CHROM. 13,058

Note

Study of the interactions between substituted phenols and alcohols and dibenzyl sulphoxide by means of gas chromatography

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(First received May 12th, 1980; revised manuscript received June 19th, 1980)

It is well established that gas chromatography is useful for the study of the molecular interactions and properties of dilute solutions. Also, in a chromatographic system with mixed stationary phases the molecular interactions can be used to improve the separation efficiency of the column. However, independently of whether gas chromatography is competitive with the more popular spectroscopic methods, it is obvious that the standard states must be very carefuly defined[1-6].

The aim of this work was to study specific interactions in the column with benzyldiphenyl and dibenzyl sulphoxide as the stationary phase and different phenols and alcohols as injected samples. The thermodynamic studies are based on the direct correlation between retention times and partition coefficients[7-10]. For a simple 1:1 association

$$A + B \rightleftharpoons AB \tag{1}$$

the partition coefficient, K_R, of a solute between a mixed stationary phase in which the concentration of the active component (A) is X_A may be written as

$$v_{A,S}^0 K_R = v_S^0 K_R^0 [1 + (\varphi + K^*) X_A] \tag{2}$$

where K_R^0 is the partition coefficient of B in the pure solvent S. $v_{A,S}$ is the molar volume of the solution A and S, so that the molar volume varies linearly with the molar fraction. φ is a factor comprising different molar volumes of a solvent, a solute and an additive, A, and is given by the equation

$$\varphi = \frac{v_A^0}{v_S^0} \cdot \frac{\exp v_B^0/v_A^0}{\exp v_B^0/v_S^0} - 1 \tag{3}$$

where v_S^0 and v_A^0 are molar volumes of pure S and A, respectively. The equilibrium constant, K^*, in eqn. 2 depends on the solvent and can therefore be defined as

$$K^* = \frac{X_{AB}}{X_A X_B} \cdot \frac{\gamma_{AB}^*}{\gamma_A^* \gamma_B^*} \tag{4}$$

The activity coefficient, γ_i^*, of the ith component is defined as $\gamma_i^* \to 1$ as $X_i \to 0$.

From the linear relationship between $v_{A,S}^0 K_R$ and X_A (eqn. 2), the equilibrium constant, K^*, can be determined.

EXPERIMENTAL

All measurements were performed on a Varian 1860 gas chromatograph with a flame-ionization detector. Stainless-steel columns loaded with packing containing 20% of liquid phase were used. The exact amount of liquid phase was determined by a combustion method. The concentration (molar fraction) of dibenzyl sulphoxide (DBSO) in benzyldiphenyl (BDP) varied from 0.00 to 0.25. Measurements were carried out at 363, 373, 383 and 393°K. The true temperature of the column was measured with a precision of $\pm 0.2°K$. A thermocouple (copper–constantan) was introduced into the oven and the temperature was measured with a potentiometer.

The sample sizes were in the range $0.1–0.2$ mm^3. Within this limit we could not observe any dependence of retention time on the amount of sample. The peaks were symmetrical, so the well known methods were used for the evaluation of specific retention data. As the solutes were solid at room temperature, they were first dissolved in diethyl ether. In all instances on-column injection was employed. Argon was used as the carrier gas at a flow-rate of 60 cm^3/min. The flow-rate was measured with a bubble flow meter at the working temperature.

TABLE I

$K_R v_{A,s}^0$ VALUES OF PHENOLS WITH THE SYSTEM OF DBSO IN BDP (dm^3)

Solute	X_A											
	363°K						373°K					
	0.00	0.05	0.10	0.15	0.20	0.25	0.00	0.05	0.10	0.15	0.20	0.25
Phenol	376	648	—	904	—	1213	217	308	—	683	—	680
2-Methylphenol	684	988	—	1796	—	2190	356	440	—	898	—	933
4-Methylphenol	766	1245	—	1847	—	2720	451	608	—	1228	—	1342
2-Ethylphenol	1534	2662	3329	4362	5201	6101	1050	1707	2202	2782	3436	3902
3-Ethylphenol	—	—	—	—	—	—	1558	2710	3626	4526	6125	7518
2-Chlorophenol	485	705	1076	1262	1555	1857	359	520	786	831	1095	1260
2-Fluorophenol	169	307	471	663	808	920	124	231	358	455	573	703
3-Fluorophenol	519	1570	2600	4025	5118	6017	374	1019	1674	2606	3326	4148

TABLE II

$K_R v_{A,s}^0$ VALUES OF n-ALCOHOLS WITH THE SYSTEM OF DBSO IN BDP (dm^3)

Solute	X_A											
	363°K						373°K					
	0.00	0.05	0.10	0.15	0.20	0.25	0.00	0.05	0.10	0.15	0.20	0.25
Ethanol	6.6	7.3	7.5	8.2	8.4	9.0	6.8	7.4	7.7	7.9	8.6	9.0
n-Propanol	14	15	16	17	19	20	13	14	14	16	16	18
n-Butanol	27	28	32	34	39	36	23	28	26	28	31	35
n-Pentanol	44	48	53	57	63	56	37	42	43	44	50	55
n-Hexanol	94	86	119	130	159	149	76	86	85	89	110	116
n-Heptanol	234	247	259	281	300	313	168	177	189	183	208	219
n-Octanol	556	604	597	663	688	720	372	426	382	406	486	478
n-Nonanol	1200	1239	1305	1333	1451	1465	777	863	860	825	963	934
n-Decanol	2577	2737	2854	3002	3166	3344	1713	1815	1869	1985	2051	2125

RESULTS AND DISCUSSION

The specific retention volumes of phenols and n-alcohols on the column of benzyldiphenyl and on the column of benzyldiphenyl plus different concentrations of dibenzyl sulphoxide were measured at four temperatures. Also, the products of the molar volumes and partition coefficients, $K_R v_{A,s}$, for all solutes were determined. Tables I and II show the results for phenols and n-alcohols. It can be seen that $K_R v_{A,s}$ increases with increasing concentration of the active additive.

The data in Table I show that specific interactions between the polar sample and the stationary phase have a considerable influence on the retention volumes. Thus, for a sample with known composition the separation of components can be improved by using a combined stationary phase. In this instance specific interactions have to exist only with components of immediate interest.

However, the data given in Table II demonstrate that the main reason for the greater specific retention volumes at greater molar fraction of the active additive under the conditions given is the chain length of alcohols and not the specific interaction.

383°K						393°K					
0.00	0.05	0.10	0.15	0.20	0.25	0.00	0.05	0.10	0.15	0.20	0.25
160	177	—	364	—	481	63	122	—	—	—	183
184	259	—	441	—	533	99	105	—	—	—	306
224	349	—	479	—	690	118	212	—	—	—	346
723	932	1505	1804	2188	2545	428	580	870	1057	1557	1629
1025	1670	2579	2829	3753	4326	603	861	1328	1615	1951	2301
246	343	516	580	685	843	164	202	287	381	475	570
95	158	249	307	362	480	65	94	154	213	267	328
275	604	1255	1532	2032	2678	171	326	780	788	1412	1535

383°K						393°K					
0.00	0.05	0.10	0.15	0.20	0.25	0.00	0.05	0.10	0.15	0.20	0.25
6.7	7.1	7.0	8.0	8.5	8.6	6.8	7.2	7.4	8.0	8.1	8.5
10	11	11	12	13	13	9.9	11	11	11	12	13
18	20	22	22	23	25	13	15	15	15	18	18
27	30	32	32	36	37	22	24	25	26	30	31
52	62	58	65	80	77	41	40	46	47	59	58
102	102	114	127	127	130	90	100	90	97	110	115
255	271	289	262	325	320	181	184	173	213	216	216
427	470	495	531	491	528	353	407	345	346	421	410
955	1022	998	1056	1160	1170	703	737	779	769	817	820

The plots of $K_R v_{A,S}^0$ versus X_A for 2-fluorophenol are shown in Fig. 1, and are straight lines, in agreement with our prediction that only the 1:1 complex can be formed.
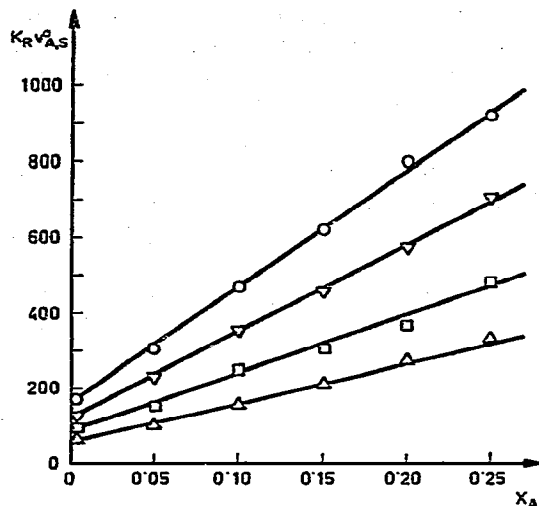

Fig. 1. Graph of $K_R v_{A,S}^0$ versus X_A for 2-fluorophenol on the column of DBSO in BDP. O, 363°K; △, 373°K; □, 383°K; △, 393°K.

From these lines, the equilibrium constants, K^*, are derived, and the results for n-alcohols and phenols are given in Tables III and IV. The values in Table III are of the same order of magnitude and as the relationships between the retention values of two neighbours are also virtually identical, it can be concluded that specific interactions between the alcohols and dibenzyl sulphoxide have no significant influence on retention values.

It follows from Table IV that the equilibrium constants for phenols are higher than those for n-alcohols. The equilibrium constant demonstrates the influence of the additive added to the stationary phase on the retention value. It is instructive to

TABLE III

VALUES OF K^* FOR n-ALCOHOLS WITH THE SYSTEM OF DBSO IN BDP

Sample	K^*			
	363°K	373°K	383°K	393°K
Ethanol	1.61	1.45	1.31	1.18
n-Propanol	1.94	1.69	1.50	1.33
n-Butanol	2.08	1.88	1.75	1.68
n-Pentanol	2.15	1.93	1.80	1.66
n-Hexanol	2.43	2.20	2.03	1.83
n-Heptanol	1.44	1.31	1.20	1.10
n-Octanol	1.25	1.21	1.10	1.04
n-Nonanol	0.94	0.86	0.76	0.71
n-Decanol	1.18	1.05	0.94	0.87

TABLE IV

VALUES OF K^* FOR PHENOLS WITH THE SYSTEM OF DBSO IN BDP

Sample	K^*			
	$363°K$	$373°K$	$383°K$	$393°K$
Phenol	9.25	8.67	8.16	7.78
2-Methylphenol	8.94	8.02	7.70	7.02
4-Methylphenol	10.32	9.26	8.46	7.82
2-Ethylphenol	11.62	11.10	10.39	9.93
3-Ethylphenol	—	12.81	11.84	11.29
2-Chlorophenol	11.15	10.37	9.54	8.92
2-Fluorophenol	20.22	18.29	16.37	15.23
3-Fluorophenol	44.41	39.55	35.12	32.02

compare o-chlorophenol and m-fluorophenol, the $K_R v^0_{A,S}$ values of which on pure benzyldiphenyl are virtually identical, but the difference in the equilibrium constant at 363°K is 33.26. The reason for the lower values for ortho substituents is that they can form intramolecular hydrogen bonds, whereas meta and para substituents cannot.

In conclusion, it has been shown that the specific interactions between a polar sample and the stationary phase can influence the retention parameters. The equilibrium constants can be determined from partition coefficients. The greater the equilibrium constant, the greater is the effect of specific interactions on the resolution of the components.

ACKNOWLEDGEMENTS

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