

STUDY ON THE THERMODYNAMIC PROPERTIES OF ADSORPTION OF ETHYL BENZOATE AND DIETHYL PHTHALATE BY PHENOLIC RESIN ADSORBENTS*

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Abstract This paper presents experimental observations on the adsorption of individual solutes by a simple thermodynamic framework, and the equilibrium adsorption of ethyl benzoate and diethyl phthalate on phenolic resin adsorbent in hexane solutions within the temperature range of 293–313 K. The experimental results show that the Freundlich adsorption law is applicable to the adsorption of ethyl benzoate and diethyl phthalate on the adsorbent, since all the correlative factors R' are larger than 0.99. The negative values of all the isosteric adsorption enthalpies for ethyl benzoate and diethyl phthalate indicate that they undergo exothermic processes, while their magnitudes (19–28 kJ/mol) manifest a hydrogen bonding sorption process. Other thermodynamic properties: the free energy changes and the entropy change associated with the adsorption have been calculated from the Gibbs adsorption equation and the Gibbs-Helmholtz equation

Keywords Phenolic resin adsorbent, Adsorption, Ethyl benzoate, Diethyl phthalate

INTRODUCTION

Adsorption is gaining wider acceptance for large-scale separation from liquids^[1]. The low-energy nature of adsorptive separation process can be advantageous compared to distillation for the separation of liquid mixtures of low volatilities or for mixtures with relative volatilities close to 1^[2]. In comparison with extraction, the high concentrating abilities of adsorption have been exploited especially for the more efficient removal of solutes from dilute aqueous solutions^[3]. However, because of the difficulties in establishing multistaged contacting, adsorption operations are generally conducted in semibatch fixed bed mode, although complex equipment can be utilized to stimulate moving bed operations^[4]. Fixed bed operation is ideally suitable for two types of problems. In the first type, fixed bed operation is utilized with a nonselective adsorbent to adsorb a wide range of solutes from a stream. An example of this problem is the removal of organics from waste water streams using activated carbon^[3]. In the second type of problem the goal would be to selectively adsorb one solute from a solute mixture. To achieve this goal highly selective adsorbents are needed. An example of such adsorbents is molecular sieves which limit nonspecific adsorption through steric constraints. Thus, by using molecular sieves, it is possible to achieve high separation factors and therefore greatly reduce the need for multistage contacting to achieve separations of one solute from a mixture of solutes^[5, 6]. The use of molecular sieves has thus demonstrated the potentiality of adsorptive separation when highly selective adsorbents are available. This presumption has also stimulated the development of alternative adsorbents which confer selectivity not through steric limitations, but rather by limiting adsorption to specific chemical interactions^[7, 8]. The development of such adsorbents has been greatly facilitated by advances in polymer synthesis methods, which have made it possible to produce polymeric

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adsorbents of well-characterized and uniform chemical surfaces. Solutes which were capable of forming hydrogen bonding could be adsorbed onto a polycarboxylic ester adsorbent (Amberlite XAD-7), while those solutes which were unable to donate a proton for the formation of a hydrogen bond (*e.g.*, benzene, anisole, and *N*-methylindole) were not adsorbed onto this adsorbent^[9].

In our research, we studied the role of hydrogen bonding as an appropriate adsorption mechanism. Hydrogen bonding is a useful interaction mechanism for separations because the low energy of this bond ensures reversibility (*i.e.*, for recovery through desorption), while the directionality and the short range of this "bond" confer selectivity. The goal of the work is to examine the selective adsorption of ethyl benzoate and diethyl phthalate through hydrogen bonding with the adsorbent with differing binding strengths. Because the ethyl benzoate and diethyl phthalate molecules are good hydrogen bonding acceptors (carbonyl group oxygen) and phenolic hydroxyl is a good hydrogen bonding donor, hydrogen bonds can form between them in hexane, and the adsorption capability of phenolic resin adsorbent for organic compounds containing hydrogen bonding acceptors should be stronger. Using phenolic resin adsorbent to study thermodynamic properties of adsorption of ethyl benzoate and diethyl phthalate will be very important for extraction of natural lactone drugs such as ginkgolide A, B and Bilobalide *etc.* from Chinese herbal drugs by adsorption methods, which has not been reported before.

EXPERIMENTAL

Materials

The phenolic resin adsorbent JDW-2 in the form of brown spherical beads was synthesized by ourselves. The weight ratio of phenol to paraformaldehyde used in the reaction mixture was 1:0.58. The macroporous phenolic resin adsorbent was synthesized under acidic conditions. Suitable porogenic agent, disperser and oil were used in the reaction. Prior to use, the resin was extracted with acetone by refluxing for 8 h and washed with absolute alcohol, then with *n*-hexane to remove organic impurities, and then dried at 333 K under vacuum for 2 h.

Ethyl benzoate and diethyl phthalate were of A.R. grade available from Tianjin Chemical Reagent First Plant.

Apparatus

The specific surface area of the adsorbent was measured using a apparatus made by the Institute of Polymer Chemistry, Nankai University; the UV-754 ultraviolet-visible spectrophotometer was made by Shanghai Third Analytical Instrument Factory, and THZ88-1 model shaker was made by Jangsu Taicang Luhe Biochemical Instrument Factory.

Methods

The characteristics of JDW-2 are given in Table 1, moisture retention was determined according to GB5757-86, content of phenolic hydroxyl group^[10], surface area^[11], apparent density (ρ_a) and real density (ρ_T)^[10] were determined using standard methods. The average diameter ($\bar{r}$) and porosity (V') of the resin were calculated from the following equation.

$$V' = 1/\rho_a - 1/\rho_T$$

$$\bar{r} = 2V'/S$$

Adsorption Assay

Adsorption equilibrium of ethyl benzoate and diethyl phthalate at three different temperatures (293 K, 303 K, 313 K) were determined as follows: a definite weight of dried resin (0.08 g, 0.12 g, 0.16 g, 0.20 g and 0.24 g) was introduced into a flask directly, 20 mL of a hexane solution of ethyl benzoate and diethyl phthalate of known concentration was added to each flask respectively. The flasks were placed in a THZ88-1 model shaker at a pre-set temperature and shaken at 100 r/min. The initial concentrations (c_0) of the hexane solution of ethyl benzoate and diethyl phthalate were 200 and 400 mg/L, respectively. After adsorption reached its equilibrium, the concentrations of ethyl benzoate and diethyl phthalate (c_e) were determined at 272 nm, 275 nm, respectively, using an ultraviolet-visible spectrophotometer. Thus the adsorbent-phase concentration of adsorbates, q_e (mg/g)

was calculated according to

$$q_e = V(c_0 - c_e) / W \tag{1}$$

where V is the volume of the solution containing ethyl benzoate or diethyl phthalate (L), W is the weight of dried resin JDW-2(g)

RESULTS AND DISCUSSION

Characteristics of Phenolic Resin Adsorbent

The typical properties of JDW-2 are compiled in Table 1.

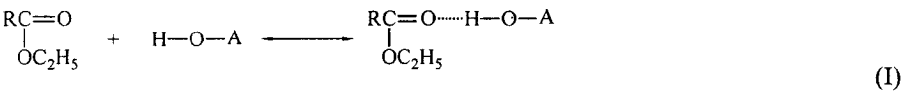
Table 1. Typical Properties of JDW-2

Property	Surface area (m ² /g)	Moisture retention (%)	Phenolic hydroxyl (mmol/g)	ρ_a (g/mL)	ρ_r (g/mL)	Average diameter (nm)	Porosity (mL/g)
JDW-2	60.9	41.7	3.72	0.805	1.164	12.58	0.383

Thermodynamic Description

Adsorption of ethyl benzoate

The adsorption of ethyl benzoate via hydrogen bonding can be represented by the reaction



where H—O— represents the phenolic hydroxyl group, or hydrogen bonding site of adsorbent. It should be noted that this approach differs from treatments in which adsorption is viewed as an exchange process where the solute replaces a previously adsorbed solvent molecule. We believe that this approach is justified in this case because it is unlikely that the solvent hexane can hydrogen bond with this carbonyl site. Assuming equilibrium, then the standard free energy change ΔG^0 for reaction (I) is given by

$$\Delta G^0 = -RT \ln K \tag{2}$$

The equilibrium constant, K , can be represented as

$$K = \alpha_{RA} / \alpha_R \alpha_A \tag{3}$$

where the activity (α) can be related to the mole fractions (X) and activity coefficients (γ) of the various species by

$$\alpha = \gamma X \tag{4}$$

By rearranging the above equations, we obtained

$$X_{RA}/X_R = (\gamma_R \gamma_A X_A / \gamma_{RA}) e^{\Delta G^0 / RT} \tag{5}$$

Combining the above equation with the thermodynamic relationship

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \tag{6}$$

it can be seen that

$$X_{RA}/X_R = (\gamma_R \gamma_A X_A / \gamma_{RA}) (e^{\Delta S^0 / R}) e^{\Delta H^0 / RT} \tag{7}$$

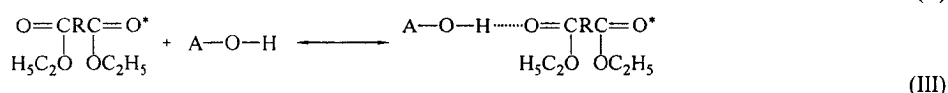
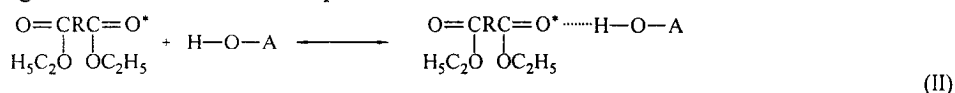
If the liquid- and solid-phase concentrations are sufficiently dilute with respect to the solute (in the case of ethyl benzoate), then the first term on the right-hand side of Eq. (7) will be constant. It should be noted that this assumption is valid only in the linear region of the adsorption isotherm where the number of sorption sites, which are occupied, is so small relative to the total number of sites that X_A is essentially unchanged by the adsorption. Further, if the standard entropy change of adsorption is constant, then the second term on the right-hand side would also be constant. Finally, if the data are presented with respect to absolute concentrations and not mole fractions, then the above equation can be simplified, and the adsorption of the ethyl benzoate can be described by

$$(q/c)_{EB} = \beta e^{\Delta H^0 / RT} \tag{8}$$

where q and c are the solid- and liquid-phase solute concentrations in mg adsorbed/g adsorbent and mg dissolved/L, respectively. If the above assumptions are valid, then β in Eq. (8) is expected to be constant.

Adsorption of diethyl phthalate

To develop an equation for describing the adsorption of diethyl phthalate, certain assumptions are required. In our case, the following assumptions are most reasonable and best supported by the data which will be presented. These assumptions are: (1) Only a single (and not both) carbonyl group oxygen atom is involved in adsorption via hydrogen bonding. (2) Each carbonyl group oxygen atom is equally capable of forming hydrogen bonds such that either of the following reactions can lead to adsorption:



where the asterisk is used to distinguish the two possible oxygen atoms of the carbonyl groups. With these two assumptions, our physical understanding of how the diethyl phthalate is adsorbed onto the phenolic resin adsorbent is illustrated in Fig. 1.

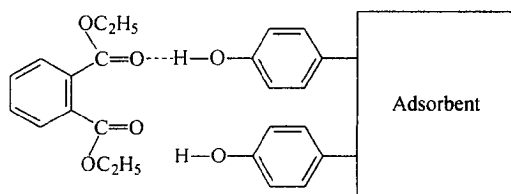


Fig. 1 Postulated adsorption mechanism for diethyl phthalate from a nonpolar solvent onto phenolic resin

To test these assumptions, we compared the adsorption of ethyl benzoate and diethyl phthalate. For comparisons, we made one further assumption – that the activity coefficients and entropy change for the adsorption of ethyl benzoate and diethyl phthalate are similar. If this latter assumption is valid, then the difference between the adsorption of these two solutes would be due solely to the fact that diethyl phthalate has two possible adsorption reactions (Reaction II and III) while ethyl benzoate has only one adsorption reaction (Reaction I).

Thus the adsorption equilibrium for diethyl phthalate should be given by

$$(q/c)_{\text{DEP}} = 2\beta e^{\Delta H^{\circ}/RT} \quad (9)$$

where β in the above equation is identical to that in Eq. (8). Also, if the enthalpy change for the formation of a single hydrogen bond is only made by the $-\text{COOC}_2\text{H}_5$, then the enthalpy change for the adsorption of ethyl benzoate should be similar to that for the adsorption of diethyl phthalate. This agrees with the first assumption that only a single hydrogen bond is involved in the adsorption of both ethyl benzoate and diethyl phthalate.

Adsorption of individual solutes

The previous thermodynamic treatment might also be used for the adsorption of individual solutes. With these assumptions, the separation factor (α) for the adsorption of diethyl phthalate and ethyl benzoate from their solutions can be predicted from Eq. (9) and Eq. (8).

$$\alpha = (q/c)_{\text{DEP}} / (q/c)_{\text{EB}} = 2 \quad (10)$$

Adsorption studies were conducted by adding JDW-2 adsorbent to hexane solutions, which contain a single solute (either diethyl phthalate or ethyl benzoate). The adsorption isotherms for these studies are shown in Fig. 2. As expected, diethyl phthalate was adsorbed better than ethyl benzoate.

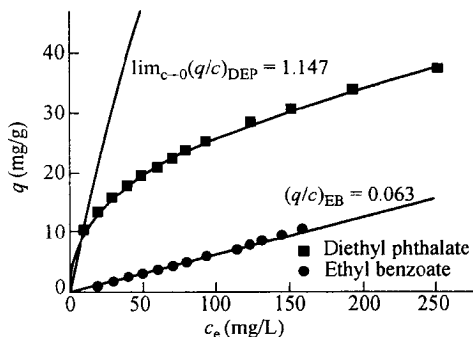


Fig. 2 Adsorption isotherms for individual solutes from JDW-2/hexane system

The values of q/c for the adsorption of diethyl phthalate and ethyl benzoate were 1.147 and 0.063 (mg adsorbed/g)/(mg dissolved/L), respectively. If our thermodynamic description of adsorption is correct, then Eqs. (8) and (9) predict that the ratio q/c for diethyl phthalate adsorption would be 2 times that for the adsorption of ethyl benzoate. On comparing with the observed value of 18.21, however, the conclusion is obviously different. It is important to note that there are two terms (β and ΔH^0) in Eqs. (8) and (9) which are assumed to be the same for the adsorption of diethyl phthalate and ethyl benzoate. But the experimental results show that these two terms are obviously different in the adsorption of the two solutes.

Equilibrium Adsorption

The equilibrium adsorption isotherms for ethyl benzoate and diethyl phthalate on JDW-2 adsorbent at 293 K, 303 K and 313 K are shown in Fig. 3 and Fig. 4. The adsorption isotherms were further correlated to the well-known Freundlich equation.

$$\ln q_e = \ln K_F + 1/n \ln c_e \quad (11)$$

where K_F and n are characteristic constants.

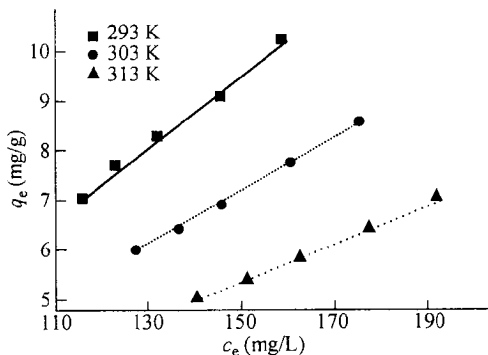


Fig. 3 Equilibrium adsorption isotherms at 303 K, 313 K and 322 K for ethyl benzoate on JDW-2

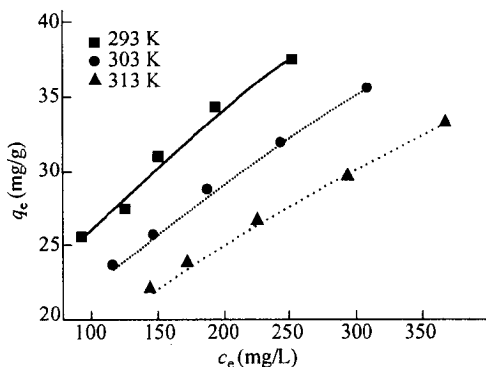


Fig. 4 Equilibrium adsorption isotherms at 303 K, 313 K and 322 K for diethyl phthalate on JDW-2

The linearity of the Freundlich isotherm (Eq. 11) was determined by least squares fit. The regression equations at 293 K, 303 K and 313 K along with the constants K_F and n , and the correlative coefficient R' are listed in Table 2. It is quite obvious that the Freundlich adsorption law is applicable to the adsorption of ethyl benzoate and diethyl phthalate on JDW-2 adsorbent. The constant is taken as a relative indicator of adsorption capacity according to the Freundlich theory. These equations are reliable since all the correlative coefficients R' are larger than 0.99. The exponents are $n > 1$ in the adsorption of diethyl phthalate on JDW-2, indicating favorable adsorptions.

Table 2. Regression equation of $\ln q_e$ versus $\ln c_e$ for Freundlich isotherms of adsorption of ethyl benzoate and diethyl phthalate on JDW-2

Adsorbate/Adsorbent	T (K)	Regression equation	K_F	n	R^2
Ethyl benzoate/JDW-2	293	$\ln q_e = -3.5930 + 1.1665 \ln c_e$	0.0275	0.8573	0.9985
	303	$\ln q_e = -3.8121 + 1.1528 \ln c_e$	0.0221	0.8675	0.9995
	313	$\ln q_e = -3.8935 + 1.1109 \ln c_e$	0.0204	0.9003	0.9992
Diethyl phthalate/JDW-2	293	$\ln q_e = 1.3815 + 0.4057 \ln c_e$	3.9808	2.4652	0.9932
	303	$\ln q_e = 1.1466 + 0.4259 \ln c_e$	3.1475	2.3480	0.9991
	313	$\ln q_e = 0.9316 + 0.4342 \ln c_e$	2.5385	2.3026	0.9990

Isosteric Enthalpies, Free Energy, Entropy Change for Compounds Adsorption

The isosteric enthalpies of adsorption were calculated with a derivative Van't Hoff's equation.

$$\ln c_e = -\ln K_0 + \Delta H/RT \tag{12}$$

where ΔH is the isosteric enthalpy of adsorption, R is the gas constant, c_e is the equilibrium concentration of solute in mg/L at the absolute temperature T . At different temperatures (293 K, 303 K and 323 K), c_e was obtained from the well-fitted isotherms. ΔH was calculated from the slope of line plotted by $\ln c_e$ versus $1/T$. Figures 5 and Fig. 6 show some of these curves for ethyl benzoate — JDW-2 and diethyl phthalate — JDW-2 systems. The isosteric enthalpies of adsorption are summarized in Table 3.

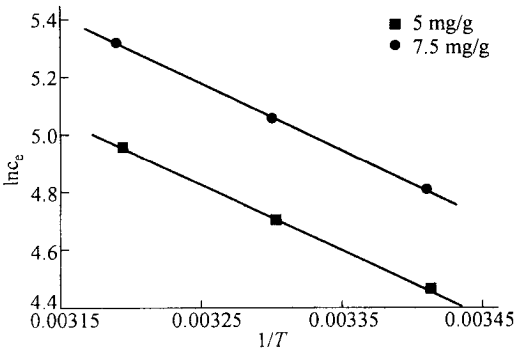


Fig. 5 Estimation of the thermodynamic parameters of the systems tested (For ethyl benzoate on JDW-2)

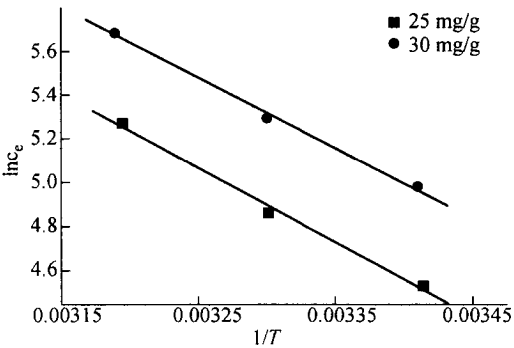


Fig. 6 Estimation of the thermodynamic parameters of the systems tested (For diethyl phthalate on JDW-2)

Table 3. Thermodynamic properties of the systems tested

Adsorbate/Adsorbent	q (mg/g)	ΔH (kJ/mol)	ΔG (kJ/mol)		ΔS (J/mol · K)	
			293 K	303 K	293 K	303 K
Ethyl benzoate/JDW-2	5	-18.83	-2.09	-2.18	-57.13	-54.95
	7.5	-19.32			-58.05	-56.57
Diethyl phthalate/JDW-2	25	-28.09	-6.00	-5.91	-75.39	-73.20
	30	-26.73			-70.75	-68.71

The free energy change of adsorption can be calculated using the following equation derived from Gibbs adsorption equation^[12].

$$\Delta G = RT \int_0^X q \frac{dX}{X} \tag{13}$$

where X represents the molar fraction of the adsorbate in solution, q represents milligram of solute adsorbed per unit mass of adsorbent, (mg/g) and R is the gas constant.

If q is related to X by the Freundlich equation

$$q = K_F X^{1/n} \tag{14}$$

then Eq. (13) becomes

$$\Delta G = nRT \quad (15)$$

where n represents Freundlich equation exponent.

Finally, we get Eq. (15) (the procedure was shown elsewhere^[12]), which can be used to calculate the free energy change per mole of solute adsorbed. The use of the Freundlich equation leads to a value for the free energy independent of q .

Free energy changes of adsorption calculated from Eq. (15) are given in Table 3. The entropy change associated with adsorption can be calculated from the Gibbs-Helmholtz equation^[12]:

$$\Delta S = (\Delta H - \Delta G)/T \quad (16)$$

Entropy changes of adsorption calculated from Eq. (16) are given in Table 3.

Table 3 shows a summary of the estimated values for these three thermodynamic properties at two kinds of adsorbate loadings. Values of the enthalpy (always negative) are indicative of an exothermic process, and their magnitudes (19–28 kJ/mol) manifest a hydrogen bonding sorption process. Absolute values decrease as the adsorption of diethyl phthalate on JDW-2 increases, a common situation when dealing with adsorption on non-homogeneous surfaces which can be related to the preferential occupation of the energetically more favorable superficial locations. A slight increase in the heat of adsorption of ethyl benzoate with JDW-2, which may be attributed to the interactions among the adsorbed molecules, can be observed at high surface coverage.

Variations of the adsorption free energy with temperature are always small. This confirms the character of the adsorption process and also indicates a compensation effect of the entropic contribution at low adsorption levels. Absolute values for the adsorption of diethyl phthalate on JDW-2 are larger than that for the adsorption of ethyl benzoate on JDW-2, indicating that diethyl phthalate is adsorbed more easily than ethyl benzoate on JDW-2.

Finally, the negative values of the adsorption entropy are consistent with the restricted mobilities of adsorbed molecules of diethyl phthalate and ethyl benzoate as compared with those in solution. Absolute entropy values decrease slightly with increasing temperature during adsorption of diethyl phthalate on JDW-2; this is more marked with increasing coverage. Bottani^[13] has obtained the same result in gas-solid adsorption. The reason can be attributed to the superficial heterogeneity of the adsorbent (and this effect would be more manifest at low surface coverage) and to the influence of the configurational factor at high adsorption levels. This factor accounts for entropy changes due to the configuration of the adsorbate molecules on the surface, which may change with increasing coverage, versus those due to the mobility of the adsorbate molecules.

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