Adsorption of phenols onto hydrous ZnS(s): effect of cosolvent and temperature

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Abstract

The adsorption of phenols onto hydrous ZnS(s) surface in the presence of cosolvent, namely, methanol, was studied. Adsorption of phenols onto hydrous ZnS(s) surface follows a linear relationship between adsorption density and equilibrium concentration. In the presence of a cosolvent, the extent of phenol adsorption decreases except catechol. Apparently, the adsorption of phenols is determined by hydrophobic partition whereas the adsorption of catchol is governed by specific chemical interaction. Adsorption of phenols is an endothermic process; the extent of phenol adsorption increases with increasing temperature. This is attributed to the hydrophobic characteristics of the phenol adsorbents.

1. Introduction

Groundwater contamination arising from disposal of hazardous chemicals has been recognized as one of the most significant environmental problems. This underscores the importance to understand the fate of contaminants in the subsurface. In modelling the transport of contaminants, some processes, such as adsorption, partitioning, degradation and ion exchange have been proposed as important reaction mechanisms. Concerning the adsorption of hydrophobic organic chemicals, it has been indicated that simple partitioning is the major reaction mechanism [1]. The partition of the hydrophobic organic chemical in the solid and aqueous phases is mainly determined by the organic carbon content of the solid and by the hydrophobicity of the chemical, mostly represented by its octanol/water partition coefficient. Recent discoveries have indicated that the presence of water-miscible organic solvents would lessen the adsorption reaction. The adsorption coefficient decreases exponentially as the fraction of organic cosolvent increases [2–6].

Table 1
Basic properties of phenols

Name	Solubility[a]	Absorption$_{max}$	log K_{ow}^b
Catechol	838,000	276	0.88
2-nitrophenol	2100	280	1.76
2, 4-dichlorophenol	4500	284	2.75
2, 4, 6-trichlorophenol	800	288	3.38

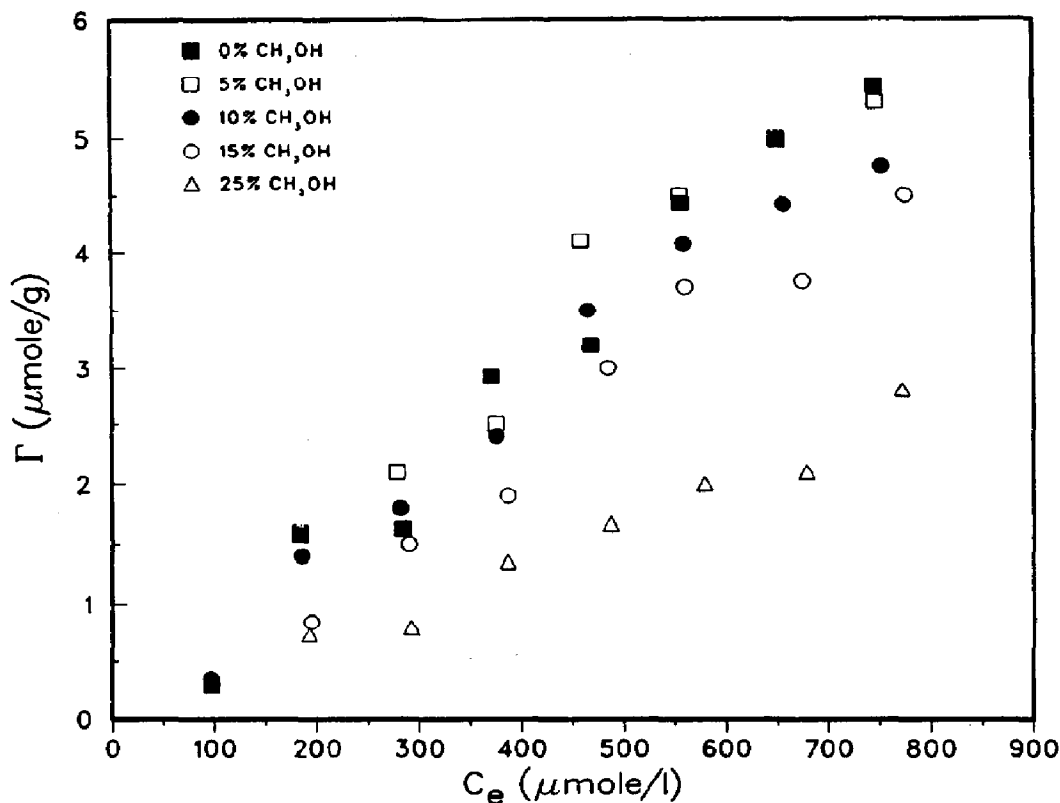[a] (mg/dm^3), Ref. [26].
[b] Leo et al. [27].

Fig. 1. Effect of cosolvent on the adsorption isotherms of 2-nitrophenol on hydrous ZnS(s). Experimental conditions: 4 g/dm^3 solid, pH = 4.0, 0.05 M NaClO$_4$.

The prime objectives of this work are to examine if cosolvent effect holds for hydrophobic adsorption on inorganic adsorbent. In addition, since most of the studies have been dealing with sparingly soluble, highly hydrophobic organic substances, we
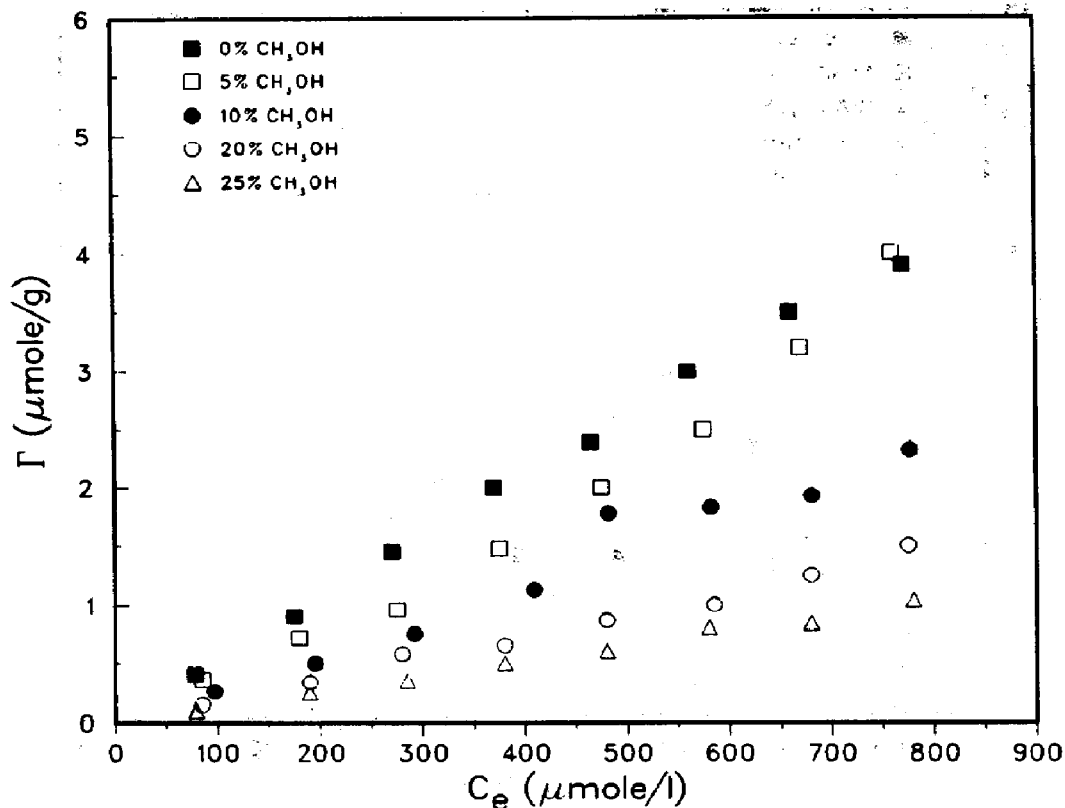
Fig. 2. Effect of cosolvent on the adsorption isotherms of 2,4-dichlorophenol on hydrous ZnS(s). Experimental conditions: $4\,g/dm^3$ solid, pH = 4.0 0.05 M $NaClO_4$.

investigated the cosolvent effect on some phenols with a range of solubilities and hydrophobicities. In addition, the temperature effect on the phenols adsorption was studied. The influence of temperature on the adsorption of organic compounds has been studied by some authors. In fact, the enhancement of adsorption of hydrophobic compounds by temperature increase has been found by other researchers. Nogami et al. [7] investigated the case in tryptophan adsorption on carbon black. The adsorption reaction increases as the temperature increases. As they discussed in another work in series [8], the iceberg must be broken down first in order to proceed the adsorption reaction. In the study of PCB adsorption by river sediment, Voice and Weber [9] found that the adsorption increases as temperature increases.

2. Methods and materials

The characterization of zinc sulfide particle was described before [10]. For the batch adsorption study, a 10^{-3} M stock solution was prepared for each phenol. Due to the low solubility of 2,4,6-trichlorophenol, the stock solution was spiked with 1 M NaOH to facilitate dissolution. Different concentrations of phenol solutions were then made by mixing specific amounts of stock solution, $NaClO_4$ and methanol in 100 ml
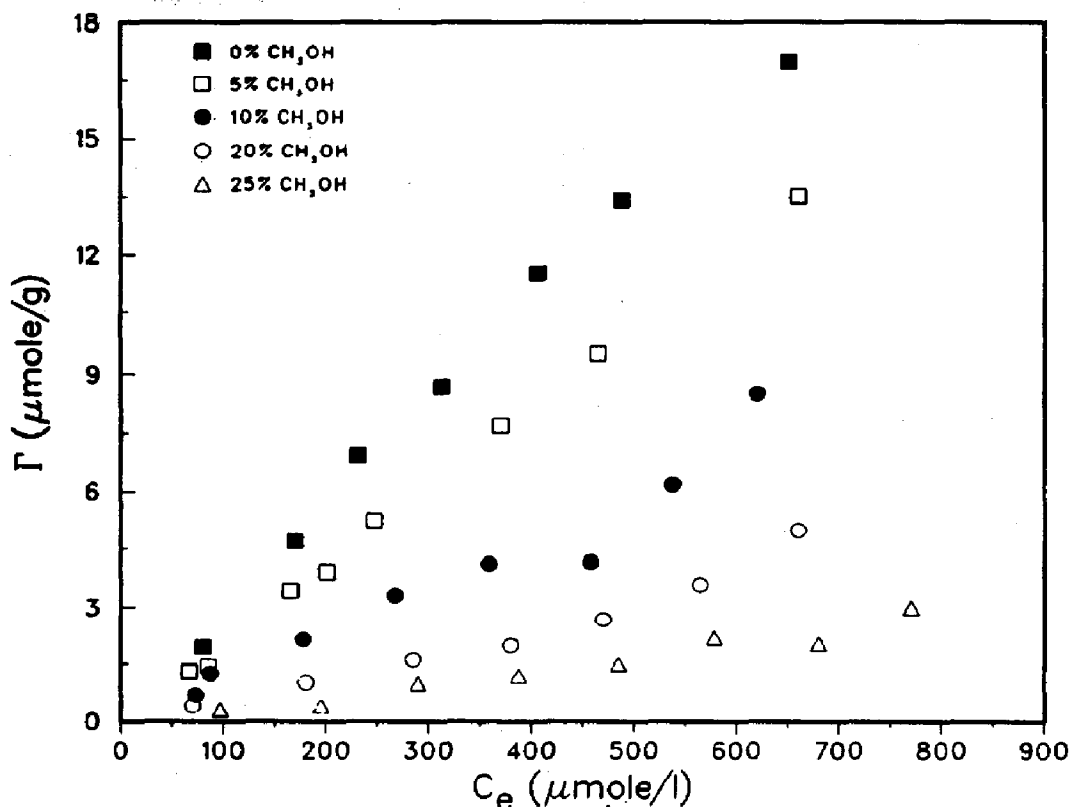
Fig. 3. Effect of cosolvent on the adsorption isotherms of 2,4,6-trichlorophenol on hydrous ZnS(s). Experimental conditions: $4 \, g/dm^3$ solid, pH = 4.0, 0.05 M $NaClO_4$.

volumetric flasks. For each concentration, samples were triplicated. The adsorption reaction was carried out in 25 ml screw-capped pyrex tube with $4 \, g/dm^3$ solid concentration and 5×10^{-2} M $NaClO_4$. The excess 25 ml of phenol solutions were saved for UV-VIS spectrophotometer's calibration. The pH value of each sample was adjusted to 4.0×0.1 M $HClO_4$. The tubes were then wrapped with aluminum foil and were placed on a shaker for overnight shaking. The samples were then filtered through 0.45 μm membrane filters (Gelman), and the phenol equilibrium concentrations were determined by a Hitachi-Perkin Elmer UV-VIS spectrophotometer (Model 139) at a wavelength of maximum absorbance (Table 1). For the experiment on temperature effect, the procedures are the same except that no methanol was added. The tubes were placed on a shaker equipped with water bath. The experiment was run at four different temperatures.

3. Results and discussion

Throughout the batch adsorption study, the linear adsorption isotherm equation was used, i.e.,
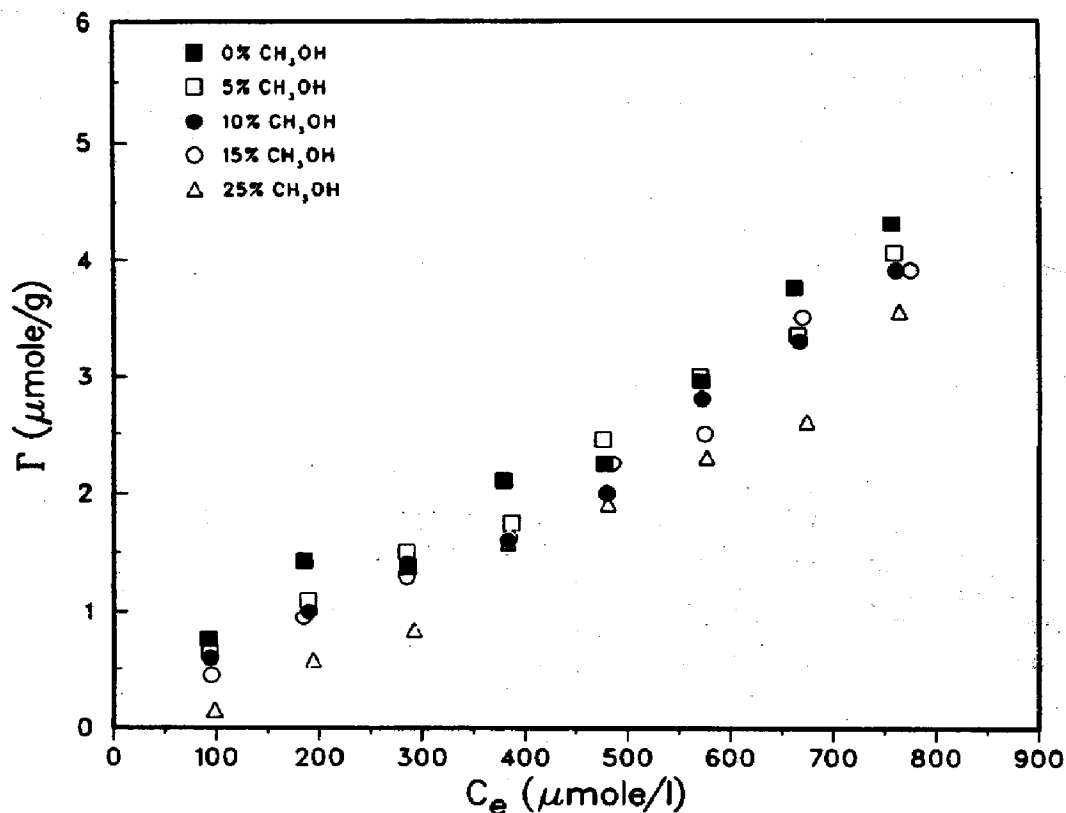
$$\Gamma = KC_e, \tag{1}$$

Fig. 4. Effect of cosolvent on the adsorption isotherms of catechol on hydrous ZnS(s). Experimental conditions: $4 \, g/dm^3$ solid, pH $= 4.0, 0.05 \, M \, NaClO_4$.

where Γ is the equilibrium adsorption density (μmol/g), K is the adsorption constant (dm³/g), and C_e is the equilibrium concentration of solute in the solution (μmol/dm³). The volume-based adsorption constant, K, is related to mole-based adsorption constant, $K_{m,i}$ (mol/g) by the following expression:

$$K_{m,i} = K/V_i, \tag{2}$$

where V_i is the molar volume of the liquid phase (dm³/mol).

3.1. The cosolvent effect

The adsorption isotherms of the four phenols from solutions of different methanol fractions are shown in Figs. 1–4 and in Table 2. For 2-nitrophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol (Figs. 1–3), the increase of cosolvent fractions significantly decreases the equilibrium K values. However, for catechol, a different trend was observed when the methanol fractions were changed. The isotherms for catechol adsorption on ZnS(s) at five different methanol fractions were so identical that there was literally no distinction (Fig. 4).

Table 2
Summaries of adsorption isotherm data

Adsorbate	Parameter (ml/g)	Volume fraction solvent, f^c					
		0	0.05	0.10	0.15	0.20	0.25
Catechol	K	5.28	5.19	4.95	4.96	—	4.74
2-nitrophenol	K	7.66	7.72	6.79	6.25	—	3.41
2,4,-dichloro	K	5.18	5.03	3.09	—	1.79	1.31
2,4,6,-trichloro	K	26.66	20.89	11.47	—	6.06	3.68

The adsorption behaviors of phenols on ZnS(s) under aqueous solution (in the absence of methanol) were first analyzed. The adsorption constants of four phenols from aqueous solution were plotted versus their solubility on log–log scale (Fig. 5). For 2-nitrophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol, the adsorption constant decreases as the solubility increases. This is consistent with what was proposed for hydrophobic adsorption [1]. After linear regression, it could be written as follows:

$$\log K_{m,i} = -0.9678 \log S + 4.1920 \quad (r^2 = 0.9748),\tag{3}$$

where S is the solubility of the adsorbent. Again, the catechol showed a drastic different behavior. Although relatively more soluble than the other three phenols, catechol had an adsorption constant which was much larger than what was expected from extrapolation from Eq. (3). This implied that the adsorption mechanism of catechol is different from the other three adsorbents. The anomaly leads us to speculate if some bonding other than hydrophobic interaction was responsible for the adsorption of catechol. Actually, this hypotheses is in accordance to what we proposed in previous work [11], in which surface complex formation was the major mechanism for catechol adsorption on ZnS(s), whereas the non-specific partitioning for other mono-substituted phenols. Similarly, specific and non-specific interactions have been found by some researchers concerning the adsorption of chlorophenols on oxide surfaces [12].

The dependence of $K_{m,i}$ on volume fraction of methanol cosolvent, f^c, for phenols adsorption by ZnS(s) is shown in Fig. 6. The lines in Fig. 6 were obtained by least-squares regression.

In fact, the model for cosolvent effect on adsorption was established on the theroretical prediction of the change of solubility from under pure aqueous phase to under cosolvent system. Groves [13] has shown the effect of cosolvent on the solubility of hydrocarbon in water. In addition, Morris et al. [14] investigated the solubility of hydrophobic organic chemicals in cosolvent and proposed that the coefficient of solute–surface interaction, σ, is related to the octanol/water partition
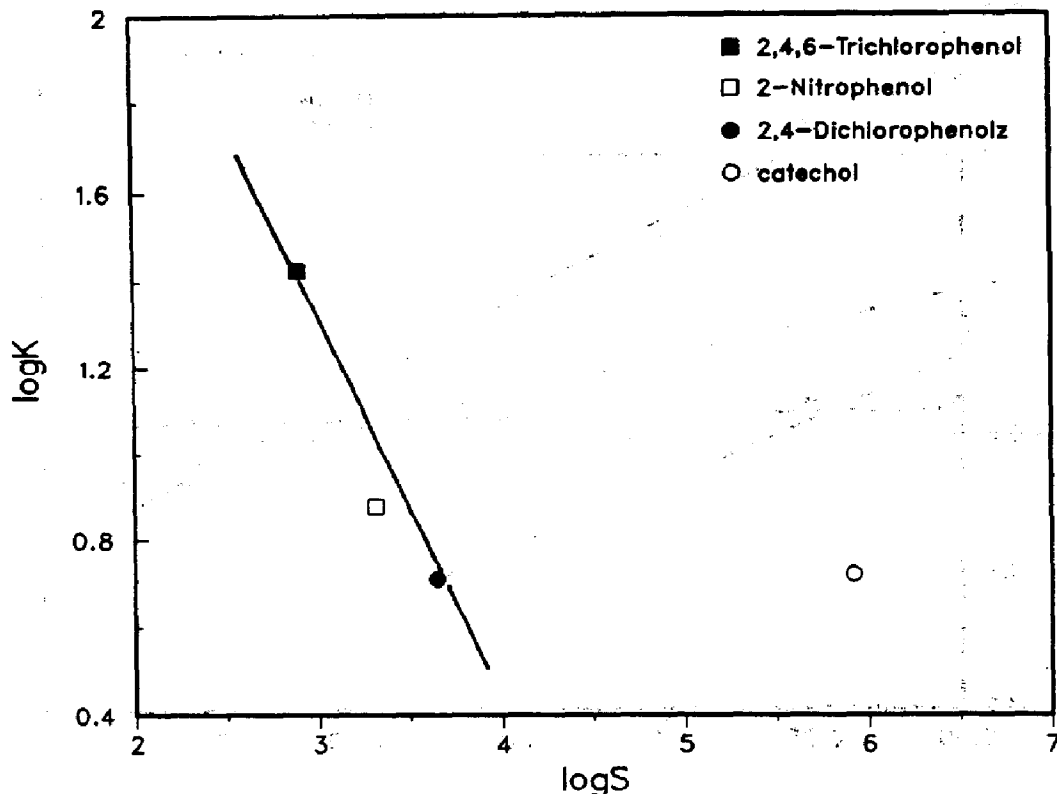
Fig. 5. The adsorption constants of catechol, 2-nitrophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol versus their solubilities. Experimental conditions: $4 g/dm^3$ solid, pH = 4.0, 0.05 M $NaClO_4$.

coefficient by the following expression:

$$\sigma = a \log K_{ow} + b, \tag{4}$$

where K_{ow} stands for the octanol/water partition coefficient. Furthermore, they have determined the a and b values for several solvent systems based on a series of experiments. In Table 3, the predicted values of σ were compared with what we have obtained from the experiment. Judging from Table 3, it was obvious that the prediction of σ values in the methanol/water system was quite satisfactory for the moderately hydrophobic 2-nitrophenol, 2,4-dichlorophenol and 2,3,4-trichlorophenol. However, anomalies were found for catechol (log K_{ow} = 0.88). The different behaviors could then be used to explain their different adsorption mechanisms.

The adsorption mechanisms of phenols adsorption on mineral surfaces have been studied, although some contradictory results were proposed [15]. According to our previous work [10], less hydrophobic phenols, such as phenol and catechol, were adsorbed on ZnS(s) mainly through specific interactions, namely covalent bonding and hydrogen bonding. Whereas simple, non-specific partitioning was responsible for the adsorption of some more hydrophobic phenols. In other words, as the value of log K_{ow} increases, the contribution of specific interactions decreases, while that of
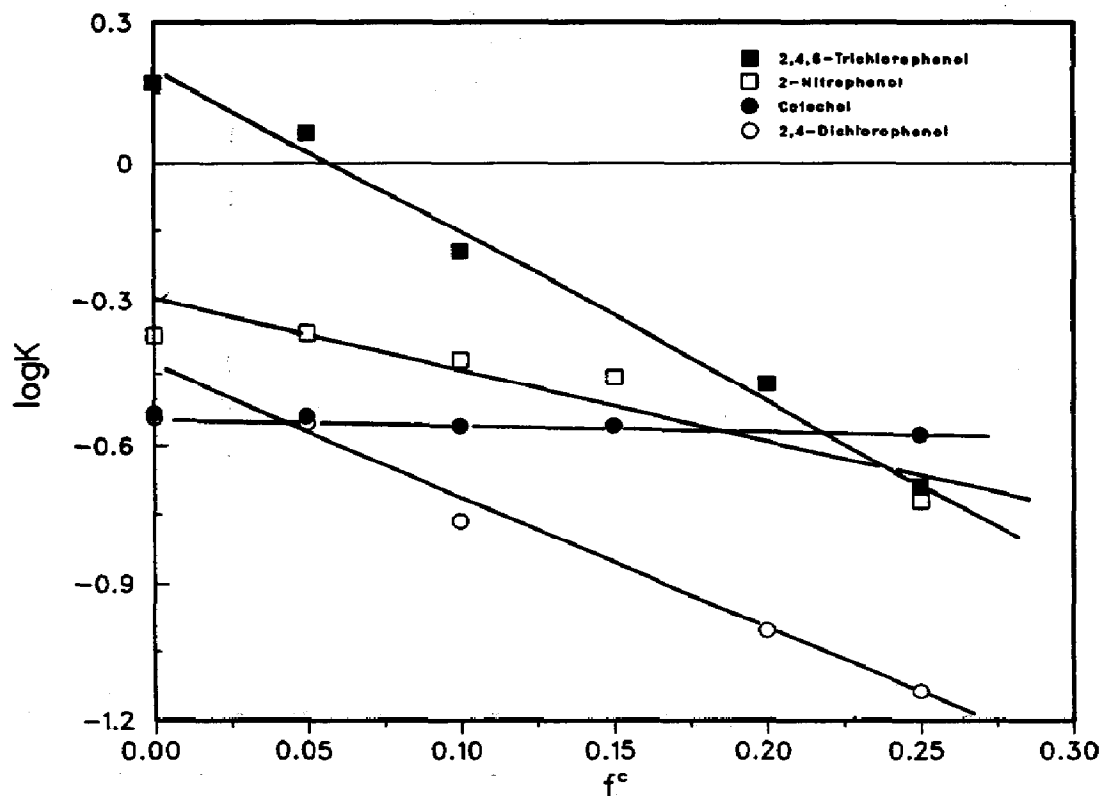
Fig. 6. The adsorption constants of catechol, 2-nitrophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol versus fraction of cosolvent. Experimental conditions: $4\,g/dm^3$ solid, pH = 4.0, 0.05 M $NaClO_4$.

Table 3
Values of σ^c in the cosolvent adsorption model

Adsorbate	σ^c predicted[a]	σ^c observed[b]	r^2
Catechol	1.67	0.22	0.9043
2-nitrophenol	2.27	1.71	0.8600
2,4-dichloro	2.94	3.06	0.9748
2,4,6-trichloro	3.37	4.16	0.9898

[a] $\sigma^c = 0.68 \log K_{ow} + 1.07$ [14].
[b] α equals 0.83 [1].

non-specific interactions increases. That explains the hydrophobic 2-nitrophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenols were adsorbed on ZnS(s) primarily due to hydrophobic interaction. However, the simple partitioning is insignificant in determining the adsorption of the hydrophilic catechol. This is why the presence of
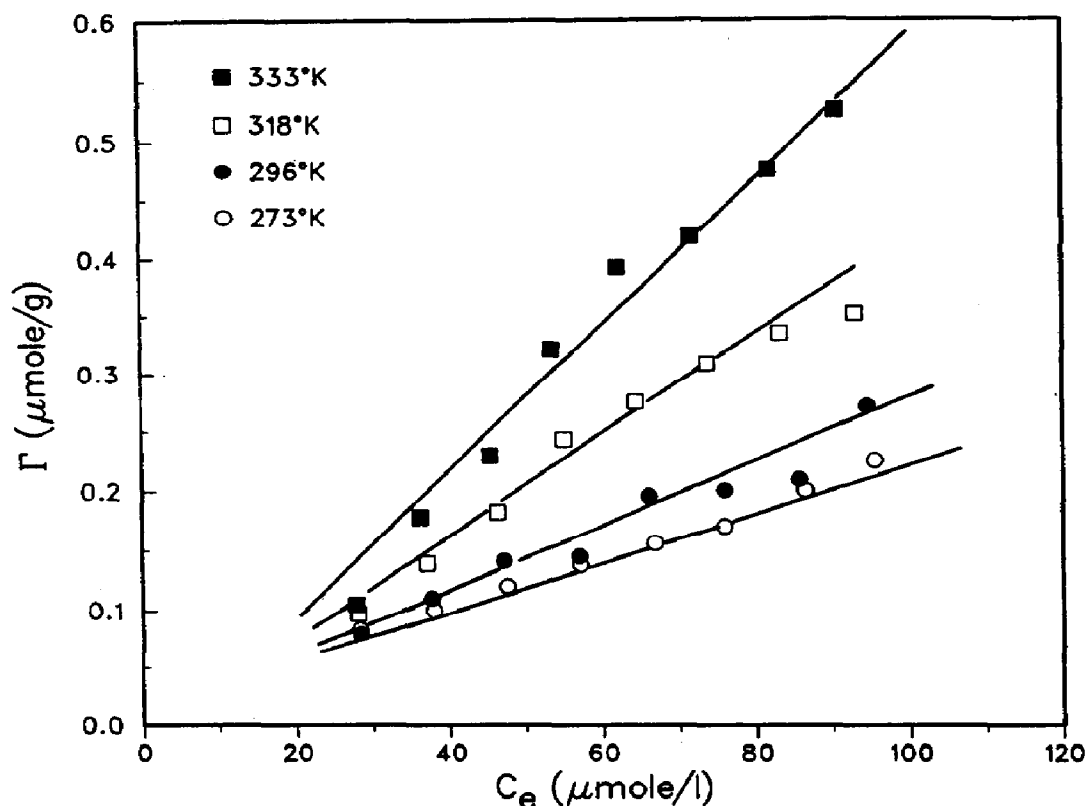
Fig. 7. Effect of temperature on the adsorption isotherms of 2-nitrophenol on hydrous ZnS(s). Experimental conditions: 4 g/dm^3 solid, pH = 4.0, 0.05 M NaClO$_4$.

cosolvent does not alter the adsorption isotherms. The value of σ^c observed for catechol under water/methanol solution was quite low. This indicated that the hydrophobic fraction (benzene ring) was relatively unimportant compared to the hydrophilic fraction (hydroxyl groups). In fact, the predicted value of σ^c for catechol could only be regarded as a reference because Eq. (4) holds only for hydrophobic chemicals.

Although many sulfides are classified as hydrophobic adsorbents [16], it has been established that hydroxyl groups would form on sulfide surfaces upon hydration [17]. The question that needs to be answered is why non-polar phenols would adsorb on the polar hydrous ZnS(s) surface, or, could it be that the phenols were adsorbed on the non-polar fraction of ZnS(s), such as elemental sulfur which has been indicated as a frequent product of sulfide surface oxidation [18–21]. Here, we are inclined to the supposition that phenols were adsorbed on hydrous ZnS(s) through surface hydroxyl groups. Since the equilibrium of hydrophobic organic chemicals on solids may be defined as a state where the adsorbate fugacity (F) in the adsorbed and aqueous phases are equal [1]. Therefore, it could be rationalized that so long as the thermodynamic equilibrium could be reached the non-polar phenols would still adsorb on the polar ZnS(s) surfaces through partitioning. That is to say if the phenols were
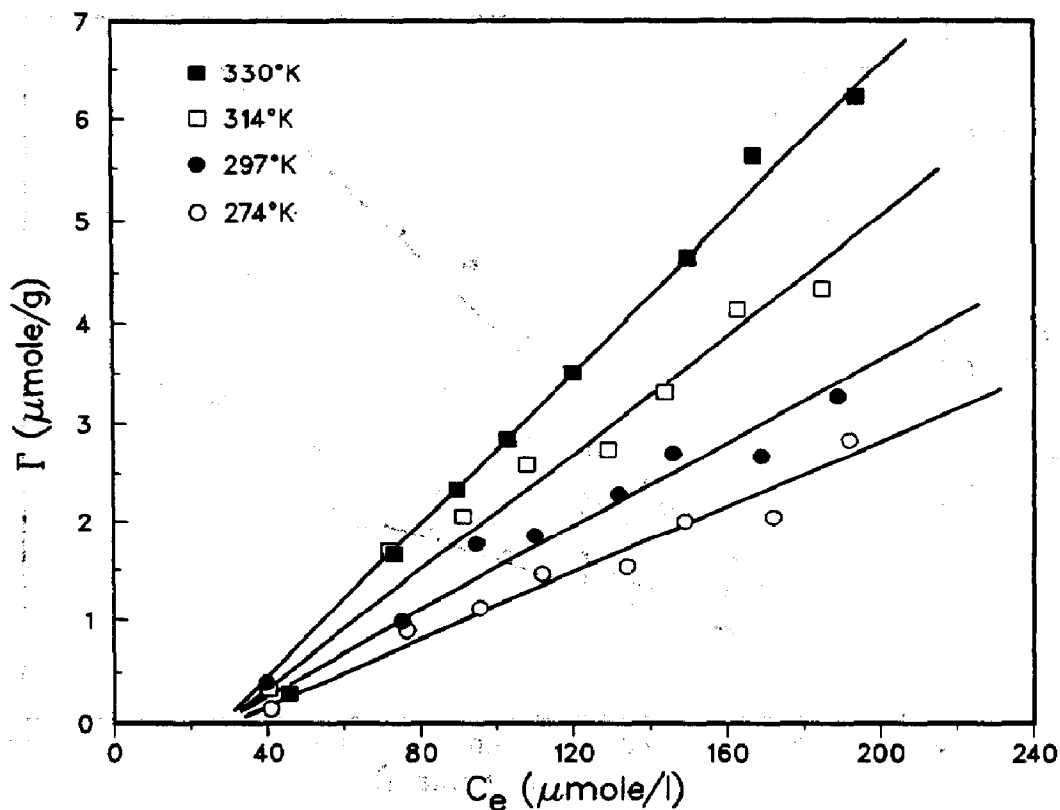
Fig. 8. Effect of temperature on the adsorption isotherms of 2,4-dichlorophenol on hydrous ZnS(s). Experimental conditions: 4 g/dm³ solid, pH = 4.0, 0.05 M NaClO₄.

thermodynamically more stable on the adsorbent surface than in the aqueous phase, they would be partitioned into the adsorbent phase. Hence, it seems the physical-chemical properties of the adsorbate are more determining than those of the adsorbent. This has been shown in some published work [22] and in our previous work [10] where the phenols adsorption characteristics were identical on hydrous ZnS(s), silica, and aluminum oxide.

3.2. The temperature effect

In order to investigate the adsorption mechanisms of phenols by hydrous ZnS(s), adsorption isotherms were investigated at different temperatures. The partition coefficient, K (dm³/g), obtained from linear adsorption isotherm has to be converted to a dimensionless constant to facilitate the calculation of the free energy of adsorption. It can be done by assuming a phenol adsorption layer thickness, L, of 5 Å [23] and
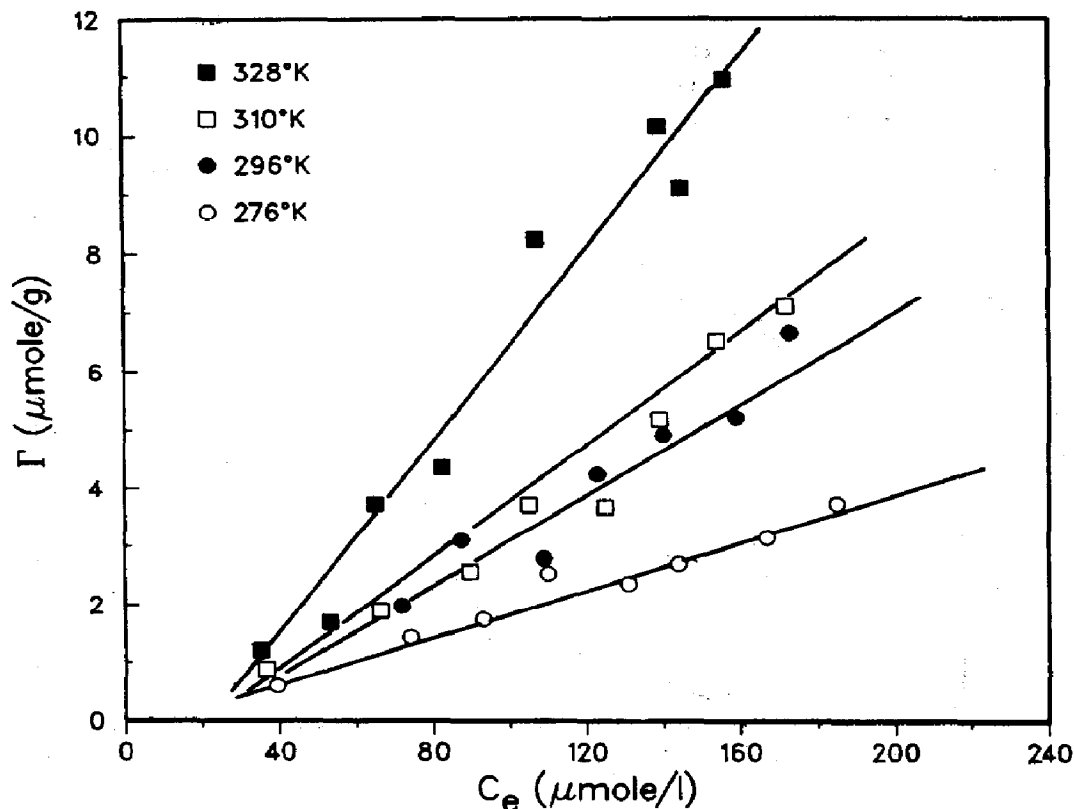
Fig. 9. Effect of temperature on the adsorption isotherms of 2,4,6-trichlorophenol on hydrous ZnS(s). Experimental conditions: 4 g/dm^3 solid, pH = 4.0, 0.05 M NaClO$_4$.

computing a dimensionless constant K_L.

$$K_L = K/L. \tag{5}$$

The adsorption was found to increase with temperature as shown in Figs. 7–9. Each isotherm was in accordance with the linear adsorption isotherm, i.e., Eq. (4). Since K_L in Eq. (5) is the equilibrium constant of adsorption reaction, the following equations are utilized to calculate the thermodynamic functions:

$$\Delta G^0 = -RT \ln K_L, \tag{6}$$

$$\Delta H^0 = \mathrm{d}(\Delta G^0/T)/\mathrm{d}(1/T), \tag{7}$$

$$\Delta S^0 = (\Delta H^0 - \Delta G^0)T, \tag{8}$$

where ΔG^0, ΔH^0, and ΔS^0 are the free energy change, the enthalpy change and the entropy change of the adsorption reaction, respectively. Figure 10 was plotted according to Eq. (7).
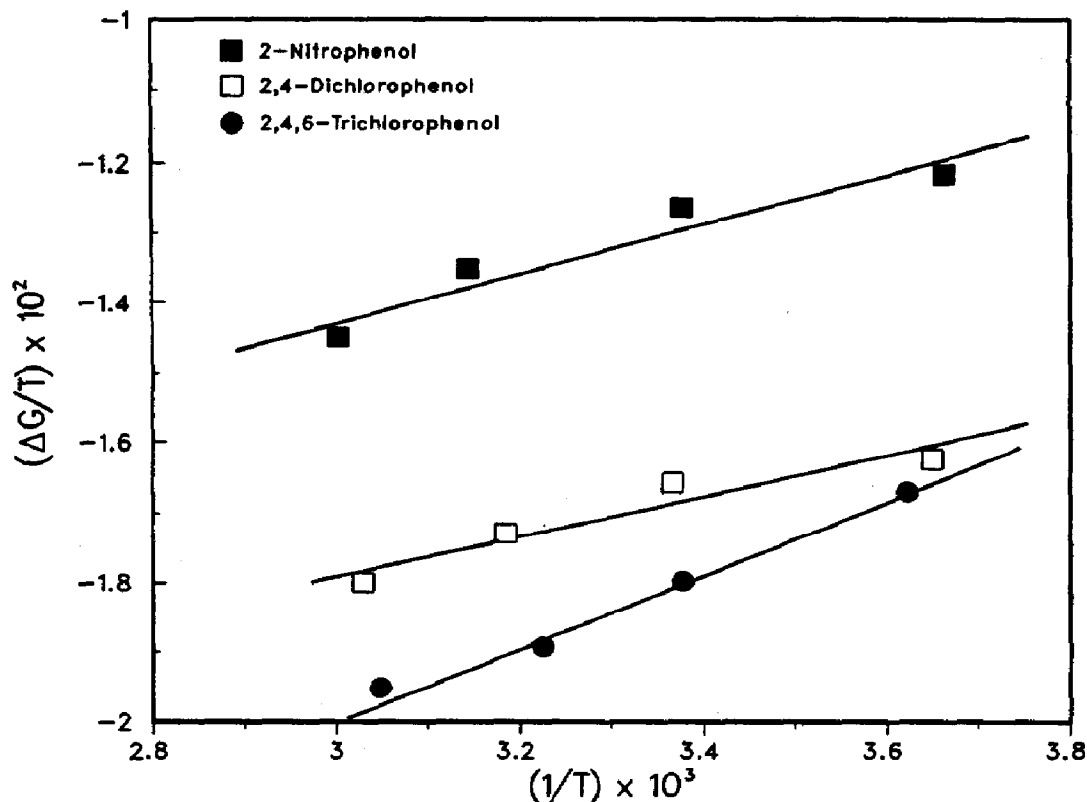
Fig. 10. The free energy of adsorption reaction divided by temperature $(\Delta G/T)$ versus the reciprocal of temperature.

Tables 4–6 show the results. Both ΔH^0 and ΔS^0 were positive and the entropy term was predominant in the free energy change. In order to interpret this phenomenon, the hydration of hydrophobic compounds was discussed first.

Franks [24] indicated in the review paper that the structure of water in the neighborhood of a non-polar molecule is modified in the direction of closer packing, which implies a reduction in the hydrogen bonding of the water. An "iceberg" tends to form around the non-polar molecule, causing enthalpy and entropy to be lost. The promotion of the structure of the neighboring water molecule is called "iceberg" effect. By analogy, the process that causes hydrophobic interactions to occur, i.e., the entropically unfavorable solution of non-polar molecules or residues in water, has been termed "hydrophobic hydration" to distinguish it from other types of interactions in aqueous solutions [24]. In all cases free energy of solution are positive, i.e., $\Delta G_s^0 > 0$, resulting from large, negative entropies, regardless of the sign of ΔH_s^0. This is also described in another work [25] that $T\Delta S$ is always greater than ΔH^0 in hydrophobic solvation. In order to proceed the adsorption reaction, the iceberg around the solute molecule must be broken down first. The endothermic effect and the entropy increase caused by the break down of iceberg might overcome the exothermic

Table 4
Linear adsorption isotherm constants and thermodynamic functions of adsorption of 2-nitrophenol onto hydrous ZnS(s)

Temperature (K)	K_L	ΔG^0 (kcal/mol)	ΔH^0 (kcal/mol)	ΔS^0 (e.u.)
273	457.3	− 3.32	3.43	24.80
296	573.4	− 3.74	3.43	24.31
318	907.5	− 4.30	3.43	24.22
333	1489.0	− 4.83	3.43	24.73

Table 5
Linear adsorption isotherm constants and thermodynamic functions of adsorption of 2,4-dichlorophenol onto hydrous ZnS(s)

Temperature (K)	K_L	ΔG^0 (kcal/mol)	ΔH^0 (kcal/mol)	ΔS^0 (e.u.)
274	3535.8	− 4.45	2.81	26.51
297	4172.9	− 4.92	2.81	26.04
314	5986.8	− 5.43	2.81	26.25
330	8609.0	− 5.94	2.81	26.53

Table 6
Linear adsorption isotherm constants and thermodynamic functions of adsorption of 2,4,6-trichlorophenol onto hydrous ZnS(s)

Temperature (K)	K_L	ΔG^0 (kcal/mol)	ΔH^0 (kcal/mol)	ΔS^0 (e.u.)
276	4475.0	− 4.61	4.74	33.86
296	8500.4	− 5.32	4.74	33.97
310	10,441.3	− 5.70	4.74	33.66
328	18,517.6	− 6.40	4.74	33.95

effect and the entropy decrease of adsorption reaction. In that case, such as what we have found, positive values of ΔH^0 and ΔS^0 are found. In other words, although an adsorption reaction usually takes place predominantly through energy change, however, the adsorption could also be driven by entropy increase through the destruction

of the iceberg. This is how hydrophobic bonding could participate in the adsorption reaction.

It is also found there is a sequence in the entropy change of adsorption of the three phenols, with the most hydrophobic 2, 4, 6-trichlorophenol possessing largest entropy change, while the least hydrophobic 2-nitrophenol possessing the smallest. This trend implies that water molecules are more structured around the more hydrophobic solute molecules.

This finding in our study showed another evidence that the adsorption of phenols onto hydrous ZnS(s) was caused by hydrophobic bonding as discussed previously.

4. Conclusions

The cosolvent effect was shown to exist in the adsorption of hydrophobic phenols onto hydrous ZnS(s). For the hydrophilic catechol, the presence of cosolvent did not affect the adsorption reaction. Further analysis of the solubility and cosolvent adsorption model supported the supposition that 2-nitro, 2, 4-dichloro, and 2, 4, 6-trichlorophenols were adsorbed onto hydrous ZnS(s) through hydrophobic interaction, while catechol was adsorbed onto hydrous ZnS(s) through specific interaction.

For the three hydrophobic phenols, the adsorption reaction increases with temperature increase. The "structure making" of hydrophobic molecules on water structure was used to interpret the endothermic adsorption reaction. The entropy change accompanying the adsorption reaction follows the trend that the more hydrophobic the solute, the larger the value of entropy change. This indicates the more hydrophobic solute molecules are capable of making the neighbouring water molecules more structured.

Acknowledgement

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