

An environmental remediation: study of molecular interactions of the poorly soluble pharmaceutical drug ibuprofen in aqueous media

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ABSTRACT

Medication disposal today is an alarming issue and gaining much more awareness from the consumers as well as healthcare professionals. Various molecular interactions surviving in aqueous drug systems may be considered responsible for these health hazards. This paper reports an experimental study of the various physico-chemical properties of poorly water soluble drug, ibuprofen in aqueous system. Conductance of ibuprofen been measured in aqueous medium at different concentrations and temperatures (from 298.15 K to 313.15 K), and the sound velocity and surface tension study are done only at 298.15 K. The experimental data have been analyzed to interpret different derived parameters as well some thermo-acoustical parameters. The surface tension values have also been determined by means of Stalagmometer and the obtained values are compared with the values computed from sound velocity and density values. Insights obtained from the present study about different molecular interactions of ibuprofen can assist public health and waste management authorities to improve pharmaceutical resource handling and management in rural and urban areas.

Keywords: *Pharmaceutical wastes; ibuprofen; association constant.*

1. INTRODUCTION

The active pharmaceutical ingredients causing environmental contamination are now an emerging global concern. Now it is clear that the increasing use of pharmaceuticals in clinical as well as veterinary practice can have disadvantageous influence on our environment [1]. It is most important for the developing world to understand the need for pharmaceutical resource management, pharmaceutical waste handling infrastructure and medication compliance [2]. Pharmacists and nurses, those who handle drugs in hospitals do not get proper training during their academic studies for hazardous waste management and though some of them are receiving such training may not be habituated with the active ingredients in numerous pharmaceutical formulations. Large scale investigations have been performed to distinguish the presence and impact of pharmaceutical pollutants in water and other environment [3].

The effect of such pharmaceutical pollutants on the human and animal health and to the environment can be interpreted if different molecular interactions existing in drug solutions can be understood. To understand and investigate the intermolecular interactions in the solution, study of bulk and thermo-physical properties is very important. Studying properties like density, viscosity, conductance and ionic mobility of solutes in aqueous solutions are of much importance to obtain a lot of information about solute-solute and solute-solvent interactions in the solution [4, 5]. Keeping these things in mind, we have studied the physico-chemical properties of poorly water soluble widely used drug, IBP

[6]. IBP also known as (\pm) 2-(4-isobutylphenyl) propionic acid, derived from propanoic acid, is a non-steroidal anti inflammatory drug (NSAID) (Fig.1). It is widely used in current pharmaceuticals as analgesic and antipyretic for all processes related to acute-on-chronic inflammation. It is weakly acidic, less soluble, but has high permeability through stomach. Considering the wide spread use of IBP, it is essential to get the idea of its physicochemical properties as the understanding promotes the design process of liquid pharmaceutical measure forms. Therefore, in order to gather a complete report about physicochemical components of such poorly water soluble drug for pharmaceutical systems, it is very much significant to determine the drug solubility of systematically.

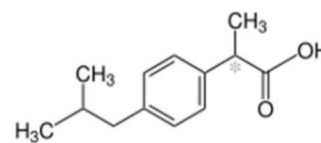


Figure 1. Structure of ibuprofen.

In continuation of our work [7], we now report the conductometric, sound velocity and surface tension values of IBP (Fig. 1) at definite and infinite dilution in aqueous medium along with the corresponding derived parameters using conductance, sound velocity and surface tension data. These elements have been explained in terms of various molecular interactions.

2. MATERIALS AND METHODS

2.1 Chemicals.

All chemicals used were of GR, BDH or AnalaR grades. Conductivity water (Sp.cond. $\sim 10^{-6}$ Scm⁻¹) was used throughout the experiment.

2.2 Determination of solubility.

As IBP is very less soluble in water, for its solubility measurement an excess quantity of IBP in 100 mL of conductivity water was taken and heated for 30 minutes maintained at 50°C.

Then the contents were kept with continuous stirring for 8 hours in a water thermostat maintained at the required temperature as described elsewhere [8]. The solution was then filtered and its concentration was determined by titration with standard NaOH solution using phenolphthalein indicator. This solution was then diluted successively to get the next four different concentrations at the corresponding temperature. The aqueous solutions were prepared on the molal basis and conversion of molal to molar was done by using the standard expression [9] considering the density differences at the respective temperatures.

2.3 Determination of Conductance.

The conductance measurements were made on a digital reading conductivity meter (Elico make) with a sensitivity of 0.1% and giving the conductance value of three digits. A dipping type conductivity cell with a platinised electrode (cell constant 1S cm⁻¹) was used. The measurements were made over the temperature range of 298.15- 313.15 K (±0.05K). The ionic strengths of the solutions were kept as low as possible (~10⁻⁴ to 10⁻² M). The conductance of different concentrations of aqueous IBP was measured making appropriate corrections for the conductance of the solvent concerned (distilled water) [10].

2.4 Determination of sound velocity.

Sound velocity measurements on the aqueous solutions of IBP were made as described earlier [11] by using Ultrasonic Interferometer (Mittal Enterprises, New Delhi, India) at 298.15 K only (frequency of 2 MHz). The accuracy of the sound velocity measurement is within ±0.5 m/s.

2.5 Determination of Surface tension.

Using experimental values of density (reported in our paper [7]) and sound velocity of IBP in water, the surface tension (γ) values were derived at 298.15 K over the entire concentration range to study different intermolecular interactions in these systems. γ values were also measured for each concentration at 298.15K using Stalagmometer [12, 13].

2.6 Calculation.

2.6.1 Conductance calculation.

The molar conductance is calculated from the specific conductance value by the relation [14]

$$\Lambda_m = 1000k_{\text{corr}}/c \quad (2.1)$$

where $k_{\text{correct}} = k_{\text{solution}} - k_{\text{solvent}}$

where Λ_m = the molar conductance,

k = the specific conductance and

c = is the concentration of the solution.

Then approximate limiting molar conductance (Λ_m^0) is obtained from the intercept of the plot between Λ_m and $c^{1/2}$ by following the methods of least squares, i.e.,

$$\Lambda_m = \Lambda_m^0 - S c^{1/2} \quad (2.2)$$

where S = the slope and

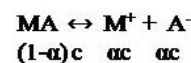
Λ_m^0 = the intercept of the plot of Λ_m vs. $c^{1/2}$.

Using the value of Λ_m^0 , Λ_m^I was calculated as

$$\Lambda_m^I = \Lambda_m^0 - S \quad (2.3)$$

The plot of Λ_m^I vs $c^{1/2}$ gives a new value of Λ_m^{0I} which is used to get a new value of Λ_m^{II} . Thus the final constant value of Λ_m^0 was obtained by following re-iteration process.

From Ostwald's dilution law, for weakly soluble drugs, say MA,



where $\alpha = \Lambda_m / \Lambda_m^0$, the degree of dissociation of the solute.

The dissociation constant $K_d = \alpha^2 c / (1 - \alpha)$, considering the activity co-efficient term and taking the mean activity co-efficient γ_{\pm} , K_d becomes K_d^I

$$K_d^I = \left[\alpha^2 c / (1 - \alpha) \right] \cdot \gamma_{\pm}^2 \quad (2.4)$$

By using Debye-Huckel limiting equation for γ_{\pm} , at 298.15 K, K_d^I can be written as

$$\log K_d^I = \log K_d - 1.018 c^{1/2} \quad (2.5)$$

The plot of $\log K_d^I$ vs $c^{1/2}$ the value of $\log K_d$ is obtained from the intercept and then the value of K_d obtained. The reciprocal of K_d (dissociation constant) gives the association constant K_A .

For the association process the free energy change, ΔG^0 was calculated using the following relation,

$$\Delta G^0 = -2.303 RT \log K_A \quad (2.6)$$

Where $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

$T = 298.15 \text{ K}$

The entropy change, ΔS^0 was calculated from the relation,

$$\Delta S^0 = \left(\partial(\Delta G^0) / \partial T \right)_p \quad (2.7)$$

The enthalpy change was calculated by using the Gibb's Helmholtz relation,

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (2.8)$$

2.6.2 Sound velocity calculation.

The sound velocity (U) have been determined from the wavelength (λ) and frequency (f) by using the relation (2.9),

$$U = \lambda \times f \quad (2.9)$$

The values of K_s , the adiabatic isentropic compressibility has been calculated from the sound velocity and density data by using the relation,

$$U = (K_s d)^{-1/2} \quad (2.10)$$

Where U = sound velocity and d = density of the solution.

For solutions of different concentrations the K_s values of K_s were fitted to an equation of the form [15]

$$K_s = K_s^0 + A c \quad (2.11)$$

Where A , B and C = empirical constants.

$K_{s,\phi}$, the apparent molar compressibility has been computed from equation,

$$K_{s,\phi} = 1000 K_s c^{-1} - K_s^0 d_0^{-1} (1000 c^{-1} d - M) \quad (2.12)$$

To obtain the limiting apparent molar compressibility $K_{s,\phi}^0$, the $K_{s,\phi}$ data were fitted to an equation of the form,

$$K_{s,\phi} = K_{s,\phi}^0 + F' c^{1/2} + G' c \quad (2.13)$$

The experimentally measured values of density and sound velocity data for aqueous IBP solutions have been used to measure other parameters at 298.15K, i.e., [16,17].

$$Z = U d \quad (2.14)$$

$$R_A = (d/d_0)(U_0/U)^{1/3} \quad (2.15)$$

$$V_f = V_m - b \quad (2.16)$$

$$\text{Where } V_m = \bar{M}/d \quad (2.17)$$

$$\pi_i = (K_s^0 - K_s) \quad (2.18)$$

$$b = \bar{M}/d[1 - (RT/\bar{M}U^2)\{(1 + \bar{M}U^2/3RT)^{1/2} - 1\}](2.19)$$

$$W = K_s^{-1} \bar{M} d^{-1} \quad (2.20)$$

$$L_f = K^1 K_s^{-1/2} \quad (2.21)$$

$$\alpha/f^2 = 4\pi^2 \tau/2U, \tau = \text{relaxation time} \quad (2.22)$$

$$S_n = n_1 n_2^{-1} [1 - V K_s (n_1 v_1^0 K_s^0)^{-1}] \quad (2.23)$$

where, V = the volume of the solution having n_2 moles of solute.
 v_1^0 = the molar volume of the solvent and n_1 is the number of moles of solvent.

The variation of the solvation number with molar concentration of the solute leads to the limiting solvation number, S_n^0 which was estimated from the relation,

$$\lim_{c \rightarrow 0} K_{s,\phi} = -S_n^0 v_1^0 K_s^0$$

2.6.3. Surface tension and surface excess calculation.

Surface tension is an essential molecular phenomenon that deals with inter-molecular forces that exists between the layers of the liquids. It is a property of the liquid which accounts for the reciprocation of cohesive and adhesive forces, the free energy of the liquid film or surface and also the thermodynamic nature of adsorption. The values of surface tension (γ) have been computed for each concentration of IBP by two methods.

(i) Surface tension from density(d) and sound velocity (U) measurement.

The surface tension (γ) values were computed from the d and U values at 298.15 K by using equation as given below,

$$\gamma = 6.3 \times 10^{-4} \times d \times U^{3/2} \quad (2.24)$$

The stoichiomolalities (m) were converted to mean ionic activities (a_{\pm}) using the mean ionic activity coefficients (γ_{\pm}) given in the following equation.

$$a_{\pm} = (Q \alpha m \gamma_{\pm}) \quad (2.25)$$

$$\text{where } Q = (v_+^{v+} v_-^{v-})^{1/v}, \quad (2.26)$$

γ_{\pm} = mean ionic activity co-efficient as given by Debye-Huckel limiting law [18]

$v = v_+ + v_-$ = total number of moles of ions [19] (v_+ and v_- are the number of moles of positive and negative ions, respectively) produced from one mole of solute.

From the conductance measurements, $\alpha = \Lambda_m/\Lambda_m^0$ = degree of dissociation

$$\log \gamma_{\pm} = -A|z^+||z^-| I^{1/2} \quad (2.27)$$

z_+ and z_- = the valences of positive and negative ions, respectively.

A = Debye-Huckel constant

$$A = 1.823 \times 10^6 / (\epsilon T^{3/2})$$

ϵ = dielectric constant

I = ionic strength of the solution = $1/2 \sum m_i z_i^2$, where m_i is m_+ or m_-

The surface excess Γ_2 can be measured from the Gibbs equation [20]

$$\Gamma_2 = -(a_{\pm}/2RT) \times (d\gamma/da_{\pm}) \quad (2.28)$$

where the $d\gamma/da_{\pm}$ is the slope obtained from the plot of γ vs. a_{\pm} .

(ii) Surface tension from drop number method using Stalagmometer.

Since surface tension (γ) illustrates itself in various effects, it offers so many paths to its measurement. The use of Traube's Stalagmometer [21] is one of the most important techniques to measure surface tension of a liquid. It is an instrument for estimating surface tension by measuring the number of drops in a known quantity of liquid. This method is based on the principle that an exact volume of liquid is freely falling from a capillary tube which is held vertically. For a given volume of liquid, as measured with a Stalagmometer, the surface tension is proportional to the density and inversely proportional to the number of drops of the solution.

Thus, surface tension (γ) of the solution was calculated using Stalagmometer at experimental temperature by the following equation,

$$\gamma_1/\gamma_2 = (n_2/n_1) \times (d_1/d_2) \quad (2.29)$$

where γ_1 and γ_2 = surface tension of water and the aqueous solution respectively

d_1 and d_2 = density of water and the aqueous solution respectively

n_1 = number of drops of water falling

n_2 = number of drops of aqueous solution falling

3. RESULTS

3.1 Conductance.

The experimental values of the conductance measurements for aqueous solutions of IBP were used to get molar conductance, Λ_m (equation (2.1) and reported in Table 1 after solvent correction. Also using the usual relations the limiting molar conductance (Λ_m^0), association constants (K_A) and Walden product ($\Lambda_m^0 \eta_0$) values of the systems under study are reported in Table 2.

A perusal of Tables-1 shows that, the molar conductance, Λ_m decreased with an increase in concentration of solution (Fig. 2 (a)) which may be due to the hydration of IBP molecules by water molecules reducing the number of free ions to move. It is observed from Table-2 that with an increase in temperature the Λ_m^0 values increased (Fig. 2 (b)) indicating higher mobility of ions or less solvation. i.e. the increased thermal energy may results in greater bond breaking and also variation in vibrational, rotational and translational energy of molecules that leads to a higher frequency

and so, higher mobility of ions [22]. Also from Tables 2, it is marked that the association constant, K_A values show an irregular variation with an increase in temperature. This may be characterized by the varying degree of exothermic ion-pair association originated due to difference in ionic stability, specific ion-solvent and solvent-solvent interactions. The Walden Product, the product of molar conductivity at infinite dilution, Λ_m^0 and viscosity, η_0 provides an evaluation of the water-structuring activity of the solute [23].

Table 1. Values of concentration, c (mol. m⁻³) molar conductance, Λ_m (S. m². mol⁻¹) of aqueous IBP solutions at different temperatures (K).

298.15 K		303.15K		308.15K		313.15K	
c	Λ_m	C	Λ_m	c	Λ_m	c	Λ_m
0.306	2.10	0.324	2.80	0.342	4.55	0.440	9.66
0.204	2.77	0.216	2.86	0.256	4.83	0.330	10.58
0.136	2.99	0.144	2.99	0.192	5.33	0.240	11.22
0.090	3.00	0.096	3.10	0.144	5.34	0.180	11.52
0.060	3.03	0.064	4.08	0.108	5.46	0.135	14.55

Table 2. Values of limiting molar conductance, Λ_m^0 ($\text{S.m}^2.\text{mol}^{-1}$), association constant, K_A ($\text{m}^3.\text{mol}^{-1}$) with their standard uncertainties and Walden product, $\Lambda_m^0\eta_0$ of aqueous IBP solutions at $T = 298.15, 303.15, 308.15$ and 313.15 K.

Temp.(T)	Λ_m^0	$K_A \times 10^2$	$\Lambda_m^0\eta_0 \times 10^4$
298.15	1.85	3.87	16.4
303.15	3.77	1.86	31.1
308.15	6.90	1.66	27.4
313.15	10.50	4.10	121.0

Standard uncertainties u are $u(T) = 0.05$ K, $u(\Lambda_m^0) = 1.01$ ($\text{S.m}^2.\text{mol}^{-1}$), $u(K_A) = 1.29 \times 10^{-2}$ ($\text{m}^3.\text{mol}^{-1}$), $u(\Lambda_m^0\eta_0) = 1.21 \times 10^{-4}$.

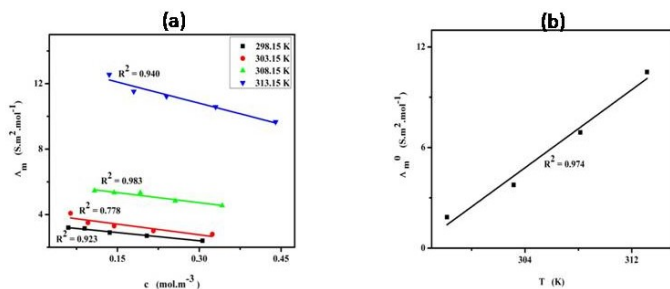


Figure 2. (a) Molar conductance, Λ_m vs concentration, c of aqueous IBP at different temperatures and (b) limiting molar conductance, Λ_m^0 vs temperature, T of aqueous IBP.

Table 3. Thermodynamic parameters ΔG_0 (kJ.mol^{-1}), ΔH_0 (kJ.mol^{-1}), ΔS_0 (J.mol^{-1}), and E_a (kJ.mol^{-1}), of aqueous IBP (mol.m^{-3}) at 298.15 K.

ΔG_0	ΔH_0	ΔS_0	E_a
-86.85	16.97	5.40	10.64

A scrutiny of Tables 3 shows that the ΔG_0 value is found to be negative and hence, suggests the process is spontaneous. The positive values of standard enthalpy and entropy change indicate endothermic in nature of the association process and so more energy consuming [24]. The activation energy, E_a has been calculated from slope of the variation of $\log(\Lambda_m^0)$ vs $1/T$ for IBP in aqueous system and found to be positive.

3.2 Sound velocity.

In the present study, values of sound velocity have been measured (using equation (2.9) from the measured density as reported in our previous paper [12] for the poorly soluble IBP, at 298.15 K. The values of U and derived parameters (using equations from 2.11 to 2.24) are given in Table 4 and 5.

Table 4. Values of U (m.s^{-1}), K_s ($\text{m.s}^2.\text{kg}^{-1}$), $K_{s,\phi}$ ($\text{m}^4.\text{kg.mol.s}^2$), Z ($\text{kg.m}^2.\text{s}$), R ($\text{m}^{-8/3}.\text{s}^{-1/3}$), R_A and W ($\text{N}^{-1}.\text{m}^{-1}$) of aqueous IBP (mol.m^{-3}) at 298.15 K.

Conc.	U	$K_s \times 10^{10}$	$K_{s,\phi} \times 10^{10}$	$Z \times 10^5$	$R \times 10^5$	$R_A \times 10$	$W \times 10^5$
0.306	1490.4	4.507	-163.8	14.89	20587.00	10.04	38992.44
0.204	1488.4	4.521	-238.4	14.86	20583.48	10.03	38986.58
0.136	1486.8	4.532	-348.3	14.84	20581.95	10.03	38984.01
0.090	1485.6	4.541	-514.9	14.82	20582.37	10.02	38984.63
0.060	1484.4	4.549	-757.0	14.81	20580.81	10.02	38982.05

Note: K_s^0 ($\text{m.s}^2.\text{kg}^{-1}$) = 4.58 and $K_{s,\phi}^0$ ($\text{m}^4.\text{kg.mol.s}^2$) = -11062.01

Standard uncertainties u are $u(T) = 0.05$ K, $u(U) = 1.35$ (m.s^{-1}), $u(K_s) = 1.00 \times 10^{-10}$ ($\text{m.s}^2.\text{kg}^{-1}$), $u(K_{s,\phi}) = 0.005 \times 10^{-10}$, $u(Z) = 0.03 \times 10^{-5}$ ($\text{kg.m}^2.\text{s}$), $u(R) = 2.36 \times 10^{-5}$ ($\text{m}^{-8/3}.\text{s}^{-1/3}$), $u(R_A) = 0.008 \times 10$, $u(W) = 3.97 \times 10^{-5}$ ($\text{N}^{-1}.\text{m}^{-1}$).

From Table 4 it can be seen that U , the sound velocity increased with an increase in concentration, c of IBP [16] and from our previous work [12] we found that, density increased with concentration of aqueous IBP solutions. This may be due to an increase in solute-solvent interaction in higher concentrations of IBP. Variation of U with d is shown in Fig. 3.

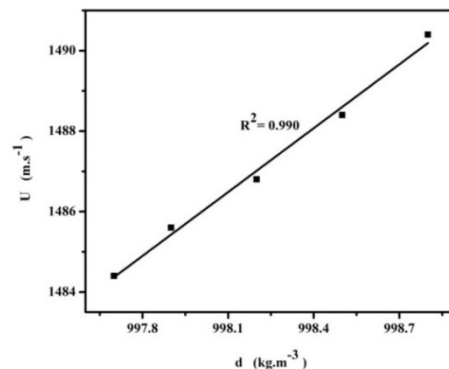


Figure 3. Sound velocity, U vs density, d of aqueous IBP at 298.15 K.

Over the total molecular environment to gather more information, several acoustic parameters (K_s , $K_{s,\phi}$, W , Z , R_A , R) has been calculated from experimentally determined density and sound data [25]. It is noticed that K_s , the isentropic compressibility decreased with an increase in concentration of drug in water.

The K_s values appear in the opposite order of its sound velocity. A typical plot of K_s vs $c^{1/2}$ is shown in Fig. 4(a). With concentration the decrease in K_s may be for the reason that the solute molecules filled interstitial spaces of water thereby making the medium less compressible, i.e., producing greater electrostriction. In addition, the decrease in compressibility with an increase in the concentration may be due to the filling of interstitial spaces of water molecules by IBP molecules shaping a tight or compact structure. This decrease in K_s is by the cause of the partial breaking of the water structure [25]. The values of $K_{s,\phi}$ are found to be negative. It is noticed that the $K_{s,\phi}$ values increased with concentration. A model plot is shown in Fig. 4(b). The negative values may be interpreted by virtue of what is called electrostriction and hydrophobic solvation. Due to strong electrostrictive forces in the vicinity of ions, the compressibility of the surrounding solvent molecules gets lost. It is known as electrostrictive solvation. Specifically, a tightened solvation skeleton structured neighboring the ion for what the medium becomes slightly compressed over the application of stress.

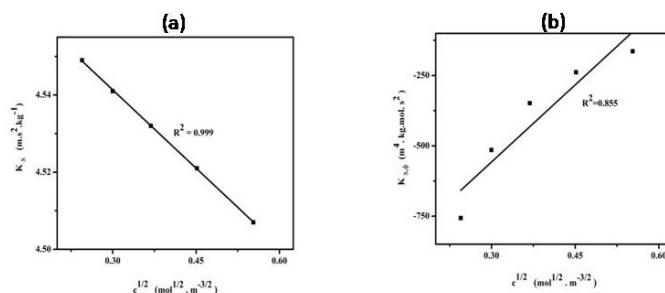


Figure 4. (a) Isentropic compressibility, K_s vs square root of concentration, $c^{1/2}$ and (b) apparent molar isentropic compressibility, $K_{s,\phi}$ vs square root of concentration, $c^{1/2}$ of aqueous IBP at 298.15 K.

As studied, the acoustic impedance, Z increased with an increase in IBP concentration [26] (from Fig. 5). Since it is a behavior of the elastic property of the system, it depends upon the structural changes in the solution. Its increasing value specifies that the solution medium starts achieving its elastic property. The molar sound velocity (R) increased with concentration of IBP. One more property [26] can also be investigated which can explain

the solute-solute or solute-solvent interactions is R_A , the relative association. It is controlled by (i) rupture of the associated solvent molecule and (ii) solvation of solute molecules. The former points to the decrease and the latter to the increase in relative association. In this study, with an increase in IBP content in water R_A increased. This implies that solvation of solute molecules takes place in most of the solvents, i.e., the solvent molecules surround the solute molecules when the solute gets dissolved in it. In the primary solvation shell, the solvent molecules get pulled towards the electrostatic field of the solute molecules. So in the presence of the solute molecules, the solvent molecules become more compacted. Such compression is called as electrostriction. The values of molar compressibility, W increased with concentration. Other essential properties such as van der Waals constant, b internal pressure, π_i free volume, V_f free length, L_f , absorption co-efficient, (α/f^2) relaxation time, τ , and solvation number (S_n) also can be analysed. These parameters are reported in Table 5.

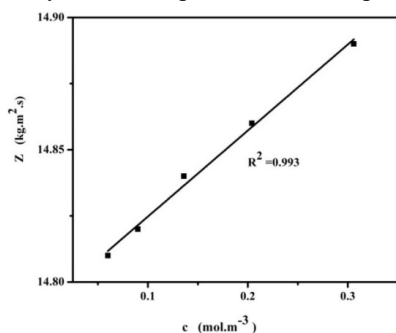


Figure 5. Acoustic impedance, Z vs concentration, cof aqueous IBP at 298.15 K.

Table 5. Values of π_i ($N.m^{-2}$), b ($m^3.mol^{-1}$), V_f ($m^3.mol^{-1}$), L_f (m), τ (s), α/f^2 , S_n of aqueous IBP ($mol.m^{-3}$) at 298.15K.

Conc.	$\pi_i \times 10^{12}$	$b \times 10^2$	$V_f \times 10^2$	$L_f \times 10^4$	$\tau \times 10^{-3}$	$\alpha/f^2 \times 10^{-3}$	$S_n \times 10$
0.306	49.3	130.36	-128.56	43.67	28.0	37.0	163.22
0.204	47.9	130.22	-128.41	43.73	27.4	36.3	244.75
0.136	46.8	130.11	-128.31	43.79	26.9	35.7	367.02
0.090	45.9	130.04	-128.24	43.83	26.6	35.3	554.49
0.060	45.1	129.96	-128.16	43.87	26.3	35.0	831.57

Note: $S_n^0 = 8205.07$ of aqueous IBP at 298.15K.

Standard uncertainties u are $u(T) = 0.05$ K, $u(\pi_i) = 1.65 \times 10^{-12}$ ($N.m^{-2}$), $u(b) = 0.15 \times 10^{-2}$ ($m^3.mol^{-1}$), $u(V_f) = 1.11 \times 10^{-2}$ ($m^3.mol^{-1}$), $u(L_f) = 0.074 \times 10^{-4}$ (m), $u(\tau) = 0.067 \times 10^5$ (s), $u(\alpha/f^2) = 0.801 \times 10^3$, $u(S_n) = 0.267 \times 10^3$.

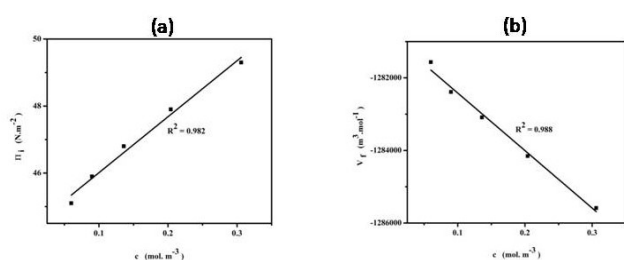


Figure 6.(a) Internal pressure, π_i vs concentration, and

(b) free volume, V_f vs concentration, cof aqueous IBP at 298.15 K.

The internal pressure, π_i values are obtained to be positive showing the existence of some distinct interactions within the molecules in the components. It is seen that the internal pressure increased with an increase in concentration (shown in Fig. 6(a)). The free volume (V_f), is, however, not the whole cell volume, but rather the average volume in which the centre of the molecule can move inside the hypothetical cell due to the repulsion of surrounding molecules [27].

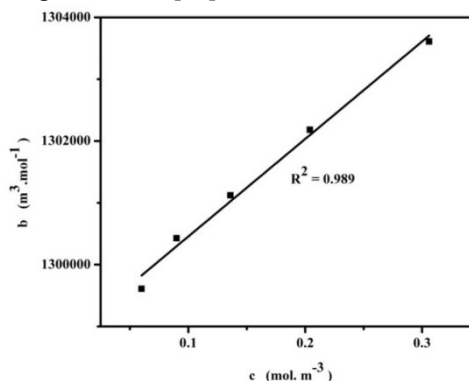


Figure 7. van der Waals constant, b vs concentration, cof aqueous IBP at 298.15 K.

The relevant thermodynamic variables, i.e., the free volume, internal pressure and temperature describe the liquid systems of a particular composition. As seen, the values of V_f (Fig. 6(b)) are found to be negative and change in a reverse way to that of internal pressure. The decrease in V_f (or increase in π_i) illustrates the formation of strong and/or tough solvation layer in the vicinity of the ion. The values of van der Waals constant, b is positive and increased with increase in IBP concentration in water (Fig. 7) which point to the fact that between the solute and solvent in the solution the binding forces become stronger and it establishes the existence of a strong molecular interaction between the solute and solvent molecules [28]. With the increase in concentration free length L_f values (found positive) are decreased which reveals the existence of remarkable interactions between solute and solvent molecules and a structure promoting behavior on the addition of solute. The values of relaxation time, τ and the absorption co-efficient, α/f^2 as studied, also increased with concentration. Table 5 shows that the decrease in solvation number S_n with concentration indicates a structure breaking process. Higher S_n value in a lower concentration of IBP indicates strong electrostriction in water [29].

Table 6. Values of mean ionic activity, a_{\pm} surface tension, γ ($N.m^{-1}$) and surface excess, Γ_2 (derived from density (d) and sound velocity (U), and drop number method) at different concentrations for IBP in water ($mol.m^{-3}$) at 298.15 K.

Conc.	$a_{\pm} \times 10^2$	Derived values from d and U		Experimental values	
		$\gamma \times 10^{-1}$	$\Gamma_2 \times 10^2$	$\gamma \times 10^{-1}$	$\Gamma_2 \times 10^2$
0.306	4.35	3620.54	-9.31	3621.85	-8.97
0.204	4.87	3612.17	-10.43	3613.21	-10.05
0.136	4.54	3605.26	-9.73	3607.40	-9.37
0.090	3.83	3599.82	-8.21	3601.92	-7.90
0.060	3.05	3594.74	-6.53	3599.59	-6.29

3.3 Surface tension.

In this section, the values of surface tension (γ), mean ionic activity (a_{\pm}) and surface excess (Γ_2) have been calculated (using

equations from 2.25 to 2.29) for aqueous IBP from the experimentally determined data of density and sound velocity at 298.15 K in different solution. The γ values are also evaluated (equation 2.30) from drop number method using Stalagmometer at 298.15 K. The results are correlated with the derived γ data from U values.

Standard uncertainties u are $u(a_{\pm}) = 0.31$, $u(\Gamma_2 \text{ Derived from U values}) = 0.40 \times 10^{-2}$, $u(\Gamma_2 \text{ From counting drop method}) = 0.39 \times 10^{-2}$.

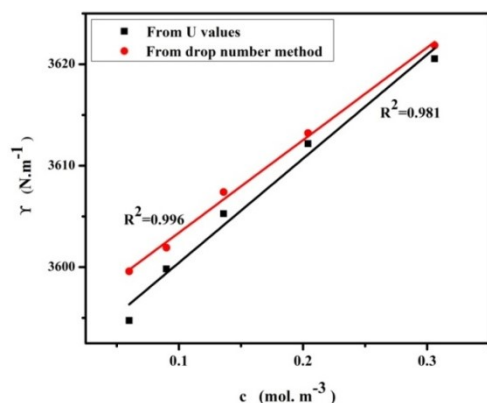


Figure 8. Surface tension, γ (derived from density and sound velocity values, and drop number method) vs concentration, c for aqueous IBP solutions at 298.15 K.

4. CONCLUSIONS

In this article we outlined the experimental conductance data at $T=298.15$, 303.15 , 308.15 and 313.15 K, and sound velocity and surface tension data at 298.15 K only. Using molar conductance values, the limiting molar conductance (Λ_m^0), association constants (K_A), Walden product ($\Lambda_m^0 \eta_0$) values of the system are evaluated. Λ_m decreased with an increase in concentration of solution. The negative ΔG_0 value suggests the process as spontaneous and the positive values of ΔH_0 and ΔS_0 implies endothermic nature of the association process and more

A perusal of Table 6 shows that the surface tension, γ values increased as the concentration of IBP increases. A model plot is presented in Fig. 8. The values of surface excess Γ_2 are negative for IBP [30]. Since Γ_2 is a measure of the solute collected in the inter phase region, the negative values indicate that its molecules are not adsorbed at the inter phase region. (Typical plot is shown in Fig. 9). A comparison of surface tension and surface excess between the two methods chosen reveals that the values are closer to each other. The results obtained using Stalagmometer are in good agreement with the promising for the use of this counting drop method in the accurate measurement of surface tension.

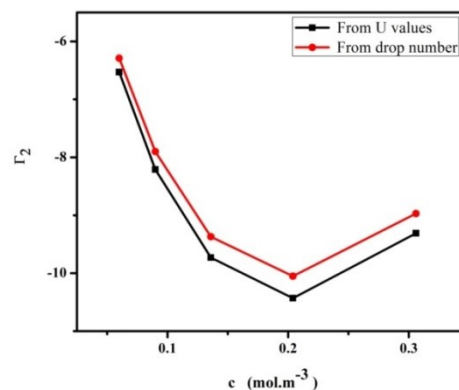


Figure 9. Surface excess, Γ_2 (obtained from density and sound velocity values, and drop number method) vs concentration, c for aqueous IBP at 298.15 K.

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