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Acoustical Studies of Ternary Mixtures at Different Temperatures

KEYWORDS: Adiabatic compressibility, free length, molar volume, ultrasonic velocity, benzaldehyde

Senthamil Selvi C
Department of Physics, Sathyabama University, Chennai

Ravichandran S
Department of Physics, Sathyabama University, Chennai

ABSTRACT *Density, viscosity and ultrasonic velocity have been measured for the ternary mixtures of benzaldehyde with acetone in hexane solution in the concentration range from 1x10^{-2}M to 1x 10^{-3}M-powers should be in superscript at 293,298,303 and 308K. From these data, adiabatic compressibility (κ), free length (L_{f-}), acoustic impedenca(Z) and internal pressure(π_{i-}) have been computed. The observed variation of these parameters helps in understanding the nature of solute-solvent interactions present in the system. The molecular interactions existing between the components are also discussed.*

INTRODUCTION

Ultrasonic investigations of ternary liquid mixtures are of considerable importance in understanding the intermolecular interactions between the component molecules and find applications in several industrial and technological processes. The ultrasonic speed and thermodynamic data derived from it has been widely used for this purpose [1]. The ultrasonic studies find extensive applications in characterizing aspects of physic-chemical behavior involving intermolecular interactions in several liquid mixtures. The study of molecular interaction in the liquid mixtures is considerable in the elucidation of the structural properties of the molecules [2]. Since, acoustic parameters provide a better insight into molecular environment to liquid mixtures, it seemed important to study molecular interactions which motivated the authors to carry out the present investigation in the ternary liquid mixtures of benzaldehyde with acetone in hexane using ultrasonic technique.

EXPERIMENTAL

All compounds used in the present work were of AnalaR grade samples and were purified before use in accordance with the procedure described elsewhere [3]. The solvent has taken as accurately weighted amount of sample was dissolved in suitable solvent to obtain solution in the concentration range 1x10^{-3}M – 1x10^{-2}M. The ultrasonic velocity (U) have been measured in ultrasonic interferometer (Model F81) supplied by Mittal enterprises, New Delhi operating at a frequency of 2MHZ with an accuracy of ±0.1%.

RESULTS AND DISCUSSION

TABLE- 1
ACOUSTICAL STUDIES VALUES OF TERNARY MIXTURES AT DIFFERENT TEMPERATURES

Conc. (M)	Density (ρ) Kgm^{-3}				Viscosity(η) 10^{-3}Nsm^{-2}				Velocity(U) ms^{-1}			
	293K	298K	303K	308K	293K	298K	303K	308K	293K	298K	303K	308K
0.001	678.2	667.7	670.1	670.3	0.5353	0.5068	0.5249	0.4951	1103.2	1087.2	1061.1	1049.3
0.002	675.6	667.0	669.2	670.1	0.5245	0.5057	0.5126	0.5024	1099.4	1090.5	1062.5	1050.9
0.003	677.6	667.1	669.6	671.2	0.5279	0.5073	0.5030	0.5073	1104.0	1090.2	1058.1	1049.0
0.004	677.1	667.3	669.8	670.9	0.5275	0.5084	0.5006	0.5030	1103.1	1090.7	1061.6	1047.5
0.005	676.7	667.4	668.9	671.6	0.5313	0.4982	0.5065	0.5164	1104.1	1089.4	1059.6	1048.6
0.006	673.4	667.2	668.8	670.7	0.5296	0.5027	0.4968	0.4938	1103.4	1087.5	1058.1	1049.0
0.007	673.2	667.5	669.3	670.5	0.5249	0.5030	0.5068	0.4980	1100.9	1086.5	1053.4	1049.9
0.008	677.0	667.6	667.1	671.3	0.5255	0.5015	0.5042	0.5005	1104.2	1090.8	1053.5	1045.4
0.009	675.7	667.8	668.8	670.4	0.5107	0.5032	0.5055	0.5145	1105.5	1086.1	1059.7	1047.9
0.010	680.5	667.9	669.0	671.2	0.5254	0.5017	0.5016	0.5042	1105.8	1087.5	1058.7	1048.2
Conc.	Adiabatic compressibility(k) 10^{-10} Kg^{-1}ms^{2}				Free length (L_f) 10^{-10}m				Free Volume(V_f) 10^{-7} m^3 mol^{-1}			
0.001	12.12	12.67	13.25	13.55	0.6961	0.7119	0.7281	0.7362	2.6731	2.8385	2.597	2.788
0.002	12.25	12.61	13.24	13.51	0.6999	0.7101	0.7277	0.7352	2.7422	2.8612	2.696	2.733
0.003	12.11	12.61	13.3	13.54	0.6959	0.7103	0.7305	0.7359	2.7325	2.8462	2.757	2.686

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0.004	12.14	12.60	13.25	13.58	0.6968	0.7098	0.7279	0.7371	2.7322	2.8392	2.790	2.715
0.005	12.12	12.63	13.32	13.54	0.6963	0.7106	0.7298	0.7360	2.7066	2.9211	2.734	2.615
0.006	12.20	12.67	13.36	13.55	0.6985	0.7120	0.7309	0.7362	2.7166	2.8743	2.808	2.797
0.007	12.26	12.69	13.47	13.53	0.7002	0.7125	0.7339	0.7357	2.7438	2.8683	2.707	2.765
0.008	12.12	12.57	13.51	13.63	0.6961	0.7096	0.7350	0.7384	2.7513	2.8981	2.729	2.727
0.009	12.11	12.69	13.32	13.58	0.6960	0.7126	0.7298	0.7371	2.8771	2.8648	2.742	2.626
0.010	12.02	12.66	13.34	13.56	0.6933	0.7116	0.7304	0.7365	2.7582	2.8829	2.770	2.708
Conc.	Internal pressure (π_i) 10^8 atm				Molar Volume(V_m) 10^{-4} m^3 mol^{-1}				Available volume(V_a) 10^{-5}			
0.001	2.992	2.952	3.099	3.078	1.2707	1.2907	1.2861	1.2857	3.946	4.137	4.332	4.425
0.002	2.959	2.942	3.058	3.097	1.2756	1.2920	1.2878	1.2860	3.991	4.114	4.326	4.414
0.003	2.969	2.948	3.037	3.119	1.2718	1.2918	1.2870	1.2839	3.943	4.116	4.359	4.422
0.004	2.967	2.951	3.025	3.107	1.2728	1.2915	1.2867	1.2845	3.953	4.111	4.330	4.436
0.005	2.976	2.923	3.043	3.148	1.2735	1.2912	1.2883	1.2831	3.947	4.121	4.351	4.422
0.006	2.962	2.939	3.016	3.076	1.2797	1.2916	1.2885	1.2848	3.972	4.137	4.364	4.425
0.007	2.952	2.942	3.055	3.087	1.2800	1.2910	1.2875	1.2852	3.993	4.143	4.398	4.419
0.008	2.960	2.932	3.040	3.104	1.2728	1.2908	1.2917	1.2837	3.944	4.108	4.412	4.449
0.009	2.913	2.944	3.040	3.140	1.2753	1.2904	1.2884	1.2854	3.941	4.144	4.351	4.435
0.010	2.968	2.938	3.030	3.111	1.2663	1.2902	1.2880	1.2838	3.911	4.133	4.358	4.428

In all the mixtures, the ultrasonic velocity (U) decreases with increase in concentration. It is observed that as the number of hydrocarbon group or chain-length of benzaldehyde increases, a gradual decrease in sound velocity is noticed. As hexane is weakly polar molecule, interactions are possible between benzaldehyde with acetone in hexane, whereas the interactions of acetone with any one of the other two is not so favored. This is further supported by the decreasing velocity trend with increasing the concentration. Table 1 indicates that the sound velocity and density in the ternary liquid system increases. This trend suggests the possibility of intermolecular interactions between the components of the system. As the medium becomes more and more compact, velocity shows nonlinear behavior is observed in the system.

The value of adiabatic compressibility (κ) shows an inverse behavior as compared to the ultrasonic velocity (U). It is primarily that the compressibility increases due to structural changes of molecules in the mixture leading to a decrease in ultrasonic velocity[4]. Such a continuous increase in adiabatic compressibility with respect to the increase of molar concentration has been qualitatively ascribed to the effect of hydrogen bonding or dipole-dipole interactions[5]. The increase in adiabatic compressibility (κ) with increasing concentration of benzaldehyde indicate significant interaction between acetone and benzaldehyde forming dipole-dipole interactions. L_f decreased with the increase in concentration due to the increasing the number of ions in a given volume or due to increase in compressibility.

TABLE- 2
ACOUSTICAL DERIVED VALUES OF TERNARY MIXTURES AT DIFFERENT TEMPERATURES

Conc.	Impedence(Z) $10^5 Kg^{-1}$ m^2 s^{-1}				Relaxation time(ζ) 10^{-13}S				Interaction parameter(χ_i)			
	293K	298K	303K	308K	293K	298K	303K	308K	293K	298K	303K	308K
0.001	7.482	7.259	7.110	7.0335	8.6471	8.5627	9.2753	8.9443	0.0519	0.0216	-0.0269	-0.0484
0.002	7.428	7.274	7.110	7.0421	8.5633	8.5004	9.0477	9.0520	0.0445	0.0277	-0.0244	-0.0456
0.003	7.481	7.273	7.085	7.0409	8.5226	8.5312	8.9458	9.1580	0.0532	0.0270	-0.0326	-0.0492
0.004	7.469	7.278	7.111	7.0277	8.5366	8.5389	8.8430	9.1108	0.0517	0.0282	-0.0259	-0.0516
0.005	7.471	7.271	7.088	7.0424	8.5873	8.3869	8.9923	9.3229	0.0531	0.0253	-0.0300	-0.0501
0.006	7.430	7.256	7.077	7.0356	8.6135	8.4949	8.8461	8.9209	0.0517	0.0216	-0.0329	-0.0495
0.007	7.411	7.252	7.050	7.0396	8.5784	8.5106	9.0985	8.9848	0.0468	0.0196	-0.0416	-0.0479
0.008	7.475	7.282	7.028	7.0178	8.4891	8.4176	9.0799	9.0964	0.0530	0.0276	-0.0415	-0.0562
0.009	7.470	7.253	7.087	7.0251	8.2458	8.5168	8.9741	9.3184	0.0554	0.0186	-0.0303	-0.0518
0.010	7.525	7.263	7.083	7.0355	8.4189	8.4688	8.9190	9.1156	0.0558	0.0212	-0.0322	-0.0513

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The increase in free length in 303 and 308K suggests that there is weak interaction between the components. The values of intermolecular free length in a ternary mixture depend on concentration and temperature. At a given concentration for ternary systems, intermolecular free length increases with increase in temperature may be due to the weakening of intermolecular attraction due to thermal agitation. At a given temperature, intermolecular free length either increases or decreases with concentration depending upon the components of the liquid mixtures. The character that determines this restriction/backward movement of sound waves is known as acoustic impedance (Z).As anticipated; acoustic impedance appears almost reciprocal to adiabatic compressibility. Free volume (V_f), is the average volume into which the molecules can move due to the repulsion by the surrounding molecule [6].

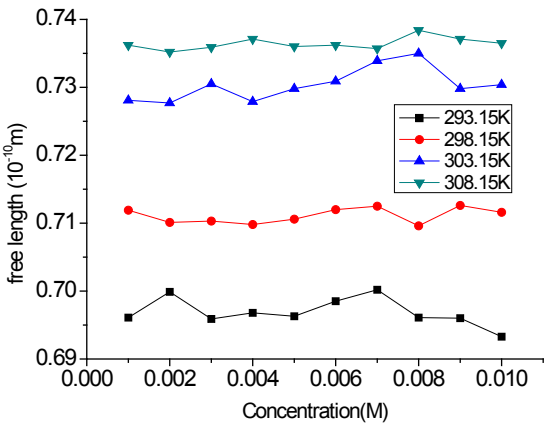

Fig. 1 free length versus concentration

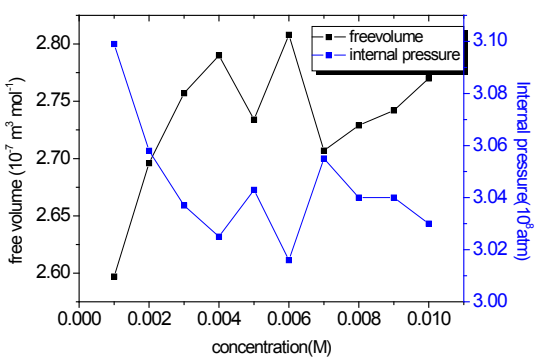

Fig. 2. internal pressure versus free volume

As the concentration increases, the free volume (V_f) decreases whereas the internal pressure (π_i) increases. This suggests that the close packing of molecules inside the shield, which may brought about by the increasing magnitude of interactions[7]. The increase in free volume indicates weak intermolecular attraction between dissimilar molecules. After the formation of a complex there may be a wide gap or weak bond between two solvent molecules which might have led to increased free volume. This increase indicates the removal of initially occupied solvent molecules on an ion by the incoming solvent molecules. Molar volume (V_m) reflects the specific variation with components of the mixture. Fig. 2 shows the comparison of free volume and internal pressure and it is in reverse trend.

Acoustic impedance (Z) values decrease with increasing concentration of benzaldehyde. And also, it is found that the acoustic impedance decreases with increase in temperature. Such a decreasing values of acoustic impedance (Z) further supports the possibility of strong molecular interactions due to dipole-dipole interaction between benzaldehyde and acetne at 293 and 298K. Moreover, molar volume (V_m) is also increases with rise in temperature. The available volume (V_a) is increases with increase in concentration. The values of relaxation time (ζ) increases with increase in concentration. It depends upon the size and shape of the rotating molecular entities in the solution.

The relaxation time (ζ) is the intrinsic properties of a charge transfer complex. These properties are almost constant. Molecular interaction parameter (χ_i) values as a function of ultrasonic velocity are calculated for the ternary system. Positive values of molecular interaction parameter for all composition at 293 and 298K indicate presence of strong attractive forces between components. The values are both positive and negative in certain concentration range for some systems, indicating strong molecular interactions in these cases.

CONCLUSIONS

The free length (L_f) increases with increase in the concentration of solute at 303 and 308K indicating that there is a weak solute-solvent interaction. The increase in intermolecular free length at 0.005M, indicates the weak interaction between the solute and solvent molecules due to which the structural arrangement in the neighborhood of constituent ions (or) molecules gets affected considerably. This may also imply the increase in number of free ions, showing the occurrence of ionic dissociation due to weak solute-solute interaction, while the free length (L_f) in the percentage of organic solvent indicating solute-solvent interaction.

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