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STUDY ON THERMODYNAMICAL PARAMETERS OF TERNARY LIQUID MIXTURES (N-N DIMETHYLFORMAMIDE + METHYL BENZOATE + TOLUENE) AT 303K, 313K AND 323K

M. Catherine Priscilla[1] , Dr. M.M. Armstrong Arasu[2]

[1]Asst. Professor Dept. of Physics, K. Ramarkrishnan College of Engg., Samayapuram Tiruchirappalli – 621 112
[2]Asst. Professor Dept. of Physics, St.Joseph's College, Tiruchirappalli – 620 002.

Abstract - The intermolecular forces of liquids in a mixture show a considerable effect on its physical and chemical properties. The ultrasonic studies in liquid mixtures can be helpful in assessing degree of interaction between molecules. The measurements of ultrasonic velocity (U), viscosity (η) and density (ρ) at various temperatures (303K, 313K, 323K) over entire composition range and its data has been used to calculate various thermodynamic and acoustic parameters like internal pressure, adiabatic compressibility, inter molecular free length, acoustic impedance, classical adsorption, Wada's constant and relaxation time. These results have been analyzed and interpreted in terms of molecular dipole-dipole interactions. The data obtained is used to understand intermolecular interactions between the unlike molecules and to test the theories of solutions.

Key words: Internal pressure, Adiabatic compressibility, inter molecular free length, acoustic impedance, classical adsorption, Wada's constant and relaxation time.

1.1 INTRODUCTION

The ultrasonic study of liquids plays an important role in understanding the nature and strength of molecular interactions. A large number of studies have been made on the molecular interaction in liquid systems by various physical methods like, Raman effect, Nuclear Magnetic Resonance, ultra violet and ultrasonic method. Velocity of sound waves in a medium is fundamentally related to the binding forces between the atoms or the molecules. The variations of ultrasonic velocity and related parameters throw some light on the intermolecular interactions and the structural changes associated with the liquid mixtures having weakly interacting components as well as strongly interacting components. The variation of ultrasonic velocity and other acoustic parameters along with their excess values in ternary liquid mixtures has been investigated by different authors. Also industries demand reliable and accessible reference data on the physical and chemical properties of a wide variety of compounds.

In the present work density and viscosity studies of ternary mixtures of N,N -Dimethylformamide + methyl benzoate + toluene over the entire range of composition, at 303K, 313K and 323K and at atmospheric pressure have been reported.

1.2 MATERIALS AND METHODS

Materials:

The chemicals used in the present work N-N Dimethylformamide (99.8%), Methyl Benzoate (99%) and toluene (99.5%) from Merck life science private limited.

Preparation of ternary mixture:

In all systems the various concentration of the ternary liquid mixtures are prepared in terms of mole fractions. The liquid mixtures were preserved in well stopped glass bottles. After mixing the liquid thoroughly, the bottles were kept undisturbed to attain thermal equilibrium.

The ultrasonic velocity in the liquid mixtures have been measured using an ultrasonic interferometer (Mittal type Model: M-83) working at frequency 2 MHz with an overall accuracy of ± 0.1 ms^{-1}, an electronically digital operated constant temperature water bath has been used to circulate water through the double walled measuring cell made up of a steel containing the experimental solution at the desired temperature. The density of pure liquids and liquid mixtures was determined using a 10ml specific gravity bottle with electronic balance of accuracy 0.0001gm. An Ostwald's viscometer was used for the viscosity measurement. All the precautions were taken to minimize the possible experimental error.

1.3 THEORY

- **Adiabatic compressibility (β_a)** has been calculated from the ultrasonic velocity (U) and the density (ρ) of the medium using the equation as:

  $\beta_a = 1 / U^2\rho$

- **Intermolecular free length** has been determined as:

  $L_f = K (\beta_a)^{1/2}$

  Where K is a Jacobson's constant.

- **Free volume** in terms of ultrasonic velocity (U) and viscosity of the liquid (η) as: $V_f = [Meff\ U / K \eta]^{3/2}$

Where Meff is the effective molecular weight ($Meff = \Sigma m_i X_i$, in which m_i and X_i are the molecular weights and the mole fraction of the individual constituents respectively). K is a temperature independent constant which is equal to 4.28×10^9 for all liquids.

- **Relaxation time** can be estimated using the relation

  $\tau = (4\eta/3\rho U^2)$

- **Classical absorption** or relaxation amplitude is given by

  $(\alpha/F2) = 8\Pi^2\eta/3\rho u^2$

- **Acoustic impedance** Z is calculated as $Z = \rho U$

- **Wada's Constant** is given by the empirical relation,

  $W = (\quad /)^{-1/7}$

1.4 RESULTS AND DISCUSSION

The experimental data relating to Density, Viscosity, Velocity and Adiabatic compressibility at 303K, 313K, 323K for the given mixture have been presented in table 1&2. The calculated values of Acoustic impedance, Free volume, Classical absorption, Wada's constant, Intermolecular free length and Relaxation time are presented in the tables 2, 3 & 4.

From the Table 1 it was observed that the ultrasonic velocity, density and viscosity of ternary liquid mixture decreases with increase in temperature.

Further the adiabatic compressibility shows an inverse behavior compared to the ultrasonic velocity in the mixtures with increase in concentration as shown in Table 1. It is primarily the compressibility that changes with the structure and this lead to the change in ultrasonic velocity. The addition of interacting molecules breaks up the molecular clustering of the other, releasing several dipoles for the interactions. In view of greater force of interaction between the molecules there will be an increase in cohesive energy and the occurrence of structural changes, take place due to the existence of electrostatic field. Thus structural arrangement of molecules results in increasing adiabatic compressibility there by showing progressively intermolecular interactions.

Acoustic impedance is used to access the strength of the intermolecular interaction. Intermolecular free length is found to be a predominating factor, which depends upon the adiabatic compressibility and shows a similar behavior as that of compressibility. On the basis of sound propagation in liquid, the increase in free length results a decrease in the velocity.

The relaxation time decreases with increase in temperature. The relaxation time, which is in the order of 10^{-10} sec is due to the structural relaxation process and in such situation it is suggested that the molecules gets rearranged due to co-operative process.

The free volume is defined as the average volume in which the centre of molecules can move inside the hypothetical cell due to repulsion of surrounding molecules.

Classical adsorption is a measure of decrease in intensity level of ultrasonic wave. Wada's constant is linear.

TABLE 1: Values of Density, Viscosity and velocity of N-N DMF (X_1) + Methyl Benzoate (X_2) + Toluene (X_3)

Sl no.	Mole Fraction			Density (ρ)X10^3 (Kg/m^3)			Viscosity (η)X10^{-3} (Nsm^{-2})			Velocity (U) m/s		
	X_1	X_2	X_3	303K	313K	323K	303K	313K	323K	303K	313K	323K
1.	0.1	0.2	0.7	1.011	0.904	0.893	0.755	0.625	0.504	1322.50	1309.20	1285.04
2.	0.1	0.4	0.5	1.047	0.924	0.904	0.913	0.734	0.645	1337.14	1331.44	1318.54
3.	0.1	0.6	0.3	1.114	1.000	0.998	1.285	0.976	0.818	1349.64	1293.40	1287.70
4.	0.2	0.2	0.6	0.997	0.902	0.886	0.804	0.627	0.592	1466.74	1330.80	1275.60
5.	0.2	0.4	0.4	1.046	0.959	0.959	1.000	0.833	0.695	1340.90	1340.10	1260.34
6.	0.2	0.5	0.3	1.099	0.965	0.951	1.142	0.914	0.802	1347.10	1325.00	1306.00
7.	0.2	0.6	0.2	1.115	1.002	0.993	1.246	1.041	0.863	1364.54	1320.84	1317.14
8.	0.3	0.2	0.5	1.026	0.921	0.798	0.846	0.679	0.526	1348.74	1345.26	1291.04

9.	0.3	0.4	0.3	1.081	0.971	0.958	1.027	0.822	0.732	1363.00	1348.74	1299.40
10.	0.3	0.3	0.4	1.057	0.943	0.940	0.916	0.738	0.666	1346.64	1342.50	1295.12
11.	0.3	0.5	0.2	1.053	0.990	0.973	1.177	0.944	0.819	1374.64	1372.00	1315.50
12.	0.4	0.2	0.4	1.041	0.932	0.894	0.877	0.703	0.599	1342.44	1336.04	1298.34
13.	0.4	0.3	0.3	1.037	0.953	0.939	0.929	0.746	0.696	1462.20	1353.34	1338.30
14.	0.4	0.4	0.2	1.063	0.972	0.949	1.150	0.916	0.789	1403.04	1364.00	1346.80
15.	0.5	0.2	0.3	1.042	0.938	0.925	0.946	0.697	0.645	1464.34	1445.00	1320.14
16.	0.5	0.3	0.2	1.030	0.944	0.928	1.015	0.787	0.714	1451.60	1366.80	1327.10
17.	0.6	0.2	0.2	1.046	0.952	0.936	0.943	0.746	0.679	1398.70	1382.80	1380.50
18.	0.7	0.1	0.2	1.037	0.937	0.923	0.911	0.728	0.633	1390.60	1389.14	1360.74

TABLE 2: Values of Adiabatic compressibility (β), Acoustic impedence and Free Volume of N-N DMF (X_1) + Methyl Benzoate (X_2) + Toluene (X_3)

Sl No.	Mole Fraction			β x10^{-10} (m^2N^{-1})			Z x10^5 (Kg/m^2s)			V_F X10^{-8} (m^3/mol)		
	X_1	X_2	X_3	303K	313K	323K	303K	313K	323K	303K	313K	323K
1.	0.1	0.2	0.7	5.651	6.451	6.776	13.37	11.84	11.48	0.257	0.337	0.453
2.	0.1	0.4	0.5	5.339	6.101	6.361	14.00	12.30	11.92	0.223	0.309	0.369
3.	0.1	0.6	0.3	4.925	5.975	6.038	15.04	12.93	12.86	0.153	0.217	0.281
4.	0.2	0.2	0.6	4.658	6.256	6.932	14.63	12.01	11.30	0.266	0.334	0.341
5.	0.2	0.4	0.4	5.312	5.800	6.559	14.03	12.86	12.09	0.191	0.251	0.300
6.	0.2	0.5	0.3	5.012	5.901	6.160	14.80	12.78	12.42	0.167	0.228	0.272
7.	0.2	0.6	0.2	4.813	5.715	5.802	15.22	13.24	13.08	0.158	0.198	0.262
8.	0.3	0.2	0.5	5.357	5.995	7.512	13.83	12.39	10.31	0.211	0.292	0.404
9.	0.3	0.4	0.3	4.975	5.657	6.177	14.74	13.10	12.45	0.183	0.252	0.283
10.	0.3	0.3	0.4	5.215	5.880	6.336	14.23	12.66	12.18	0.200	0.275	0.304
11.	0.3	0.5	0.2	5.023	5.363	5.934	14.48	13.58	12.81	0.160	0.223	0.259
12.	0.4	0.2	0.4	5.328	6.008	6.630	13.98	12.45	11.61	0.192	0.266	0.325
13.	0.4	0.3	0.3	4.510	5.726	5.946	15.16	12.90	12.56	0.215	0.266	0.291
14.	0.4	0.4	0.2	4.774	5.524	5.804	14.92	13.27	12.79	0.156	0.212	0.260

TABLE 3: Values of Classical absorption and Wada's constant of N-N DMF (X_1) + Methyl Benzoate (X_2) + Toluene (X_3)

Sl No.	Mole Fraction			(α/f^2) X10^{-8} (m^{-1} s^{-2})			Wada's Constant (W) x10^3		
	X_1	X_2	X_3	303K	313K	323K	303K	313K	323K
1.	0.1	0.2	0.7	1.122	1.061	0.889	2.050	2.250	2.262
2.	0.1	0.4	0.5	1.282	1.177	1.079	2.174	2.416	2.456
3.	0.1	0.6	0.3	1.664	1.533	1.298	2.235	2.423	2.423
4.	0.2	0.2	0.6	9.858	1.031	1.080	2.096	2.221	2.229
5.	0.2	0.4	0.4	1.397	1.270	1.200	2.138	2.303	2.263
6.	0.2	0.5	0.3	1.506	1.418	1.300	2.138	2.379	2.398
7.	0.2	0.6	0.2	1.577	1.564	1.316	2.203	2.392	2.410
8.	0.3	0.2	0.5	1.191	1.071	1.038	1.958	2.145	2.398
9.	0.3	0.4	0.3	1.344	1.223	1.189	2.051	2.242	2.244
10.	0.3	0.3	0.4	1.256	1.142	1.110	1.996	2.199	2.182
11.	0.3	0.5	0.2	1.554	1.331	1.278	2.192	2.310	2.316
12.	0.4	0.2	0.4	1.229	1.111	1.044	1.892	2.078	2.135
13.	0.4	0.3	0.3	1.102	1.123	1.088	2.038	2.142	2.164
14.	0.4	0.4	0.2	1.444	1.330	1.204	2.059	2.205	2.243
15.	0.5	0.2	0.3	1.113	9.358	1.052	1.899	2.069	2.041
16.	0.5	0.3	0.2	1.230	1.173	1.148	2.005	2.124	2.137
17.	0.6	0.2	0.2	1.212	1.076	1.000	1.830	1.975	2.004
18.	0.7	0.1	0.2	1.194	1.058	9.744	1.710	1.865	1.878

TABLE 4: Values of Intermolecular free length and Relaxation time of N-N DMF (X_1) + Methyl Benzoate (X_2) + Toluene (X_3)

Sl No.	Mole Fraction			L_F X10^{-11} (m)			τ X10^{-10} sec		
	X_1	X_2	X_3	303K	313K	323K	303K	313K	323K
1.	0.1	0.2	0.7	4.754	5.156	5.362	5.693	5.383	4.558
2.	0.1	0.4	0.5	4.621	5.014	5.195	6.505	5.973	5.473
3.	0.1	0.6	0.3	4.438	4.962	5.061	8.440	7.777	6.586
4.	0.2	0.2	0.6	4.316	5.077	5.423	4.999	5.231	5.479
5.	0.2	0.4	0.4	4.609	4.889	5.275	7.089	6.444	6.085
6.	0.2	0.5	0.3	4.477	4.931	5.112	7.639	7.195	6.592
7.	0.2	0.6	0.2	4.387	4.853	4.962	8.001	7.934	6.678
8.	0.3	0.2	0.5	4.629	4.970	5.646	6.043	5.433	5.268
9.	0.3	0.4	0.3	4.461	4.828	5.120	6.818	6.202	6.031

10.	0.3	0.3	0.4	4.567	4.922	5.185	6.369	5.791	5.631
11.	0.3	0.5	0.2	4.482	4.701	5.018	7.883	6.751	6.481
12.	0.4	0.2	0.4	4.616	4.975	5.304	6.233	5.635	5.296
13.	0.4	0.3	0.3	4.247	4.857	5.023	5.589	5.699	5.520
14.	0.4	0.4	0.2	4.370	4.771	4.963	7.325	6.749	6.108
15.	0.5	0.2	0.3	4.230	4.584	5.129	5.647	4.745	5.335
16.	0.5	0.3	0.2	4.292	4.833	5.093	6.238	5.951	5.824
17.	0.6	0.2	0.2	4.421	4.755	4.875	6.149	5.458	5.072
18.	0.7	0.1	0.2	4.465	4.773	4.982	6.055	5.370	4.941

1.5 CONCLUSION

The result in the present study indicates that thermodynamic parameters are sensitive to the molecular interactions in the liquid mixture. Also it is concluded that the there exist interactions like hydrogen bonding, dipole dipole and dipole induced dipole and charge transfer between unlike molecules in ternary liquid mixture N-N Dimethylformamide, Methyl Benzoate and Toluene.

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