

CHAPTER 8

RESULTS

8.1 Theoretical aspects – Evaluation of excess sound velocity

The excess thermodynamic functions are useful in understanding the solute-solvent interactions in liquid mixtures. The magnitude and sign of the excess thermodynamic property of a mixture are a measure of the deviation of the mixture from ideality and reflect the nature of molecular interactions. The solute-solvent interactions in binary mixtures of water and nonelectrolytes and of nonelectrolytes themselves are extensively studied now-a-days by determining the excess compressibilities, excess heat capacity, excess internal pressure, excess Gruneisen parameter, excess Gibb's free energy and excess enthalphy.

The survey of literature indicates that the studies on the use of the excess sound velocity parameter in understanding the solute-solvent interactions in liquid mixtures are not extensive due to the fact that the sound velocity being not a primary thermodynamic parameter and also as well that there is no single agree view regarding the method of evaluation of the ideal value of the sound velocity in a mixture. Eventhough Lara and Desnoyers [16] and Kiyohara *et al.* [151] attempted to interpret the solution structure based on the extrema observed in the concentration dependence of excess sound velocity, the very procedure of evaluation of excess sound velocity has been questioned [152] since it is not thermodynamically valid. However the attempts made by Ernst and Glinski [152] and Kiyohara *et al.* [153] indicate that sound velocities evaluated making use of thermodynamically valid expressions may be utilized to obtain excess sound velocities which are useful in understanding the solute-solvent interactions.

In the present work, excess sound velocity data have been utilized to elucidate the solute-solvent interactions in binary dilute solutions of water in nonelectrolytes. As such, a detailed account of the evaluation of excess sound velocity in a binary mixture is given below.

The thermodynamic excess function F^E can be defined as the excess of the thermodynamic property F of a real mixture over F_{id} , the value for an ideal mixture of the same temperature, pressure and composition. Thus

$$F^E = F - F_{id} \quad \dots \quad 8.1.1$$

The accuracy of F^E depends not only on the accuracy of the determination of F , but also on the accuracy of any approximations adopted in estimating F_{id} .

From the above definition of an excess function, the excess sound velocity u^E in a binary mixture can be given by

$$u^E = u - u_{id} \quad \dots \quad 8.1.2$$

where u represents the experimentally determined diffraction corrected velocity of sound in the mixture and u_{id} represents the velocity of sound in the ideal mixture. u_{id} can be expressed as additive on mole fraction basis [16, 151] or weight fraction basis [154]. But the excess sound velocity so obtained does not property characterize the deviations of acoustic properties of the mixture from identity.

The thermodynamic criterion of ideality of a mixture is given by

$$G = \sum_i X_i \mu_i + RT \sum_i X_i \ln X_i \quad \dots \quad 8.1.3$$

where G , μ_i , X_i , R and T represent mean molar free enthalpy, chemical potential of the i^{th} component, mole fraction of the i^{th} component, gas constant and temperature of the mixture in absolute scale respectively. According to the above equation, the sound velocity in an ideal mixture should differ from the mole fraction average of the velocities in the pure component since neither energy nor volume effects accompany the mixing of the components of an ideal mixture. The time of propagation of a plane acoustic wave through an ideal mixture layer of thickness 'L' should be equal to the sum of the times the wave needs to pass through the separate layers of the pure components of thickness $L\phi_i$ where ϕ_i represents the volume fraction of the i^{th} component. Hence

$$\frac{L}{u_{id}} = \sum_i \frac{L\phi_i}{u} \quad \dots \quad 8.1.4$$

Therefore

$$u_{id} = \left[\sum \frac{\phi_i}{u_i} \right]^{-1} \quad \dots \quad 8.1.5$$

For a binary mixture

$$u_{id} = \left[\frac{\phi_1}{u_1} + \frac{\phi_2}{u_2} \right]^{-2} \quad \dots \quad 8.1.6$$

or

$$u_{id} = \left[\frac{u_1 u_2}{\phi_1 u_2 + \phi_2 u_1} \right] \quad \dots \quad 8.1.7$$

where u_1 , u_2 and ϕ_1 , ϕ_2 represent the sound velocities and volume fractions respectively. Suffix 1 and suffix 2 correspond to the first and second components of the binary mixture respectively.

The ideal sound velocity can also be calculated on the basis of the Laplace equation and is given by

$$u_{id} = [\beta_{id} \rho_{id}]^{-1/2} \quad \dots \quad 8.1.8$$

where

$$\rho_{id} = \phi_1 \rho_1 + \phi_2 \rho_2 \quad \dots \quad 8.1.9$$

$$\beta_{id} = \phi_1 \beta_1 + \phi_2 \beta_2 \quad \dots \quad 8.1.10$$

Here ρ_1 , ρ_2 and β_1 , β_2 represent the densities and adiabatic compressibilities respectively of pure components in the binary mixture.

The isothermal compressibility K of a liquid is related to the adiabatic compressibility β via the relation

$$K = \beta + \frac{TV\alpha^2}{C_p} \quad \dots \quad 8.1.11$$

where V , α and C_p represent molar volume, thermal expansion coefficient and molar heat capacity of constant pressure of the liquid respectively. β_{id} of the mixture can be evaluated using the following expression

$$\beta_{id} = K_{id} - \frac{TV_{id}\alpha_{id}^2}{C_{p_{id}}} \quad \dots \quad 8.1.12$$

where

$$K_{id} = \phi_1 K_1 + \phi_2 K_2 \quad \dots \quad 8.1.13$$

$$V_{id} = X_1 V_1 + X_2 V_2 \quad \dots \quad 8.1.14$$

$$\alpha_{id} = \phi_1 \alpha_1 + \phi_2 \alpha_2 \quad \dots \quad 8.1.15$$

$$C_{p id} = X_1 C_{p 1} + X_2 C_{p 2} \quad \dots \quad 8.1.16$$

Kiyohara *et al.* [151] used the following expression to obtain deviation of u from ideality on mole fraction basis to understand the acoustic behaviour of a mixture.

$$\Delta u = u - (X_1 u_1 + X_2 u_2) \quad \dots \quad 8.1.17$$

But, they agree with the view of Ernst and Glinski [152] that Δu does not properly characterize the deviation of the acoustic properties of the mixture from ideality.

Kiyohara *et al.* [153] point out that the Eqn. 8.1.17 which depends on an intuitive model for the passage of a wave through layers at the unmixed components is unsuitable for defining an ideal thermodynamic value for u . They also state that Eqn. 8.1.8 which follows from Laplace equation under conditions where dispersion is negligible is the correct way of relating u to the thermodynamic properties and ideal thermodynamic behaviour.

Ernst and Glinski [152] point out that Eqn. 8.1.7 is more reliable than Eqn. 8.1.8 from their calculations of excess sound velocities in (heavy water + water) mixture.

Thus the excess sound velocity in a binary liquid mixture can be evaluated using Eqns. 8.1.2 and 8.1.7 (Formula 1); Eqns. 8.1.2, 8.1.8, 8.1.9 and 8.1.10 (Formula II) and Eqns. 8.1.2, 8.1.8 and 8.1.12 (Formula III).

The relative merits and adaptability of each of the above three formulae have been tested by Manohara Murthy and Nagabhushanam [155-157] on a large number of binary mixtures of water + nonelectrolytes and nonelectrolytes themselves namely n-alcohol + n-alkane mixtures. They concluded that Formula III may be taken as more appropriate to evaluate the excess sound velocity in binary mixtures. Since the parameters involved (isothermal compressibility and molar heat capacity at constant pressure) in the estimation of u^E truly depict the nonideality of the mixtures and are also thermodynamically consistent.

In the present study formula III has been used to evaluate excess sound velocities in dilute solutions of water in the nonelectrolytes. The pure liquid parameters required for the evaluation of excess sound velocities in the solutions of water in the nonelectrolytes studied in the present work are presented in Table 8.1.1.

Table 8.1.1 u , ρ , C_p , α , β , and k of pure liquids at 298.15 K

Liquid	u (m s ⁻¹)	ρ (kg m ⁻³)	C_p (J mol ⁻¹ K ⁻¹)	$\alpha \times 10^4$ (K ⁻¹)	$\beta \times 10^{11}$ (N ⁻¹ m ²)	$K \times 10^{11}$ (N ⁻¹ m ²)	Ref
Water	1496.7	997.07	75.3	2.59	44.77	45.25	[23]
PEG- 200	1606.4	1120.55	372.2	6.81	34.63	41.26	[119]
PEG - 300	1592.6	1122.08	562.9	6.30	35.11	40.73	[119]
PEG - 400	1591.4	1122.28	729.1	6.24	35.11	40.79	[119]
PEG - 600	1586.0	1122.80	1090.0	5.08	35.36	39.04	[14]
Diethylene glycol	1583.5	1113.00	244.8	7.16	35.76	41.80	[158]
Methanol	1097.6	786.44	81.2	12.01	104.04	125.14	[17]
Ethanol	1144.3	785.06	112.6	10.92	97.28	116.34	[17]
n-butanol	1239.9	805.70	177.0	9.32	80.73	94.25	[23]
2-methyl ethanol	1344.8	960.03	176.4	8.23	57.52	66.60	[159]
2-ethynol ethanol	1309.3	925.01	210.3	8.40	63.03	72.78	[159]
2-butyl ethanol	1304.8	896.31	270.6	10.41	65.50	81.24	[159]
Diethylamine	1120.2	702.56	169.2	12.94	113.27	143.01	[158]
Triethylamine	1115.1	725.56	219.9	12.45	110.81	140.12	[158]
Dibutylamine	1249.1	755.62	292.9	11.11	84.70	106.19	[158]
Di-sec-butylamine	1182.0	748.84	253.2	11.46	95.81	134.26	[158]

8.2. Results – Ultrasonic velocity in dilute solutions of water in nonelectrolytes

Triple distilled degassed water was used to prepare the dilute solutions of water in the nonelectrolytes. Solutions of desired concentration were prepared by weighing the samples using mono pan balance with an accuracy of ± 0.1 mg. Ultrasonic velocities in the solutions have been determined using the variable path interferometer working at 3 MHz, the details of which are described in Chapter 2. The interferometer filled with the solution is kept inside U-10 thermostat controlled at 298.15 K with an accuracy of ± 0.01 K. One hour was allowed for the experimental liquid to attain thermal equilibrium. The wavelength of the ultrasonic wave in the solution was determined by measuring the path length for 60 dips. Knowing the frequency of the oscillator at which the quartz transducer has been excited (determined by using Digital Frequency Meter), the ultrasonic velocity in the solution was determined. Six measurements were made for each solution and the average value was taken as the velocity in the solution.

The ultrasonic velocities determined in the solutions were corrected for diffraction effects. The diffraction corrected ultrasonic velocities (u) in dilute solutions of water in glycols; n-alcohols; 2-alkoxy ethanols and amines as a function of concentration of water (mole fraction X_2) are presented in Tables 8.2.1 to 8.2.4 respectively. The excess sound velocities evaluated using the Formula III as detailed in Section 8.2.1 are also presented in the Tables 8.2.1 to 8.2.4. The molecular weights of pure liquids were taken to be the formula weights. The atomic weights of the elements were taken from C-12 isotope scale as given in "Lange Hand Book of chemistry" [160]. The excess sound velocities determined are accurate to ± 0.2 m s⁻¹.

TABLE 8.2.1 u , u_{id} and u^E versus X_2 of water in (glycols + water) at 298.15K

X_2	$u(\text{ms}^{-1})$	$u_{id}(\text{ms}^{-1})$	$u^E(\text{ms}^{-1})$
(Diethylene glycol + water)			
0.0000	1583.5	-	-
0.0019	1584.7	1583.1	1.6
0.0029	1585.3	1583.1	2.2
0.0036	1585.9	1583.1	2.8
0.0046	1586.0	1583.1	2.9
0.0062	1586.2	1583.1	3.1
0.0079	1587.5	1583.0	4.5
0.0087	1587.5	1583.0	4.5
0.0095	1588.0	1583.0	5.0
PEG (polyethylene glycol) - 200 + water			
0.0000	1606.4	-	-
0.0010	1606.6	1605.7	0.9
0.0021	1606.8	1605.7	1.1
0.0028	1607.0	1605.6	1.4
0.0042	1607.9	1605.6	2.3
0.0052	1608.4	1605.6	2.8
0.0060	1608.6	1605.5	3.1
0.0083	1609.3	1605.5	3.8
0.0094	1609.7	1605.4	4.3
PEG - 300 + water			
0.0000	1592.6	-	-
0.0014	1593.0	1593.3	-0.3
0.0023	1594.1	1593.3	0.8
0.0031	1594.5	1593.2	1.3
0.0042	1594.7	1593.2	1.5
0.0062	1596.2	1593.1	3.1
0.0074	1596.3	1593.1	3.2
0.0087	1596.5	1593.1	3.4
0.0095	1596.8	1593.0	3.8

TABLE 8.2.1 (continued)

X_2	$u(\text{ms}^{-1})$	$u_{id}(\text{ms}^{-1})$	$u^E(\text{ms}^{-1})$
PEG - 400 + water			
0.0000	1591.4	-	-
0.0017	1592.5	1593.0	-0.5
0.0039	1593.0	1592.9	0.1
0.0050	1593.2	1592.9	0.3
0.0068	1593.7	1592.8	0.9
0.0075	1593.8	1592.7	1.1
0.0091	1594.4	1592.7	1.7
0.0100	1594.7	1592.6	2.1
PEG - 600 + water			
0.0000	1586.0	-	-
0.0011	1586.8	1589.1	-2.3
0.0024	1587.0	1589.1	-1.9
0.0039	1587.4	1589.1	-1.7
0.0047	1588.0	1589.1	-1.1
0.0062	1588.4	1589.1	-0.7
0.0067	1588.6	1589.1	-0.5
0.0076	1588.6	1589.1	-0.5
0.0088	1588.8	1589.1	-0.3
0.0099	1589.4	1589.0	0.4

TABLE 8.2.2 u , u_{id} and u^E versus X_2 of water in (n-Alcohols + water) at 298.15 K

X_2	$u(\text{m s}^{-1})$	$u_{id}(\text{m s}^{-1})$	$u^E(\text{m s}^{-1})$
Methanol + water			
0.0000	1097.6	-	-
0.0011	1098.9	1097.7	1.2
0.0027	1099.2	1097.6	1.6
0.0037	1099.9	1097.6	2.3
0.0044	1100.2	1097.5	2.7
0.0054	1100.8	1097.5	3.3
0.0070	1102.6	1097.5	5.1
0.0074	1103.8	1097.5	6.3
0.0088	1104.7	1097.4	7.3
0.0100	1106.5	1097.4	9.1
Ethanol + water			
0.0000	1144.6	-	-
0.0013	1145.9	1141.1	4.8
0.0028	1146.5	1141.0	5.5
0.0033	1146.8	1141.0	5.8
0.0053	1147.1	1141.0	6.1
0.0069	1147.1	1141.0	6.1
0.0084	1147.7	1140.9	6.8
0.0094	1148.3	1140.9	7.4
n-butanol + water			
0.0000	1240.3	-	-
0.0007	1240.5	1239.4	1.1
0.0014	1241.1	1239.4	1.7
0.0028	1241.7	1239.4	2.3
0.0037	1241.7	1239.4	2.3
0.0043	1242.0	1239.4	2.6
0.0052	1242.1	1239.4	2.7
0.0075	1242.6	1239.4	3.2
0.0088	1242.9	1239.4	3.5
0.0100	1243.4	1239.4	4.0

TABLE 8.2.3 u , u_{id} and u^E versus X_2 of water in (2-alkoxy ethanols + water) at
298.15 K

X_2	$u(\text{m s}^{-1})$	$u_{id}(\text{m s}^{-1})$	$u^E(\text{m s}^{-1})$
2 - Methoxy ethanol + water			
0.0000	1344.8	-	-
0.0005	1345.0	1344.8	0.2
0.0022	1345.4	1344.8	0.6
0.0033	1345.9	1344.8	1.1
0.0043	1346.9	1344.7	2.2
0.0056	1347.2	1344.7	2.5
0.0068	1347.5	1344.6	2.9
0.0078	1347.8	1344.6	3.2
0.0087	1348.1	1344.6	3.5
0.0094	1348.9	1344.6	4.3
2-Ethoxy ethanol + water			
0.0000	1309.3	-	-
0.0008	1310.1	1309.2	0.9
0.0017	1311.4	1309.2	2.2
0.0028	1312.1	1309.2	2.9
0.0035	1312.6	1309.2	3.4
0.0046	1312.6	1309.2	3.4
0.0057	1313.1	1309.2	3.9
0.0064	1313.5	1309.1	4.4
0.0072	1313.8	1309.1	4.7
0.0088	1314.5	1309.1	5.4
2 - Butoxy ethanol + water			
0.0000	1304.5	-	-
0.0009	1306.0	1304.2	1.8
0.0020	1307.1	1304.1	2.9
0.0036	1308.2	1304.1	4.1
0.0047	1309.1	1304.0	5.0
0.0060	1309.8	1304.0	5.8
0.0075	1310.2	1304.0	6.2
0.0083	1310.5	1304.0	6.5
0.0092	1311.1	1304.0	7.1

TABLE 8.2.4 u , u_{id} and u^E versus X_2 of water in (amines + water) at 298.15 K

X_2	$u(\text{m s}^{-1})$	$u_{id}(\text{m s}^{-1})$	$u^E(\text{m s}^{-1})$
Diethylamine + water			
0.0000	1120.2	-	-
0.0010	1121.1	1122.9	-1.8
0.0028	1122.0	1122.9	-0.9
0.0031	1122.4	1122.8	-0.4
0.0045	1122.9	1122.8	0.1
0.0063	1123.5	1122.8	0.7
0.0073	1123.8	1122.7	1.1
0.0085	1124.5	1122.7	1.8
Triethylamine + water			
0.0000	1115.4	-	-
0.0018	1116.0	1115.2	0.8
0.0032	1116.7	1115.2	1.5
0.0036	1117.1	1115.2	1.9
0.0054	1117.5	1115.2	2.3
0.0061	1118.1	1115.2	2.9
0.008	1118.4	1115.1	3.3
0.0084	1119.0	1115.1	3.9
0.0094	1119.3	1115.1	4.2
Dibutylamine + water			
0.0000	1249.5	-	-
0.0014	1250.1	1250.0	0.1
0.0024	1250.7	1250.0	0.7
0.0032	1251.3	1250.0	1.3
0.0044	1251.6	1250.0	1.6
0.0060	1252.2	1249.9	2.3
0.0067	1251.9	1249.9	2.0
0.0083	1252.5	1249.9	2.6
0.0092	1252.5	1249.9	2.6
0.0100	1252.8	1249.8	3.0
Di-sec-butylamine + water			
0.0000	1182.0	-	-
0.0013	1183.2	1181.0	2.2
0.0028	1183.8	1181.0	2.5
0.0039	1184.1	1181.0	3.1
0.0050	1184.4	1181.0	3.4
0.0068	1184.4	1180.9	3.5
0.0079	1184.5	1180.9	3.6
0.0088	1185.6	1180.9	4.7
0.0096	1185.9	1180.9	5.0