

Solubility parameter treatment for the characterization of the stationary phase in the reversed-phase chromatography of benzene derivatives

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ABSTRACT

Non-polar benzene derivatives were chromatographed on seven commercially available octadecyl columns with aqueous methanol as eluent. To interpret the differences in the retention behaviour on these columns, the role of the stationary phase was investigated by means of the solubility concept model. An apparent solubility parameter of the stationary phase, δ_s' , was determined for the seven columns by using toluene as a standard solute. The values ranged from 14.32 to 14.91 (cal/cm³)¹⁻² with an 80% aqueous methanol eluent. The absolute value of the enthalpy change of solutes in the phase-transfer process, ΔH^0 , was larger on C₁₈ columns with a smaller δ_s' . The ΔH^0 value was predictable from the δ_s' when the physico-chemical parameters of the solute and of the mobile phase were given. The δ_s' was useful for characterizing the retention properties of the stationary phase.

INTRODUCTION

Chemically bonded octadecylsilica gel is the most popular packing material for reversed-phase chromatography. Various silica-based C₁₈ materials have been provided by several manufacturers. Recently, new types of packings, such as capsule-type silica-based C₁₈ materials and polymer-based C₁₈ materials have become available. These C₁₈ materials have different retention properties. It is well known that the retention data obtained with different columns under identical mobile phase conditions are hardly comparable. The need for characterization and classification of these materials has been expressed¹.

In reversed-phase chromatography, retention of solutes on a C₁₈ column depends mainly on non-specific interactions, such as hydrophobic interactions, between the solute, mobile phase and stationary phase. The solubility concept model has been applied in semi-empirical descriptions of retention behaviour in this type of chromatography²⁻⁶ and the polarities of solutes and mobile phases have been investigated to elucidate their role in retention. In previous papers^{7,8}, we expressed the polarity of the stationary phase by an apparent solubility parameter of the stationary

phase, δ'_s , by using the concept of solubility. The value of δ'_s was determined on a Nucleosil C₁₈ column from chromatographic data for toluene with various compositions of methanol-containing eluents. A relationship between the δ'_s value and the methanol concentration in the mobile phase was reported⁷. In this paper, the δ'_s value was determined for seven different C₁₈ columns and their characterization was studied on the basis of their δ'_s values.

EXPERIMENTAL

A Shimadzu LC-3A chromatograph including a Model SPD-2A UV detector and a Model CTO-2A column temperature controller (Shimadzu, Kyoto, Japan) was employed with a Model RI-SE51 refractometer (Showa Denko, Tokyo, Japan).

The octadecylsilica packing materials (all of particle size 5 μ m) used were Cosmosil C₁₈ (Nacalai Tesque, Kyoto, Japan), LiChrosorb RP-18 (E. Merck, Darmstadt, F.R.G.), Spherosil XOA 600, (Rhône Poulenc, France), Nucleosil C₁₈ (Macherey, Nagel & Co., Düren, F.R.G.) and Chemcosorb UH-ODS (Chemco, Osaka, Japan). These packings were slurry-packed into 25 \times 0.4 cm I.D. or 15 \times 0.46 cm I.D. columns, using the balanced-density technique. Asahipak ODP-50 (5 μ m), with a vinyl alcohol copolymer-based structure (Asahi Chemical Industry, Tokyo, Japan), and Capcellpak C₁₈ (5 μ m) (Shiseido, Tokyo, Japan) were also used to compare their retention properties with those of the silica-based gels. Capcellpak C₁₈ is a new type of C₁₈ material prepared by coating the silica surface with a silicone polymer film and thereafter modifying the coated polymer with octadecyl groups⁹.

Benzene derivatives, used as solutes, and other chemicals were purchased from Nacalai Tesque (Kyoto, Japan). Chromatography was performed with 30% or 80% aqueous methanol as the eluent at a flow-rate of 0.5 ml/min. The eluate was monitored with the UV detector for aromatic hydrocarbons and with the refractometer for *n*-alkanes.

RESULTS AND DISCUSSION

In the solubility concept model, the enthalpy change in the phase-transfer process, ΔH^0 , is represented as the difference between the partial molar enthalpy changes, Δh^0 , on dissolving a solute in the two phases. The value of Δh^0 is controlled with the molar volume and the solubility parameter. In chromatography, the enthalpy change on transferring a solute from the mobile phase to the stationary phase is represented as follows;

$$\Delta H^0 = \Delta h_{is}^0 - \Delta h_{im}^0 = V_i[(\delta_i - \delta_s)^2 - (\delta_i - \delta_m)^2] \quad (1)$$

where V_i is the molar volume of the solute, δ is the solubility parameter and the subscripts i, m and s refer to the solute, mobile phase and stationary phase, respectively. V_i , δ_i and δ_m are physico-chemical parameters, the values of which are obtained from non-chromatographic data^{5,10}. Table I gives the values for the parameters used here. The solubility parameter of the mobile phase δ_m , was calculated from that of the pure solvent, δ_j , by using the following equation;

$$\delta_m = \sum v_j \delta_j \quad (2)$$

TABLE I
PHYSICO-CHEMICAL PARAMETERS FOR VARIOUS SOLUTES

<i>Solute</i>	V_i (cm^3)	δ_i (cal/cm^3) ^{1/2}	<i>Solute</i>	V_i (cm^3)	δ_i (cal/cm^3) ^{1/2}
<i>n</i> -Pentane	115.3	7.1	<i>n</i> -Propylbenzene	139.4	8.64
<i>n</i> -Hexane	130.8	7.3	Ethylbenzene	122.5	8.84
<i>n</i> -Heptane	146.5	7.4	Toluene	106.3	8.93
<i>n</i> -Octane	164.0	7.5	Benzene	88.9	9.1
<i>n</i> -Nonane	178.6	7.5 ^a	Naphthalene	147.6	9.96
<i>n</i> -Amylbenzene	171.8	8.44 ^a	Phenanthrene	196.7	9.8
<i>n</i> -Butylbenzene	156.1	8.58	Anthracene	196.7	9.9

^a Values calculated from the heat of evaporation at 25°C by using the Hildebrand rule.

where v is the volume fraction of a constituent of the mobile phase. The values of δ_m for 30% and 80% aqueous methanol eluents were 20.83 and 16.31 (cal/cm^3)^{1/2}, respectively.

The stationary phase in reversed-phase chromatography is recognized as a ternary complex phase, consisting of octadecyl and unreacted silanol residues on the silica surface and a solvating layer on the residues. The polarity of such a stationary phase cannot be determined physico-chemically. However, the value of δ_s can be calculated by substituting the values of V_i , δ_i and δ_m into eqn. 1, when the ΔH^0 value for a solute is obtained experimentally from the van't Hoff plots. Thus, we determined the value of δ_s by using the retention data for toluene. The calculated δ_s was expressed as the "apparent" parameter, δ'_s , which is a semi-experimental value for the polarity of the stationary phase.

Table II gives the δ'_s values for the seven different C₁₈ columns with 30% and 80% aqueous methanol eluents. The δ'_s values for these C₁₈ columns ranged from 14.32 to 14.91 (cal/cm^3)^{1/2} with 80% aqueous methanol and from 18.24 to 19.01 (cal/cm^3)^{1/2} with 30% aqueous methanol as eluent. As reported previously⁷, it should be noted that the δ'_s values are larger than the solubility parameter of octadecane, which is assumed

TABLE II
 δ'_s VALUES FOR VARIOUS C₁₈ COLUMNS

<i>Column</i>	80% aqueous methanol $\delta_m = 16.31$ (cal/cm^3) ^{1/2}	30% aqueous methanol eluent, $\delta_m = 20.83$ (cal/cm^3) ^{1/2}
Capcellpak C ₁₈	14.32	18.24
LiChrosorb RP-18	14.67	18.77
Chemcosorb UH-ODS	14.68	18.73
Nucleosil C ₁₈	14.70	19.03
Cosmosil C ₁₈	14.85	18.94
Spherosil XOA-600	14.88	18.75
Asahipak ODP	14.91	18.42

to be about 7 (ref. 6). The δ'_s value did not depend on the polarity of the fixed alkyl groups but on that of the complex stationary phase composed of the alkyl chains, the solvating layer on the residues. The δ'_s value changed on varying the polarity of the mobile phase, being lower with 80% than with 30% aqueous methanol.

The effect of the mobile phase composition on the δ'_s value was characteristic of the C_{18} materials. With conventional silica-based C_{18} materials, the difference in the δ'_s values under the two elution conditions ranged from $4.35 \text{ (cal/cm}^3)^{1/2}$ for Nucleosil C_{18} to $3.87 \text{ (cal/cm}^3)^{1/2}$ for Spherosil XOA. On a Capcellpak C_{18} , a capsule-type silica gel, the difference between the δ'_s values under the two elution conditions was $3.92 \text{ (cal/cm}^3)^{1/2}$. On polymer-based Asahipak ODP, the effect of the composition of the mobile phase on the δ'_s value was $3.51 \text{ (cal/cm}^3)^{1/2}$, which is smaller than those for the conventional silica-based C_{18} columns. The difference in the δ'_s values between C_{18} columns may reflect the difference in the solvation of the materials in aqueous methanol solution.

Fig. 1 shows the relationship between $-\Delta H^0$ and δ_s for benzene and n -alkylbenzenes with 80% aqueous methanol as eluent. The curves were drawn with a CAD (computer-aided design) system by substituting the values of V_i and δ_i for n -alkylbenzenes and the values of δ_m for 80% aqueous methanol into eqn. 1. The curves cross the horizontal line ($-\Delta H^0 = 0$) at the points δ_m and $2\delta_i - \delta_m$. When the polarity of the stationary phase is higher than that of the solute, the absolute value of ΔH^0 decreases with increasing δ_s . The chromatographic conditions in this work are an example of such a case.

In Table III the experimental $-\Delta H^0$ and the calculated $-\Delta H^0$ values for n -alkylbenzenes on the various C_{18} columns are given. The experimental $-\Delta H^0$ values were evaluated from the Van 't Hoff plots of the retention data on the columns in the temperature range 40–70°C. The calculated $-\Delta H^0$ values were obtained from the plots in Fig. 1. The experimental values agreed with the calculated values, within experimental error. On the Capcellpak C_{18} and Asahipak ODP columns the absolute mean deviations were 0.75% and 1.07%, respectively. The structure of the materials,

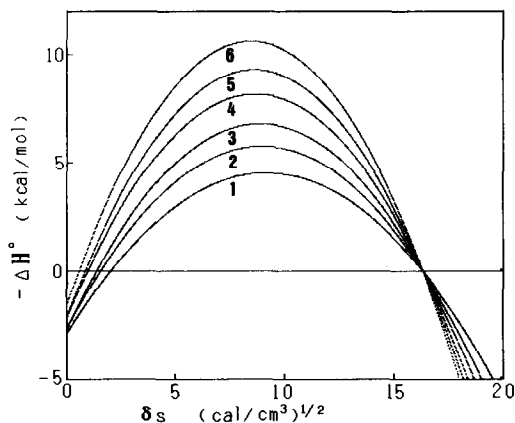


Fig. 1. Correlation curves for $-\Delta H^0$ and δ_s . Solutes: 1 = benzene; 2 = toluene; 3 = ethylbenzene; 4 = n -propylbenzene; 5 = n -butylbenzene; 6 = n -amylnbenzene. Eluent: 80% aqueous methanol.

TABLE III
 CHROMATOGRAPHICALLY MEASURED (obs) AND CALCULATED (cal) $-\Delta H^{\circ}$ VALUES (kcal/mol) FOR *n*-ALKYLBENZENES
 Deviation: $|\Delta H^{\circ}(\text{obs}) - \Delta H^{\circ}(\text{cal})| \cdot 100/\Delta H^{\circ}(\text{obs})$. Eluent: 80% aqueous methanol.

Solute	Capcellpak C ₁₈		LiChrosorb RP-18		Chemcosorb UH-ODS		Nucleosil C ₁₈	
	$-\Delta H^{\circ}(\text{obs})$	$-\Delta H^{\circ}(\text{cal})$	$-\Delta H^{\circ}(\text{obs})$	$-\Delta H^{\circ}(\text{cal})$	$-\Delta H^{\circ}(\text{obs})$	$-\Delta H^{\circ}(\text{cal})$	$-\Delta H^{\circ}(\text{obs})$	$-\Delta H^{\circ}(\text{cal})$
Benzene	2.15	2.18	1.91	1.85	1.83	1.84	1.83	1.82
Ethylbenzene	3.14	3.16	2.62	2.67	2.66	2.66	2.60	2.63
<i>n</i> -Propylbenzene	3.62	3.70	3.02	3.13	3.08	3.12	3.00	3.08
<i>n</i> -Butylbenzene	4.09	4.18	3.46	3.54	3.46	3.52	3.44	3.48
<i>n</i> -Amylbenzene	4.65	4.70	3.89	3.97	3.95	3.95	3.87	3.91
Av. deviation (%)	1.50		2.61		0.72		0.80	
δ'_s (cal/cm ³) ^{1/2}	14.32		14.67		14.68		14.70	
Spherosil C ₁₈ Cosmosil C ₁₈ Asahipak ODP-50								
	$-\Delta H^{\circ}(\text{obs})$	$-\Delta H^{\circ}(\text{cal})$	$-\Delta H^{\circ}(\text{obs})$	$-\Delta H^{\circ}(\text{cal})$	$-\Delta H^{\circ}(\text{obs})$	$-\Delta H^{\circ}(\text{cal})$	$-\Delta H^{\circ}(\text{obs})$	$-\Delta H^{\circ}(\text{cal})$
Benzene	1.65	1.67	1.61	1.64	1.59	1.61		
Ethylbenzene	2.40	2.41	2.36	2.37	2.30	2.32		
<i>n</i> -Propylbenzene	2.78	2.83	2.74	2.78	2.66	2.72		
<i>n</i> -Butylbenzene	3.18	3.19	3.18	3.13	3.10	3.07		
<i>n</i> -Amylbenzene	3.58	3.58	3.56	3.53	3.45	3.45		
Av. deviation (%)	0.75		0.59		1.07			
δ'_s (cal/cm ³) ^{1/2}	14.85		14.88		14.91			

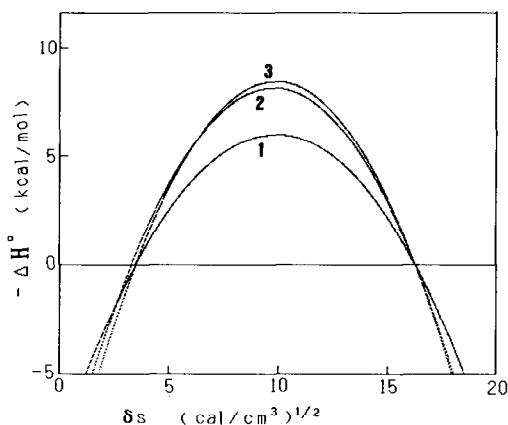


Fig. 2. Correlation curves for $-\Delta H^0$ and δ_s . Solutes: 1 = naphthalene; 2 = phenanthrene; 3 = anthracene. Eluent: 80% aqueous methanol.

whether silicone-coated silica or organic polymer-based, did not affect the $-\Delta H^0$ values for the retention of these *n*-alkylbenzenes.

The experimental and calculated $-\Delta H^0$ values for condensed aromatic hydrocarbons, such as naphthalene, phenanthrene and anthracene, and the absolute mean deviation on each column are given in Table IV. First, the $-\Delta H^0$ values for these aromatics were calculated by using the values of V_i in Table I, obtained by the method of Le Bas¹¹. The absolute mean deviation for aromatics was larger than that for *n*-alkylbenzenes. This resulted from the large difference between the calculated and experimental $-\Delta H^0$ values for phenanthrene and for anthracene. The calculated $-\Delta H^0$ values for phenanthrene on the seven C_{18} columns were larger than the experimental values, whereas the calculated $-\Delta H^0$ values for anthracene were smaller than the experimental values. However, the correlation coefficients between the calculated and experimental $-\Delta H^0$ values for the retentions of these two aromatics on five columns (*i.e.*, not including the Spherosil XOA and Asahipak ODP columns) were

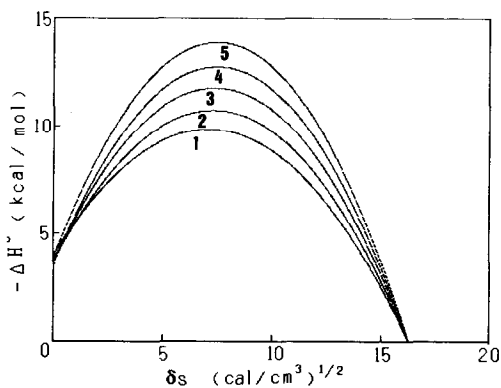


Fig. 3. Correlation curves for $-\Delta H^0$ and δ_s . Solutes: 1 = *n*-pentane; 2 = *n*-hexane; 3 = *n*-heptane; 4 = *n*-octane; 5 = *n*-nonane. Eluent: 80% aqueous methanol.

TABLE V

CHROMATOGRAPHICALLY MEASURED (obs) AND CALCULATED (cal) $-\Delta H^0$ VALUES (kcal/mol) FOR *n*-ALKANESDeviation: $|\Delta H^0(\text{obs}) - \Delta H^0(\text{cal})| \cdot 100/\Delta H^0(\text{obs})$. Eluent: 80% aqueous methanol.

Solute	Capcellpak C ₁₈		Nucleosil C ₁₈		Asahipak ODP-50	
	$-\Delta H^0(\text{obs})$	$-\Delta H^0(\text{cal})$	$-\Delta H^0(\text{obs})$	$-\Delta H^0(\text{cal})$	$-\Delta H^0(\text{obs})$	$-\Delta H^0(\text{cal})$
<i>n</i> -Pentane	3.70	3.77	3.06	3.12	2.78	2.76
<i>n</i> -Hexane	4.13	4.17	3.42	3.46	3.06	3.07
<i>n</i> -Heptane	4.53	4.62	3.82	3.82	3.38	3.40
<i>n</i> -Octane	5.01	5.10	4.17	4.23	3.74	3.72
<i>n</i> -Nonane	5.44	5.55	4.61	4.60	4.05	4.06
Av. deviation (%)	1.73		0.96		0.48	
δ'_s (cal/cm ³) ^{1/2}	14.32		14.70		14.91	

0.996 and 0.994, respectively. The deviation for the aromatics was assumed to be due to the error in the calculation of V_i values by the method of Le Bas¹¹.

Next, the values of V_i for the condensed aromatics were calculated by substituting the experimental $-\Delta H^0$ values into eqn. 1. We used the data for the Nucleosil C₁₈ column as a standard. The V_i values obtained for naphthalene, phenanthrene and anthracene were 148.5, 191.6, and 209.4 cm³, respectively. These V_i values differed from those obtained by the method of Le Bas by 0.6, 2.6, 6.5%, respectively. The recalculated $-\Delta H^0$ values are given in parentheses in Table IV. The absolute mean deviation for each column was improved by the recalculation. However, exceptions were found for the Spherosil XOA and Asahipak ODP columns. The experimental $-\Delta H^0$ values for the condensed aromatics on those columns were much larger than the values calculated from their δ'_s values. Hence the specific interaction may be due to the steric structure of the C₁₈ materials. Fig. 2 shows the relationship between $-\Delta H^0$ for the three condensed aromatics and δ'_s . Here, the recalculated V_i values were used for the molar volume of the condensed aromatics.

Fig. 3 shows the correlation curves between $-\Delta H^0$ and δ'_s for *n*-alkanes. Table V gives the experimental and calculated $-\Delta H^0$ values for the retention of the five *n*-alkanes on three types of columns: Capcellpak C₁₈, Nucleosil C₁₈ and Asahipak ODP. The absolute mean deviation between the experimental and calculated $-\Delta H^0$ values was sufficiently small on these three columns.

CONCLUSIONS

The polarity of the stationary phase was different for the different commercial C₁₈ materials. The concentration of the organic modifier in the mobile phase also affected the polarity of the stationary phase. Seven C₁₈ columns were characterized by their δ'_s values. On the C₁₈ column having a larger δ'_s value, a smaller absolute value of $-\Delta H^0$ was obtained in the retention of non-polar benzene derivatives. In other words, the larger the δ'_s values, the smaller was the observed temperature effect on the retention. The $-\Delta H^0$ values for the retention of benzene derivatives were predictable from the physico-chemical parameters and the δ'_s values.

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