Preparation and capillary column gas chromatographic characterization of aza-crown ether polysiloxane stationary phases

Caiying Wu*, Jinshong Cheng, Wenhui Gao☆, Zaorui Zeng, Xueran Lu and Shulin Gong

Chemistry Department, Wuhan University, Wuhan 430072, Hubei Province (China)

ABSTRACT

Two new kinds of aza-crown ethers, ω-undecylene aza-18-crown-6 polysiloxane (PUAC-18-C-6) and ω-undecylene aza-15-crown-5 polysiloxane (PUAC-15-C-5), were synthesized for use as stationary phases in capillary column gas chromatography. These two stationary phases demonstrate high column efficiency, a wide operating temperature range, good thermal stability, medium polarity and excellent selectivity for *n*-alcohols, esters and aromatic compounds, similarly to ω-undecyloxymethyl-18-crown-6 polysiloxane phase (PSO-11-18-C-6), and they have unique characteristics which are responsible for the success of separating aniline and other basic compounds without derivatization. The factors which affect the separation mechanism, including dipole–dipole interactions, hydrogen-bonding forces and fitting of solute molecules in the crown ether cavity, are discussed.

INTRODUCTION

Crown ethers are becoming increasingly important as stationary phases in gas chromatography (GC) owing to the cavity structure and the strong electronegative effect of heteroatoms on the crown ether ring [1–4]; especially polymeric crown ethers are suitable for this purpose because of their ease of coating on capillary columns and their high column efficiency, wide operating temperature and good thermal stability [5–8], and they can also be used in temperature-programmed work.

In 1988, Rouse *et al.* [5] first synthesized a crown ether-substituted polysiloane with a polymer spacing of three methylene groups, which showed unique selectivity for nitrogen-containing polycyclic aromatic compounds. In recent work [6–8], we developed PSO-11-18-C-6 substituted polysiloxane

with a polymer spacing of 11 methylene groups, which is convenient for cross-linking on fused-silica capillary columns with aza-*tert*.-butane (ATB) and dicumyl peroxide (DCUP) [6,7]. We also introduced another new method for preparing crown ether polysiloxane stationary phases by direct cross-linking a crown ether with SE-54 in different proportions inside a column [8]. We succeeded in separating aromatic compounds and their derivatives, phenols and their isomers, ethyl-substituted diphenyl ketone isomeric mixtures, etc.

In this work, two new kinds of aza-crown ether, ω-undecylene aza-18-crown-6 and ω-undecylene aza-15-C-5, were substituted on a polysiloxane backbone to yield two stationary phases for capillary GC (Fig. 1). The tertiary nitrogen atom in the crown ether ring makes these two polymeric stationary phases basic, and they were expected to have strong abilities for separating anilines and other basic compounds without derivatization; these compounds are difficult to separate by GC.

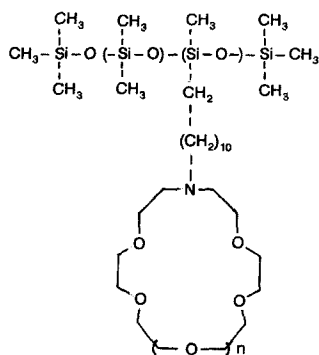☆ Present address: Hebei Chemical and Light Engineering Institute, Hebai, China.

Fig. 1. Structure of the aza-crown ethers: $n = 0$, PUAC-15-C-5; $n = 1$, PUAC-18-C-6.

EXPERIMENTAL

Syntheses

The two aza-crown ether polymers were synthesized with a hydrosilylation technique [9]. ω-Undecylene aza-18-C-6 and ω-undecylene aza-15-C-5 were obtained from the Department of Chemistry, Polymeric Major, Wuhan University, China. These starting materials were both purified by passing them through a silica gel G column, using in order pure chloroform, ethyl acetate, acetone and ethanol as eluents. Polymethylhydrosiloxane (40%) was obtained from Xing Huo Chemical Plant, Jiang Xi Province, China.

Synthesis of ω-undecylamine aza-18-crown-6polysiloxane (PUAC-18-C-6). Purified ω-undecylene aza-18-C-6 (0.35 g) and 0.06 g of 40% polymethylhydrosiloxane were mixed in 5 ml of pure benzene and the mixture was heated at 90°C for 1 h in a three-necked flask under an argon atmosphere. A 10-μl volume of chloroplatinic acid solution (1% $H_2PtCl_6 \cdot 6H_1O$, 1% ethanol and 98% tetrahydrofuran) was then added to the mixture, and the reaction was nearly completed after 16 h, when the products became viscous, as measured by the remaining Si–H band in the IR spectrum. A 1-ml volume of n-decylene was then added to the mixture to react with all of the residual Si–H units under the same conditions as above, and after 1 h the mixture was allowed to cool, the gummy product was dissolved in 2 ml of dichloromethane and precipitated with 10 ml of methanol–water (1:1). The precipitate was centrifuged and the solvents were

decanted. The process of precipitation with aqueous methanol was repeated seven more times to remove the catalyst. The product (0.4 g), a yellow gum, was dried overnight under reduced pressure.

Synthesis of ω-undecylamine aza-15-crown-5polysiloxane (PUAC-15-C-5). The synthesis of PUAC-15-C-5 was similar to that for PUAC-18-C-6, except that the weight of polymethylhydrosiloxane was 0.12 g and that of purified ω-undecylene aza-15-C-5 was 0.59.

Column preparation

Fused-silica capillary columns (Yong Nian Optical Fibre Factory, Hebei Province, China) were rinsed with 10 ml of methanol and purged with nitrogen at 250°C for 2 h to remove acidic impurities. The columns were then statically coated with a solution of 0.4–0.6% (w/v) PUAC-15-C-5 or PUAC-18-C-6 in dichloromethane at 30°C. Following the coating procedure and flushing with nitrogen for 3 h, the columns were conditioned at 280°C for 10 h under a slow flow of nitrogen before use.

Column evaluation

An Sc-7 gas chromatograph (Sichuan Analytical Apparatus Plant, Sichuan, China) equipped with a capillary split injection system and flame ionization detector was used throughout. Nitrogen was the carrier gas at a linear velocity of 12–15 cm/s. Solutes (0.5 μl) were injected using the split mode (80:1) and the injector and detector temperatures were maintained at 250 and 280°C, respectively.

The efficiency of the columns was determined as the number of plates per metre for naphthalene at 120°C. The polarity of the stationary phases was characterized by the McReynold's constants and A values (the slope of the graph obtained when the logarithm of the adjusted retention times of n-alkanes is plotted as a function of the number of carbon atoms at 170°C). The A value represents only dispersion forces, but the McReynold's constants include dispersion forces, dipole–dipole forces, hydrogen-bonding forces, etc. The glass transition temperature was determined by the change in slope of the plot of the logarithm of capacity factor *versus* reciprocal absolute temperature for naphthalene. Some standard mixtures of alcohols, normal fatty acid methyl esters and aromatic hydrocarbons and also some polar positional isomers were used to

demonstrate the unique selectivity of these two stationary phases. The thermal stabilities of these two stationary phases were tested by measuring column bleeding; after measuring column bleeding, the column efficiency remain unchanged and the column capacity factors had decreased by 3–5%.

RESULTS AND DISCUSSION

PUAC-15-C-5 and PUAC-18-C-6 have a non-polar polysiloxane chain, a long aliphatic spacer arm and a polar crown ether ring, with a tertiary nitrogen atom in the polar crown ether ring. They are predicted to have good film-forming ability and high thermal stability [10] and a unique selectivity for aniline compounds.

Table I shows the characteristics of these two crown ether capillary columns. The data indicate that the columns have an efficiency above 3850 plates/m, decreasing slightly with increase in film thickness. The coating efficiencies are more than 81% and the reproducibility is good. The peak-area ratio of acidic 2,6-dimethylphenol and basic 2,4-dimethylaniline between 0.32 and 0.43 indicates that these two stationary phases exhibit basic properties. The peak asymmetry factors for octanol on the fused-silica columns are close to 1.0, indicating that

the aza-crown ether polysiloxanes possess the good film-forming ability.

Fig. 2 shows chromatograms for the Grob test mixture obtained on the PUAC-18-C-6 and PUAC-15-C-5 columns. They show that the mixtures were well separated and each peak is symmetrical. It is notable that 1-octanol and 1,3-butanediol both eluted behind n-dodecane, which has the highest molecular weight of the three. It is obvious that these two stationary have strong hydrogen-bonding forces to alcohols.

The selectivities and average polarities of the two aza-crown ether polysiloxane stationary phases, represented by the McReynold's constants and A values, are shown in Table II. It can be seen that they both have an average polarity similar to that of PSO-11-18-C-6 which was cross-linked by ATB [6], and lower than that of Carbowax 20M owing to their long non-polar alkyl groups and polysiloxane chain. The A values decrease with increasing polarity of the phases, indicating that these crown ether stationry phases are more suitable than Carbowax 20M for separating non-polar compounds.

The operating temperature range is determined by the glass transition temperature and column bleeding. These transitions occur at temperatures which may correspond to the glass transition temperature

TABLE I

CHROMATOGRAPHIC PROPERTIES OF PUAC-15-C-5 AND PUAC-18-C-6 COLUMNS

| Parameter	PUAC-15-C-5				PUAC-18-C-6		
Column No.	1	2	3	4	5	6	7
Synthesis No.	1	2	3	3	4	5	5
Column dimensions, length × I.D. (m × mm)	13 × 0.25	14 × 0.25	11.5 × 0.25	22.5 × 0.25	12 × 0.25	15 × 0.25	15 × 0.25
Coating efficiency (%)	89.8	98.3	93.3	81	102	101.8	102.7
Film thickness (μm)	0.4	0.4	0.4	0.4	0.44	0.44	0.3
Column efficiency (plates/m)	4489	4715	4428	3850	4621	4627	4839
Naphthalene capacity factor (k')	2.44	3.63	4.04	3.93	7.45	7.03	4.4
Peak asymmetry	1.05	1.04	1.05	1.06	1.0	1.0	1.0
Peak-area ratio[a]	0.39	0.36	0.40	0.41	0.4	0.32	0.43

[a] 2,6-Dimethylphenol to 2,4-dimethylaniline.
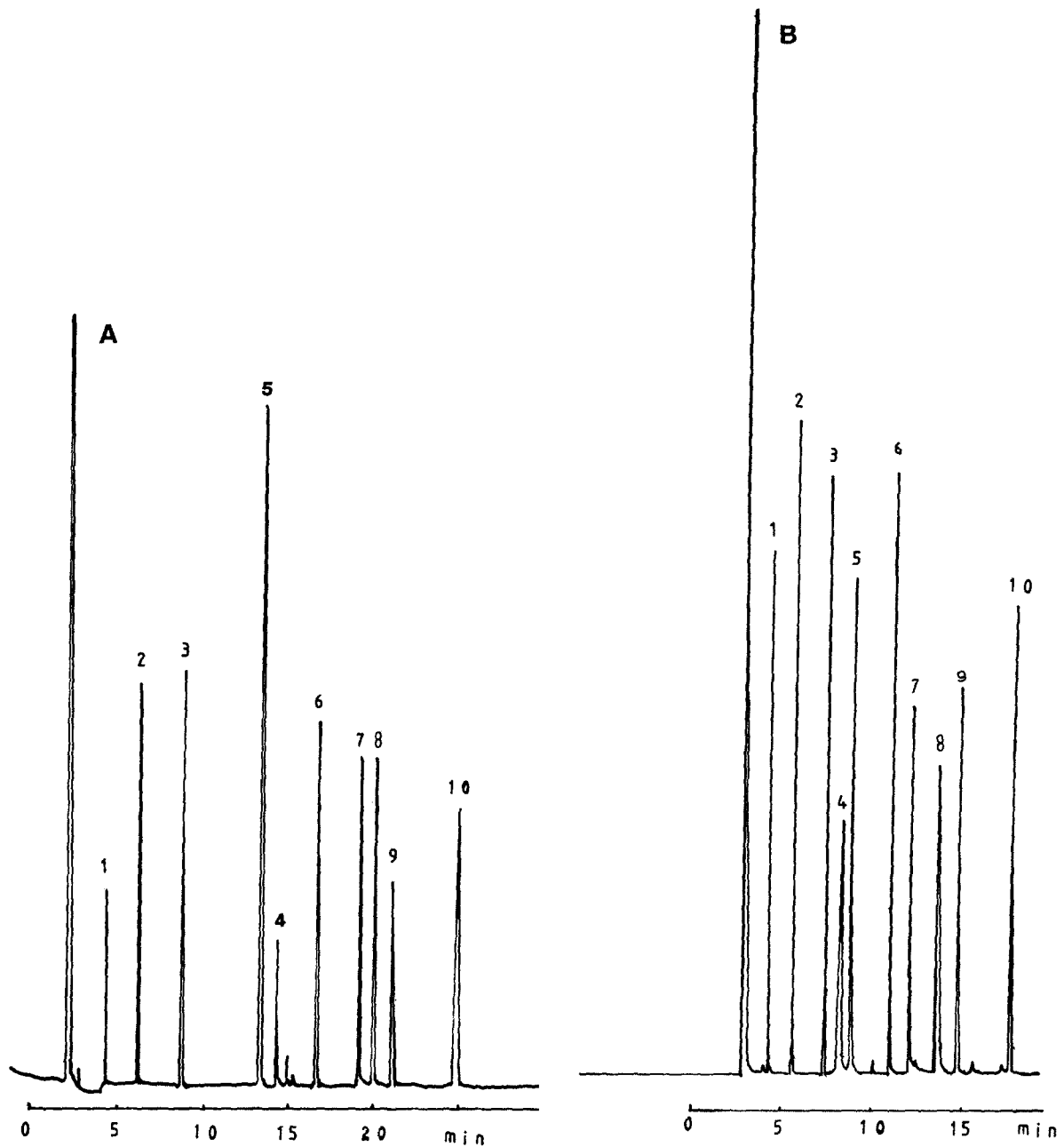
Fig. 2. Chromatogram of Grob test mixture on (A) the PUEC-18-C-6 and (B) the PUAC-15-C-5 columns. Temperature programmed from 80 to 150°C at 4°C/min. Peaks: 1 = *n*-decane; 2 = *n*-undecane; 3 = *n*-dodecane; 4 = 1,3-butanediol; 5 = 1-octanol; 6 = naphthalene; 7 = 2,4-dimethylaniline; 8 = 2,6-dimethylphenol; 9 = methyl undecanoate; 10 = methyl dodecanoate. The unlabelled peak represents the solvent.

TABLE II

McREYNOLD'S CONSTANTS AND A OF VALUES FOR THE VARIOUS STATIONARY PHASES

Stationary phase	Benzene	Butanol	2-Pentanone	Nitropropane	Pyridine	Mean	A
PUAC-15-C-5	147.5	258	263	261	224	231	0.1962
PUAC-18-C-6	150	300.5	283	254	211	239	0.1965
PSO-11-18-C-6	304	229	141	252	218	229	0.1975
Carbowax 20M	332	536	368	572	510	464	0.1905

and a liquid–liquid transition [3]. Fig. 3 shows the plot of the logarithm of the capacity factor for naphthalene on the PUAC-18-C-6 and PUAC-15-C-5 columns. The changes in slope at 119°C for PUAC-15-C-5 and 121°C for PUAC-18-C-6 correspond to the changes. These results also corresponded to the glass transition temperature determined by differential scanning calorimetry (DSC) of these two polymers. Such a change in slope was not observed with PSO-11-18-C-6, which is not cross-linked, and the transition points are lower than that of PSO-11-18-C-6, because the aza-crown ether molecules are regular and the interaction forces of
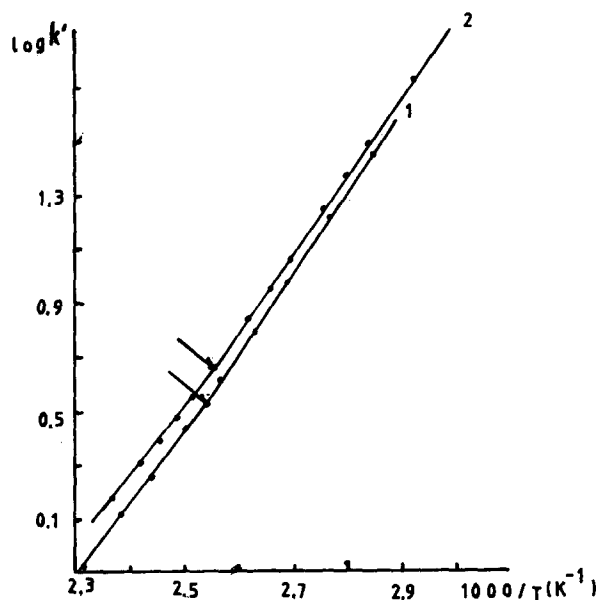

Fig. 3. Logarithm of capacity factor (k') vs. reciprocal absolute temperature for naphthalene on (1) PUAC-18-C-6 and (2) PUAC-15-C-5 columns.

the molecules are lower than those with PSO-11-18-C-6. This indicates that aza-crown ethers have lower minimum operating temperature than PSO-11-18-C-6. Xylene mixtures can be separated very well on the PUAC-18-C-6 column at 55°C (Fig. 4). Also, the efficiencies of both columns are more than 3300 plates/m at 70°C.

The column bleeding was measured by heating the columns from 120 to 300°C. The baseline did not increase when the column temperature was below 250°C and the shift of the baseline was $4.5 \cdot 10^{-13}$ A for PUAC-15-C-5 and $6.5 \cdot 10^{-13}$ A for PUAC-18-C-6 at 300°C. It can be seen that aza-crown ether stationary phases have a wider operating temperature range than PSO-11-18-C-6, which represents an appreciable improvement over the crown ether polysiloxane stationary phase reported by Rouse et al. [5]. These capillary columns were used at about 200°C for 3 months without a decrease in column efficiency and capacity factor.

Fig. 5 shows the relationship between the logarithm of the adjusted retention times and the number of carbon atoms in alcohol and normal fatty acid methyl ester homologues. The slopes of the straight lines for PUAC-15-C-5 and PUAC-18-C-6 are higher than that for Carbowax 20M and similar to that for PSO-11-18-C-6. These results indicate that the crown ether polysiloxane phases have a strong directional force and a higher selectivity for alcohols and esters than Carbowax 20M. The slopes are given in Table III.

Crown ethers show special selectivity, especially for aromatic compounds and their derivatives, amines, anilines, etc. [11]. These two aza-crown ether stationary phases give good separations of aniline compounds without derivatization (Fig. 6). It is interesting that the solutes did not elute only
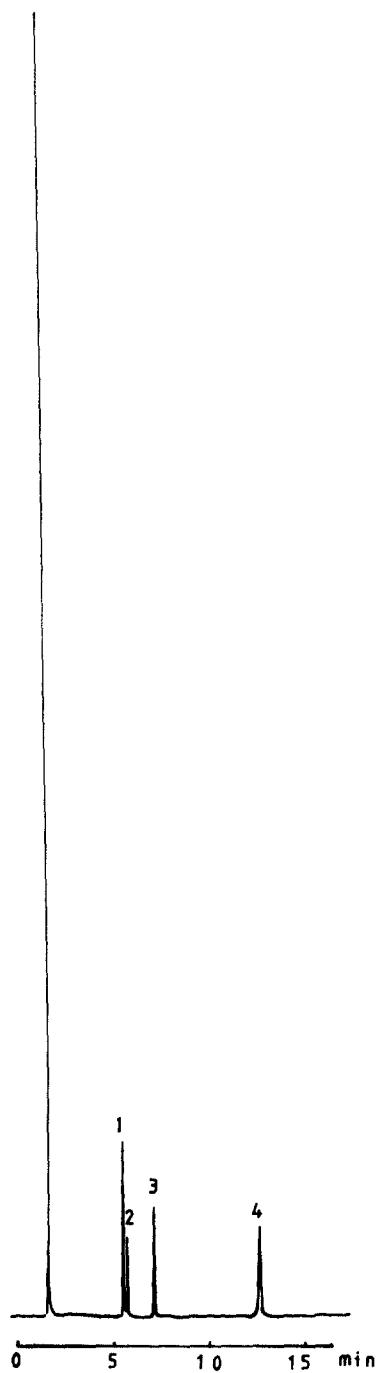
Fig. 4. Chromatogram of methyl-substituted benzene compounds on the PUAC-18-C-6 column (15 m × 0.25 mm I.D.). Temperature, 55°C (isothermal). Peaks: 1 = *p*-xylene; 2 = *m*-xylene; 3 = *o*-xylene; 4 = 1,3,5-trimethylbenzene.
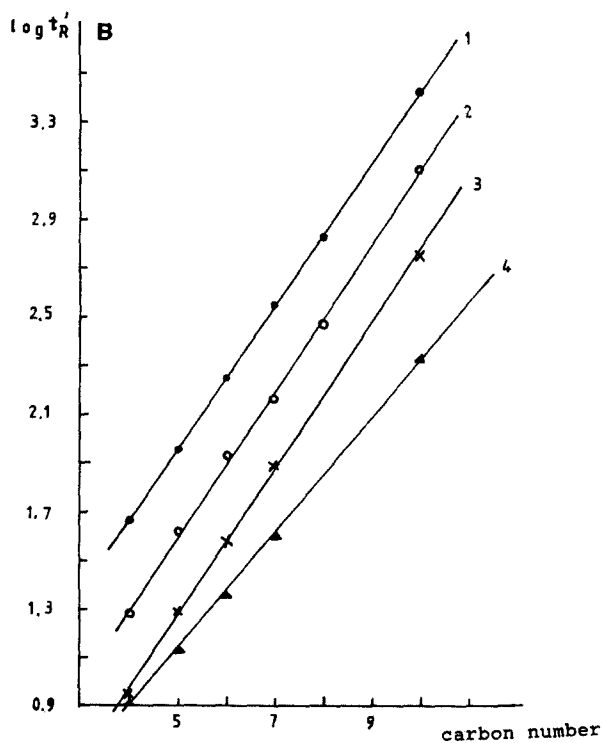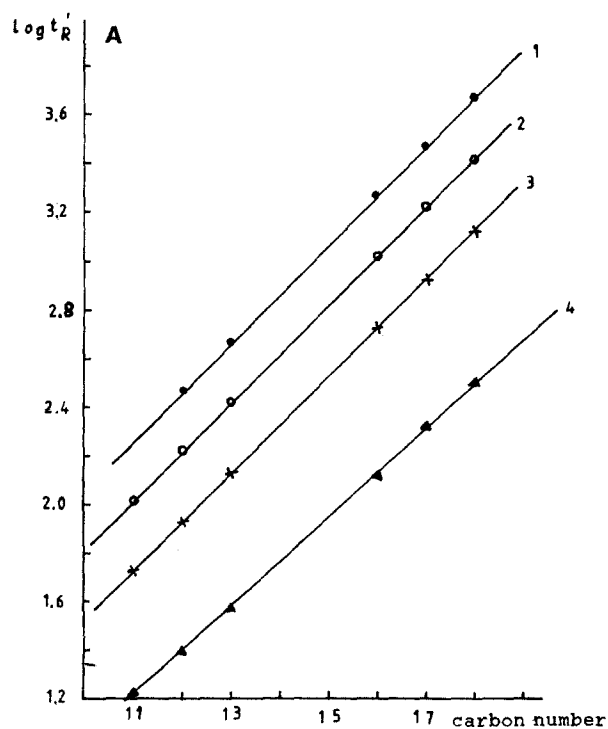

Fig. 5. Logarithm of the adjusted retention time (t_R') *vs.* carbon number for homologous (A) normal fatty acid methyl esters and (B) alcohols. Column: (1) PUAC-18-C-6; (2) PUAC-15-C-5; (3) PSO-11-18-C-6; (4) Carbowax 20M.

TABLE III

SLOPES OF THE STRAIGHT LINE OF LOGARITHM
OF ADJUSTED TIMES *VERSUS* CARBON NUMBER OF
HOMOLOGOUS ALCOHOLS (110°C) AND NORMAL
FATTY ACID METHYL ESTERS (170°C)

Stationary phase	Alcohols	Esters
PUAC-18-C-6	0.2943	0.1997
PUAC-15-C-5	0.298	0.1988
PSO-11-18-C-6	0.2983	0.1979
Carbowax 20M	0.2368	0.1827

according to the dipole–dipole interactions; the decreasing order of dipole–dipole force of methylaniline (MA) isomers is *o*-MA, *m*-MA and *p*-MA, but the sequence of elution of MA isomers on the PUAC-18-C-6 column is *o*-MA, *p*-MA and *m*-MA. This may be caused by the co-action of dipole–dipole and hydrogen-bonding forces. The retention times of N-ethyl-substituted *m*-MA isomers increase in the order *m*-MA, N,N-diethyl-*m*-MA and N-ethyl *m*-MA. These differences in elution may be due to the fact that the N,N-diethyl-*m*-MA molecule does not fit well in the cavity of the crown ether ring and does not have hydrogen atoms to form hydrogen bonds with the crown ether ring.

Aza-crown ethers also provide selectivity for strongly polar organic compounds such as nitrobenzene positional isomers (Fig. 7). Relatively small molecules which have few substituent groups and cannot form hydrogen bonds elute in the order of dipole–dipole interactions. For example, xylene isomers elute from the PUAC-18-C-6 columns in the order *p*-xylene, *m*-xylene and *o*-xylene, which is the sequence of the dipole–dipole interactions (Fig. 4). Mononitrotoluene (MNT) isomers elute from the PUAC-18-C-6 column in the order *o*-MNT, *m*-MNT and *p*-MNT, which is also the sequence of dipole–dipole interactions (Fig. 7). However, dinitrotoluene (DNT) isomers eluted from the PUAC-18-C-6 column in the order 2,6-DNT, 2,5-DNT, 2,4-DNT, 3,5-DNT and 3,4-DNT (Fig. 7), whereas the increasing sequence of dipole–dipole forces is 2,5-DNT, 2,4-DNT, 2,6-DNT, 3,5-DNT and 3,4-DNT. This different elution is also possibly caused by the 2,6-DNT molecule not fitting well in the cavity of the aza crown ether ring.
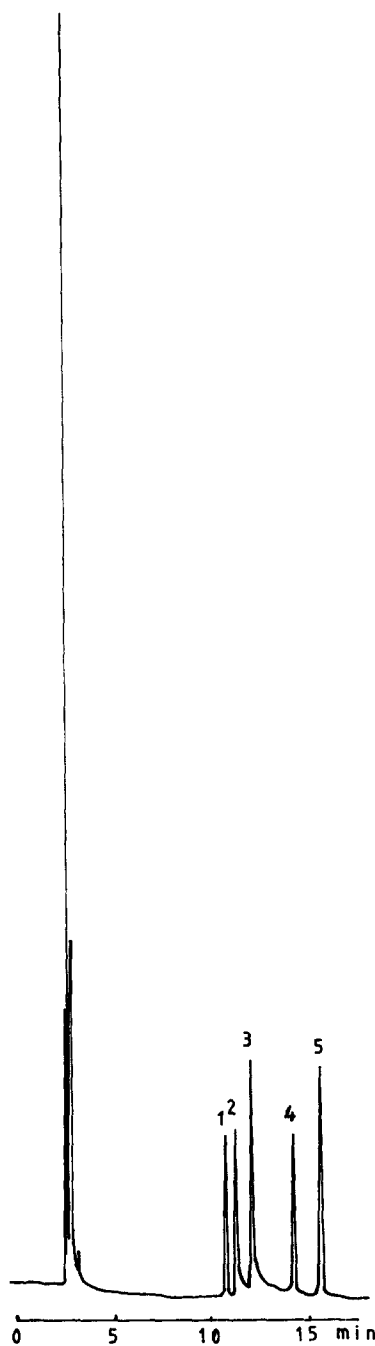

Fig. 6. Chromatogram of aniline compounds on the PUAC-18-C-6 column (15 m × 0.25 mm I.D.). Temperature, 120°C (isothermal). Peaks: 1 = *o*-methylaniline; 2 = *p*-methylaniline; 3 = *m*-methylaniline; 4 = N,N-diethyl-*m*-methylaniline; 5 = N-ethyl-*m*-methylaniline.
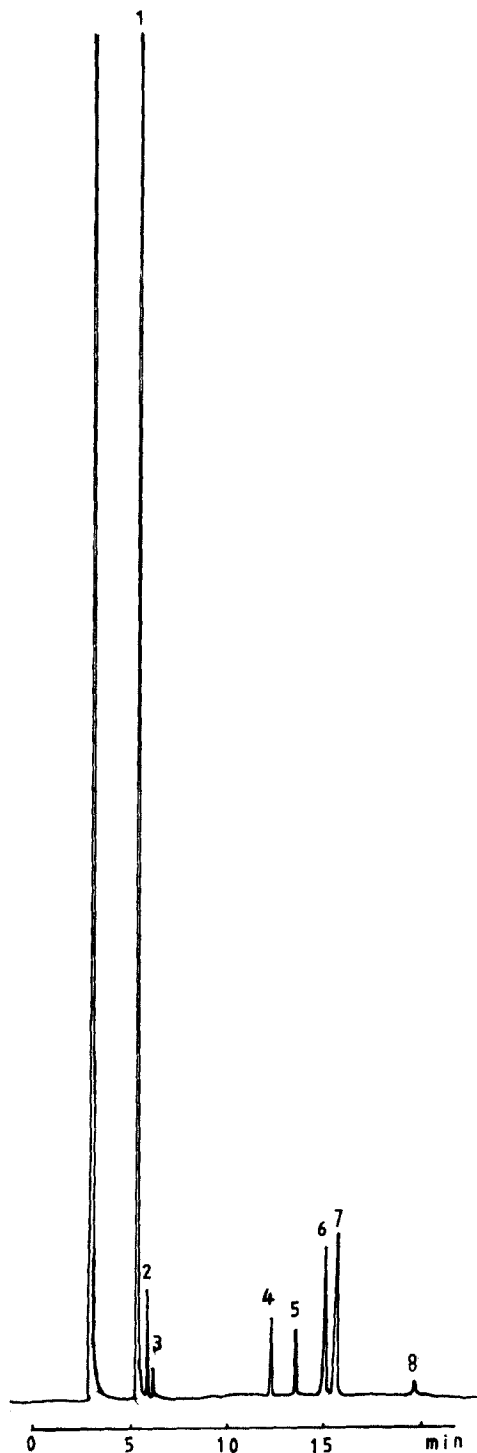
Fig. 7. Chromatogram of nitro compounds on the PUAC-18-C-6 column (15 m × 0.25 mm I.D.). Temperature programmed from 160 to 200°C at 4°C/min. Peaks: 1 = o-MNT; 2 = m-MNT; 3 = p-MNT; 4 = 2,6-DNT; 5 = 2,5-DNT; 6 = 2,4-DNT; 7 = 3,5-DNT; 8 = 3,4-DNT.
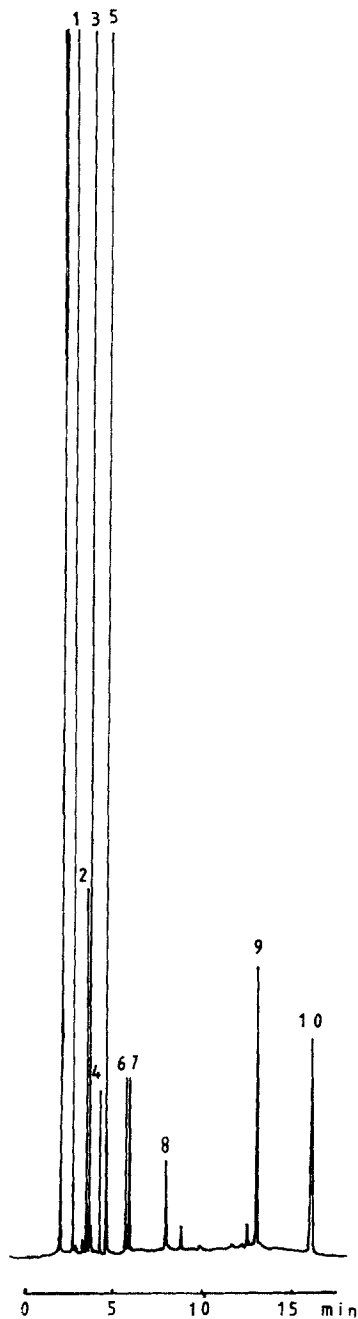
Fig. 8. Chromatogram of aromatic hydrocarbons on the PUAC-15-C-5 column (14 m × 0.25 mm I.D.). Temperature programmed from 150 to 200°C at 4°C/min. Peaks: 1 = naphthalene; 2 = 2-methylnaphthalene; 3 = 1-methylnaphthalene; 4 = biphenyl; 5 = diphenylmethane; 6 = bibenzil; 7 = acenaphthalene; 8 = fluorene; 9 = phenanthrene; 10 = triphenylmethane.
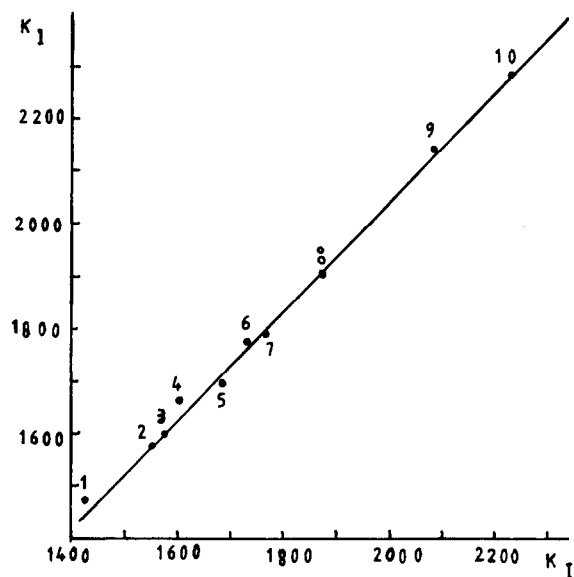
Fig. 9. Kováts retention indices of a series of aromatic hydrocarbons on PUAC-18-C-6 (ordinate) plotted against those on PSO-11-18-C-6 (abscissa). Column temperature, 170°C (isothermal). Compound numbers as in Fig. 8.

Fig. 8 shows that aza-crown ethers also provide good selectivity for easily polarizable aromatic hydrocarbons. Fig. 9 shows a plot of the Kováts retention indices of these aromatic compounds on PUAC-18-C-6 against those on PSO-11-18-C-6. There is a good linear relationship for most aromatic hydrocarbons, indicating that aza-crown ethers have the same mechanism as PSO-11-18-C-6 in separating easily polarizable aromatic compounds.

CONCLUSIONS

Aza-crown ether stationary phases are medium-polarity stationary phases that possess good film-forming ability and a wide operating temperature range of 55–300°C. These stationary phases present excellent selectivity for non-polar compounds, easily polarizable aromatic compounds and polar compounds such as alcohols, esters, nitrobenzene compounds and anilines.

ACKNOWLEDGEMENT

REFERENCES

1 R.-S. Li, SEPU, 4 (1986) 304.
2 Y.-H. Jin, R.-N. Fu and Z.-F. Huang, J. Chromatogr., 469 (1989) 153.
3 D. D. Fine, H. L. Geargart, II and H. A. Mottola, Talanta, 32 (1985) 751.
4 Y.-H. Jin and R.-N. Fu, Huaxue Shiji, 11 (1989) 339.
5 C. A. Rouse, A. C. Fintinson, B. J. Tarbet, J. C. Pixton, N. M. Djordjevic, K. Z. Markides, J. S. Bradshaw and M. L. Lee, Anal. Chem., 60 (1988) 901.
6 C.-Y. Wu, C.-M. Wang, Z.-R. Zeng and X.-R. Lu, Anal. Chem., 62 (1990) 968.
7 C.-Y. Wu, H.-Y. Li, Y.-Y. Chen and X.-R. Lu, J. Chromatogr., 504 (1990) 279.
8 C.-Y. Wu, C.-M. Wang, J.-S. Cheng and X.-R. Lu, SEPU, 8 (1990) 355.
9 B. A. Jones, J. S. Bradshaw, M. Nishioka and M. L. Lee, J. Org. Chem., 49 (1984) 4947.
10 L. Blomberg, J. High Resolut. Chromatogr. Chromatogr. Commun., 5 (1982) 520.
11 E. V. Zagorevskaya and N. Y. Kovaleva, J. Chromatogr., 365 (1986) 7.