International Journal of Current Research in Chemistry and Pharmaceutical Sciences
www.ijcrcps.com Volume 1 Issue: 4 2014 Pages:24-30

(p-ISSN: 2348-5213; e-ISSN: 2348-5221)

RESEARCH ARTICLE

DETERMINATION OF ACOUSTIC PARAMETERS AND UNDERSTANDING THE INTERMOLECULAR INTERACTIONS OF THE SULFOLANE-HALOMETHANE BINARY SYSTEMS.

B.GANESHBABU[1], AND P.S.RAGHAVAN[2]

[1]Department of Chemistry, Ramakrishna Mission Vivekananda College, (Autonomous) Mylapore, Chennai-600 004, Tamilnadu ,India
[2]Department of Chemistry, Madras Christian College, (Autonomous) Tambaram, Chennai-600 059, Tamilnadu, India.

Corresponding Author: ps_raghavan@rediffmail.com

Abstract

The ultrasonic velocity, density and viscosity were measured for the binary mixtures of sulfolane-dichloromethane, sulfolane-chloroform and sulfolane- carbon tetrachloride binary mixture at 303K. These experimental data have been used to calculate the acoustical parameters, namely adiabatic compressibility (ß) free volume, free length, internal pressure and absorption coefficient. From the acoustical parameter values, the nature and the quality of molecular interaction have been deduced.

Keywords: Ultrasonic velocity, sulfolane, halomethane, density, viscosity

Introduction

Solvent parameters such as its nature, structural features, dielectric constant, polarity, etc, play very important role in many reactions(Erwin Buncel et al., 2003). However, as the solubility of many substances are limited in a given solvent, very often the use of binary mixture of solvents having complementary characteristics have become important. Under such circumstances, the physical interaction of the components in the binary mixture might alter the properties of the individual components and hence influence the reaction differently. For example, in sulfolane – water binary mixture the highly unusual protonated hydronium dication H_4O^{2+} has been shown to exist(Jean-Claude Bollinger et al., 1987). Thus, a well informed knowledge about interactions in the mixed solvent system is highly helpful to design the experiments and understand the course of reaction.

The nature of interactions in solvent systems and over all idea about their liquid structural features could be ascertained by the ease with which the velocities of ultrasonic waves are transmitted in these liquids and the viscosity of the binary mixture(Jagan Nath et al., 1990; Robert Amme et al., 1957;Manoj Ku Praharaj et al., 2012; Sumathi et al., 2012; Kannappan et al., 2008) . Sulfolane, a weakly basic aprotic solvent with high dielectric constant exhibits(Edward M. Arnett et al., 1964) many unusual properties and hence this paper concerns with the measurment of ultrasonic velocity, density and viscosity of binary mixtures consisting of sulfolane, an alicyclicdiketone solvent, and any one of the halomethanes, viz: methylenechloride (CH_2Cl_2), chloroform ($CHCl_3$) and carbon tetrachloride (CCl_4).

Experimental

The chemicals used in the present work were of analytical grade with minimum assay of 99.9% (sd fine chemicals India and Merck, Germany). The densities of pure liquid and liquid mixtures were determined using a specific gravity bottle by relative measurement method with an excellent (+/- 0.0001g/ml) reproducibility. An Oswald's viscometer of 10 mL capacity was used for the viscosity measurement of pure liquids and liquid mixtures and efflux time was determined using a digital chronometer to within +/-0.01s. Ultrasonic interferometer (Mittal enterprises, New Delhi) having the frequency 2 MHZ with an overall accuracy of 2 ms^{-1} has been used for velocity measurement. An electronically controlled digital temperature bath (RAAGA Industries, Chennai) has been used to circulate water through the double walled measuring cell made up of steel containing experimental mixtures at the desired temperature. The accuracy in the temperature measurement is 0.1K.

In a typical experiment, appropriate volume of the chosen halomethane was mixed with a predetermined volume of sulfolane and the ultrasonic velocity, viscosity and density were measured. By changing the volume of liquids, different compositions of the mixture were prepared and the above physical parameters were determined. From the experimental data of ultrasonic velocity (U),density (ρ), viscosity (η), the acoustical parameter such as internal pressure (π_i), free volume (V_f), free length(L_f), adiabatic compressibility(β) and absorption coefficient (α/f^2),were calculated using the reported equations(Kubendran et al., 2007; Pandey et al., 1999).

Results and Discussion

The three physical parameters – ultrasonic velocity, density and viscosity have been experimentally determined for the pure liquids, viz: Sulfolane ,carbon tetrachloride, chloroform and dichloromethane as well as for the binary mitures of sulfolane with each of these halomethanes. The data are presented in tables 1,2, and 3. First to understand the intermolecular interactions in the pure liquids, the corresponding data for pure liquids alone are discussed below.

The data in table-1 reveal that sulfolane posseses markedly different values. High value of velocity as well as viscosity indicates significant intermolecular interaction in sulfolane. Among the halomethanes CCl_4 being a symmetric tetrahedral molecule has a zero dipole moment while $CHCl_3$ and CH_2Cl_2 would have relatively higher dipole moment due to the introduction of the electronegative chlorine atom. On the other hand sulfolane with its diketonic structure could exist in canonical forms as shown in scheme1.

Thus, CCl_4 would have the least possible Vander Waal's intermolecular forces, followed by $CHCl_3$ and CH_2Cl_2. Sulfolane due to its ionic canonical contribution,(scheme 1) would involve stronger electrostatic intermolecular forces. Consequently the ultrasonic velocity values also run parallel to the intermolecular forces and follow the order

$$CCl_4 < CHCl_3 < CH_2Cl_2 < \text{sulfolane}$$

Besides, the repulsion of the possible anionic canonical forms of sulfolane would keep the molecules at a distance and hence the density,(number of sulfolane molecules per unit volume) is the least among the four solvents studied.

Physical parameters of binary mixtures

It is obvious from the data in table 1 that the velocity and viscosity of the binary mixtures decrease appreciably with increase in mole fraction of CH_2Cl_2 while a reverse trend is observed for density. A similar variation has been noted for both $CHCl_3$ – sulfolane and CCl_4- sulfolane binary mixtures also (table 2 and 3). It is quite interesting to observe that the density of the binary mixtures of sulfolane with CH_2Cl_2 is marginally affected while those with $CHCl_3$ and with CCl_4 progressively increases. This suggests that the packing (ie) number of molecules per unit volume is increasing in both $CHCl_3$ and CCl_4 – sulfolane systems, packing becomes tightened on increasing sulfolane content. Obviously, CCl_4 with zero dipolemoment, involving only attractive vander wall's intermolecular force would reduce the ionic repultion in sulfolane and be packed tightly. The monotonous decreases in velocity and viscosity value of the mixtures with increase in halomethane content, inspite of the increase in density, reveals that the effective strength of molecular interactions in these solvent mixtures follow the order

$$A\text{-}A < B\text{-}B < A\text{-}B$$

where A is sulfolane and B represents any of the three halomethanes.

Scheme 1

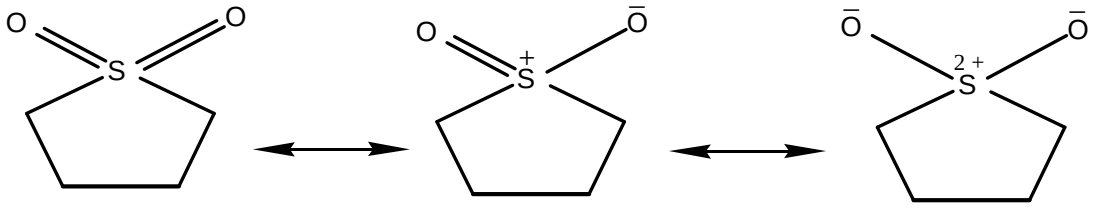


Table-1 Physical parameters of the CH_2Cl_2 -sulfolane binary mixtures

Molefraction of CH_2Cl_2	Ultrasonic velocity m/sec	Density (g/ml)	Viscosity (mPa.s)
0.000	1590	1.265	10.07
0.058	1568	1.239	5.35
0.271	1461	1.256	2.97
0.498	1339	1.270	1.88
0.691	1240	1.235	1.19
0.856	1142	1.290	1.07
0.973	1074	1.310	1.02
1.000	1059	1.330	0.39

Table-2 Physical parameters of the $CHCl_3$ -sulfolane binary mixtures

Molefraction of $CHCl_3$	Ultrasonic velocity m/sec	Density (g/ml)	Viscosity (mPa.s)
0.000	1590	1.265	10.07
0.049	1547	1.256	7.05
0.229	1438	1.300	4.83
0.441	1311	1.337	2.93
0.640	1182	1.381	2.01
0.826	1080	1.402	1.51
0.966	998	1.463	1.35
1.000	997	1.472	0.55

Table-3 Physical parameters of the CCl_4 -sulfolane binary mixtures

Molefraction of CCl_4	Ultrasonic velocity m/sec	Density (g/ml)	Viscosity (mPa.s)
0.000	1590	1.265	10.07
0.039	1563	1.287	9.02
0.197	1441	1.342	6.47
0.396	1292	1.409	4.26
0.596	1132	1.500	2.22
0.797	962	1.550	1.99
0.959	932	1.577	1.66
1.000	913	1.587	0.80

Thus the entire binary solvent mixture might be visualized as islands of halomethanes floating in a sea of sulfolane at higher sulfolane content and vice versa at lower sulfolane compositions.

Acoustic parameters of the pure liquids

The experimentally determined physical parameters have been used to derive the acoustic parameters such as the internal pressure, free volume, free length, adiabatic compressibility and absorption coefficient. The derived acoustical parameters are listed in table-4.

The internal pressure of the pure liquids follow the order sulfolane > CH_2Cl_2 >$CHCl_3$ > CCl_4, which is in line with our earlier conclusion that the intermolecular attractive forces are greater in sulfolane and least in CCl_4. As the intermolecular attraction is greater in sulfolane, obviously the free length (i.e) intermolecular distance, free volume and adiabatic compressibility are low. This is also further correlated with a higher absorbtion coefficient value for sulfolane. The well knitted liquid structure of sulfolane, due to strong intermolecular attraction would facilate absorbtion rather than transmission of ultrasonic sound.

Acoustic parameters of the halomethanes-sulfolane binary mixtures

The acoustic parameters calculated for halomethane -sulfolane binary mixtures are given in table-5,6, and 7.

Table-4 Acoustic parameters of the pure liquids

Liquid	Internal pressure π_i x10^3 (atm)	Free volume V_f x10^{-03} m^2mol^{-1}	Free length L_f x10^{-09} m	Adiabatic Compressibilty βx10^{-7} $Kg^{-1}ms^2$	Absorbtion coefficient α/f^2 10^{-11} NPm^{-2}
CH_2Cl_2	1.35	12.51	1.63	6.72	0.651
$CHCl_3$	1.19	11.38	1.64	6.86	0.990
CCl_4	1.17	8.32	1.72	7.55	1.74
sulfolane	3.63	0.295	1.11	3.14	5.23

Table-5 Acoustic data for CH_2Cl_2 –sulfolane binary mixtures

Molefraction of CH_2Cl_2	Internal pressure π_i x10^3 (atm)	Free volume V_f x10^{-7} m^2mol^{-1}	Free length L_f x10^{-9}m	Adiabatic Compressibilty βx10^{-7} $Kg^{-}ms^2$	Absorbtion coefficient α/f^2 10^{-11} $NPm^{-}{}_s^2$
0.000	3.63	0.295	1.11	3.14	5.23
0.058	2.68	0.727	1.14	3.28	2.94
0.271	2.25	1.437	1.21	3.73	1.99
0.498	2.06	2.224	1.32	4.39	1.62
0.691	1.81	3.582	1.44	5.27	1.32
0.856	1.98	3.371	1.53	5.96	1.46
0.973	2.12	3.096	1.62	6.64	1.64
1.000	1.35	12.51	1.63	6.72	0.68

Table-6 Acoustic data for $CHCl_3$ –sulfolane binary mixtures

Molefraction of **$CHCl_3$**	Internal pressure **π_i x10^3 (atm)**	Free volume **V_f x10^{-3} m^2mol^{-1}**	Free length **L_f x10^{-9} m**	Adiabatic Compressibilty **βx10^{-7} $Kg^{-1}ms^2$**	Absorbtion coefficient **α/f^2 10^{-11} $NPm^{-}{}_s^2$**
0.000	3.63	0.295	1.11	3.14	5.23
0.047	3.07	4.83	1.15	3.33	3.99
0.229	2.70	7.63	1.21	3.72	3.28
0.441	2.24	1.40	1.31	4.35	2.56
0.640	2.01	2.10	1.43	5.19	2.32
0.826	1.84	2.81	1.55	6.12	2.26
0.966	1.86	2.96	1.64	6.86	2.44
1.000	1.19	11.38	1.64	6.86	0.96

Table-7 Acoustic data for CCl_4 –sulfolane binary mixtures

Molefraction of **CCl_4**	Internal pressure **π_i x10^3 (atm)**	Free volume **V_f x10^{-3} m^2mol^{-1}**	Free length **L_f x10^{-9} m**	Adiabatic Compressibilty **βx10^{-7} $Kg^{-1}ms^2$**	Absorbtion coefficient **α/f^2 10^{-11} $NPm^{-}{}_s^2$**
0.000	3.63	2.95	1.11	3.14	5.23
0.039	3.46	3.45	1.12	3.18	4.82
0.197	2.93	5.36	1.20	3.69	4.35
0.396	2.48	9.20	1.29	4.25	3.68
0.596	1.83	2.16	1.46	5.45	2.80
0.797	1.87	2.14	1.65	6.97	3.79
0.959	1.69	2.83	1.71	7.43	3.47
1.000	1.17	8.32	1.72	7.55	1.73

Fig 1 Plot of ultrasonic velocity Vs molefraction of Halomethane

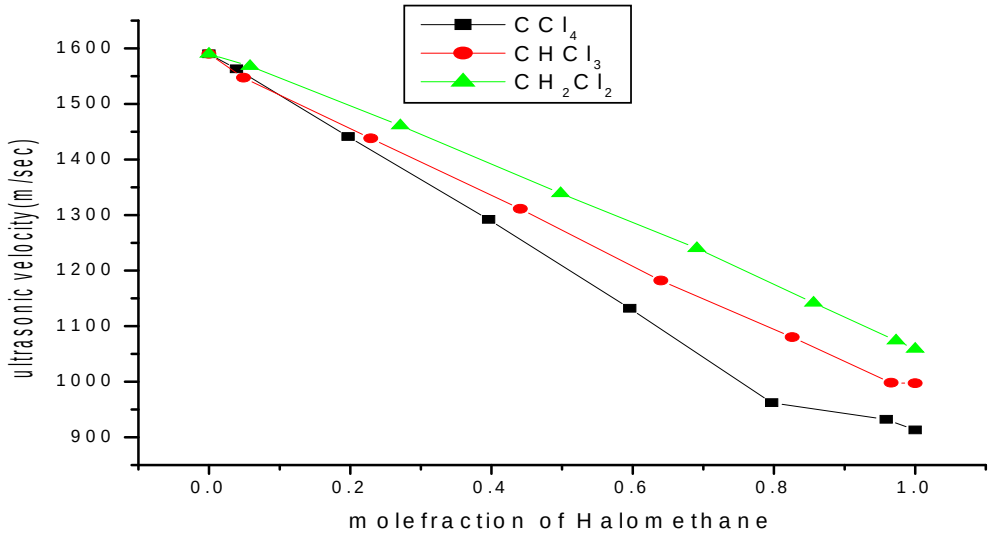
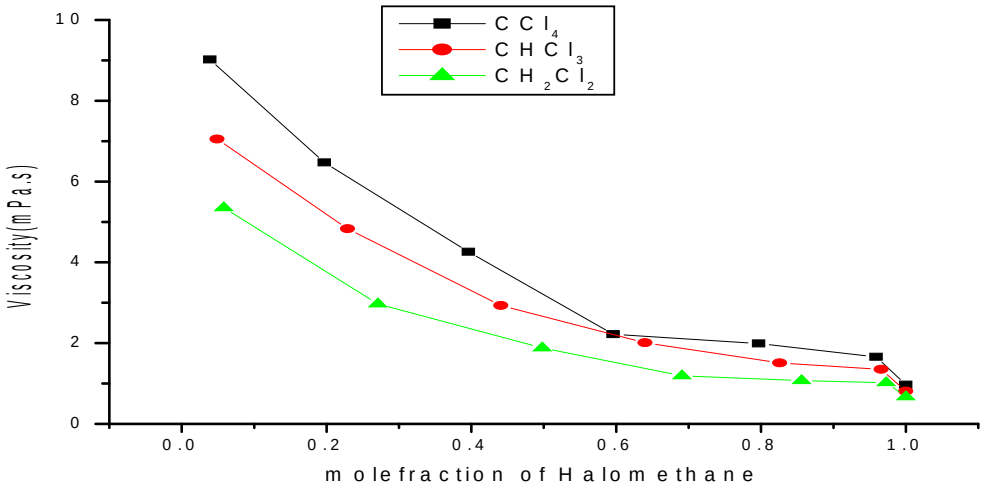


Fig 2 Plot of Viscosity Vs molefraction of Halomethane



The CH_2Cl_2-sulfolane mixtures (table-5) involve decreasing intermolecular interaction as indicated by the continuous decrease in internal pressure with increasing CH_2Cl_2 content. Decrease in internal pressure is usually accompanied by an increase in free volume.However such a straight relation is not observed; instead, upto a certain amount of halomethane added (about 23% for $CHCl_3$ and 40% for CCl_4) free volume increases as expected but further increase in addition of halomethane drastically reduces the free volume. This may be ascribed to the fact that the addition of higher mole fraction of halomethane with lower polarity would replace the strong electrostatic intermolecular forces between sulfolane molecules with much weaker forces and thus reducing both the internal pressure and the free volume. Obviously, with decrease in intermolecular forces the liquid structure would become loosend and hence an increase in compressibility accompanied with corresponding increase in sound velocity absorption resulted. Thus the data in table-5 are straightforward in indicating the well-knit liquid structure of the CH_2Cl_2 -sulfolane binary mixtures with increase in sulfolane composition.

The trend in acoustic data for the $CHCl_3$- sulfolane (table-6) and CCl_4- sulfolane (table-7) are also very much similar to that for the CH_2Cl_2 -sulfolane mixture.

Comparatively the CH_2Cl_2 –sulfolane system has a higher ability to transmit ultrasonic velocity and the CCl_4- sulfolane, the least (fig 1). From the viscosity profile shown in fig-2 it is noted that addition of any one of these halomethanes progressively reduced the viscosity of sulfolane, directly corroborating our inference that strong molecular interaction forces are replaced with weak forces on increasing the halomethane content in the binary mixture.

Conclusion

Among the four liquids studied, sulfolane emerges as a good ultrasonic sound transmitter while CCl_4 has the least capacity. Besides, comparing the experimental data for the liquids and the binary mixtures it is understood that the intermolecular interactions between sulpholane molecules predominates over that between any of the three halomethanes studied and the strong interaction forces between sulfolane molecules are replaced with weak forces on progressive addition of halomethanes to sulfolane.

References

Edward M. Arnett and Charles F. Douty, 1964. J. Am. Chem. Soc. 86(3): 409.

Erwin Buncel, Robert A. Stairs and Herald Wilson,. 2003. “The role of solvent in chemical reactions”, Oxford University Press, I Ed.

Jagan Nath and Renu Saini. 1990.J. Chem. Soc. Faraday Trans. 86: 645.

Jean-Claude Bollinger, Rene Fause and Theophile Yvernault, 1987. Chem.Phys. Lett., 140(6): 579.

Kannappan, A.N, Kesavasamy R , and Ponnusamy, V. 2008. American. J. Eng Appl. Sci. 1 (2):95.

Kubendran , T. R. and Baskaran, R. 2007. Int. J. Appl. Sci. Eng.2: 115.

Manoj Ku Praharaj, Abhiram Satapathy, Prativarani Mishra and Sarmistha Mishra. 2012.

Pandey, J.D., Dubey, G. P and Tripathi, N., 1999. Proc. Indian Acad. Sci.(Chem. Sci.) 111(2):361.
Robert Amme and Sam Legvold, 1957. J. Chem. Phys. 26: 514.
Sumathi, T., and Govindarajan, S..2012. IJBPAS.1:1153.

