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Note

Liquid chromatography of chlorinated biphenylols

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The metabolism of polychlorinated biphenyls yields phenolic compounds in which hydroxyl groups take the place of the chlorine atoms or are inserted as substituents in addition to chlorine atoms originally present[1]. In our liquid chromatographic analysis of treated sewage[2] we have found evidence of biphenylols. The first step in identifying the peaks of such substances in liquid chromatography is to record retention volumes of pure model compounds under specified chromatographic conditions. We wish to report such retention volumes obtained on a bonded silica-C_{18} column, using aqueous methanol eluents.

EXPERIMENTAL

The data here reported were obtained with a Partisil PXS-10-25-ODS column (Whatman). Similar data were also obtained with a Zorbax ODS column (DuPont). The chromatographic system included a Model 6000A pump and U6K injector (Waters Assoc.), a variable-wavelength ultraviolet absorbance detector (Kratos-Schoeffel Model SF 770) and a controlled-temperature column heating jacket (Bio-Analytical Systems). The biphenylols were obtained in better than 99% purity from Ultra Scientific Company, Hope, RI, U.S.A.

Methanol and water were mixed by volume: that is, "40% methanol" was made by mixing 40 volumes of methanol with 60 volumes of water. The flow-rate was 1.00 ml/min; the void volume, measured by injections of sulfosalicyclic acid or potassium bromide, was 3.1 ml. Retention volumes were reproducible to within 0.1 ml.

RESULTS AND DISCUSSION

At least three methanol concentrations were used with each compound, and all compounds were run at three temperatures, 23, 35 and 45°C. All were run in 50% and 60% methanol, and the retention volumes, expressed as logarithms of capacity factors, are shown in Table I. It was shown that adding 0.1%–0.5% phosphoric acid to the eluent did not measurably change the retention of the phenols. Table I shows that chlorine atoms increase retention, while hydroxyl groups decrease retention by almost the same amounts. The C_{18} packing discriminates between isomers only slightly, if at all.

TABLE I

LOGARITHMS OF CAPACITY FACTORS (k') OF MODEL COMPOUNDS

Compound	*Log k'*					
	50% Methanol			*60% Methanol*		
	23°C	*35°C*	*45°C*	*23°C*	*35°C*	*45°C*
Biphenyl	0.86	0.73	0.62	0.42	0.35	0.27
Terphenyl	1.65	1.50	1.37	1.07	0.96	0.85
p-Di-(*tert.*-butyl)benzene	1.62	1.47	1.35	1.08	0.96	0.86
2-Biphenylol	0.50	0.27	0.22	0.1	−0.1	−0.2
4-Biphenylol	0.48	0.31	0.23	0.05	0.0	−0.1
2,2'-Biphenyldiol	0.11	0.0	−0.1	−0.3	−0.4	–
4,4'-Biphenyldiol	0.0	−0.1	−0.3	−0.5	−0.5	–
2-Chloro-4-biphenylol	0.80	0.62	0.52	0.33	0.22	0.14
3-Chloro-4-biphenylol	0.78	0.62	0.52	0.34	0.22	0.15
4-Chloro-4'-biphenylol	0.84	0.66	0.55	0.39	0.27	0.14
3-Chloro-2-biphenylol	0.64	0.50	0.42	0.22	0.14	0.04

Figs. 1 and 2 show the variation of corrected retention volume with temperature and solvent composition. Linear plots of free energy of retention against volume fraction of the solvent are common with methanol–water mixtures and are observed here. The lines for the hydrocarbons (Fig. 1; *p*-di-*tert.*-butylbenzene gives a similar graph) converge as the methanol concentration rises, indicating that the enthalpy of sorption falls. Enthalpies calculated from the graphs are shown in Table II. For the hydrocarbons, the enthalpy changes with solvent composition to about the same extent as does the free energy, showing the absence of any large entropy effects. This

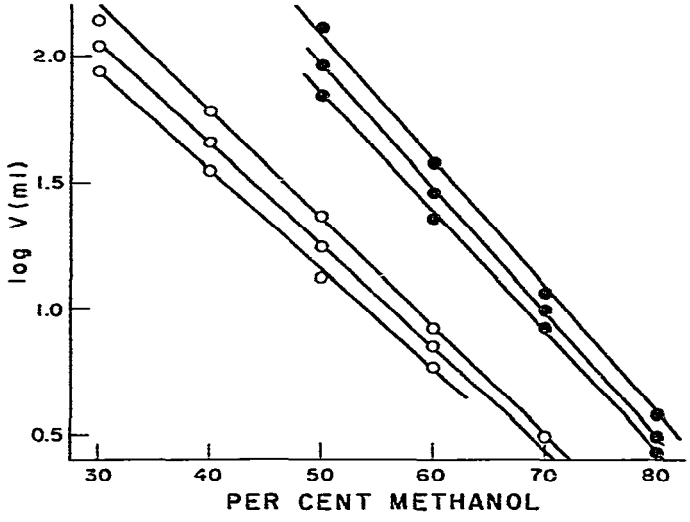

Fig. 1. Corrected retention volumes of *p*-di-*tert.*-butyl benzene (closed circles) and biphenyl (open circles), at temperatures 23 (upper line), 35 and 45°C (lower line). Volumes were read to ±0.1 ml.

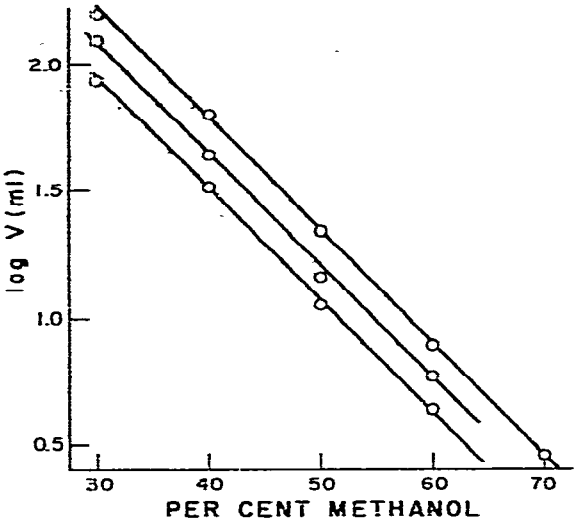

Fig. 2. Corrected retention volumes of 4-chloro-4′-biphenylol at 23, 35 and 45°C.

TABLE II

ENTHALPY OF SORPTION ON C_{18}-SILICA

Compound	*Methanol (%)*	*ΔH (cal/mole)*
Biphenyl	30	4200
	60	2100
Terphenyl	50	5300
	80	2900
Di-*tert.*-butylbenzene	50	4100
	80	2900
4-Chloro-4′-biphenylol	30	4000
	60	4000

is not the case with the phenolic compounds. Fig. 2 indicates that the enthalpy of sorption of 4-chloro-4′-biphenylol does not change with methanol concentration, yet the free energy of sorption changes substantially. A similar effect is seen with the other phenols. Evidently hydrogen bonding causes significant entropy changes. It is difficult to make precise thermodynamic deductions with materials as ill-defined as bonded silica absorbents, but it would be interesting to examine this effect further.

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