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ULTRASONIC STUDIES ON MOLECULAR INTERACTION IN TERNARY LIQUID MIXTURES OF N-N DIMETHYL FORMAMIDE, METHYL BENZOATE, AND CYCLOHEXANE At 303K, 313K, and 323K

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ABSTRACT: The ultrasonic velocity measurements are highly sensitive to molecular interaction and can be used to provide qualitative information about the physical nature and strength of molecular interaction in the liquid mixture. Ultrasonic velocity of a liquid was related to the binding forces between the atoms or the molecules. Ultrasonic velocity (U), Density (ρ), and Viscosity (η) of N-N Dimethyl Formamide, Methyl Benzoate and Cyclohexane at different temperatures 303K, 313K & 323K were determined. The acoustic parameters provided a better insight into molecular environments in liquid mixtures. The various acoustical parameters such as acoustic impedance (Z), Adiabatic Compressibility (β), Relaxation Time (τ), Wada's Constant (W), Free Volume (V_F), Classical absorption, and Intermolecular free length (L_f), have been calculated for the present ternary system. The calculated values had their own physical significance and lead to better understanding between the liquids.

Key Words: Acoustic Impedance (Z), Adiabatic Compressibility (β), Relaxation Time (τ).

INTRODUCTION

Ultrasonic investigation of liquid mixtures containing polar and Non Polar components is of considerable importance in understanding intermolecular interaction between the component molecules as that finds application in several industrial and technological processes. Knowledge of thermodynamic and acoustical properties is of great significance in studying the Pysico – Chemical behavior and molecular interactions in a variety of liquid mixtures. Acoustic and thermodynamic parameters have been used to understand different kinds of association, the molecular packing, molecular motion, and various types of intermolecular interactions and their strengths. In the present study molecules of N-N-Dimethyl formamide (DMF) as a polar solvent and this is a colourless liquid. The ultrasonic investigation of DMF is important because of its use in industry and medicine. Methyl benzoate is a colorless liquid that is poorly soluble in water, but miscible with organic solvents. Methyl benzoate has a pleasant smell strongly reminiscent of the fruit of the feijoa tree and it is used in perfumery. The Cyclohexane is non polar, a solvent and used in the production of nylon. Cyclohexane is mainly used for the industrial production of adipic acid and caprolactam which are precursors to nylon.

EXPERIMENTAL

All the chemicals used in this present research work are analytical reagent (AR) grades of minimum assay of 99.8%, 99.5%, 99% obtained from E-Merck, Germany and Sd Fine Chemicals, India, which are used as such without further purification. The purities of the above chemicals were checked by density determination at 303, 313 and 323K ± 0.1K which showed an accuracy of ± 1×10^{-4}g on a electronic digital balance (Model: SHIMADZU AX 200). The density was measured using pycnometer of capacity 10 ml and gave an estimated reproducibility of +0.0001g cm^{-3}. The viscosity was measured using an Ostwald's Viscometer having time of effulix 0.01s and the accuracy was found to be 3×10^{-6} $Nm^{-2}S$. An electronically digital operated constant temperature bath (Mittal Enterprises, New Delhi) has been used to circulate water through double walled measuring cell made up of steel containing the experimental solution

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at the desired temperature. The speed of sound waves was obtained by using ultrasonic interferometer, (Mittal Enterprises, New Delhi) at a fixed frequency of 2MHZ.

THEORETICAL ASPECTS

The following thermodynamic parameters were calculated:

1 Adiabatic compressibility (β) has been calculated from the ultrasonic velocity (U), and the density (ρ) of the medium using the Newton-Laplace equation as follows:

$\beta = 1/U^2\rho)$ Kg^{-1} ms ………….. (1) ρ =

Density of liquid in kg/m^3, U = Ultrasonic velocity in m/s

2 Intermolecular free length (L_f) has been determined as follows:

$Lf = K_T (\beta)^{1/2}$ ……………. (2)

K is Jacobson's constant which depends on the temperature
Where KT is the temperature-dependent constant known as Jacobson's constant

(KT = 2.131×10^{-6} at 303,313 and 323K), and β is

the adiabatic compressibility that can be calculated from the speed of sound (U) and the density of the medium (ρ) as

β = (u ρ). …………… (3)

Where ρ is density of the solution in Kg/m^3, U is the ultrasonic velocity in m/sec

3 The relation for free volume in terms of ultrasonic velocity and the viscosity (η) of liquid as follows:

$V_f = (MeffU / k\eta)^{1/2}$ ……………. (4)

Where Meff is the effective molecular weight of the mixture ($M_{eff} = \Sigma m_i X_i$, where m_i and X_i are the molecular weight and mole fraction of individual constituents, respectively),

K is a temperature independent constant which is equal to (4.281 × 109) for all liquids.

4 Relaxation time (τ) in terms of adiabatic compressibility (β) and viscosity (η) of the liquid is as follows:

τ = 4/3.(βη) ……………. (5)
Where η is viscosity of the solution in Ns/m^2, ρ is density of the solution in Kg/m^3
U is the ultrasonic velocity in m/s.

5 The acoustic impedance (Z) of a material is defined as the product of its density (ρ) and ultrasonic velocity (U).

Z = ρ U kg m^{-2} s^{-1} ………………. (6)

Where U and ρ are the velocity and density of the mixture respectively**6** Wada's analyzed the variation of molar compressibility with concentration for many liquid systems and has derived the empirical relation

$vv - \frac{M_{[illegible]}}{r} \rho^{-1}/$ ………………….. (7)

Where, M_{eff} is the effective mass, is the density of the solution, β Adiabatic Compressibility.

7 The classical absorption or relaxation amplitude is given by

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

RESULT AND DISCUSSION

TABLE – 1: Measured Values of Density (ρ), Viscosity (η) for the ternary system – N – N DimethylFormamide + Methyl Benzoate + Cyclohexane at 303K, 313K and 323K

Sl. No	Ratio			Density (ρ)X10³ (Kg/m³)			Viscosity (η)X10⁻³ (Nsm⁻²)			Velocity (U) m/s		
	X1	X2	X3	303K	313K	323K	303K	313K	323K	303K	313K	323K
1	0.1	0.3	0.6	1.0470	0.9805	0.9734	1.0576	0.8447	0.8121	1267	1249	1225
2	0.1	0.5	0.4	1.0130	0.9684	0.9629	1.0611	0.9066	0.8582	1287	1274	1266
3	0.1	0.7	0.2	1.0813	1.0008	0.9837	1.2782	1.0184	1.0182	1350	1332	1311
4	0.2	0.1	0.7	0.9955	0.9773	0.9727	0.9087	0.8022	0.8251	1310	1305	1265
5	0.3	0.1	0.6	1.0089	0.9750	0.9625	0.9285	0.8003	0.8232	1339	1302	1268
6	0.4	0.1	0.5	1.0136	0.9751	0.9667	0.9859	0.8136	0.8478	1308	1249	1236
7	0.2	0.6	0.2	1.0225	1.0440	0.9998	1.1399	1.0482	0.9845	1331	1309	1289
8	0.3	0.2	0.5	1.0430	1.0020	0.9552	0.9911	0.8429	0.8239	1270	1262	1258
9	0.3	0.3	0.4	1.0157	0.9750	0.9623	0.9727	0.8069	0.8161	1292	1275	1251
10	0.3	0.4	0.3	1.0122	0.9909	0.9738	1.0388	0.8537	0.8959	1332	1314	1291
11	0.3	0.5	0.2	1.0517	0.9900	0.9829	1.1488	0.9201	0.9423	1361	1350	1330
12	0.4	0.2	0.4	1.0068	0.9817	0.9643	0.9642	0.8325	0.8042	1306	1291	1277
13	0.4	0.3	0.3	1.0741	0.9763	0.9631	1.0689	0.8544	0.8168	1327	1310	1287
14	0.4	0.4	0.2	1.0363	0.9895	0.9634	1.1398	0.9398	0.8448	1269	1252	1241
15	0.5	0.2	0.3	1.0209	0.9788	0.9624	0.9854	0.8300	0.8231	1343	1329	1319
16	0.5	0.3	0.2	1.0178	0.9795	0.9643	1.0357	0.8572	0.8872	1274	1253	1250
17	0.6	0.2	0.2	1.0492	0.9744	0.9661	0.9734	0.8395	0.8194	1354	1345	1322
18	0.7	0.1	0.2	1.0209	0.9777	0.9654	0.9243	0.7761	0.8119	1384	1344	1343

TABLE – 2: Measured Values of Velocity (U), Adiabatic Compressibility (β) for the ternary system N – N Dimethyl Formamide + Methyl Benzoate + Cyclohexane at 303K, 313K and 323K

Sl. No	Ratio			β x10^{-10} (m^{2}N^{-1})			Z (Kg/m^{2}s)			Wada's constant (W)		
	X_1	X_2	X_3	303K	313K	323K	303K	313K	323K	303K	313K	323K
1	0.1	0.3	0.6	5.9493	6.5360	6.8351	1326.59	1225.07	1193.37	1.9592	2.0642	2.0659
2	0.1	0.5	0.4	5.9593	6.3621	6.4789	1303.79	1233.73	1219.08	2.2378	2.3192	2.3263
3	0.1	0.7	0.2	5.0703	5.6297	5.9145	1460.33	1333.28	1289.66	2.3500	2.5014	2.5269
4	0.2	0.1	0.7	5.8451	6.0081	6.4236	1305.03	1275.36	1230.56	1.8248	1.8516	1.8425
5	0.3	0.1	0.6	5.5278	6.0493	6.4615	1350.96	1269.55	1220.48	1.7919	1.8305	1.8369
6	0.4	0.1	0.5	5.7623	6.5735	6.7699	1326.29	1217.92	1194.98	1.7502	1.7855	1.7933
7	0.2	0.6	0.2	5.5201	5.5837	6.0117	1360.98	1367.36	1289.61	2.6260	2.5677	2.6530
8	0.3	0.2	0.5	5.9444	6.2617	6.6148	1324.59	1265.14	1201.70	1.8191	1.8795	1.9561
9	0.3	0.3	0.4	5.8973	6.3027	6.6398	1312.35	1243.77	1203.86	1.9767	2.0397	2.0513
10	0.3	0.4	0.3	5.5675	5.8444	6.1531	1348.36	1302.10	1258.03	2.1076	2.1381	2.1597
11	0.3	0.5	0.2	5.1293	5.5424	5.7514	1431.88	1336.48	1307.24	2.1575	2.2667	2.2711
12	0.4	0.2	0.4	5.8203	6.1115	6.3585	1315.19	1267.42	1231.50	1.8673	1.9016	1.9250
13	0.4	0.3	0.3	5.2864	5.9664	6.2680	1425.41	1279.17	1239.58	1.8768	2.0295	2.0428
14	0.4	0.4	0.2	5.9919	6.4447	6.7398	1315.10	1239.08	1195.57	2.0150	2.0885	2.1314
15	0.5	0.2	0.3	5.4281	5.7837	5.9722	1371.39	1300.87	1269.40	1.8371	1.8988	1.9224
16	0.5	0.3	0.2	6.0453	6.5017	6.6308	1297.53	1227.41	1205.95	1.9205	1.9749	2.0004
17	0.6	0.2	0.2	5.1948	5.6723	5.9223	1421.14	1310.68	1277.21	1.7765	1.8888	1.8934
18	0.7	0.1	0.2	5.1132	5.6616	5.7421	1413.02	1314.11	1296.66	1.6985	1.7480	1.7666

TABLE – 3: Measured Values of Free Volume (V_f), Relaxation Time (τ) for the ternary system N – N Dimethyl Formamide + Methyl Benzoate + Cyclohexane at 303K, 313K and 323K

Sl.No	Ratio			(V_F) X10^{-8} (m^3)			(τ) X10^{-10} sec		
	X_1	X_2	X_3	303K	313K	323K	303K	313K	323K
1	0.1	0.3	0.6	0.1451	0.1990	0.2052	8.3893	7.3615	7.4011
2	0.1	0.5	0.4	0.1717	0.2142	0.2304	8.4313	7.6901	7.4135
3	0.1	0.7	0.2	0.1601	0.2206	0.2154	8.6412	7.6442	8.0291
4	0.2	0.1	0.7	0.1591	0.1906	0.1744	7.0819	6.4260	7.0668
5	0.3	0.1	0.6	0.1560	0.1870	0.1722	6.8435	6.4553	7.0926

6	0.4	0.1	0.5	0.1351	0.1681	0.1556	7.5748	7.1312	7.6523
7	0.2	0.6	0.2	0.2057	0.2277	0.2445	8.3898	7.8036	7.8915
8	0.3	0.2	0.5	0.1427	0.1804	0.1856	7.8553	7.0372	7.2666
9	0.3	0.3	0.4	0.1637	0.2125	0.2029	7.6484	6.7812	7.2254
10	0.3	0.4	0.3	0.1680	0.2209	0.2003	7.7114	6.6526	7.3502
11	0.3	0.5	0.2	0.1609	0.2216	0.2091	7.8567	6.7991	7.2263
12	0.4	0.2	0.4	0.1523	0.1866	0.1933	7.4826	6.7837	6.8180
13	0.4	0.3	0.3	0.1454	0.1996	0.2079	7.5342	6.7966	6.8265
14	0.4	0.4	0.2	0.1337	0.1750	0.2026	9.1062	8.0753	7.5915
15	0.5	0.2	0.3	0.1509	0.1922	0.1924	7.1318	6.4005	6.5545
16	0.5	0.3	0.2	0.1410	0.1825	0.1728	8.3481	7.4311	7.8437
17	0.6	0.2	0.2	0.1528	0.1887	0.1908	6.7421	6.3494	6.4701
18	0.7	0.1	0.2	0.1525	0.1897	0.1771	6.3015	5.8583	6.2158

TABLE – 4: Measured Values of Classical Absorption (α), Intermolecular Free Length (L_f) for the ternary system N – N Dimethyl Formamide + Methyl Benzoate + Cyclohexane at 303K, 313K and 323K

Sl.No	Ratio			(α/F^2) X10^{-8} ($m^{-1} s^{-2}$)			(L_F) X10^{-9} (m)		
	X_1	X_2	X_3	303K	313K	323K	303K	313K	323K
1	0.1	0.3	0.6	1.6543	1.4509	1.4594	4.88E-09	5.19E-09	5.39E-09
2	0.1	0.5	0.4	1.6625	1.5164	1.4618	4.88E-09	5.12E-09	5.24E-09
3	0.1	0.7	0.2	1.7039	1.5073	1.5832	4.50E-09	4.82E-09	5.01E-09
4	0.2	0.1	0.7	1.3965	1.2671	1.3935	4.84E-09	4.98E-09	5.22E-09
5	0.3	0.1	0.6	1.3494	1.2729	1.3986	4.70E-09	4.99E-09	5.24E-09
6	0.4	0.1	0.5	1.4936	1.4062	1.5089	4.80E-09	5.20E-09	5.36E-09
7	0.2	0.6	0.2	1.6544	1.5388	1.5561	4.70E-09	4.80E-09	5.05E-09
8	0.3	0.2	0.5	1.5490	1.3877	1.4329	4.88E-09	5.08E-09	5.30E-09
9	0.3	0.3	0.4	1.5082	1.3372	1.4248	4.86E-09	5.10E-09	5.31E-09
10	0.3	0.4	0.3	1.5206	1.3118	1.4494	4.72E-09	4.91E-09	5.11E-09
11	0.3	0.5	0.2	1.5493	1.3407	1.4249	4.53E-09	4.78E-09	4.94E-09
12	0.4	0.2	0.4	1.4755	1.3376	1.3444	4.83E-09	5.02E-09	5.19E-09
13	0.4	0.3	0.3	1.4856	1.3402	1.3461	4.60E-09	4.96E-09	5.16E-09
14	0.4	0.4	0.2	1.7956	1.5924	1.4969	4.90E-09	5.15E-09	5.35E-09
15	0.5	0.2	0.3	1.4063	1.2621	1.2925	4.66E-09	4.88E-09	5.03E-09

16	0.5	0.3	0.2	1.6461	1.4653	1.5467	4.92E-09	5.18E-09	5.30E-09
17	0.6	0.2	0.2	1.3295	1.2520	1.2758	4.56E-09	4.83E-09	5.01E-09
18	0.7	0.1	0.2	1.2426	1.1552	1.2257	4.52E-09	4.83E-09	4.94E-09

The experimentally determined values of Density (ρ), Viscosity (η) and Ultrasonic Velocity (u) of all the three liquid systems at three different temperatures of 303K, 313K and 323K are give in the Table5.1,Table5.2and Table 5.3. The Values of Adiabatic Compressibility, Acoustic Impedance, Wada's Constant, free volume, relaxation time, Classical Absorption and intermolecular free length for the system of pure and ternary mixtures of N – N Dimethyl Formamide, Methylbanzoate and Cyclohexane are given in Table5.4, Table 5.5, Table 5.6, Table 5.7, Table 5.8, Table 5.9, and Table
5.10.

For the system of ternary mixtures N – N Dimethyl Formamide, Methylbenzoate, and Cyclohexane in these liquids Density (ρ), Viscosity (η) decreases with increasing the temperature and ultrasonic velocity (u) Decreases with increasing the temperature of N – N Dimethyl Formamide, Methylbenzoate and Cyclohexane in liquid. However the ultrasonic velocity, density and viscosity decrease in all cases as temperature is increased.

For the system of ternary mixtures N – N Dimethyl Formamide, Methylbenzoate and Cyclohexane the adiabatic compressibility and free volume values are also positive which indicates that influence of OH bonding interaction or chemical forces and positive value indicate interstitial accommodation of one liquid molecule into another. Further the adiabatic compressibility shows an inverse behavior compared to the ultrasonic velocity in the mixtures with increase in temperature.

Acoustic Impedance is used to access the strength of the intermolecular attraction. Positive values length of free length indicates that there is an increase in free length. It gives the interaction between the mixtures of molecules. This interaction leads to the structural rearrangement. This depends upon the size and shape of the molecule.

The free volume is defined as the average volume in which the center of molecules can move inside the hypothetical cell due to repulsion of surrounding molecules. Classical absorption is a measure of decrease in intensity level of ultrasonic wave. Constant while the other two liquids have been varied.

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

CONCLUSION

Ultrasonic method is a powerful probe for characterizing the physico-chemical properties and existence of molecular interaction in the mixture. In addition, the density, viscosity and the derived acoustical parameters provide evidence of confirmation. The temperature variation of the ternary mixtures indicates that the strength of the intermolecular interaction increases with rise in temperature.

REFERENCE

1. Ali A & Nain A K, Acoust Lett, 19 (1996) 181.

2.Tewari K, Patra C & Chakraborrty V, Acoust Lett, 19 (1996) 53.

3.Kannappan AN and Rajendran V. 1992. Acoustic parameters of some ternary liquid mixtures. Ind. J. Pure. Appl. Phys. Vol. 30, pp. 240-242.

4.K.Ramasamy, and Ranganathan, V., Indian J. Pure & Appl. Phys., **27** (1983). 579.Spencer, J.N., Jeffery E. and Robert, C., J. of Phys. Chem., **83**, 1249 (1979).

5.J. Mohan, Liew, C.N. and Mather, A.E., J. Sol. Chem., **31**, 743 (2002).

6.Berry R S, Rice S A & Ross J, Physical Chemistry, 2nd edn Wiley (2000).

7.Kannappan V, Mahendran S & Kothai S, J Acous Soc Ind, 28 (2000).

8.Manoj Ku. Praharaj; Sarmistha Mishra, Research journal of chemical sciences, 2015.

9.Berry R S, Rice S A & Ross J, Physical Chemistry, 2nd edn Wiley (2000).

10.Kothai S, Ph D Thesis, March 2003.

11.Bhandakkar V D, IOSR Journal of applied Physics, 2012.

12.Kannappam V and Chidambara Vinayagam S, Indian J. Pure & Applied Physics, 2006.

13. Jain DVS and Dhar N S, Ind. J.Tech, 1992.

14. Large Man R J and Dunbar W S, *J. Phys. Chem.,* 1945.

15. Arul G. and Palaniappan L. 2001. Molecular interaction studies in the ternary mixtures of cyclohexane + toluene + 2-propanol. Ind. J. Pure. Appl. Phys. Vol. 39, pp. 561-564.

16. Surjit Singh Bhatti and Devinder Pal Singh. 1983. Molecular association in some n-butanol systems. Ind. J. Pure Appl. Phys. Vol. 21, pp. 506-509.