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Studies of Solute-Chain Interaction under
Reordering/Resolvation Conditions: Correlation between
Solute Structure and Changes in Retention for Hydroxylated
Aliphatic and Aromatic Compounds

by

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Studies of Solute-Chain Interaction under Reordering/Resolvation

Conditions: 1) Correlations between Solute Structure and Changes

in Retention for Hydroxylated Aliphatic and Aromatic Compounds

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ABSTRACT

The current investigation is an extension of previous studies of conformational changes of n-alkyl bonded phases under totally aquoeus mobile phase conditions. Relative changes in retention, $\Delta k'_r$, before and after reordering/resolvation of an octyl phase have been studied using various linear, branched, cyclic and aromatic compounds. The magnitude of $\Delta k'_r$ can be correlated to structural features in the solute, such as size, shape, rigidity and substitution. The largest values of $\Delta k'_r$ were obtained from rigid solutes with multiple hydroxylated groups.

INTRODUCTION

Reversed-phase liquid chromatography is perhaps the most important means of separating thermally labile low molecular weight compounds. In a majority of cases, separations are carried out using linear alkyl phases. Hence developing a better understanding of such bonded materials and the fundamental processes controlling solute retention and selectivity continues to be important.

There have been a number of theories suggested to describe the nature of the bonded microlayer (1,2). A common view is that the immobilized chains are surrounded by intercloated solvent, the composition of which may or may not be close to that of the bulk mobile phase. Further the microlayer can swell or shrink depending on solvent composition. This latter property has been discussed in terms of a "breathing" model (3).

Previously we have systematically investigated thermally induced reordering/resolvation of both polar and nonpolar bonded phases in contact with water (1, 4-6). Likewise, the influence of entrapped solvent used to precondition the surface has been examined (7). Although separations are not typically carried using totally aqueous mobile phases, results from these studies have been useful in developing a better understanding of the orientation and dynamics of the bonded chains. The surface immobilized chains assume a folded conformation (an aggregated state) when the mobile phase is changed from an organic solvent to totally aqueous conditions. However, the bonded chains may undergo reorientation to an extended state upon heating. Water molecules pene-

trate into the bonded phase to form hydrogen bonds with unreacted surface silanols. For nonpolar chains, this behavior can be explained by differences between the two conformations in terms of; a) cohesive interactions between bonded chains, b) hydrophobic interactions between bonded chains and the contact solvent , water, and c) specific interactions resulting from hydrogen bonding between the aqueous mobile phase and unreacted surface silanols (5). However, for bonded alkyl chains containing a polar functional group, the specific interactions between it and the mobile phase, water, also must be considered (6).

The onset temperature (T_o) for reordering/resolvation can be obtained from nonlinearity in a plot of ln k' vs 1/T. This is illustrated in figure 1 for a silica surface with immobilized octyl chains. The experimental details of this procedure have been described previously (4). T_o has been determined for a number of polar and nonpolar phases. For a particular homologous series of anchored groups, a linear correlation exists between the reordering/resolvation temperature and the boiling point of the corresponding nonimmobilized compounds (5,6). This same type of experiment also has been used to examine the influence of bonding chemistry on resolution (8). The onset for reordering has been found to begin at approximately the same temperature irrespective of the attachment chemistry.

Relative changes in retention before /after resolution have been shown to be a function of surface coverage and solute structure (4). The current investigation represents an extension of these earlier surface resolution experiments and is a systematic effort to examine orientationally how (i.e., what difference in ordering occur when) mole-

cules interact with the bonded phase. Relative changes in retention

following resolvation have been determined using various linear,

branched, cyclic and aromatic compounds.

EXPERIMENTAL SECTION

Chemicals and Instruments:

All compounds listed in Table 1 and the HPLC grade acetonitrile were purchased from the Alrich Chemical Co., (Milwaukee, WI, USA). Deionized water was purified using a Milli-Q reagent water system (Milliopore Corp., El Paso, TX, USA) and was used as the mobile phase. n-octyldimethylchlorosilane was obtained from Petrarch System Inc., (Levittown, PA, USA) and was used as received. LiChrosorb Si60 ($d_p \approx 10$ μm and surface area 550 m²/g) was from E. Merck (Darmstadt, West Germany).

All chromatographic studies were carried out using a Laboratory Data Control (Riviera Beach, FL, USA) model constametric II G liquid chromatographic pump equipped with uv and reflective index detectors. Column temperature was controlled in a water bath with a Tempunit (Techne, Princeton, NJ, USA) model TU-14 zero cross-over proportional controller and a Neslab (Neslab Instruments, Portsmouth, NH, USA) model EN-350 flowthru liquid cooler. The flow rate was monitored with a liquid flowmeter (Model F1080A, Phase Separations Limited, Queensferry, Clwyd, UK). Retention data were recorded and processed using an IBM Instruments model 9000 data system.

Column preparation:

LiChrosorb Si60 (3.0 g) was slurried with deionized water and allowed to stand for three hours. Excess water was removed and the material dried at 110 °C for three hours. The dried silica was refluxed

overnight with 50 ml of a 15 % solution of the n-octyldimethylchlorosilane in toluene. During this process, a stream of dry nitrogen was continuously bubbled through the solution. After reaction, the modified silica was washed five times with 50 ml portions of toluene and two portions of ethyl ether. The material was dried at 110 °C for four hours to remove the solvent. The surface coverage (w/w %, carbon/silica) determined by microcombustion analysis was 11.2 %.

Empty 5 cm columns were prepared from 4.6 mm I.D. stainless steel tubing (Handy-Harman, Norristown, PA, USA). The column blanks were cleaned thoroughly with nonpolar and polar solvents and then rinsed with acetone. The modified materials were packed into the empty columns using a dynamic procedure (9).

Chromatographic studies: Solute retention was measured before/after resolvation of the bonded phases as follows:

(a) Initial studies: The column was first conditioned with 100 ml of acetonitrile followed by 100 ml of deionized water at a temperature of 20.0 ± 0.1 °C. Acetonitrile was chosen as the conditioning solvent to minimize entrapment problems (7). The flow rate was 4.0 ml/min. The retention of each compound was measured at least twice. Void volume was determined using D_2O.

(b) Thermal treatment: The pump was switched off and the column temperature increased to 70 °C. The column was maintained at this temperature for 20 minutes to assure thermal equilibrium. Subsequently, the pump was restarted and allowed to run for 15 minutes (60 ml water)

while maintaining the column at 70 °C. The pump was again switched off and the column cooled to 20.0 °C.

(c) Studies following thermal treatment: The pump was restarted and all compounds injected as in step (a).

The above three steps were repeated three times.

Calculations: The capacity factors (k') for all solutes were calculated and $\Delta k'_r$ (retention before/after reordering/reorientation) determined according to equation 1:

$$\Delta k'_r = (k'_a - k'_b)/k'_a \times 100\% \qquad \text{eq.1}$$

where k'_a is the capacity factor measured at 20.0 °C before thermal treatment, and k'_b is the capacity factor measured at the same temperature after heating and cooling.

RESULTS AND DISCUSSION

Shown in figure 1 are representative plots of ln k' vs 1/T for phenol chromatographed on an octyl phase before and after thermal treatment. In the presence of a totally aqueous mobile phase, the conformation of the bonded chains may be in either an aggregated or an extended state at a given temperature (4-6). At temperatures lower than T_o (i.e., ~40 °C for an octyl phase), the bonded chains are in an aggregated state (line A) and following thermal treatment above T_o the chains are in an extended state (line B). Differences in retention before and after resolvation, $\Delta k'_r$, is illustrated in figure 1 by line C.

Listed in Table 1 and 2 are k' and $\Delta k'_r$ values for the twenty-six solutes studied. These solutes were chosen on the basis of small changes in size (i.e., addition of methylene carbons), shape (i.e., linear, branching, cyclic, etc.), position of hydrophillic substitution and aliphatic vs. aromatic character. They cover a k' range from less than one to over two hundred and thus represent different degrees of solute-phase interaction. Interestingly, the trends to be discussed are independent of overall differences in retention but rather depend on structural features in the solutes. The relative magnitude of $\Delta k'_r$ for the solutes was in the following order; (a) dihydroxy compounds > monohydroxy compounds > nonpolar compounds, (b) aromatic compounds > cyclic or branched aliphatic compounds > linear aliphatic compounds. The largest values of $\Delta k'_r$ were obtained with rigid solutes with multiple polar functional groups. The smallest values of $\Delta k'_r$ were obtained for small flexible solutes.

Shown in figure 2 are plots of ln k' vs carbon number for three hcmologous series of solutes. These were linear alcohols (● & O) branched alcohols (■ & □) and alkyl phenols (▲ & △). Data are shown before and after thermal treatment. For a given homologous series, the slopes for the linear fits are related to the incremental change in selectivity per addition of a methylene carbon. Values for the slope are given in Table 3. A smaller incremental change was noted in case of branched alcohols compared to the linear alcohols which is reasonable based on steric arguments. The 35 to 40% reduction in slope reflects a decrease in interaction per carbon in the more hindered system.

The two linear fits for a given series of solutes were parallel with similar slopes before and after reordering/resolvation indicating a similar degree of solute-chain interaction regardless of the bonded chain's conformation. Relative changes in retention appear to reflect the increased orientation necessary (i.e., loss in ΔS) for a solute to have the same degree of interaction (ΔH) regardless of the phase's conformation. Thus, $\Delta k'_r$ can be correlated to hydrophobicity of the solute and how substitution and rigidity influences solute-chain interaction. For rigid molecules with the hydrophobic portion more sterically hindered, $\Delta k'_r$ was largest, whereas, for flexible solutes or for solutes where the polar group was removed to one end of the molecule, $\Delta k'_r$ was smallest. For example, considering the aromatic solutes, a relatively small change in retention ($\Delta k'_r$) was observed for benzene (7.5%). Likewise, $\Delta k'_r$ was only slightly higher for toluene (9.0%). However, the $\Delta k'_r$ values for phenol and the dihydroxy bezenes were significantly larger (i.e., 28.3% and 32.2 to 34.0% respectively).

Shown in figure 3 are plots of ln k' vs hydroxy substitution for an aromatic ring. Two linear relationships were observed with slopes of -1.04 and -1.14 for retention measurements made before and after reordering/resolvation of the surface. These lines were nonparallel and show that increasing hydrophillic substitution on the ring results in relatively higher values of $\Delta k'_r$. However, for substituted aromatic solutes where the hydrophobicity and rigidity were similar (e.g., chlorophenols and methylphenols), $\Delta k'_r$ were not significantly different. For the chlorophenols $\Delta k'_r$ was 29.4±0.4% and for the methylphenols $\Delta k'_r$ was 28.6±1.4%.

The rigidity of solutes studied is in the order of; aromatic compounds > branched or cyclic aliphatic compounds > linear aliphatic compounds. Data in Table 1 and 2 also show a good correlation between solute rigidity and $\Delta k'_r$. For example; phenol (28.3 %) > cyclohexanol (17.6 %), cyclopentanol (16.0 %) or t-pentanol (15.8 %) > n-pentanol (11.4 %), etc. These data further support the idea that $\Delta k'_r$ is a measure of the conformational changes of the solute necessary for similar solute-chain interaction to occur.

Changes in retention and selectivity for a pair of solutes before/after surface reorientation, $\Delta k'_r$, have been correlated to structural features in the solutes such as size, shape, rigidity and substitution. The magnitude of $\Delta k'_r$ for a pair of structurally similar solutes are within a narrow range and selectivity changes little between conformational states of the bonded phase. For a pair of solutes with different features $\Delta k'_r$ may be relatively large and elution order and selectivity may change.

CONCLUSION

The types of measurements made in the current study provide a means of examining the influence of a solute's structure and the bonded phase's conformation on the mechanism governing reversed-phase separations. Additional studies are now in progress using solutes which contain different functional groups in an effort to characterize the influence of functionality on retention and selectivity.

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Table 1: $\Delta k'_r$ values for aromatic solutes calculated from equation 1

Compounds	k'_a*	k'_b*	$\Delta k'_r$*
benzene	53.0	49.0	7.5 ± 2.0
toluene	224.2	204.0	9.0 ± 2.0
phenol	18.7	13.4	28.3 ± 0.5
benzyl alcohol	27.2	20.7	23.8 ± 0.8
pyrogallol	2.3	1.5	34.0 ± 0.4
catechol	6.8	4.6	32.3 ± 0.6
resorcinol	6.5	4.3	33.8 ± 0.4
hydroquinone	3.4	2.3	32.5 ± 0.6
2,7-DHNT**	147.7	93.4	37.0 ± 0.5
o-methylphenol	66.1	46.3	29.9 ± 0.7
m-methylphenol	67.8	48.9	27.9 ± 0.4
p-methylphenol	65.6	47.8	27.2 ± 0.3
p-ethylphenol	250.5	173.0	30.9 ± 0.5
o-chlorophenol	66.1	46.5	29.7 ± 0.5
m-chlorophenol	94.3	66.9	29.1 ± 0.3
p-chlorophenol	84.4	59.7	29.3 ± 0.5

 * the average value of data from each cycle

** 2,7-DHNT = 2,7-dihydroxynaphthalene

Table 2: $\Delta k'_r$ values for aliphatic solutes calculated from
equation 1.

Compounds	k'_a*	k'_b*	$\Delta k'_r$*
methanol	0.31	0.29	4.0 ± 2.0
ethanol	0.92	0.87	5.0 ± 2.0
n-propanol	3.4	3.1	9.2 ± 0.4
n-butanol	12.6	11.3	10.6 ± 0.5
n-pentanol	53.7	47.5	11.4 ± 0.5
propandiol	0.43	0.30	31.0 ± 2.0
iso-propanol	2.8	2.5	11.0 ± 1.0
t-butanol	6.9	6.0	13.2 ± 0.4
t-pentanol	22.7	19.1	15.8 ± 1.0
cyclopentanol	11.6	9.7	16.0 ± 1.0
cyclohexanol	39.0	32.0	18.0 ± 2.0

* see Table 1.

Table 3: Methylene selectivity for various homologous series of
solutes before/after reordering/resolvation

compounds	slope*	Y-int.	correlation
linear cpds	1.38/1.37	-2.94/-2.99	0.999/0.999
branched cpds	1.04/1.02	-2.15/-2.17	0.994/0.993
aromatic cpds	1.30/1.27	-4.86/-5.05	1.000/1.000

* calculated from plots of ln k' vs carbon number (figure 2).

List fo Figures

(1). Plot of ln k' vs 1/T for an octyl phase.

Mobile phase : water. Test solute : phenol. Evaluation cycle:

(A) initial run, (B) rerun following thermal conditioning.

Dashed line (C): $\Delta k'_r$ at 20 °C (i.e., measurements of solute retention

taken before (point a) and after (point b) surface

. reordering/resolvation).

(2) Plots of ln k' vs carbon number which reflect incremental

changes in retention. Solid line: data obtained before

surface reordering/resolvation. Dashed line: data obtained

after surface reordering/resolvation.

● & O : n-propanol, n-butanol, n-pentanol.
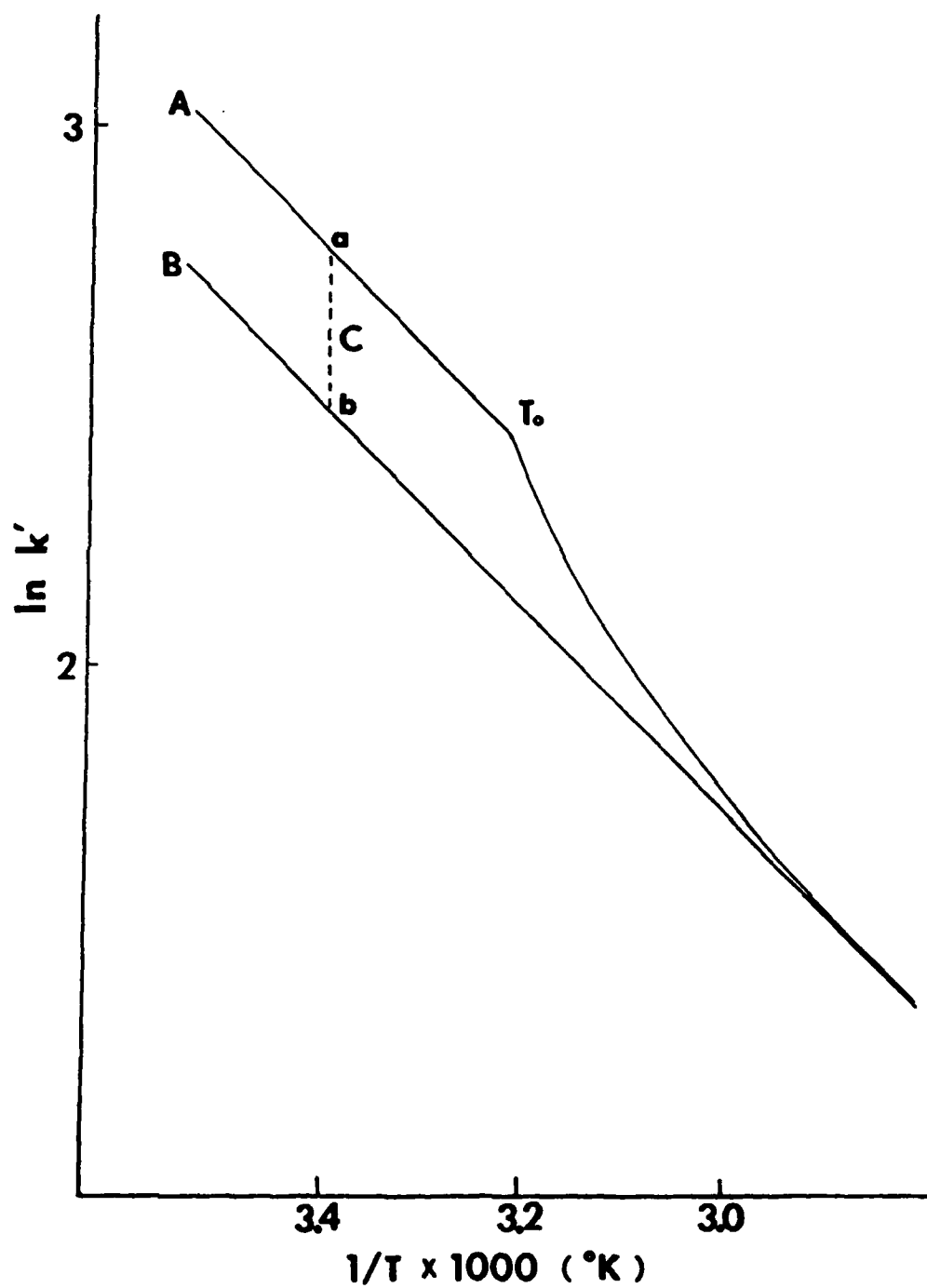
▲ & △ : phenol, p-methylphenol, p-ethylphenol.
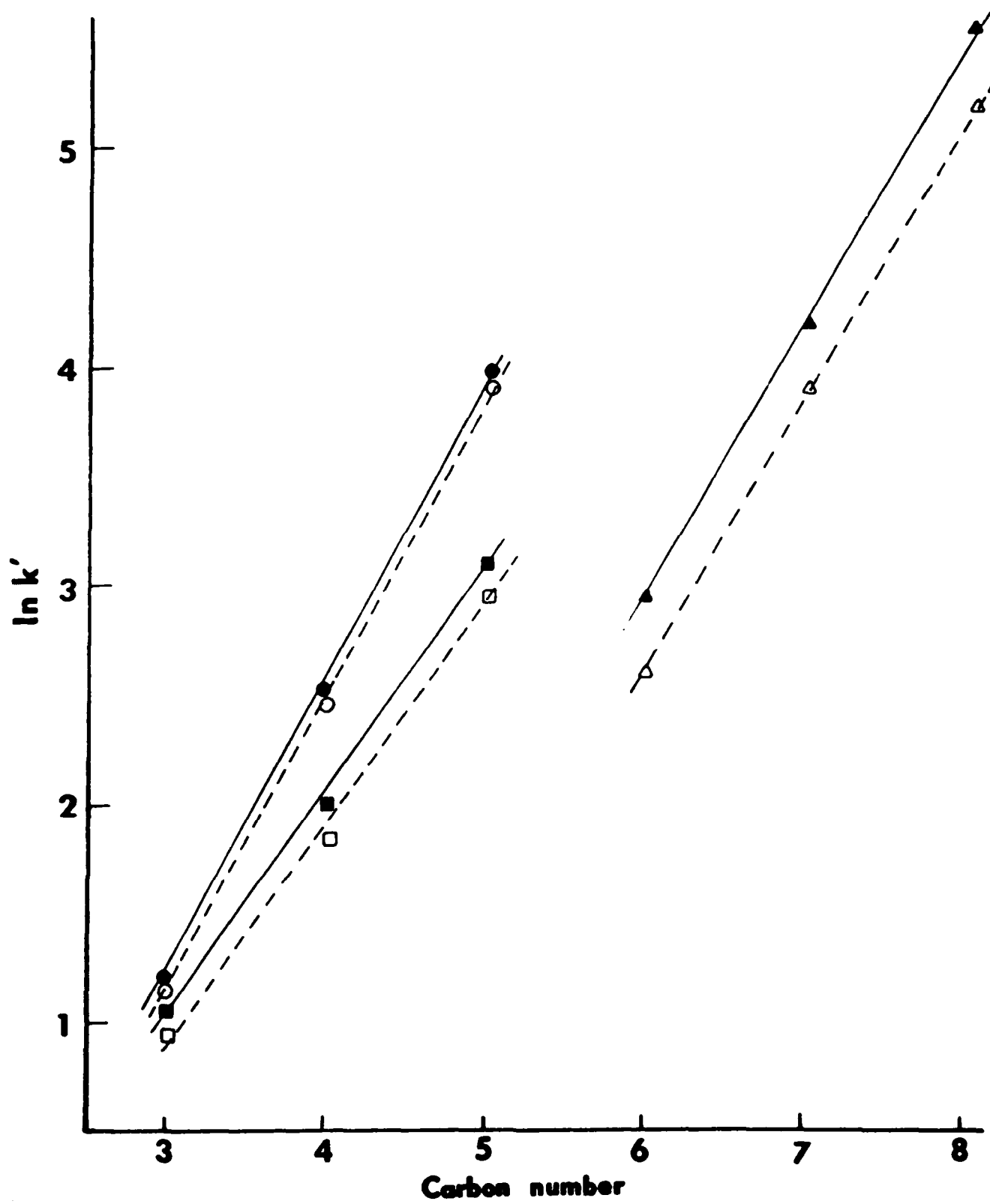
■ & □ : i-propanol, t-butanol, t-pentanol.

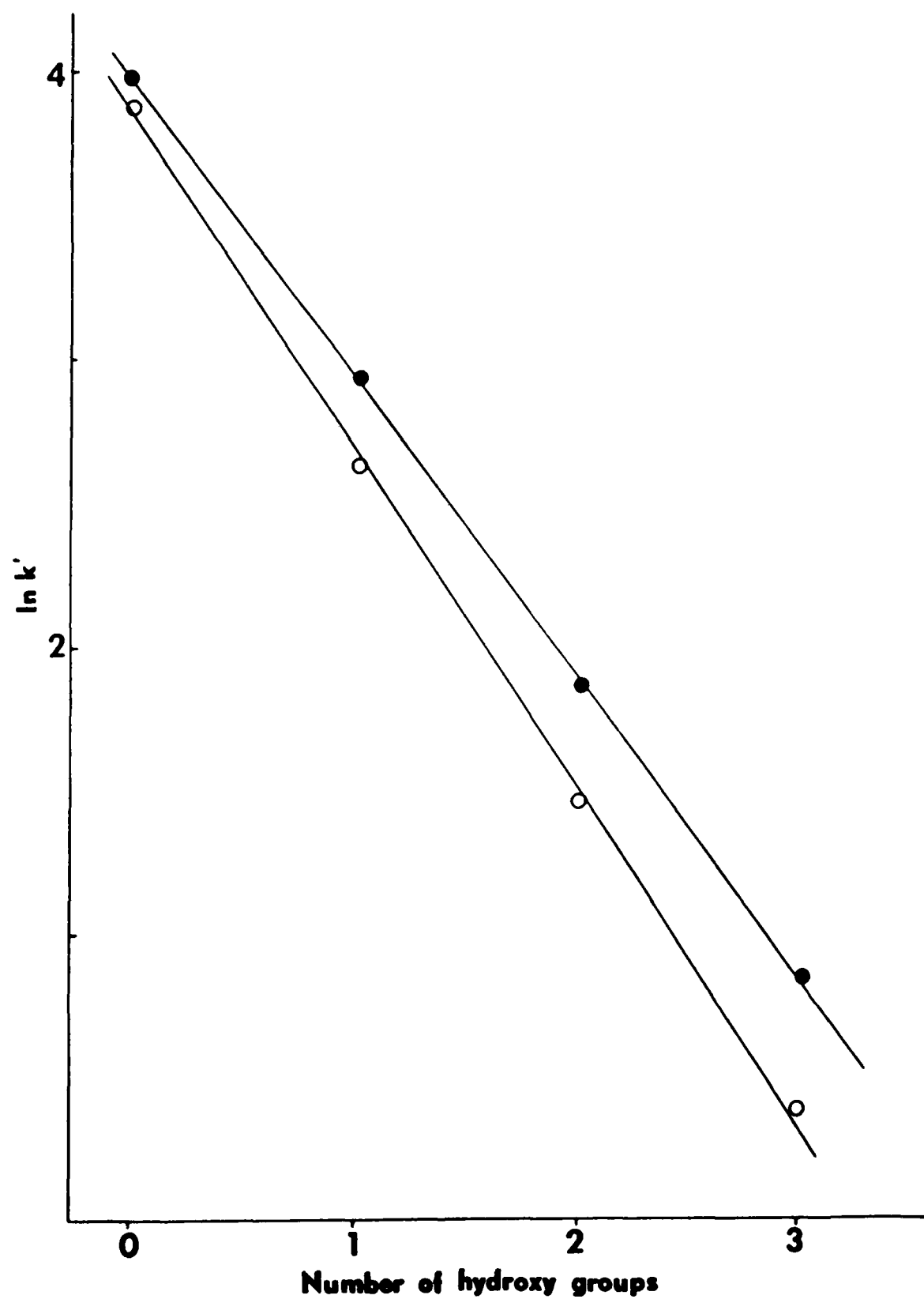(3) Plots of ln k' vs. number of hydroxy groups on an aromatic ring

solid line : see figure 2.

dashed line : see figure 2.

solutes: bezene, phenol, resorcinol and pyrogallol.

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