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Research Article

Phase Transition Thermodynamic Properties Of 2-Methylquinoline, 2-Chloroquinoline And 2-Phenylquinoline

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Abstract

Derivatives of quinoline are widely utilized in both industries and in healthcare. To understand the quinolines' quality and stability in usage, it is crucial to study their phase transition chemical thermodynamic characteristics. In this work, the phase transition thermodynamic characters of 2-methylquinoline (quinaldine), 2-chloroquinoline, and 2-phenylquinoline were investigated. Moreover, the sublimation/vaporization enthalpy of the compounds were determined the solution calorimetry-additivity scheme approach at 298.15 K. The solution calorimetry was applied to measure solution enthalpies of the compounds in benzene solvent at 298.15 K. While, the solvation enthalpy of the compounds were calculated additivity scheme approach. In addition, the transpiration method applied to estimate vapor pressure to temperature dependency to 2-Chloroquinoline. In consequence, the vapor pressure values with respect to temperature variation was determined to 2-Chloroquinoline compound for the first time. As a result, the phase transition chemical thermodynamic properties; enthalpy, entropy, and Gibbs energy for 2-methylquinoline, 2-chloroquinoline and 2-phenylquinoline were determined from crystalline/liquid to gas phase. Furthermore, in this work the thermochemical characteristics values of the studied compounds exhibited higher accuracy to those in literature data. Finally, the phase transition thermodynamically studied on 2-position of the quinoline compound, where it substituted to methyl, chloro and phenyl groups.

Keywords: *Quinoline derivatives; sublimation/vaporizatin enthalpy; solvation enthalpy; solution calorimetry; additive scheme approach; transpiration method; Gibbs energy; entropy.*

1. Introduction

Quinoline derivative compounds have many applications in both medicine and industry [1]. In medicine, due to their antibacterial properties, quinoline derivatives were utilized in the manufacturing of drugs for the treatment of influenza B-Mass virus [2]. Additionally, the quinolines have been used to treat diseases including cancer, malaria, and anti-inflammatory illnesses [3], [4], antidotes against poisoning, antidiabetic activities and antiviral HCV [5]. In the light of industry, the quinoline compounds have been applied in production electro-optical display devices [6] and researching studies to magnetic properties, [7] photochemistry, [8] materials science, solution studies, and homogeneous catalysis owing to the versatility of their steric and electronic properties [9].

Due to mentioned implementations quinoline derivative compounds, it is necessary to study phase transition thermochemistry to use the quinolines in right way. Therefore, phase transition thermodynamics quinolines studying is essential. Phase transition of the compounds means transfer in chemical phase and properties. By the way, it makes drugs and devices are unusable or poisoned, where they were made from the quinolines, in another word, it has been expired. Thus, the phase transition thermochemical properties of the basic compounds (quinolines) in drugs and in devices are detected quality and stability drugs and manufacture devices.

The thermodynamic properties of phase transition presents energy transfer (enthalpy, entropy and Gibbs free energy (in this work)) of a chemical compound from its standard state (liquid or crystalline) to gas phase at constant temperature and 0.1 MPa pressure. The enthalpy of evaporation (sublimation/vaporization) of a chemical compound is a phase transition thermodynamics property was measured directly by calorimetric methods [10], [11] or indirectly from determination vapor pressure as a function to temperature [12], [13]. As consequence, the solution calorimetry was employed to determine the evaporation enthalpy of various compounds in specific solvents from solution enthalpy and solvation enthalpy values as estimated in previous works [14], [15], [16]–[20]. In this method, the solution enthalpy of the chemical compounds was measured solution calorimetry at standard temperature and solvation enthalpy the compounds in same solvent was established additivity scheme approach at 298.15 K [21]–[23]. Solution calorimetry technique was applied in obtaining enthalpy of sublimation/vaporization of the compounds as from following equation;

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$$\Delta^{g}_{cr,liq}H^{Ai}_{m} = \Delta_{soln}H^{Ai/Bz}_{m} - \Delta_{solv}H^{Ai/Bz}_{m} \quad (1)$$

Where, $\Delta^{g}_{cr,liq}H^{Ai}_{m}$ is the sublimation/vaporization enthalpy of chemical compound Ai, $\Delta_{soln}H^{Ai/Bz}_{m}$ is the solution enthalpy of chemical compound Ai in benzene solvent and $\Delta_{solv}H^{Ai/Bz}_{m}$ is the solvation enthalpy of Ai compound in benzene solvent. The solvation enthalpy of the compounds were worked out additive scheme approach at 298.15 K (in detail described from section 3.2).

In addition, transpiration method as indirect method was applied to estimate sublimation/vaporization enthalpy to the chemical compounds. The transpiration method has been used in measuring vapor pressure to temperature dependency. From data, vapor pressure to temperature relation values of the studied compound will establish chemical thermodynamic properties, according to the following equation;

$$Rln(P_t/P_0) = -\frac{\Delta^{g}_{cr,liq}G^{0}_{m}}{T_0} + \Delta^{g}_{cr,liq}H^{0}_{m}\left(\frac{1}{T_0} - \frac{1}{T}\right) + \Delta^{g}_{cr,liq}C^{0}_{p,m}\left(\left(\frac{T_0}{T}\right) - 1 + ln\left(\frac{T}{T_0}\right)\right) \quad (2)$$

Where P_t saturated vapor pressure at T temperature, P_0 is the standard vapor pressure, T_0 is the standard temperature (298.15 K), $\Delta^{g}_{cr,liq}G^{0}_{m}$ Gibbs energy of evaporation, $\Delta^{g}_{cr,liq}C^{0}_{p,m}$ evaporation heat capacity. Then, the value of entropy of phase transition ($\Delta^{g}_{cr,liq}S$) of the compound could be measure as from following equation;

$$\Delta^{g}_{cr,liq}S = \Delta^{g}_{cr,liq}H/T \quad (3)$$

Consequently, the chemical thermodynamic characters were measured through equations used from vapor pressure to temperature correlation data from the transpiration method.

The phase transition of the chemical thermodynamic properties distinguish the stability and quality of drugs and devices were manufactured from chemical compounds. Especially, the phase transition thermodynamic properties; enthalpy, Gibbs energy and entropy. In this work, the thermochemical properties were estimated for the compounds 2-methylquinoline, 2-chloroquinoline and 2-phenylquinoline. As from figure (1) (chemical structure) the studied compounds are heterocyclic aromatic compounds where substituted at two-cite of the quinoline compound.

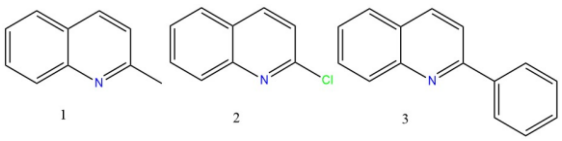

Figure 1. Chemical structure of the quinolines.1) 2-methylquinoline, 2) 2-chloroquinoline, 3) 2-phenylquinoline.

Furthermore, the solution calorimetry-additive scheme approach and the transpiration method were applied in this work to determine the phase transition thermochemical properties of the studied compounds. The evaporation enthalpy was determined at 298.15 K to the three compounds solution calorimetry-additivity scheme approach. Besides, the thermochemical properties study of phase transition on these compounds were also investigated from transpiration method.

2. Experimental Part

2.1 Materials

The quinoline derivatives are commercial origin materials. The quinoline solute compounds were in high mass fraction purity, the purity percent were more than 97% (table 1), in solution calorimetry the quinoline compounds were dissolved in benzene solvent. The benzene solvent was local commercial origin. Additionally, the benzene solvent was purified by standard methods [24], [15] through fraction distillation. Hence, the fraction mass purity of the solvent was raised to 99 %, gas chromatography GC Agilent 7820 A was tested.

Table 1. CAS number, origin and purity of the quinolines.

Compound	CAS	Origin	Purity %
2-Methylquinoline	91-63-4	Alfa Aesar	97+
2-Chloroquinoline	612-62-4	SIGMA-ALDRICH	99
2-Phenylquinoline	612-96-4	ACROS ORGANICS	99+

2.2 Solution Calorimetry

Enthalpy of solution quinoline compounds was measured with commercial TAM III solution calorimetry (TA Instruments, USA). First, small amount of a quinoline derivative compound (Quinaldine (2-methylquinoline), 2-Chloroquinoline or 2-phenylquinoline) was dissolved in the benzene solvent to get infinite dilution solution into the solution calorimetry glass cell. Furthermore, there are used two standard compounds with respect the state of the materials (crystalline and liquid) to measure solution enthalpy in solution calorimetry technique at 298.15 K. Moreover, the crystalline compound, first it was grinded to make like powder substance then weighted about 500 mg and it was dissolved into the glass cell, which it contained about 90 mL of the solvent. While, the liquid samples, small portions of the liquid compound between 50-300 µL were injected electronically by operated syringe connected with long gold cannula immersed into the solvent [14][15].

First, the solution calorimetry was calibrated up on using standard crystalline and liquid compounds. The standard crystalline compound was potassium chloride. The KCl standard crystalline was dissolved in a purified water (distillated twice and deionized) into the calorimetry cell, its solution enthalpy at 298.15 was 17.475 ± 0.08 kJ.mol^{-1}, and in the literature, solution enthalpy of KCl was 17.205 kJ.mol^{-1} at same temperature [25]. Identically, to the liquid compounds, the calorimetry was tested by propan-1-ol as standard liquid solute in the purified water and the value solution enthalpy was -10.16 ± 0.05 kJ.mol^{-1} as well as the propanol-1 solution enthalpy value in the literature was -10.18 ± 0.03 kJ.mol^{-1} [26]. Therefore, the values of solution enthalpies of our standards were well agree with the literature values.

2.3 Transpiration Method

Vapor pressure was measured over the liquefied compound of 2-chloroquinoline as a function to temperature through the transpiration method. First, about 0.5 g of the sample was mixed with glass beads and placed into the U-tube thermostatic at constant temperature ± 0.1 K. Then, the amount of the evaporated compound into the thermostat tube at a definite temperature carried out by Nitrogen gas flow stream with known rate and specific amount of time. After that, the sample condensed into the second cooling part tube.

The amount of condensed compound m_i was measured by the gas chromatography at each temperature with respect to an organic standard liquid compound. The nitrogen flow stream in a definite flow rate passed through the tube at selected temperature T_i. Definitely, the amount of saturated vapor pressure of the sample condensed in the cold trap was measured at definite time to know the volume V_{N2} transported nitrogen gas at the specific rate according to general gas law, the procedure described elsewhere [12], [15], [27], [28] [29].

$$p_i = m_i \cdot R \cdot Ta / (V \cdot M_i) \quad (4)$$

Where; $V = V_{N2} + V_i = (n_{N2} + n_i) \cdot R \cdot T_a / P_a$

Where V is the volume of the gas phase consisting of the n_{N2} moles of the carrier gas and n_i mole of gaseous compound under study at the atmospheric pressure P_a and the ambient temperature T_a. The volume of the carrier gas V_{N2} was calculated through a digital flow rate microcontroller. The digital flow rate sensor was worked in an uncertainty at the level of 2.5 %. The flow rate of the nitrogen stream was also controlled by using soap bubble flow pipette and optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. The volume of the carrier gas V_{N2} read from the calibrated digital flow rate sensor.

3. Results and Discussion

Enthalpy of sublimation/vaporization (evaporation) is the enthalpy transfer of a compound from its standard state (crystalline or liquid) to gaseous phase at constant temperature and pressure 0.1 MPa. Solution calorimetry-additivity scheme approach and transpiration method were applied to measure the evaporation enthalpy to the three compounds substituted quinolines (2-methylquinoline, 2-chloroquinoline and 2-phenylquinoline) at 298.15 K. In addition, the other thermochemical properties of the compounds were estimated to the studied compounds. Accordingly, the chemical thermodynamic properties have been found to 2-chloroquinoline compound from transpiration method in this work and for the other compounds the properties were collected in the literature data. The quinoline derivative compounds chemical thermodynamic characters are established the stability and thermochemical energy of the compounds from standard state to gas phase as well as the impact of substituted groups at 2-position of the quinoline compound. Consequently, the stability and quality of the drugs and the devises, which made from the studied quinolines, could be known.

Hence, the evaporation enthalpy of the studied compounds was measured by the solution calorimetry-additive scheme approach and the transpiration methods at 298.15 K. Then, from solution calorimetry-additive scheme approach was determined the vaporization/sublimation enthalpy for quinoline derivatives according to equation (1). While, the solution enthalpy was determined directly from the solution calorimetry at 298.15 K in benzene solvent and the solvation enthalpy was calculated by additivity scheme approach.

3.1 Solution Enthalpy

Solution enthalpy is the enthalpy of a compound in standard state (solid or liquid) to dissolve in solvent to make a solution infinite dilute solution at standard temperature and pressure 0.1 *MPa*. Solution enthalpy was determined directly from solution calorimetry at 298.15 K for the studied compounds. Moreover, according to the solution enthalpy values (table 2) indicate that all three compound exist the endothermic heat affect when dissolve in the benzene solvent. Furthermore, the low value solution enthalpy 2-methylquinoline due to the methyl group attached to the quinoline compound and the interaction with the benzene solvent as well as it is in liquid state. While, the solution enthalpy values 2-chloroquinoline and 2-phenylquinoline were close to each other because they are in crystalline state, the solution enthalpy values contain destroy crystalline lattice then process heat of solvation.

3.2 Solvation Enthalpy

Solvation enthalpy is the transfer enthalpy of a compound from gaseous state to a solvent to make a solution of infinite dilution at standard temperature and pressure 0.1 *MPa*. The solvation enthalpy is another phase transition chemical thermodynamic character indicates the solubility heat effect of compound. In this work, the solvation enthalpy was calculated to the three quinolines with respect to additivity scheme approach [15], [21], [22], [30]. According to the additive scheme approach, the solvation enthalpy was estimated.

Solvation enthalpy was calculated for the quinoline (as heterocyclic compound);

$$\Delta_{\mathrm{solv}}\mathrm{H}^{\mathrm{ArXi/S}} = \Delta_{\mathrm{solv}}\mathrm{H}^{\mathrm{ArH/S}} + \Sigma\, \Delta_{\mathrm{solv}}\mathrm{H}^{\mathrm{Xi\rightarrow CH/S}} \quad (5)$$

Where $\Delta_{solv}H^{ArXi/S}$ is the solvation enthalpy of quinoline compound in solvent *S*, $\Delta_{solv}H^{ArH/S}$ is the solvation enthalpy of the naphthalene compound (removed nitrogen atom into the quinoline ring) in the solvent *S* and $\Delta_{solv}H^{\mathrm{Xi\rightarrow CH}/S}$ is the solvation enthalpy of the substituted group with CH, it means azo group into the quinoline compound in solvent *S*. As notify, the solvents *S* must be same solvent to all components of a compound.

In addition, the solvation enthalpy of quinoline with attached group was measured as following equation;

$$\Delta_{solv}H^{ArXi/S} = \Delta_{solv}H^{ArH/S} + \Delta_{solv}H^{Xi/S} \quad (6)$$

Where $\Delta_{solv}H^{ArXi/S}$ is the solvation enthalpy of the substituted quinoline compounds *ArXi* in solvent *S*, $\Delta_{solv}H^{ArH/S}$ is solvation enthalpy of the compound without

Table 2. The values of solution enthalpy, solvation enthalpy and evaporation enthalpy in kJ.mol^{-1} at 298.15 K.

Compound	$-\boldsymbol{\Delta_{solv}H_m^{Ai/Bz}}$ [b]	$\Delta_{soln}\boldsymbol{H_m^{Ai/Bz}}$ [c]	$\Delta_{liq,cr}^{g}H_m$ [a]
2-Methylquinoline	63.8	1.45	65.25 ± 0.13
2-Chloroquinoline	66.4	21.21	87.61 ± 0.89
2-Phenylquinoline	82.68	19.92	108.0 ± 0.04

[a] the values of standard uncertainty were calculated from standard deviation of repeating experiments of the solution calorimetry in this work. [b] the values were calculated from equations (5), (6) and (7). [c] the values were measured from solution calorimetry technique in this work.

any attached group (quinoline in this work) in solvent *S*, $\Delta_{solv}H^{Xi/S}$ is solvation enthalpy of the branched group (methyl, chloro and phenyl in this study) in the same solvent. Notably, the *S* solvent must be the same to all parts of the study compound [15].

Thereupon, solvation enthalpy was measured to 2-methylquinoline and 2-chloroquinoline. After that, the evaporation enthalpy for the two compounds was obtained. In another hand, the equation (7) was used in calculation enthalpy of solvation for 2-Phenyl quinoline compound, because the 2-phenyl quinoline compound didn't obey to the two above equations due to high deviation of the solvation enthalpy value. Therefore, the 2-phenyl quinoline compound has three aromatic rings and it was estimated as poly aromatic compound with respect to the additive scheme approach [19], as from following equation;

$$\Delta_{\mathrm{solv}}\mathrm{H}^{2\mathrm{PQ/Bz}} = \mathrm{n}.\,1/6.\,\Delta_{\mathrm{solv}}\mathrm{H}^{\mathrm{Bz/Bz}} + 1.08\,.\,\mathrm{Y} \quad (7)$$

Where $\Delta_{solv}H^{2PQ/Bz}$ is the solvation enthalpy of 2-phenylquinoline in benzene solvent, $\Delta_{solv}H^{Bz/Bz}$ is solvation enthalpy of benzene in benzene solvent, *n* is the number of carbon atoms and *Y* is the difference between carbon and hydrogen atoms. Consequently, the solvation enthalpy value for the 2-phenylquinoline compound was -82.68 kJ.mol^{-1} (table 2).

3.3 Evaporation Enthalpy

The sublimation/vaporization enthalpy was determined for 2-methyl quinoline, 2-chloro quinoline and 2-phenyl quinoline in applying the solution calorimetry-additivity scheme approach at standard temperature. Uniquely, the sublimation/vaporization enthalpy values in this work were in high accuracy observed the solution calorimetry at 298.15 K according to equations (mentioned above) with respect to standard uncertainty values. In addition, to establish values from solution calorimetry-additivity scheme approach of the 2-chloroquinoline and because it had only one literature value on its thermochemical properties (sublimation enthalpy), therefore, the thermochemical properties were determined through the transpiration method. In this method, the thermodynamic parameters were indirectly calculated in relation between temperature and saturated vapor pressure values of the studied compound.

First, determination of the heat capacity by vapor pressure to temperature dependency applying the Clausius-Clayperon equation, as shown below;

$$R\,ln\,p_i = a + \frac{b}{T} + \Delta^g_{liq,cr}C^o_{p,m}ln\left(\frac{T}{T_0}\right) \quad (8)$$

Where R is the general gas constant (8.31447 J.mol^{-1}.K^{-1}), p_i is vapor pressure of compound *i*, *a* and b are adjustable constants, $\Delta^g_{liq,cr}C^o_{p,m}$ is molar heat capacity change of a compound from liquid or crystalline state to the gaseous phase at constant pressure and standard temperature, and *T*, T_o are selected temperature and reference temperature (298.15 K) respectively. Then, enthalpy of evaporation was measured, where, expressed below and adjusted to reference temperature 298.15 K;

$$\Delta^g_{cr,liq}H^{Ai} = -b + \Delta^g_{liq,cr}C^o_{p,m} \times T \quad (9)$$

From equation (9), it is possible to determine the enthalpy of sublimation/vaporiztion of the studied compound, knowing the constant *b* and the change in heat capacity from the solid or liquid state to the gas phase at temperature *T*.

Moreover, the molar heat capacity phase transition the three compounds were calculated from Acree, Jr. and S. Chickos estimation equations for liquid and crystalline states respectively [31];

$$\Delta^{\mathrm{g}}_{\mathrm{liq}}\mathrm{C}_{\mathrm{p,liq}} = 10.58 + 0.26\mathrm{C}_{\mathrm{p,liq}} \quad (10)$$

$$\Delta^{\mathrm{g}}_{\mathrm{cr}}\mathrm{C}_{\mathrm{p,cr}} = 0.75 + 0.15\mathrm{C}_{\mathrm{p,cr}} \quad (11)$$

Therefore, from value molar heat capacity change and constant *b* at *T* temperature was measured the vaporization enthalpy for 2-chloroquinoline;

To confirm the sublimation enthalpy value of 2-chloroquinoline because only one value was found. Therefore, the vapor pressure to temperature dependency, vaporization/sublimation enthalpy, entropy change and Gibbs energy change values were determined by transpiration method in this work for the 2-chloroquinoline compound at the selected temperature and at suitable nitrogen flow rate to obtain the amount of evaporated vapor over the sample (table 3). Vapor pressure to temperature relation data over 2-chloroquinonline was measured for the first time and its thermochemical properties at reference temperature 298.15 K were determined temperature [29]. The uncertainties of vaporization/ sublimation enthalpies combined in literature values assessed. Additionally, the transpiration method uncertainties measurements were described in detail elsewhere [32].

Table 3. Vapor pressure of liquefied 2-Chloroquinoline from transpiration method.

$$\ln(p/p^{\circ}) = \frac{249.39}{R} - \frac{73847.58}{RT} - \frac{48.8}{R}\ln\frac{T}{298.15}$$

$$\Delta^g_{liq}H_{298.15\,\mathrm{K}} = 66.76 \pm 0.55\ \mathrm{kJ.mol^{-1}}$$

Tm, K	*m, mg*	*V(N$_2$), L*	*Gas-flow, L.hr^{-1}*	*P, Pa*	$\Delta^g_{liq}H_{Tm\,K}$ *kJ.mol^{-1}*	$\Delta^g_{liq}S_{Tm}$ *J.K^{-1}.mol^{-1}*
313.4	*2.40*	*8.721*	*4.19*	*4.19*	*66.02*	*126.9*
319.5	*2.53*	*5.233*	*4.19*	*7.35*	*65.72*	*126.6*
328.8	*2.28*	*2.428*	*4.16*	*14.34*	*65.27*	*125.0*
331.1	*2.81*	*2.428*	*4.16*	*17.65*	*65.16*	*125.0*
335.7	*3.05*	*1.953*	*4.19*	*23.48*	*64.93*	*120.7*
339.3	*3.11*	*1.535*	*4.19*	*30.87*	*64.76*	*121.7*
340.2	*2.28*	*1.047*	*4.19*	*33.23*	*64.71*	*121.4*
343.0	*2.49*	*0.986*	*1.69*	*38.48*	*64.58*	*122.0*
345.6	*2.09*	*0.704*	*1.69*	*45.23*	*64.45*	*122.5*
348.9	*2.06*	*0.563*	*1.69*	*55.87*	*64.29*	*122.9*
351.7	*2.47*	*0.563*	*1.69*	*66.92*	*64.15*	*123.7*
353.4	*2.74*	*0.563*	*1.69*	*74.11*	*64.07*	*123.7*
357.4	*2.59*	*0.423*	*1.69*	*93.31*	*63.87*	*124.0*

According to the vapor pressure to temperature values, the 2-Chloroquinoline enthalpy of vaporization value was 66.76 ± 0.55 kJ.mol^{-1} at reference temperature (298.15 K) because the compound has been liquefied then evaporated into the thermostat tube then it condensed after that the condensed state measured through gas chromatography method. Furthermore, with respect to the works [22], [33] the solution enthalpy (crystalline form, 2-Chloroquinoline) approximately equal to the fusion enthalpy $\Delta_{cr}^{liq} H^{Ai}$ at fusion temperature for the same compound. Consequently, sublimation enthalpy $\Delta_{cr}^{g} H_m^0$ for 2-Chloroquinoline was evaluated, following equations;

$$\Delta_{\mathrm{cr}}^{\mathrm{g}}\mathrm{H}_{\mathrm{m}}^{0} = \Delta_{\mathrm{cr}}^{\mathrm{liq}}\mathrm{H}^{\mathrm{Ai}} + \Delta_{\mathrm{liq}}^{\mathrm{g}}\mathrm{H}_{\mathrm{m}}^{0} \quad (12)$$

Where; $\Delta_{\mathrm{soln}}\mathrm{H}_{298.15\,\mathrm{K}} \approx \Delta_{\mathrm{cr}}^{\mathrm{liq}}\mathrm{H}^{\mathrm{Ai}}$,

$$\text{Then, } \Delta_{\mathrm{cr}}^{\mathrm{g}}\mathrm{H}_{\mathrm{m}}^{0} = \Delta_{\mathrm{soln}}\mathrm{H}_{298.15\,\mathrm{K}} + \Delta_{\mathrm{liq}}^{\mathrm{g}}\mathrm{H}_{\mathrm{m}}^{0} \quad (13)$$

Therefore, the sublimation enthalpy values 2-Chloroquinoline from solution calorimetry-additivity scheme approach and the transpiration method were 87.61 ± 0.89 kJ.mol^{-1} and 87.97 ± 0.55 kJ.mol^{-1} at 298.15 K respectively. While, the value of sublimation enthalpy for 2-Chloroquinoline by the microcalorimetry method was 84.3 ± 2.6 kJ.mol^{-1} [34] with higher uncertainty (standard deviation) than the values were obtained in this work (table 4). Hence, our values of sublimation enthalpy are higher accuracy (lower standard deviation). Besides, the sublimation enthalpy value of 2-Phenylquinoline was 108.0 ± 0.04 kJ.mol^{-1} in solution calorimetry-additivity scheme approach. In addition, it was compared with the literature average value was 104.8 ± 2.2 kJ.mol^{-1}, when it was done by Knudsen mass-loss effusion method with higher uncertainty [27] than the value was observed in this work. The sublimation enthalpy difference between our method and the literature value where estimated by Knudson-mass loss effusion method was 3.57 kJ.mol^{-1} however, it agrees with each other when compare uncertainty values. Likewise, vaporization enthalpy 2-methylquinoline in this work by solution calorimetry method was 65.25 ± 0.13 kJ.mol^{-1} at 298.15 K and vaporization enthalpy of same compound at 298 K in microcalorimetry method was 66.1 ± 1.9 kJ.mol^{-1} well agree with the value in this work. While, the other values of vaporization enthalpy didn't agree with our value due to they were measured in higher temperature like, in reference [35] the enthalpy was measured in temperature range 319-553 and applied Ebulliometry method, however, adjusted to reference temperature.

3.4 Gibbs Free Energy And Entropy of Phase Transition

Gibbs energy and entropy of the phase transition were estimated for the studied compounds at temperature 298.15 K (table 5). The Gibbs energy of the phase transition of the compounds from liquid or crystalline state to the gas phase were generally no favorably changed. Moreover, the highest value of the Gibbs energy was 44.3 ± 0.04 kJ.mol^{-1} for the 2-Phenylquinoline compound because it was in most stable crystalline state due to it has the maximum value of sublimation enthalpy. While, the minimum value of Gibbs energy was 13.36 kJ.mol^{-1} was due to the chemical structure quinoline compound, where, it has not substituted group and it was in liquid state.

In another hand, the evaporation entropy values were obtained to quinoline and the substituted quinolines. The compounds of 2-Phenylquinoline and 2-Chloroquinoline were present maximum value of sublimation entropy because they were in crystalline state and they exist the highest values of sublimation enthalpy. Furthermore, the entropy of evaporation was determined at various temperature for 2-Chloroquinoline through the transpiration method. In consequence, the chemical thermodynamic parameters were evaluated and adjusted to the reference temperature 298.15 K.

In addition, the standard uncertainties values were combined in the transpiration method and in the solution calorimetry uncertainties where the vapor pressure and temperature uncertainties adjusted to the reference

Table 4. Various techniques to determine evaporation enthalpy.

Compound	*M* [a]	*T /K*	$\Delta_{liq,cr}^{g} C_{p,298\,K}$ [b] *J.K^{-1}.mol^{-1}*	$\Delta_{liq,cr}^{g} H_{298.15\,K}$ *kJ.mol^{-1}*	$\Delta_{liq,cr}^{g} H_{T/K}$ [c] *kJ.mol^{-1}*	*Ref.*
Quinoline(liq) [d]	*IPM,E*	*298–559*			*57.9 ± 0.1*	[31]
	GS	*298*		*58.1*		[31]
	IPM,E	*440*			*50.7 ± 0.1*	[31]
	GC				*53.3*	[31]
	SC		*63.59*			*This work*
2-Methylquinoline(liq)	*E*	*319–553*			*62.6 ± 0.1*	[35]
	M	*298*		*66.1 ± 1.9*		[31]
	GS	*281–313*			*61.2*	[31]
	E	*443–521*			*54.7*	[31]
	SC	*298.15*	*70.98*	*65.25 ± 0.13*		*This work*
2-Chloroquinoline(cr)	*CM*	*298.15*			*84.3 ± 2.6*	[34]
	SC	*298.15*	*26.64*	*87.61 ± 0.89*		*This work*
	T	*298.15*		*87.97 ± 0.55*		*This work*
2-Phenylquinoline(cr)	*KM*	*337-351*			*105.4±0.9*	[36]
	KM	*337-351*			*103.1±0.8*	[36]
	KM	*298.15*		*104.8 ± 2.2*		[27]
	SC	*298.15*	*36.81*	*108.0 ± 0.04*		*This work*

[a] methods, E= Ebulliometer, M=Microcalorimetric, V=vaporization method, GC= gas chromatography, GS =Gas saturation vaporization method, SC=Solution Calorimetry, CM= Calvet microcalorimetry, T= Transpiration method and KM=Knudsen mass-loss effusion. IPM= Inclined piston manometry. [b] the values were measured from estimation equation method (see text). [c] the values were calculated in literature data at mean temperature. [d] the quinoline compound was set just to comparison with the other compounds in this work.

Table 5. The thermodynamic properties of the quinolines.

Compound	$\Delta^{g}_{liq,cr}H_{298\,K}$ [a] *kJ.mol^{-1}*	$\Delta^{g}_{liq,cr}G_{298\,K}$ *kJ.mol^{-1}*	$\Delta^{g}_{liq,cr}S$ *J.K^{-1}.mol^{-1}*
Quinoline(liq)	*58.1* [e]	*13.36* [g]	*150.05* [f]
2-Methylquinoline(liq)	*65.25 ± 0.13*	*24.1 ± 0.03* [d]	*126.8* [d]
2-Chloroquinoline(cr)	*87.61 ± 0.89*	*28.1 ± 0.05* [c]	*199.7 ± 1.9* [c]
2-Phenylquinoline(cr)	*108.0 ± 0.04*	*44.3 ± 0.04* [b]	*202.7 ± 2.7* [b]

[a] values were measured by solution calorimetry-additive scheme method in this work (table 2). [b] values were determined from vapor pressure measurements [37]. [c] measured in this work by transpiration method. [d] according to Clark-Glaw equation from reference [38]. [e] from table 3. [f] the value was calculated from equation ($\Delta^{g}_{liq,cr}S_{298\,K} = \Delta^{g}_{liq,cr}H_{298\,K}/T_b$) T_b boiling point from reference [39]. [g] the value was calculated from equation: $\Delta^{g}_{liq,cr}G_{298\,K} = \Delta^{g}_{liq,cr}H_{298\,K} - (298.15\ K).\Delta^{g}_{liq,cr}S_{298\,K}$

In summing up, the evaporation enthalpy values studied compounds were determined from solution enthalpy values, which directly measured from solution calorimetry at 298.15 K. While, the solvation enthalpy values were calculated additivity scheme approach at standard temperature into the same solvent. Meanwhile, the evaporation enthalpy values were determined by solution calorimetry in high accuracy (lowest value of the standard deviation) for the three compounds of Quinaldine, 2-Chloroquinoline and 2-Phenylquinoline. In addition, the transpiration method was applied to determine vapor pressures to temperature dependency and the vaporization enthalpy of 2-Chloroquinoline was determined. Further, in the transpiration method calculated uncertainties of the thermochemical properties of vaporization enthalpy, free energy change and entropy change. By the way, the vaporization enthalpy of liquid 2-Chloroquinoline was modified to sublimation enthalpy without measuring fusion enthalpy instead used solution enthalpy of its solid state at temperature 298.15 K. The evaporation entropy from crystalline state to gas phase of 2-Chloroquinoline and 2-Phenylquinoline close to each other. However, the 2-Chloroquinoline and 2-Phenylquinoline considerably had high difference in their free energy change from solid state to gas phase due to the substituted groups of the chloro and phenyl.

4. Conclusion

Sublimation/vaporization enthalpy for the compounds Quinaldine (2-Methylquinoline), 2-Chloroquinoline, and 2-Phenylquinoline were determined using the solution calorimetry-additive scheme approach at 298.15 K. In addition, the chemical thermodynamic properties were established to studied compounds and the values were adjusted to the standard temperature. Accordingly, for the first time, vapor pressure over 2-Chloroquinoline to temperature dependence and other chemical thermodynamic properties were determined at various temperatures by the transpiration method. In the present study, the values evaporation enthalpies of the compounds were exist lower standard deviations in compare with those obtained in literature data. According to the three compounds were studied, comparatively the thermochemical properties were determined to 2-position substitution of quinolines in comparison to quinoline thermodynamic properties values where substituted to methyl, chloro and phenyl groups. Consequently, phase transition thermodynamic properties observed that the stability especially the energy require to evaporate the compounds as well as the amount of evaporation energy. In that case, the thermodynamic characters indicate the quality and usable of the compounds in fields of medicine and industry.

Nomenclature

Bz benzene solvent
C heat capacity (is the amount of heat require to raise the temperature of a compound one degree)
cr crystalline (standard state of the compound)
g gas
G Gibbs free energy in kJ
H enthalpy in kJ
J joule
k kilo
K kelvin
hr hour unit
L litter
liq liquid
m mass in *mg*
M molecular mass
MPa mega Pascal
P pressure
R general gas constant in (8.31447 kJ/(mol. K))
S entropy in J
soln solution
solv solvation
T temperature in K
V volume
Δ change or transfer state

References:

[1] K. Li, T. Zou, Y. Chen, X. Guan, and C. Che, "Pincer-Type Platinum (II) Complexes Containing N-Heterocyclic Carbene (NHC) Ligand: Structures, Photophysical and Anion-Binding Properties, and Anticancer Activities," *Chem. Eur. J.*, vol. 21, no. 20, pp. 7441–7453, 2015, doi: 10.1002/chem.201406453.

[2] M. Islamuddin, O. Afzal, W. H. Khan, M. Hisamuddin, A. S. A. Altamimi, I. Husain, K. Kato, M. A. Alamri, and S. Parveen, "Inhibition of Chikungunya Virus Infection by 4-Hydroxy-1-Methyl-3-(3-morpholinopropanoyl)quinoline-2(1 H)-one (QVIR) Targeting nsP2 and E2 Proteins," *ACS Omega*, vol. 6, no. 14, pp. 9791–9803, 2021, doi: 10.1021/acsomega.1c00447.

[3] R. Pingaew, S. Prachayasittikul, and S. Ruchirawat, "Synthesis, Cytotoxic and Antimalarial Activities of Benzoyl Thiosemicarbazone Analogs of Isoquinoline and Related Compounds," *Molecules* , vol. 15, no. 2. 2010. doi: 10.3390/molecules15020988.

[4] S. M. A. Hussaini, "Therapeutic significance of

quinolines: a patent review (2013-2015)," *Expert Opin. Ther. Pat.*, vol. 26, no. 10, pp. 1201–1221, Oct. 2016, doi: 10.1080/13543776.2016.1216545.

[5] A. A. Altaf, A. Shahzad, Z. Gul, N. Rasool, A. Badshah, B. Lal, and E. Khan, "A review on the medicinal importance of pyridine derivatives," *J. Drug Des. Med. Chem*, vol. 1, no. 1, pp. 1–11, 2015, [Online]. Available: doi: 10.11648/j.jddmc.20150101.11

[6] G. Albrecht, C. Rössiger, J. M. Herr, H. Locke, H. Yanagi, R. Göttlich, and D. Schlettwein, "Optimization of the Substitution Pattern of 1, 3-Disubstituted Imidazo [1, 5-a] Pyridines and-Quinolines for Electro-Optical Applications," *Phys. status solidi*, vol. 257, no. 5, p. 1900677, 2020, doi: 10.1002/pssb.201900677.

[7] J. Qian, J. Hu, H. Yoshikawa, J. Zhang, K. Awaga, and C. Zhang, "External-Template-Assisted Formation of Octacyanometalate-Based MV–MnII (M= W, Mo) Bimetallic Coordination Polymers with Magnetic Properties," *Eur. J. Inorg. Chem.*, vol. 2015, no. 12, pp. 2110–2119, 2015, doi: DOI: 10.1002/ejic.201403223.

[8] A. Y. Tam, W. H. Lam, K. M. Wong, N. Zhu, and V. W. Yam, "Luminescent Alkynylplatinum (II) Complexes of 2, 6-Bis (N-alkylbenzimidazol-2′-yl) pyridine-Type Ligands with Ready Tunability of the Nature of the Emissive States by Solvent and Electronic Property Modulation," *Chem. Eur. J.*, vol. 14, no. 15, pp. 4562–4576, 2008, doi: DOI: 10.1002/chem.200701914.

[9] S. Günnaz, A. G. Gökçe, and H. Türkmen, "Synthesis of bimetallic complexes bridged by 2,6-bis(benzimidazol-2-yl) pyridine derivatives and their catalytic properties in transfer hydrogenation," *Dalt. Trans.*, vol. 47, no. 48, pp. 17317–17328, 2018, doi: 10.1039/C8DT03178A.

[10] L. M. P. F. Amaral and M. A. V Ribeiro da Silva, "Calorimetric study of bromoacetophenone isomers," *J. Chem. Thermodyn.*, vol. 78, pp. 254–259, 2014, doi: https://doi.org/10.1016/j.jct.2014.06.028.

[11] A. L. R. Silva, Á. Cimas, and M. D. M. C. Ribeiro da Silva, "Energetic study of benzothiazole and two methylbenzothiazole derivatives: Calorimetric and computational approaches," *J. Chem. Thermodyn.*, vol. 73, pp. 3–11, 2014, doi: https://doi.org/10.1016/j.jct.2013.06.021.

[12] S. P. Verevkin and V. N. Emel'yanenko, "Transpiration method: Vapor pressures and enthalpies of vaporization of some low-boiling esters," *Fluid Phase Equilib.*, vol. 266, no. 1, pp. 64–75, 2008, doi: https://doi.org/10.1016/j.fluid.2008.02.001.

[13] A. Delle Site, "The vapor pressure of environmentally significant organic chemicals: a review of methods and data at ambient temperature," *J. Phys. Chem. Ref. Data*, vol. 26, no. 1, pp. 157–193, 1997.

[14] R. S. Abdullah, "Phase Transition Thermodynamics: Evaporation Enthalpy of 13 Naphthalene Derivatives," *Russ. J. Phys. Chem. A*, vol. 97, no. 7, pp. 1361–1367, 2023, doi: 10.1134/S0036024423070245.

[15] R. S. Abdullah and B. N. Solomonov, "Sublimation/vaporization and solvation enthalpies of monosubstituted pyridine derivatives," *Chem. Thermodyn. Therm. Anal.*, vol. 8, p. 100087, Dec. 2022, doi: 10.1016/J.CTTA.2022.100087.

[16] R. N. Nagrimanov, A. A. Samatov, T. M. Nasyrova, A. V Buzyurov, T. A. Mukhametzyanov, C. Schick, B. N. Solomonov, and S. P. Verevkin, "Long-chain linear alcohols: Reconciliation of phase transition enthalpies," *J. Chem. Thermodyn.*, vol. 146, p. 106103, 2020, doi: https://doi.org/10.1016/j.jct.2020.106103.

[17] R. N. Nagrimanov, A. A. Samatov, A. V Buzyurov, A. G. Kurshev, M. A. Ziganshin, D. H. Zaitsau, and B. N. Solomonov, "Thermochemical properties of mono- and di-cyano-aromatic compounds at 298.15 K," *Thermochim. Acta*, vol. 668, pp. 152–158, 2018, doi: https://doi.org/10.1016/j.tca.2018.07.026.

[18] B. N. Solomonov, M. A. Varfolomeev, R. N. Nagrimanov, T. A. Mukhametzyanov, and V. B. Novikov, "Enthalpies of solution, enthalpies of fusion and enthalpies of solvation of polyaromatic hydrocarbons: Instruments for determination of sublimation enthalpy at 298.15K," *Thermochim. Acta*, vol. 622, pp. 107–112, 2015, doi: https://doi.org/10.1016/j.tca.2015.10.020.

[19] B. N. Solomonov, R. N. Nagrimanov, and T. A. Mukhametzyanov, "Additive scheme for calculation of solvation enthalpies of heterocyclic aromatic compounds. Sublimation/vaporization enthalpy at 298.15K," *Thermochim. Acta*, vol. 633, pp. 37–47, 2016, doi: https://doi.org/10.1016/j.tca.2016.03.031.

[20] B. N. Solomonov, M. I. Yagofarov, and R. N. Nagrimanov, "Additivity of vaporization enthalpy: Group and molecular contributions exemplified by alkylaromatic compounds and their derivatives," *J. Mol. Liq.*, vol. 342, p. 117472, 2021, doi: https://doi.org/10.1016/j.molliq.2021.117472.

[21] B. N. Solomonov, M. A. Varfolomeev, R. N. Nagrimanov, V. B. Novikov, A. V. Buzyurov, Y. V. Fedorova, and T. A. Mukhametzyanov, "New method for determination of vaporization and sublimation enthalpy of aromatic compounds at 298.15 K using solution calorimetry technique and group-additivity scheme," *Thermochim. Acta*, vol. 622, pp. 88–96, 2015, doi: 10.1016/j.tca.2015.09.022.

[22] B. N. Solomonov, R. N. Nagrimanov, M. A. Varfolomeev, A. V Buzyurov, and T. A. Mukhametzyanov, "Enthalpies of fusion and enthalpies of solvation of aromatic hydrocarbons derivatives: Estimation of sublimation enthalpies at 298.15K," *Thermochim. Acta*, vol. 627–629, pp. 77–82, 2016, doi: https://doi.org/10.1016/j.tca.2016.02.001.

[23] M. I. Yagofarov, R. N. Nagrimanov, and B. N. Solomonov, "Thermochemistry of phase transitions of aromatic amines: Estimation of the sublimation enthalpy at 298.15K through the fusion enthalpy," *J. Chem. Thermodyn.*, vol. 113, pp. 301–307, 2017, doi: https://doi.org/10.1016/j.jct.2017.06.017.

[24] W. L. F. Armarego and C. L. L. Chai, "Purification of organic chemicals," *Purif. Lab. Chem.*, vol. 7, pp. 103–554, 2009.

[25] H. Li, X. Chen, and F. Guo, "Enthalpy of solution for thiourea in triglycol and water," *Russ. J. Phys. Chem. A*, vol. 84, no. 13, pp. 2259–2261, 2010, doi:

10.1134/S0036024410130091.

[26] E. V Ivanov, V. K. Abrosimov, and V. I. Smirnov, "Enthalpies of solution of 1,1,3,3-tetramethylurea in normal and branched alkanols (C2–C4) at 298.15K," *J. Chem. Thermodyn.*, vol. 39, no. 12, pp. 1614–1619, 2007, doi: https://doi.org/10.1016/j.jct.2007.04.008.

[27] S. P. Verevkin, S. P. Safronov, A. A. Samarov, and S. V Vostrikov, "Hydrogen Storage: Thermodynamic Analysis of Alkyl-Quinolines and Alkyl-Pyridines as Potential Liquid Organic Hydrogen Carriers (LOHC)," *Appl. Sci.*, vol. 11, no. 24, 2021, doi: 10.3390/app112411758.

[28] A. A. Zhabina, R. N. Nagrimanov, V. N. Emel'yanenko, B. N. Solomonov, and S. P. Verevkin, "Nicotinamides: Evaluation of thermochemical experimental properties," *J. Chem. Thermodyn.*, vol. 103, pp. 69–75, 2016, doi: https://doi.org/10.1016/j.jct.2016.08.002.

[29] R. N. Nagrimanov, D. H. Zaitsau, R. S. Abdullah, A. V Blokhin, and B. N. Solomonov, "Thermochemistry of formation and phase transitions of substituted thiophenes at 298.15 K," *J. Chem. Thermodyn.*, vol. 186, p. 107123, 2023, doi: https://doi.org/10.1016/j.jct.2023.107123.

[30] A. A. Samatov, R. N. Nagrimanov, E. A. Miroshnichenko, and B. N. Solomonov, "Vaporization/sublimation enthalpies of mono- and dimethyl-esters estimated by solution calorimetry method," *Thermochim. Acta*, vol. 685, p. 178529, 2020, doi: https://doi.org/10.1016/j.tca.2020.178529.

[31] W. Acree Jr and J. S. Chickos, "Phase transition enthalpy measurements of organic and organometallic compounds. Sublimation, vaporization and fusion enthalpies from 1880 to 2015. Part 1. C1− C10," *J. Phys. Chem. Ref. Data*, vol. 45, no. 3, p. 33101, 2016, doi: 10.1063/1.4948363.

[32] S. P. Verevkin, A. Y. Sazonova, V. N. Emel'yanenko, D. H. Zaitsau, M. A. Varfolomeev, B. N. Solomonov, and K. V Zherikova, "Thermochemistry of halogen-substituted methylbenzenes," *J. Chem. Eng. Data*, vol. 60, no. 1, pp. 89–103, 2015, doi: doi.org/10.1021/je500784s.

[33] B. N. Solomonov, M. A. Varfolomeev, R. N. Nagrimanov, T. A. Mukhametzyanov, and V. B. Novikov, "Enthalpies of solution, enthalpies of fusion and enthalpies of solvation of polyaromatic hydrocarbons: Instruments for determination of sublimation enthalpy at 298.15 K," *Thermochim. Acta*, vol. 622, pp. 107–112, 2015, doi: 10.1016/j.tca.2015.10.020.

[34] M. A. V. R. da Silva, M. A. R. Matos, and L. M. P. F. Amaral, "Standard molar enthalpies of formation of 2-chloroquinoline, 4-chloroquinoline, 6-chloroquinoline and 4, 7-dichloroquinoline by rotating-bomb calorimetry," *J. Chem. Thermodyn.*, vol. 38, no. 1, pp. 49–55, 2006, doi: 10.1016/j.jct.2005.03.011.

[35] R. D. Chirico and W. V Steele, "Thermodynamic Properties of 2-Methylquinoline and 8-Methylquinoline," *J. Chem. Eng. Data*, vol. 50, no. 2, pp. 697–708, Mar. 2005, doi: 10.1021/je049595u.

[36] W. Acree Jr and J. S. Chickos, "Phase transition enthalpy measurements of organic and organometallic compounds and ionic liquids. Sublimation, vaporization, and fusion enthalpies from 1880 to 2015. Part 2. C11–C192," *J. Phys. Chem. Ref. Data*, vol. 46, no. 1, p. 13104, 2017, doi: 10.1063/1.4948363.

[37] M. A. V Ribeiro da Silva and M. A. R. Matos, "Recent work on the thermochemistry of some nitrogen heterocycles," *Pure Appl. Chem.*, vol. 69, p. 2305, 1997, doi: 10.1351/pac199769112295.

[38] S. P. Safronov, S. V. Vostrikov, A. A. Samarov, and S. P. Verevkin, "Reversible storage and release of hydrogen with LOHC: Evaluation of thermochemical data for methyl-quinolines with complementary experimental and computational methods," *Fuel*, vol. 317, Jun. 2022, doi: 10.1016/J.FUEL.2022.123501.

[39] R. M. Stephenson, *Handbook of the thermodynamics of organic compounds*. Springer Science & Business Media, 2012.