for various cross associated hydrogen bonded molecules are mentioned in Table 6

The stabilization energy between lone pair of electrons (n) of the proton acceptor and anti-bonding orbitals (σ^*) of the proton donor were compared for various intermolecular hydrogen bonding complexes.

From Table 6 it is concluded that in **COM1** (self associated 2-Methoxyaniline) the amine group "N" offers its lone pair to σ (N–H)* which stabilizes the system with the interactive energy 5.01 kcal mol^{-1}. But in the self association of all N-Alkyl amides(NMF,NMA,NEA) in **COM2, COM3, COM4** the bond formation is basically due to the oxygen atom offers their p electrons to the σ (N–H)* which were stabilized with interaction energies lies in between 4.69 and 11.23 kcal mol^{-1}. The orbital interactions for cross associated molecules (**COM5, COM6, COM7**) have second-order perturbation stabilization energy E (2) range of 1.76–6.16 kcal mol^{-1} with the orbital interactions LP (O) → σ (N–H)*, LP (N) → σ (N–H)*. Whereas the orbital interactions LP (O) → σ (N–H)*, LP (N) → σ (N–H)* in 2-methoxyaniline and N-methylacetamide (NMA) complexes (**COM8 – COM10**) having stabilization energy E (2) in range of 2.71–6.47 kcal mol^{-1}. Similarly the orbital interactions in

Table 7
Interaction energy corrected with BSSE (ΔE_{cp}. kJ mol^{-1}) for all dimmers at B3LYP/6-311++G (d,p) level.

Complexes	X–H···Y	ΔE	BSSE	ΔE_{CP}
COM1	N2–H15···N1	−14.3624	0.36	−12.4947
COM 2	N2–H7···O1	−48.8373	1.87	−14.8183
COM 3	N2–H5···O1	−57.3814	1. 97	−14.9573
COM 4	N1–H1···O2	−32.3421	1.41	−15.8058
COM 5	N1–H5···O2	−11.2142	0.86	−10.3542
COM 6	N2–H11···N1	−20.3526	1.26	−12.6847
COM 7	N2–H11···O1	−13.9447	1.66	−12.2847
COM 8	N1–H6···O2	−18.7641	0.88	−17.8841
COM 9	N2–H10···N1	−19.3644	1.46	−17.9044
COM 10	N2–H10···O1	−29.3644	1.66	−27.7044
COM 11	N3–H4···O2	−15.8750	0.91	−14.9650
COM 12	N1–H1···N2	−17.9993	0.94	−17.0593
COM 13	N1–H2···O2	−31.9192	1.24	−30.6792

2-methoxyaniline and N-ethylacetamide (NEA) complexes (**COM11–COM13**) have second-order perturbation stabilization energies E(2) are 0.50–7.41 kcal mol^{-1}. With this observation it suggests that the cross associations of H–N···O=C combinations are stronger than N–H···N combinations in 2-Methoxyanelene with Isomeric N-Alkylamides.

From Table 6 in the self-associated 2-methoxyaniline complex (**COM1**) the major interaction is that N (amine group) offers its lone pair to the σ (N–H)* antibond; this interaction stabilizes the system with energy 5.01 kcal mol^{-1}. Where as in the N-methylformamide (NMF), N-methylacetamide (NMA) and N-ethylacetamide (NEA) self associated complexes (**COM 2–COM 4**) the major interaction are the oxygen atom offers their p electrons to the σ (N–H)* and these interaction stabilizes the systems with energies lies between 4.73 and 10.54 kcal mol^{-1}. The orbital interactions LP (O)→ σ(N–H)*, LP(N)→ σ(N–H)* in 2-methoxyaniline and N-methylformamide (NMF) complexes (**COM5–COM7**) have second-order perturbation stabilization energy E (2) range of 1.76–6.16 kcal mol^{-1}. Whereas the orbital interactions LP (O)→ σ (N–H)*, LP (N)→ σ (N–H)* in 2-methoxyaniline and N-methylacetamide (NMA) complexes (**COM8–COM10**) having stabilization energy E (2) in range of 2.71–6.47 kcal mol^{-1}. Similarly the orbital interactions in 2-methoxyaniline and N-ethylacetamide (NEA) complexes (**COM11–COM13**) have second-order perturbation stabilization energies E(2) are 0.50–7.41 kcal mol^{-1}. Hence it is observed that in the cross-associations H–N···O=C interactions stronger than N–H···N interactions in 2-methoxyaniline and isomeric N-alkylamides mixtures.

3.4.3. Interactive energy

To analyze the stable geometrical optimized hydrogen bonded complexes, precise interaction energies are always required. The interaction energy of two hydrogen bonded monomers (X, Y) was evaluated by using the following formula:

$$\Delta E_{\text{int}} = E(XY) - E(X) - E(Y) \tag{8}$$

where $E(XY)$ is the total energy of XY pair and $E(X)$, $E(Y)$ are energies of monomeric moieties. The calculated interaction energies contain overestimated values that can cause an error called basis set superposition error (BSSE) [48] and this occurs due to the overlapping of basis set function of monomers.The counterpoise-corrected method proposed by Boys-Bernardi is used to rectify BSSE error. The counterpoise-corrected interaction energies, ΔE^{cp} for all the dimers were computed at $\mathrm{B3LYP/6-311G++(d,p)}$ level and the values are summarized in Table 7.

The calculated interaction energies in Table 7 show that among all the 13 complexes the main interaction (H–bond) is happening between 2-methoxyaniline and N-alkylamides mixtures (**COM5–COM7**)· In 2-methoxyaniline with N-methylformamide 1:1 complex (**COM 5–COM 7**) the interactive energies are in the range of −10.3542 kJ mol^{-1} to −12.2847 kJ mol^{-1}. In the case of 2-methoxyaniline and N-methylacetamide (NMA) 1:1 complex (**COM 8–COM 10**) the interaction energies are in the range of −17.8841 kJ mol^{-1} to −27.7044 kJ mol^{-1}. Finally In the case of 2-methoxyaniline and N-Ethylacetamide 1:1 complex (**COM 11–COM 13**) the interactive energies are in the range of −14.9650 kJ.mol^{-1} and −30.6792 kJ mol^{-1}. It is found that **COM 13(**N–H···O**)** has noticeable interactive energy (−30.6792 kJ mol^{-1}) when compared to all self and cross-associated due to the presence of the shorter N–H···O hydrogen bond (1.97610 Å). i.e. The computational results of the interaction energies also supports the strong intermolecular cross-association in **COM 13**. And also the computational calculations of the interaction energies, stabilization energies and geometries shows that the intermolecular cross-associated combinations are much stronger than the intermolecular self-associated combinations between the monomers.

3.4.4. Quantum theory of atoms in molecules (QTAIM) studies

QTAIM analysis was used to investigate the electron charge densities of hydrogen bond interactions in 2-methoxyaniline and N-alkylamides complexes at $\mathrm{B3LYP/6-311++G(d,p)}$ level of theory. .In this analysis a chemical bond is characterized by a point called bonding critical point (BCP) with a (3,−1) topology between the atoms connected by a hydrogen bond.

The values of electron density ($\rho(r)$) and Laplacian of the electron density ($\nabla^2\rho(r)$) at BCP of all the dimers are summarized in Table S4. Koch and Popelier [49] proposed the following three local topological properties to detect and characterize the hydrogen bond.

(1) Existence of BCP between proton (H) and acceptor (Y) contact is the conformation of formation of H–bond
(2) At BCP of the H···Y the electron density ($\rho(r)$) lies in the range of 0.002–0.040 a.u
(3) Laplacian electronic density ($\nabla^2\rho(r)$) is positive and lies in the range 0.015–0.15 a.u

In the current work, the values of $\rho(r)$ and $\nabla^2\rho(r)$ are obtained at BCP between hydrogen and the other atoms and they varies from 0.016328 to 0.030776 a.u and 0.047733 to 0.10298 a.u. Maximum electron density in the self-association is 0.04702 a.u and in cross-association is 0.03389 a.u shows strong hydrogen bonds are observed for O–H···N interaction with high stability.

Furthermore, the values of Laplacian charge density all possible combinations are found to be positive. These results support the closed shell [50] interactions of hydrogen bonds in the chosen complexes. The hydrogen bond length and electron density are inversely proportional to each other which shows that the increase in the hydrogen bond length leads to decrease in the electron charge density. As there is a increase in the distance of hydrogen bond length, this leads to reduced orbital overlapping and electron density decreases along the bond length. It is also noticed that the Laplacian electron density and hydrogen bond lengths are also inversely related to each other.

According to virial theorem the Laplacian of the electron density $\nabla^2\ \rho(r)$ is directly connected with the local kinetic energy density (K_{BCP}) and potential energy density (V_{BCP}) in every point of the system.

$$\frac{1}{4}\nabla^2\rho(r)_{BCP} = 2K_{BCP} + V_{BCP} \tag{8}$$

$$H_{BCP} = K_{BCP} + V_{BCP} \tag{9}$$

where H_{BCP} Represents the electronic energy density. The sign of the H_{BCP} will depend on the local kinetic energy density (K_{BCP}) and potential energy density (V_{BCP}).

According to Grabowski et al. [51] Laplacian of the electron density $\nabla^2\ \rho(r)$ and total electronic energy density H_{BCP} follows the below conditions at BCP of hydrogen bond:

(1) For weak and medium hydrogen bonds both $\nabla^2\ \rho(r)$ and $H_{BCP} > 0$
(2) For strong hydrogen bonds $\nabla^2\ \rho(r) > 0$ and $H_{CP}\ ^{<0}$
(3) For very strong hydrogen bonds both $\nabla^2\ \rho(r)$ and $H_{BCP}\ ^{<0}$

From Table S4 both $\nabla^2\ \rho(r)$ and HBCP and weak hydrogen bonds, reveals the information that only electrostatic interactions are present in all the complexes [52].

3.4.5. NCI analysis

We can use the Reduced Density gradient (RDG) curves which are suggested by Yang and Co-worker [54], that supports the Hydrogen bond interaction between selected cross associated complexes (**COM13, COM10**, and **COM8**) and are presented in Figs. 7–9.

Further, the strength of the hydrogen bond interaction between selected dimers (**COM13, COM10**, and **COM8**) can effectively exhibited by reduced density gradient (RDG) curves proposed by Yang and co-worker [53] are shown in Figs. 6–8. The decreased density gradient versus sign $(\lambda_2)\rho$ along with the reduced density gradient isosurfaces with the value of $s = 0.50$ a.u. of the 3 associations are studied by the typical characteristic of sharp spike(s) which belongs to weak intermolecular interactions in the low-density region of component molecules. There are different cross-associated dimers are possible in which N–H···O hydrogen bonds shows a stronger interaction when compared to other bond interactions.

In the case of **COM13, COM10** and **COM8** dimers, the two low-reduced gradient spikes at low density now lies at negative values of −0.02458 a.u and −0.01822 a.u. respectively, indicates a stabilizing bond interaction. In accordance with the note of the sharp spike associations **COM13, COM10** and **COM8** contain a strong H-bond interaction at $\sin(\lambda_2)\rho = -0.02458$ a.u (N1–H2···O2 (**COM13**)), −0.019709 a.u (N2–H10···O1 (**COM10**)) and −0.01822 a.u (N1–H6···O2 (**COM8**)), respectively. So the stability order of the dimers is **COM13**>**COM10**>**COM8** that coincides the interaction energy calculation with the help of compared result.

Along with this, the RDG isosurfaces shows a productive visualisation of NCI analysis in the broad regions in real space. For three associations which are employed, it is possible to obtain the strong H–bonds, weaker H–bonds and weaker repulsive interactions according to the gradient isosurfaces. The more blue colour region represents the stronger interaction and can be indentified in the different regions from the colour-filled RDG isosurface. From the colour-filled RDG isosurface, we can identify different type regions by colour the more blue means the stronger interactive interaction. In this the light blue region shows us that there is a hydrogen bond formation and is in elliptical slab between oxygen and hydrogen shows light blue colour, so we can conclude that there is a hydrogen bond.

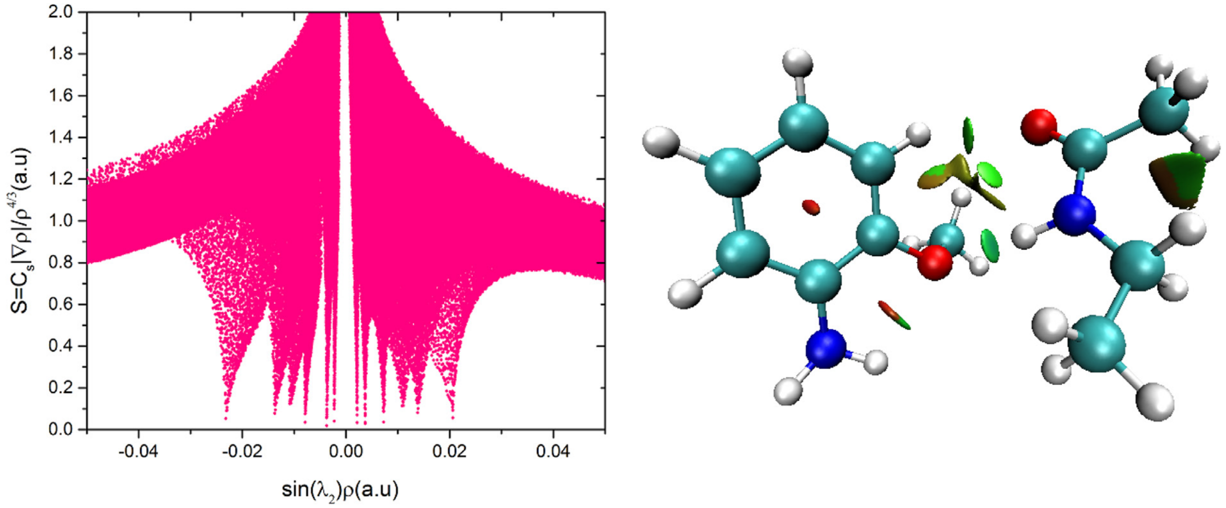


Fig. 7. Plots of the reduced density gradient versus the electron density multiplied by the sign of the second hessian eigenvalues and gradient isosurfaces with $s = 0.5a.u$ for the for the hydrogen bond association2-methoxyaniline +N-methylformamide.

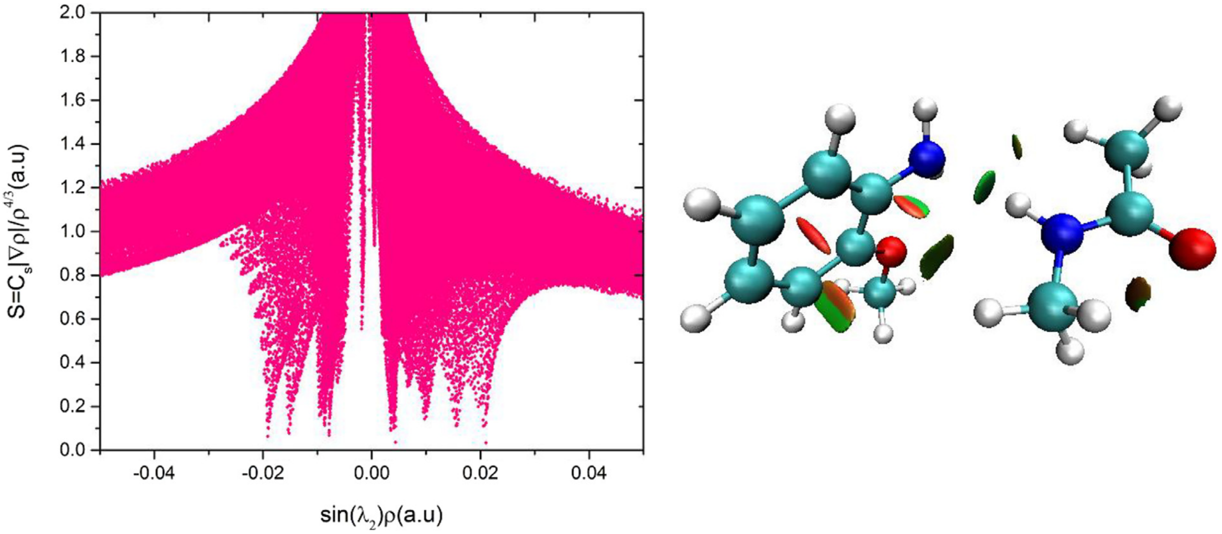


Fig. 8. Plots of the reduced density gradient versus the electron density multiplied by the sign of the second hessian eigenvalues and gradient isosurfaces with $s = 0.5a.u$ for the for the hydrogen bond association2-methoxyaniline+ N-methylacetamide.

4. Site–Site intermolecular radial distribution function (RDF)

Radial distribution functions (RDFs) is the fundamental property that characterize the averaged spatial structure and the local molecular distribution. The study on the RDFs directly provides the microscopic structure information of the system. Radial distribution functions (RDFs) are useful in studying intermolecular structure and interactions in bulk systems [54,55]. Site-site radial distribution functions of 2-methoxyaniline - N-alkylamides at equi-molefraction were obtained through molecular dynamic simulations.

RDF's of pure 2-methoxyaniline and N-alkylamides reveals the presence of N1···H5 hydrogen bond in pure 2-chloroaniline which is shown in Fig.S6. For N1···H5 pair, it has two peaks in which the first peak is a sharp one and it is located at 2.213 Å, and the second one is located at a distance of 3.386 Å. These values are agrees with the intermolecular distances of the cross-associated dimer of O–H...N and it is calculated at $B3LP/6-311++G(d,P)$ which is shown in Fig. S5.1. The location of the first peak is a bit lesser than the total value of the Vander Waals radii of hydrogen and nitrogen atoms [$R_N \cdots H_N \leq 2.52$ Å (threshold distance)] which is an indication of an intermolecular hydrogen bond between H and N atoms of component molecules. The second peak is a broad one and located at 3.386 Å that does not refer to an H-bond and this peak might be a combination of 3 different intermolecular interactions. The very first one is related to the interaction of N atom to the central molecule with the second H_N atoms of other molecules and are located in the nearest layer, whereas

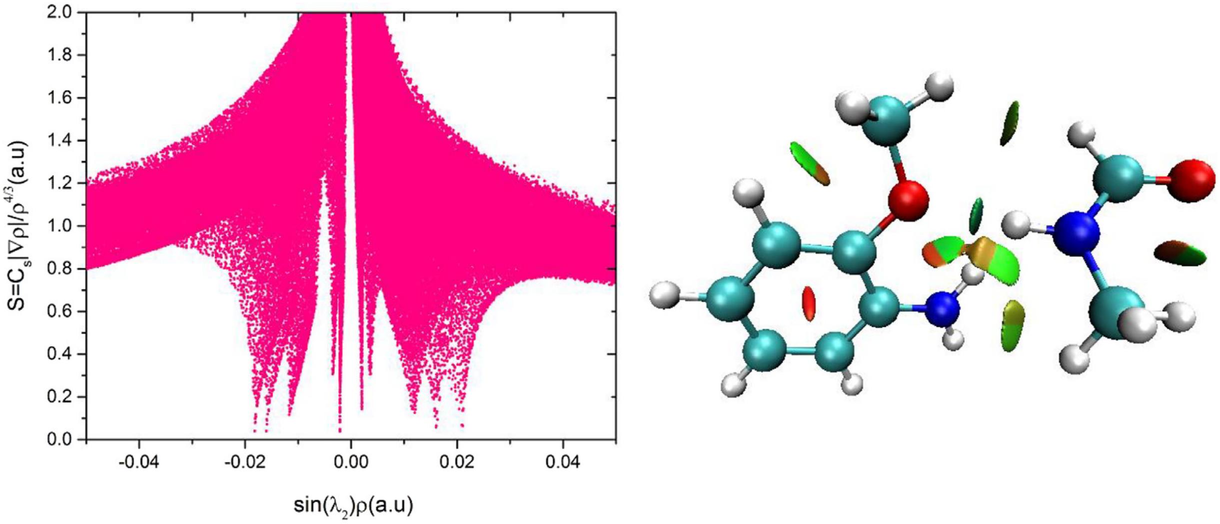


Fig. 9. Plots of the reduced density gradient versus the electron density multiplied by the sign of the second hessian eigenvalues and gradient isosurfaces with $s = 0.5a.u$ for the for the hydrogen bond association2-methoxyaniline+ N-ethylacetamide.

second and third interactions are related to the interaction of 2 H_N of the central molecule with N of the other molecules which are located in the closest shell.

For N-Alkylamides NMF, NMA and NEA are computed with RDFs of N–H···O=C hydrogen bond interactions have been shown in Fig. S7. The mean value of N–H···O=C contacts and it can be accredited to a single NMF, NMA and NEA molecules, these can be estimated by calculating the $g(r)$ RDF of the pairs which are gained by an amide hydrogen atom (acting as donor) & a carbonyl oxygen atom (acceptor). In Fig. S7 the $g_{(OH)}$ function executes a well noticeable at initial peak for H···O site occurs at $r_{(OH)} = 1.9283$ Å for NMF, $r_{(OH)} = 1.9366$ Å for NMA and $r_{(OH)} = 1.875$ Å for NEA. This is an indication of strong hydrogen bonding between the adjacent self associated molecules of carbonyl's oxygen and the amide hydrogen of neighbor self-associated molecules. A close observation of first peak values in Fig. S7 reveals that H···O interactions are strong in N-Ethylacetamide (NEA) molecules compared to N-Methylformamide (NMF), N-Methylacetamide (NMA).

The RDF of carbonyl oxygen of N-alkylamides surrounded by H atoms of 2-methoxyaniline at the equi-mole fractional values at 303.15 K are presented by Fig. S8. The position of first and second peaks for H···O site occurs at $r_1 = 1.955$ Å, $r_2 = 3.375$ Å for (MOA+NMF), $r_1 = 1.925$ Å, $r_2 = 3.335$ Å for(MOA+NMA) and $r_1 = 1.8933$ A^0, $r_2 = 3.323$ Å for(MOA+NEA). Intermolecular interactions are revealed by all these peaks reveal. Due to steric hindrance, RDFs of O … H_N peak is sharper. In all the three mixtures location of the first peaks are in the range 1.8933–1.955 Å shows a H-bond as this indicates distance is lesser than the total sum of the vander Waals radii of H and O atoms [$R_O \cdots H_N \leq 2.48$ Å (threshold distance)].The second broad peak located in the range 3.323–3.375 Å does not refer to the H–bond and it can be related to O of the molecule which is at center with H atom of the other molecules that are presented in the nearest layer.

So, a close observation of first and second peaks values in Fig. S8 reveals that O…H–N interactions are strong in MOA+NEA binary mixture compared to MOA+NMA and MOA+NMF binary mixtures. These MD outcomes are good in corresponds with the practical and DFT calculations.

Conclusion

Intermolecular interactions between the self and cross-associated structures of 2-methoxyaniline - N-alkylamides complexes were investigated in experimental and theoretical methods. Excess molar volume and isentropic compressibility retrieved from the density and speed of sound at temperatures from 303.15 K to 318.15 K were found to be negative at all compositions. The predominant contribution to the excess properties is due to volume contraction, interstitial accommodation of unlike molecules in mixtures. The interaction observed is stronger in case of 2-methoxyaniline and N-ethylacetamide (NEA) mixture than 2-methoxyaniline and N-methylformamide (NMF), N-methylacetamide (NMA) mixtures. The characteristics of these complexes are essentially controlled by intermolecular hydrogen bonds .The study of optimized geometries, interaction energies, QTAIM and NBO reveals that, COM13(2-methoxyaniline and N-ethylacetamide) with N–H···O hydrogen bond is the most stable complex among the thirteen self and cross associated dimers. The molecular dynamics simulations in liquid phase using the RDF revels a good agreement with their values retrieved form quantum mechanical simulations and experimental results.

Acknowledgements

The authors are thankful to Anton Paar company pvt. ltd., Hyderabad for providing the research facilities and Department of physics, Vignan Institute of Technology and Science for their encouragement towards the research work. They are also very thankful to Bioinformatics Resources and Applications Facility (BRAF) C-DAC, Pune, India for providing the computational work.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cdc.2019.100241.

References

[1] S. Scheiner (Ed.), Molecular Interactions: From Van Der Waals to Strongly Bound Complexes, Wiley, Chichester ; New York, 1997.

[2] G.A. Jeffrey, W. Saenger, Hydrogen Bonding in Biological Structures, Study ed., Springer-Verlag, Berlin ; New York, 1994.

[3] P. Hobza, Z. Havlas, Blue-shifting hydrogen bonds, Chem. Rev. 100 (2000) 4253–4264, doi:10.1021/cr990050q.

[4] L. Sobczyk, S.J. Grabowski, T.M. Krygowski, Interrelation between H-bond and Pi-electron delocalization, Chem. Rev. 105 (2005) 3513–3560, doi:10.1021/cr030083c.

[5] J. Schwöbel, R.-U. Ebert, R. Kühne, G. Schüürmann, Modeling the H bond donor strength of -OH, -NH, and -CH sites by local molecular parameters, J. Comput. Chem. 30 (2009) 1454–1464, doi:10.1002/jcc.21166.

[6] K.V. Tretiakov, K.J.M. Bishop, B. Kowalczyk, A. Jaiswal, M.A. Poggi, B.A. Grzybowski, Mechanism of the cooperative adsorption of oppositely charged nanoparticles †, J. Phys. Chem. A 113 (2009) 3799–3803, doi:10.1021/jp809447m.

[7] H. Qian, P.-Z. Shi, Fluctuating enzyme and its biological functions: positive cooperativity without multiple states, J. Phys. Chem. B 113 (2009) 2225–2230, doi:10.1021/jp810657j.

[8] J. Dudowicz, J.F. Douglas, K.F. Freed, Self-assembly by mutual association: basic thermodynamic properties †, J. Phys. Chem. B 112 (2008) 16193–16204, doi:10.1021/jp806859w.

[9] Q. Li, X. An, F. Luan, W. Li, B. Gong, J. Cheng, J. Sun, Cooperativity between two types of hydrogen bond in H3C–HCN–HCN and H3C–HNC–HNC complexes, J. Chem. Phys. 128 (2008) 154102, doi:10.1063/1.2898499.

[10] P.D. Vaz, P.J.A. Ribeiro-Claro, $C \equiv H \cdot s$ O hydrogen bonds in small ring carbonyl compounds: vibrational spectroscopy and ab initio calculations, Struct. Chem. 16 (2005) 287–293, doi:10.1007/s11224-005-4460-y.

[11] M.K. Patwari, R.K. Bachu, S. Boodida, S. Nallani, Densities, viscosities, and speeds of sound of binary liquid mixtures of sulfolane with ethyl acetate, n -propyl acetate, and n -butyl acetate at temperature of (303.15, 308.15, and 313.15) K, J. Chem. Eng. Data 54 (2009) 1069–1072, doi:10.1021/je800653d.

[12] S. Scheiner, Hydrogen Bonding: A Theoretical Perspective, Oxford University Press, New York, 1997.

[13] D. Hadži, Theoretical Treatments of Hydrogen Bonding, John Wiley Sons, Chichester ; New York, 1997.

[14] O.V. Shishkin, I.S. Konovalova, L. Gorb, J. Leszczynski, Novel type of mixed O–H···N/O–H···π hydrogen bonds: monohydrate of pyridine, Struct. Chem. 20 (2009) 37–41, doi:10.1007/s11224-009-9412-5.

[15] A. Zabardasti, A. Kakanejadifard, A.-A. Hoseini, M. Solimannejad, Competition between hydrogen and dihydrogen bonding: interaction of B_2H_6 with CH_3OH and $CHnX_3-nOH$ derivatives, Dalton Trans. 39 (2010) 5918, doi:10.1039/b925091c.

[16] H. Roohi, A.-R. Nowroozi, E. Anjomshoa, H-bonded complexes of uracil with parent nitrosamine: a quantum chemical study, Comput. Theor. Chem. 965 (2011) 211–220, doi:10.1016/j.comptc.2011.01.048.

[17] S.J. Grabowski, Theoretical studies of strong hydrogen bonds, Annu. Rep. Sect. “C” 102 (2006) 131–165, doi:10.1039/b417200k.

[18] L. Sacconi, P. Paoletti, M. Ciampolini, Thermochemical studies. I. Thermodynamic functions of solutions of pyridine bases in water [1], J. Am. Chem. Soc. 82 (1960) 3828–3831, doi:10.1021/ja01500a008.

[19] B. Mukesh, M. Gowri Sankar, M. Chandra Shekar, T. Srikanth, Effect of placement of hydroxyl groups in isomeric butanol on the behavior of thermophysical and spectroscopic properties of 2-methoxyaniline, J. Solut. Chem. 44 (2015) 2267–2296, doi:10.1007/s10953-015-0406-1.

[20] F. Palombo, M. Paolantoni, P. Sassi, A. Morresi, R.S. Cataliotti, Spectroscopic studies of the “free” OH stretching bands in liquid alcohols, J. Mol. Liq. 125 (2006) 139–146, doi:10.1016/j.molliq.2005.11.006.

[21] B. Jović, A. Nikolić, B. Kordić, Densitometric and spectroscopic investigation of interactions of selected N-substituted amides and acetonitrile, J. Mol. Liq. 191 (2014) 10–15, doi:10.1016/j.molliq.2013.11.016.

[22] A. Nikolić, L. Gobor, V. Krstić, S. Petrović, Excess molar volumes of N-methylacetamide+tetrahydrofuran, +2-butanone, +ethylacetate at the temperatures between 303.15 K and 318.15 K, J. Mol. Liq. 121 (2005) 139–142, doi:10.1016/j.molliq.2004.12.001.

[23] P.J. Victor, D.K. Hazra, Excess molar volumes, viscosity deviations, and isentropic compressibility changes in binary mixtures of N -methylacetamide + 2-methoxyethanol and N -methylacetamide + water at (308.15, 313.15, and 318.15) K, J. Chem. Eng. Data 47 (2002) 79–82, doi:10.1021/je0101451.

[24] S. Boodida, R.K. Bachu, M.K. Patwari, S. Nallani, Volumetric and transport properties of binary liquid mixtures of N-methylacetamide with lactones at temperatures (303.15–318.15)K, J. Chem. Thermodyn. 40 (2008) 1422–1427, doi:10.1016/j.jct.2008.05.004.

[25] R. Balaji, M. Gowri Sankar, M. Chandra Sekhar, M. Chandra Shekar, FT-IR Spectroscopic study of excess thermodynamic properties of liquid mixtures containing N-methylformamide with 2-alkoxyethanols at various temperatures, J. Mol. Liq. 216 (2016) 330–341, doi:10.1016/j.molliq.2015.12.051.

[26] A.D. Becke, Density-functional exchange-energy approximation with correct asymptotic behavior, Phys. Rev. A 38 (1988) 3098–3100, doi:10.1103/PhysRevA.38.3098.

[27] C. Lee, W. Yang, R.G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, Phys. Rev. B 37 (1988) 785–789, doi:10.1103/PhysRevB.37.785.

[28] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox. Gaussian 09. Revision C01. Wallingford: Gaussian Inc.; 2010.

[29] T. Lu, Multiwfn Program, Version 2.3. <http://multiwfn.codeplex.com>.

[30] S. Pronk, S. Páll, R. Schulz, P. Larsson, P. Bjelkmar, R. Apostolov, M.R. Shirts, J.C. Smith, P.M. Kasson, D. van der Spoel, B. Hess, E. Lindahl, GROMACS 4.5: a high-throughput and highly parallel open source molecular simulation toolkit, Bioinformatics 29 (2013) 845–854, doi:10.1093/bioinformatics/btt055.

[31] W.L. Jorgensen, D.S. Maxwell, J. Tirado-Rives, Development and testing of the OPLS all-atom force field on conformational energetics and properties of organic liquids, J. Am. Chem. Soc. 118 (1996) 11225–11236, doi:10.1021/ja9621760.

[32] B. Hess, H. Bekker, H.J.C. Berendsen, J.G.E.M. Fraaije, LINCS: a linear constraint solver for molecular simulations, J. Comput. Chem. 18 (1997) 1463–1472 (199709)18:12<1463::AID-JCC4>3.0.CO;2-H, doi:10.1002/(SICI)1096-987X.

[33] O. Kiyohara, G.C. Benson, Ultrasonic speeds and isentropic compressibilities of n-alkanol + n-heptane mixtures at 298.15 K, J. Chem. Thermodyn. 11 (1979) 861–873, doi:10.1016/0021-9614(79)90067-3.

[34] G. Douhéreta, C. Salgado, M.I. Davis, J. Loya, Ultrasonic speeds and isentropic functions of 2-(2-alkoxyethoxy)ethanol + water at 298.15 K, Thermochim. Acta 207 (1992) 313–328, doi:10.1016/0040-6031(92)80145-M.

[35] G. Douhéret, C. Moreau, A. Viallard, Excess thermodynamic quantities in binary systems of non electrolytes, Fluid Phase Equilib. 22 (1985) 277–287, doi:10.1016/0378-3812(85)87027-8.

[36] G. Douheret, M.B. Holczer, R. Peyrelier, M.I. Davis, Speeds of sound and excess volumetric properties of mixtures of water with 2-propanol and with ethylene glycol monoisopropyl ether at 298.15 K, J. Chem. Eng. Data 39 (1994) 868–872, doi:10.1021/je00016a053.

[37] G. Douhéret, A. Pal, M.I. Davis, Ultrasonic speeds and isentropic functions of (a 2-alkoxyethanol + water) at 298.15 K, J. Chem. Thermodyn. 22 (1990) 99–108, doi:10.1016/0021-9614(90)90036-P.

[38] D.N. Rihani, L.K. Doraiswamy, Estimation of heat capacity of organic compounds from group contributions, Ind. Eng. Chem. Fundam. 4 (1965) 17–21, doi:10.1021/i160013a003.

[39] O. Redlich, A.T. Kister, Algebraic representation of thermodynamic properties and the classification of solutions, Ind. Eng. Chem. 40 (1948) 345–348.

[40] S.E. Wood, R. Battino, Thermodynamics of Chemical Systems, Cambridge University Press, Cambridge [England] ; New York, 1990.

[41] A. Cipiciani, G. Onori, G. Savelli, Structural properties of water-ethanol mixtures: a correlation with the formation of micellar aggregates, Chem. Phys. Lett. 143 (1988) 505–509, doi:10.1016/0009-2614(88)87404-9.

[42] A. Pal, A. Kumar, H. Kumar, Volumetric properties of binary mixtures of some *n*-alkoxyethanols with 2-pyrrolidinone and N-methyl-2-pyrrolidinone at 298.15 K, Indian J. Chem. 41 (2002) 2017–2024.

[43] I.R. Radovic, M.L. Kijevcanin, A.Z. Tasic, B.D. Djordjevic, S.P. Serbanovic, Densities and excess molar volumes of alcohol + cyclohexylamine mixtures, J. Serb. Chem. Soc. 74 (2009) 1303–1318.

[44] M. Karthika, L. Senthilkumar, R. Kanakaraju, Hydrogen-bond interactions in hydrated 6-selenoguanine tautomers: a theoretical study, Struct. Chem. 25 (2014) 197–213, doi:10.1007/s11224-013-0239-8.

[45] A.J.L. Jesus, M.T.S. Rosado, I. Reva, R. Fausto, M.E.S. Eusébio, J.S. Redinha, Structure of isolated 1,4-butanediol: combination of MP2 calculations, NBO Analysis, and matrix-isolation infrared spectroscopy, J. Phys. Chem. A 112 (2008) 4669–4678, doi:10.1021/jp7116196.

[46] R.F.W. Bader, H. Essén, The characterization of atomic interactions, J. Chem. Phys. 80 (1984) 1943–1960, doi:10.1063/1.446956.

[47] A. Bondi, Van der Waals volumes and radii, J. Phys. Chem. 68 (1964) 441–451, doi:10.1021/j100785a001.

[48] M. Chandra Sekhar, A. Venkatesulu, M. Gowrisankar, T. Srinivasa Krishna, Thermodynamic study of interactions in binary liquid mixtures of 2-Chloroaniline with some carboxylic acids, Phys. Chem. Liq. 55 (2017) 196–217, doi:10.1080/00319104.2016.1183201.

[49] U. Koch, P.L.A. Popelier, Characterization of C-H-O hydrogen bonds on the basis of the charge density, J. Phys. Chem. 99 (1995) 9747–9754, doi:10.1021/j100024a016.

[50] R.F.W. Bader, H. Essén, The characterization of atomic interactions, J. Chem. Phys. 80 (1984) 1943–1960, doi:10.1063/1.446956.

[51] S.J. Grabowski, W.A. Sokalski, J. Leszczynski, Nature of $X{-}H^{+\delta}\cdots{}^{-\delta}$ H−Y dihydrogen bonds and $X{-}H{\cdots}\sigma$ interactions, J. Phys. Chem. A 108 (2004) 5823–5830, doi:10.1021/jp049874o.

[52] D. Cremer, E. Kraka, Chemical bonds without bonding electron density? Does the difference electron-density analysis suffice for a description of the chemical bond? Angew. Chem. Int. Ed. Engl. 23 (1984) 627–628, doi:10.1002/anie.198406271.

[53] E.R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A.J. Cohen, W. Yang, Revealing noncovalent interactions, J. Am. Chem. Soc. 132 (2010) 6498–6506, doi:10.1021/ja100936w.

[54] Y. Lei, H. Li, H. Pan, S. Han, Structures and hydrogen bonding analysis of *N, N* -dimethylformamide and *N, N* -dimethylformamide−water mixtures by molecular dynamics simulations, J. Phys. Chem. A 107 (2003) 1574–1583, doi:10.1021/jp026638+.

[55] G.G. Almeida, A. Borges, J.M.M. Cordeiro, On the hydrogen bonding between N-methylformamide and acetone and tetrahydrofuran, Chem. Phys. 434 (2014) 25–29, doi:10.1016/j.chemphys.2014.02.013.