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Ultrasonic Studies of Molecular Interactions in Ternary Liquid Mixtures at Different Temperatures

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Abstract

The behavior of mixture of pyridine, N- N dimethylformamide and cyclohexane as a function of temperature and composition has been investigated by measuring ultrasonic velocity in conjunction with density and viscosity at 288, 298, 308 and 318 K for frequency 2 MHz. From the velocity, density and viscosity data values, various acoustical and thermodynamics parameters namely, adiabatic compressibility (β), intermolecular free length (Lf), viscous relaxation time (τ), Gibbs' free energy (ΔG), internal pressure (Π) free volume (Vf) and specific acoustic impedance (Z) have been calculated. Also their excess values are calculated. All these parameters and their excess values have been discussed to throw light on intermolecular interactions between the components of ternary mixture.

Keywords- Ternary mixtures, dimethylformamide, pyridine, ultrasonic studies, dipole- dipole interaction, free length, excess values.

1. Introduction

The measurement of ultrasonic speed in liquid mixture enables accurate determination of some useful acoustical and thermodynamical parameters and their excess values which are highly sensitive to molecular interactions in their 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 influenced by the size in pure components and in the mixtures [1-5]. Excess parameters play a vital role in assessing the compactness due to molecular arrangement and the extent of molecular interactions in the liquid mixtures through charge transfer, dipole-dipole and dipole-induced dipole interactions [6]. The sign and the extent of deviation of these functions from ideality depend on the strength of interactions between unlike molecules [7]. We intend to measure the ultrasonic parameters and their excess values for ternary mixture of N-N Dimethylformamide (DMF) and pyridine along with Cyclohexane at different concentration of the

components of the mixture and at different temperatures (288 K, 298 K, 308 K, and 318 K).

DMF is a versatile solvent with a high dielectric constant (38 at 298 K) and a high dipole moment (3.82 D). Its linear aliphatic configuration contributes to the volume contraction of the mixture. Pyridine is a polar aprotic solvent. It is used in wide variety of reaction including electrophilic substitution, nucleophilic substitution, oxidation and reduction as it has the property to form complexes with many salts. It has a dipole moment 2.2 D at 298 K, which is small, compared to that of DMF. Since pyridine molecules are spherical in shape and monomers, they have weak interaction with their neighbors. Cyclohexane has a closed chain structure and is non- polar in nature. Dispersive forces caused by co-related movements of electrons are responsible between cyclohexane and the other components [8-9].

2. Experimental Techniques

All the chemicals namely, pyridine N-N dimethylformamide and cyclohexane were obtained

from E-Merck Chemicals Ltd., India. These liquids were used without any further purification. The velocity of ultrasonic waves was measured, using a multi-frequency ultrasonic interferometer with a high degree of accuracy operating at 11 different frequencies (Model M-84) supplied by M/s Mittal Enterprises, New Delhi, at a fixed frequency of 2MHz. The measuring cell of interferometer is a special designed double walled vessel with provision for temperature constancy. An electronically operated digital constant temperature bath (Model SSI-03spl) supplied by M/s Mittal Enterprises, New Delhi, operating in the temperature range -10°C to 85°C with an accuracy of ± 0.1 K has been used to circulate water through the outer jacket of the double walled measuring cell containing the experimental liquid. The density was measured using pycnometer of capacity 10ml. The specific gravity bottle with the experimental mixture was immersed in a temperature controlled water bath. The density was measured using the formula

$$\rho_2 = (w_2/w_1) \cdot \rho_1$$

Where, w_1 = weight of distilled water, w_2 = Weight of experimental liquid,

ρ_1 = Density of water, ρ_2 = Density of experimental liquid.

Viscosity measurements were carried out with an Oswald's viscometer having time of efflux 0.01s. The time of flow was measured using a digital racer stop watch with an accuracy of 0.1 sec. The temperature around the viscometer was maintained in an electronically controlled thermostatic water bath. The viscosity was determined using the relation,

$$\eta_2 = \eta_1 (t_2/t_1) (\rho_2/\rho_1)$$

Where, η_1 = Viscosity of water, η_2 = Viscosity of mixture, ρ_1 = Density of water,

ρ_2 = Density of mixture, t_1 = Time of flow of water, t_2 = Time of flow of mixture..

3. Theory

The ultrasonic velocity (U), density (ρ) and viscosity (η) in pure liquids and liquid mixture of various concentrations have been measured at 288,

298, 308 and 318K. Thermodynamic and acoustical parameters such as adiabatic compressibility (β), intermolecular free length (Lf), viscous relaxation time (τ), Gibbs' free energy (ΔG), internal pressure (Π_i) free volume (Vf), specific acoustic impedance (Z) and attenuation coefficient (α / f^2) were determined using the observed values of velocity, density and viscosity using respective equations^[10-14] and the excess values of these parameters were evaluated using the equation given below.

$$\beta = 1 / U^2 \cdot \rho \quad \text{----- (1)}$$

$$L_f = K T \cdot \beta^{1/2} \quad \text{----- (2)}$$

$$\tau = 4/3 \cdot (\beta \cdot \eta) \quad \text{----- (3)}$$

$$\Delta G = k T \cdot \ln (k T \tau / h) \quad \text{----- (4)}$$

$$\Pi_i = b R T (k \eta / U)^{1/2} (\rho^{2/3} / M_{eff}^{7/6}) \quad \text{----- (5)}$$

$$V_f = (M_{eff} \cdot U / K \cdot \eta)^{3/2} \quad \text{----- (6)}$$

$$Z = U \cdot \rho \quad \text{----- (7)}$$

$$\alpha / f^2 = 8 \pi^2 \eta / 3 \rho U^2 \quad \text{----- (8)}$$

Where 'KT' is the temperature dependent constant known as Jacobson's constant, 'k' is Boltzmann's constant, 'h' is the Planck's constant, 'b' stands for cubic packing, which is assumed to be '2' for all liquids, 'R' is gas constant, 'T' is absolute temperature, 'Meff' is the effective mass of liquid mixture, 'K' is a dimensionless constant independent of temperature and liquid, its value is 4.281×10^9 .

The excess values of parameters has been calculated by using the relation

$$A^E = A \exp - A_{id}$$

Where, $A \exp = \sum A_i X_i$, $i=1$ to n , A_i is any acoustical parameters and X_i is the mole fraction of the liquid component.

4. Result And Discussion

The experimental data relating to density, viscosity and ultrasonic velocity at 288 k, 298 k, 308 k and 318 K for frequency 2MHz of the mixture are given in table-5.1. The calculated values of adiabatic compressibility (β) and free length (Lf) are reported in table-5.2. Viscous relaxation time (τ) and Gibb's free energy (ΔG) are reported in table-5.3. Further free volume (Vf) and Internal pressure (Π_i) are reported in table-5.4 and acoustic impedance (Z) and absorption coefficient (α / f^2) are reported in

Mole fraction		Acoustic impedance (Z)				Absorption coefficient (α/f^2)			
X1	X3	288K	298K	308K	318K	288K	298K	308K	318K
0.0000	0.6000	1.212	1.165	1.129	1.085	1.2165	1.0746	0.9703	0.8909
0.0999	0.4999	1.217	1.171	1.129	1.082	1.2187	1.0841	0.9920	0.9306
0.1998	0.4001	1.224	1.174	1.129	1.081	1.2203	1.0902	1.0090	0.9467
0.3001	0.3000	1.231	1.178	1.129	1.081	1.2233	1.0990	1.0189	0.9677

table-5.5. The excess values of above parameters are presented in table-5.6, 5.7 and 5.8. The variation of different parameters and their excess values with temperature are shown in fig.6.1 to 6.15.

It is observed that at a fixed temperature, with increase in concentration of DMF, density of the medium decreases where velocity increases which may be due to the structural changes occurring in the mixture resulting in increase of intermolecular forces. However, when temperature increases, the intermolecular distance increases, resulting in decrease of the intermolecular forces and hence velocity.

Adiabatic compressibility decreases with increasing concentration of DMF, which is in conformation with the above fact. Compressibility gives the ease with which a medium can be compressed. In this case the medium appears to be more compact. This is also confirmed by the decreasing trend of free length ^[15-16].

$$L_f = KT.\beta^{1/2}$$

Internal pressure is a broader concept and is a measure of the totality of the forces (dispersion + ionic + dipolar) of interaction that contribute to the overall cohesion / adhesion of the liquid system. When concentration of pyridine decreases and that of DMF increases, internal pressure increases fast, as the force of cohesion increases. When temperature increases, the force of cohesion also decreases, hence internal pressure decreases.

Table – 5.1: Values of Density (ρ), Viscosity (η) and velocity (U) of mixtures at 288k, 298k, 308k and 318k.

Viscous relaxation time and the Gibbs' free energy both increases as concentration of DMF increases. Increase in Gibbs' free energy suggests shorter time for rearrangement of molecules. Relaxation time is the time taken for the excitation energy to appear as translational energy. The above fact confirms the minimum interaction between the molecules in the mixture.

Viscous relaxation time and the Gibbs' free energy both decreases as temperature increases. As temperature increases, excitation energy increases and hence relaxation time decreases. Further, since the kinetic energy of the molecule increases, longer time is taken for rearrangement of molecules and this suggest a decrease in Gibbs' free energy.

Free volume is the average volume in which the centre of a molecule can move due to the repulsion of the surrounding molecules. When concentration of DMF increases and that of pyridine decreases, ultrasonic velocity (U) increases and viscosity increases but free volume decreases. This indicates increase in molecular attraction. With increase in temperature, ultrasonic velocity as well as viscosity decreases, where as free volume increases. Thermal energy of the molecules increases with temperature, hence available free volume should be more.

Acoustic impedance is given by,

$$Z = U.\rho.$$

0.4000	0.1999	1.231	1.179	1.130	1.083	1.2278	1.1376	1.0326	0.9736
0.4998	0.1001	1.231	1.179	1.129	1.083	1.2413	1.1779	1.0630	0.9903
0.5997	0.0000	1.229	1.175	1.126	1.079	1.2523	1.2031	1.0729	0.9943

Table – 5.2: Values of Adiabatic compressibility (β) and free length (Lf) of mixtures at 288k, 298k, 308k and 318.

Mole fraction		Adiabatic compressibility (β) ($10^{-10} \text{N}^{-1} \cdot \text{m}^2$)				Free length (Lf) (10^{-10}m)			
X1	X3	288K	298K	308K	318K	288K	298K	308K	318K
0.0000	0.6000	6.044	6.501	6.884	7.3932	0.4819	0.5049	0.5303	0.5522
0.0999	0.4999	5.974	6.414	6.853	7.3844	0.4791	0.5015	0.5291	0.5519
0.1998	0.4001	5.884	6.366	6.818	7.3724	0.4755	0.4997	0.5278	0.5515
0.3001	0.3000	5.797	6.300	6.794	7.351	0.4720	0.4970	0.5268	0.5506
0.4000	0.1999	5.767	6.270	6.754	7.287	0.4708	0.4959	0.5253	0.5483
0.4998	0.1001	5.748	6.236	6.731	7.257	0.4700	0.4945	0.5244	0.5471
0.5997	0.0000	5.728	6.214	6.706	7.227	0.4692	0.4937	0.5234	0.5460

Table –5.3: Values of Viscous relaxation time (τ) & Gibb's free energy (ΔG) of mixtures at 288k, 298k, 308k and 318k

Mole fraction		Viscous relaxation time(τ) (x 10^{-12}s)				Gibb's free energy (ΔG) (x $10^{-20} \text{k.J.mol}^{-1}$)			
X1	X3	288K	298K	308K	318K	288K	298K	308K	318K
0.0000	0.6000	0.841	0.719	0.633	0.563	0.644	0.615	0.596	0.578
0.0999	0.4999	0.851	0.731	0.649	0.590	0.648	0.622	0.607	0.598
0.1998	0.4001	0.858	0.739	0.664	0.602	0.652	0.627	0.616	0.607
0.3001	0.3000	0.865	0.750	0.673	0.617	0.655	0.633	0.622	0.618
0.4000	0.1999	0.876	0.779	0.685	0.625	0.660	0.649	0.630	0.624
0.4998	0.1001	0.889	0.811	0.708	0.638	0.666	0.665	0.644	0.633
0.5997	0.0000	0.901	0.834	0.720	0.646	0.671	0.677	0.651	0.638

Table –5.4: Values of Free volume (Vf) & Internal pressure (Π_i) of mixtures at 288k, 298k, 308k and 318k.

Mole fraction		Free volume (Vf) ($10^{-7} \text{m}^3 \cdot \text{mol}^{-1}$)				Internal pressure(Π_i) (x 10^6N.m^{-2})			
X1	X3	288K	298K	308K	318K	288K	298K	308K	318K
0.0000	0.6000	1.234	1.658	2.105	2.664	474.06	442.89	420.90	399.54
0.0999	0.4999	1.192	1.585	2.000	2.462	481.07	450.89	429.12	410.77
0.1998	0.4001	1.154	1.537	1.914	2.367	487.66	457.12	436.39	417.04
0.3001	0.3000	1.119	1.479	1.855	2.255	493.74	464.06	441.86	425.00
0.4000	0.1999	1.084	1.378	1.782	2.181	500.11	476.88	449.21	430.80
0.4998	0.1001	1.049	1.282	1.678	2.088	506.77	488.86	458.99	438.02
0.5997	0.0000	1.018	1.221	1.626	2.039	512.58	496.38	463.13	440.48

Table – 5.5: Values of acoustic impedance (Z) and attenuation coefficient (α / f^2) of mixtures at 288k, 298k, 308k and 318k.

Table – 5.6: Excess values of adiabatic compressibility (β), free length (Lf) and free volume (Vf) at 288k, 298k, 308k and 318k.

Mole fraction		Adiabatic compressibility(β^E) ($10^{-10} N^{-1}.m^2$)				Free length (L_f^E) (10-10 m)				Free Volume (V_f^E) ($10^{-7} m^3.mol^{-1}$)			
X1	X3	288K	298K	308K	318K	288K	298K	308K	318K	288K	298K	308K	318K
0.0000	0.6000	0.196	0.186	0.042	0.015	0.011	0.011	0.006	0.005	-0.066	-0.115	-0.390	-0.456
0.0999	0.4999	0.148	0.118	0.035	0.033	0.009	0.009	0.006	0.006	-0.103	-0.172	-0.440	-0.568
0.1998	0.4001	0.080	0.087	0.022	0.045	0.007	0.007	0.006	0.007	-0.136	-0.205	-0.473	-0.577
0.3001	0.3000	0.013	0.037	0.019	0.047	0.004	0.006	0.006	0.007	-0.167	-0.249	-0.480	-0.605
0.4000	0.1999	0.006	0.026	0.004	0.010	0.004	0.005	0.005	0.006	-0.196	-0.333	-0.500	-0.594
0.4998	0.1001	0.008	0.009	0.003	0.005	0.004	0.005	0.005	0.006	-0.225	-0.414	-0.552	-0.603
0.5997	0.0000	0.011	0.006	0.001	0.001	0.004	0.005	0.005	0.006	-0.250	-0.458	-0.552	-0.570

Table – 5.7: Excess values of Internal pressure (π_i), Acoustic impedance (Z) and Gibb’s free energy (ΔG) at 288k, 298k, 308k & 318k

Mole fraction		Internal pressure(Π_i^E) (x $10^6 N.m^{-2}$)				Acoustic impedance (Z^E) (x $10^6 Kg.m^2.s^{-1}$)				Gibb’s free energy (G^E) (x $10^{-20} k.J.mol^{-1}$)			
X1	X3	288K	298K	308K	318K	288K	298K	308K	318K	288K	298K	308K	318K

Mole fraction		Acoustic impedance (Z)				Absorption coefficient (α/f^2)			
X1	X3	288K	298K	308K	318K	288K	298K	308K	318K
0.0000	0.6000	1.212	1.165	1.129	1.085	1.2165	1.0746	0.9703	0.8909
0.0999	0.4999	1.217	1.171	1.129	1.082	1.2187	1.0841	0.9920	0.9306
0.1998	0.4001	1.224	1.174	1.129	1.081	1.2203	1.0902	1.0090	0.9467
0.3001	0.3000	1.231	1.178	1.129	1.081	1.2233	1.0990	1.0189	0.9677
0.4000	0.1999	1.231	1.179	1.130	1.083	1.2278	1.1376	1.0326	0.9736
0.4998	0.1001	1.231	1.179	1.129	1.083	1.2413	1.1779	1.0630	0.9903
0.5997	0.0000	1.229	1.175	1.126	1.079	1.2523	1.2031	1.0729	0.9943

0.0000	0.6000	1.34	4.75	18.80	16.31	-0.062	-0.060	-0.047	-0.044	0.026	0.031	0.057	0.055
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0.0999	0.4999	6.00	10.00	22.44	22.10	-0.058	-0.053	-0.047	-0.046	0.032	0.039	0.065	0.071
0.1998	0.4001	10.10	13.34	25.00	22.80	-0.051	-0.050	-0.047	-0.049	0.038	0.043	0.072	0.075
0.3001	0.3000	13.63	17.34	25.69	25.13	-0.046	-0.047	-0.048	-0.049	0.043	0.050	0.075	0.080
0.4000	0.1999	17.65	27.41	28.46	25.49	-0.046	-0.045	-0.047	-0.047	0.050	0.066	0.079	0.081
0.4998	0.1001	21.87	36.55	33.57	27.18	-0.048	-0.045	-0.049	-0.048	0.058	0.084	0.091	0.085
0.5997	0.0000	25.34	41.33	33.13	24.20	-0.050	-0.048	-0.052	-0.052	0.065	0.096	0.095	0.086

Table – 5.8: Excess values of Acoustic impedance (Z) at 288k, 298k, 308k and 318k.

Mole fraction		Acoustic impedance (Z ^E)			
X1	X3	288K	298K	308K	318K
0.0000	0.6000	-0.062	-0.060	-0.047	-0.044
0.0999	0.4999	-0.058	-0.053	-0.047	-0.046
0.1998	0.4001	-0.051	-0.050	-0.047	-0.049
0.3001	0.3000	-0.046	-0.047	-0.048	-0.049
0.4000	0.1999	-0.046	-0.045	-0.047	-0.047
0.4998	0.1001	-0.048	-0.045	-0.049	-0.048
0.5997	0.0000	-0.050	-0.048	-0.052	-0.052

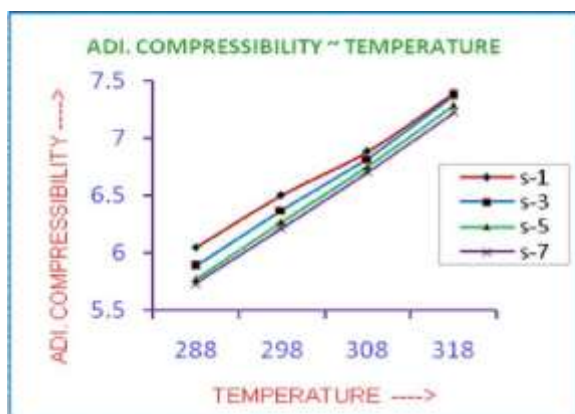


Fig-6.2: Variation of free length with temperature

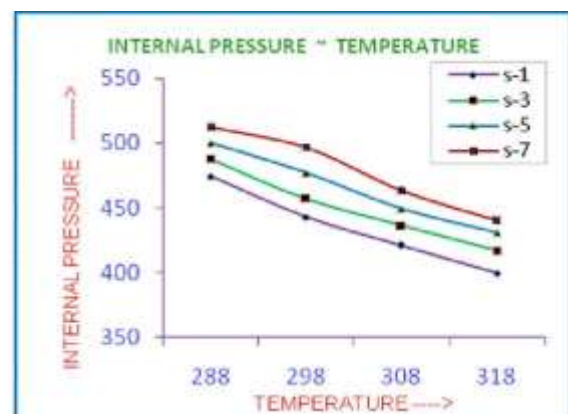


Fig-6.5: Variation of relaxation time with temperature

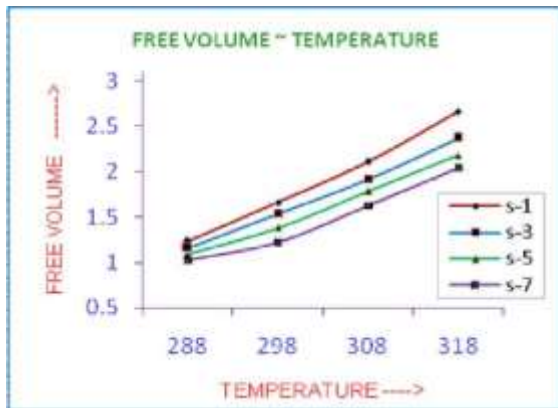


Fig-6.3: Variation of free volume with temperature with temperature

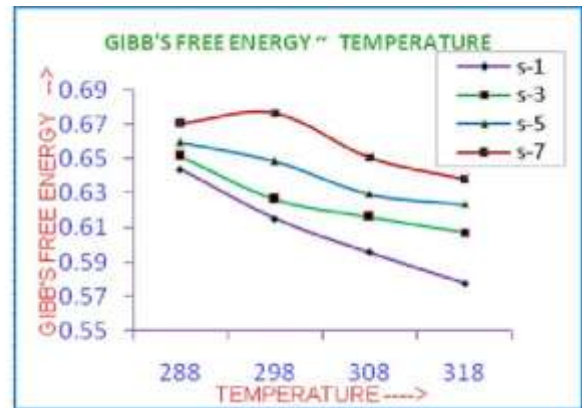


Fig-6.6: Variation of Gibbs free energy with temperature

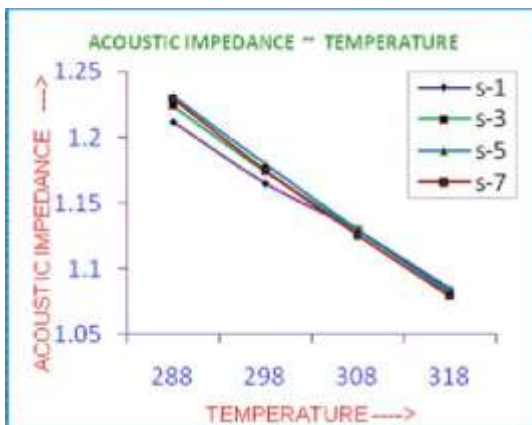


Fig-6.7: Variation of acoustic impedance with temperature.

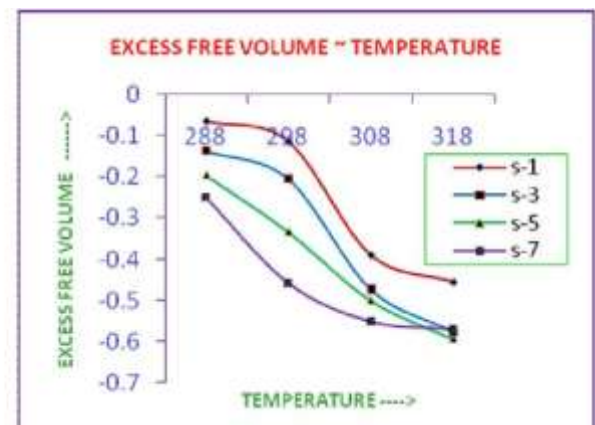


Fig-6.10: Variation of excess free length with Temperature.

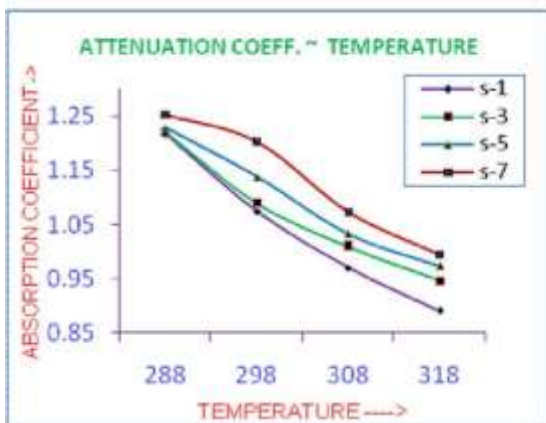


Fig-6.8: Variation of attenuation coefficient with temperature

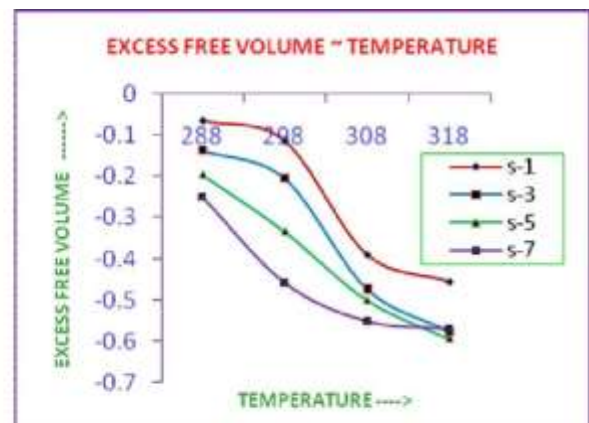


Fig-6.11: Variation of excess free

volume with Temperature

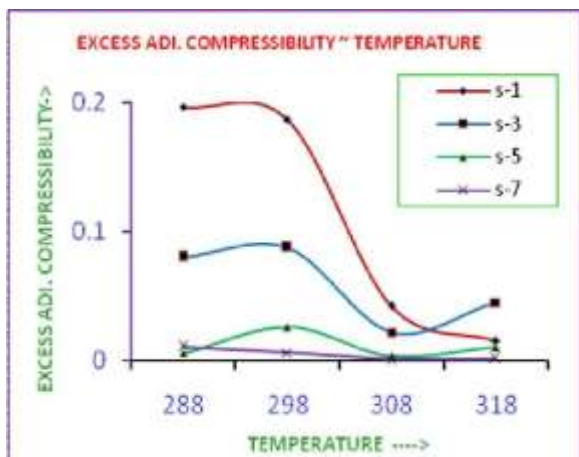


Fig-6.9: Variation of excess adiabatic compressibility with temperature

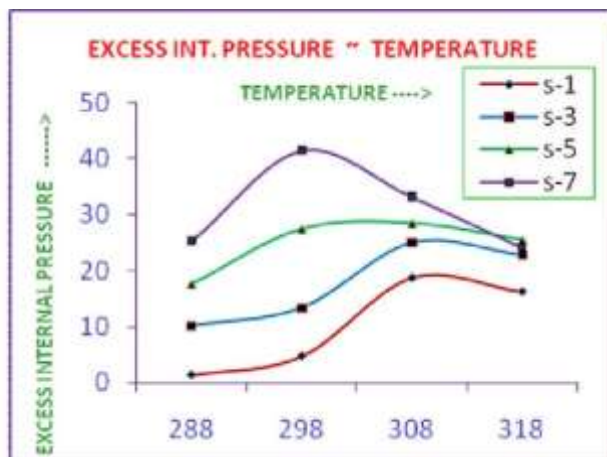


Fig-6.12: Variation of excess int. pressure with temperature

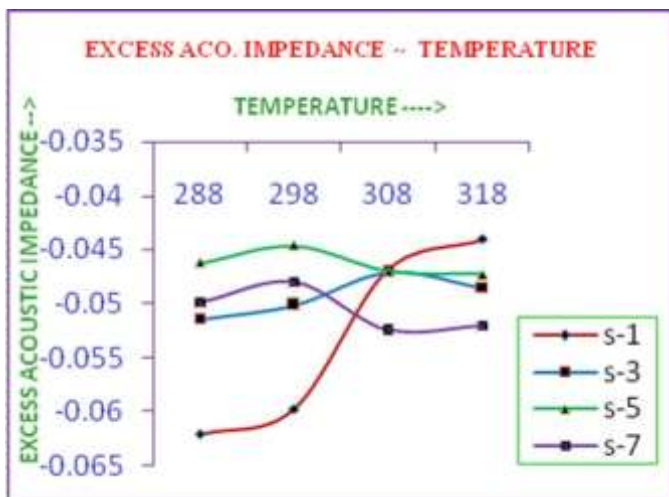


Fig-6.13: Variation of excess relaxation time with temperature.

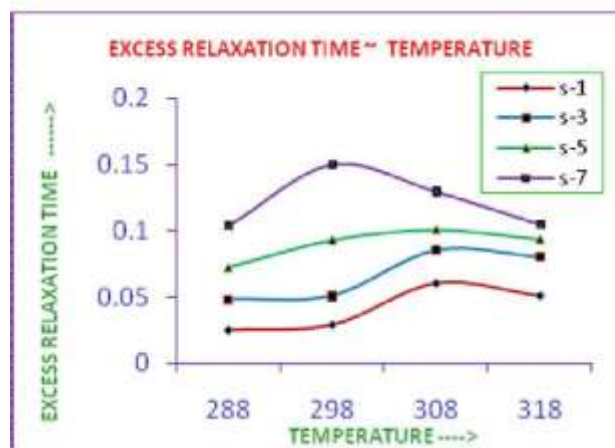


Fig-6.14: Variation of excess Gibbs' free energy with temperature.

Fig-6.15: Variation of excess acoustic impedance with temperature.

With increase in concentration of pyridine, density of the mixture increases and velocity decreases where as acoustic impedance increases very slowly.

This indicates a slower release of pyridine molecules (dipoles) for interaction. Concentration remaining constant, when temperature is increased, acoustic impedance decreases. This decrease in acoustic impedance indicates the possibility of significant interaction between the component molecules. Acoustic impedance is also used for assessing the absorption of sound in medium

Attenuation coefficient is given by,

$$\alpha / f^2 = 8\pi^2\eta / 3\rho U^2$$

Variation in the attenuation coefficient is a measure of spatial rate of decrease in the intensity level of the ultrasonic wave. When concentration of DMF increases the attenuation coefficient increases and the wave is more and more attenuated.

When concentration of pyridine is low, excess value of adiabatic compressibility and excess value of free length are positive and gradually decreases with increase in concentration of pyridine. This confirms that, initially the intermolecular interactions are low¹⁷⁻¹⁸ and gradually increases with concentration of pyridine. With increase in temperature, excess values of adiabatic compressibility and excess values of free length are positive and small indicating weak interaction. Excess negative value of free volume indicates the contraction in volume. The excess internal pressure is positive confirming the fact that excess free volume and excess internal pressure must be of converse nature to each other.

The excess value of acoustic impedance is negative. It becomes less and less negative with increase of temperature and also with decrease in concentration of pyridine indicating that the intermolecular interaction becomes weaker and weaker.

5. Conclusion

There exists a dipole-dipole interaction between DMF and pyridine. Since pyridine molecules are spherical in shape and monomers, the intramolecular interaction dominates intermolecular interaction. Thus, when concentration of DMF increases and that of pyridine decreases free volume decreases and the waves get more and more

attenuated. The elevation of temperature however facilitates an agitation in thermal energy resulting in an increase in the molecular separation in the liquid mixtures.

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