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Thermodynamic analysis of 1,4-diaminoanthraquinone adsorption on polyethylene terephthalate in alkane media

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Abstract

Thermodynamic adsorption parameters of 1,4-diaminoanthraquinone on polyethylene terephthalate (PET) were determined using several alkane media ranging from pentane to decane. In the range from pentane to decane, as the number of carbon atoms in the alkane decreased, the standard affinity ($-\Delta\mu^0$) increased. From the results of the enthalpy change (ΔH^0) and the entropy change (ΔS^0), it is found that when adsorbed in the longer chain of alkane medium than in the shorter one, the dye molecules were more strongly embedded within the PET substrate. The diffusion coefficient (D_T) of the dye decreased and the activation energy (E_D) increased with increasing number of carbon atoms in the alkane.

Keywords: Thermodynamic parameters; 1,4-Diaminoanthraquinone; Diffusion; Adsorption; PET; Alkane

1. Introduction

In the previous study [1,2], the adsorption properties of disperse dyes towards PET fiber using various organic solvents were discussed in terms of solubility properties and substituent effects. According to the previous findings, the adsorption of the dye in alkanes was as high as in water and the adsorption amount was inversely proportional to the dye solubility in the solvent used as adsorption medium, which represents that the dye solubility in alkanes was much lower than in the other solvents.

Several physicochemical parameters, such as standard affinity ($-\Delta\mu^0$), enthalpy change (ΔH^0), entropy change (ΔS^0) and activation energy of the diffusion (E_D), can be commonly used to interpret the thermodynamic behaviors of the dye in the adsorption system [3–6]. These factors, which are known as thermodynamic parameters, are usually calculated by the equations using the experimental adsorption data [7–9].

In this study, the thermodynamic adsorption parameters using alkane systems ranging from pentane to decane are discussed.

2. Experimental

2.1. Materials

PET fabric (75 den./36 fil., 106 × 97 yarns/inch, 70 ± 5 g/m^3) was used after scouring in a solution containing 2.0 g/l of nonionic surfactant at 60 °C for 30 min. The liquor ratio was 100:1. The fabric was then washed completely in cold distilled water and dried in the open air. A disperse dye, 1,4-diaminoanthraquinone, was purchased from Aldrich Chemical Co. and was used without further purification.

2.2. Adsorption isotherms

The dye was adsorbed onto PET fabric (0.01 g) in several alkanes containing 0.01, 0.02 and 0.03 g/l of the dye at various

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temperatures of 110, 120 and 130 °C until equilibrium adsorption was obtained. The ratio of the dye solution to fabric (liquor ratio) was 5000:1 (w/w), which could be considered as an infinite liquor ratio.

2.3. Partition coefficient and standard affinity

The partition coefficient (K) of the dye between the fiber substrates ($[D]_f$) and the adsorption solution ($[D]_s$) was obtained from the adsorption isotherms. The standard affinity ($-\Delta\mu^0$) of the dye was calculated using Eq. (1)

$$-\Delta\mu^0 = -\left(\mu_f^0 - \mu_s^0\right) = RT\ln\frac{[D]_f}{[D]_s} = RT\ln K \quad (1)$$

where $-\Delta\mu^0$ is standard affinity (cal/mol); μ_f^0, standard chemical potentials of dye in the fiber; μ_s^0, standard chemical potentials of dye in the adsorption solution; R, gas constant (1.9872 cal/mol K); T, absolute temperature (K); $[D]_f$, dye concentration in the fiber (mol/kg); $[D]_s$, dye concentration in the adsorption solution (mol/L); and K, partition coefficient.

2.4. Enthalpy change

The enthalpy change (ΔH^0) in adsorption process was obtained from the empirical plot that shows the relationship between $\Delta\mu^0/T$ and $1/T$ using Eq. (2)

$$\Delta H^0 = \frac{\delta(\Delta\mu^0/T)}{\delta(1/T)}\frac{\Delta H^0}{T} = \frac{\Delta\mu^0}{T} + C \quad (2)$$

where ΔH^0 is heat of adsorption (cal/mol); $-\Delta\mu^0$, standard affinity (cal/mol); T, absolute temperature (K); and C, integral constant.

2.5. Entropy change

The entropy change (ΔS^0) was calculated using Eq. (3)

$$\Delta\mu^0 = \Delta H^0 - T\Delta S^0 \quad (3)$$

where $-\Delta\mu^0$ is standard affinity (cal/mol); ΔH^0, heat of adsorption (cal/mol); ΔS^0, change in entropy (cal/mol K); and T, absolute temperature (K).

2.6. Adsorption rate

For the adsorption rate, the PET fabric (0.01 g) was adsorbed in several alkanes containing 0.1 g/l of the dye at temperatures of 110, 115, 120 and 125 °C. The liquor ratio was 5000:1.

2.7. Diffusion coefficient

According to Eq. (4), the diffusion coefficient (D_T) was calculated from the plot that shows the relationship between C_t/C_{eq} and $t^{1/2}$ in the initial stage of adsorption

$$\frac{C_t}{C_{eq}} = 4\sqrt{\frac{D_T}{\pi r^2}} \quad (4)$$

where C_t is dye exhaustion at time t (mol/kg); C_{eq}, dye exhaustion at equilibrium (mol/kg); D_T, diffusion coefficient (cm^2/min); and r, radius of fiber (cm).

2.8. Activation energy of diffusion

Using Eq. (5), the activation energy of the diffusion (E_D) was calculated from the relationship between $\ln D_T$ and $1/T$

$$\ln D_T = \ln D_0 - \frac{E}{RT} \quad (5)$$

where D_T is diffusion coefficient at a temperature T (cm^2/min); D_0, constant; E, activation energy; R, gas constant (1.9872 cal/mol K); and T, absolute temperature (K).

2.9. Determination of adsorption amount of the dye

At the end of adsorption, the samples were completely washed with cold acetone and dried in a vacuum oven. The dried samples were weighed and then dyes were extracted using *N*,*N*-dimethylformamide at 95 °C until the samples became colorless. The dye concentration in the extracts was measured using a UV–vis spectrophotometer and the extent of dye adsorption was calculated.

3. Results and discussion

3.1. Standard affinity

The standard affinity ($-\Delta\mu^0$) of the dye in adsorption medium towards fiber substrate is the most basic thermodynamic parameter. This parameter can be defined as a difference between the chemical potential of the dye in the fiber and that of the dye in the adsorption medium in a standard state. This quantity is the measure of the tendency of the dye to move from its standard state of the adsorption solution to its standard state of the fiber substrate [7,10]. In order to calculate the standard affinity of 1,4-diaminoanthraquinone towards PET substrate in alkanes, the isotherm data of dye adsorption were obtained at several different temperatures.

Fig. 1 shows the adsorption isotherms of 1,4-diaminoanthraquinone on PET substrate using several alkanes as adsorption media and the linear relationship between the initial dye concentration and the adsorption amount of the dye on PET [9]. The slopes of the straight lines in the isotherms are the partition coefficients (K) of the dye between the adsorption media and the PET. From Eq. (1), the standard affinity can be calculated and its data are summarized in Table 1.

It is found from Table 1 that as the number of carbon atoms in the alkane decreased, the partition coefficient and the standard affinity increased. This result means that the tendency of the dye to move from the adsorption solution to PET increased

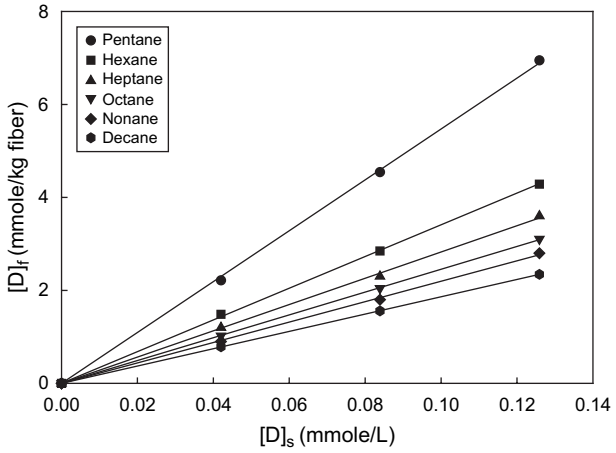

Fig. 1. Adsorption isotherms of 1,4-diaminoanthraquinone on PET in alkanes at 130 °C.

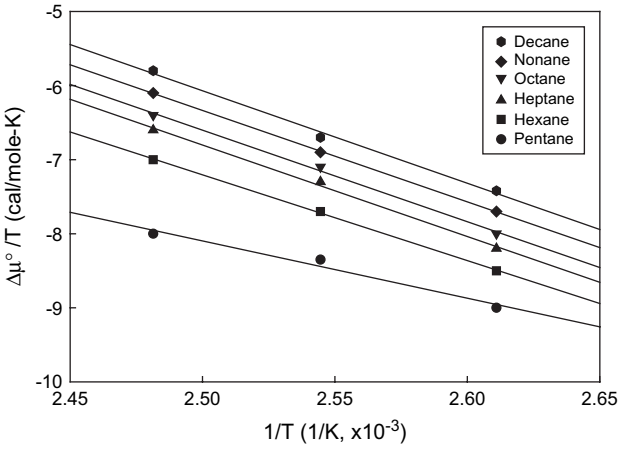

Fig. 2. Relationship between $\Delta\mu^0/T$ and $1/T$ in alkanes.

with decreasing chain length of the alkane molecule. In the range of pentane to decane, it is found that the dye adsorption gradually increased with decreasing number of carbon atoms in the alkane. On the contrary, the dye solubility increased with increasing number of carbon atoms in the alkane [1]. Thus, it is proposed that the molecular length of alkane could influence different reaction properties of the dyes in terms of adsorption and solubility. In addition, as the temperature increased, the standard affinity decreased in all alkane media. These results can be explained as follows: because the adsorption of dye on the fiber substrate is well known as an exothermic reaction process, corresponding higher adsorption temperature gives a negative effect on the thermodynamic adsorption [8].

3.2. Enthalpy and entropy change

The enthalpy change (ΔH^0) is considered as the measure of the adsorption strength of dyes on the substrate. Meanwhile, the entropy change (ΔS^0) in adsorption process represents the entropy difference of the dye molecules between fiber substrate and adsorption medium [8]. This entropy change shows negative values in most adsorption processes, because adsorbed dye molecules become more restrained within the fiber molecules than adsorption medium. Therefore, the value of the entropy change could be considered as the measure of immobility of dyes within the fiber molecules. Fig. 2 shows the relationship between $\Delta\mu^0/T$ and $1/T$ on enthalpy change (ΔH^0). As expected from Eq. (2), they show linear relationship. From the slopes ($\Delta H^0/T$) of the straight lines, the enthalpy change can be calculated.

From Fig. 3 and Eq. (3) showing the linear relationship between $\Delta\mu^0$ and T, the entropy change can also be obtained. The enthalpy and the entropy change obtained are presented in Table 2. Table 2 reveals that as the number of carbon atoms of the alkane molecule increased the released heat energy during the adsorption gradually increased.

The enthalpy change corresponds to the amount of the released thermal energy when dye molecules are adsorbed into polymer molecules. The negatively larger value represents that the dye molecules are more strongly embedded within the polymer chains. In Table 2, an interesting result was observed. Although the higher standard affinity was achieved in the shorter length of the alkane molecule, namely pentane medium, the enthalpy change was of low value. Also, the adsorption amount, which is proportional to the standard affinity, is of high value in the shorter chain of the alkane medium compared to that in the longer chain of adsorption medium. However, the dye molecules were more strongly embedded within the PET when adsorbed using the longer chain of the alkane.

Table 1
The partition coefficient (K) and the standard affinity ($-\Delta\mu^0$) of 1,4-diaminoanthraquinone between PET and alkanes

Adsorption media	K			$-\Delta\mu^0$ (cal/mol)		
	110 °C	120 °C	130 °C	110 °C	120 °C	130 °C
Pentane	92.3	65.2	54.7	3443	3262	3205
Hexane	71.8	48.3	34.1	3252	3027	2826
Heptane	63.5	40.2	28.3	3159	2885	2676
Octane	56.7	34.3	24.5	3073	2760	2563
Nonane	48.0	32.0	22.0	2946	2706	2474
Decane	39.7	30.3	18.6	2801	2662	2341

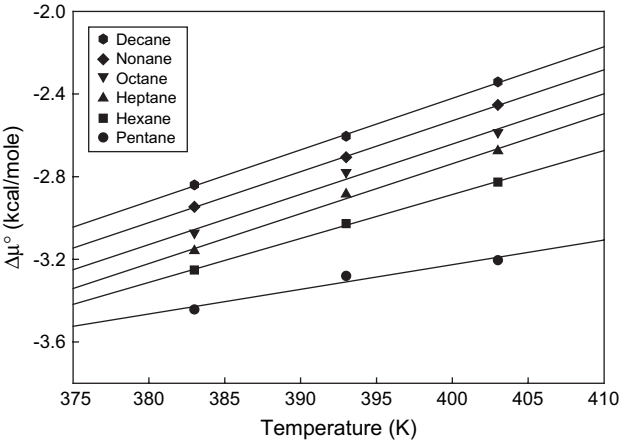

Fig. 3. Relationship between $\Delta\mu^0$ and T in alkanes.

Table 2
The enthalpy change (ΔH^0) and the entropy change (ΔS^0) of 1,4-diaminoanthraquinone on PET in alkanes

Adsorption media	ΔH^0 (cal/mol)	ΔS^0 (cal/mol K)
Pentane	−7736	−11.9
Hexane	−11,580	−21.3
Heptane	−12,358	−24.2
Octane	−12,358	−24.3
Nonane	−12,345	−24.7
Decane	−12,488	−24.9

The entropy change represents the extent of the reduced freedom of dye molecules after the completion of adsorption [8]. The negatively larger value of the entropy change means that the mobility of the dye molecules significantly decreased after adsorption. In Table 2, as the number of carbon atoms of the alkane increased, the entropy change increased in the direction of negative value. This result represents that the dye molecules adsorbed on PET in the longer chain of the alkane are more strongly restrained and immobilized within the fiber molecules than in the shorter chain of the alkane.

3.3. Adsorption rate and diffusion coefficient

To investigate the diffusion properties of 1,4-diaminoanthraquinone on PET in several alkanes, the adsorption rate was determined at temperatures of 110, 115, 120 and 125 °C. Fig. 4 shows the adsorption rate curves of the dye on PET at 125 °C.

According to Eq. (4), the C_t/C_{eq} is linearly proportional to the $t^{1/2}$ and from the slope of the relationship the diffusion coefficient (D_T) can be calculated. Fig. 5 shows the relationship between C_t/C_{eq} and $t^{1/2}$ on PET at 125 °C. In addition, the diffusion coefficients obtained in all ranges of temperatures of 110, 115, 120 and 125 °C are presented in Table 3.

Fig. 5 and Table 3 show that as the temperature increased, the diffusion coefficients also increased. This result displays that the mobility of the polymer chains generally increased with increasing adsorption temperature. Also, the diffusion coefficient of the dye decreased with increasing chain length of alkane molecules at all temperatures. These data support the findings obtained in the part of the entropy study: in the longer chain of the alkane medium the adsorption rate was slow when compared to that in the shorter chain of the alkane due to the different dye solubility in alkane.

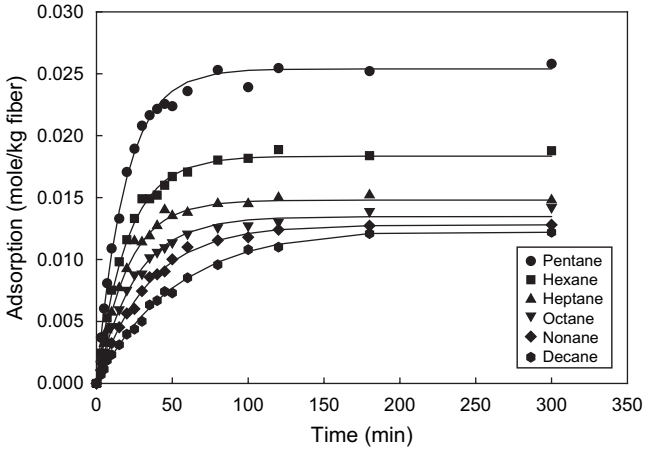

Fig. 4. Adsorption rate of 1,4-diaminoanthraquinone on PET in alkanes at 125 °C.

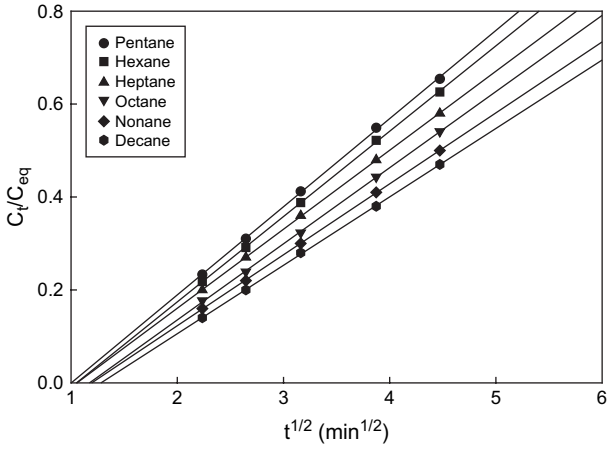

Fig. 5. Relationship between C_t/C_{eq} and $t^{1/2}$ in alkanes at 125 °C.

3.4. Activation energy of diffusion

The activation energy of the diffusion can be calculated by Eq. (5) that is known as the Arrhenius equation. This parameter represents the dependence of the diffusion coefficient on the application temperature and also describes the energy barrier that a dye molecule should overcome to diffuse into the fiber molecules [9]. The activation energy of the diffusion can be calculated from the slope in the linear relationship between $\ln D_T$ and $1/T$ shown in Fig. 6. The calculated activation energy is presented in Table 4. In Table 4, the activation energy of diffusion increased with increasing chain length of the alkane molecule. This result means that the energy barrier for the dye to overcome to diffuse into the PET is high in the longer chain of the alkane medium. This finding can also be explained in terms of the density of alkanes (Table 4).

The alkanes consist of almost the same hydrocarbon, such as methyl and methylene groups. The density of alkane increases with increasing number of carbon atoms in the alkane [11]. In a dye solution, the dye molecules are surrounded by the neighboring solvent molecules. The dye molecules should

Table 3
The diffusion coefficient (D_T) of 1,4-diaminoanthraquinone on PET in alkanes

Adsorption media	D_T (cm^2/min, $\times 10^{-9}$)			
	110 °C	115 °C	120 °C	125 °C
Pentane	0.66	1.19	2.13	3.55
Hexane	0.51	1.08	1.98	3.34
Heptane	0.42	0.84	1.55	3.04
Octane	0.36	0.67	1.34	2.69
Nonane	0.31	0.63	1.22	2.42
Decane	0.28	0.56	1.10	2.25

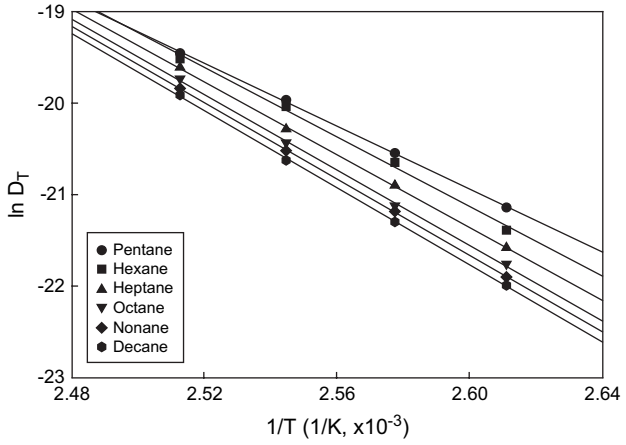

Fig. 6. Relationship between $\ln D_T$ and $1/T$ in alkanes.

have enough thermodynamic energy to diffuse from the alkane molecules into PET. If the dye molecules are in the adsorption medium of higher density, the dye molecules are surrounded by more hydrocarbons than in lower density. Therefore, to separate the dye molecules from the solvent molecules, more energy is needed and this would cause an increase in the activation energy. This could be the reason why the activation energy increased with increasing chain length of the alkanes.

4. Conclusions

Thermodynamic adsorption parameters of 1,4-diaminoanthraquinone on polyethylene terephthalate (PET) were investigated with several alkane media such as pentane, hexane, heptane, octane, nonane, and decane. As the number of carbon atoms in the alkane decreased, the partition coefficients and the standard affinity increased. As the temperature increased, the standard affinity decreased in all alkane media. From the results of the enthalpy and entropy change, it is found that the dye molecules are embedded more strongly within the substrates when adsorbed in the longer chain of the alkane medium than in the shorter one. The activation energy increased with increasing chain length of the alkane molecules.

Table 4
The activation energy of diffusion (E_D) for 1,4-diaminoanthraquinone and the density (ρ) of alkanes

Adsorption media	E_D (cal/mol)	ρ (g/ml, 20 °C)
Pentane	34,164	0.626
Hexane	37,780	0.655
Heptane	39,850	0.684
Octane	40,978	0.699
Nonane	41,500	0.718
Decane	41,650	0.730

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