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Volumetric study of Imidazole in aqueous solutions at 298.15,303 and 308.15 k

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Abstract

This paper reports the experimental density (ρ) of binary mixture of Imidazole in aqueous solutions at 298.15, 303.15 and 308.15 k. From these experimental data apparent molar volume (Φ_v) and limiting partial molar volume (Φ_v^0) have been calculated. The results show that solvated Imidazole shows different types of solute – solute interactions as a result of its dissociation spatially at low concentrations, the results also shows that the solvated Imidazole has the property of breaking structure of liquid water with increasing temperature with this range.

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دراسة حجمية للاميدازول في محاليله المائية في الدرجات الحرارية 298.15 , 303.15 و308.15 درجة مطلقة

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في هذه الدراسة تم الحصول على النتائج التجريبية لكثافة المزيج الثنائي للايميدازول في محاليله المائية (ρ) في الدرجات الحرارية 298.15 ، 303.15 و 308.15 درجة مطلقة ، من هذه النتائج تم حساب الحجم المولاري الظاهري (Φ_v) و الحجم المولاريالمحدد(Φ_v^0) حيث بينت تلك النتائج ان الاميدازول المتمذوب يظهر انواع مختلفة من تداخلات مذاب – مذاب كنتيجة لتفككه خاصة عند التراكيزالواطئة ، كذلك فان الاميدازول يسلك كعامل مهدم لتركيب الماء السائل مع زيادة درجة الحرارة .

Introduction

Imidazole as a molecule or moiety has a great importance from biological and modern chemical point of view it is exists in Histamine and Histidine the first compound is metabolic product in the living systems play a rule as stimulating cellular agent[1] , Histadine is building unit in enzymes , proteins and Oligopeptides also as a member of constituents of groups that form the active site[2,3] in many enzymes Imidazole also exist in many synthetic drugs such as Phentolamine, Naphazoline and Tolazoline[4].

One of the most interesting features to the Imidazole ring specific activity is its tendency to inter proton transfer reactions and their property is the main reason that make Imidazole group important in must above examples [5]now days many researches concerned in incorporate Imidazole unit in partial enzyme mimics[6] and nano - devises as a proton transfer unit[7,8] for this reason it is important to know about structural properties of Imidazole in aqueous solution and its structure dimension and the constituents of its hydrated layer, most researches concerned with Imidzole derivative (Histidine) for its biological importance [9] but we did not fined much works about Imidazole independent unit.

Experimental

Imidazole was obtained from Aldrich chemical company used with out further treatment. The water used in the

preparations of the binary mixtures was deionized distilled water.

All solutions were prepared in molar concentrations by dissolving(10 g) of Imidazole in (1 dm^3) volumetric flask which sated as a stock solution , from this solution a series of twelve concentrations were prepared by dilution then converted to molality units using the following expression:

$$m = 1000C/ (1000\rho – M)$$

…….. (1

Where (m) is the molality (g/Kg), (C) molar concentration (mole/dm^3), (ρ) is the density of solution (g/cm^3).

Measurements

Densities were measured by using a single capillary density bottle equipped with thermometer to insure a definite temperature.

Temperature was controlled using a Scott- Gerate CT1150 thermostat with a precision of (± 0.01 k).

All mixtures were prepared by mass using an Electronic balance Sartorins Lab. BL210S, Germany with an accuracy of (10^{-4}g) covering whole composition range of the binary mixtures.

Results and discussion

The measured densities at 298.15, 303.15 and 308.15 k are listed in table (1) at different molal concentrations of

Imidazole. Apparent molar volume (m^3/mol) was calculated from solution densities using standard expression [10]:

$$\Phi_v = \left[\frac{1000+mM}{\rho} - \frac{1000}{\rho_0}\right]/m$$

…… (2

Where (m) is the molality of solution (mol/Kg), (M) is the molar mass of solute (g/mol) and (ρ_0) and (ρ) are the densities of solvent and solute respectively ((g/cm^3) the values of (Φ_v) (m^3/mol) are plotted vs. (m) and shown in figure (1). Table (1) shows that the densities of Imidazole solution were increased by increasing concentration but generally decreasing with increase of temperature in agreement with general behavior of liquid solutions[11] ,(Φ_v) also show slightly increase with increasing concentration and increase with increasing temperature but the difference in apparent molar volume at low concentrations with temperature is larger than that in higher concentrations , this may be a result of increase of ionization at low concentrations .

In the mathematical treatment of value variety of (Φ_v) with concentration in polar solutions some references used linear expression as relation between (Φ_v) and concentration of solution spatially in the case of none-ionic solutes [12,9] , other used linear relation between square root of concentration (as equivalent to ionic strength of solution) and (Φ_v) for ionic solutes[13,14,15] , we have summed between the two methods to get better understanding to the

interaction between solute particles with each others and with solvent molecules .

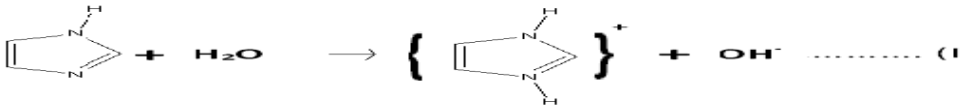
Limiting value of apparent molar volume at infinite dilution (Φ_v^0) was calculated from the relation:

$$\Phi_v = \Phi_v^0 + S_v m$$

…… (3

Which is equal to the partial molar volume at infinite dilution [13], (Φ_v^0) considered as a measure of solute – solvent interactions and a measure of molecular volume of solute [16], (S_v) is the experimental slop which is a parameter of solute – solute interactions [17] both values of (Φ_v^0) and (S_v) are listed in table (2) with both values were obtained by least squares fitting of (Φ_v) to equation (2).

To realize the phenomena of ionization of Imidazole which show weak base character through the reaction:



We postulate the equation:

$\Phi_v = a + b\, m^{1/2} + c\, m + d\, m^{3/2}$ …….. (4

This equation represented by plotting (Φ_v) vs. ($\sqrt{m}$) and treated it as polynomial from the third order as shown in

figure (3), the numerical values of (a),(b),(c) and (d) are listed in table(2).

To describe the variety of interactions among different species in the solution according to equation (4) we give the following explanation:

(a) Parameter is analogous to (Φ_v^0) in equation (3) describe the interactions between solute and solvent qualitatively not quantitatively because the deviations that take place as a result of ionization at low concentrations will get a large deviation in (Φ_v^0) value, for this reason the values of (Φ_v^0) obtained from equation (2) are considered more realist than that obtained from eq. (2)

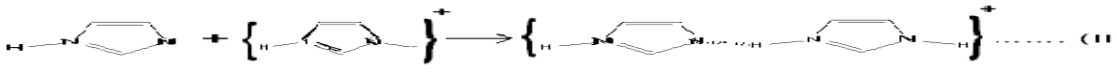
Especially they much close to the theoretical molecular volume of Imidazole molecule.

(b), (c) and (d) values are analogous to (S_v) (they describe the interactions among solute species as follows:

(b) Define the interaction between ions mainly between (OH^-) and ($I\text{-}H^+$).

(c) Define none ionic binary interactions between Imidazole molecules.

(d) Define the interactions among ions and neutral molecules of solute such as:



From table (2) we observe increase of (Φ_v^0) value with increase temperature suggesting the solute- solvent interaction increased by increasing temperature , (S_v) values are found to be positive indicate strong solute – solute interaction , by increasing temperature (S_v) decreases which show that the interactions become less strong.

Solute – solute interactions can be represented more clearly by considering the coefficients of equation (4) that shown in table (2) the ionic type solute – solute interaction which be predicted from coefficient (b) weakened by increasing temperature this may be due to decrease in ionization of Imidazole by increasing temperature.

None – ionic interaction type between Imidazole molecule which represented by (c) coefficient is negative indicate weak interaction, this interaction become more strong [(c) is less negative] with increasing temperature.

Remaining (d) coefficient that give indication to ionic – nonionic solute – solute interactions also begin with large positive value meaning strong solute – solute interaction and this interaction become weak with increasing temperature as Shown from (d) values this result may be explained as the explanation of ionic solute – solute interaction [coefficient (b)] because the decrease of ionization of Imidazole in water with increasing temperature.

The temperature dependence of (Φ_v^0) follows the equation [18]:

$\Phi_v^0 = \alpha + \beta T + \gamma T^2$ ..... (6

Values of coefficients (α), (β) and (γ) have been calculated and are listed with first and second derivatives in table (3), first derivative called partial molar expansibility [18] which is a measure to structure – forming, structure – breaking tendency to solute molecules on long range order of solvent molecules from table (3) we observe the structure breaking tendency of the Imidazole increases with increasing temperature.

Helper [19] has proposed a method by which qualitative information on hydration of solutes can be obtained from thermal expansion of aqueous solution by the following relation:

$(\frac{\partial C_P^0}{\partial P})_T = -T(\frac{\partial^2 \Phi_v^0}{\partial T^2})_P$

..... (7

According to this , the left hand side of the above equation should be positive for structure – breaking solutes , and therefore , structure – breaking solutes posses negative values of $[\frac{\partial^2 \Phi_v^0}{\partial T^2}]_P$ on the other hand , positive values of $[\frac{\partial^2 \Phi_v^0}{\partial T^2}]_P$ should be associated with structure – making solutes.

In the present study the values of second derivative have been obtained from equation (6) and are listed in table (3) shows that the values are negative thus Imidazole behave as structure – breaking in the liquid water and these results

are in agreement with the results that obtained from partial molar expansibility .

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298.15 k		303.15 k		308.15 k	
m (mol/Kg)	ρ (g/cm^3)	m (mol/Kg)	ρ (g/cm^3)	m (mol/Kg)	ρ (g/cm^3)
0	0.99707	0	0.99568	0	0.99406
0.007371	0.998072	0.007383	0.996403	0.007397	0.994497
0.014746	0.998267	0.014771	0.996591	0.014799	0.994698

Table (1) densities of solutions (ρ) at 298.15, 303.15 and 308.15 K

0.022126	0.998468	0.022164	0.996758	0.022201	0.995104
0.02951	0.998667	0.029557	0.997071	0.029604	0.995509
0.036897	0.998926	0.036958	0.997257	0.03702	0.995594
0.044289	0.999133	0.044362	0.997483	0.044438	0.995799
0.051688	0.9993	0.051774	0.997635	0.051857	0.996049
0.059089	0.999513	0.059188	0.997848	0.059283	0.996242
0.066498	0.999659	0.066611	0.997978	0.066722	0.996326
0.073905	0.999924	0.074015	0.998433	0.074134	0.996846
0.081326	1.000048	0.081458	0.998439	0.081584	0.996897
0.088743	1.000282	0.088889	0.998646	0.089030	0.996976

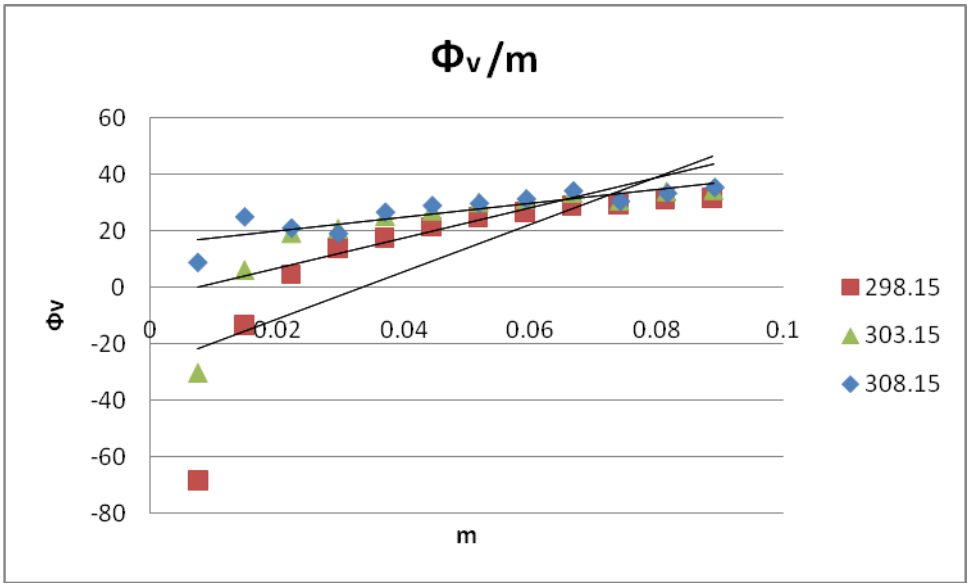

Figure (1) apparent molar volume of Imidazole Aqueous solution

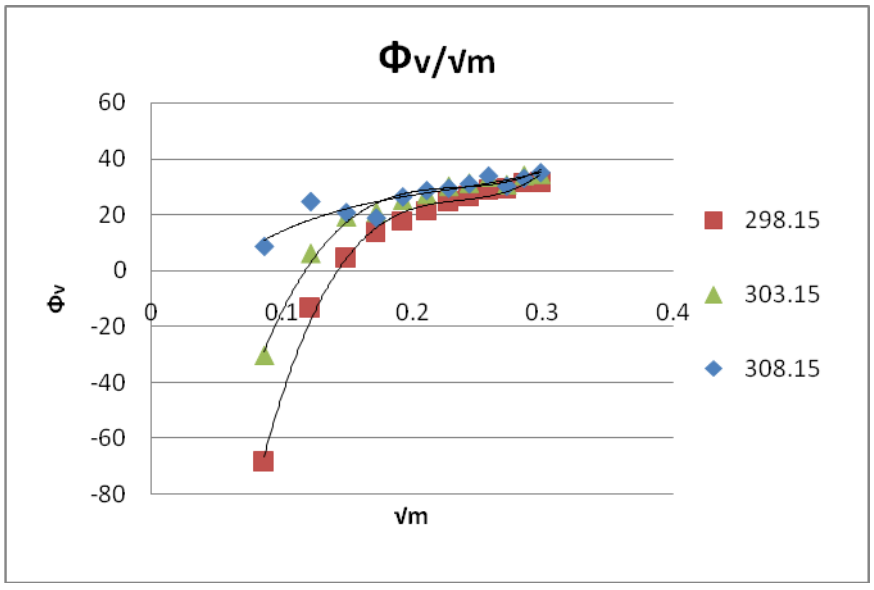

Figure (2) plots of (Φ_v) vs.($\sqrt{m}$)

	a	b	c	d	Rp	σ	Φ_v^0	Sv	RL
298.15	-312	4181	-17503	24733	0.966	18.6113	-28.12	842.3	0.787
303.15	-192	2800	-11879	16960	0.993	13.5949	-3.806	533.4	0.775
308.15	-21.45	529	-2039	3021	0.920	4.43541	14.89	246.8	0.868

Table (2) Limiting partial molar volume (Φ_v^0) experimental slope (Sv) with standard (σ) deviation and parameters of equation (4), (Rp, RL) are correlation coefficient for polynomial and linear form respectively

Table (3) Limiting partial molar volume with its derivatives

T	Φ_v^o	$\partial\Phi_v^o/\partial T$	$\partial^2\Phi_v^o/\partial T^2$
298.15	-28.12	5.6344	-0.224
303.15	-	4.5144	-0.224

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	3.806		
308.15	14.89	3.3944	-0.224