# Viscosities and excess properties For 7-[2,2-(1-phenylidene amino)-1,3,4 –( Thiadiazole- 5-yl)-thio acetamido]-Desacetoxy cephalosporanic Acid[PATDCA]

And water at several temperatures

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#### Abstract :

Experimental values of viscosity are presented for the mixtures of 7-[2,2-(1-phenylidene amino)-1,3,4 – (Thiadiazole- 5-yl)- thio acetamido]- Desacetoxy cephalosporanic Acid [PATDCA] with water over the whole mole fraction range at 298.15 , 308.15 , 318.15 and 328.15 K.The data were used to calculate excess viscosity ,  $\Delta ln \eta$  and excess Gibbs energy of activation of flow , $\Delta G^{*E}$ .Both  $\Delta ln \eta$  and  $\Delta G^{*E}$  show a significant positive deviation from ideal mixing behavior over the whole mole fraction range and decreased with increasing temperature . The results have been discussed in terms of the nature of solvent – solute interaction in the mixture.

#### Introduction:

Knowledge of mixing properties of binary mixtures has relevance in theoretical and applied areas of research such results are needed for design processes in chemical and petrochemical industries. Some drugs such as morpholine finds application as an extractant agent for aromatic hydrocarbons from petroleum cuts [1-3]. Therefore an understanding the mixing properties of aqueous mixtures of this solvent has values in extraction processes industry . The present investigation is a continuation of our previous study [4] on volume of mixing and deviation in molar refractivity for the mixtures of aqueous solution of morpholine .So the study of thermodynamic properties of binary mixtures containing PATDCA and water in varying mole fraction and temperatures provides a continuous adjustment of these properties and by using this solvent through demonstrate the information about the intermolecular forces in liquid mixtures which effect on this properties. The present work regarded as a continuous investigation among a series of researching related in this field [5 -9].

#### Experimental

#### Materials :

Water used in the present study is deionized and doubly distilled its specific conductivity was always below  $(1*10^{-6} \text{ s. cm}^{-1})$ , 7-[2,2-(1-phenylidene amino)-1,3,4 –( Thiadiazole- 5-yl)-thio acetamido]-Desacetoxy cephalosporanic Acid [PATDCA], scheme(1), was prepared according to the ref. [10]. The water as determined by gas-liquid chromatography (Pye Unican Series 104) was less than 0.01% .the uncertainly in the mole fraction was less than  $2*10^{-4}$ .

#### **Measurements :**

Viscosity was measured with a Schott-Gerate viscometer AVS 300. The flow time was measured electronically by two light barriers across the viscometer with a precision of  $\pm$  0.01 s .The calibration of the viscometer and the experimental data its are the same as given previously [11] .The viscosities are accurate to 0.003 centipoise , in all measurements a Schott-Genate CT1150 thermostat

was used a constant digital temperature control of  $\pm 0.01$  K at the desired temperature .

#### The equations:

The densities  $\rho$ , from a previous study [4] and the measured kinematics viscosity  $\nu$ , in this work were used to calculate the absolute viscosity  $\eta$ . The obtained data are listed in table 1 and plotted as a function of x, the mole fraction of (PATDCA),

scheme2 . Excess viscosity ,  $\Delta ln~\eta$  was calculated from the following equation :

Where  $\eta_1$ ,  $\eta_2$  and  $\eta$  represent the viscosity of pure (PATDCA) ,water and the mixture respectively .The obtained results are plotted in scheme3 .The excess molar Gibbs free energy of activation  $\Delta G^{*E}$  is defined by the viscosity equation [13] :

 $\eta = hN_A/Mexp \Delta G^{*E}/RT$  ......2

Where M, h and  $N_A$  are molecular weight ,Planck's constant and Avogadro's constant respectively .

By definition :  $\mathbb{R}^{*E}$ 

Where  $\Delta G^*$  and  $\Delta G^*$  ideal are the molar Gibbs free energy activation of the binary mixture and the ideal, respectively.

For an ideal binary mixtures [12]:

 $\Delta G^* ideal = x_1 \Delta G^*_{1} - x_2 \Delta G^*_{2} \dots 4$ 

Thus for binary mixture [14]:

 $\Delta G^{*E} = RT \{ \ln \eta \ v -x_1 \ \ln \eta \ _1v_1 - x_2 \ \ln \eta \ _2v_2 \} \dots 5$ 

Where  $\eta$  and v are the viscosity and molar volume of the mixture respectively .  $\eta_1$ ,  $\eta_2$  and  $v_1$  and  $v_2$  are the viscosity and molar volume of pure component liquids 1 and 2.

#### **Results and Discussion :**

The obtained data of  $\Delta G^{*E}$  are plotted as a function of x .

 $\Delta \ln \eta$  and  $\Delta G^{*E}$  in schemes 3 and 4 show a significant positive deviation from ideal mixing behavior above the whole mole fraction range .Both  $\Delta \ln \eta$  and  $\Delta G^{*E}$ decreases with increasing temperature ,and  $\eta$ increases (at the same temperature) as the mole fraction  $x_1$  increases ( introducing (PATDCA) to (PATDCA)–water mixture), scheme 2. This is explained by strong hydrogen bonding between (PATDCA) and water at the same time destruction of self-associated molecules of water till reach the maximum at mole fraction ( $x_1 \ge 0.8$  of "PATDCA").

As a result of that a close pocked structure is formed which gives a high viscosity , as the concentration of (PATDCA) increases ( $x_1 \ge 0.8$ ) the viscosity start decreasing till reach the viscosity of pure (PATDCA)

 $\Delta \ln \eta$  and  $\Delta G^{*E}$ , schemes 3 and 4 show the maximum positive deviation from ideal at the mole fraction of (PATDCA)  $x_1 = 0.3$  this supports the previous results of the excess molar volume  $v^E$ , and indicates that 2 mole of water interact with 1 mole of (PATDCA) through hydrogen bonding .Our results were verified by comparing the measured properties with those reported in literatures [5-9] as follows : according to [5], a negative values of excess viscosities n and positive values of Gibbs free energy of activation of flow  $\Delta G^{*E}$  for all binary systems used are occurs. [6], the viscosities of all mixtures used decrease with increasing temperatures , and at any particular temperature , as the mole fraction  $x_1$  increases , the absolute viscosity ,  $\eta$  decreases for all mixtures , and  $\Delta \eta$  and  $\Delta G^{*E}$  values both are shows a negative deviations over the whole mole fraction range .[7],  $\Delta ln \eta$  and  $\Delta G^{*E}$  values both are shows positive deviations over the whole mole fraction range of all mixtures used . [8] ,  $\Delta \eta$  is found negative for all binary mixtures over the entire composition range, and the absolute values of  $\Delta \eta$  decrease as temperature is raised ,but shows variation in  $\Delta G^{^{\ast}E}$ between a negative and positive values . And finally [9] , show that a negative  $\Delta \eta$  and positive  $\Delta G^{*E}$ values over the entire range of composition used . From this comparisons, we show agreements and differences between our results and that obtained by [5-9] which are due to the varying in binary mixtures composition and environmental conditions in the works, where the H-bond (which is the main cause of the viscosity increase ) is not only the alone factor influencing in the viscosity deviation of binary mixtures ,but another factors are important like the molecular size and shape of the components of the mixtures and also could be related to the spatial hindrance of a certain groups in the H-bonded network, in addition to the complex formation, and the dispersion forces may be dominance in these mixtures . However , precise conclusion can hardly be drawn about the molecular interactions in liquid mixtures from the nature of the mixture components ,though suggestion can be given about the interactions from the studied physical properties, deviations from additivity and other related phenomena. As for example, when the liquids are together mixed there may be either contraction(increase in density by association ) or expansion in volume from additivity (decrease in density by decrease in association ). Thus excess

properties can give valuable information about molecular interactions between binary mixtures.

Table 1. Experimental viscosity ,  $\eta$  for the binary mixture of  $x_1$ , 7-[2,2-(1-phenylidene amino)-1,3,4 –( Thiadiazole- 5-yl)-thio acetamido]-Desacetoxy cephalosporanic Acid + $x_2$  water at 298.15 , 308.15 , 318.15 and

328.15 K

X <sub>1</sub>	η / mPa.s			
	298.15	308.15	318.15	328.15
0.0000	0.888	0.715	0.590	0.497
0.0224	1.729	1.315	1.020	0.792
0.0423	2.415	1.715	1.369	1.060
0.0636	2.911	2.092	1.507	1.141
0.0859	4.153	2.853	2.019	1.475
0.0993	5.183	3.445	2.406	1.730
0.1974	13.496	8.132	5.153	3.424
0.2976	23.892	13.467	8.075	5.062
0.4008	29.006	16.455	9.636	5.933
0.4992	31.770	18.110	10.604	6.829
0.5945	34.001	19.499	11.517	8.973
0.6884	35.413	20.159	12.244	7.828
0.7859	35.853	20.642	12.463	7.881
0.8802	29.220	17.456	10.858	7.111
0.9500	26.030	16.242	10.052	6.892
1.0000	25.635	15.511	9.887	6.573



Scheme 1 :(PATDCA)



Scheme 2 : Viscosity η versus PATDCA mole fraction x<sub>1</sub>



Scheme 3: Excess viscosity  $\Delta ln \eta$  versus PATDCA mole fraction  $x_1$ 



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# Scheme 4: Excess Gibbs free energy of activation $\Delta G^{*E}$ versus PATDCA mole fraction $x_1$ .

### Conclusions

The excess properties of the aqueous solutions of PATDCA reflect the interaction between PATDCA and water , and the experimental values of these binary mixture (PATDCA- water) , viscosities at different mole fraction  $x_1$  were determined at T=(298.15,308.15,318.15,328.15) K and atmospheric pressure . Both  $\Delta ln~\eta~$  and  $\Delta G^{*E}$  decreases with increasing temperature, and  $\eta$  increases at the same temperature as the mole fraction  $x_1$  increases and the effect of the interactions of binary mixtures on these properties are discussed. The agreement between our results and those reported by [5-9] is reasonable in spite of certain differences which belong to the composition of binary mixture components and the conditions environment .

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## دراسة خواص اللزوجة لمخاليط ثنائيه المكون من :-

# 7-[2,2-(1-phenylidene amino)-1,3,4 –( Thiadiazole- 5-yl)-thio acetamido]-Desacetoxy cephalosporanic Acid [PATDCA]

## مع الماء وبدرجات حرارة مختلفة .

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#### الملخص :

تم في هذا البحث دراسة خواص اللزوجه لمخاليط ثنائية المكون من :

7-[2,2-(1-phenylidene amino)-1,3,4 -( Thiadiazole- 5-yl)-thio acetamido]-Desacetoxy cephalosporanic Acid [PATDCA]

مع الماء على مدى الكسر المولي ودرجات حرارة ٣٢٨,١٥ و ٣١٨,١٥ و٣٢٨,١٥ و٢٩٨,١٥ كلفن حيث تم حساب الخواص الفائقة للزوجة وطاقه التنشيط واظهرت حيوداً موجباً في السلوك المثالي للمخاليط على مدى الكسر المولي ويقل هذا الحيود بارتفاع درجه الحرارة . تمت مناقشه النتائج بمفهوم طبيعة التداخلات الجزيئيه المذيب – المذاب في المخاليط الثنائية .