Evaluation of adsorption of organic solvents to modified hydrophobic silica adsorbents based on Hansen solubility parameter

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ABSTRACT

Adsorption is an effective methodology for the removal of organic matter. Several studies have shown that adsorption performance is dependent on pore size, specific surface area, and the affinity between the adsorbent and adsorbed material. In this study, we concentrated on the effect of the affinity between the surface of the adsorbent and the adsorbed matter by examining the adsorption of organic solvents from organic/aqueous mixtures using three types of hydrophobic silica adsorbents. The Hansen solubility parameters (HSPs) of the adsorbents were determined using the group contribution method. A linear relationship between the logarithm of the amount of adsorbed organic solvent and the difference between the HSP values of the organic solvents and adsorbents was obtained with a high correlation coefficient. These experimental results suggest that the affinity between the adsorbent and adsorbed matter can be well-described by the HSPs of the components.

1. Introduction

Adsorption is a well-established and effective methodology for the removal of micro pollutants and is widely applied in wastewater treatment. Solid materials are used extensively as absorbents because of their large accessible surface areas and pore volumes and the possibility of regenerating the adsorbent at a later time [1,2].

However, adsorption isotherm is required for the adsorption process design. Time, cost, and toxicity may prevent the extensive collection of experimental adsorption data. Therefore, for the sake of preliminary design, a correlation capable of predicting adsorption equilibrium capacities from commonly available physicochemical properties of these compounds is highly needed [3].

Several studies have shown that adsorption is dependent on pore size, specific surface area, and the affinity between the adsorbent and adsorbed material [4–6]. However, there have been few quantitative reports that evaluate the effect of affinity on adsorption. Thus, it is necessary to numerically verify the effects of affinity.

The linear solvation energy relationship (LSER) model has been proposed as an affinity (interaction) evaluation method in adsorption [3,7].

The LSER model takes into account the hydrogen bonding or dipole-dipole force as an interaction. Zhang et al. reported adaptation to solid-liquid adsorption of LSER model [3]. However, it is difficult to determine the parameters. It is thought that it is necessary to propose more simple indicators.

To elucidate the mechanisms by which affinity affects adsorption, we focused on the Hansen solubility parameters (HSPs) of various materials [8].

The Hildebrand solubility parameter (δt) [9,10] is commonly used to evaluate the cohesion energies of substances. The solubility parameter, a physical property representing the cohesion energy density of a substance, is useful for evaluating the compatibility, wettability, and cohesiveness or dispersibility of substances. Hansen further defined the Hildebrand solubility parameter as comprising three components based on the type of molecular interaction involved: namely, dispersion forces (δ_d), intermolecular dipole interactions (δ_p), and hydrogen-bonding interactions (δ_h).

Sato et al. evaluated the correlation between oxygen solubility in pure organic solvents and R_a, i.e., the 3D-HSP distance between oxygen and the solvent [12].

Moreover, good correlation between R_a and solubility was observed for the HSPs of oxygen.

In the present study, for adsorbents with constant specific surface area and pore diameter, we investigated changes in the adsorption performance related to the adsorbent affinity. We performed adsorption experiments using silica with different functional groups to test the effect of the affinity between the adsorbent and organic solvent and to clarify the effect of the surface functional groups on the adsorption amount.

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Nomenclature

E	cohesive energy, J/mol
E_d	cohesive energy of dispersion interaction, J/mol
E_p	cohesive energy of dipole interaction, J/mol
E_h	cohesive energy of hydrogen-bonding interaction, J/mol
V	volume of solvent, L
δ_t	solubility parameter, MPa$^{1/2}$
δ_d	Hansen solubility parameter of dispersion interaction, MPa$^{1/2}$
δ_p	Hansen solubility parameter of dipole interaction, MPa$^{1/2}$
δ_p	Hansen solubility parameter of hydrogen-bonding

	interaction, MPa$^{1/2}$
R_a	distance between Hansen solubility parameters, MPa$^{1/2}$
φ	volume ratio, −
R	correlation coefficient, −
q	adsorbed amount, mmol/g
C	concentration of solvents, mol/L
W	weight of adsorbent, g
V_M	molar volume, cm^3/mol
F_{di}	Dispersion component of molar attraction function, J$^{1/2}$ cm$^{3/2}$/mol
F_{pi}	Polar component of molar attraction function, J$^{1/2}$ cm$^{3/2}$/mol

Araki et al. reported that the flux of an organic compound through a membrane is related to the difference between the HSPs of the membrane and organic compound [6]. In other words, the affinity between the organic compounds and membrane is the dominant factor in membrane separation.

Using this approach, we established the HSPs of the adsorbent and found a correlation between R_a and the amount of solvent adsorbed, similar to the correlation previously reported for oxygen [12].

2. Experimental section

2.1. Theory of Hansen solubility parameter

The solubility parameter δ_t [(MPa)$^{1/2}$] used in the solubility evaluation was defined as

$$\delta_t = \left(\frac{\Delta E^V}{V_M}\right)^{1/2} \tag{1}$$

where ΔE is the liquid cohesion energy [J] and VM is the molar volume [cm^3/mol] [9].

Hansen divided the cohesion energy ΔE [J] of the Hildebrand solubility parameter into three components (i.e., dispersion interactions Ed [J/mol], dipole interactions Ep [J/mol], and hydrogen-bonding interaction Eh [J/mol]), which can be expressed as follows: [13]

$$\Delta E^V = \Delta E_d^V + \Delta E_p^V + \Delta E_h^V \tag{2}$$

$$\delta_d = \left(\frac{\Delta E_d^V}{V_M}\right)^{1/2}, \ \delta_p = \left(\frac{\Delta E_p^V}{V_M}\right)^{1/2}, \ \delta_h = \left(\frac{\Delta E_h^V}{V_M}\right)^{1/2} \tag{3}$$

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{4}$$

Here, δ_d [(MPa)$^{1/2}$], δ_p [(MPa)$^{1/2}$], and δ_h [(MPa)$^{1/2}$] represent the dispersion force factor, dipole interaction force factor, and hydrogen-bonding force factor of the HSP, respectively. Quantitative evaluation of the solubility can be represented by the value of R_a [(MPa)$^{1/2}$], which reflects the distance of the HSPs of both substances:

$$R_a = [4 \cdot (\delta_{d,1} - \delta_{d,2})^2 + (\delta_{p,1} - \delta_{p,2})^2 + (\delta_{h,1} - \delta_{h,2})^2]^{1/2} \tag{5}$$

A smaller R_a means a higher solubility of each substance because the interaction forces acting between the molecules are similar. Thus, substances with large R_a values exhibit low solubility.

The solubility parameter of a mixed solvent is calculated using the following equation:

$$\delta_i = \varphi_1 \delta_{i,1} + \varphi_2 \delta_{i,2} \tag{6}$$

where φ is the volume fraction of each of the mixed solvents, with the subscripts 1 and 2 representing components 1 and 2, respectively. The subscript i can be d, p, or h (representing the dispersion interaction, dipole interaction, or hydrogen-bonding interaction factors, respectively).

2.2. Calculation of HSPs of adsorbents

We calculated the HSPs of hydrophobic silica samples (modified with different functional groups) using the Hoftyzer–van Krevelen group contribution method [14]. The following equations were used to estimate the HSPs:

$$\delta_d = \frac{\sum F_{di}}{V_M} \tag{7}$$

$$\delta_p = \frac{\sqrt{\sum F_{pi}^2}}{V_M} \tag{8}$$

$$\delta_h = \sqrt{\frac{\sum E_{hi}}{V_M}} \tag{9}$$

where δ_d is the dispersion HSP, δ_p is the polar HSP, δ_h is the hydrogen-bonding HSP, v is the molar volume, F_{di} is the group contribution of the dispersion component of structural group i, F_{pi} is the group contribution of the polar component, and E_{hi} is the hydrogen-bonding energy. If two identical polar groups are present in a symmetrical position, the value of δ_p calculated using Eq. (8) must be multiplied by a symmetry factor of 0.5, 0.25, or 0 for one, two, or more-than-two planes of symmetry, respectively. For molecules with several planes of symmetry, $\delta_h = 0$. The molar volume was estimated using Hoy's method [6,14].

In addition, the HSP value of a polymer with a molecular structure consisting of repetition of a basic structure, such as the hydrophobic silica adsorbent used in this research, can be estimated using the group contribution method for one segment of the structure [6].

The HSPs of the adsorbents were calculated from the amounts of organic solvent adsorbed from organic/aqueous mixtures. The detailed procedure for the calculation of the HSPs of the adsorbents was as follows. First, the amounts adsorbed from the organic/aqueous mixtures with known HSPs were measured. Second, we assumed that the HSP values of the adsorbents, R_a could be calculated from the HSP values of the adsorbents and solvents. The correlation coefficient between R_a and the logarithm of the amount of solvent adsorbed was calculated. Finally, the HSPs of the adsorbents were determined.

2.3. Preparation of hydrophobic silica sol adsorbents

To prepare the phenyltrimethoxysilane (PhTMS) sol adsorbent, a PhTMS silica sol was first prepared by hydrolysis and copolymerization of PhTMS (0.1 mol) in the presence of cetyltrimethylammonium bromide (CTAB) (0.008 mol) in 25 mL of ethanol with gentle stirring. This concentration of CTAB was higher than the critical micelle concentration of CTAB in ethanol (0.24 mol mL^{-1}) [6]. The hydrolysis and condensation reactions of the PhTMS silica sol were promoted by adding 7.5 mL of 1 mol L^{-1} HNO$_3$ dropwise to the mixture. Then, the mixture was stirred continuously at room temperature for 3 h. Next, 3 mL of the mixture was extracted, placed on a square alumina plate, and calcined at 453 K for 3 h. The adsorbents were then washed with ethanol to