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Thermodynamic properties study of dissolution of 2-hydroxbenzoic acid in binary solvent (ethanol+ water) at various temperatures

Ebaa A Hamooshy [a] and Hanaa. H .Hussein[b] *

[a] *Basic science section, College of agricultural engineering, University of Baghdad, Baghdad, Iraq*

[b] *Mustansiriyah University/College of Science, Chemistry department, Baghdad, Iraq*

Abstract

The dissolution of 2-hydroxbenzoic acid in binary solvent (ethanol+water) mixed with various ethanol concentrations was experimentally tested at temperatures from (293 to 313) K under atmospheric pressure by the equilibrium process. As the temperature rose, the degradation of 2-hydroxbenzoic acid in all ethanol concentrations rose. Tower thermodynamic models like the van't Hoff equation, modified Apelblate equation, were correlated with the dissolution results. The measured dissolution with the modified Apelblate equation was found to provide good agreement with experimental values for the behaviors of 2-hydroxbenzoic acid dissolution. On the basis of the van't Hoff study, the thermodynamic properties of the standard dissolution enthalpy ΔH, standard entropy ΔS, and the standard Gibbs free energy ΔG were evaluated. The values of free energy ΔG and enthalpy ΔH were increased as the percentage of ethanol and temperature increased while the values of entropy ΔS were decreased at the same values. The Nonlinear variation of ΔG, ΔH, and ΔS with mole % indicate there is specific solvation occurring in a water-ethanol mixture Discovered iso-kinetic temperature. 268.7 (less than 300) means that there is a weak interaction between solvent and solvent, or there is a slow shift in the solvent or reactant structure, or both.

Keywords: 2-hydroxbenzoic acid, binary solvent (ethanol+ water), modified Apelblat equation, van 't Hoff equation.

1. Introduction

Solvent possesses an important effect on the determination of chemical reactivity, especially in elementary reactions the rate of reaction may be changed obviously if the solvent has been changed. The solvent can affect the chemical reaction kinetically in different media through the term solvent polarity which represents the whole specific and non-specific interaction of the media initial and transition state. Recently great attempts were oriented toward understanding the effect of solvent and great progress has been made in this field [1, 3]. Often referred to as ortho-hydroxybenzoic acid or salicylic acid, 2-hydroxbenzoic acid was used as early as 400 B.C. As an analgesic and, by its glucosides, it is naturally popular in willow leaves, as well as in poplar and birch trees. 2, hydroxybenzoic acid (figure 1) is a phenolic compound of chemical formula (C7H6O3) (Salicylic acid SA) has been studied for more than 200 years because of its application in human medicinal and it is also regarded as a plant hormone in Flowering, disease resistance and leaf senescence which is a slow apoptosis phenomenon and allows to plants to assemble the nutrient from the senescing cells to storage organ and active growing tissues or seeds [4, 7]. Park et al record the antibacterial activity for salicylic acid [8]. SA is typically used in scaling condition and hyperkeratotic to promote the loss rate of surface scales also used as an assistant therapeutic agent for treated viral infections [9]. Salicylic acid is known to be the primary therapeutic catalytic in microemulsion drug used to treat various skin conditions caused by hard and thickened skin such as (verrucas, warts, psoriasis, scaly skin conditions and some on nail infections) by working to reduce the outer layer of skin and allow it to lose and shed [10]. SA had the ability to relieve aches, pains and reduce fevers these therapeutic properties for SA were known before several decades also SA was used as an anti-inflammatory drug [11]. SA is poorly soluble in water [12]. In the pharmacy field the low solubility of drugs remain as a challenge; therefore ethanol is widely used as a Cosolvent in pharmaceutical industries because it has high solubility. Sometimes ethanol used as a solvent with a concentration of less than 50% but sometimes it used at high concentrations [13]. Solubility in Ethanol-water mixture provides a good knowledge for development studies and discovery of drugs also the mixture can be used for drug

*Corresponding author: (Hanaa. H. Hussein).

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formulation, drug recrestilazation studies and experimental measurements [14]. The most popular technique used for enhancing the solubility of drugs is by using a mix of organic co solvent and water the most popular co solvents used in pharmaceutical industry are propylene glycol, ethanol, glycerin, polyethylene glycols and glycofural [15]. SA is a solid weak acid the degree of dissociation is affected by the solvent. The best way to study the solvent effect on the dissociation reaction is by study the activation thermodynamic parameters (ΔG, ΔH, and ΔS) for the reaction [16]. In this paper, the correlated of solubility with temperature effect of solvent on the dissociation of SA was investigated at different solvents concentrations and different temperatures.

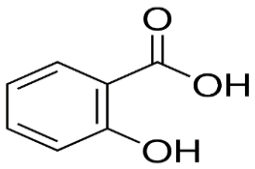

Figure 1: 2-hydroxbenzoic acid

2. Experimental Section

In the ethanol water mixture solvent, the 2-hydroxbenzoic acid was calculated gravimetrically in the temperature range (293-313) K, the temperature regulated by thermostatic baths, and the true temperature was tested using the mercury calibration thermometer (Thermo-Schneider, Wertheim, Germany) and the solution pH measured by the pH meter (inolap pH7110). The analytical balance with a precision of 0.1 mg (Sartorius BP301S) was used for solvent weighting and exceeded the solvent quantity.

2.1.Materials

Sigma-Aldrich purchased 2-hydroxbenzoic acid (CAS no. 69-72-7), purity > 99 percent, ethanol purchased from VWR / Merck: (HiperSolv, > 99.8 percent), water distilled, deionized, and filtered by 0.2 μm.

2.2 Solubility Measurement.

The equilibrium method [17, 18] and the dynamic method [19, 20] are commonly used methods for determining the solubility. 2-hydroxbenzoic acid dissolution in the binary solvent (ethanol+ water) the dynamic approach was used to investigate mixed in various concentration solutions at temperatures ranging from 293 to 313 K under atmospheric pressure. The procedure determined was followed by the procedure reported in Reference [21]. Dissolution of 2-hydroxbenzoic acid expressed in mole fractions (X) was measured as follows [18]: equation (1).

$$\boldsymbol{X = \frac{m1/M1}{m1/M1+m2/M2+m3/M3}} \qquad \textbf{(1)}$$

Where m1, m2 and m3 represent the mass of 2-hydroxbenzoic acid, ethanol and water respectively, while M1, M2 and M3 represent the molecular weight of 2-hydroxbenzoic acid, ethanol and water respectively.

3. Thermodynamic Models

1. The equation Apelblat [22] is as follows in equation (2):

$$\boldsymbol{\ln(x) = A + \frac{B}{T} + C\ln(T)} \qquad \textbf{(2)}$$

Where (X) is the dissolution of the mole fraction of 2-hydroxbenzoic acid, (T) is the absolute temperature and the empirical parameters that can be measured using the least square method are A, B and C. Values of parameters A and B reflect the difference between the non-idealities on solvent solubility induced by solution behavior and the solution action. The relation between temperature and fusion enthalpy is expressed by the parameter C [23].

2. Van't Hoff Model:

The van't Hoff equation is a universal equation used according to the thermodynamic concepts of the solid-liquid balance [24] to compare the mole fraction of the dissolution of a solute with temperatures.

$$\boldsymbol{\ln x = A + \frac{B}{(T/K)}} \qquad (3)$$

3. Deviation

Where x in the mole fraction represents 2-Hydroxybenzoic acid dissolution, parameters A and B can be acquired using multidimensional, nonlinear minimization by dissolution regression.

4.The root mean square deviation (rmsd)

$$\boldsymbol{rmsd = \sqrt{\frac{\sum_{i=1}^{N}(x_i^{cal} - x_i)^2}{N}}} \qquad \textbf{(4)}$$

If N is the number of experimental points, x_i^{cal} is the measured dissolution, and xi is the dissolution of the experiment.

5. The equations polynomial and exponential

Some equations that can be used to Correlated between dissolution and temperature are polynomial and exponential equations as show in equations (5) and (6) respectively.

$$\boldsymbol{S_p = A+BT+CT^2} \qquad \textbf{(5)}$$

$S_{exp} = A\ ex^{BT}$ **(6)**

Where S_p and S_{exp} are the solubility calculated by polynomial and exponential equations respectively. A, B and C Parameters of the equations referred to in (table 3). T is the absolute temperature.

4. Results and discussion

Dissolution Data 2-hydroxbenzoic acid mal fraction dissolution data in binary solvent (ethanol+ water) at temperatures ranging from (293 to 313) K are mentioned in Table 1. Temperature dependence of 2-hydroxbenzoic acid dissolution was present in (Figure 2**)** which shows that the dissolution data of 2-hydroxbenzoic acid are increased nonlinear as the temperature increased which means the volume-fraction depended of the solvent- solvent interaction.

Dissolution Modeling Four thermodynamic models were implemented to expand the field of application to 2-hydroxbenzoic acid to establish a connection between temperature and dissolution values in the selected binary solvent (ethanol+ water). The optimized parameters are shown in tables (2-4).

Table 1: Mole fraction of dissolution of 2-hydroxbenzoic acid in binary solvent (ethanol+ water) at various temperatures

$X10^{-3}$	T/K									
	293		298		303		308		313	
	X_i^{cal} 10^{-5}	X 10^{-5}	X_i^{cal} 10^{-5}	X 10^{-5}	X_i^{cal} 10^{-4}	X 10^{-4}	X_i^{cal} 10^{-4}	X 10^{-4}	X_i^{cal} 10^{-3}	X 10^{-3}
71.63	669	674	789	766	953	999	1178	1140	1487	1500
170.2	521	517	614	625	742	745	916	897	1155	1168
317	285	287	344	339	413	420	493	490	585.8	586
553	705.5	705	800	798	892.8	897	979.2	976	105.7	105.8
1000	107.5	109	118.4	114.9	129.2	131	139.9	141.9	148.7	150

Table 2: parameters of Apelblat equation and rmsd for dissolution of 2-hydroxbenzoic acid in binary solvent (ethanol-water)

X 10-3	A	B	C	Rmsd 10-4
71.63	-715.717	28955.44	107.72	2.92015
170.2	-704.224	28435.57	105.968	1.15847
317	-16.388	-2208.87	3.586	4.19746
554	340.29	-10740.9	-50.137	2.62703
1000	138.527	-7643.85	-20.187	22

Table 3: parameters of Polynomial equation and rmsd for dissolution of 2-hydroxbenzoic acid in binary solvent (ethanol-water)

$X10^{-3}$	A	B	$C\ 10^{-3}$	Rmsd
71.63	700.3735	-4.848	8.44	0.19348
170.2	4678.56	-32.327	56.18	0.8797
317	9339.08	-67.573	123.3	8.19
554	2717.91	-23.784	52.3	8.7268
1000	-2770.03	14.423	-13.6	7.59

Table 4: parameters of Exponential equation and rmsd for dissolution of 2-hydroxbenzoic acid in binary solvent (ethanol+water)

$X10^{-3}$	A 10^{-4}	B		Rmsd
71.63	0.375	0.0397		0.232
170.2	3.05	0.0390		1.77
317	26.9	0.0368		5.2188
554	1.590	0.025		15.79
1000	15.320	0.01788	7.62	

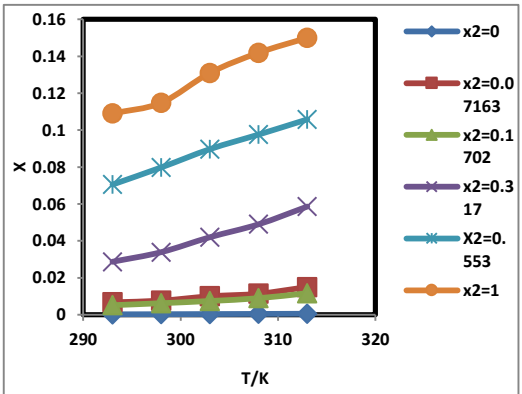

Figure 2. dissolution of 2-hydroxybenzoic acid with mole fraction (X) in binary solvent (ethanol+ water) at various tempertures

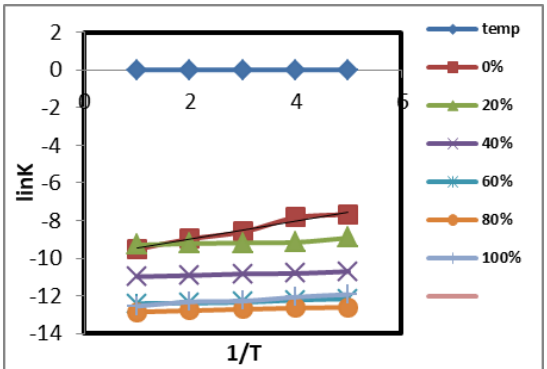

Figure 3: vant-hoff equation for variation of lnK for 2- hydroxybenzoic acid with temperatures at different concentrations of solven

Plots in (figure 2) show that the dissolution of 2-hydroxybenzoic acid increased nonlinear as the temperature increased, also the calculated Apelblat data of dissolution (table 1) and (table 2) show good agreements with experimental data. And there is little difference between calculated and experimental data also the values of rmsd found to be increase as X increased but it still gives good agreement between calculated and experimental values. The data listed in (table 3) and (table 4) show that the polynomial and exponential equation gives good results at low values for X. By comparing the results for the three equations Apelblate equation give better agreement because it give more precise results and low values for rmsd.

Thermodynamic Analysis of the 2-hydroxybenzoic acid dissolution process in binary solvents: The values of the acid dissociation constant (Ka) for 2-hydroxybenzoic acid were calculated from the data of solubility in mole/l and from the pH data for each temperature and concentration of solvent in order to calculate activation free energy ΔG from the equation.

$$\Delta G = -RT \ln Ka \quad \text{---------- (7)}$$

From the data in (table 5) the values of ΔG in (kJ $mol^{-1}K^{-1}$) found to be increased as the percentage of ethanol increased in the solvent also it increased obviously as the temperature is increased except for data of 0% ethanol figure (3) the same results were recorded by Singh [25]. The values of ΔG are proportionally inverses with lnK. It's also noted that the values of ΔG are increased as the organic mole ratio increased in the solvent this increment is nonlinear and it is varied smoothly with an organic mole fraction of the solvent. The values of enthalpy (ΔH) in (kJ mol^{-1}) (table 5) were calculated from vant-Hoff equation (equation 8) by plotting lnK against 1/T the slope represent (ΔH/R) (figure 3).

$$\ln K = \Delta H/RT - \Delta S/R \quad \text{---------- (8)}$$

These values found to be smoothly decreased as the % ethanol are increased the decreased was sharp (figure 4). The entropy (ΔS) values in (J K^{-1} mol^{-1}) (table 5) were calculated from the intercept of equation (8) and it found to be decreased as the organic mole ratio increased these values are indicating that the reaction activates the ΔH and control over the ΔS this can be explained through the figure (4) which are given nonlinear variation for both ΔH and ΔS this give indicate for presence of specific dissolution of 2-hydroxybenzoic acid in binary solvent (ethanol +water). The values of activation energy are calculated through (equation 4) [26].

$$Ea = \Delta H + RT \quad \text{---------- (9)}$$

The entropy ΔS can be defined as the measuring of randomness the data in (table 5) shows there are decreased in ΔS values as the organic % are increased in spite of there were increased in the solubility. These decrements give an indicator there were restricted to the soluble matter. This fact can be confirmed through the values acid constant Ka and pH which were measured for the solutions which are given clear decrement as the % of organic solvent are increased in the solvent. This decrement in Ka values can be explained by decreased the degree of dissociation of 2-hydroxybenzoic acid as the % of water decreased in

the solvent and its give indicates that the initial state is less dissolved than transition state [16]. In order to evaluate the solvent-solute interaction and iso-kinetic temperature, Barclay and butler relationship was used for this purpose [27]. This relation is represented mathematically by equation (10).

$$\delta m\ (\Delta H^*) = \beta \delta m(\Delta S^*) \text{……..(10)}$$

The value of β which is represent the iso-kinetic temperature for water-ethanol can be calculated from the slop of plotting ΔH* against (ΔS*+200) at 303 K (figure 5) and found to be 268.7 science this value is less than 300 that is an indication there is a weak interaction between solute and solvent presents in reaction media or due to slow change in the structure of solvent or the reactant the same way for calculation iso-kinetic temperature was recorded recently by Singh AK[2]

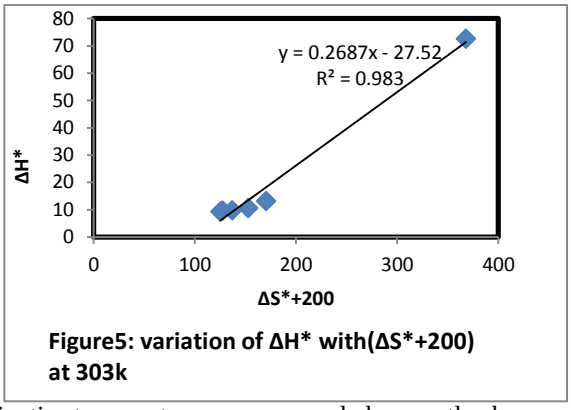

Figure5: variation of ΔH* with(ΔS*+200) at 303k

Table 5: thermodynamic data ΔH (KJ.mol^{-1}), ΔS (J.mol^{-1}.K^{-1}), ΔG (KJ.mol^{-1} K^{-1}) for the dissolution in binary solvent (ethanol-water) of 2-hydroxybenzoic acid at various temperatures

X10^{-3}	T(K)														
	293			298			303			308			313		
	ΔH	ΔS	ΔG	ΔH	ΔS	ΔG	ΔH	ΔS	ΔG	ΔH	ΔS	ΔG	ΔH	ΔS	ΔG
71.63	12.238	38.1	22.64	14.757	33.23	22.141	9.506	35.9	23.122	23.74	36.34	23.431	23.48	35	23.196
170.2	9.847	57.65	26.74	12.366	55.84	26.210	9.764	58.49	27.279	28.14	57.82	27.658	28.32	57.59	27.847
317	9.764	69.76	30.204	12.283	66.94	29.715	9.847	70.31	31.071	31,45	69.81	31.267	31.59	69.83	31.623
553	9.506	74.37	31.297	12.025	71.09	30.692	12.23	74.23	32	32.98	74.194	32.358	33.40	74.38	32.788
1000	22.472	27.55	30.547	22.472	23.82	29.571	72.61	27.81	30.9	31.10	27.25	30.866	31.23	27.27	31.008

In this work, the correlated between dissolution of 2-hydroxybenzoic acid in binary solvent (ethanol-water) at various temperatures dissolution and ethanol concentrations temperature was studied according to Apelblta, polynomial and exponential equations the results found to be better agree with Apelblat than the other equations .The reaction constant for solvation of 2-hydroxybenzoic acid in binary solvent (ethanol-water) was found to be decreased for all temperature as the percentage of ethanol increased that Indicates the initial state is less dissolved than transition state [16]. Nonlinear variation of indicating there is specific salvation occurring in the water-ethanol mixture [28]. The iso-kinetic temperature was 268.7 (less than 300) suggesting that there is a bad interaction between solute and solvent or a slow shift in solvent or reactant structure or both.

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