

Surface tension and ultrasonic velocity of binary liquid mixtures at 298.15 K

J D PANDEY^a, G P DUBEY^{b*} and N TRIPATHI^b

^aDepartment of Chemistry, University of Allahabad, Allahabad 211 002, India

^bDepartment of Chemistry, Kurukshetra University, Kurukshetra 136 119, India

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Abstract. Using the Brock and Bird relation and the Flory statistical theory, the surface tension of five binary mixtures of 1,1,2,2-tetrachloroethane with benzene, toluene, *p*-xylene, acetone and cyclohexane have been evaluated at 298.15 K. The values of surface tension thus obtained have been utilized to compute ultrasonic velocity via the Auerbach relation. Theoretical values have been compared with experimental data and deviations in the ultrasonic velocity have been interpreted in terms of intermolecular interactions.

Keywords. Binary liquid mixtures; Brock and Bird relation; Flory statistical theory; ultrasonic velocity.

1. Introduction

Surface tension is a diagnostic parameter for describing various properties of liquids and liquid mixtures. A number of empirical, semi-empirical and statistical theories have been developed by several workers^{1–5} for evaluation of surface tension. Brock and Bird⁶ have designed a semi-empirical relation for the estimation of surface tension of pure liquids for which only the critical data of temperature, pressure and volume are required. Further, this approach can also be extended to binary liquid mixtures. Another important method for theoretical evaluation of surface tension of mixtures is the Flory statistical theory^{7,8}. Patterson and Rastogi⁹ studied this theory for the evaluation of surface tension using reduced parameters. Mishra¹⁰ and Pandey *et al*^{11–13} have examined this theory for computing the sound velocity of pure liquids and binary liquid mixtures.

In the present investigation, surface tension of binary liquid mixtures have been evaluated using the theory given by Brock and Bird as well as the Flory statistical theory. The values of surface tension thus obtained have been utilized to calculate ultrasonic velocity employing the Auerbach¹⁴ relation. A comparison has been made between the experimentally obtained values with those evaluated theoretically through two different approaches. Results are given in terms of percentage deviations in ultrasonic velocity. Good agreement is seen between the two approaches. Binary mixtures used for the present study are 1,1,2,2-tetrachloroethane with benzene, toluene, *p*-xylene, acetone and cyclohexane at 298.15 K. The experimental data needed for the purpose have been taken from the literature^{15,16}.

*For correspondence

2. Theoretical

Brock and Bird⁶ have found the following correlation between critical constants and surface tension,

$$\frac{\sigma}{(P_c^2 T_c)^{1/3}} = \left(-0.951 + \frac{0.432}{Z_c} \right) (1 - T_r)^{11/9}. \quad (1)$$

In the above equation Z_c and T_r are critical compressibility factor and reduced temperature respectively. These are expressed as

$$Z_c = P_c V_c / (RT_c), \quad (2)$$

$$T_r = T / T_c, \quad (3)$$

where T and R stand for absolute temperature and gas constant respectively and P_c , V_c and T_c are the critical constants of the liquid.

In case of binary liquid mixtures, pseudo-critical constant values can be taken and (1) can be written as,

$$\frac{\sigma_m}{(P_{c_m}^2 T_{c_m})^{1/3}} = \left(-0.951 + \frac{0.432}{Z_{c_m}} \right) (1 - T_{r_m})^{11/9}. \quad (4)$$

These pseudo-critical constants (P_{c_m} , V_{c_m} and T_{c_m}) for binary liquid mixtures are calculated assuming that these are all mole fraction averages⁵:

$$P_{c_m} = x_1 P_{c_1} + x_2 P_{c_2}, \quad (5)$$

$$V_{c_m} = x_1 V_{c_1} + x_2 V_{c_2}, \quad (6)$$

$$T_{c_m} = x_1 T_{c_1} + x_2 T_{c_2}, \quad (7)$$

and the values of T_{r_m} and Z_{c_m} are obtained from the relations,

$$T_{r_m} = T / T_{c_m}, \quad (8)$$

$$Z_{c_m} = P_{c_m} V_{c_m} / (RT_{c_m}). \quad (9)$$

Another method used to evaluate the ultrasonic velocity in binary liquid mixtures is the Flory statistical theory which has no direct link with ultrasonic velocity. Patterson and coworkers used this theory to calculate surface tension which in turn is used to evaluate ultrasonic velocity in liquid mixtures. Patterson and Rastogi⁹ used the following relation to calculate characteristic surface tension,

$$\sigma^* = k^{1/3} P^{*2/3} T^{*1/3}, \quad (10)$$

where k denotes the Boltzmann constant, and P^* and T^* are the characteristic pressure and temperature respectively. Here,

$$P^* = \gamma T \bar{V}^2, \quad (11)$$

where $\gamma = (\partial P / \partial T)_v = (\alpha / \beta_T)$ is the thermal pressure coefficient at $P = 0$, α is the thermal expansion coefficient and β_T the isothermal compressibility.

The reduced volume \bar{V} for a pure substance in terms of thermal expansion coefficient is given as,

$$\bar{V} = \left(\frac{1 + (4/3)\alpha T}{1 + \alpha T} \right)^3. \quad (12)$$

The characteristic temperature T^* is given as,

$$T^* = T \left(\frac{\bar{V}^{4/3}}{\bar{V}^{1/3} - 1} \right). \quad (13)$$

The characteristic and reduced parameters used to evaluate the surface tension of binary liquid mixtures, are given by the following expressions,

$$V_m^* = x_1 V_1^* + x_2 V_2^*, \quad (14)$$

$$\bar{V}_m = V / [x_1 V_1^* + x_2 V_2^*], \quad (15)$$

$$P^* = \Psi_1 P_1^* + \Psi_2 P_2^* - \Psi_1 \theta_2 X_{12}, \quad (16)$$

and

$$T^* = P^* / \left[\frac{\Psi_1 P_1^*}{T_1^*} + \frac{\Psi_2 P_2^*}{T_2^*} \right], \quad (17)$$

where Ψ is the segment fraction, X_{12} the interaction parameter and θ_2 the site fraction. This is expressed as,

$$\Psi_1 = \frac{x_1 V_1^*}{x_1 V_1^* + x_2 V_2^*}, \quad (18)$$

$$\Psi_2 = 1 - \Psi_1, \quad (19)$$

$$\theta_2 = \Psi_2 / \left[\Psi_2 + \Psi_1 \left(\frac{V_2^*}{V_1^*} \right)^{1/3} \right], \quad (20)$$

and

$$X_{12} = R_1^* \left[1 - \left(\frac{V_2^*}{V_1^*} \right)^{1/6} \left(\frac{P_2^*}{P_1^*} \right)^{1/2} \right]^2 \quad (21)$$

Starting from the work of Prigogine and Saraga¹⁷, the equation for reduced surface tension is,

$$\bar{\sigma}(\bar{V}) = M\bar{V}^{-5/3} \frac{\bar{V}^{1/3} - 1}{\bar{V}^2} \left[\frac{\bar{V}^{1/3} - 0.5}{\bar{V}^{1/3} - 1} \right], \quad (22)$$

where M is the fractional decrease in the nearest neighbours of a cell due to migration from bulk phases to the surface phases, whose value varies from 0.26–0.31 for a closely packed lattice. In the present calculations, we have used $M = 0.29$.

Thus the surface tension of a liquid mixture is given by the relation,

$$\sigma_m = \sigma^* \bar{\sigma}(\bar{V}). \quad (23)$$

The values of surface tension obtained by the Brock and Bird relation for binary mixtures, (4), and by the Flory theory, (23), have been used to evaluate ultrasonic velocity, making use of the well-known Auerbach relation¹⁴,

$$U = \left(\frac{\sigma_m}{6.3 \times 10^{-4} \rho_m} \right)^{2/3}, \quad (24)$$

where ρ_m is the density of the mixture.

3. Results and discussion

The ultrasonic velocity in binary mixtures of 1,1,2,2-tetrachloroethane with benzene, toluene, *p*-xylene, acetone and cyclohexane at 298.15 K have been computed using (4) and (24) as well as (23) and (24). Table 1 comprises the values of different parameters for pure components such as thermal expansion coefficient, isothermal compressibility, reduced volume, characteristic volume, pressure and temperature. The necessary data required for the evaluation of ultrasonic velocity as well as the experimental ultrasonic velocity values have been taken from different sources^{15,16}.

In table 2 the percentage deviations of ultrasonic velocity obtained by two different methods have been given. The percentage deviation of ultrasonic velocity has been found to decrease with increase in the concentration of tetrachloroethane in both the methods. The variation in the percentage deviation with change in concentration of the components indicates the existence of molecular interaction between the components of different binary systems.

Table 2 reveals that for binary mixtures of tetrachloroethane, both positive and negative values of deviations of ultrasonic velocity are obtained. The maximum deviation is observed for the system tetrachloroethane + acetone by both the methods which provides evidence of the formation of a strong molecular complex between tetrachloroethane and acetone in the liquid state. The complexation between acetone and

Table 1. Values of molar volume (V), reduced volume (\bar{V}), thermal expansion coefficient (α), isothermal compressibility (β_T) and characteristic parameters (P^* , V^* and T^*) for pure liquids at 298.15 K.

Liquid components	$V \times 10^6$ ($\text{m}^3 \text{mol}^{-1}$)	\bar{V}	$\alpha \times 10^3$ (K^{-1})	β_T (TPa^{-1})	$P^* \times 10^6$ (J cm^{-3})	$V^* \times 10^6$ ($\text{m}^3 \text{mol}^{-1}$)	T^* (K)
1,1,2,2-Tetrachloroethane	105.63	1.2473	0.998	617.0	774	84.69	5237
Benzene	89.5	1.2917	1.223	967.0	648	69.14	4709
Toluene	106.81	1.2627	1.074	896.0	573	84.57	5033
<i>p</i> -Xylene	123.94	1.2508	1.051	859.0	548	98.98	5188
Acetone	73.98	1.3309	1.437	1239.0	632	55.57	4366
Cyclohexane	108.79	1.2903	1.215	1140.0	534	84.29	4724

tetrachloroethane can be attributed to the formation of strong hydrogen bonds between the hydrogen atoms of tetrachloroethane and the lone-pair electrons of the oxygen atom of acetone. The association of tetrachloroethane with aromatic hydrocarbons can be attributed to the existence of a specific interaction. It may be due to the formation of a weak hydrogen bond between the hydrogen atoms of the tetrachloroethane and the π -electrons of the aromatic ring.

The minimum value of mean percentage deviation is obtained for the system tetrachloroethane + cyclohexane. These values are -0.93 and -0.29 respectively by the two methods. The variation of mean percentage deviation from -2.73 to $+0.07$ (method 1) and from -3.09 to -0.31 (method 2) for the systems tetrachloroethane + benzene to tetrachloroethane + *p*-xylene suggests that with the increase of the number of $-\text{CH}_3$ groups attached to the benzene nucleus, the π -electron density above and below the benzene nucleus increases, which in turn causes increased interaction between the molecules. Since M in (22) is the fractional decrease in the number of neighbours of a cell in the surface phases compared to the bulk phase, it should have values which vary with temperature and pressure. Patterson and Rastogi⁹ have suggested a range of values from 0.26 to 0.31 . Auxiliary calculations show that the values of percentage deviations can be further improved by adopting a value higher than 0.29 . Since the Flory theory is strictly applicable to spherical molecules and (22) ignores the effect of shape, larger deviations are expected in the present systems. However the values of deviations obtained via the Brock and Bird relations show good agreement with that obtained through the Flory theory except in the tetrachloroethane + acetone system where the deviation obtained via the Brock and Bird method is larger.

Thus, it can be concluded that the Brock and Bird relation as well as the Flory-Patterson theory are very useful for evaluating surface tension which in turn can be used to predict the sound velocity of a binary liquid mixture. This relation, however, is not very suitable for mixtures where hydrogen bonding is expected.

All the reduced and characteristic parameters given by the Flory theory have been computed from the reduced equations of state. Such equations are assumed to hold universally but avoid unrealistic parametrization of intermolecular energies as stipulated by the theorem of corresponding states. The basic advantage of the Flory theory over other theories in computing the sound velocity is that all the essential parameters can be

Table 2. Experimental values of ultrasonic velocity and their percentage deviations for binary liquid mixtures of 1,1,2,2-tetrachloroethane at 298.15 K. D = mean percentage deviation.

x_1	U_{exp} (ms^{-1})	ΔU (Brock & Bird)	ΔU (Flory)
<i>1,1,2,2-Tetrachloroethane (x_1) + benzene ($1-x_1$) system</i>			
0.0660	1276	3.8	0.39
0.1858	1243	1.1	-0.65
0.1860	1243	1.1	-0.73
0.2606	1227	-0.4	-1.32
0.4252	1201	-3.3	-2.74
0.5705	1181	-4.9	3.69
0.6562	1172	-5.3	-4.36
0.7000	1168	-5.9	-4.47
0.8679	1160	-7.7	-6.62
0.9337	1158	-8.2	-6.73
		$D = -2.73$	$D = -3.09$
<i>1,1,2,2-Tetrachloroethane (x_1) + toluene ($1-x_1$) system</i>			
0.2923	1237	3.3	1.51
0.4200	1212	0.3	-0.50
0.4364	1207	0.3	-0.42
0.4586	1202	0.0	-0.50
0.5325	1190	-1.0	-1.19
0.6841	1175	-3.6	-3.07
0.8942	1161	-6.9	-5.74
0.9001	1159	-6.9	-5.65
		$D = -1.47$	$D = -1.95$
<i>1,1,2,2-Tetrachloroethane (x_1) + p-xylene ($1-x_1$) system</i>			
0.0926	1282	6.4	4.90
0.2279	1253	3.9	3.20
0.2927	1239	2.9	2.44
0.4536	1209	0.3	0.82
0.4964	1202	-0.3	0.25
0.5000	1201	-0.3	-6.10
0.5654	1193	-2.3	-0.59
0.6447	1181	-3.5	-4.46
0.7785	1168	-5.0	-43.27
		$D = 0.07$	$D = -0.31$
<i>1,1,2,2-Tetrachloroethane (x_1) + acetone ($1-x_1$) system</i>			
0.0604	1154	31.4	0.08
0.0713	1152	30.4	7.62
0.2374	1137	17.5	1.47
0.4579	1133	6.1	0.69
0.4964	1135	4.9	0.00
0.6507	1138	-0.7	-2.12
0.9267	1146	-6.8	-5.39
		$D = -12.47$	$D = 1.48$

Contd.....

Table 2. (Contd.)

x_1	U_{exp} (ms^{-1})	ΔU (Brock & Bird)	ΔU (Flory)
<i>1,1,2,2-Tetrachloroethane (x_1) + cyclohexane ($1-x_1$) system</i>			
0.0537	1238	5.6	5.68
0.3000	1181	2.9	1.75
0.4164	1162	1.6	0.51
0.5000	1154	0.1	0.43
0.6904	1150	-3.1	1.12
0.8832	1152	-6.5	-5.69
0.9139	1150	-7.0	-5.98
		$D = -0.93$	$D = -0.29$

precisely determined experimentally. Moreover, this theory is simple to elaborate. Thus, there is no probability of serious errors in the prediction of sound velocity from the Flory statistical theory and it is clear from the above discussion that both the approaches agree with experimental values satisfactorily and reasonably and can be used if all the required data are available in correct form.

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