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Acoustical and molecular interaction studies of amide with aliphatic amines in benzene at various temperatures

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ABSTRACT

The ultrasonic velocity, density and viscosity have been measured for the mixtures of amines, namely, Di-methyl amine, Di-ethylamine and Tri-ethyl amine with amide in benzene at 303 K 313K and 323K. The experimental data have been used to calculate the thermo dynamical parameters namely adiabatic compressibility (β), free length (L_f), free volume (V_f) and internal pressure (π_i) viscous relaxation time (τ) and Gibbs' free energy (ΔG). Present study helped to find the existence of strong molecular association. Such a molecular association is found to be by hydrogen bonding and through dipole-dipole interaction.

Keywords: Thermo dynamical parameters, Molecular association, Dipole-Dipole interaction.

INTRODUCTION

The present study is concerned with the ternary mixtures of N,N- Di-methyforamide + Benzene + Di-methyl amine, N,N-Di-methyforamide + Benzene + Di-Ethyl amine and N,N- Di-methyforamide + Benzene + Tri-ethyl amine. Basically they are H-Bond in nature and in recent years, studying molecular association among pure and liquid mixtures gives the idea about their physical and thermo dynamical properties [1-4].

In the present investigation N,N-Dimethylformamide (DMF) is taken as one of the liquid, which is a polar solvent used widely in a variety of industrial process. N,N-Dimethylformamide is very much useful in manufacturing synthetic fibers, leathers, films and surface coating [5-7]. N,N-Dimethylformamide is a stable compound with a strong electron-pair donating and accepting ability and is widely used in studies on solvent reactivity relationships [8,9]. N,N-Dimethylformamide is of particular interest, because any significant structural effects are absent due to the lack of hydrogen bonds. Therefore it may be used as an aprotic protophilic solvent with a large dipole-moment, a

high dielectric constant and good donor-acceptor properties, which is enable it to dissolve a wide range of both organic and inorganic substance [10].

Benzene is a non polar solvent which can freely miscible with many organic solvents [11] and it has slightly polar nature due to the delocalized electron cloud, which result in the solute-solvent molecular associates [12]. Benzene exists as dimer [13].

EXPERIMENTAL SECTION

Analytical reagent (AR) chemicals with minimum assay of 99.9% were used for the present investigation (obtained from Merck), the chemical are pure in nature so they are used directly without any further purification. The selected liquids are mixed with the concentration of mole fraction, in that the mole fraction of benzene is fixed as 0.3 (i.e. $X_2=0.3$). And the mole fraction of the other compounds like N,N-Dimethylformamide and aliphatic amines are varied from 0.0 to 0.7. Ultrasonic velocity is measured using an ultrasonic interferometer with an operating frequency of 2MHz (manufactured by Mittal enterprises, New Delhi). Viscosity has been measured by an Oswald's Viscometer of with 10 ml capacity. The flow time of water and liquid mixtures are measured by a digital stop watch (manufactured by Racer). The density of the pure and liquid mixtures has been measured by relative measurement using specific gravity bottle of 10 ml capacity.

Theory and calculation

Ultrasonic velocity (U), Viscosity (η) and Density (ρ) of the liquid mixtures have been calculated using the standard relations. And using the measured data, the acoustical parameters, such as adiabatic compressibility (β), Free length (L_f), Free Volume (V_f), Internal pressure(π_i), Viscous relaxation time (τ) and Gibb's Free energy (ΔG) also have been calculated using the following relations,

$$\beta = (U^2 \rho)^{-1} \dots \dots \dots (N^{-1} m^2) \quad (1)$$

$$L_f = K_T \beta^{\frac{1}{2}} \dots \dots \dots (m) \quad (2)$$

$$V_f = \left[\frac{M_{eff} U}{K \eta} \right]^{\frac{3}{2}} \dots \dots \dots (m^3 mol^{-1}) \quad (3)$$

$$\delta_i = bRT \left[\frac{K \rho}{U} \right]^{\frac{1}{2}} \left[\frac{\bar{n}^{\frac{1}{3}}}{M^{\frac{1}{6}}} \right] \dots \dots (Pa) \quad (4)$$

$$\hat{\delta} = \frac{4}{3} \hat{\alpha} \rho \dots \dots \dots (s) \quad (5)$$

$$-\Delta G = -KT \log \left(\frac{h}{KT \hat{\delta}} \right) \dots (KJ mol^{-1}) \quad (6)$$

Where, K_T is Jacob's constant, M_{eff} is the effective molecular weight ($M_{eff} = \sum m_i x_i$ in which m_i and x_i are the molecular weight and the mole fraction of the individual constituents respectively), K is a temperature independent constant equal to 4.28×10^9 for all liquids [14], T is the Absolute temperature in Kelvin, R is the universal gas constant and B is the cubic packing fraction factor is assumed to be '2' for all liquid systems [15].

RESULT AND DISCUSSION

The experimentally calculated values of density (ρ), viscosity (η), and ultrasonic velocity (U) increases with increases in molar concentration of N,N-Dimethylformamide shown in Table-1. The increase in these parameter indicates that the presence of molecular interaction between the component molecules. N,N-Dimethylformamide is the organic solvent widely used in binary and ternary liquid systems, and it is a polar aprotic in nature [16]. When this is mixed with benzene, there is dipole-dipole interaction between N,N-Dimethylformamide and benzene [17].

Table -1: Density (ρ), Viscosity (η) and Velocity (U) of N, N-Dimethylformamide + Benzene + Di-methylamine, N, N-Dimethylformamide + Benzene + Di-Ethylamine and N, N-Dimethylformamide + Benzene + Tri-Ethylamine at 303K, 313K and 323K

Mole fraction		Density (ρ) (Kgm ⁻³)			Viscosity (η) (10 ⁻³ NSm ⁻²)			Velocity (U) (ms ⁻¹)		
X ₁	X ₃	303K	313K	323K	303K	313K	323K	303K	313K	323K
N,N-Dimethylformamide + Benzene + Di-methylamine										
0.000	0.705	816.8	812.7	808.7	0.7001	0.648	0.5852	1354.7	1348.3	1343.5
0.100	0.606	826.8	821.8	816.1	0.7495	0.6859	0.6226	1358.4	1351.6	1347.9
0.197	0.498	831.4	825.7	820.8	0.8612	0.7802	0.7001	1364.7	1355.6	1351.4
0.301	0.403	834.7	830.5	825.7	0.9465	0.8673	0.7955	1369.3	1360.4	1354.2
0.399	0.297	839.7	834.2	829.8	1.1092	1.0451	0.9732	1372.7	1364.9	1360.4
0.497	0.195	844.3	839.4	833.2	1.3327	1.238	1.1586	1377.5	1370.6	1366.3
0.607	0.104	848.4	844.7	838.7	1.4251	1.3551	1.2786	1386.4	1378.4	1374.8
0.705	0.000	857.4	852.9	849.2	1.5684	1.5012	1.4728	1392.6	1388.4	1380.5
N,N-Dimethylformamide + Benzene + Di-Ethylamine										
0.000	0.701	810.9	808.4	806.5	0.6892	0.6437	0.6017	1351.9	1345.7	1341.8
0.102	0.604	813.8	810.8	807.8	0.7281	0.6709	0.6242	1354.7	1349.9	1344.6
0.199	0.501	822.6	816.5	811.8	0.7992	0.7398	0.6838	1360.4	1353.8	1347.8
0.305	0.398	829.6	825.5	822.5	0.8678	0.8119	0.7643	1367.8	1357.3	1351.4
0.398	0.301	836.8	831.1	828.4	1.0457	0.9392	0.8845	1371.4	1360.7	1355.6
0.504	0.200	846.8	841.2	837.4	1.3047	1.2313	1.1152	1375.2	1365.4	1361.4
0.601	0.098	856.2	852.6	846	1.4057	1.3417	1.2552	1382.6	1373.9	1367.5
0.700	0.000	868.1	863	857.8	1.5238	1.4855	1.463	1387.8	1382.6	1373.3
N,N-Dimethylformamide + Benzene + Tri-Ethylamine										
0.000	0.700	809.5	806.9	802.9	0.6745	0.6365	0.5931	1349.6	1343.6	1340.4
0.101	0.603	811.1	808.6	804.3	0.7024	0.678	0.6159	1353.4	1347.4	1343.7
0.203	0.501	816.4	812.2	809.7	0.7542	0.7054	0.6388	1357.4	1350.6	1346.8
0.299	0.404	825.2	820.4	812.8	0.8047	0.7742	0.7103	1362.6	1354.8	1349.6
0.403	0.308	830.3	825.6	819.3	0.9678	0.9326	0.8657	1366.4	1358.7	1354.6
0.503	0.199	846.1	837.7	829.4	1.2174	1.1456	1.0924	1370.7	1362.5	1358.7
0.599	0.104	850.8	846.7	837.4	1.3745	1.2967	1.2365	1375.6	1369.5	1365.6
0.703	0.000	854.4	849.2	841.1	1.5047	1.4773	1.4013	1383.7	1380.1	1376.7

In the first concentration onwards amines are purposefully introduced, it behaves as Lewis bases since they contain nitrogen as the basic center with lone pair of electrons. Aromatic amines also contain π electrons [18], but these electrons are used for resonance.

In the present study donor-acceptor complexes expected between benzene and N,N-Dimethylformamide that is possible because of π electron clouds in benzene can be donated to C ^{$\delta+$} of N,N-Dimethylformamide. In addition, when amines are introduced in between this, there is a possibility of intermolecular hydrogen bonding between carbonyl oxygen and Hydrogen in amine. Since such hydrogen is in between two highly electronegative elements. The C=O group is exhibiting negative inductive effect over the electron density of the hydrogen of amines. Therefore the possibility of forming intermolecular hydrogen bonding is greater.

This holds good for first two systems, because nitrogen in di-methyl and di-ethyl amine contains at least one hydrogen in its group. But in the case of Tri-ethyl amine (last system) there is no hydrogen, because of this there is no possibility of hydrogen bonding. Further the possibility for dipole-dipole interaction in that is also difficult.

Table- 2: Adiabatic compressibility (β), Free length (L_f) and Free Volume (V_f) of N,N-Dimethylformamide+Benzene+Di-methylamine, N,N-Dimethylformamide+Benzene+Di-Ethylamine and N,N-Dimethylformamide+Benzene+Tri-Ethylamine at 303K, 313K and 323K

Mole fraction		Adiabatic compressibility (β) ($10^{-10} \text{ N}^{-1} \text{ m}^2$)			Free length (L_f) (10^{-10} m)			Free Volume (V_f) ($10^{-7} \text{ m}^3 \text{ mol}^{-1}$)		
X_1	X_3	303K	313K	323K	303K	313K	323K	303K	313K	323K
N,N-Dimethylformamide + Benzene + Di-methylamine										
0.000	0.705	6.6711	6.7685	6.8507	5.0979	5.1350	5.1660	1.1230	1.2520	1.4513
0.100	0.606	6.5545	6.6609	6.7443	5.0531	5.0940	5.1258	1.0881	1.2336	1.4206
0.197	0.498	6.4582	6.5904	6.6710	5.0159	5.0669	5.0978	0.9560	1.0976	1.2853
0.301	0.403	6.3895	6.5062	6.6040	4.9891	5.0344	5.0722	0.8972	1.0129	1.1452
0.399	0.297	6.3201	6.4347	6.5116	4.9619	5.0067	5.0366	0.7693	0.8340	0.9236
0.497	0.195	6.2419	6.3417	6.4292	4.9311	4.9704	5.0046	0.6385	0.7078	0.7781
0.607	0.104	6.1322	6.2308	6.3083	4.8876	4.9268	4.9573	0.6321	0.6758	0.7345
0.705	0.000	6.0140	6.0823	6.1789	4.8403	4.8677	4.9062	0.6060	0.6442	0.6573
N,N-Dimethylformamide + Benzene + Di-Ethylamine										
0.000	0.701	6.7475	6.8308	6.8868	5.1270	5.1585	5.1796	1.9914	2.1911	2.4139
0.102	0.604	6.6957	6.7683	6.8471	5.1072	5.1349	5.1647	1.8392	2.0683	2.2912
0.199	0.501	6.5686	6.6824	6.7811	5.0586	5.1022	5.1397	1.6096	1.7941	2.0056
0.305	0.398	6.4429	6.5755	6.6572	5.0099	5.0612	5.0926	1.4339	1.5663	1.7037
0.398	0.301	6.3540	6.4986	6.5689	4.9752	5.0315	5.0587	1.0883	1.2637	1.3749
0.504	0.200	6.2443	6.3764	6.4431	4.9321	4.9840	5.0100	0.7840	0.8460	0.9772
0.601	0.098	6.1098	6.2136	6.3208	4.8787	4.9199	4.9622	0.7067	0.7507	0.8239
0.700	0.000	5.9810	6.0617	6.1813	4.8270	4.8594	4.9072	0.6296	0.6505	0.6588
N,N-Dimethylformamide + Benzene + Tri-Ethylamine										
0.000	0.700	6.7822	6.8650	6.9321	5.1401	5.1714	5.1966	2.8556	3.0944	3.4279
0.101	0.603	6.7309	6.8119	6.8861	5.1206	5.1514	5.1794	2.5621	2.6837	3.0869
0.203	0.501	6.6478	6.7496	6.8087	5.0890	5.1278	5.1502	2.1978	2.4115	2.7865
0.299	0.404	6.5268	6.6408	6.7547	5.0424	5.0863	5.1297	1.9139	2.0108	2.2750
0.403	0.308	6.4507	6.5612	6.6517	5.0129	5.0557	5.0904	1.3909	1.4580	1.6228
0.503	0.199	6.2906	6.4304	6.5311	4.9503	5.0050	5.0441	0.9439	1.0248	1.0959
0.599	0.104	6.2113	6.2971	6.4035	4.9191	4.9529	4.9946	0.7584	0.8221	0.8791
0.703	0.000	6.1130	6.1825	6.2729	4.8800	4.9076	4.9434	0.6388	0.6541	0.7054

Adiabatic compressibility (β) exhibits reverse trend to that of ultrasonic velocity (U) shown in Table-2, when the molar concentration of N,N-Dimethylformamide increases, adiabatic compressibility (β) decreases gradually, because this depends on strength of electron donor and acceptor. The same trend exhibits to free length also, because there also a possibility of breaking dipoles in N,N-Dimethylformamide molecules by mixing benzene [17], this is evident from Table-2

From table-2, it is also evident that the free volume (V_f) decreases with increasing molar concentration of N,N-Dimethylformamide and subsequently concentration of amines is decreases,

therefore there is very weaker hydrogen bonding interaction among N,N-Dimethylformamide and amines. The concentration of benzene is fixed as constant, (i.e,0.3M), when the concentration of N,N-Dimethylformamide increases, $C^{\delta+}$ will be available more in number. So there is decreasing trend in free volume(V_f).

Table- 3: Internal Pressure (π_i),Viscous relaxation Time (τ) and Gibb's Free Energy (ΔG) of N,N-Dimethylformamide+Benzene+Di-methylamine, N,N-Dimethylformamide+Benzene+Di-Ethyl amine and N,N-Dimethylformamide+Benzene+Tri-Ethylamine at 303K, 313K and 323K

Mole fraction		Internal Pressure (π_i) (10^{-6} Pa)			Viscous Relaxation Time (τ) (10^{-12} S)			Gibb's Free Energy (ΔG) (10^{-20} KJ mol $^{-1}$)		
X_1	X_3	303K	313K	323K	303K	313K	323K	303K	313K	323K
N,N-Dimethylformamide + Benzene + Di-methylamine										
0.000	0.705	5.7306	5.5078	5.2263	6.2272	5.8480	5.3454	0.6667	0.6829	0.6934
0.100	0.606	5.6679	5.4138	5.1411	6.5502	6.0916	5.5987	0.6759	0.6906	0.7024
0.197	0.498	5.7526	5.4686	5.1677	7.4158	6.8558	6.2272	0.6984	0.7128	0.7230
0.301	0.403	5.7029	5.4586	5.2195	8.0636	7.5237	7.0047	0.7136	0.7302	0.7458
0.399	0.297	5.8148	5.6357	5.4282	9.3470	8.9665	8.4495	0.7404	0.7632	0.7821
0.497	0.195	5.9836	5.7592	5.5527	11.0915	10.4681	9.9318	0.7715	0.7922	0.8134
0.607	0.104	5.8105	5.6658	5.4847	11.6522	11.2579	10.7544	0.7804	0.8058	0.8288
0.705	0.000	5.6892	5.5548	5.5018	12.5765	12.1745	12.1339	0.7943	0.8205	0.8522
N,N-Dimethylformamide + Benzene + Di-Ethylamine										
0.000	0.701	3.6860	3.5631	3.4445	6.2005	5.8627	5.5250	0.6659	0.6834	0.6999
0.102	0.604	3.7943	3.6397	3.5090	6.5001	6.0545	5.6986	0.6616	0.6895	0.7059
0.199	0.501	3.9952	3.8342	3.6802	6.9995	6.5915	6.1825	0.6879	0.7054	0.7217
0.305	0.398	4.1760	4.0414	3.9202	7.4549	7.1182	6.7842	0.6993	0.7198	0.7396
0.398	0.301	4.6044	4.3608	4.2307	8.8592	8.1380	7.7470	0.7307	0.7449	0.7653
0.504	0.200	5.1777	5.0257	4.7755	10.8627	10.4685	9.5804	0.7677	0.7922	0.8064
0.601	0.098	5.3993	5.2768	5.0894	11.4515	11.1157	10.5786	0.7773	0.8034	0.8256
0.700	0.000	5.6634	5.5803	5.5342	12.1519	12.0063	12.0577	0.7881	0.8179	0.8509
N,N-Dimethylformamide + Benzene + Tri-Ethylamine										
0.000	0.700	2.8186	2.7383	2.6377	6.0994	5.8260	5.4819	0.6629	0.6823	0.6984
0.101	0.603	2.9945	2.9425	2.7984	6.3037	6.1580	5.6549	0.6689	0.6984	0.7044
0.203	0.501	3.2380	3.1286	2.9753	6.6850	6.3483	5.7992	0.6795	0.6984	0.7097
0.299	0.404	3.4868	3.4166	3.2586	7.0028	6.8551	6.3971	0.6878	0.7128	0.7283
0.403	0.308	3.9757	3.8990	3.7431	8.3240	8.1586	7.6778	0.7194	0.7454	0.7636
0.503	0.199	4.6805	4.5238	4.3945	10.2109	9.8222	9.5128	0.7565	0.7802	0.8051
0.599	0.104	5.1488	4.9960	4.8498	11.3834	10.8874	10.5570	0.7762	0.7996	0.8252
0.703	0.000	5.5770	5.5107	5.3395	12.2645	12.1782	11.7204	0.7897	0.8206	0.8455

However, internal pressure (π_i) decreases with increase in concentration of N,N-Dimethylformamide must be noted. But reverse trend is observed because of the introduction of amines ,this is contributing interaction by means of hydrogen bonding , which may be attributed to increase in magnitude of interaction [19] and which is given in the Table -3.

Viscous relaxation time (τ) increases with increasing molar concentration of N,N-Dimethylformamide. Viscous relaxation time (τ) is measured in the order of 10^{-12} Sec, this is due to

structural relaxation process [19, 20] and nonlinear variation of relaxation time is due to thermal variation. The same trend observed in the case of Gibb's free energy (ΔG), this suggest the closer approach of unlike molecules due to hydrogen bonding [17, 21], whereas in the case of last system, the reduction of free energy indicated that the need for smaller time for the cooperative process [22].

CONCLUSION

The present study prevails that there exists dipole-dipole interaction and hydrogen bonding between Di-methyl amine and Di-ethyl amine with N,N-Dimethylformamide and order of interaction is found to be greater in Di-methyl amine than Di-ethyl amine. However in the case of last system (Tri-ethyl amine) reverse trend is observed because of the absence of H. The temperature variation of the ternary mixtures indicated that the strength of intermolecular interaction increases with rise in temperature.

REFERENCES

- [1] Johnson I, Kalidoss M and Srinivasamoorthy R, *Proceedings of the 17th international congress on acoustics (ROME)*, Part B, **2001**, Vol.1, 12-13.
- [2] Ramamurthy M and Sastry O S, *Ind J pure and appl phy*, **1983**, 21, 579.
- [3] Ramasany K and Ranganathan V, *Ind J pure and appl phy*, **1970**, 8, 144.
- [4] Kincaid J F and Eyring H, *J chem phy*, **1937**, 5, 587.
- [5] Zagar E and Zigon M, *Polymer*, **2000**, 41, 3513.
- [6] Borrmann H, Presson I, Sandstrom M and Stalhandske C M V, *J Chem. Soc Ferkin Trans*, **2000**, 2, 395.
- [7] Kang Y K and Park H S, *J Mol Stru (Theochem)*, **2004**,676, 171.
- [8] Venkatesu P, Lee M J and Lin H M, *J Chem Thermodyn*, **2005**, 53,996.
- [9] Umebayashi Y, Matsumoto K, Watanabe M and Ishiguro S, *Phys Chem Chem Phys*, **2001**, 3,5475.
- [10] Riddick J A, Bunger W B and Sakano T K, *Organic solvents*, 4th Edu, Wiley-Inter Science, Newyork, **1986**.
- [11] Jain R P, *Text book of Engineering chemistry*, Sulthan Chand and sons, New Delhi, **1944**.
- [12] Asghar J, Liakath Ali Khan F and Subramani K, *Rasayan J Chem*, **2010**, No.16, Vol.3(4), 697,
- [13] Kannapan A N, Kesavasamy and Ponnusamy, *American J Eng. and Appli Sci*, **2008**, 1(2), 95.
- [14] Surayanarayana. C V and kuppusamy, *J.Acoss.Soc.Ind*, **1976**, 4, 75.
- [15] Surayanarayana. C V, *J.Acou.Soc.Ind*, **1979**, 7, 131.
- [16] San Jun Peng, Hzi-yun Hou, Lang-shu and Tao Yan *J.Chem Thermodyn*, **2007**, 39, 474.
- [17] Thirumaran S and Sudha S, *J Chem and Pharm Research*, **2010**, 2(1), 327.
- [18] Kannapan V and Indragandhi N, *Ind J pure and appl phy*, **2007**, 45(3), 221.
- [19] Bender J M and Pecora, *J Phy Chem*, **1986**, 90, 1700.
- [20] Kinser L E, Fray A R, *Fundamentals of Acoustics*, Wisely Eastern, New Delhi, **1989**.
- [21] Fort R J, and Moore W R, *Trans Faraday Soc*, **1962**, 61, 2102.
- [22] Kannapan A N and Palani R, *Ind J pure and appl phy*, **2007**, 45, 573.