Available online at www.derpharmachemica.com

ISSN 0975-413X
CODEN (USA): PCHHAX

Der Pharma Chemica, 2021, 13(12): 24-28
(http://www.derpharmachemica.com/archive.html)

Thermodynamic Study of Substituted Chalcone Dibromide in Ethanol, 1,4-Dioxane and Carbontetrachloride

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ABSTRACT

The thermodynamic measurement of 2-hydroxy substituted chalcone dibromide in a different solvents like ethanol, 1,4-dioxane and carbontetrachloride. Density and viscosity measurements were carried out in 0.01 M solution in different solvents at different temperatures. The viscometric measurements were done with the help of Ostwald's viscometer. The data so obtained were analyzed by using Jones-Dole equation. This study helps to predict the molecular interaction in solution mixture. The present study deals with the determination of the thermodynamic parameters such as Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS).

Keywords: Substituted chalcone dibromide; Thermodynamic parameters

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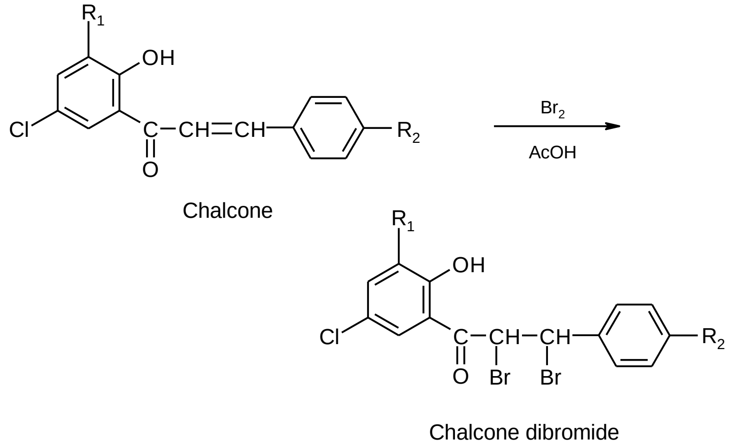
INTRODUCTION

The study of viscous behaviour of molecules in solutions and thermodynamic parameters is important in understanding the mechanism of transport process provide valuable information regarding the size and shape of these molecules were studied by Pan HP [1]. The thermodynamic parameters like ΔG*, ΔH* and ΔS* decided the molecular reaction dynamics [2]. Studies on thermodynamic and transport properties of curcumin mixture at 303.15, 308.15, 313.15, 318.15 and 323.15 K were carried out by Archana Pandey [3]. Thermodynamic and structural studies of Triton X-100 micelles in ethylene glycol-water mixed solvent were carried out by C. Carnero Ruiz [4]. Solvent effect on the thermodynamic parameters of $Ca(OH)_2$ by conductivity method were studies by Azhar Ali and Atya Hassan [5]. Studies on thermodynamic properties of streptomycin aqueous solution from T = (298.15 to 308.15) K by K.C. Patil and C.M. Dudhe [6]. Viscometric and thermodynamic study of substituted-N, N'-bis (salicyliden) arylmethanediamine in a binary system of 70% DMF-water [7]. Thermo-acoustic investigations on L-valine in aqueous salt [8]. Thermal kinetics study of 4-(naphthalene-1-yl methylene amino)-benzene sulfonamide using TG/DTG techniques [9]. Thermodynamics of removal of cadmium by adsorption on Barley husk biomass [10].

In the present investigation deals with the thermodynamic study of substituted chalcone dibromide in the 0.01 M solution of ligands were prepared in different solvents like ethanol, 1,4-dioxane and carbon tetrachloride (Scheme 1).



Scheme 1: Synthesis of Chalcone Dibromide

Where, $R_1 = –H, –Br$
$R_2 = –H, –OCH_3$

Ligand IIIa = 2'-Hydroxy-5'- chloro-4-methoxy chalcone dibromide
Ligand IIIb = 2'-Hydroxy-5'-chloro chalcone dibromide
Ligand IIIc = 2'-Hydroxy-3'-bromo-5'-chloro-4-methoxy chalcone dibromide
Ligand IIId = 2'-Hydroxy-3'-bromo-5'-chloro chalcone dibromide

MATERIALS AND METHODS

All the chemicals used were of A.R. grade. Ethanol was purified by described method [11]. 1,4-Dioxane were purified by described method[12]. Carbon tetrachloride was purified by described method [13].

Viscosities of the solutions were determined with the help of calibrated Ostwald viscometer (±0.11% $Kgm^{-1}s^{-1}$). The densities of solution were determined by a bicapillary Pyknometer having a bulb volume of about 10 cm^3 and capillary having an internal diameter of 1 mm and calibrated with deionised doubly distilled water at 297, 301 and 305 K. The accuracy of density measurements was ±0.1 Kg m^{-3}. Weighing was made on one pan digital balance (Citizen CY 104) with an accuracy of ±0.001 gm.

The 0.01 M solutions of ligands IIIa, IIIb, IIIc and IIId were prepared in ethanol, 1,4-dioxane and CCl_4. The densities and viscosities of each ligand solution were measured at 297 K, 301 K and 305 K. The constant temperature was maintained with the help of elite thermostatic water bath (±0.01 K). For each measurement, sufficient time was allowed to attain the thermal equilibrium.

The thermodynamic parameters can be evaluated from the following expressions.

$$\eta = \left(\frac{hN_0}{V}\right)\exp\left(\frac{-\Delta G^*}{RT}\right)$$

Where, h = Plank's constant
N_0 = Avogadro's number
R = Gas constant
T = Temperature in Kelvin, and
ΔG^* = Standard free energy of activation.

$$\left(\frac{\delta \ln \eta}{\delta (1/T)}\right)_P = \frac{\Delta H^*}{R}$$

Where, ΔH^* = Enthalpy change of activation process.
$\Delta G^* = \Delta H^* - T\Delta S^*$
ΔS^* = Entropy of activation.

RESULTS AND DISCUSSION

The thermodynamic parameters is important in understanding mechanism of transport process provide valuable information regarding the size and shape of these molecules. The thermodynamic parameters were calculated and are enlisted in the table 1 to 3 (Figure 1-3).

Table 1: Determination of Thermodynamic parameters (ΔG*)

Ligands	Ethanol	1,4-Dioxane	Carbon tetrachloride
IIIa	-61131.15988	-61131.41211	-61093.5777
IIIb	-61226.64877	-61249.2158	-61168.95461
IIIc	-61056.19284	-60988.50699	-60987.97657
IIId	-61024.50432	-61051.90124	-61027.56192

Table 2: Determination of Thermodynamic parameters (ΔH*)

Ligands	Ethanol	1,4-Dioxane	Carbon tetrachloride
IIIa	7972.285465	7541.715245	9917.956265
IIIb	7213.244725	5643.984115	8496.24533
IIIc	7642.319345	7411.21564	7730.43772
IIId	7550.984755	6518.343535	8016.812435

Table 3: Determination of Thermodynamic parameters (ΔS*)

Ligands	Ethanol	1,4-Dioxane	Carbon tetrachloride
IIIa	226.56867	225.1577946	232.824701
IIIb	224.39309	219.32197	228.4104916
IIIc	225.241024	224.261386	225.306276
IIId	224.83767	221.541786	226.374998

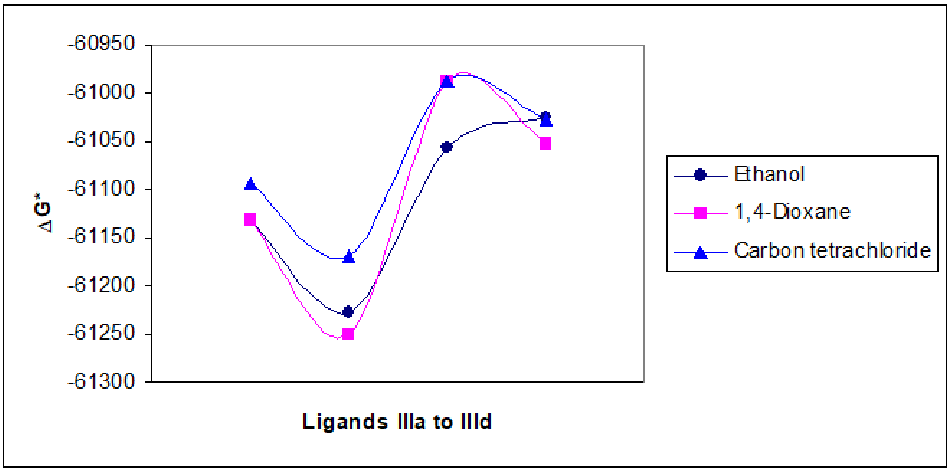


Figure 1: Thermodynamic parameters (ΔG*)

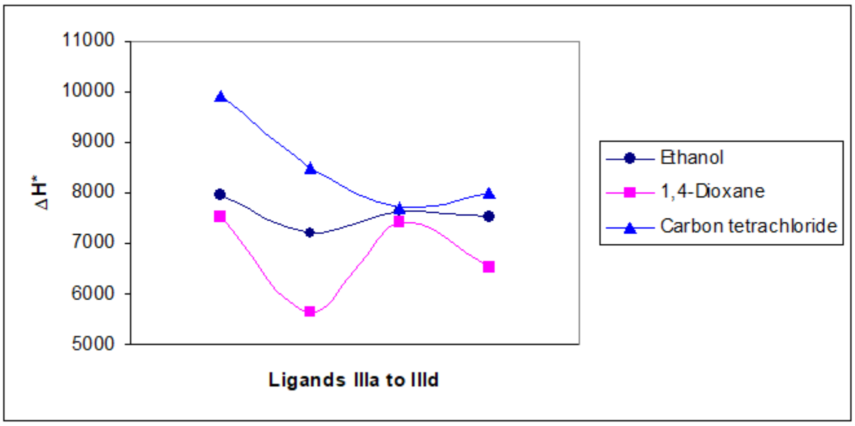


Figure 2: Thermodynamic parameters (ΔH*)

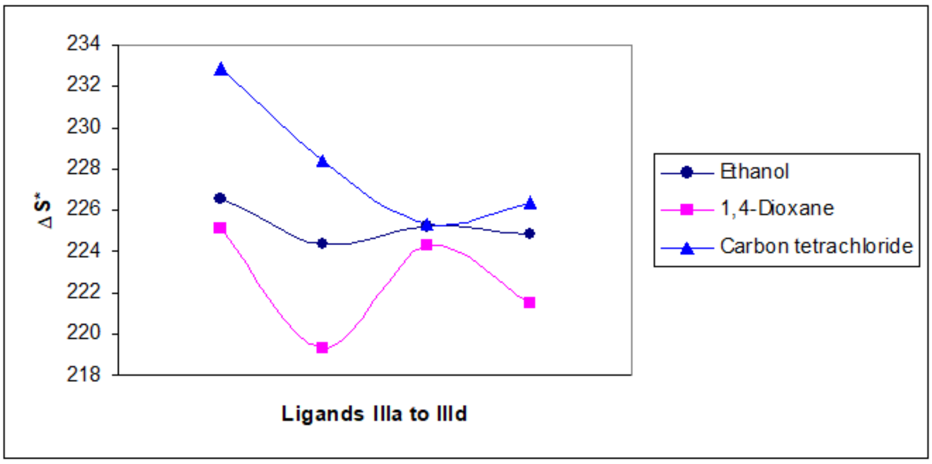


Figure 3: Thermodynamic parameters (ΔS*)

In ΔG*,

CCl_4 > Ethanol > Dioxane

The Gibbs free energy is found to be greater in CCl_4 than in ethanol which is further greater than 1,4- dioxane.
ΔG* values are lowest in case of dioxane and highest for CCl_4 whereas ΔS* values are maximum for CCl_4 and minimum for dioxane. Whereas ΔH values are lowest in case of dioxane and highest for CCl_4. This may be due to higher solute-solute interaction of molecule of ligand.
Gibbs free energy is observed to be increasing in the following order, the trend is observed as follows.

In case of ethanol,

Ligand - IIId > IIIc > IIIa > IIIb

In case of 1,4- dioxane,

Ligand - IIIc > IIId > IIIa > IIIb

In case of CCl_4,

Ligand - IIIc > IIId > IIIa > IIIb

The increase in Gibbs free energy also suggests shorter time for rearrangement of the molecules in the mixtures. The case is just reverse when temperature increases keeping the concentration of DMF constant [14].

Larger the negative ΔG value higher will be the stability of the species in that solution. Observed large negative value of ΔG indicate the stability of the species in solvent media than in water is supported by the exothermic character of the reaction [15].
In ΔH*,

CCl_4 > Ethanol > Dioxane

The enthalpy values are greater in CCl_4 than in ethanol which is further observed to be greater than dioxane. Enthalpy decreases in the following order for the ligands, the trend is observed as follows.

In case of ethanol,

Ligands - IIIa > IIIc > IIId > IIIb

In case of 1,4-dioxane,

Ligands -IIIa > IIIc > IIId > IIIb

In case of CCl_4,

Ligands -IIIa > IIIb > IIId > IIIc

Positive and negative deviations over the entire range of mole fraction. The viscosity of the mixture strongly depends on the entropy of mixture, which is related with liquid's structure and enthalpy, consequently with the molecular interactions between the components of the mixtures. Therefore, the viscosity deviation depends on molecular interactions as well as on the size and shape of the molecules [16].

In ΔS^*,

CCl_4 > Ethanol > Dioxane

The entropy values are greater in CCl_4 than in ethanol which is further observed to be greater than dioxane. Entropy decreases in the following order for the ligands the trend is observed as follows.

In case of ethanol,

Ligands - IIIa > IIIc > IIId > IIIb

In case of 1,4-dioxane,

Ligands - IIIa > IIIc > IIId > IIIb

In case of CCl_4,

Ligands - IIIa > IIIb > IIId > IIIc

The free energy increases and entropy decreases reducing the spontaneity and stability. This may be due to the strong hydrogen bonding which reduces the interaction between ligand molecules and the solvent.

The negative ΔG^* values and positive ΔS^* value are obtained indicating that the process is spontaneous in nature. Where ΔS^* is positive and ΔH^* is also positive, a process is spontaneous at high temperature, where exothermicity plays a small role in the balance. In a spontaneous process, every reactant has a tendency to form the corresponding product. This tendency is related to stability. Stability is gained only if energy is minimum and randomness is maximum. Hence negative ΔG^* and positive ΔS^* values shows a stable and spontaneous process. The knowledge of thermodynamic parameters is essential to interpret the nature of the chemical reaction.

ACKNOWLEDGEMENT

The authors are very much thankful to Prof. V.D. Thakare, Head, Department of Chemistry, G.V.I.S.H., Amravati for giving laboratory facilities. They are also thankful to Dr. A.R. Raut, G.V.I.S.H., Amravati and Dr. Naik, Department of Chemical Technology, S.G.B.A.U., Amravati for their kind cooperation.

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