Available online at www.elixirpublishers.com (Elixir International Journal)

Ultrasonics

Elixir Ultrasonics 95 (2016) 41252-41255

ISSN: 2229-712X

Validity of Velocity of Mixing Rules in Methylmethacrylate Solutions at 318 K

R.G. Indhumathi

Voorhees College, Thiruvalluvar University, Vellore 632 102, TN, India.

ARTICLE INFO

Article history:
Received: 29 March 2016;
Received in revised form:
22 June 2016;
Accepted: 27 June 2016;

Keywords
Free length theory,
Impedance dependence relation,
Jungie's relation,
Nomoto's relation,
Ultrasonic velocity,
Vandeal-Vangeel relation,.

ABSTRACT

Ultrasonic velocity at 318 K in the binary systems of Methyl methacrylate + Toluene and Methyl methacrylate + Dimethylacetamide has been evaluated as a function of concentration and temperature, by using theoretical models viz., Nomoto's relation, Impedance dependence relation, VanDeal and Vangeel ideal mix relations, Free length theory and Jungie's method. The experimental values of ultrasonic velocity are compared with theoretical values. The best suitable theoretical relation was found by calculating the percentage deviation and chi-square test.

Introduction

Measurement of ultrasonic investigations found extensive applications in determining the Physio-chemical behaviour of liquid mixtures [1, 2]. Several researchers [6–9] carried out ultrasonic investigation and correlated the experimental results of ultrasonic velocity with the theoretical relations of Nomoto's relation (NOMO) [5,6], VanDeal and Vangeel ideal mix relations (VV) [7] impedance relation [8] Free length theory (FLT) [9] and Junjie's relation [10] and interpreted the results in terms of molecular interactions. Ultrasonic study of liquid mixtures, due to its non destructive nature, ultrasonic technique has been extensively carried out in different branches of science to measure the thermodynamic properties to predict the nature of molecular interaction between the molecules in a medium. The ultrasonic sound velocity and the thermodynamic parameters derived from it have been widely used to interpret the interactions between unlike molecules in the binary liquid mixtures. This investigation presents the evaluation of ultrasonic velocity using Nomoto's relation, Impedance dependence relation, VanDeal and Vangeel ideal mix relations, Free length theory and Jungie's relation for the binary liquid mixtures of Methyl methacrylate(MMA) with Toluene and Dimethylacetamide(DMAC).

Experimental method

Methyl methacrylate solutions in two different organic solvents (Toluene and Dimethyl Acetamide). Solutions were prepared in the concentration range 0% to 100% in steps of 10%. The samples were added to the solvent taken in bottles with air tight bids. The content of the bottle were shaken periodically and allow dissolving at the required temperature. Enough time was given for MMA to dissolve and clear solutions were obtained. All measurements were made within 2 or 3 days of preparation. The binary mixtures were prepared by using analytical regent grade of Toluene and Dimethylacetamide(DMAC) with different concentration of Methyl methacrylate from 0% to 100% in steps of 10%. The density of pure liquids and mixtures are measured using a 10 ml specific gravity bottle. The specific gravity bottle with the experimental liquid is immersed in a temperature controlled water bath. The viscosities of MMA + Toluene and DMAC were determined using an Ubbelohode viscometer. The ultrasonic velocity was measured using an ultrasonic interferometer at a frequency of a MHZ at temperature 318 K. Its accuracy is ±5m/s.Comparison of theoretical values of ultrasonic velocities with those obtained experimentally in the present binary liquid mixtures is expected to reveal the nature of interaction between component molecules in the mixture. Such theoretical study is useful in finding the comprehensive theoretical model for the liquid mixtures.

Results and discussion

The observed values through experiment and calculated values of velocity by the theoretical relations mentioned for the system MMA + Toluene is given in Table 1 and for the system MMA + DMAC is given in Table2. For MMA + Toluene system, the calculated velocities using given theoretical formulae are much deviated from the observed velocities. For MMA + DMAC, all the computed values are close to experimental values. It is noticed that Impedance dependence relation is very close to experimental values. Further it is followed by Nomoto's relation, Vandeal-Vangeel relation and Free length theory. It is clear that Nomoto's, Vandeal-Vangeel and Free length theory show almost same velocity. Jungie's relation is slightly deviated compared to other relations.

Since it is not much deviated from the observed velocities, Impedance dependence relation can be utilized to calculate the velocity for various concentrations providing the velocities of MMA and DMAC are known.

The validity of different theoretical formulae is checked by percentage deviation for MMA with Toluene and DMAC.

Tele:
E-mail address: indhu3686@gmail.com

Table 1.Experimental and Calculated values of Velocity for MMA with Toluene and Dimethylacetamide using mixing rules at 318 K.

Concentration of solute (In vol. %)	Experimental Values ms^{-1}		Calculated Values ms^{-1}									
			NOMO		VV		IMP		FLT		JUNJIE	
	Toluene	DMAC	Toluene	DMAC	Toluene	DMAC	Toluene	DMAC	Toluene	DMAC	Toluene	DMAC
0	1397	1384	1397	1384	1397	1384	1397	1384	1397	1384	1397	1384
10	1218	1367	1368	1356	1362	1356	1368	1361	1364	1355	1361	1348
20	1199	1354	1338	1328	1329	1328	1338	1337	1333	1328	1328	1315
30	1189	1318	1309	1300	1297	1300	1309	1313	1302	1300	1296	1284
40	1182	1297	1281	1273	1268	1273	1281	1288	1273	1273	1267	1256
50	1170	1273	1252	1247	1240	1246	1253	1262	1245	1246	1239	1229
60	1164	1230	1225	1225	1213	1220	1225	1235	1218	1220	1212	1204
70	1144	1206	1198	1194	1187	1194	1198	1207	1191	1194	1186	1181
80	1140	1174	1171	1169	1163	1168	1171	1179	1166	1168	1163	1158
90	1131	1143	1144	1143	1140	1143	1144	1149	1142	1143	1140	1138
100	1118	1118	1118	1118	1118	1118	1118	1118	1118	1118	1118	1118

The limitations and approximations incorporated in these theories are responsible for the deviations between theoretical and experimental values. The percentage deviation is calculated using the formula,

$$PD = \frac{U_{obs.} - U_{cal}}{U_{obs.}} x100\%$$

The deviations for Toluene and Dimethylacetamide are given in Table2. It is observed that the deviations are so high in each of the relations for Toluene. It is shown by the figure1. Compared to Toluene the percentage deviations are less in MMA+DMAC system. It is shown in figure 2.

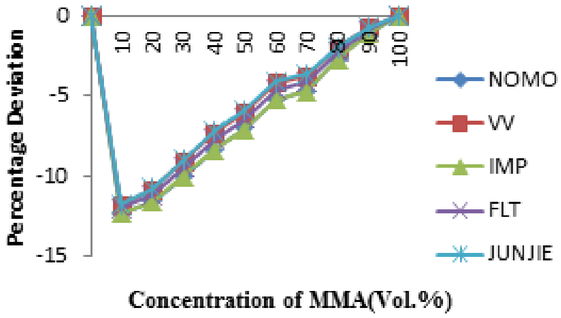

Figure 1. Relation between percentage deviation and concentration of MMA in Toluene.

The % deviation is found to be 1.26 as the maximum in Impedance dependence relation. Therefore, if ± 1.3 is taken as error, then Impedance dependence relation can be utilized to compute velocity. The maximum deviation in Nomoto's relation is 2.05%. The maximum deviation in Van deal-Van geal and free length theory is ± 2.13. Therefore, if ± 2.13 is taken as the error, then Impedance dependence relation, Nomoto's relation, Vandeal-Vangeel relation and Free length theory can be utilized to compute velocity. In Junjie'e relation the deviation is large. It is up to 3.46%.

To obey the Vandeal-Vangeel relation both the components must have same molar volume. For Nomoto's relation, the components have same molar sound velocity which is an additive property. The assumption is free length theory shows that the molecules are in spherical shape. It is evidenced that Impedance dependence relation shows least deviation for MMA+DMAC system which is evidenced by figure 2.

The validity of the theories is also checked by applying Chi-square test. The 'goodness of fit' of the theories for the binary liquid mixtures under study is evaluated. In both the systems, the number of degrees of degrees of freedom is 10.

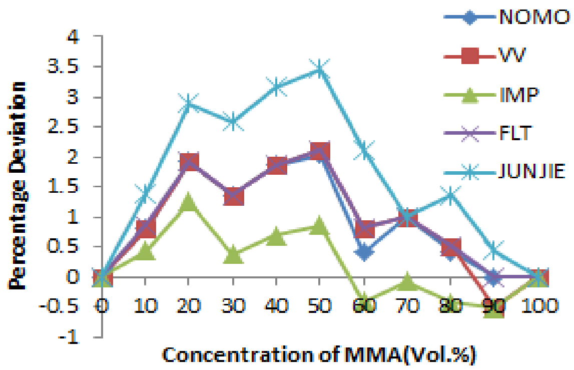

Figure 2. Relation between percentage deviation and concentration of MMA in DMAC.

Table 2.Percentage Deviation of velocity for MMA with Toluene and Dimethylacetamide using mixing rules at 318K.

Concentration Of Solute (In Vol. %)	Percentage Deviation									
	NOMO		VV		IMP		FLT		JUNJIE	
	Toluene	DMAC	Toluene	DMAC	Toluene	DMAC	Toluene	DMAC	Toluene	DMAC
0	0	0	0	0	0	0	0	0	0	0
10	-12.3152	0.8047	-11.8227	0.8047	-12.3153	0.4389	-11.9869	0.8778	-11.7405	1.3899
20	-11.5930	1.9202	-10.8424	1.9202	-11.5930	1.2555	-11.1760	1.9202	-10.7590	2.8803
30	-10.0925	1.3657	-9.0833	1.3657	-10.0083	0.3794	-9.5038	1.3657	-8.9991	2.5797
40	-8.3756	1.8504	-7.2758	1.8504	-8.3756	0.6939	-7.6988	1.8504	-7.1912	3.1611
50	-7.0085	2.0424	-5.9829	2.1210	-7.0940	0.8641	-6.4103	2.1210	-5.8974	3.4564
60	-5.2405	0.4065	-4.2096	0.8130	-5.2405	-0.4065	-4.6392	0.8130	-4.1237	2.1138
70	-4.7202	0.9950	-3.7587	0.9950	-4.7203	-0.0829	-4.1084	0.9950	-3.6713	0.9950
80	-2.7193	0.4259	-2.0175	0.5111	-2.7193	-0.4259	-2.2807	0.5111	-2.0175	1.3629
90	-1.1494	0	-0.7895	-0.5249	-1.1494	-0.5249	-0.9726	0	-0.7958	0.4374
100	0	0	0	0	0	0	0	0	0	0

For this, the χ^2 value for 'goodness of fit' at 1% level is equal to 23.209 and at 5% level is equal to 18.307. According to Karl Pearson, the χ^2 value is calculated using the formula,

$$\chi^2 = \sum_{i=1}^{n} \frac{(U_{obs.} - U_{cal.})^2}{U_{cal.}}$$

For (n-1) degrees of freedom, where n is the number of data used.

The calculated Chi-square values are given in Table3 for both the systems. It is observed that chi-square values for system MMA+DMAC are least which is evidenced by the figures 3 and 4. Hence, the theoretical formulae are well suited to calculate the ultrasonic velocity for MMA+DMAC system.

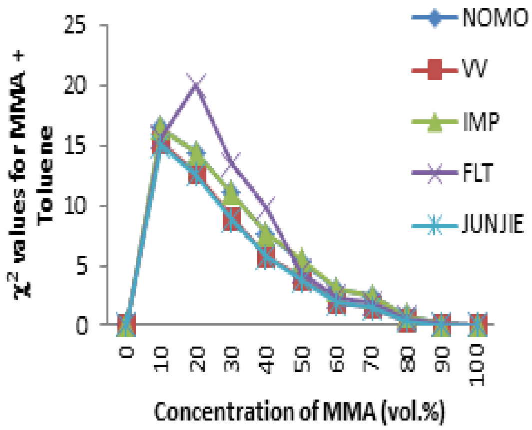

Figure 3. Relation between χ^2 values and concentration of MMA in Toluene .

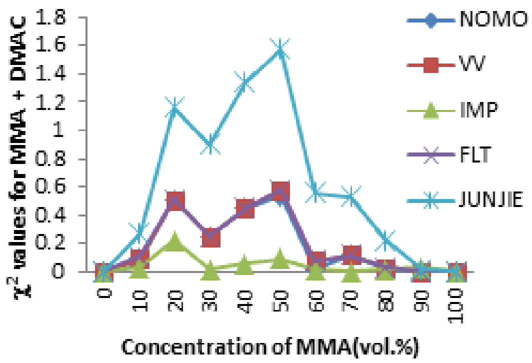

Figure 4. Relation between χ^2 values and concentration of MMA in DMAC.

It can be seen from Table1 that the theoretical values of ultrasonic velocity computed by various theories show deviation from experimental values. The reason may be the limitations and approximations incorporated in these theories. For DMAC in MMA, the chi-square test and percentage deviation values are minimum for *Impedance dependence* relation than those obtained by other theories. When two liquids are mixed, the interaction between the molecules of the two liquids takes place because of the presence of various forces like dispersive force, charge transfer, hydrogen bonding, dipole-dipole and dipole-induced dipole interactions. Hence, the observed deviation shows that the molecular interaction is taking place between the unlike molecules in the liquid mixture.

Conclusion

The Ultrasonic velocity, viscosity, density and other related parameters were calculated. The Ultrasonic velocities were calculated using various theoretical formulae. The study of velocity mixing rules show that Impedance dependence relation is best suited for MMA+DMAC to calculate Ultrasonic velocity. If $\pm$2.13 is taken as the error, then Impedance dependence relation, Nomoto's relation, Van deal_Van geel relation and free length theory can be utilized to compute velocity in MMA+DMAC system. The study of Van deal_Van geel relation shows both the components MMA and DMAC may have same molar volume. From the study of Nomoto's relation, the same molar sound velocity is found in MMA+DMAC. The molecule of MMA is almost spherical in shape as inferred from the study of MMA+DMAC. The theoretical formulae hold good for MMA+DMAC system which is evidenced by the application of chi-square test.

References:

1. P. Vasantharani, S. Muthu Shailaja, A. N. Kannappan, and R. Ezhil Pavai, "Theoretical evaluation of ultrasonic velocity in organic liquid mixtures," Journal of Applied Sciences, vol. 8, no. 12, pp. 2329–2332, 2008.
2. T. Sumathi and J. U. Maheswari, "Ultrasonic and theoretical studies of some ternary liquid mixtures at Various temperatures," Indian Journal of Pure and Applied Physics, vol. 47, no. 11, pp. 782–786, 2009.
3. S. Baluja and S. Oza, "Studies of some acoustical properties in binary solutions," The Journal of Pure and Applied Ultrasonics, vol. 24, p. 580, 2002.
4. A. Ali, A. Yasmin, and A. K. Nain, "Study of intermolecular interactions in binary liquid mixtures through ultrasonic speed measurement," Indian Journal of Pure and Applied Physics, vol. 40, no. 5, pp. 315–322, 2002.
5. O. Nomoto, Journal of the Physical Society of Japan, vol. 4, p. 280, 1949.

Table 3. χ^2 test for MMA with Toluene and Dimethylacetamide.

Concentration (In Vol. %)	NOMO		VV		IMP		FLT		JUNJIE	
	Toluene	DMAC	Toluene	DMAC	Toluene	DMAC	Toluene	DMAC	Toluene	DMAC
0	0	0	0	0	0	0	0	0	0	0
10	16.45	0.09	15.22	0.09	16.45	0.03	15.63	0.11	15.02	0.27
20	14.44	0.51	12.72	0.51	14.44	0.22	19.96	0.51	12.53	1.16
30	11	0.25	8.99	0.25	11	0.02	13.47	0.25	8.83	0.90
40	7.65	0.45	5.83	0.45	7.65	0.06	9.81	0.45	5.70	1.34
50	5.37	0.54	3.95	0.58	5.50	0.09	4.52	0.58	3.84	1.57
60	3.04	0.02	1.98	0.08	3.03	0.02	2.39	0.08	1.90	0.56
70	2.43	0.12	1.56	0.12	2.43	0	1.85	0.12	1.49	0.53
80	0.82	0.02	0.45	0.03	0.82	0.02	0.58	0.03	0.45	0.22
90	0.15	0	0.07	0	0.15	0.03	0.11	0	0.07	0.02
100	0	0	0	0	0	0	0	0	0	0
$\sum \chi^2 =$	61.35	2	50.77	2.11	61.47	0.49	68.32	2.13	49.83	6.57

6. O. Nomoto, "Empirical Formula for Sound Velocity in Liquid Mixtures," Journal of the Physical Society of Japan, vol. 13, pp. 1528–1532, 1958.
7. W. Van Deal and E. Vangeel, in Proceedings of the International Conference on Calorimetry and Thermodynamics, p. 555, Warsaw, Poland, 1955.
8. S. Baluja and R. H. Parsania, "Studies on acoustical properties of diclofanac sodium methanol-water system at 30◦C," Asian Journal of Chemistry, vol. 9, no. 1, pp. 149–152, 1997.
9. K. Rayapa Reddy, D. Bala Karuna Kumar, C. Rambabu, and G. Srinivasa Rao, "Theoretical evaluation of ultrasonic velocities in binary liquid mixtures of N-Methyl-2-pyrrolidone at differ- ent temperatures with Some cyclic compounds," E-Journal of Chemistry, vol. 9, no. 2, pp. 553–562, 2012.
10. Z. Junjie, Journal of University of Science and Technology of China, vol. 14, p. 298, 1984.
11. R. T. Langeman and J .E. Correy, "Velocity of sound as a bond property," Journal of Chemical Physics, vol. 10, no. 12, p. 759, 1942.
12. G.R.Rendall,"Dispersionofsoundvelocityinsomealcohols," Proceedings of the Indian Academy of Sciences A, vol. 16, no. 6, pp. 369–378, 1942.
13. D. Auslander and L. Onitni, Acustica, vol. 24, p. 205, 1971.
14. K. Samal and S. C. Misra, "Ultrasonic absorption in binary mixtures of carbon disulphide in comparison with Bauer's theory," Journal of the Physical Society of Japan, vol. 32, no. 6, pp. 1615–1618, 1972.
15. R. A. Aziz and D. H. Bowman, "The law of corresponding states as applied to sound velocity in liquids consisting of elliptical molecules," Canadian Journal of Physics, vol. 50, no. 7, pp. 721–727, 1972.
16. G. R. Poole, R. A. Aziz, and C. C. Lim, "An examination of the relationship between sound velocity and density in liquids," Canadian Journal of Physics, vol. 50, pp. 646–654 , 1972.
17. B. A. Younglove, "Speed of sound in fluid parahydrogen," Journal of the Acoustical Society of America, vol. 38, pp. 433– 438, 1965.
18. A. Prash, S. Prakash, and Q. Prakash, Proceedings of the National Academy of Sciences, vol. 55, p. 114, 1985.
19. R. Sabeson, Natarajan, and R. Varadha Rajan, Indian Journal of Pure and Applied Physics, vol. 25, p. 489, 1987.
20. A. Pal and Y. P. Singh, "Excess molar volumes and apparent molar volumes of some amide + water systems at 303.15 and 308.15 K," Journal of Chemical & Engineering Data, vol. 40, no. 4, pp. 818–822, 1995.
21. M. J. Blandamer and D. Waddington, "Analysis of sound velocities in aqueous mixtures in terms of excess isentropic compressibilities," Journal of Physical Chemistry, vol. 74, no. 12, pp. 2569–2570, 1970.
22. P. S. Nikam, B. S. Jagdale, A. B. Sawant, and M. Hasan, Journal of Pureand Applied Ultrasonics, vol. 22, p. 115, 2000.
23. A. Ali and A. K. Nain, "Study of molecular interactions in non-aqueous binary liquid mixtures through ultrasonic mea- surements," Journal of Pure and Applied Ultrasonics, vol. 22, p. 10, 2000.