Vol 15 No 9, September 2006
1009-1963/2006/15(09)/2030-06

Chinese Physics

© 2006 Chin. Phys. Soc.
and IOP Publishing Ltd

Ultrasonic study on organic liquid and binary organic liquid mixtures by using Schaaffs' collision factor theory

Lu Yi-Gang(卢义刚)[a)†] and Dong Yan-Wu(董彦武)[b)]

[a)] *School of Physics, South China University of Technology, Guangzhou* 510640, *China*

[b)] *Applied Acoustics Institute, Shaanxi Normal University, Xi'an* 710062, *China*

(Received 10 August 2005; revised manuscript received 15 May 2006)

Based on Schaaff's collision factor theory (CFT) in liquids, the equations for nonlinear ultrasonic parameters in both organic liquid and binary organic liquid mixtures are deduced. The nonlinear ultrasonic parameters, including pressure coefficient, temperature coefficients of ultrasonic velocity, and nonlinear acoustic parameter B/A in both organic liquid and binary organic liquid mixtures, are evaluated for comparison with the measured results and data from other sources. The equations show that the coefficient of ultrasonic velocity and nonlinear acoustic parameter B/A are closely related to molecular interactions. These nonlinear ultrasonic parameters reflect some information of internal structure and outside status of the medium or mixtures. From the exponent of repulsive forces of the molecules, several thermodynamic parameters, pressure and temperature of the medium, the nonlinear ultrasonic parameters and ultrasonic nature of the medium can be evaluated. When evaluating and studying nonlinear acoustic parameter B/A of binary organic liquid mixtures, there is no need to know the nonlinear acoustic parameter B/A of the components. Obviously, the equation reveals the connection between the nonlinear ultrasonic nature and internal structure and outside status of the mixtures more directly and distinctly than traditional mixture law for B/A, e.g. Apfel's and Sehgal's laws for liquid binary mixtures.

Keywords: nonlinear acoustic parameter B/A, coefficient of ultrasonic velocity, organic liquid, binary organic liquid mixtures

PACC: 4325, 4335

1. Introduction

The ultrasonic nature of liquids is closely related to the molecular structure. Study of the ultrasonic nature of liquids can help us understand their thermodynamic property and the information of their molecular structure. Based on Tanks equation, Kittle[1] and Hartman[2] have studied the special property of ultrasonic velocity. Based on Schaaffs' theory, Tong and Dong[3] have studied ultrasonic velocity and nonlinear acoustic parameter B/A in organic liquid. Krzesińska found the formula of absolute temperature coefficients of ultrasonic velocity in solutions of coal products.[4] Yadava and Aniruddh measured the velocity of ultrasound for binary mixtures of bromobutane, and evaluated the adiabatic compressibility and Wada's constant.[5] Kamila *et al* measured the ultrasonic velocities, viscosities and densities of some liquid ion exchangers.[6] Based on Jacobson's molecular free length theory (FLT) and the relationship between ultrasonic velocity and the molecular free length in organic liquid,[7,8] we have studied ultrasonic nature of organic liquid and binary organic liquid mixtures.[9−13] Based on Schaaff's collision factor theory for liquids, this paper focuses on the equations for nonlinear ultrasonic parameters in both organic liquid and binary organic liquid mixtures. This paper is organized as follows. Section 1 introduces the Schaaff's collision factor theory (CFT) for liquids and the conception of nonlinear acoustic parameter B/A. Section 2 deduces equations of coefficient of ultrasonic velocity and nonlinear acoustic parameter B/A in both organic liquid and binary organic liquid mixtures. Section 3 briefly describes our measurement method, then gives calculations and measurements of the nonlinear ultrasonic parameters in nine types of organic liquid and two mixtures, and the comparison of the results with those published by other researchers[3,14−17] and the results we obtained in our earlier works.[9−13] Finally, the conclusions are summarized in Section 4.

†E-mail: phyiglu@scut.edu.cn

2. Schaaffs' collision factor theory and the conception of nonlinear acoustic parameter

According to Schaaffs' collision factor theory (CFT), the ultrasonic velocity in the liquid is determined by the space filling factor and the elasticity collision factor of molecules, expressed as follows:[18]

$$C = KS\gamma = KSV_0/V, \tag{1}$$

where C is the ultrasonic velocity, K is a constant equal to 1600 m/s, S is the collision factor determining the elasticity of the collision between molecules of the liquid, γ is the space filling factor, V_0 is the specific volume of a mol of molecules and V is the molar volume of the liquid. The equation for the ultrasonic velocity in binary liquid mixtures is given by[19]

$$C = K\left(X_1S_1 + X_2S_2\right)\frac{X_1V_{01} + X_2V_{02}}{V}, \tag{2}$$

where X stands for mole fraction of the components, and the subscripts 1 and 2 stand for components 1 and 2 of the mixtures respectively. Suppose the mixing is ideal, that is

$$S = X_1S_1 + X_2S_2, \tag{3}$$

$$V = X_1V_1 + X_2V_2, \tag{4}$$

$$\rho = X_1\rho_1 + X_2\rho_2, \tag{5}$$

where S is the collision factor, V is molar volume and ρ is density of the binary mixtures.

The nonlinear acoustic parameter B/A in the liquid is defined as[20]

$$\begin{aligned} B/A =& \rho\left(\frac{\partial C^2}{\partial P}\right)_s \\ =& 2\rho_0 C\left(\frac{\partial C}{\partial P}\right)_T + \frac{2\alpha CT}{C_P}\left(\frac{\partial C}{\partial T}\right)_P, \end{aligned} \tag{6}$$

where P is pressure and the subscript s stands for constant entropy.

3. Equations for coefficient of ultrasonic velocity and nonlinear acoustic parameter B/A from Schaaffs' theory

Supposing the size of the liquid molecules does not vary with pressure at constant temperature, we can differentiate Eq.(1) with respect to pressure and obtain

$$\begin{aligned} \left(\frac{\partial C}{\partial P}\right)_T =& KV_0\left(\frac{\partial\left(\dfrac{S}{V}\right)}{\partial P}\right)_T \\ =& \frac{KV_0S}{V}\left(\frac{1}{S}\left(\frac{\partial S}{\partial P}\right)_T - \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T\right) \\ =& C\left(\frac{1}{S}\left(\frac{\partial S}{\partial P}\right)_T + \kappa_T\right). \end{aligned} \tag{7}$$

If the size of the liquid molecules does not vary with temperature at constant pressure, we can differentiate Eq.(1) with respect to temperature and obtain

$$\begin{aligned} \left(\frac{\partial C}{\partial T}\right)_P =& KV_0\left(\frac{\partial\left(\dfrac{S}{V}\right)}{\partial T}\right)_P \\ =& \frac{KV_0S}{V}\left(\frac{1}{S}\left(\frac{\partial S}{\partial T}\right)_P - \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P\right) \\ =& C\left(\frac{1}{S}\left(\frac{\partial S}{\partial T}\right)_P - \alpha\right), \end{aligned} \tag{8}$$

where $\kappa_T = -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial P}\right)_T$ is the coefficient of compressibility at constant temperature, and $\alpha = \dfrac{1}{V}\left(\dfrac{\partial V}{\partial T}\right)_P$ is the bulk coefficient of expansion of the liquid at constant pressure.

When studying the relationship between collision factor S, pressure P and temperature T, Soczkiewicz obtained two equations in Ref.[21] as follows:

$$\frac{1}{S}\left(\frac{\partial S}{\partial P}\right)_T = \frac{n+1}{6}\kappa_T, \tag{9}$$

$$\frac{1}{S}\left(\frac{\partial S}{\partial T}\right)_P = \left(1 - \frac{n}{6}\right)\alpha, \tag{10}$$

where n is the individual exponent for each liquid for describing the magnitude of the repulsion forces of the molecules. Substituting Eq.(9) into Eq.(7) and Eq.(10) into Eq.(8), we obtain the equations for pressure coefficient and temperature coefficient of ultrasonic velocity in organic liquid as follows:

$$\left(\frac{\partial C}{\partial P}\right)_T = \frac{n+7}{6}\kappa_T C, \tag{11}$$

$$\left(\frac{\partial C}{\partial T}\right)_P = -\frac{n}{6}\alpha C. \tag{12}$$

Substituting Eqs.(11), (12) into Eq.(6), we obtain the equation for nonlinear acoustic parameter B/A in organic liquid as follows:

$$\frac{B}{A} = \frac{n+7}{3}\rho\kappa_T C^2 - \frac{n}{3}\frac{\alpha C^2 T}{C_P}. \tag{13}$$

In binary liquid mixtures, X_1, X_2, V_{01} and V_{02} are constants. Differentiating Eq.(2) with respect to pressure$P$ and to temperature T respectively, we obtain Eq.(14) and Eq.(15), the equations for pressure coefficient and temperature coefficient of ultrasonic velocity in binary liquid mixtures respectively:

$$\begin{aligned}\left(\frac{\partial C}{\partial P}\right)_T =& K\left(X_1V_{01}+X_2V_{02}\right)\frac{\partial}{\partial P}\left(\frac{X_1S_1+X_2S_2}{X_1V_1+X_2V_2}\right)_T\\ =& C\left[\kappa_{T1}\left(\frac{n_1+1}{6}\frac{X_1S_1}{S}+\frac{X_1V_1}{V}\right)+\kappa_{T2}\left(\frac{n_2+1}{6}\frac{X_2S_2}{S}+\frac{X_2V_2}{V}\right)\right]\\ =& C\left[\kappa_{T1}\left(\frac{n_1+1}{6}l_1+m_1\right)+\kappa_{T2}\left(\frac{n_2+1}{6}l_2+m_2\right)\right], \qquad (14)\\ \left(\frac{\partial C}{\partial T}\right)_P =& C\left[\alpha_1\left(\frac{6-n_1}{6}l_1-m_1\right)+\alpha_2\left(\frac{6-n_2}{6}l_2-m_2\right)\right]\\ =& -C\left[\alpha_1\left(\frac{n_1-6}{6}l_1+m_1\right)+\alpha_2\left(\frac{n_2-6}{6}l_2+m_2\right)\right], \qquad (15)\end{aligned}$$

where $l_1=\dfrac{X_1S_1}{X_1S_1+X_2S_2}$, $m_1=\dfrac{X_1V_1}{X_1V_1+X_2V_2}$, $l_2=\dfrac{X_2S_2}{X_1S_1+X_2S_2}$, $m_2=\dfrac{X_2V_2}{X_1V_1+X_2V_2}$, and $l_1+l_2=1$, $m_1+m_2=1$. We call l_1, l_2 the fractions of collision factor of the components, and n_1, n_2 the fractions of volume.

Substituting Eqs.(14), (15) into Eq.(6), we obtain the equation for nonlinear acoustic parameter B/A in organic liquid mixtures as follows:

$$\begin{aligned}\frac{B}{A} =& 2\rho C^2\left[\kappa_{T1}\left(\frac{n_1+1}{6}l_1+m_1\right)+\kappa_{T2}\left(\frac{n_2+1}{6}l_2+m_2\right)\right]\\ &-\frac{2\alpha TC^2}{C_P}\left[\alpha_1\left(\frac{6-n_1}{6}l_1-m_1\right)+\alpha_2\left(\frac{6-n_2}{6}l_2-m_2\right)\right]. \qquad (16)\end{aligned}$$

4. Discussion

In Eqs.(13) and (16), the first term on the right side is the pressure coefficient and the second one is the temperature coefficient; comparatively the second term contributes to the nonlinear acoustic parameter B/A much less than the first term.[21] Therefore Eqs.(13) and (16) can be expressed approximately as follows:

$$\frac{B}{A}=\frac{n+7}{3}\rho\kappa_TC^2, \qquad (17)$$

$$\begin{aligned}\frac{B}{A} =& 2\rho C^2\left[\kappa_{T1}\left(\frac{n_1+1}{6}l_1+m_1\right)\right.\\ &\left.+\kappa_{T2}\left(\frac{n_2+1}{6}l_2+m_2\right)\right]. \qquad (18)\end{aligned}$$

Equations (11)–(16) link the nonlinear ultrasonic parameters with several thermodynamic parameters, exponent of repulsive forces of the molecules, and the pressure and temperature of the liquid. So the nonlinear acoustic parameter of the binary organic liquid mixtures can be calculated from the equations of nonlinear acoustic parameter B/A when several thermodynamic parameters, exponents of repulsive forces of the molecules of the components of the mixture are given. In contrast, the internal structure and outside status of both the organic liquid and the binary organic liquid mixtures can be analysed with the measurements of the parameter B/A.

Supposing $\kappa_{T1}=\kappa_{T2}=\kappa_T$ and $\alpha_1=\alpha_2=\alpha$, equations (14)–(16) can be expressed as follows:

$$\left(\frac{\partial C}{\partial P}\right)_T=\frac{(l_1n_1+l_2n_2)+7}{6}\kappa_TC, \qquad (19)$$

$$\left(\frac{\partial C}{\partial T}\right)_P=-\frac{(l_1n_1+l_2n_2)}{6}\alpha C, \qquad (20)$$

$$\frac{B}{A}\approx\frac{(l_1n_1+l_2n_2)+7}{3}\rho\kappa_TC^2. \qquad (21)$$

Under this condition, the fractions of volume m_1 or m_2 have nothing to do with the nonlinear ultrasonic parameters in binary organic liquid mixtures, and then the nonlinear ultrasonic parameters are determined by the exponent of repulsive forces of the

molecules, mole fraction, etc. of the components. We can treat $(l_1n_1 + l_2n_2)$ as the repulsive forces of the binary organic liquid mixtures.

To verify Eqs.(11)–(16), we calculate and measure the nonlinear ultrasonic parameters. The principle for measurement of the pressure and temperature coefficients of ultrasonic velocity is similar to that of the nonlinear acoustic parameter B/A, which was illustrated in our earlier papers.[10,12,13] We compare the results with those published by other researchers[3,14−17] and the results from Jacobson's molecular free length theory (FLT) in our earlier papers.[10,12,13] Data of the liquids used in calculation are listed in Table 1. Calculated values, measured values and data from references for nine types of organic liquids (at 20°C) are listed in Table 2. The data of collision factor for three components of two mixtures are taken from Ref.[22]. From the data, we calculate any related data which are used in the calculation of the nonlinear acoustic parameter B/A in binary organic liquid mixtures and list the related data in Table 3. Similarly, the nonlinear ultrasonic parameters (at 20°C) for two binary organic liquid mixtures are calculated and listed in Tables 4 and 5. To compare the equation of B/A in binary organic liquid mixtures with Apfel's and Sehgal's mixture laws, we calculate the values of B/A of the mixtures by Apfel's and Sehgal's mixture laws.

Table 1. Data of liquids (20°C).

Liquid	$C/(\mathrm{m{\cdot}s^{-1}})$	$\rho/(\mathrm{kg{\cdot}m^{-3}})$	$\kappa_T\times10^{-11}/\mathrm{Pa^{-1}}$	$\alpha\times10^{-5}/\mathrm{K^{-1}}$	n[12]
Benzene	1324	878	94.86	123	17.5
Carbon tetrachloride	938	1595	91.60	123	16.1
methanol	1123	792	120.00	126	16.5
Acetone	1190	792	111.00	149	16.3
n-pentane	1008	621	210.80	161	15.5
n-hex ane	1116	654	157.17	135	17.5
n-heptane	1154	684	142.61	124	16.8
n-octane	1192	703	124.10	116	16.9
n-nonane	1234	738	112.50	107	17.3

Table 2. Calculated, measured and reference values for organic liquid (20°C).

Liquid	$\left(\frac{\partial C}{\partial P}\right)\Big/(\times10^{-6}\mathrm{m\cdot s^{-1}\cdot N^{-1}})_T$		$\left(\frac{\partial C}{\partial T}\right)_P\Big/(\mathrm{m\cdot s^{-1}\cdot K^{-1}})$		B/A		
	Calculated	Reference	Calculated	Reference	Calculated	Measured	Reference
Benzene	5.13	5.73[9]	4.75	4.45[9]	11.92	9.21	8.17[10]
		5.23[14]		4.8[15]			10.69[14]
Carbon	3.31	3.74[9]	3.10	2.89[9]	9.90	9.08	8.73[10]
tetrachloride		3.92[3]		3.0[15]			9.62[14]
methanol	5.28	5.86[9]	3.89	3.61[9]	9.39	9.24	8.69[10]
		5.64[3]		3.3[3]			9.34[14]
Acetone	5.13	5.97[9]	4.82	5.30[9]	9.67	9.11	9.05[10]
		5.59[3]		4.52[2]			9.55[14]
n-pentane	7.97		4.19	4.63[9]	9.98	8.71	8.49[10]
				4.2[15]			
n-hex ane	7.16		4.39	4.36[9]	10.45	9.23	9.21[10],
				4.4[15]			9.9(30°C)[14]
n-heptane	6.53		4.01	3.75[9]	10.31	9.12	8.93[10],
				4.0[15]			10.0(30°C)[14]
n-octane	5.89		3.89	3.52[9]	9.88	9.07	9.00[10]
				3.9[15]			
n-nonane	5.62		3.81	3.21[9]	10.24	9.14	9.10[10]
				3.8[15]			

Table 3. Data of components of the mixtures (20°C).

Mixtures	X_1	$c/(\mathrm{m{\cdot}s^{-1}})$	$\rho/(\mathrm{kg{\cdot}m^{-3}})$	l_1	n_1
Acetone(X_1)- Benzene(X_2) $\begin{bmatrix} V_1 = 73.2\times10^{-2}\mathrm{m}^3, S_1 = 1.7822^{[22]} \\ V_2 = 89.0\times10^{-2}\mathrm{m}^3, S_2 = 1.5231^{[22]} \end{bmatrix}$	0.2	1278	860.8	0.2263	0.1705
	0.4	1257	843.6	0.4382	0.3541
	0.6	1233	826.4	0.6370	0.5523
	0.8	1207	809.2	0.8240	0.7669
Carbon tetrachloride (X_1)- Benzene (X_2) $\begin{bmatrix} V_1 = 96.6\times10^{-2}\mathrm{m}^3, S_1 = 1.5835^{[22]} \\ V_2 = 89.0\times10^{-2}\mathrm{m}^3, S_2 = 1.5231^{[22]} \end{bmatrix}$	0.2	1152	1021.4	0.2063	0.2134
	0.4	1092	1164.8	0.4094	0.4198
	0.5	1025	1236.5	0.5097	0.5205
	0.7	975	1379.9	0.7081	0.7169
	0.8	945	1451.6	0.8061	0.8128

Table 4. Calculated, measured and reference values of coefficient of ultrasonic velocity in Acetone(X_1)- Benzene(X_2) (20°C).

X_1	$\left(\frac{\partial C}{\partial P}\right)\Big/(\times10^{-6}\mathrm{m\cdot s^{-1}\cdot N^{-1}})_T$			$-\left(\frac{\partial C}{\partial T}\right)_P\Big/(\mathrm{m\cdot s^{-1}\cdot K^{-1}})$			B/A		
	Calculated	From Ref.[11]	Measured	Calculated	From Ref.[12]	Measured	Calculated	Apfel[16]	Sehgal[17]
0.2	5.07	5.66	5.54	4.70	4.48	4.51	11.15	11.49	10.94
0.4	5.09	5.70	5.73	4.74	4.62	4.59	10.79	11.05	10.63
0.6	5.10	5.76	5.80	4.76	4.79	4.77	10.39	10.59	10.26
0.8	5.10	5.81	5.84	4.77	4.98	5.02	9.96	10.13	9.85

Table 5. Calculated, measured and reference values of B/A in Acetone(X_1)- Carbon tetrachloride (X_2) (20°C).

X_1	$\left(\frac{\partial C}{\partial P}\right)\Big/(\times10^{-6}\mathrm{m\cdot s^{-1}\cdot N^{-1}})_T$			$-\left(\frac{\partial C}{\partial T}\right)_P\Big/(\mathrm{m\cdot s^{-1}\cdot K^{-1}})$			B/A		
	Calculated	From Ref.[11]	Measured	Calculated	From Ref.[12]	Measured	Calculated	Apfel[16]	Sehgal[17]
0.2	4.38	4.91	5.06	4.06	3.80	4.06	10.31	11.43	9.69
0.4	4.07	4.58	4.52	3.79	3.54	3.61	10.35	11.00	9.94
0.5	3.79	4.25	4.29	3.53	3.29	3.24	9.61	10.80	8.95
0.7	3.54	3.96	3.96	3.30	3.08	3.00	9.53	10.42	9.01
0.8	3.40	3.83	3.78	3.17	2.92	2.92	9.33	10.24	8.83

From Tables 3, 4, and 5, one can find that the calculated values are in good agreement with both of the measured values and the reference data from other researchers.

In the homologous series, the values of pressure coefficient of ultrasonic velocity decrease when the number of the homologue grows.

By comparing the results with the results we obtained in our earlier work, it is obvious that the proposed formula for pressure coefficient, temperature coefficients of ultrasonic velocity and nonlinear acoustic parameter B/A in both the organic liquids and the binary organic liquid mixtures are suitable for the study of ultrasonic nature in organic liquid and binary organic liquid mixtures.

5. Conclusions

(1) Schaaffs' collision factor theory can be used to calculate not only ultrasonic velocity but also the coefficient of ultrasonic velocity and nonlinear acoustic parameter B/A for bath organic liquid and binary organic liquid mixtures.

(2) Coefficients of ultrasonic velocity and nonlinear acoustic parameter B/A for both the organic liquid and the binary organic liquid mixtures are determined by its internal structure, thermodynamic parameters and outside status. The bigger the exponent of repulsive forces of the molecules, the larger the coefficient of ultrasonic velocity and the nonlinear acoustic parameter B/A.

(3) Mole fraction and some physical parameters of the components can be utilized to estimate nonlinear

acoustic parameter B/A of the binary organic liquid mixtures, therefore there is no need to measure the nonlinear acoustic parameter B/A of the components. Conversely, internal structure information of the liquid, especially the information of interactions between the molecules, can be acquired through measuring the acoustic parameter of the medium.

References

[1] Kittle C 1964 *J. Chem. Phys.* **61** 614
[2] Hartman B 1979 *J. Acoust. Soc. Am.* **65** 1392
[3] Tong J and Dong Y W 1993 *J. Acoust. Soc. Am.* **93** 291
[4] Krzesińska M 2000 *Fuel* **79** 1907
[5] Yadava S S and Aniruddh Y 2005 *Ultrasonics* **43** 732
[6] Kamila S, Mukherjee A and Chakravortty V 2004 *J. Molecular Liquids* **115** 127
[7] Jacobson B 1952 *Acta Chem. Scand.* **6** 1485
[8] Jacobson B 1952 *J. Chem. Phys.* **20** 927
[9] Lu Y G, Peng J X, Dong Y W and Tong J 1999 *Chin. Sci. Bull.* **44** 1770
[10] Lu Y G, Peng J X, Dong Y W and Tong J 2000 *Chin. J. Acoustics* **19** 285
[11] Lu Y G, Feng J Y, Dong Y and Tong J 1999 *Acta Phys. Sin.* **48** 2087 (in Chinese)
[12] Lu Y G, Feng J Y, Dong Y W and Tong J 1999 *Acta Phys. Sin.* **48** 2082 (in Chinese)
[13] Lu Y G, Feng J Y, Dong Y W and Tong J 2000 *Chin. Sci. Bull.* **45** 414
[14] Coppens A B and Beyer R T 1965 *J. Acoust. Soc. Am.* **38** 797
[15] Soczkiewicz E 1977 *Archives of Acoustics* **2** 325
[16] Apfel R E 1983 *J. Acoust. Soc. Am.* **74** 1866
[17] Sehgal C M 1986 *Ultrasound in Med. and Biol.* **12** 865
[18] Schaaffs W 1963 *Molekurlrakustik* (Berlin: Springer) p278
[19] Schaaffs W 1965 *Acustica* **11** 351
[20] Qian Z W 1992 *Nonlinear Acoustics* (Beijing: Science Press) p249 (in Chinese)
[21] Soczkiewicz E 1978 *Arch. Aco.* **3** 267
[22] Chaturvedi B R, Verma S K and Pant N 1980 *Acoust. Lett.* **4** 53