

CHROM. 3560

PERFLUOROCYCLIC ETHERS AS VERY WEAK SOLVENTS FOR THE SEPARATION OF SATURATED AND OLEFINIC HYDROCARBONS BY LIQUID-SOLID CHROMATOGRAPHY

L. R. SNYDER

Union Oil Company of California, Union Research Center, Brea, Calif., 92621 (U.S.A.)

(Received April 8th, 1968)

SUMMARY

The perfluorocyclic ethers have been shown to be very weak solvents in separations by adsorption chromatography. In this respect they resemble the perfluoroalkanes, but are much cheaper. The separability of various saturated and olefinic hydrocarbons on alumina or silica, using these solvents or mixtures with saturated hydrocarbons, has been examined in detail. A number of potentially useful separations can be recognized.

INTRODUCTION

Liquid adsorption chromatography (*e.g.* thin-layer chromatography) has seldom been applied to the separation of mixtures of saturated and olefinic hydrocarbons. These compounds (with the exception of the polyenes) are adsorbed only slightly, even from weak chromatographic solvents such as the saturated hydrocarbons. As a result mixtures of the saturated and olefinic hydrocarbons migrate together near the solvent front, without undergoing appreciable separation. A few workers have attempted to solve this problem by means of low temperature separation¹ or the use of highly active, high surface area adsorbents (see data of Table XIV, ref. 2). The formation of mercuric acetate addition compounds from olefinic hydrocarbons, which increases the adsorption of the starting olefin, has also been suggested in this connection³. In all of these cases the adsorption of monoolefins can be increased to the point where these compounds are separated from saturated hydrocarbons. However, these techniques often provide only marginal separation of individual olefins, and they give no separation among the saturated hydrocarbons of the sample. Furthermore, those samples which are difficultly soluble cannot be run at very low temperatures, while samples which are prone to adsorbent catalyzed reaction cannot be subjected to highly active adsorbents. Finally, with the exception of separations on highly active adsorbents, these techniques are experimentally inconvenient to carry out.

ATTAWAY and coworkers^{4,5} have recently shown that the perfluoroalkanes are

considerably weaker solvents than the saturated hydrocarbons. As a result it is possible to carry out useful separations of weakly adsorbing hydrocarbons by means of thin-layer chromatography (TLC) with perfluoroalkane solvents. However, the use of these solvents is presently limited by their cost (\$ 0.25-4.50 per ml in liter quantities). Preparative separations are virtually ruled out, and even microscale separations can be relatively expensive. The systematic investigation of separations based on the perfluoroalkane solvents is likewise discouraged. We have recently found that the so-called perfluorocyclic ethers (sold as Inert Fluorochemical Liquids by 3M Co.) are quite similar to the perfluoroalkanes as chromatographic solvents, while their cost (\$ 0.04 per ml in gallon quantities) is substantially less. We have therefore carried out a systematic investigation of the solvent properties of the perfluorocyclic ethers in order to define their potential for separations of saturated and olefinic hydrocarbons on polar adsorbents. These studies also provide further insight into the fundamental theory of adsorption chromatography, specifically with regard to the role of dispersion forces in such separations (see ref. 6).

EXPERIMENTAL

All separations were carried out at $23^{\circ} \pm 1^{\circ}$. The alumina was Alcoa F-20 (Aluminum Co. of America), initially heated in air at 400° for 16 h (surface area at this point equal to $229 \text{ m}^2/\text{g}$), followed by addition of varying amounts of water. The final product was chromatographically standardized, using naphthalene as sample and pentane as solvent (see Table I of ref. 7). The silica was Davison grade 62 (Grace Chemical), initially heated in air at 200° for 8 h, followed by addition of 4% water.

Retention volume measurements were carried out in one of two ways. For saturated and olefinic samples, continuous detection (by differential refractive index) of the column eluate (using apparatus described in ref. 8) gave peak retention volumes directly. For aromatic samples, individual fractions were collected and these were scanned in the ultraviolet as previously (e.g. ref. 9). Retention volumes were then calculated as 50% elution values (as in ref. 9).

RESULTS

Table I summarizes some of the physical properties of the perfluorocyclic ethers sold by 3M Co. The boiling points and viscosities of these materials are such that FC-78 is best for room-temperature separations, and FC-77 or FC-75 are preferred for separations

TABLE I

PROPERTIES OF THE INERT FLUORO-CHEMICAL LIQUIDS (PERFLUOROCYCLIC ETHERS) SOLD BY 3M

	FC-78	FC-77	FC-75
Boiling point ($^{\circ}\text{C}$)	50	97	102
Kinematic viscosity at 25° (cS)	0.44	0.80	0.82
Surface tension at 25° (dynes/cm)	13	15	15
$\alpha_d(\epsilon_p - \epsilon_d)(24^{\circ})$ alumina	-0.174	(-0.19) ^a	-0.191
silica	-0.125	(-0.14) ^a	-0.139

^a Estimated value.

at 40–90°. While liquid–solid chromatography is usually carried out at room temperature, the limited solubility of high molecular weight samples in the perfluorocyclic ethers may require high temperature separation in some cases. The surface tensions of the perfluorocyclic ethers are uniformly low, which means that the development times in thin-layer chromatography tend to be long (*e.g.* see ref. 10). Finally, Table I summarizes the effective strengths of these various solvents, relative to pentane: $\alpha_a(\epsilon_d - \epsilon_p)$ (see below).

The role of the solvent

Tables II–V present retention volume data for elution of various hydrocarbons and halogen substituted benzenes from alumina and silica by FC-78 and FC-75, solutions of FC-78 in pentane, and pentane. Values of \bar{R}° , the linear-isotherm equivalent retention volume (ml/g, corrected for column void-volume) are reported. In every case the perfluorocyclic ethers and their solutions in pentane are seen to be weaker solvents than pentane (retention volumes with pentane are smaller). For solvents such as these, whose adsorption involves dispersion rather than so-called “specific” interactions, a previous treatment⁶ has given a general relationship for the change in sample retention volume with solvent:

$$\log (R_1/R_2) = \alpha_a A_s (\epsilon'_2 - \epsilon'_1) \quad (1)$$

Here R_1 and R_2 refer to \bar{R}° values for a particular compound X eluted by solvents 1 and 2, respectively, α_a is the adsorbent activity function for dispersion interactions only, A_s is the area required by adsorbed X on the adsorbent surface, and ϵ'_1 and ϵ'_2

TABLE II

SOLVENT STRENGTH OF FC-78 ON 4% H₂O-SiO₂

Compound	$\log \bar{R}^\circ$		$\log(R_2/R_1)$	A_s^b
	Pentane ^a	FC-78 ^a		
Acetylene	-0.10	0.29	0.39	3.2
Methyl iodide	-0.33	0.46	0.79	3.7
Methylene chloride	-0.10	0.53	0.63	4.1
Benzene	-0.15	0.68	0.83	6.0
Bromobenzene	-0.21	0.64	0.85	6.6
Toluene	-0.11	0.79	0.90	6.8
<i>m</i> -Fluorochlorobenzene	-0.36	0.38	0.74	7.1
<i>p</i> -Dibromobenzene	-0.29	0.68	0.97	7.2
<i>p</i> -Xylene	-0.05	0.86	0.91	7.6
1,3,5-Tribromobenzene	-0.54	0.69	1.23	7.8
1,3,5-Trimethylbenzene	0.01	0.99	0.98	8.4
Naphthalene	-0.15			
<i>n</i> -Pentane	-1.15 ^c	-0.47	0.68	5.9
<i>n</i> -Octane	-1.25 ^c	-0.30	0.95	8.1
<i>n</i> -Decane	-1.32 ^c	-0.27	1.05	9.6
<i>n</i> -Dodecane	-1.40 ^c	-0.12	1.28	11.1
<i>n</i> -Tetradecane	-1.47 ^c	0.01	1.48	12.6
<i>n</i> -Hexadecane	-1.54 ^c	0.08	1.62	14.1
<i>n</i> -Eicosane	-1.68 ^c	0.36	2.04	17.1

^a Solvent.^b Calculated according to ref. 11, with α_i (-CH₂-) equal 0.75 (see ref. 12).^c Calculated value (see text).

TABLE III
SOLVENT STRENGTH OF FC-78 ON 2.8% H₂O-Al₂O₃

Compound	log \bar{R}°		log (R_1/R_2)	A_s^b
	Pentane ^a	FC-78 ^a		
Methyl iodide	-0.44	0.45	0.89	3.7
Benzene	-0.33	0.62	0.95	6.0
Bromobenzene	-0.09	1.12	1.21	6.6
Toluene	-0.28	0.92	1.20	6.8
<i>m</i> -Chlorofluorobenzene	-0.21	0.81	1.03	7.1
<i>p</i> -Xylene	-0.20	1.13	1.33	7.6
1,3,5-Trimethylbenzene	-0.14	1.27	1.41	8.4
<i>n</i> -Pentane	-1.58 ^c	-0.41	1.17	5.9
<i>n</i> -Hexane	-1.57 ^c	-0.32	1.25	6.7
<i>n</i> -Heptane	-1.55 ^c	-0.20	1.35	7.4
<i>n</i> -Octane	-1.54 ^c	-0.11	1.43	8.2
<i>n</i> -Nonane	-1.52 ^c	-0.02	1.50	8.9
<i>n</i> -Decane	-1.51 ^c	0.11	1.62	9.7
<i>n</i> -Dodecane	-1.48 ^c	0.34	1.82	11.1

^a Solvent.

^b Calculated according to ref. 11, with a_i (-CH₂-) equal 0.75 (see ref. 12).

^c Calculated value (see text).

TABLE IV
SOLVENT STRENGTH OF FC-78 ON ALUMINA VERSUS ADSORBENT ACTIVITY

Compound	log \bar{R}°				A_s^c
	0.0% H ₂ O-Al ₂ O ₃ ^a		4.0% H ₂ O-Al ₂ O ₃ ^b		
	Pentane ^d	FC-78	Pentane ^d	FC-78	
Propane	-1.14	-0.69			4.4
<i>n</i> -Butane	-1.12	-0.34			5.2
<i>n</i> -Pentane	-1.10	-0.24			5.9
<i>n</i> -Hexane	-1.08	-0.07	-1.84	-0.46	6.7
<i>n</i> -Heptane	-1.06	0.12			7.4
<i>n</i> -Octane	-1.04	0.35	-1.81	-0.28	8.2
<i>n</i> -Decane			-1.78	-0.12	9.7
<i>n</i> -Dodecane			-1.75	0.07	11.1
<i>n</i> -Hexadecane			-1.69	0.46	14.1

^a Log V_a equal -1.10 (BET surface area determination, see ref. 11), α equal 1.00.

^b Log V_a equal -1.85, α equal 0.63⁷.

^c Calculated according to ref. 11, with a_i (-CH₂-) equal 0.75 (see ref. 12).

^d Calculated value (see text).

refer to the ε_a values of solvents 1 and 2, respectively. ε_a is the dispersion interaction energy per unit area of adsorbed solvent (for a given solvent and adsorbent type). It will prove convenient to relate the \bar{R}° values of Tables II-V to corresponding \bar{R}° values for pentane as solvent. If solvent 1 is one of the perfluorocyclic ethers (or its solution with pentane) and solvent 2 is pentane, we can rewrite eqn. 1 as follows:

$$\log (R/R_p) = \alpha_d A_s (\varepsilon_p - \varepsilon_a) \quad (1a)$$

TABLE V
SOLVENT STRENGTH OF FC-75 AND MIXTURES OF FC-78/PENTANE ON ALUMINA AND SILICA

Solvent	2.8% H ₂ O-Al ₂ O ₃		4% H ₂ O-SiO ₂		$\alpha_d(\epsilon_p - \epsilon_d)^a$
	$\log R^o$ C ₆ H ₅ -Br	$\log R^o$ <i>p</i> -xylene 1,3,5-tri- methyl- benzene	$\log R^o$ C ₆ H ₅ -Br	$\log R^o$ <i>p</i> -xylene 1,3,5-tri- methyl- benzene	
Pentane	-0.09	-0.20	-0.21	-0.05	0.000
FC-75	1.26	1.24	0.75	0.99	0.139
10% v pentane/FC-78	0.97	0.89	0.64	0.75	0.111
25% v pentane/FC-78	0.74	0.68	0.48	0.63	0.090
50% v pentane/FC-78	0.38	0.34	0.17	0.43	0.056
FC-78					0.125 ^c

^a Average value for three sample compounds.

^b Value from Table III and Fig. 2.

^c Value from Table II and Fig. 1.

R and R_p now refer to the \underline{R}° values of some solvent (1) and of pentane (2), ϵ_a is the ϵ_a value for solvent (1) and ϵ_p is the corresponding value (of ϵ_a) for pentane. According to eqn. 1a, the quantity $\log (R/R_p)$ should be proportional to the area of the adsorbing sample molecule X . This relationship is tested in Figs. 1 and 2 for adsorption from FC-78 and pentane, on silica and alumina respectively. In each case there is good agreement between experimental data and eqn. 1a, verifying the proportionality of $\log (R/R_p)$ and A_s . Values of \underline{R}° for the n -alkanes eluted by pentane are too small for experimental measurement in any of these cases (dark circles of Figs. 1 and 2).

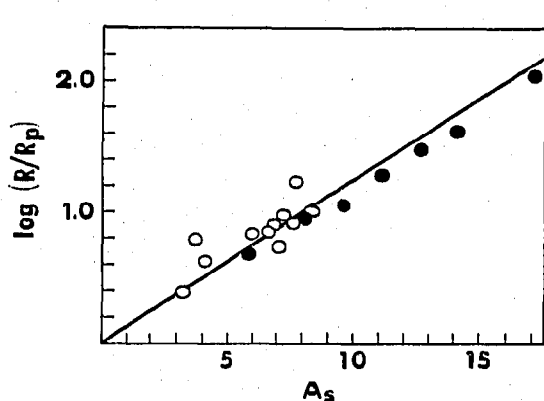


Fig. 1. Dependence of $\log (R/R_p)$ on A_s value of the sample; adsorption on 4% H_2O-SiO_2 (data of Table II). ● = Values for n -alkanes.

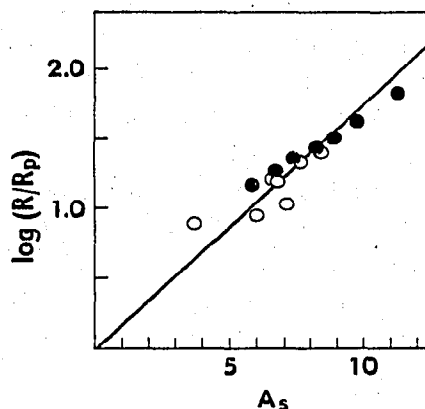


Fig. 2. Dependence of $\log (R/R_p)$ on A_s value of the sample; adsorption on 2.8% $H_2O-Al_2O_3$ (data of Table III). ● = Values for n -alkanes.

However, values of R_p for the n -alkanes eluted by pentane can be calculated from previous data (see refs. 2 and 9), according to the relationships

$$\log R_p = \log V_a + 0.02 \alpha (n - 5) \text{ (alumina)} \quad (2)$$

and

$$\log R_p = \log V_a + 0.05 \alpha (5 - n) \text{ (silica)}. \quad (2a)$$

Eqns. 2 and 2a recognize that the \underline{R}° value of pentane itself, eluted by pentane, is equal to the adsorbent surface volume V_a , while each additional methylene group adds $0.02 \alpha \log$ units to $\log \underline{R}^\circ$ on alumina, and $-0.05 \alpha \log$ units on silica. α refers to the adsorbent surface activity function (specific interactions only, see ref. 6). Values of $\log V_a$ can be calculated from the starting adsorbent surface area and the quantity of added water (see section 6-2A of ref. 11). Values of α and $\log V_a$ for the adsorbents of Tables II-IV have also been tabulated (see ref. 11).

The relative strength of one of these very weak solvents (e.g. FC-78) compared to that of pentane, is given by the quantity $\alpha_a(\epsilon_a - \epsilon_p)$. The more negative this quantity is for a given solvent, the greater will be the \underline{R}° values of all sample components eluted by that solvent. From eqn. 1a we see that the slope of the plot in Fig. 1 or 2 is equal to $\alpha_a(\epsilon_p - \epsilon_a)$; i.e. the weaker the solvent (eqn. 1), the steeper is the curve. Previously it has been shown⁶ that α_a is relatively insensitive to adsorbent water content. Consequently the quantity $\alpha_a(\epsilon_p - \epsilon_a)$ should be constant for a given adsorbent type (e.g. alumina or silica) as its water content is varied. This is verified in Fig. 3 for

the data of Table IV. Values of $\log (R/R_p)$ versus A_s for 0 and 4 % $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$ fall on the same curve which applies to the data of Fig. 2 (for 2.8 % $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$). That is, $\alpha_d(\varepsilon_p - \varepsilon_d)$ is essentially constant for all three samples of alumina.

Table IV presents retention volume data for three standard samples (bromobenzene, *p*-xylene, and 1,3,5-trimethylbenzene) eluted by several different solvents from both alumina and silica. From these data average values of $\alpha_d(\varepsilon_d - \varepsilon_p)$ for each solvent can be derived (eqn. 1a), as shown in Table IV. FC-75 is seen to be slightly weaker than FC-78, and the solvent strengths of the various FC-78/pentane blends increase regularly with increasing pentane concentrations (as expected). Thus solvents of any strength between that of FC-78 and pentane are easily available.

The relative strengths of the perfluorocyclic ethers appear comparable to those of the perfluoroalkanes. Examination of the data of ATTAWAY *et al.*⁴ suggests that $\alpha_d(\varepsilon_d - \varepsilon_p)$ for a perfluoroalkane is equal to about -0.11 on silica, versus -0.125 for FC-78. R_F values for limonene developed by FC-78 and perfluoroalkane-70 (Peninsular Chemresearch, Inc.) were found by us to equal 0.29 and 0.14, respectively, on Silica Gel G plates (TLC). This suggests a slightly lower solvent strength for this particular perfluoroalkane. In any case we will see that the strengths of the perfluorocyclic ethers are sufficiently low for any desired separation of saturated or olefinic hydrocarbons.

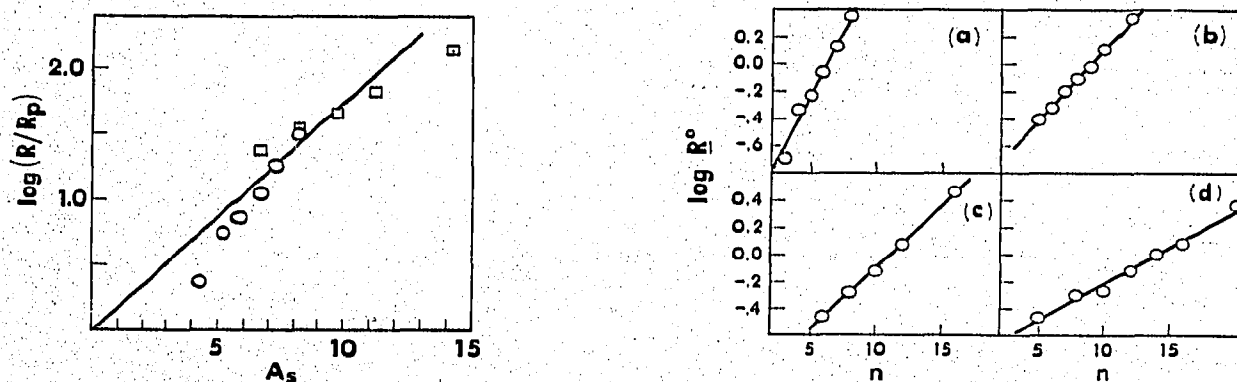


Fig. 3. Dependence of $\log (R/R_p)$ on adsorbent activity; adsorption on alumina (data of Table IV). $\circ = 0\%$ $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$; $\square = 4\%$ $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$; $- 2.8\%$ $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$.

Fig. 4. Dependence of $\log \underline{R}^\circ$ on carbon number n for the n -alkanes; elution by FC-78 from 0% $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$ (a), 2.8% $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$ (b), 4% $\text{H}_2\text{O}-\text{Al}_2\text{O}_3$ (c), and 4% $\text{H}_2\text{O}-\text{SiO}_2$ (d). Experimental data of Tables II-IV.

The role of sample structure

Let us look first at the \underline{R}° values of the n -alkanes (Tables II-IV). We can calculate $\log \underline{R}^\circ$ for any of the n -alkanes from eqns. 1a and 2 or 2a, in terms of $\alpha_d(\varepsilon_d - \varepsilon_p)$, α , and $\log V_a$. The resulting expression for $\log \underline{R}^\circ$ (for an n -alkane) is of the form

$$\log \underline{R}^\circ = C + Dn.$$

Here C and D are constants for a particular separation system, and n refers to the carbon number of the n -alkane. That is, $\log \underline{R}^\circ$ for an n -alkane increases linearly with carbon number. This is illustrated in Fig. 4 for the data of Tables II-IV. Since we can calculate (or know) values of $\alpha_d(\varepsilon_d - \varepsilon_p)$, α , and $\log V_a$ for various solvents and adsorbents, (*i.e.* those studied here) and since α_d is known as a function of temperature⁶, we can calculate $\log \underline{R}^\circ$ for the n -alkanes as a function of carbon number n for a wide

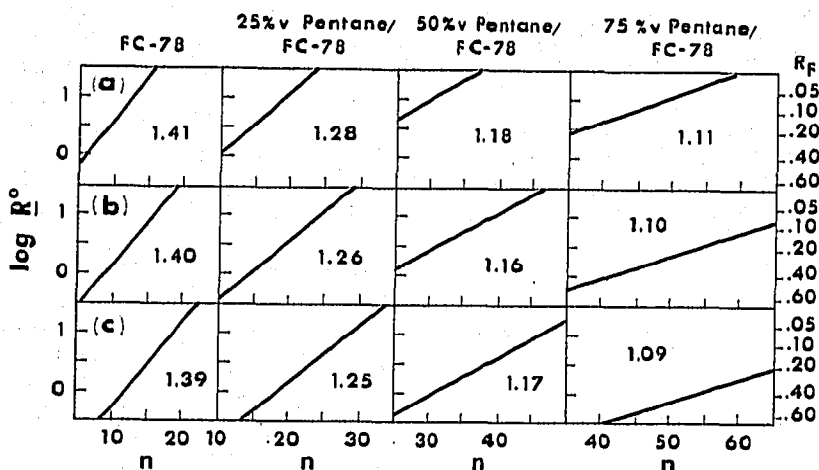


Fig. 5. Calculated dependence of $\log R^o$ for n -alkanes on adsorbent water content and solvent composition in elution from alumina at 24°. (a) = 0% $H_2O-Al_2O_3$; (b) = 3% $H_2O-Al_2O_3$; (c) = 6% $H_2O-Al_2O_3$.

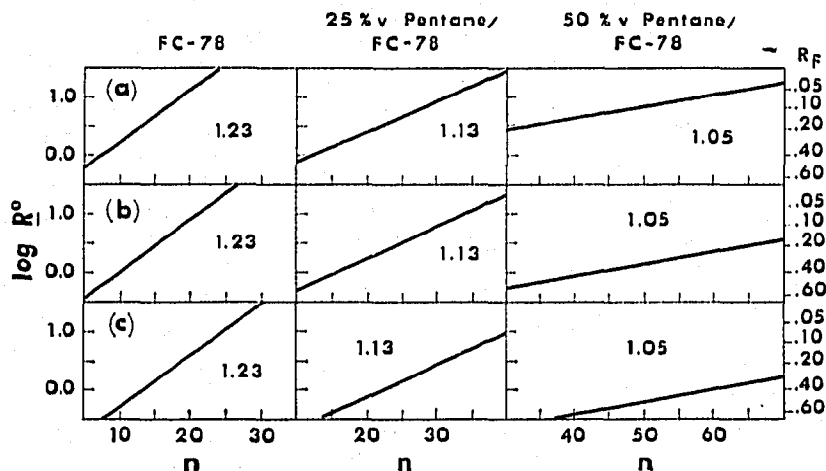


Fig. 6. Calculated dependence of $\log R^o$ for n -alkanes on adsorbent water content and solvent composition in elution from silica (Davison grade 62) at 24°. (a) = 0% H_2O-SiO_2 ; (b) = 4% H_2O-SiO_2 ; (c) = 8% H_2O-SiO_2 .

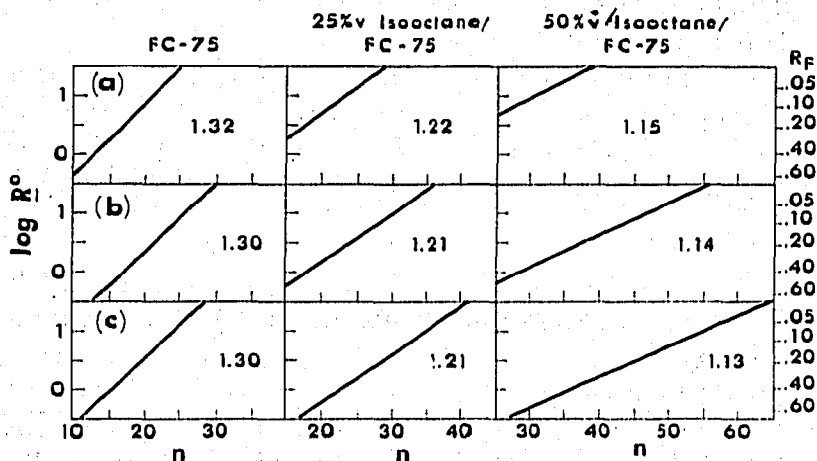


Fig. 7. Calculated dependence of $\log R^o$ for n -alkanes on adsorbent water content and solvent composition in elution from alumina at 80°. (a) = 0% $H_2O-Al_2O_3$; (b) = 3% $H_2O-Al_2O_3$; (c) = 6% $H_2O-Al_2O_3$.

TABLE VI

EFFECT OF SAMPLE STRUCTURE ON THE RETENTION VOLUMES OF SATURATED AND OLEFINIC HYDROCARBONS; FC-78 SOLVENT

Compound	4% H ₂ O-SiO ₂		2.8% H ₂ O-Al ₂ O ₃	
	log R°	Δ	log R°	Δ
Cycloalkanes				
<i>n</i> -Propylcyclohexane	-0.26	0.01		
<i>n</i> -Decylcyclopentane	0.08	0.03		
<i>trans</i> -Decalin	-0.15	0.07	0.10	-0.01
Monoolefins				
Monoalkylethylenes				
1-Nonene	0.23	0.50	0.37	0.36
1-Hexadecene	0.54	0.44	0.37	0.36
Dialkylethylenes				
<i>cis</i> -2-Hexene	0.16	0.60	0.06	0.37
<i>trans</i> -2-Hexene	0.16	0.60	-0.01	0.30
<i>cis</i> -3-Hexene	0.19	0.63		
2-Methyl-1-pentene	0.17	0.61	0.03	0.34
4-Methyl- <i>cis</i> -2-pentene	0.14	0.58		
2-Methyl-1-hexene	0.25	0.63		
<i>trans</i> -4-Octene	0.19	0.52		
Trialkylethylenes				
2-Methyl-2-pentene	0.25	0.69	0.02	0.29
3-Methyl- <i>cis</i> -2-pentene	0.25	0.69		
3-Methyl- <i>trans</i> -3-hexene	0.33	0.71		
Tetraalkylethylenes				
2,3-Dimethylbutene	0.33	0.77	0.05	0.36
Cyclic olefins				
Vinylcyclopentane	0.20			
Diolefins				
1,3-Pentadiene	0.37	0.86		
1,5-Hexadiene	0.41	0.85		

range of experimental conditions. Figs. 5 through 7 present some calculations of this type, showing R° as a function of adsorbent type, adsorbent water content, solvent, and temperature. The usefulness of these data will be apparent shortly.

Let us turn now to the effect of cycloalkyl, isoalkyl, or olefinic groups on the R° value of a hydrocarbon. Table VI provides some relevant data for elution from alumina and silica by FC-78. Previous work (see ref. 11) has shown for compounds of the type under discussion (*i.e.* compounds which do not undergo so-called "delocalized" adsorption) that

$$\log R_p = \log V_a + aS^{\circ}, \quad (3)$$

where the standard sample adsorption energy (specific interactions only) S° is in turn given as the sum of group contributions Q°_i :

$$S^{\circ} = \sum_i Q^{\circ}_i. \quad (3a)$$

For the saturated and unsaturated hydrocarbons, the latter relationship may be written

$$S^{\circ} = (S^{\circ})_{\text{alk}} + a(Q^{\circ}_i)_{\text{cyc}} + b(Q^{\circ}_i)_{\text{iso}} + c(Q^{\circ}_i)_{\text{olef.}} \quad (3b)$$

That is, the S° value of the compound in question is equal to the S° value of the n -alkane of equal carbon number $(S^\circ)_{\text{alk}}$, plus the adsorption energy of a cycloalkane group $(Q^\circ i)_{\text{cyc}}$ times the number a of such groups in the molecule, plus the adsorption energy of an iso branch $(-\text{CH} <)$ $(Q^\circ i)_{\text{iso}}$ times the number b of such branches in the molecule, plus the adsorption energy of an olefin group $(Q^\circ i)_{\text{olef}}$ times the number c of such groups in the molecule. From eqns. 1a and 3 we have

$$\log \underline{R}^\circ = \log V_a + aS^\circ + a_d A_s (\varepsilon_p - \varepsilon_d) \quad (4)$$

Now the value of A_s for an n -alkane is approximately equal to that for a cycloalkane, isoalkane, or olefin of the same carbon number (see ref. 12), so for any solvent

$$\log \underline{R}^\circ = (\log \underline{R}^\circ)_{\text{alk}} + a[a(Q^\circ i)_{\text{cyc}} + b(Q^\circ i)_{\text{iso}} + c(Q^\circ i)_{\text{olef}}] = (\log \underline{R}^\circ)_{\text{alk}} + \Delta \quad (4a)$$

Values of Δ are shown for the various compounds of Table VI, and corresponding values of $(Q^\circ i)_{\text{cyc}}$ and $(Q^\circ i)_{\text{olef}}$ can be derived from these data (see Table VII). We see first that the Δ values for the various cycloalkanes of Table VI are small, so that in general cycloalkanes are adsorbed on alumina and silica about as strongly as the

TABLE VII

GROUP ADSORPTION PARAMETERS FOR CALCULATING R° FOR SATURATED AND OLEFINIC HYDROCARBONS

Group	Q_i^a	
	Silica	Alumina
Cycloalkyl	0.04	0.00
Isoalkyl	-0.09 ^b	-0.11 ^c
Olefin		
R-CH=CH ₂	0.67	0.51
R-CH=CH-R	0.86	0.49
R ₂ -C=CH ₂	1.00	0.41
R ₂ -C=CH-R	1.10	0.51
R ₂ -C=C-R ₂		

^a Derived from data of Table VI; $\alpha = 0.70$ for both adsorbents.

^b Derived from gas-solid chromatographic studies of ref. 13.

^c Derived from gas-solid chromatographic studies of ref. 14.

corresponding n -alkanes. We have grouped the various monoolefins of Table VI according to the number of alkyl substituents on the two carbons forming the double bond. In the case of silica, we see that Δ values tend to be approximately constant for an olefin of given substitution type, but Δ increases regularly with increasing number of groups attached to the olefin: monoalkylethylenes, 0.47 ± 0.04 std. dev.; dialkylethylenes, 0.60 ± 0.04 ; trialkylethylenes, 0.70 ± 0.01 ; tetraalkylethylenes, 0.77 . There appears to be little difference in the absorption of isomeric *cis*, *trans*, or asymmetrical dialkylethylenes on silica. In the case of adsorption on alumina, however, Δ changes little with the number of alkyl groups substituted onto the double bond, and the relative adsorption of the dialkylethylenes is *cis* > asymmetric > *trans*. Thus the relative adsorption of isomeric olefins on silica seems to depend largely on the number of groups substituted on the double bond, while the relative positions of these groups seems to be of greater importance in adsorption on alumina. These variations in \underline{R}° :

with alkyl substitution pattern can be explained in terms of the contrasting effects of intramolecular electronic and steric effects (see Chapter 11 of ref. 11). Attaching an alkyl group to the olefin group increases its electron density and its adsorption energy. At the same time, however, these added alkyl groups sterically interfere with the interaction between the olefin double bond and the adsorbent surface. For adsorption on silica, it appears that electronic effects outweigh steric effects. For adsorption on alumina, these two effects are apparently of similar magnitude.

PRACTICAL APPLICATIONS OF THE PERFLUOROCYCLIC ETHERS

The potential usefulness of the perfluorocyclic ethers (and their solutions with saturated hydrocarbons) as solvents in adsorption chromatography should be apparent from the preceding data and Figures, and the applications of the related perfluoroalkanes^{4, 5}. The preceding data permit us to estimate R° values for a given compound as a function of separation conditions, and this in turn allows a quick decision on the best set of experimental conditions for a given separation. Eqn. 4a, Figs. 5-7 and Table VII are of the greatest value in this respect. In using eqn. 4a, we should recall that α for silica is relatively constant as adsorbent water content is varied (see ref. 6), and we can assume α equals 0.7-0.8 for most silicas. In the case of alumina, α varies from 1.00 for 0 % $H_2O-Al_2O_3$ to 0.6 for alumina which contains 6 % or more of added water.

Separations by molecular weight

It is apparent from Figs. 4-7 that separations by molecular weight are a characteristic feature in adsorption chromatography with the perfluorocyclic ethers as solvents. The numbers within each box of Figs. 5-7 refer to the fractional increase in R° per added methylene group. Mixtures of the *n*-alkanes have been separated in the past by gas chromatography. However, the upper molecular weight limit on these separations appears to be about *n*- $C_{40}H_{82}$ ¹⁵. The data of Figs. 5-7 suggest that liquid-solid chromatography with a suitable solvent can extend this molecular weight limit to at least C_{60} . The only limitations are the separation efficiencies required and the problem of sample solubility which has been referred to earlier. Those systems of Figs. 5-7 which give reasonable values of R° for *n*-alkanes larger than C_{40} have rather small differences in R° between adjacent homologs. For separations of the C_{40} - C_{60} alkanes, good resolution between neighboring homologs would require about 1600 theoretical plates. However, this is not impractical at the present time (see ref. 16).

Under comparable experimental conditions (same solvent, temperature), alumina exhibits a much greater molecular weight selectivity than does silica. This can be seen in Figs. 4-7. As a result, for comparable separation of the band centers of two adjacent homologs (and comparable resolution of these bands) silica will require the use of a solvent with higher concentration of perfluorocyclic ether, or a lower separation temperature. Both of these factors reduce solubility, and are therefore undesirable. Alumina therefore seems preferable for the separation of high molecular weight hydrocarbons.

ATTAWAY and coworkers^{4, 5} have noted in separations on alumina with the perfluoroalkanes as solvents that monoterpenes migrate less rapidly than do sesquiterpenes. Presumably a similar difference would be found in separations with the per-

fluorocyclic ethers. This observation seems to contradict the fact that higher molecular weight compounds are in general more strongly held in such separations. The reason for this apparent discrepancy is not immediately apparent, but it can be explained in part by the fact that many of the sesquiterpenes are large-ring compounds (e.g. cycloundecane derivatives). Such compounds are calculated to have much larger A_s values than corresponding acyclic isomers, or isomers with smaller rings. These abnormally large A_s values in turn lead to much lower values of R° (see eqn. 4).

Separations of isomers

The data of Table VII suggest that saturated hydrocarbons can be separated according to the relative branching along the alkyl chain. Isoalkanes migrate more rapidly than isomeric *n*-alkanes, although the effect is predicted to be rather small. Little separation of aliphatic from cyclic saturated hydrocarbons is predicted.

Isomeric olefins should be separable on silica according to the extent of alkyl substitution around the olefinic bond. While the separation of isomers such as the *cis*, *trans*, and asymmetric dialkylethylenes does not occur to any significant extent on silica, silver impregnated silicas exhibit marked differences in the adsorption of these compounds (see ref. 11). Consequently in some cases, for maximum differentiation of individual olefin isomers, it may be useful to carry out two-dimensional separations: first on silica, then on silver impregnated silica. In this way individual olefin isomers can be separated according to both the number and relative position of the alkyl groups attached to the double bond.

Separations of hydrocarbons by class

In some cases it is desirable to effect the separation of total saturated hydrocarbons from olefins, or of olefins according to the number of double bonds present in the molecule. The separation of saturated hydrocarbons from olefins is possible by means of high surface area silica and hydrocarbon solvents. However, some overlap of these two groups of compounds generally occurs, especially in the case of broad boiling samples such as petroleum fractions. One of the fundamental problems in such separations is the molecular weight selectivity of the separation. High molecular weight saturated hydrocarbons may have R° values greater than those of low molecular weight olefins, or vice versa. From eqns. 1a and 2 it is easy to show that when $\alpha_a(\epsilon_a - \epsilon_p)$ is equal to 0.02α for alumina, or -0.05α for silica, the addition of a methylene group to an alkane molecule will cause no net change in R° . That is, the separation system then exhibits no net molecular weight selectivity. Assuming separation on adsorbents with no added water (which is optimum for this separation), it can be shown that the best value of $\alpha_a(\epsilon_a - \epsilon_p)$ for alumina is 0.02α and for silica it is -0.05α . In the case of alumina, an $\alpha_a(\epsilon_a - \epsilon_p)$ value of 0.02 means quite small R° values for both saturated and olefinic hydrocarbons, and little or no separation of these two groups of compounds. Consequently the best system for the separation of saturated hydrocarbons as a class from all olefins in the sample is 0% H_2O - SiO_2 (high surface area) with a solvent containing about 60% of FC-78 (room temperature) or FC-75 (elevated temperature), depending upon the molecular weight and solubility of the sample. Because the mono- and dialkylethylenes are least strongly adsorbed on silica, there will be a tendency for these compounds to overlap the elution band for the saturated hydrocarbons. Addition of silver nitrate to the silica (see ref. 11) is not

expected to affect the migration of saturated hydrocarbons or the more highly substituted olefins, but it significantly retards the migration of the less highly substituted olefins. The use of silver impregnated silica, rather than ordinary silica, should therefore further improve the separation of saturated from olefinic hydrocarbons.

Separations of monoolefins from diolefins on alumina tend to be poor, at least for samples with an appreciable molecular weight spread. On silica the variation of R° with olefin substitution is expected to lead to extensive overlap of the mono- and diolefin classes. This problem should be much alleviated by use of silver impregnated silica, because of the tendency of the silver to selectively increase the adsorption of those olefins which are normally less strongly adsorbed. By adjustment of the concentration of silver on the silica, it should be possible to just cancel the normal effect of alkyl substitution on R° .

REFERENCES

- 1 R. L. CLEMENTS, *Science*, 128 (1958) 899.
- 2 L. R. SNYDER, *J. Chromatog.*, 11 (1963) 195.
- 3 E. STAHL AND H. YORK, in E. STAHL (Editor), *Thin-Layer Chromatography. A Laboratory Handbook*, Academic Press, New York, 1965, p. 189.
- 4 J. A. ATTAWAY, J. BARABAS AND R. W. WOLFORD, *Anal. Chem.*, 37 (1965) 1289.
- 5 J. A. ATTAWAY, *J. Chromatog.*, 31 (1967) 231.
- 6 L. R. SNYDER, *J. Chromatog.*, 36 (1968) 455.
- 7 L. R. SNYDER, *J. Chromatog.*, 16 (1964) 55.
- 8 L. R. SNYDER, *Anal. Chem.*, 39 (1967) 698.
- 9 L. R. SNYDER, *J. Chromatog.*, 6 (1961) 22.
- 10 G. H. STEWART, *Separ. Sci.*, 1 (1966) 747.
- 11 L. R. SNYDER, *Principles of Adsorption Chromatography*, Marcel Dekker, New York, 1968.
- 12 L. R. SNYDER AND E. R. FETT, *J. Chromatog.*, 18 (1965) 461.
- 13 T. A. BELLAR AND J. E. SIGSEY, JR., *Environ. Sci. Tech.*, 1 (1967) 242.
- 14 C. G. SCOTT, *J. Inst. Petrol.*, 45 (1959) 118.
- 15 C. G. SCOTT, *J. Gas Chromatog.*, 4 (1966) 4.
- 16 L. R. SNIJDER, *Anal. Chem.*, 39 (1967) 705.

J. Chromatog., 36 (1968) 476-488