

Ultrasonic Studies on Intermolecular Interaction in Binary Mixture of N-Methyl Formate with 1-Butanol at 308K.

S. Elangovan

Department of Physics, Easwari Engineering College,
Chennai 600 089, Tamil Nadu, India

Abstract: Density, viscosity and ultrasonic velocity have been measured for a binary mixture composed of n-methyl formate and 1-butanol at 308K. The adiabatic compressibility, acoustic impedance, free length, free volume, internal pressure, viscous relaxation time and Gibbs free energy have been deduced from the experimental data. The excess values of these parameters have also been calculated and elucidated in terms of molecular interactions. The deviations in the sign and values of these excess parameters from the ideal mixing reveal that intermolecular interactions obtaining in the liquid mixture.

Keywords : n-methyl formate, 1-butanol, ultrasonic velocity and hydrogen bonding.

Introduction

Intermolecular interaction in liquid mixtures plays a vital role in many field of applied and theoretical research. Ultrasonic technique is one of the sensitive techniques to elucidate the intermolecular interaction between the liquid systems[1-3]. N-methyl formate is an ester. It is used in the chemical industry as a solvent for cellulose nitrate. In continuous with our earlier work [4], the present study is an attempt to elucidate the molecular interaction between various concentrations of the binary liquid mixtures of n-methyl formate and 1-butanol at 308K.

Experimental and Theoretical Aspects

Binary liquid mixture preparations and the various methods involved in theoretical part have been described in the earlier article [5].

Result and Discussions

The experimentally measured values of density (ρ), viscosity (η), ultrasonic velocity (U) and computed values of adiabatic compressibility (β), acoustic impedance (Z), free length (L_f), free volume (V_f), internal pressure (π_i), viscous relaxation time (τ), Gibbs free energy (ΔG) for a binary mixture of n-methyl formate and 1-butanol at 308K are listed in Table 1.

Density of the binary mixtures decreases with increasing concentration of the n-methyl formate is as shown in Table1. It may due to the increasing concentration of the n-methyl formate leads to decrease the number of particles in the liquid mixtures. Similar trend has been observed in the viscosity measurement. Fig.1 signifies that ultrasonic velocity decreased with increasing mole fraction of n-methyl formate in 1-butanol medium. Acoustic impedance supports the same trend of ultrasonic velocity. It suggests the specific interaction occurring in the liquid mixtures resulting in weakening of intermolecular forces [6].

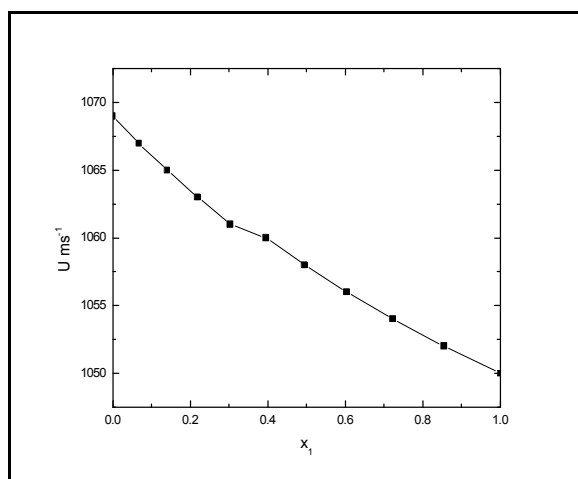


Fig.1. Plots of mole fraction Vs Ultrasonic velocity, of n-methyl formate with1- butanol at308K

Adiabatic compressibility has been increased with increasing concentration of 1-butanol elucidated that the medium is more and more easily compressed. The free volume and free length have been observed in increasing trend. It signifies that the carbonyl group of n-methyl formate and hydroxyl group present in the 1-butanol can mutually form dipoles and this dipolar interaction also supports the existence of more space between the components [7]. Internal pressure and viscous relaxation time decreased with increase in mole fraction of n-methyl formate. Moreover the reduction of Gibbs free energy in the liquid mixture reveals that the need less time for the rearrangement of the molecules in the liquid mixture decreases the energy that leads to dissociation [8].

The excess values of β^E , L_f^E , V_f^E , τ^E and ΔG^E are listed in Table 2. The positive excess values represent the dispersion forces, while the negative values interpreted that the dipole-dipole, charge transfer interaction and hydrogen bonding between the unlike molecules [9, 10].

Excess compressibility β^E and excess free length L_f^E values are negative values increased in the lower concentrations and decreased with the higher concentrations of n-methyl formate[11]. It is due to the existence of the dispersion and dipolar interaction between the unlike molecules.

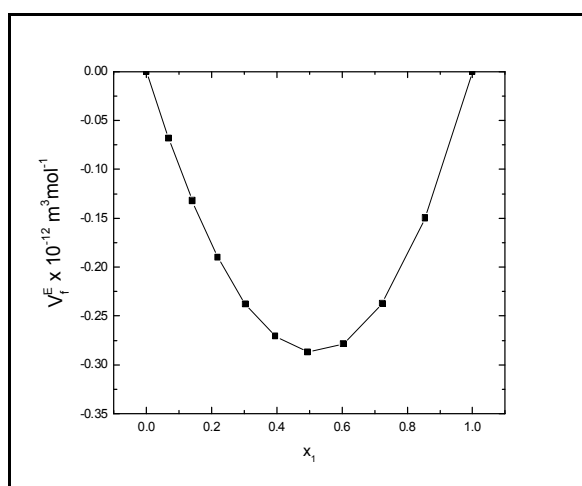


Fig.2. Plots of mole fraction Vs Excess free volume of n-methyl formate with1- butanol at308K

Excess free volume deviation against the mole fraction of n-methyl formate is plotted as shown in Fig.2. It signifies that the negative excess free volume increased up to a critical mole fraction of n-methyl formate ($x_1=0.4$) then decreased in the higher concentration. Thus, the observed variation of excess free volume can be confirmed the predominance of an energetically favored hydrogen bonding ($-\text{OH} \cdots \text{O}=\text{C}$) formed in the liquid system [12]. The negative values of excess relaxation time τ^E and excess Gibbs free energy ΔG^E increased with the increasing at the lower concentrations of n-methyl formate. It is suggested that the disassociation takes place in 1-butanol rich concentration.

Table 1 : Values of density (ρ), viscosity (η), ultrasonic velocity (U), adiabatic compressibility (β), acoustic impedance (Z) and free length (L_f) of n-methyl formate + 1-butanol at 308 K.

x_1	(ρ) kgm^{-3}	(η) $\times 10^{-3}$ Nsm^{-2}	(U) ms^{-1}	(β) $\times 10^{-10}$ m^2N^{-1}	(Z) $\times 10^6$ $\text{kgm}^{-2}\text{s}^{-1}$	(L_f) $\times 10^{-10}$ m	(V_f) $\times 10^{-7}$ $\text{m}^3\text{mol}^{-1}$	(R) $\times 10^{-3}$ m^5N^{-1}	(W) $\times 10^{-3}$ m^4s	(π_i) $\times 10^9$ Nm^{-2}	(τ) $\times 10^{-12}$ s	(ΔG) $\times 10^{-20}$ kJmol^{-1}
0.0000	798.2	1.9819	1210	8.5569	0.9658	0.6125	0.3427	0.9892	0.1833	0.7682	2.2612	1.1368
0.1431	813.7	1.8152	1194	8.6203	0.9716	0.6147	0.3676	0.9400	0.1747	0.7744	2.0863	1.1026
0.2731	829.3	1.6485	1178	8.6896	0.9769	0.6172	0.4004	0.8953	0.1670	0.7754	1.9100	1.0651
0.3917	844.8	1.4817	1162	8.7667	0.9817	0.6199	0.4440	0.8537	0.1598	0.7708	1.7320	1.0235
0.5004	860.4	1.315	1146	8.8497	0.9862	0.6229	0.5028	0.8161	0.1532	0.7599	1.5517	0.9768
0.6004	875.9	1.1483	1130	8.941	0.9898	0.6261	0.5845	0.7813	0.1472	0.7418	1.3689	0.9235
0.6927	891.4	0.9816	1114	9.0398	0.9930	0.6295	0.7025	0.7489	0.1415	0.7153	1.1831	0.8615
0.7781	907.0	0.8149	1098	9.1451	0.9959	0.6332	0.8836	0.7189	0.1363	0.6788	0.9936	0.7873
0.8574	922.5	0.6481	1082	9.2593	0.9981	0.6371	1.1868	0.6911	0.1314	0.6296	0.8001	0.6953
0.9311	938.1	0.4814	1066	9.3807	1.0000	0.6413	1.7678	0.6643	0.1267	0.5638	0.6021	0.5744
1.0000	953.6	0.3147	1050	9.5116	1.0013	0.6457	3.1928	0.6406	0.1226	0.4731	0.3991	0.3996

Table 2: Excess values of adiabatic compressibility (β^E), free length (L_f^E), free volume (V_f^E), of internal pressure (π_i^E), viscous relaxation time (τ^E) and Gibb's free energy (ΔG^E) of n-methyl formate + 1-butanol at 308K .

x_1	(β^E) $\times 10^{-10} \text{ m}^2 \text{ N}^{-1}$	(L_f^E) $\times 10^{-12} \text{ m}$	(V_f^E) $\times 10^{-12} \text{ m}^3 \text{ mol}^{-1}$	(π_i^E) $\times 10^8 \text{ Nm}^{-2}$	(τ^E) $\times 10^{-13} \text{ s}$	(ΔG^E) $\times 10^{-20} \text{ kJmol}^{-1}$
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1431	-0.0143	-0.2591	-0.3864	0.0488	0.0938	0.0468
0.2731	-0.0361	-0.4430	-0.7261	0.0884	0.1609	0.0838
0.3917	-0.0497	-0.5681	-1.0216	0.1189	0.2045	0.1113
0.5004	-0.0561	-0.6293	-1.2729	0.1401	0.2268	0.1296
0.6004	-0.0559	-0.6410	-1.4760	0.1515	0.2300	0.1385
0.6927	-0.0503	-0.6064	-1.6202	0.1522	0.2155	0.1377
0.7781	-0.0396	-0.5186	-1.6813	0.1408	0.1843	0.1260
0.8574	-0.0245	-0.3902	-1.6027	0.1148	0.1375	0.1016
0.9311	-0.0055	-0.2136	-1.2306	0.0707	0.0760	0.0615
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Conclusions

Physical and thermo dynamical parameters were determined in the binary mixture of n-methyl formate and 1-butanol at 308K. The determined variations in sign and excess values from the ideal mixture confirmed the specific hydrogen bonding interaction between carbonyl group of the n-methyl formate and hydroxyl group present in the 1-butanol.

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References

1. S. Punitha, R. Uvarani and A. Panneerselvam, *Int. J. ChemTech. Res.*, 7, 629 (2015).
2. Ritesh R. Naik, S. V. Bawankar, P. V. Tekade, Om A. Mahodaya, *Russian. J Phys. Chem A.*, 89, 152 (2015).
3. M.Chandra Sekhar, T. Madhu Mohan, T. Vijaya Krishna, A. Venkatesulu, and K. Siva Kumar, *J. Sol. Chem.*, 44, 237 (2015).
4. S. Elangovan and S. Mullainathan, *Russian J. Phys Chem A.*, 88, 2108 (2014).
5. S. Elangovan and S. Mullainathan, *Indian J. Phys.*, 87, 659 (2013).
6. S. Acharya, B. K. Das, G. C. Mohanty, *Indian J. Phys.*, 83, 185 (2009).
7. Suman Gahlyan, Manju Rani, Inkyu Lee, Il Moon and Sanjeev Kumar Maken, *Korean J. Chem. Eng.* 32,168 (2015).
8. L. Venkatramana, R. L. Gardas, C. Narasimha Rao, K. Sivakumar, K. Dayananda Reddy, *J. Sol. Chem.*, 44, 327 (2015).
9. R. J. Fort and W. R. Moore, *Trans. Faraday Soc.*, 62, 1112 (1966).
10. V. Vanathi, S. Mullainathan and S. Nithyanantham, *J. Comp Theo. Nano Sci.*, 10, 1952 (2013).
11. S. Elangovan and S. Mullainathan, *Indian J. Phys.*, 87, 373 (2013).
12. S. Elangovan and S. Mullainathan, *Russian J. Phys Chem A.*, 88, 601 (2014).
