Thermodynamic Properties of Pentanol Deduced from Ultrasonic Velocity Data of its Aqueous Solutions

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THERMODYNAMIC PROPERTIES OF PENTANOL DEDUCED FROM ULTRASONIC VELOCITY DATA OF ITS AQUEOUS SOLUTIONS

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The thermodynamic method of Eyring and Hirschfelder has been employed to evaluate intermolecular free length L_f whereas free length theory FLT of Jacobson was used to compute the theoretical data of ultrasonic sound velocity C_{FLT}. A maximum variation of 0.06% is observed between experimental velocity and the velocity deduced from free length theory ($C_{exp} > C_{FLT}$), while uncertainty for C_{exp} data is as high as $\pm 0.02\%$. The ultrasonic velocity data C_{FLT} and density ρ of pentanol in water have been used to compute coefficient of thermal expansion α, isothermal compressibility β_T, ratio of heat capacity γ, internal pressure p_i and pseudo-Gruneisen parameter Γ for the system. The results confirm that, upon increasing the temperature of the system, the solutions become easier to compress.

KEY WORDS: Ultrasonic velocity, density, free length theory.

INTRODUCTION

The internal pressure of liquids has been a subject of extensive investigation since the appearance of a review by Barton[1], although its physical significance and other details were originally discussed by Hildebrand and co-workers[2–4]. Major work has since been done on pure liquids[5–9]. The study of pseudo-Gruneisen parameter, a dimensionless quantity, for the structural and interaction investigations of liquids was initiated in the recent past[10–15]. Pandey *et al.*[16–20] and Subrahmanyam *et al.*[21] and others[22] have emphasised the role of internal pressure and the pseudo-Gruneisen parameter for investigating intermolecular interactions in binary liquid mixtures. It has been concluded that both internal pressure p_i and the pseudo-Gruneisen parameter Γ are thermodynamic properties.

The present study embodies calculations on pentanol in water where the internal pressure and Gruneisen parameter are computed from ultrasonic velocity C_{FLT} and density ρ alone. In the traditional procedure, however, one requires the values of thermal expansion coefficients α, isothermal compressibility β_T and the heat capacity at constant pressure C_p or constant volume C_v, in addition to C and ρ values, in the evaluation of these thermodynamic properties.

EXPERIMENTAL

1-Pentanol (Merk) was purified by refluxing the reagent over calcium hydride for 10h followed by fractional distillation. All solutions were prepared by weight using degassed conductance water. The solutions were kept at a constant temperature for about 2h in a thermostat. The data for density were taken from Ref. 23. The density were reportedly measured using a vibrating tube flow densimeter[23] (Sodev Inc. model 03D) sensitive to 3 ppm.

A multi frequency ultrasonic interferometer (M-83, Mittal Enterprises, New Delhi), operating at 4 MH$_z$, was used to measure the ultrasonic velocity of the solutions at different temperatures. The maximum uncertainty of velocity results was $\pm 0.02\%$.

THEORETICAL

The intermolecular free length L_f have been evaluated employing thermodynamic method of Eyring and Hirschfelder[24] using the following equations,

$$L_f = 2V_a/Y \tag{1}$$

$$V_a = V_T - V_0 \tag{2}$$

$$V_0 = V_t[1 - (T/T_c)^{0.3}] \tag{3}$$

where V_a, V_T, T signify for available volume, molar volume, experimental temperature and T_c is 0 K. The surface area per mole is given by

$$Y = [36\pi N V_0^2]^{1/3} \tag{4}$$

where N is Avogadro's number and V_0 is the molar volume at 0 K. The theoretical values of adiabatic compressibility β_s and ultrasonic velocity C were then computed,

$$\beta_s = L_f^2 K \tag{5}$$

$$C = \left[\frac{1}{\beta_s \cdot \rho}\right]^{1/2} \tag{6}$$

where K is the temperature dependent Jacobson's constant[25] and ρ is density of the solutions.

The internal pressure P_i, of a liquid can be obtained from the relation,

$$P_i = (\alpha T/\beta_T) - P \tag{7}$$

at atmospheric pressure ($P = 1$ atm) this reduces to,

$$P_i = \alpha T/\beta_T \tag{8}$$

The Gruneisen parameter Γ is a dimensionless measure of the change in entropy with volume or the thermal pressure coefficient, it is usually investigated, through the relation

$$\Gamma = \frac{\alpha v}{\beta_T C_v} = \frac{\alpha v}{\beta_s C} = \frac{-1}{C_v}\left(\frac{\delta S}{\delta \ln v}\right) = \frac{V}{C_v}\left(\frac{\delta P}{\delta T}\right)_v = \frac{C^2 \alpha}{C_P} = \frac{\gamma - 1}{\alpha T} \tag{9}$$

RESULTS AND DISCUSSION

The intermolecular free length L_f have been computed by thermodynamic method of Eyring and Hirschfelder[24] employing equations (1-4). The data of ultrasonic velocity C for pentanol in water at different temperatures were subsequently evaluated using Eqs. (5 and 6). A maximum variation of 0.06% is observed between experimental velocity and the velocity deduced from free length theory FLT ($C_{exp} > C_{FLT}$), while uncertainty for C_{exp} data is as high as $\pm 0.02\%$. It is found (Table 1) that both ultrasonic velocity as well as intermolecular free length decrease whereas data for available volume V_a, surface area per mole Y and adiabatic compressibility β_s increase with increasing the temperature. Figure 1 explicitly shows the effect of temperature and concentration on ultrasonic velocity, and the variation between experimental and deduced data of ultrasonic sound velocity for the given system.

From the density values of pentanol in water taken from Ref. 23, coefficient of thermal expansion α was obtained using the relation,

$$\alpha = \rho \left(\frac{\delta \rho - 1}{\delta T} \right)_P \tag{10}$$

The isothermal compressibility β_T of pentanol was obtained from the relation[26]

$$B_T \sigma^{4/3} = 1.2 \times 10^{-3} \; T^{1/3} \tag{11}$$

where σ is the surface tension. The values of σ were obtained using the well tested[20,27,28] Auerbach[29] relation,

$$C = \left(\frac{\sigma}{6.3 \times 10^{-4} \rho} \right)^{2/3} \tag{12}$$

where C is the ultrasonic velocity. The values of α and β_T for pentanol were computed from the relations (10), (11) and (12). The ratio of the heat capacities γ was obtained from,

$$\gamma = C_P / C_v = \beta_T / \beta_s \tag{13}$$

where B_s is the adiabatic compressibility. In order to carry out the evaluations of P_i and Γ for pentanol, the Eqs. (8) and (9) were employed.

The values of various thermodynamic properties of pentanol at different temperature are recorded in Table 2.

It is observed (Table 2) that both internal pressure as well as pseudo-Gruneisen parameter decrease whereas isothermal compressibility and the ratio of specific heats increase with increasing temperature. These results (Table 2) confirm that, upon increasing the temperature of the given system, the solutions tend to become more compressible i.e. easier to compress.

Table 1 Parameters for computing ultrasonic velocity of pentanol in water at different temperatures.

| Temp. (K)	m(Pent OH) (k mol/1000 kg)	ρ^* (kg m⁻³)	$V_T \times 10^3$ (m³ mol⁻¹)	$V_a \times 10^6$ (m³)	$Y \times 10^{-3}$ (m²)	$L_f \times 10^{10}$ (m)	$\beta_s \times 10^{10}$ (m² N⁻¹)	v (ms⁻¹)
288.15	0.05000	998.444	0.08829	89.72	51.77	34.66	1.046	3094.07
	0.06195	998.290	0.08830	89.73	51.80	34.47	1.035	3094.10
	0.07504	998.124	0.08832	89.75	51.80	34.65	1.046	3094.20
	0.08500	998.004	0.08833	89.76	51.80	34.66	1.046	3094.20
	0.09995	997.814	0.08834	89.77	51.80	34.66	1.046	3094.30
	0.11990	997.570	0.08836	89.79	51.80	34.67	1.047	3094.39
298.15	0.02498	996.712	0.08844	90.79	72.28	25.12	1.186	2908.40
	0.05000	996.381	0.08847	90.82	72.30	25.12	1.186	2908.76
	0.07501	996.049	0.08850	90.86	72.32	25.13	1.186	2909.00
	0.10000	995.726	0.08853	90.89	72.34	25.13	1.186	2909.35
	0.12500	995.400	0.08856	90.92	72.36	25.13	1.187	9009.58
	0.15000	995.077	0.08859	90.95	72.36	25.14	1.187	2909.07
	0.20000	995.441	0.08864	91.00	72.40	25.14	1.188	2910.50
308.15	0.02500	993.699	0.08871	91.98	89.93	20.46	1.913	2293.89
	0.03999	993.496	0.08873	92.00	89.95	20.46	1.913	2294.12
	0.06002	993.328	0.08875	90.02	89.97	20.46	1.913	2294.31
	0.07499	993.025	0.08877	92.04	89.99	20.46	1.913	2294.42
	0.10000	992.687	0.08880	92.07	90.00	20.46	1.913	2294.64
	0.14000	992.158	0.08885	92.12	90.02	20.47	1.914	2294.90

* density data taken from reference 23.
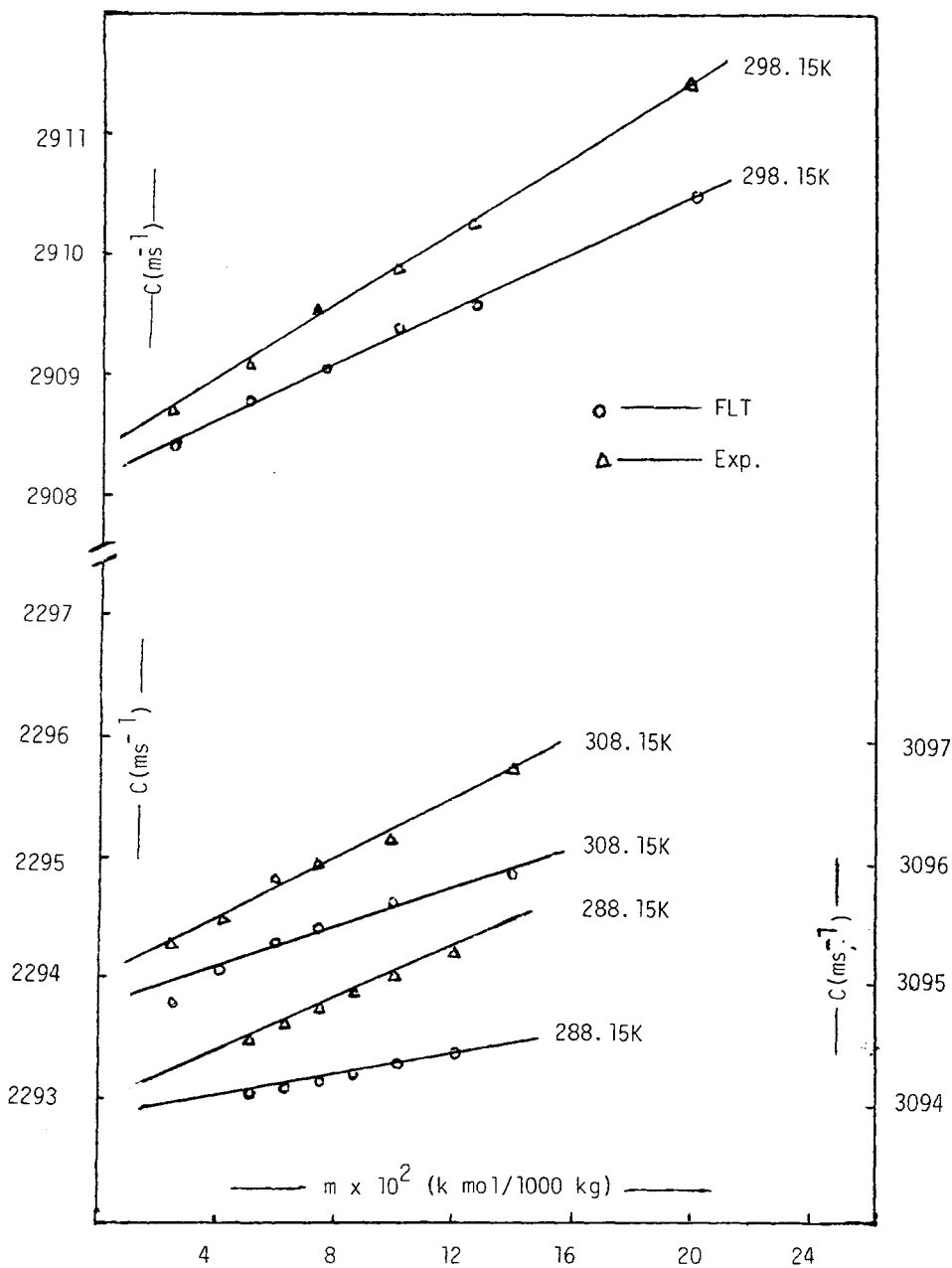
Figure 1 Plots of ultrasonic velocity C (ms^{-1}) as a function of pentanol concentration m (k mol/1000 kg) in water at different temperatures.

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Table 2   Computed values of thermodynamic properties for pentanol at different temperatures.

Temp. (K)	x (deg^{-1})	$\beta_T \times 10^4$ (atm^{-1})	γ	$P_i \times 10^{-4}$ (atm)	Γ
288.15	0.0995	1.557	14.69	18.41	0.477
298.15	0.0993	1.786	14.86	16.61	0.467
308.15	0.0991	2.914	15.04	10.48	0.460

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