

Gas Chromatographic Separation of Unsaturated Hydrocarbons Using Silver Nitrate in Ethylene Glycol as the Stationary Phase

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Silver nitrate in ethylene glycol has been investigated as a stationary phase for the separation of unsaturated hydrocarbons by gas chromatography. It is demonstrated, that this substrate has a high selectivity for various types of unsaturated hydrocarbons and is a valuable instrument for solving analytical problems related to hydrocarbons. Retention data are given for about 75 unsaturated hydrocarbons.

The usefulness of silver nitrate solutions as stationary phases for the gas chromatographic analysis of hydrocarbons was first recognized by Bradford *et al.*¹ They separated ethane and ethylene using a column containing silver nitrate in ethylene glycol. A comparative study of ethylene glycol, polyethylene glycol and glycerole as solvents for silver nitrate was made by Bednas and Russel² using a material consisting of alkanes and alkenes. They pointed out the difference in retention times between alkanes and alkenes as well as between *cis*- and *trans*-alkenes. The polyethylene glycol column was found to be inferior to the other two columns. Tenney³, in connection with studies of various liquid substrates used in gas chromatography, also investigated a solution of silver nitrate in triethylene glycol and demonstrated its ability to separate certain types of olefins. Van de Craats⁴ and later Luchsinger⁵ and Armitage⁶ utilized benzyl cyanide as a solvent for the silver nitrate. From the retention values given by Armitage it appears that the selectivity of this stationary phase for various hydrocarbon types is low. This fact can, at least in part, be attributed to the limited solubility of silver nitrate in benzyl cyanide. Thus, although this stationary phase has been stated to be more stable than other silver nitrate solutions, it seems to have a limited analytical value.

Cope *et al.*⁷⁻⁹ and Sauers¹⁰ used silver nitrate in di- or tetraethylene glycol as stationary phases when analyzing alkenes, methylcycloalkenes, methylenecycloalkanes and menthenes. The same types of unsaturated hydrocarbons have been investigated by means of silver nitrate/ethylene glycol^{11,12}. An interesting application of stationary phases containing silver nitrate was made by Cope *et al.*¹³ in the analysis of the *cis*- and *trans*-forms of cyclononene,

cyclodecene, cycloundecene and cyclododecene. Camphene and tricyclene were separated at 80°C by Powell and Whiting¹⁴ using silver nitrate/diethylene glycol. It can be questioned whether the silver nitrate plays any roll in this case in view of the reported inactivation of silver nitrate solutions above 65°C². Recently silver nitrate in various solvents has been used in a number of investigations principally dealing with C₂—C₄ hydrocarbons¹⁵⁻²².

The potential analytical value of silver nitrate solutions as stationary phases in gas chromatography is evident from the preceding review. However, these results have not included enough compounds to permit a thorough evaluation of this kind of packing. On that account it was decided to investigate the performance of about 75 unsaturated hydrocarbons of various types on a stationary phase consisting of silver nitrate in ethylene glycol. The first separation of 3- and 4-methyl-1-pentene by the present authors using this stationary phase was previously reported²³.

EXPERIMENTAL

Material. Most of the hydrocarbons used were prepared in this laboratory. The synthesis of some of them will be described elsewhere.

Apparatus and column. A Perkin-Elmer Vapor Fractometer model 154 was used in the experiments. The preparation of the stationary phase * and of the column has been described previously²³.

Procedure. [Relative retention times (R_T), using *trans*-2-pentene as internal standard, were determined throughout. An appropriate number of hydrocarbons were mixed with 2-pentene and the mixture run on a 2 m column at 25°C and 40 ml He/min. The retention times counted from the air top were measured and for each compound the retention time relative to *trans*-2-pentene was calculated.

It will be emphasized that the retention values are dependent on the concentration of silver nitrate in the solvent. As a certain change of composition takes place during use due to elution of the solvent, one might expect a change in the retention data with time. At 25°C, however, no serious variations in retention time have been observed, even after running the column daily for several months. The values obtained are collected in Table 1.

RESULTS AND DISCUSSION

The differing behaviour of the various unsaturated hydrocarbons on the silver nitrate/ethylene glycol stationary phase can largely be attributed to the presence of silver nitrate. Silver ions are known to form complex compounds with unsaturated hydrocarbons. There is also a certain parallelism between the established complex constants²⁴ and the retention values obtained in this work. This is to be expected since the same forces are active in both cases, although the environments are dissimilar.

The separation obtained between two hydrocarbons on the AgEG stationary phase is largely dependent on three factors, namely the vapour pressure of the compounds, the structural environment of the unsaturated bonds and the nature and number of the latter. Thus, for compounds with the same general structure there is as a rule a steady increase in retention time when going from one compound to the next higher in a series, partly as a consequence of the increased stability of the silver ion complex with decreased vapour pressure (*cf.* Ref.²⁴). The structural environment of the unsaturated bond has a pro-

* In the following the silver nitrate/ethylene glycol stationary phase will be denoted the AgEG stationary phase.

found influence on the retention time. Substitution of alkyl groups at the unsaturated bond for hydrogen atoms is often accompanied by a considerable decrease in retention time*. This latter effect dominates over the vapour pressure effect. On that account we get, for example, about the same retention time for 1-butene (b.p. -6°) and 3-methyl-3-hexene (b.p. 95°). *Cis*-isomers are retained more strongly than *trans*-isomers, reflecting another structural influence. The favourable conditions for complex formation present in cyclic alkenes are evident from their appreciably larger retention times in comparison with those for straight chain alkenes with similar structure and boiling point e.g. *cis*-2-pentene (b.p. 37° , $R_T = 3.8$) and cyclopentene (b.p. 44° , $R_T = 18.9$). Naturally, the type and number of the unsaturated bonds are also of importance. The retention time increases with the number of unsaturated bonds in the molecule. Thus diolefins are retarded more than monoolefins**. The retention time is also dependent on the relative position of two or more unsaturated bonds in a molecule. Acetylenic hydrocarbons travel more slowly than olefins in the same boiling range***.

The gas chromatographic separation of unsaturated hydrocarbons with different boiling points can be achieved using various stationary phases separating according to boiling point. The separation of unsaturated hydrocarbons in the same boiling range presents a more difficult problem. For this purpose a number of stationary phases have been used with more or less success (*cf.* Ref.²⁶). The application of the AgEG stationary phase to this problem will now be discussed in some detail. Fig. 1 gives a clear view of the separation possibilities for various types of unsaturated hydrocarbons on this stationary phase.

Saturated and unsaturated hydrocarbons. It has been pointed out previously² and will be further stressed here that this stationary phase is ideally suited to the separation of saturated from unsaturated hydrocarbons. Of the unsaturated hydrocarbons investigated *trans*-2-butene (b.p. -1°) has the lowest relative retention time (0.50), the same as that for the saturated hydrocarbon 2,4,4-trimethylpentane (b.p. 99°). This means that any saturated hydrocarbon boiling below about 90° will be released from this column before any unsaturated, even before ethene with the b.p. -104° , and have a relative retention time below 0.50.

Treatment of an unknown sample. Prior to an analysis of an unknown hydrocarbon sample using the AgEG stationary phase, it has to be divided into narrow fractions by distillation or better by gas chromatography using a "boiling point column", e.g. a squalane column†. The resulting fractions are then further analyzed on the AgEG stationary phase.

* Studies conducted on the stability of complex compounds between unsaturated hydrocarbons and various metal ions indicate that this substitution effect is partly of steric origin, partly connected with the influence exerted by the substituent on the electron density at the unsaturated bond. A bonding theory advanced by Dewar²⁵ seems to give the best explanation of the experimental facts.

** Certain monoolefins are more strongly retarded than 1,2-dienes in the same boiling range.

*** 1-Alkynes are retained on this column, a fact which may be utilized for the identification of this hydrocarbon type.

† If saturated hydrocarbons are present, it may be advantageous first to sort out these using the AgEG column, the approximate boiling range of the sample being ascertained beforehand.

Hydrocarbon type	Log relative retention time																
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6
Saturates (b.p. < 90°)	<-0.3																
1-Alkenes	CH ₂ =CH(CH ₂) _n CH ₃		3(-48°)			4(-6°)	5(30°)		6(64°)	7(94°)			8(121°)				
	CH ₂ =C(CH ₃)(CH ₂) _n CH ₃			4(-7°)	5(31°)		6(61°)		7(92°)								
	CH ₂ =CHCH(CH ₃)(CH ₂) _n CH ₃						5(20°)	6(54°)									
	CH ₂ =CHCH ₂ CH(CH ₃)(CH ₂) _n CH ₃							6(54°)									
	CH ₂ =C(CH ₃)CH(CH ₃)(CH ₂) _n CH ₃				6(56°)		7(84°)										
	CH ₂ =C(CH ₃)CH ₂ CH(CH ₃)(CH ₂) _n CH ₃					7(82°)											
	CH ₂ =CHC(CH ₃) ₂ (CH ₂) _n CH ₃							6(41°)									
	CH ₂ =C(CH ₃)C(CH ₃) ₂ (CH ₂) _n CH ₃							8(108°)									
	CH ₂ =C(CH ₃)CH ₂ C(CH ₃) ₂ (CH ₂) _n CH ₃						8(101°)										
	CH ₂ =C(C ₂ H ₅)(CH ₂) _n CH ₃							6(65°)		7(94°)							
2-Alkenes	CH ₃ CH=CH(CH ₂) _n CH ₃ - <i>cis</i>				4(4°)		5(37°)	6(69°)	7(99°)				8(126°)				
	CH ₃ CH=CH(CH ₂) _n CH ₃ - <i>trans</i>		5(36°)	6(68°)		7(98°)		8(125°)									
	(CH ₃) ₂ C=CH(CH ₂) _n CH ₃			6(67°)	7(95°)												
	CH ₃ CH=C(CH ₃)(CH ₂) _n CH ₃ - <i>cis</i>		6(71°)		7(94°)												
	CH ₃ CH=C(CH ₃)(CH ₂) _n CH ₃ - <i>trans</i>		6(68°)		7(94°)												
	CH ₃ CH=CHCH(CH ₃)(CH ₂) _n CH ₃ - <i>cis</i>						6(56°)										
	CH ₃ CH=CHCH(CH ₃)(CH ₂) _n CH ₃ - <i>trans</i>			6(59°)													
	(CH ₃) ₂ C=C(CH ₃)(CH ₂) _n CH ₃	6(73°)	7(97°)														
	(CH ₃) ₂ C=CHCH(CH ₃)(CH ₂) _n CH ₃			7(83°)													
	(CH ₃) ₂ C=CHC(CH ₃) ₂ (CH ₂) _n CH ₃				8(105°)												
	CH ₃ CH=C(C ₂ H ₅) ₂					9(96°)											
3-Alkenes	CH ₂ CH ₂ CH=CH(CH ₂) _n CH ₃ - <i>cis</i>							6(66°)	7(96°)								
	CH ₂ CH ₂ CH=CH(CH ₂) _n CH ₃ - <i>trans</i>					6(67°)	7(96°)										
	CH ₂ CH ₂ C(CH ₃)=CH(CH ₂) _n CH ₃ - <i>cis</i>						7(95°)										
	CH ₂ CH ₂ C(CH ₃)=CH(CH ₂) _n CH ₃ - <i>trans</i>						7(94°)										
Alkadienes	CH ₂ =C=CH(CH ₂) _n CH ₃				5(45°)	6(78°)	7(105°)										
	CH ₂ =CHCH=CH ₂																
	CH ₂ =CHCH=CH(CH ₂) _n CH ₃ - <i>cis</i>													5(44°)	6(73°)		
	CH ₂ =CHCH=CH(CH ₂) _n CH ₃ - <i>trans</i>													5(42°)	6(73°)		
	CH ₂ =C(CH ₃)CH=CH ₂																
	CH ₂ =CHCH=C(CH ₃) ₂																
	CH ₂ =CH(CH ₂) _n CH=CH ₂																
	CH ₃ CH=CHCH=CH(CH ₂) _n CH ₃ - <i>cis/cis</i>														5(26°)	6(60°)	
	CH ₃ CH=CHCH=CH(CH ₂) _n CH ₃ - <i>cis/trans</i>															6(83°)	
	CH ₃ CH=CHCH=CH(CH ₂) _n CH ₃ - <i>trans/trans</i>															6(81°)	
	CH ₃ CH=CHCH=CH(CH ₂) _n CH ₃ - <i>trans</i>															6(79°)	
Allyl Cyclo-nes	CH=CH-(CH ₂) _n														5(44°)	6(83°)	
	CH ₃ C=CH-(CH ₂) _n														6(76°)		
	CH=CH-(CH ₂) _n -CH=CH															5(43°)	6(82°)
Allyl Cyclo-nes	CH ₃ C=C(CH ₂) _n CH ₃					4(27°)									5(56°)		
	CH ₃ CH ₂ C=C(CH ₂) _n CH ₃															6(80°)	7(111°)
Aromatics																	8(139°)

Fig. 1. Log. relative retention time (*trans*-2-pentene internal standard) for various types of unsaturated hydrocarbons on a silver nitrate/ethylene glycol column. (The first number denotes the number of carbon atoms in the molecule and the number within parenthesis denotes the b.p. of the compound.)

Alkene types $RCH=CHR(I)$, $R_2C=CHR(II)$ and $R_2C=CR_2(III)$ *. The possibility of separating close-boiling *cis*- and *trans*-isomers on the AgEG stationary phase was pointed out already by Bednas and Russel². However, not always can a separation be achieved. A necessary condition is that the structural environment of the two forms be distinctly dissimilar. This is the case for the type $RCH=CHR(I)$ but not always for the types $R_2C=CHR(II)$ or $R_2C=CRR(III)$. In the *cis*-form of type I the hydrogen side is considerably more open than the other and than the two sides in the *trans*-form. In the *cis*-

* R may denote the same or different alkyl groups.

Table 1. Relative retention times for hydrocarbons on a silver nitrate/ethylene glycol column.

Hydrocarbon	Boiling point °C	Relative retention time (R_T) (trans-2-pentene = 1.00)
Saturates		
<i>n</i> -Pentane	36.1	0.07
<i>n</i> -Hexane	68.7	0.14
2,2,4-Trimethylpentane	99.2	0.50
Cyclohexane	60.7	0.37
Aromatics		
Benzene	80.1	6.91
Toluene	110.6	12.9
<i>m</i> -Xylene	139.1	22.0
<i>p</i> -Xylene	138.4	21.8
Alkenes		
C ₂ Ethene	-103.7	0.67
C ₃ Propene	-47.7	1.04
C ₄ 1-Butene	-6.3	2.38
<i>cis</i> -2-Butene	3.7	2.09
<i>trans</i> -2-Butene	0.9	0.50
Isobutene	-6.9	1.44
C ₅ 1-Pentene	30.0	3.29
<i>cis</i> -2-Pentene	36.9	3.77
<i>trans</i> -2-Pentene	36.4	1.00
2-Methyl-1-butene	31.2	2.77
3-Methyl-1-butene	20.1	2.69
2-Methyl-2-butene	38.6	0.71
C ₆ 1-Hexene	63.5	5.65
<i>cis</i> -2-Hexene	68.8	5.35
<i>trans</i> -2-Hexene	67.9	1.47
<i>cis</i> -3-Hexene	66.4	6.73
<i>trans</i> -3-Hexene	67.1	1.91
2-Methyl-1-pentene	60.7	3.30
3-Methyl-1-pentene	54.1	3.79
4-Methyl-1-pentene	53.9	3.06
2-Methyl-2-pentene	67.3	1.48
3-Methyl- <i>cis</i> -2-pentene	70.5	1.49
3-Methyl- <i>trans</i> -2-penten	67.6	1.49
4-Methyl- <i>cis</i> -2-pentene	56.3	3.73
4-Methyl- <i>trans</i> -2-pentene	58.6	1.10
2,3-Dimethyl-1-butene	55.7	3.15
3,3-Dimethyl-1-butene	41.2	2.94
2-Ethyl-1-butene	64.7	5.25
2,3-Dimethyl-2-butene	73.2	1.00
C ₇ 1-Heptene	93.6	9.14
<i>cis</i> -2-Heptene	98.5	8.17
<i>trans</i> -2-Heptene	98.0	2.50
<i>cis</i> -3-Heptene	95.8	8.17
<i>trans</i> -3-Heptene	95.7	2.70
2-Methyl-1-hexene	92.0	5.65
2-Methyl-2-hexene	95.4	2.06
<i>cis</i> -3-Methyl-2-hexene	94.0	2.00
<i>trans</i> -3-Methyl-2-hexene	94.0	2.00
<i>cis</i> -3-Methyl-3-hexene	95.3	2.50
<i>trans</i> -3-Methyl-3-hexene	93.5	2.50
2,3-Dimethyl-1-pentene	84.3	3.30

Table 1, continued.

	2,4-Dimethyl-1-pentene	81.6	2.30
	2-Ethyl-1-pentene	94.0	6.75
	2,3-Dimethyl-2-pentene	97.4	1.03
	2,4-Dimethyl-2-pentene	83.3	1.19
	3-Ethyl-2-pentene	96.0	2.66
C ₈	1-Octene	121.3	16.1
	<i>cis</i> -2-Octene	125.6	16.1
	<i>trans</i> -2-Octene	124.9	5.03
	2,3,3-Trimethyl-1-pentene	108.3	2.89
	2,4,4-Trimethyl-1-pentene	101.4	2.33
	2,4,4-Trimethyl-2-pentene	104.9	1.86
Alkadienes			
C ₄	1,3-Butadiene	-4.4	5.17
C ₅	1,2-Pentadiene	44.9	1.92
	1, <i>cis</i> -3-Pentadiene	44.1	18.0
	1, <i>trans</i> -3-Pentadiene	42.0	10.2
	1,4-Pentadiene	26.0	18.7
	2-Methyl-1,3-butadiene	34.1	7.87
C ₆	1,2-Hexadiene	76	3.32
	1, <i>cis</i> -3-Hexadiene	72.5	24.2
	1, <i>trans</i> -3-Hexadiene	72.5	16.5
	1,5-Hexadiene	59.5	32.2
	<i>cis</i> -2- <i>cis</i> -4-Hexadiene	83	41.5
	<i>cis</i> -2- <i>trans</i> -4-Hexadiene	81	19.8
	<i>trans</i> -2- <i>trans</i> -4-Hexadiene	79	8.75
	4-Methyl-1,3-pentadiene	76.3	12.3
C ₇	1,2-Heptadiene	105	5.60
Cycloalkenes			
	Cyclopentene	44.2	18.9
	Cyclohexene	83.0	26.6
	1-Methylcyclopentene	75.8	10.4
Cycloalkadienes			
	1,3-Cyclopentadiene	42.5	28.9
	1,3-Cyclohexadiene	81.5	31.9
Alkynes			
	2-Butyne	27.0	2.38
	2-Pentyne	56.1	10.2
	3-Hexyne	81.4	14.9

forms of types II and III the structures on both sides are more alike and similar to those in the *trans*-forms. On that account *cis*- and *trans*-isomers of the two latter types have very nearly the same retention times. The reason for this is obviously steric. In the *cis*-form of type I the silver ion can get into closer contact with the double bond than in the *trans*-form and in the isomers of types II and III.

A further consequence is that it will be difficult to separate the *trans*-form of type I from the isomers of type II, if they have similar boiling points. Thus *trans*-2-hexene, 2-methyl-2-pentene and *cis*- and *trans*-3-methyl-2-pentene all boil at about 70°C, while *trans*-2-heptene, 2-methyl-2-hexene and *cis*- and *trans*-3-methyl-2-hexene all boil near 95°C. Neither of these groups is resolved on the AgEG column. Further examples in the latter boiling range are *trans*-3-heptene, *cis*- and *trans*-3-methyl-3-hexene and 3-ethyl-2-pentene. However, the data suggests that alkenes of type III can be separated from the *trans*-

form of type I and alkenes of type II, *cf.* 2,3-dimethyl-2-pentene and the above-mentioned heptenes.

Sometimes one may encounter difficulties in separating *cis*-forms of various alkenes of type I and also these from alkenes of the type $\text{CH}_2=\text{CHR}$ (IV); *cf.* *cis*-2- and *cis*-3-heptene, 1-octene and *cis*-2-octene.

Alkene types $\text{CH}_2=\text{CHR}$ (IV) and $\text{CH}_2=\text{CR}_2$ (V). As might be expected, alkenes belonging to type V generally are released before alkenes belonging to type IV, when they appear in the same boiling range. This fact is exemplified by 1-pentene and 2-methyl-1-butene and by the corresponding hexenes and heptenes. A further example is given by 1-heptene and 2-ethyl-1-pentene. The risk of coincidence between alkenes of type IV and the *cis*-forms of type I was mentioned previously.

Influence of substituents elsewhere than at the C=C bond. It is of particular interest that the retention times of alkenes on the AgEG stationary phase are also influenced by substituents elsewhere than at the ethylenic bond. This is of value since close-boiling isomers only differing in having methyl groups in the β - and γ -positions to the ethylenic bond are difficult to separate on other types of stationary phases. The γ -isomers generally have the shortest retention times*. This difference in retention time was previously utilized for the separation of 3- and 4-methyl-1-pentene²³. Other examples are given by 2,3-dimethyl-1-pentene and 2,4-dimethyl-1-pentene and by 2,3,3-trimethyl-1-pentene and 2,4,4-trimethyl-1-pentene.

Cycloolefins, alkadienes and alkynes. Hydrocarbons belonging to this group travel more slowly than monounsaturated straight chain alkenes and can generally be separated from the latter ones. There is, however, one exception. 1,2-Alkadienes** which are released before the other types of hydrocarbons discussed in this section may be mixed up with certain monounsaturated straight chain alkenes.

Thus, while 1,2-alkadienes may be sorted out from the rest of hydrocarbons mentioned in the heading, the separation of close-boiling specimens of other types of alkadienes, cycloolefins and alkynes is not always feasible on the AgEG stationary phase.

Considering the influence of stereoisomerism and replacement of hydrogen atoms at various positions by alkyl groups, the same rules as previously outlined for alkenes apply. The retention data for the three close-boiling isomers of 2,4-hexadiene give a particularly clear demonstration of the influence of stereoisomerism and of the analytical usefulness of this stationary phase.

Aromatic hydrocarbons are, in accordance with their less olefinic nature, less retarded than cyclic unsaturated hydrocarbons, *e.g.* benzene (b.p. 80°, $R_T = 6.9$) and cyclohexene (b.p. 83°, $R_T = 26.6$). Because aromatic hydrocarbons appear together with alkenes, it is advantageous to remove them before the separation on the AgEG column, *e.g.* by using a picrate column²⁷.

Analytical use. The principal analytical use of the AgEG stationary phase may be summarized. (1) For type separation of saturated hydrocarbons from

* The greater shielding of the double bond by a methyl group in γ -position is evident from an inspection of molecular models of the compounds.

** A similar behaviour can be expected from other types of alkenes.

all types of unsaturated. (2) For type separation of monounsaturated alkenes from alkadienes (except 1,2-dienes and possibly other allenes), cycloolefins and alkynes. (3) For separating close-boiling isomers of various types of unsaturated hydrocarbons. Of special importance is the possibility of separating *cis*- and *trans*-isomers with certain exceptions. Further separation possibilities arise from substitution at or in the vicinity of the unsaturated bond. (4) For determination, on the basis of the retention time, if a certain hydrocarbon is unsaturated or not. The combination of gas chromatography using the AgEG stationary phase with the hydrogenation methods recently described by the present authors²⁸ has proved to be especially fruitful for the identification of unsaturated hydrocarbons.

It is hoped that the present attempt to broaden the knowledge of the behaviour of unsaturated hydrocarbons on the AgEG stationary phase will be of use not only for the separation and identification of hydrocarbons in the actual boiling range but will also facilitate the analysis of higher boiling fractions.

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