

Ultrasonic velocity of binary systems at elevated pressures

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Abstract. Various empirical theories of ultrasonic velocity have been applied to three binary liquid mixtures, under pressures up to 200 MPa and their validity have been tested. A pressure dependent study of ultrasonic velocities has been made at 303.15 K. The agreement between theory and experiment is found to be quite satisfactory.

Keywords. Ultrasonic velocity; pressure dependence; theoretical evaluation; binary mixtures at elevated pressures.

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1. Introduction

There has been an increasing interest in the study of molecular interactions and a number of experimental techniques have been used to investigate the interactions between the components of binary liquid mixtures. The ultrasonic speed and thermodynamic data derived from it have been widely used for this purpose. Measurement of sound velocity offers a convenient method for determining certain thermodynamic properties of liquids not easily obtained by other means. Successful attempts have been made in the recent past [1–4] on theoretical evaluation of ultrasonic velocity and its correlation with other thermodynamic properties in binary liquids using statistical and semi-empirical theories. But such studies have been limited to binary liquid mixtures at zero pressure. Due to the lack of experimental data on ultrasonic velocity at elevated pressures, such studies could not be extended at elevated pressure. For the first time, Takagi *et al* [5–8] have carried out experimental measurements of ultrasonic velocity and related thermodynamic properties of a few binary liquid mixtures at elevated pressures over a wide range of temperatures. Although, of late [9–17], some work on ultrasonic speed and thermodynamic parameters has been carried out, however, to our knowledge, the use of ultrasonic velocity at elevated pressures is rare. Therefore, in the present investigation, we report the results of theoretical calculations of ultrasonic velocity at elevated pressures using various semiempirical theories in the mixtures. Ultrasonic investigations of the systems have been reported by Takagi *et al* [6,8]. A comparative study has then been made thereof.

2. Theoretical

Nomoto [18] took into account the linearity of molecular sound velocity and additivity of molar volumes and suggested an empirical formula for sound velocity in binary liquid mixtures U_{mix} as

$$U_{\text{mix}} = \left(\frac{R_{\text{mix}}}{V_{\text{mix}}} \right)^3 = \left(\frac{x_1 R_1 + x_2 R_2}{x_1 V_1 + x_2 V_2} \right)^3, \quad (1)$$

where R_{mix} is molar sound velocity and V_{mix} is the molar volume of mixture.

The Van Dael ideal mixing relation [10] which has been successfully employed to investigate the acoustical behaviour of binary liquid mixtures gives the expression for the velocity of sound as

$$\left(\frac{1}{x_1 M_1 + x_2 M_2} \right) \frac{1}{u^2} = \left[\frac{x_1}{M_1 u_1^2} + \frac{x_2}{M_2 u_2^2} \right], \quad (2)$$

where x_1, x_2, M_1, M_2 and u_1 and u_2 are the mole fractions, molecular weights and ultrasonic velocities of first and second component respectively.

Schaaffs [19,20] and Nutsch-Kunhies developed an expression for evaluating sound velocity in binary liquid mixture as

$$u_{\text{mix}} = u_{\infty} (x_1 S_1 + x_2 S_2) \left(\frac{x_1 B_1 + x_2 B_2}{V} \right), \quad (3)$$

where $u_{\infty} = 1600 \text{ m sec}^{-1}$, S_1, S_2 and B_1 and B_2 are the collision factors and actual volumes of the molecule per mole of first and second component respectively.

3. Results and discussions

Theoretical values of ultrasonic velocity computed from the aforesaid theories for the binary mixtures, viz., (i) chlorobenzene + bromobenzene, (ii) toluene + aniline and (iii) toluene + *o*-xylene at 303.15 K up to 200 MPa have been recorded in tables 1–3 at varying mole fractions.

3.1 Chlorobenzene + Bromobenzene (polar + polar) mixture

Literature values [7] show when pressure is raised, the ultrasonic speed in each mixture increases indicating a curve of second order in pressure over the whole range used in the present investigation. Furthermore, in order to examine solution behaviour for the present mixture, plotted values of β_S^E , the excess isentropic compressibility, against x_2 exhibit small positive values at all compositions and pressures. This finding and the behaviour is due to dipole–dipole interactions between the two components.

According to X-ray investigations [22], on the crystal and spectrographic investigations of gas, the Van der Waals radius of Br atom is 0.195 nm which is relatively greater than for other atoms. This finding leads us to the conclusion that the free volume of mixing of

a mixture containing bromobenzene will be much larger as compared to others at atmospheric pressure. Thus, with rise in pressure, increase of this free volume plays a leading role in determining the large pressure effect on the interaction and the excess isoentropic compressibility in lower-pressure region. A close perusal of table 1 shows that the minimum deviations are observed in the case of collision factor theory, followed by case of ideal mixing relation. The average percentage deviations for collision factor theory, Nomoto's relation and ideal mixing relation are 2.09, 6.97 and 6.72 for 0.2; 2.42, 3.17 and 3.55 for 0.4; 2.41, 1.02 and 0.56 for 0.6 and 2.85, 5.60 and 5.28 for 0.8 mole fraction of chlorobenzene respectively.

3.2 Toluene + Aniline (non polar + polar) mixture

For this binary liquid mixture, ultrasonic velocity has been calculated using the previously mentioned theories over a pressure range up to 160 MPa at 303.15 K. The freezing pressure for pure aniline is 188.5 MPa at 303.15 K. Hence computed values of ultrasonic velocity in this mixture are in the range of pressures up to 160 MPa, in concurrence with literature [6].

Table 1. Average percentage deviations calculated from Nomoto, ideal mixing and collision factor theory for the binary system chlorobenzene + bromobenzene at $x_2 = 0.2, 0.4, 0.6$ and 0.8 at 303.15 K.

Pressure (P) MPa	Percentage deviation											
	MF = 0.2			MF = 0.4			MF = 0.6			MF = 0.8		
	Nomoto	Vandael	CFT	Nomoto	Vandael	CFT	Nomoto	Vandael	CFT	Nomoto	Vandael	CFT
0.1	-5.53	-6.02	2.57	-2.34	-2.95	2.92	1.35	0.77	3.07	5.16	4.82	2.91
5.0	-5.43	-5.92	2.65	-2.88	-2.88	2.99	1.28	1.28	3.11	5.22	4.89	2.90
10.0	-5.08	-5.09	2.47	-2.44	-3.05	2.84	1.06	0.51	2.79	5.08	4.76	2.88
15.0	-6.04	-6.47	2.31	-2.61	-3.21	2.64	0.98	0.43	2.55	5.09	4.76	2.85
20.0	-6.69	-6.26	2.30	-3.21	-3.04	2.84	1.06	0.51	2.64	5.12	4.79	2.88
25.0	-7.08	-6.31	2.34	-3.83	-3.01	2.82	1.08	0.52	2.38	5.19	4.86	2.89
30.0	-6.13	-6.55	2.11	-4.12	-3.30	2.54	1.00	0.43	2.57	5.22	4.88	2.84
40.0	-7.95	-6.85	2.02	-2.81	-3.41	2.45	0.69	0.36	2.45	5.21	4.89	2.86
50.0	-6.54	-6.95	2.16	-2.86	-3.46	2.52	0.90	0.36	2.41	5.27	4.96	2.84
60.0	-6.60	-7.00	0.66	-2.97	-3.56	1.48	0.88	0.35	1.79	5.45	5.14	2.81
70.0	-6.72	-7.14	2.11	-3.11	-3.11	2.28	1.04	0.49	2.38	5.49	5.17	2.86
80.0	-6.88	-7.33	2.09	-3.28	-3.74	2.37	1.06	0.54	2.35	5.86	5.56	2.89
90.0	-6.93	-7.33	2.16	-3.11	-3.71	2.40	1.24	0.70	2.48	6.02	5.76	2.86
100.0	-6.96	-7.39	2.21	-3.09	-3.68	2.41	1.00	0.46	2.30	5.95	5.56	2.85
110.0	-7.01	-7.44	1.91	-3.12	-3.78	2.21	0.92	0.39	2.19	5.74	5.43	2.83
120.0	-7.19	-7.33	2.32	-3.69	-3.63	2.51	1.06	0.52	2.36	5.99	5.68	2.85
130.0	-6.67	-7.09	2.21	-2.84	-3.60	2.53	1.14	1.14	2.55	5.83	5.82	2.87
140.0	-6.87	-7.30	2.11	-3.24	-3.80	2.25	1.12	0.58	2.48	5.90	5.57	2.85
150.0	-6.81	-7.28	2.12	-3.08	-3.80	2.30	0.91	1.09	2.24	5.69	5.38	2.83
160.0	-6.90	-7.30	2.23	-2.86	-3.75	2.40	1.13	0.60	2.48	6.11	5.78	2.87
170.0	-7.37	-7.77	1.89	-3.66	-4.08	2.01	0.81	0.28	1.93	5.87	5.57	2.80
180.0	-7.22	-7.65	1.95	-3.39	-4.04	2.08	1.05	0.52	2.21	5.97	5.68	2.83
190.0	-7.33	-7.74	1.83	-4.11	-4.48	2.19	0.97	0.44	2.12	6.07	5.77	2.83
200.0	-7.42	-7.83	1.63	-3.55	-4.16	2.09	0.86	0.35	2.04	5.96	5.67	2.83
Avg =	-6.72	-6.97	2.09	-3.17	-3.55	2.42	1.02	0.56	2.41	5.60	5.28	2.85

Close perusal of table 2 again indicates that the minimum deviations are observed in the case of collision factor theory while the deviations obtained for Nomoto's relation and the ideal mixing relation hold equally good, keeping in accordance with literature values. The average percentage deviations for collision factor theory, Nomoto's relation and ideal mixing relation are 1.06, 9.99 and 9.67 for 0.2; 1.98, 3.86 and 3.63 for 0.4; 2.67, 2.05 and 2.20 for 0.6 and 3.01, 7.89 and 7.95 for 0.8 mole fraction of aniline respectively.

Aniline molecules are known to be associated through hydrogen bonding in the pure state. The self-association is decreased when aniline is mixed with other aromatic hydrocarbons [6]. Literatures [6] values indicate that pressure effects of β_S^E for various binary mixtures qualitatively suggest that β_S^E values and the composition where β_S^E showed the maximum or minimum were scarcely affected by pressure changes when the mixture had strong molecular interactions. These facts lead us to the conclusion that the association in toluene-aniline is weaker than that of benzene-aniline and thus the results for the present mixture may be presumed to cause the large pressure effect on β_S^E .

3.3 Toluene + o-xylene (nonpolar – weakly polar) mixture

As in the previous system (toluene + aniline), ultrasonic velocity has been computed under similar conditions of temperature and pressure. Perusal of table 3 reveals that the average percentage deviations for collision factor theory, Nomoto's relation and ideal mixing relation are 0.22, 1.28 and 1.28 for 0.2; 0.22, 0.37 and 0.22 for 0.4; 0.221, 0.48 and 0.70 for 0.6 and 1.63, 1.38 and 1.54 for 0.8 mole fraction of o-xylene respectively.

Table 2. Average percentage deviations calculated from Nomoto, ideal mixing and collision factor theory for the binary system toluene + aniline at $x_2 = 0.2, 0.4, 0.6$ and 0.8 at 303.15 K

Pressure (P) MPa	Percentage deviation											
	MF = 0.2			MF = 0.4			MF = 0.6			MF = 0.8		
	Nomoto	Vandael	CFT	Nomoto	Vandael	CFT	Nomoto	Vandael	CFT	Nomoto	Vandael	CFT
0.1	18.18	15.72	1.33	6.42	5.17	2.70	-2.59	-4.09	3.76	-12.36	-12.81	3.98
10.0	14.37	13.90	1.28	5.29	4.65	2.23	-3.80	-3.83	2.98	-12.25	-12.25	3.09
20.0	13.37	12.98	1.25	4.83	4.31	1.87	-4.34	-3.53	2.78	-10.78	-11.02	2.35
30.0	12.46	12.14	1.34	4.77	4.35	2.02	-2.54	-3.04	2.71	-10.53	-10.18	2.96
40.0	11.45	11.20	1.01	4.46	4.11	2.00	-2.91	-2.79	2.73	-9.17	-9.34	3.09
50.0	10.46	9.28	1.08	4.26	3.84	1.86	-2.24	-2.50	2.75	-8.47	-8.60	3.09
60.0	10.01	9.87	1.11	4.00	3.79	1.91	-2.02	-2.02	2.62	-8.21	-8.21	2.85
70.0	9.75	9.61	1.07	3.81	3.81	1.80	-2.06	-2.24	2.50	-7.82	-7.82	2.93
80.0	9.18	9.07	1.00	3.40	3.66	1.90	-1.70	-1.84	2.66	-7.22	-7.30	3.03
90.0	8.90	8.80	1.04	3.54	3.40	1.95	-1.41	-1.54	2.84	-6.84	-6.91	3.18
100.0	8.38	8.30	0.81	3.22	3.08	1.79	-1.59	-1.68	2.57	-6.67	-6.75	2.94
110.0	7.08	7.95	0.84	3.19	3.08	1.87	-1.51	-1.60	2.49	-6.39	-6.42	2.86
120.0	7.63	7.57	0.76	3.03	2.86	1.82	-1.51	-1.59	2.28	-6.15	-6.19	2.70
130.0	7.56	7.50	1.08	3.05	2.96	1.96	-1.36	-1.41	2.36	-5.80	-5.83	2.97
140.0	7.05	7.05	1.00	2.74	3.04	2.02	-1.16	-1.57	2.46	-5.38	-5.39	3.13
150.0	6.98	0.97	1.13	2.92	2.92	1.98	-1.06	-1.09	2.53	-5.18	-5.20	3.05
160.0	6.66	6.64	1.05	2.82	2.79	2.07	-1.07	-1.12	2.37	-5.08	-5.09	3.08
Avg =	9.99	9.67	1.06	3.86	3.63	1.98	-2.05	-2.20	2.67	-7.89	-7.95	3.01

Table 3. Average percentage deviations calculated from Nomoto, ideal mixing and collision factor theory for the binary system toluene + *o*-xylene at $x_2 = 0.2, 0.4, 0.6$ and 0.8 at 303.15 K.

Pressure (<i>P</i>) MPa	Percentage deviation											
	<i>MF</i> = 0.2			<i>MF</i> = 0.4			<i>MF</i> = 0.6			<i>MF</i> = 0.8		
	Nomoto	Vandael	CFT	Nomoto	Vandael	CFT	Nomoto	Vandael	CFT	Nomoto	Vandael	CFT
0.1	2.14	-0.51	1.08	0.79	0.53	0.44	-0.47	-0.73	0.50	-1.90	-2.06	0.24
10.0	1.80	1.98	0.29	0.68	1.90	0.22	-0.55	-0.79	0.36	-1.51	-1.98	0.23
20.0	1.42	1.59	0.09	0.45	0.20	0.10	-0.64	-0.34	0.17	-1.76	-1.91	0.64
30.0	1.50	1.50	0.30	0.18	0.18	0.22	-0.52	-0.76	0.28	-1.65	-1.65	0.10
40.0	1.53	1.70	0.11	0.77	0.26	0.18	-0.57	-0.82	0.20	-1.73	-1.73	0.18
50.0	1.43	2.93	0.14	0.56	0.33	0.18	-0.55	-0.78	0.24	-1.59	-1.74	0.15
60.0	1.74	1.92	0.20	0.72	0.47	0.41	-0.40	-0.64	0.43	-1.39	-1.55	0.52
70.0	1.28	1.45	0.12	0.63	0.37	0.066	-0.58	-0.82	0.09	-1.62	-1.78	0.012
80.0	1.42	1.29	0.02	0.47	0.22	0.29	-0.47	-0.70	0.22	-1.47	-1.63	0.11
90.0	1.09	1.25	0.06	0.36	0.11	0.15	-0.46	-0.46	0.13	-1.40	-1.56	0.18
100.0	0.89	1.05	0.107	0.19	-0.03	0.17	-0.48	-0.71	0.17	-1.10	-1.26	0.25
110.0	0.90	1.07	0.016	0.16	-0.07	0.18	-0.39	-0.61	0.36	-1.17	-1.33	0.25
120.0	0.76	0.93	-0.017	0.20	-0.04	0.20	-0.54	-0.78	0.26	-1.23	-1.39	0.13
130.0	0.70	0.86	0.045	0.10	-0.03	0.07	-0.56	-0.77	0.10	-1.20	-1.36	-0.16
140.0	0.78	0.94	0.30	0.25	0.005	0.30	-0.53	-0.77	0.15	-0.95	-1.11	-0.022
150.0	0.75	0.94	0.75	0.27	0.02	0.30	-0.30	-0.54	-0.66	-0.91	-1.07	0.12
160.0	1.75	1.03	0.24	0.32	0.07	0.27	-0.27	-0.97	0.39	-0.98	-1.08	0.15
Avg =	1.28	1.28	0.22	0.37	0.21	0.22	-0.48	-0.70	0.21	-1.38	-1.54	1.63

The values are in agreement with the literature values [25] as both Nomoto's relation and ideal mixing relations give almost identical results but the collision factor theory proves to be better than both of these.

Thus, keeping in view the behaviour of the three aforementioned systems under the present investigation, it can be said that the positive deviations in velocity are attributed to (a) molecular association and (b) complex formation, whereas negative deviations in velocity are attributed to the molecular dissociation of an associated species caused by addition of an inert solvent or an active solvent. The actual sign and magnitude of the deviations observed experimentally would depend upon the relative strength of the two opposing effects (molecular association and dissociation).

According to Keesom's theory, the intermolecular energy for binary mixtures including polar substances is proportional to the product of squares of the dipole moments for each component and is inversely proportional to the temperature and to r^6 , where r is intermolecular separation between the two components. These facts, when applied to the systems under the present investigations bring about the conclusion that the irregularities observed over the wide range of mole fraction is strongly subject to polarity of each substance and moreover it depends largely on the pressure change compared with those for (nonpolar + polar) and (weakly polar + polar) mixtures. However, if the binary mixtures have a strong molecular interaction between two components, it is in general that the physicochemical quantities are changed successively with composition.

Whereas interstitial accommodation effect is more prominent in hydrogen bonded solvent systems, the dispersion forces are likely to be dominant in mixed dipolar aprotic and nonpolar or binary mixtures of nonpolar solvents. Lack in smoothness of deviations are due to interactions between the component molecules. Interactions are a result of active collisions between the molecules. In the collision factor theory, molecules are treated as real, non-elastic molecules. In the case of system I (chlorobenzene + bromobenzene), both the components are polar organic liquids which have strong molecular forces of attraction. Hence their collisions are likely to be less elastic, resulting in greater extent of interaction. Furthermore, both positive and negative deviations are observed in the aforementioned liquid mixture.

Fort *et al* [25] have studied some fourteen binary liquid mixtures and clearly established that the positive contributions for excess values should be contributed to dispersion forces and the negative excess values should be due to charge transfer, dipole induced dipole and dipole-dipole interactions. Since both positive and negative deviations are found in three types of liquid mixtures hence they can be attributed to molecular interactions.

In conclusion, it appears from the preceding discussion that the collision factor theory seems to provide the best results followed by Nomoto's relation, ideal mixing relation respectively for the polar-polar (I) liquid system. The reason behind this can be attributed to the presence of two empirical factors, S_1 and S_2 , contained in the Schaaffs equation (3), which are known as collision factors and are in fact correction terms which can be adjusted to give better results. This also seems to be in agreement with the conclusion arrived at by Prasad *et al* [23] and Kaulgud and Tarsekar [24] for different binary liquid mixtures. However, in the case of polar-nonpolar and nonpolar-nonpolar, both Nomoto's relation and the ideal mixing relation give almost identical results, but the best results are obtained by the collision factor theory.

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