

Short Communication

Studies on the retention and thermodynamic properties of aromatic compounds on two types of crown ether polysiloxane stationary phase

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(First received March 29th, 1993; revised manuscript received July 5th, 1993)

ABSTRACT

We separated 37 aromatic compounds, including twelve groups of positional isomers, on two new types of crown ether polysiloxane, di(*tert.*-butylbenzo)-propyl-15-crown-5 polysiloxane (PSO-DTB-3-15C5) and dibenzopropyl-15-crown-5 polysiloxane (PSO-DB-3-15C5). It is shown that when these new crown ethers polysiloxanes are used as stationary phases in capillary column gas chromatography they possess excellent chromatographic properties and are unique in the separation of some polar aromatic positional isomers, especially phenols and nitro compounds. The mechanism and retention are discussed by measuring various thermodynamic parameters: the enthalpy of solution, ΔH , the entropy of solution, ΔS , the free energy of solution, ΔG , and differences in ΔH [$\Delta(\Delta H)$] and ΔS [$\Delta(\Delta S)$]. The results were compared with those obtained on OV-1701 and PEG 20M GC columns.

INTRODUCTION

It is well known that crown ethers are useful chromatographic stationary phases because of their high chemical stability and good selectivity [1–4] resulting from the cavity structure and the strong electronegative effect of heteroatoms on the crown ether ring. The polymeric crown ether stationary phases (PCSPs) are superior to small molecule crown ethers, because the latter have poor thermal stability and are associated with poor column efficiency, coating difficulty and column bleeding at high temperature, while the

former may alleviate some of these problems. In recent years, many polymeric crown ethers have been used in GC, and their chromatographic properties have been studied [5–10].

We coated fused-silica capillaries with two new types of crown ether and demonstrated excellent chromatographic properties, such as a wide range of operating temperature, high column efficiency, good thermal stability and unique selectivity in the separation of some polar aromatic positional isomers, especially phenols and nitro compounds. In order to study the retention and separation mechanism of these PCSPs, thermodynamic parameters of solution, the enthalpy of solution (ΔH), the entropy of solution (ΔS), the free energy of solution (ΔG) and the differences in ΔH [$\Delta(\Delta H)$] and ΔS [$\Delta(\Delta S)$] were

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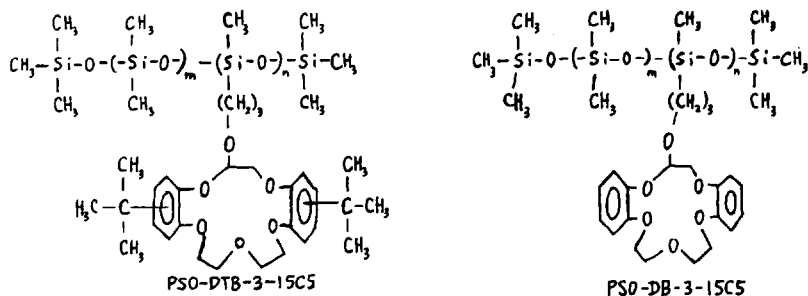


Fig. 1. Structures of the crown ether polysiloxanes used in this study.

measured. The last two parameters are independent of column temperature: $\Delta(\Delta H)$ and $\Delta(\Delta S)$ reflect the forces of interaction and the goodness of fit of solute molecules within the cavity of the crown ether. Thirty-seven aromatic compounds can be separated on these two new PCSPs between 90 and 240°C.

Theoretical

Two well-known equations can be applied. First:

$$\ln k' = \frac{-\Delta H}{R} \cdot \frac{1}{T} + \frac{\Delta S}{R} - \ln \beta \quad (1)$$

The slope $\Delta H/R$ and the intercept $(\Delta S/R - \ln \beta)$ of the graph of $\ln k'$ against $1/T$ were calculated by the least-squares method from at least five measurements within the temperature range 90–240°C. Solution enthalpy, ΔH , is the measure of the forces of interaction between solute molecules and stationary phase; solution entropy, ΔS , reveals the degree of mixing of the solute molecules and stationary phase. Second:

$$\begin{aligned} \ln \alpha &= \frac{-(\Delta H_1 - \Delta H_2)}{RT} + \frac{\Delta S_1 - \Delta S_2}{R} \\ &= \frac{-\Delta(\Delta H)}{RT} + \frac{\Delta(\Delta S)}{R} \end{aligned} \quad (2)$$

Here the difference in the enthalpy of solution, $\Delta(\Delta H)$, and the difference in the entropy of solution, $\Delta(\Delta S)$, were calculated by the least-squares method, as in eqn. 1.

EXPERIMENTAL

Instrumentation

An SC-7 gas chromatograph (Sichuan Analytical Apparatus Plants, Sichuan, China) equipped with a capillary split injection system and a flame ionization detector was used.

Gas chromatographic procedure

PSO-DTB-3-15C5 and PSO-DB-3-15C5 were prepared by hydrosilylation as previously described [2]. Their structures are shown in Fig. 1 and their chromatographic properties are listed in Table I.

The carrier gas was nitrogen at a linear velocity of 12–15 cm/s. The injector temperature was maintained at 250–280°C and the detector temperature was held at 280°C. A split ratio of 100:1 was used throughout. The retention time (t_R) of all aromatic compounds and the separation factor (α) of all isomeric pairs were measured at 10°C intervals in the temperature range

TABLE I
CHROMATOGRAPHIC PROPERTIES OF THE CROWN ETHER POLYSILOXANES USED IN THIS STUDY

Stationary phase	Column No.	Column dimensions: length (m) × I.D. (mm)	Column efficiency (plates/m)	Capacity factor (k')	Peak asymmetry
PSO-DTB-3-15C5	1	9 × 0.25	4500	3.63	1.05
	2	14.5 × 0.25	4590	5.01	1.03
PSO-DB-3-15C5	1	14 × 0.25	4443	3.8	1.05
	2	14.5 × 0.25	5206	4.98	1.01

TABLE II

THE VALUES OF ΔH , ΔS AND ΔG ON PCSPs, OV-1701 AND PEG 20MUnits: $\Delta H = \text{kJ/mol}$; $\Delta S = \text{J/mol/K}$; $\Delta G = \text{kJ/mol}$.

Elution order	PSO-DTB-3-15CS			PSO-DB-3-15CS			OV-1701			PEG-20M		
	$-\Delta H$	$-\Delta S$	$-\Delta G$	$-\Delta H$	$-\Delta S$	$-\Delta G$	$-\Delta H$	$-\Delta S$	$-\Delta G$	$-\Delta H$	$-\Delta S$	$-\Delta G$
Dichlorobenzene	<i>p</i>	42.15	103.76	3.448	39.69	(<i>m</i>) 100.58	2.174	(<i>m</i>) 36.71	(<i>m</i>) 49.53	18.24	(<i>m</i>) 41.33	19.96
	<i>o</i>	41.92	102.68	3.620	41.00	(<i>p</i>) 103.17	2.518	(<i>p</i>) 37.54	(<i>p</i>) 51.18	18.45	(<i>p</i>) 42.17	20.46
	<i>m</i>	43.12	103.93	3.354	41.86	(<i>o</i>) 103.24	3.351	(<i>o</i>) 38.25	(<i>o</i>) 51.40	19.08	(<i>o</i>) 42.64	21.15
Cresol	<i>o</i>	55.26	128.12	7.471	53.71	123.21	7.753				57.35	(<i>m</i>) 75.58
	<i>m</i>	57.59	131.69	8.470	55.49	(<i>p</i>) 125.18	8.798	(<i>p</i>) 45.70	64.91	21.49	59.29	(<i>p</i>) 77.49
	<i>p</i>	57.91	132.11	8.633	55.37	(<i>m</i>) 124.51	8.928	(<i>m</i>) 47.26	67.08	22.24	59.17	(<i>o</i>) 76.91
Nitrochlorobenzene	<i>m</i>	51.41	112.49	9.451	47.50	102.51	9.264	45.87	59.48	23.68	50.71	62.86
	<i>p</i>	51.62	112.07	9.818	48.23	103.18	9.744	45.94	59.15	23.88	51.63	63.77
	<i>o</i>	52.24	112.90	10.13	49.35	104.59	10.34	46.97	60.37	24.45	53.22	65.40
Dinitrobenzene	<i>o</i>	59.12	116.89	15.52	66.19	130.20	17.63	53.49	66.27	28.77	52.43	52.80
	<i>m</i>	60.92	120.14	16.11	67.53	132.36	18.16	54.31	67.04	29.30	52.94	53.45
	<i>p</i>	59.63	116.06	16.34	68.51	132.53	19.08	55.82	68.16	30.39	57.58	59.20
Methylnaphthalene	β	50.12	109.25	9.370	48.03	104.67	8.988	45.99	59.04	23.97	48.05	58.24
	α	51.44	111.16	9.977	48.58	104.59	9.568	46.47	59.43	24.30	49.63	58.50
Quindine	<i>n</i>	49.16	107.00	9.249	49.08	105.92	9.572	45.24	58.10	23.57	48.90	57.82
	Iso	49.13	105.59	9.745	50.38	107.75	10.19	45.92	58.53	24.09	49.84	58.87
Anthracene phenanthrene	an-	62.50	116.15	19.18	67.79	(<i>ph</i>) 126.71	20.53	(<i>ph</i>) 55.71	63.07	(<i>ph</i>) 32.19		
	ph-	62.89	116.56	19.41	67.96	126.79	20.67	56.13	63.69	32.37		
Nitrotoluene	<i>m</i>	50.38	109.58	9.507	50.49	109.83	9.523	38.38	45.62	(<i>o</i>) 21.36		
	<i>p</i>	50.65	109.41	9.840	50.96	109.83	9.993	39.79	47.06	(<i>m</i>) 22.24		
	<i>o</i>	51.39	110.49	10.18	52.37	111.99	10.60	41.28	49.45	(<i>p</i>) 22.83		
Dinitrotoluene	3,4-	43.50	97.77	7.032	41.52	94.03	6.447	53.22	(2, 6) 65.42	(2, 6) 28.82		
	2,3-	46.11	100.93	8.463	45.80	100.52	8.306	54.13	(2, 5) 65.85	(2, 5) 29.56		
	2,6-	58.37	116.31	14.99	58.76	116.35	15.36	55.18	(2, 4) 66.42	(2, 4) 30.40		
	2,5-	61.31	120.55	16.34	61.83	120.54	16.87	56.44	(3, 5) 68.36	(3, 5) 30.94		
	2,4-	61.38	118.47	17.19	62.59	119.97	17.84	57.98	(3, 4) 68.88	(3, 4) 32.29		
3,5-	62.44	120.30	17.57	63.12	120.54	18.16						
Phenyl dihydroxide	<i>o</i>	61.27	126.87	13.95	59.98	123.13	14.05					
	<i>p</i>	65.93	133.77	16.03	67.53	133.27	17.82					
	<i>m</i>	69.03	139.01	17.18	69.30	135.85	18.63					
Tetrahydronaphthalene		46.77	109.08	6.083	42.55	101.16	4.817					
		40.33	97.94	3.798	40.62	99.73	3.421					
Triphenylisomer	<i>o</i>	57.09	105.75	17.65	74.66	143.17	21.26					
	<i>m</i>	64.67	111.99	22.90	77.04	137.01	25.94					
	<i>p</i>	64.13	109.25	23.38	77.79	136.68	26.81					
Decahydronaphthalene	<i>trans</i>	40.69	102.26	2.547	36.47	97.77	-0.0018					
	<i>cis</i>	41.97	103.09	3.517	36.79	95.94	1.004					

90–240°C and at least five data points were obtained for each compound. Correlation coefficients of $\ln k'$ versus $1/T$ plots were higher than 0.99. Solution free energy (ΔG) values at 373K were calculated.

RESULTS AND DISCUSSION

Table II shows that the size of the ΔG values agrees with the retention order of isomers. Aromatic compounds are well separated on the

two new PCSP columns, while their ΔG values are smaller than those on OV-1701 and polyethylene glycol (PEG) 20M; hence, the two new PCSP columns produce smaller retention times for the same compounds than PEG-20M. The range of ΔG values on PSO-DB-3-15C5 is larger than on PSO-DTB-3-15C5, resulting in better separation of the isomers on PSO-DB-3-15C5.

Table II also shows that 3,4-DNT and 2,3-DNP are well separated on the two new PCSP columns, but they cannot be separated on OV-

TABLE III

THE VALUES OF $\Delta(\Delta H)$ AND $\Delta(\Delta S)$ ON PCSPs, OV-1701 AND PEG-20M

Units: $\Delta(\Delta H)$ = kJ/mol; $\Delta(\Delta S)$ = J/mol/K.

		PSO-DTB-3-15C5		PSO-DB-3-15C5		OV-1701		PEG-20M	
		$\Delta(\Delta H)$	$\Delta(\Delta S)$	$\Delta(\Delta H)$	$\Delta(\Delta S)$	$\Delta(\Delta H)$	$\Delta(\Delta S)$	$\Delta(\Delta H)$	$\Delta(\Delta S)$
Dichlorobenzene	<i>o/p</i>	0.2314 ^a	1.116 ^a	-1.309 (<i>p/m</i>)	-2.572 (<i>p/m</i>)				
	<i>m/p</i>	-0.9727	-0.167	-2.158 (<i>o/m</i>)	-2.634 (<i>o/m</i>)				
Cresol	<i>m/o</i>	-2.327	-3.552	-1.784 (<i>p/o</i>)	-1.985 (<i>p/o</i>)	-1.561	2.1656	-1.819	1.330
	<i>p/o</i>	2.641	-3.961	-1.664 (<i>m/o</i>)	-1.299 (<i>m/o</i>)			0.120	-0.576
Nitrochlorobenzene	<i>p/m</i>	-0.2148 ^a	0.4110 ^a	-0.7481	-0.6963	0.071	0.339	0.920	-0.915
	<i>o/m</i>	-0.8267	-0.3654	-1.845	-2.074	1.100	-0.887	2.513	2.629
Dinitrobenzene	<i>m/o</i>	-1.778	-3.168	-1.346	-2.192	0.820	-0.770	0.509	-0.651
	<i>p/o</i>	-0.5057 ^a	0.8572 ^a	-2.323	-2.295	2.327	-1.887	5.144	-6.398
Methylnaphthalene	α/β	-1.625	-2.635	-0.5729 ^a	0.09677 ^a	0.481	-0.39	0.584	-0.259
Quindine	<i>iso/n</i>	0.1784 ^a	1.299 ^a	-1.260	-1.680	0.682	-0.436	0.944	-1.047
Anthracene phenanthrene	<i>ph/an</i>	-0.3649	-0.4322	-0.2142 (<i>an/ph</i>)	-0.193 (<i>an/ph</i>)				
Nitrotoluene	<i>p/m</i>	-0.3524 ^a	0.1379 ^a	-0.8089	-0.8230				
	<i>o/m</i>	-1.093	-0.9212	-1.971 ^a	-2.591 ^a				
Dinitrotoluene	2,3/3,4	-2.614 ^a	-3.203 ^a	-4.294	-6.537				
	2,6/3,4	-16.69	-22.65	-17.27	-22.41				
	2,5/3,4	-19.63	-26.93	-19.52	-24.87				
	2,4/3,4	-19.68	-24.80	-21.08	-26.01				
	3,5/3,4	-20.74	-26.60	-21.55	-26.43				
Phenyl dihydroxide	<i>p/o</i>	-5.160	-6.934	-7.597	-10.29				
	<i>m/o</i>	-8.251	-12.10	-9.262	-12.61				
Decahydronaphthalene	<i>cis</i>	-1.304	-0.8846	-0.3097	1.904				
	<i>trans</i>								
Diphenylbenzene	<i>m/o</i>	-7.560	-6.242	-0.471 ^a	11.04 ^a				
	<i>p/o</i>	-7.119	-3.732	-0.8229 ^a	11.33 ^a				

^a The correlation coefficient is less than 0.6.

1701 and PEG 20M. *o*-Cresol and *p*-cresol cannot be separated on OV-1701 but are separated on PEG 20M. They can be even better resolved on the two new PCSPs.

The retention of solute on the PCSPs depends mainly on hydrogen bonds formed by the high electron cloud density on the crown ether ring, the fit of the solute molecules within the crown ether cavity and dipole–dipole interaction between isomeric analytes and PCSPs. Both ΔH and ΔS contribute to the retention order of positional isomers. The ΔS values on the two new PCSPs show small differences, and all are larger, more than 40–80 J/mol·K larger, than on OV-1701 and PEG 20M columns and 20–40 J/mol·K larger than on PSOB-3-18C6 [11]. This shows that the steric hindrance due to the crown ether moiety is greater. From Table II we know that the ΔH values of positional isomers, which do not form hydrogen bonds, are similar, while the ΔH values of cresol isomers, which can form hydrogen bonds with PCSPs and PEG-20M, give values which are about 10 kJ/mol higher than on OV-1701.

From Table III, the $\Delta(\Delta H)$ values of all isomers are larger than on the OV-1701 column, hence the PCSPs are more effective for the separation of isomers. Most $\Delta(\Delta H)$ values on PSO-DB-3-15C5 are higher than for the same compounds on PSO-DTB-3-15C5.

For fifteen pairs of isomers the correlation coefficients of $\ln \alpha$ versus $1/T$ plots are higher than 0.9 on the PSO-DTB-3-15C5 column. The same is true of the PSO-DB-3-15C5 column. For six pairs of isomers on the PSO-DTB-3-15C5 column and four pairs of isomers on the PSO-DB-3-15C5 column, the correlation coefficients of $\ln \alpha$ versus $1/T$ plots are smaller than 0.6. The results show that the plots of $\ln \alpha$ versus $1/T$ of these compounds are non-linear and that the influence of temperature on these isomers is not the same. These isomers are *o/p*-dichlorobenzene, *p/m*-nitrochlorobenzene, *p/o*-dinitrobenzene, *n/iso*-quinidine, *p/o*-nitrotoluene and 2,3/3,4-dinitrotoluene on PSO-DTB-3-15C5 and α/β -methylnaphthalene, *o/m*-nitrotoluene, *m/o*-

diphenylbenzene and *p/o*-diphenylbenzene on PSO-DB-3-15C5.

The graphs of $\ln k'$ against $1/T$ on the PCSPs clearly show that the separation efficiency of aromatic compounds on PSO-DB-3-15C5 is better than on PSO-DTB-15C5. The optimum temperature range is 200–210°C, at which temperatures seventeen aromatic compounds can be separated. If two compounds have a point of intersection, this indicates that these two compounds cannot be separated at this temperature. There are many points of intersection in the temperature range 130–170°C.

CONCLUSIONS

Two new PCSPs exhibit good chromatographic properties and high selectivity for aromatic compounds. Solution thermodynamic parameters show that hydrogen bonding forces and dipole forces caused by the high electron density of the crown ether ring are the main cause of the separation. Both ΔH and ΔS contribute to the retention order of positional isomers.

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