



## Study of thermodynamic values in different temperature from partition coefficient for some organic acids immiscible di-solvents mixtures



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### Abstract

In the present work the partition co-efficient was studied for some organic aromatic acids quinoline-2- carboxylic acid, salicylic acid, aliphatic acid and succinic acid Oxalic acid in different mixtures solvents not mixing diethyl ether + water, chloroform + water and carbontetrachloride + water at different temperature range from (293-318)K. Also the thermodynamic properties, Gibbs free energy change  $\Delta G$ , otherwise enthalpy change  $\Delta H$  and entropy change  $\Delta S$  of partition co-efficient  $k_p$  have been studied for the dependence of the equilibrium constant ( $k$ ) to temperature using the van Hoff equation, over the temperature range (293-318)K. The work shows the effects of temperature on the distribution processes. The results show also the effects of temperature and the number of acidity one acid or diacidic. The thermodynamic values indicated that the distribution processes were spontaneous and endothermic these processes increasing in entropy depending upon spontaneous hydrogen bonding in either spontaneous or strengthened.

**Key words:** -partition coefficient, thermodynamic of partition, Interamolecular bond, degree and intensity acidic.

### -Introduction:-

The partition coefficient ( $P$ ) also called the distribution coefficient ( $D$ ) defined as the equilibrium ratio of the dissolved test substance in a two phases system organic phase ( $C_o$  mg/ml) to aqueous phase ( $C_w$  mg/ml) expressed in molarity, it is abbreviated as  $k_{o/w}$  by equation .

$$P = C_o / C_w \dots\dots\dots 1$$

It may be also expressed as its logarithm ( $\log k_{o/w}$ ) [1]. In this work the partition coefficient  $k_p$  of some organic aromatic acids quinoline-2- carboxylic acid salicylic acid -5- solfo and aliphatic acids succinic acid oxalic acid quinoline-2- carboxylic is heterocyclic aromatic compound using mainly in the manufacture of dyes and their derivatives are a group of compound known to possess wide range of biological activities. Salicylic acid is widely used in organic synthesis and functions as a plant hormone. In addition to serving as an important active metabolite of aspirin. Succinic acid is involved in several chemical processes it is used for symptoms related to menopause such as hot flashes are irritability and also applied to the skin for arthritis and joint pain oxalic acid is an essential

household chemical that can be used remove a cleaning agent on wood work as a stain lifter.

### -Determination of thermodynamic properties

Also the thermodynamic parameters  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  were calculated. The experimental data obtained from partition co-efficient with temperature were used to investigate the thermodynamic according to van Hoff equation [2,3]

$$\ln k_p = -\Delta H / R(1/T) + \Delta S / R \dots\dots\dots 2$$

For the determination of  $\Delta H$  and  $\Delta S$  by plot  $\ln k_p$  against  $1/T$  was done the values calculated from the slope and intercept of plot according to the van Hoff equation [2,4,5] where:  $k_p$  is the partition constant without units,  $\Delta H$  is the molar enthalpy change kJ/mol,  $\Delta S$  is the molar entropy kJ/mol,  $R$  is the universal gas constant 8.314 J/mol.K and  $T$  is the temperature by kelvin. Free energy change ( $\Delta G$ ) or Gibbs energy change of reaction was obtained at the various temperature by using equation below [6,7].

$$\Delta G = \Delta H - T\Delta S \dots\dots\dots 3$$

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## 2. Experimental

### 3-1. chemicals

Fresh acids samples were taken quinoline-2-carboxylic acid salicylic acid and aliphatic acids succinic acid oxalic acid ,solvents: Diethylether, chloroform and carbon tetra chloride was used as supplied by suppliers

- 3-1-1. Distilled water was used to prepare the solutions of various carboxylic and prepare solvents two phases system .
- 3-1-2. Hydroxide sodium used for titration and was supplied.

3-1-3. phenolphthalein solution was prepared by (dissolved phenolphthalein in water+ ethanol) used as indicator for titration.

### 2. Procedure

- 3-2-1. The solutions was prepare by disolved same concentration of the sample of studying acid in two-phase systems (organic /aqueous ) containing diethyl-ether 50%+50% water, chloroform 50%+50% water and carboutetra chlorid 50%+50% water was dissolved[9].
- 3-2-2. separation processes experiments by shake flask involve shaking of equal volumes of aqueous and organic phase with test dissolved then the mixture were stirred on amechanical shakere for one hour .The samples were placed on water path thermostat (optima) for 1 hr at temperature range 293-318 k

3-2-3. The apparent molal partition co-efficient  $k_o/k_w$  for individual acids were calculated by mass balance of carboxylic acid concentration in each diluent between at temprature over rang 293-318 according to Eq.1

### 4-Result and Discussion:

Partition coefficient:-  $K_p$  values measured for all aromatic and aliphatic organic acids at varying temperature Eq. 1. Detailed values are presented in table (1).

According to table (1) the partition coefficient  $K_p$  was obtained from solubility of the studying carboxylic acids in different two-system solvents, in all cases  $K_p$  values were affected by temperature that greater than unit and increasing with rising temperature. Also when comparing the results obtained for all organic solvents the solubility happened interacts with by hydrogen bonding through carbonyl and carboxyl groups present, in addition to weak interactions such as London dispersion forces. The aromatic acid more solubility from aliphatic because of resonance. Quinoline-2-carboxylic acid form hydrogen bonds as a donor with diethylether because the pair edelectron on nitrogen atom (resonance). Salicylic acid from hydrogen bonds as a donor with diethylether because of carboxyl group. The aliphatic acids that less five atoms of carbon good solubility with solvents oxalic acid and succinic acid formed hydrogen bonding through double acidic. Based on molecular structure, they are classified[8] as:-Inorganic solvents, the most popular inorganic (not containing carbon) like water, the hydrogen bond ability of water is much greater than of the other solvent.[11]Oxygenated solvents: oxygenated solvent are organic solvent, molecules of which contain oxygen, oxygenated solvents are widely used in points, in Ks, pharmaceuticals, fragrance sectors, adhesive, cosmetics, detergents, food industries like diethylether. In the other system ( $\text{CHCl}_3/\text{H}_2\text{O}$ ) and ( $\text{CCl}_4/\text{H}_2\text{O}$ ) are used in this kind of study classified as halogenated solvents that are an organic solvents, molecules of which contain halogenic atoms chlorine (Cl) and carbon.  $\text{CHCl}_3$  it acts mainly as a hydrogen donor for establishing hydrogen bonds or acceptor.  $\text{CCl}_4$  is aprotic solvent able to form hydrogen bonds as acceptor by losing atom of chloride.

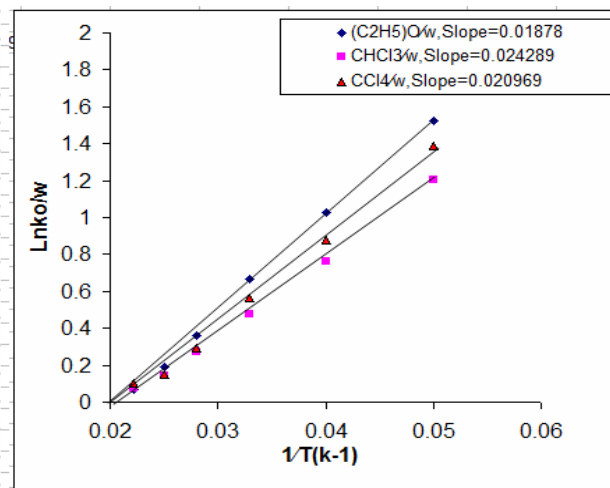
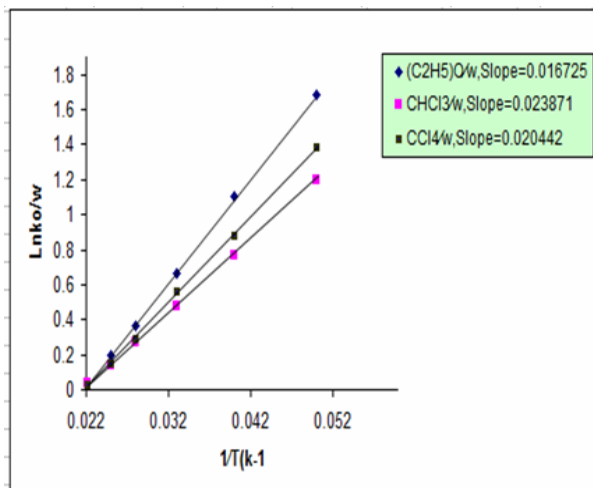
### Thermodynamic studies

The determination of the thermodynamic values ( $\Delta H$ ,  $\Delta S$  and  $\Delta G$ ) for partition coefficient by vant Hoff plots for ( $\text{C}_2\text{H}_5\text{O}/\text{H}_2\text{O}$ ,  $\text{CHCl}_3/\text{H}_2\text{O}$  and  $\text{CCl}_4/\text{H}_2\text{O}$  partition of carboxylic acids are shown in figures 1,2,3,4 respectively

Table (1). Partition coefficient ( $K_p$ ) of aromatic and aliphatic acids in different system as a function of temperature ( $\pm 0,05 \text{ c}^0$ ).

system	$1/Tc^0 (k-1)$					
	0.022	0.025	0.028	0.033	0.040	0.050
salicylic acid(Lnko/w)						
$(\text{C}_2\text{H}_5)\text{O/w}$	0.038	0.192	0.362	0.666	1.106	1.685
$\text{CHCl}_3/\text{w}$	0.0381	0.143	0.274	0.476	0.765	1.202
$\text{CCl}_4/\text{w}$	0.029	0.152	0.292	0.566	0.876	1.385
quinoline-2- carboxylic acid(Lnko/w)						
$(\text{C}_2\text{H}_5)\text{O/w}$	0.068	0.192	0.362	0.666	1.026	1.525
$\text{CHCl}_3/\text{w}$	0.0781	0.143	0.274	0.476	0.765	1.202
$\text{CCl}_4/\text{w}$	0.099	0.152	0.292	0.566	0.876	1.385

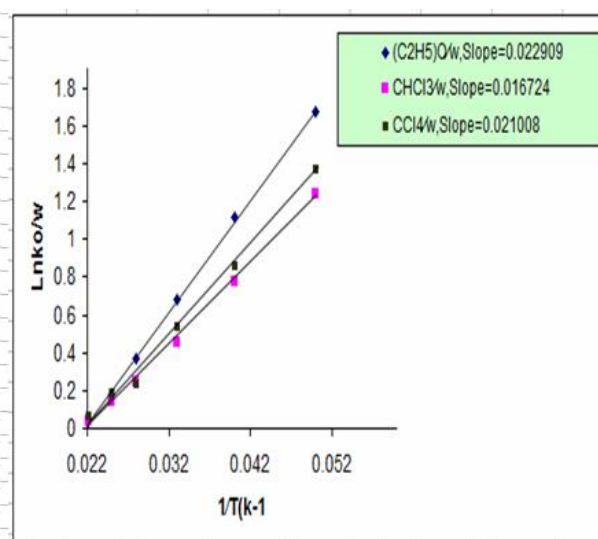
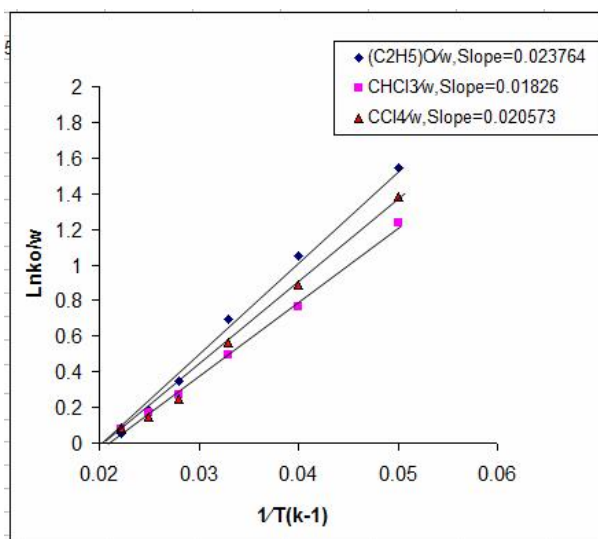
succinic acid(Lnko/w)						
(C <sub>2</sub> H <sub>5</sub> )O/w	0.035	0.182	0.369	0.676	1.116	1.676
CHCl <sub>3</sub> /w	0.037	0.143	0.249	0.454	0.776	1.243
CCl <sub>4</sub> /w	0.064	0.192	0.237	0.538	0.858	1.367
oxalic acid(Lnko/w)						
(C <sub>2</sub> H <sub>5</sub> )O/w	0.056	0.187	0.348	0.698	1.048	1.548
CHCl <sub>3</sub> /w	0.078	0.167	0.267	0.495	0.765	1.239
CCl <sub>4</sub> /w	0.087	0.149	0.249	0.566	0.887	1.385



Vant hoff plot for the partition

Figure 1: salicylic acid in the (C<sub>2</sub>H<sub>5</sub>)O/H<sub>2</sub>O, CHCl<sub>3</sub>/H<sub>2</sub>O and CCl<sub>4</sub>/H<sub>2</sub>O.

Figure 2: Quinoline-2-carboxylic acid in the (C<sub>2</sub>H<sub>5</sub>)O/H<sub>2</sub>O, CHCl<sub>3</sub>/H<sub>2</sub>O and CCl<sub>4</sub>/H<sub>2</sub>O.



Vant hoff plot for the partition

Figure 3: succinic acid in (C<sub>2</sub>H<sub>5</sub>)O/H<sub>2</sub>O, CHCl<sub>3</sub>/H<sub>2</sub>O and CCl<sub>4</sub>/H<sub>2</sub>O.

Figure 4: Oxalic acid in (C<sub>2</sub>H<sub>5</sub>)O/H<sub>2</sub>O, CHCl<sub>3</sub>/H<sub>2</sub>O and CCl<sub>4</sub>/H<sub>2</sub>O.

From the estimated slopes in the (C<sub>2</sub>H<sub>5</sub>)O/H<sub>2</sub>O, CHCl<sub>3</sub>/H<sub>2</sub>O and CCl<sub>4</sub>/H<sub>2</sub>O systems, the respective standard enthalpic changes for partition were calculated by using Eq. 2. Then transfer enthalpies ( $\Delta H$ ) were calculated as the product of slopes multiplied by R (that is 8.314 J.mol<sup>-1</sup>.K<sup>-1</sup>) on the other hand the entropy change ( $\Delta S$ ) values for partition were

calculated from Eq. 2. In addition to standard Gibbs free energy for transfer ( $\Delta G$ ) of from Eq. 3 The obtained values for this thermodynamic functions are summarized in table (2). From the values can be observed that for all cases were endothermic. In all cases,  $\Delta G$  was negative in sign indicating spontaneous process.

**-Conclusion and result:**

- 1- This study aimed compare the partition constant and valuation behavior of some aromatic and aliphatic carboxylic acids in solvents were difference in polarity. From the obtained values of corresponding thermodynamic transfer functions, an interpretation based on solute-solvent, these values are property is not dependent on the concentration, dependent on solutes molecular.
- 2- The values of partition coefficient of mixtures showed that increased with an increase in temperature, and shows a close relationship with the chemical nature of solvent.
- 3- The position heat of enthalpy change ( $\Delta H$ ) are indicative of the endothermic processes and increase with increase of temperature.
- 4- The negative values of the free energy change ( $\Delta G$ ) indicative of spontaneous of the process in each case.
- 5- The position entropy values change ( $\Delta S$ ) indicate some degree of randomness during the distribution process.

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