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THERMODYNAMIC STUDIES OF BROMPHENOL BLUE REMOVAL FROM WATER USING SOLVENT SUBLATION

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Abstract. The investigation of thermodynamic peculiarities of bromphenol blue (BB) elimination from aqueous solutions using solvent sublation technique has been carried out. Thermodynamic properties of acid dye (BB) interaction with cationic surfactant cetylpyridinium chloride (CPC), applying Kharash method and HyperCube HyperChem Professional software were studied. It was proven that dye-surfactant ion complex formation is a spontaneous process and does not require any external forces for its run.

Keywords: Hess's law, enthalpy, Gibbs free energy, ion complex, molecular mechanics, sublimate.

1. Introduction

Unfortunately, Ukraine does not remain uninvolved in water pollution problem, moreover it experiences its exacerbation phase. According to international standards, all of our big rivers and their tributaries belong to the category of polluted or highly polluted waters. At the same time synthetic dyes play one of the key roles in water contaminating. These compounds can not be biochemically decomposed in aqueous systems due to their complicated chemical structure, hence local sewage treatment plants can not cope with such impurities. Because of the potentiating effect the result of dyes interactions with other water pollutants is often unpredictable. In addition, dyestuff is quite toxic for some flora and fauna species due to aromatic rings and chlorine substituents in its structure, entailing the extinction of different water inhabitants.

Since dyes can cause self-treatment processes disruption and bring a serious risk of human diseases, they are extremely hazardous and have to be eliminated from surface water basins [1].

There are numerous water treatment techniques that provide either elimination or destruction of synthetic dyes. However, they are often inappropriate due to their

expensive application, ineffectiveness or sludge production. In this case solvent sublation is a good alternative. It is a kind of special adsorptive bubble separation technique that excludes the possibility of foam formation. Some amount of organic solvent placed on the top of aqueous phase is used to collect the sublimate adsorbed on bubble surfaces of an ascending gas stream. This method, with its advantages of simultaneous separation and concentration, has recently attracted much attention in many fields [2-4].

Previous work of this team [5] addressed the following: experimental evaluation of solvent sublation effectiveness in the case of acid dye (BB) removal, investigation of its main principles, adequate mathematical model derivation, and determination of optimum conditions. However, physicochemical properties of analysed system remained undiscussed. Thermodynamic studies of processes occurring at different solvent sublation stages were carried out by several authors. For instance, K. Valsaraj [6] focused on the investigation of such thermodynamic parameters as: free energy, interfacial energy, enthalpy, and entropy of mass transfer from the bulk aqueous solution to the air-water interface for hydrophobic compounds of environmental interest. Lu and Zhu [7] studied the energy of the dye-surfactant complex attraction to the surface of ascending bubble. They also compared solvation-sublation to flotation process and proposed to use the same equation expressing the surface excess value for both techniques. In [8] researchers conducted studies on thermodynamic behaviour (surface tension, surface excess, molecular area, and the free adsorption energy) of surface active agents during their adsorption on the air-water interface (bubbles surface).

Our current investigation deals with thermodynamic parameters of the interaction between anionic dye BB and the surface active agent with opposite charge – CPC at surfactant concentrations below the critical micelle concentration (CMC). Calculations were made using Kharash method and HyperCube HyperChem Professional v8.0.6.

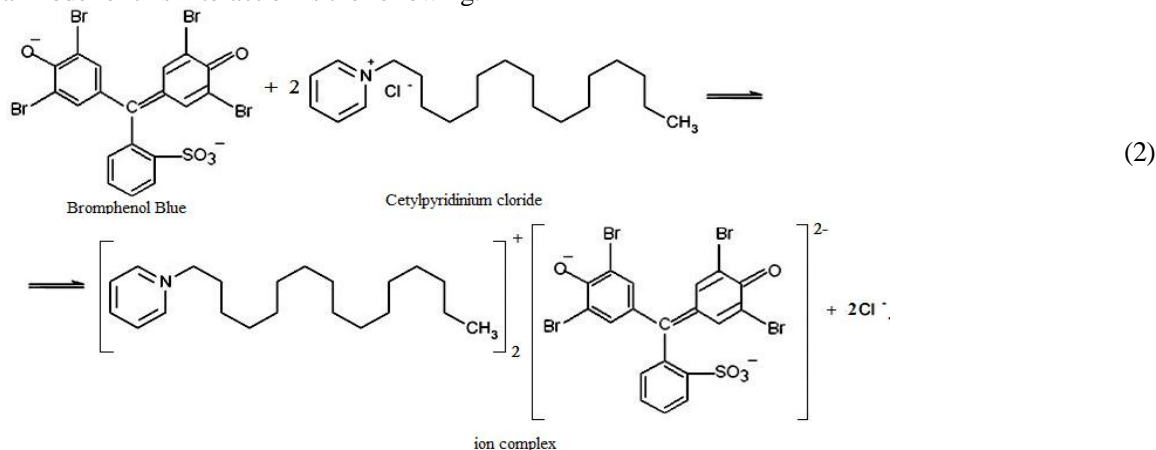
2. Theoretical

2.1. Process Mechanism

Before carrying out thermodynamic calculations it is necessary to define the mechanism of formation of cetylpyridinium-bromphenol blue (CP-BB) ion associates after the interaction between cationic surface agent CPC and anionic dye BB at submicellar surfactant concentration (Eqs. (1) and (2)).



Structural model of this interaction is the following:



The reliability of determined mechanism of sublate formation had been proved before by the study of UV-visible spectra of examined aqueous solutions, indicating the occurrence of characteristic absorbance peak at 463 nm. Nevertheless, the mechanism needed the additional proof. Therefore, thermodynamic calculations were used to confirm ion complex formation as the free Gibbs energy value shows whether the reaction is thermodynamically favourable or not at a constant temperature and pressure. In addition, thermodynamic investigation would dramatically simplify and accelerate the search for new suitable surface active agents.

2.2. Kharash Method

Since no experimental data on BB and CPC thermodynamic characteristics were available, our choice fell exactly on Kharash method, although it is not completely accurate. Usually, this method is used to determine heat of combustion for organic compounds in liquid state at 298 K.

As specified by Kharash formula, heat of combustion is defined as:

$$\Delta H_{comp}^{comb.} = 109 \cdot r + \sum \Delta_i \cdot k \quad (3)$$

where r is a number of electrons which are tightly bonded with atoms and substitute hydrogen atoms in organic compound $r = c_4 \cdot 4 + c_3 \cdot 3 + c_2 \cdot 2 + c_1 \cdot 1 + H \cdot 1$

(c_4, c_3, c_2, c_1 are the amounts of carbon atoms that act as electron donors and donate 4, 3, 2 and 1 electrons, respectively; H is the amount of hydrogen atoms that donate 1 electron each); Δ_i is the thermal correction which depends on the type of substituent; k is the amount of the same substituents.

The heat of formation can be found using the consequence of the Hess's law:

$$\Delta H_{comp}^{form.} = \sum n \cdot \Delta H_{el.}^{comb.} - \Delta H_{comp}^{comb.} \quad (4)$$

where n is the amount of atoms of one element within the molecule; $\Delta H_{el.}^{comb.}$ is the heat of combustion change for 1 kg/atom of element, kJ; $\Delta H_{comp}^{comb.}$ is the heat of combustion change for every compound kJ/(kg/mol).

According to Hess's law, total enthalpy change during the complete course of a chemical reaction (1) is equal to algebraic sum of enthalpy changes for products and reactants. Thus:

$$\Delta H_{ch.reaction}^0 = \sum n_i \cdot \Delta H_{i(products)}^0 - \sum n_i \cdot \Delta H_{i(reactants)}^0 = \left(\Delta H_{(CP-BB)}^0 + 2 \cdot \Delta H_{(Cl^-)}^0 \right) - \left(2 \cdot \Delta H_{(CPC)}^0 + \Delta H_{(BB)}^0 \right), \quad (5)$$

where n_i is the amount of i -component.

The value of Gibbs free energy change under standard conditions is given by:

$$\Delta G_{ch.reaction}^0 = \Delta H_{ch.reaction}^0 - T \cdot \Delta S_{ch.reaction}^0 \quad (6)$$

where T is the temperature of the system, K; $\Delta S_{ch.reaction}^0$ is the standard entropy change during the process run, kJ/(mol·K).

2.3. HyperCube HyperChem Professional

HyperChem is a kind of molecular modelling software that calculates the energy of various conformations of molecules and finds the one characterized by the lowest energy. It is also a simulation program that lets scientist construct (draw) representations of molecules, perform geometry optimizations (energy minimizations) to determine the lowest energy conformations of molecules, and perform quantum chemical, thermodynamic and other complex calculations.

3. Results and Discussion

3.1. Kharash Method Application

The heat of combustion change for every compound in the system was calculated according to Eq. (3), as shown below.

$$\Delta H_{comp.(BB)}^{comb} = 109 \cdot r + \sum \Delta_i \cdot k = 109 \cdot 71 + (-97.9 + 14.6 + 27.2 + 4 \cdot 54.4) = 7900.5 \text{ J/(kg/mol)}$$

$$\Delta H_{comp.(CPC)}^{comb} = 109 \cdot r + \sum \Delta_i \cdot k = 109 \cdot 91 + (54.4 - 14.6 + 54.4) = 10013.2 \text{ kJ/(kg/mol)}$$

$$\Delta H_{comp.(CP-BB)}^{comb} = 109 \cdot r + \sum \Delta_i \cdot k = 109 \cdot 253 + (27.2 + 14.6 + 4 \cdot 54.4 - 97.2 + 2(54.4 - 14.6)) = 27818.1 \text{ kJ/(kg/mol)}$$

At the following stage the heat of formation change for every component of the system under standard conditions was found, as specified by Eq. (4):

$$\Delta H_{comp.(BB)}^0 = 394.9 \cdot 19 + 143.03 \cdot 8 + 289.9 - 7900.5 = 1036.74 \text{ kJ/mol}$$

$$\Delta H_{comp.(CPC)}^0 = 394.9 \cdot 21 + 143.03 \cdot 38 - 10013.2 = 3714.84 \text{ kJ/mol}$$

$$\Delta H_{comp.(CP-BB)}^0 = 394.9 \cdot (19 + 21.2) + 143.03 \cdot (8 + 38.2) + 289.9 - 27818.1 = 8575.22 \text{ kJ/mol}$$

The value of standard enthalpy of formation change for chlorine ions in aqueous solution was taken from reference book [9]: $\Delta H_{Cl^-}^0 = 167.07 \text{ kJ/mol}$

After that, in accordance with Eq. (5), the heat of reaction value was determined:

$$\begin{aligned} \Delta H_{ch.reaction}^0 &= (\Delta H_{(CP-BB)}^0 + 2 \cdot \Delta H_{(Cl^-)}^0) - \\ &= (2 \cdot \Delta H_{(CPC)}^0 + \Delta H_{(BB)}^0) = \\ &= (8575.22 - 2 \cdot 167.07) - \\ &= (2 \cdot 3714.84 + 1036.74) = -225.34 \text{ kJ/mol} \end{aligned}$$

Standard entropies of formation for examined compounds were unknown. Therefore, HyperCube HyperChem Professional v8.0.6 software was used to determine their approximate values. Calculations were made using semi-empirical method AM1. Results are represented in Table 1.

The reference book value of the standard entropy of formation for chlorine ions ($S_{Cl^-}^{o,form}$) is equal to 0.05674 kJ/(mol·K) [9].

Next the change in entropy of the system was found:

$$\begin{aligned} \Delta S_{ch.reaction}^0 &= \sum (n_i \cdot S_i^0)_{products} - \sum (n_i \cdot S_i^0)_{react.} = \\ &= (2.025 + 2 \cdot 0.05674) - (2 \cdot 0.8368 + 0.7824) = \\ &= -0.3175 \text{ kJ/(mol·K)} \end{aligned}$$

Table 1

Obtained values of standard entropies of formation for studied compounds

Compound	$S_i^{o,form}$, kJ/(mol·K)
BB	0.7824
CPC	0.8368
BB-CP	2.025

Table 2

Thermodynamic parameters of investigated compounds

Compound	BB	CPC	CP-BB
Total energy, kJ/mol	1340.22	2846.28	6776.62
Entropy, J/mol·K	665.3	677.4	1395.4
Free energy, kJ/mol	1142.11	2644.46	6360.81
Heat capacity, J/mol·K	308.78	276.56	816.72

Eventually, in compliance with Eq. (6), the value of standard Gibbs energy change was determined:

$$\Delta G_{ch.reaction}^0 = \Delta H_{ch.reaction}^0 - T \cdot \Delta S_{ch.reaction}^0 = \\ = -225.34 - 298 \cdot (-0.3175) = -130.73 \text{ kJ/(mol}\cdot\text{K)}.$$

Consequently, according to obtained value of Gibbs free energy change under standard conditions, the process runs spontaneously in the direction of sublate (CP-BB ion complex) formation.

3.2. Calculations *via* HyperChem Software

Thermodynamic characteristics of reactants – BB, CPC and the product of reaction – CP-BB (in solid state at 298 K) were calculated, using the model of molecular mechanics called Amber. Obtained results are shown in Table 2.

The value of standard Gibbs energy change of formation for chlorine ions was taken from the reference book [9]:

$$\Delta G_{Cl^-}^{0\text{ form.}} = -131.29 \text{ kJ/mol.}$$

Finally, the change of standard free enthalpy of the interaction process was defined:

$$\Delta G_{ch.reaction}^0 = \sum (n_i \cdot \Delta G_i^0)_{products} - \sum (n_i \cdot \Delta G_i^0)_{react.} = \\ = (6360.81 - 2 \cdot 131.29) - (2 \cdot 2644.46 + 1142.11) = \\ = -332.804 \text{ kJ/mol.}$$

As in the previous case, the obtained value of standard Gibbs free energy change indicates that the process of interaction between BB and CPC proceeds spontaneously and does not require any external forces for its run.

4. Conclusions

Thermodynamic investigations not only are the additional evidence of spontaneous ion associates formation but also ease further studies of solvent sublation, particularly surfactants selection. In this work thermodynamic parameters of investigated compounds were studied. Kharash method and HyperCube HyperChem Professional software were applied in order

to calculate the values of thermodynamic properties of analyzed system. It was found that the value of standard Gibbs energy change for system components in liquid phase was equal to -130.73 kJ/mol and in the case of solid state -332.804 kJ/mol . Thus, the process runs spontaneously in the direction of cetylpyridinium-bromphenol blue ion complex formation. The obtained results can be used in further investigations, especially those related to the selection and application of other surface active agents in solvent sublation.

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ТЕРМОДИНАМІЧНЕ ДОСЛІДЖЕННЯ ВИЛУЧЕННЯ БРОМФЕНОЛОВОГО СИНЬОГО З ВОДИ МЕТОДОМ ФЛОТОЕКСТРАКЦІЇ

Анотація. Проведені дослідження термодинамічних особливостей вилучення бромфенолового синього (БС) з водних розчинів, використовуючи технологію флотоекстракції. Вивчено термодинамічні характеристики взаємодії кислотного барвника (БС) з катіонною поверхнево-активною речовиною (ПАР) – хлоридом цетилпіридинію (ЦПХ), використовуючи метод Караша та програмне середовище HyperCube HyperChem Professional. Доведено, що формування йонного комплексу барвник-ПАР є самочинним процесом і не потребує жодних зовнішніх сил для його перебігу.

Ключові слова: закон Гесса, ентальпія, вільна енергія Гіббса, йонний комплекс, молекулярна механіка, сублат.