Reviews

Superselective aqueous inorganic phases in vapor-phase gas chromatography

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Chromatographic characteristcs of aqueous solutions of inorganic electrolytes, a new class of stationary liquid phases (SLP) for vapor-phase chromatography, are considered. The SLP are characterized by an unusually high selectivity to organic compounds of the R—X type (R is a hydrocarbon radical, X is a polar group, *e.g.*, hydroxyl, carboxyl, and amine; for instance, light C_1—C_6 alcohols are eluted from the column with a water-containing phase in the following order: hexanol < pentanol < butanol < propanol < ethanol < methanol). The nature of the electrolyte used and its concentration in the water-containing SLP have a crucial influence on the column selectivity and the degree of separation of the compounds subjected to chromatography. This feature provides the possibility of controlling the column selectivity by changing the content of water vapor in the mobile phase.

Key words: gas chromatography, superselective stationary liquid phases, vapor-phase chromatography, water-containing stationary liquid phases, properties of water—inorganic electrolyte systems, determination of impurities, complex-forming stationary liquid phases, preparative chromatography.

Introduction

An important problem of applied chromatography is separation of compounds with similar physicochemical properties.[1—3] Separation of two compounds *i* and *j* is characterized quantitatively by peak resolution $R_{S_{ij}}$, which is determined by three factors, namely, the selectivity (*S*), efficiency (*E*), and capacity (*C*)[4]:

$$R_{S_{ij}} = S \cdot E \cdot C, \quad (1)$$

$$S_{ij} = (\alpha_{ij} - 1)/\alpha_{ij}, \quad (2)$$

$$E_j = \sqrt{N_j}/4, \quad (3)$$

$$C_j = k_j/(k_j + 1), \quad (4)$$

where $\alpha_{ij} = k_j/k_i$ is the separation factor or the relative retention time (indices *i* and *j* refer to the first and second compounds eluted from the column); N_j is the number of theoretical plates in the column; and k_i and k_j are retention factors for compounds *i* and *j*, respectively.

The main characteristic determining the separation factor is the selectivity of the stationary liquid phase (SLP) used. Even a slight increase in the separation factor α_{ij} results in a sharp increase in the R_{ij} value and, therefore, it permits a substantial decrease in the number of theoretical plates needed to ensure an effective separation of compounds. The decrease in the number of theoretical plates makes it possible to reduce the duration of the analysis. Therefore, extensive studies dealing with the search for and investigation of new selective

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SLP (see, for example, Refs. 1—3 and 5—7) are carried out with gas chromatography. As a rule, new selective SLP possess specific physicochemical and chromatographic characteristics (capacity for complexation, molecular-sieve properties, *etc.*).

Water with its unusual properties and unique structure[8—16] has long been attracting the attention of researchers, among other aspects, as a promising SLP.

The main promising fields of application of water-containing SLP include determination of impurities in aqueous media, determination of polar impurities in nonpolar media (for example, in hydrocarbons), extension of the range of applicability of complexation chromatography (for example, the use of an aqueous solution of $AgNO_3$ as an SLP), and determination of physicochemical characteristics of aqueous solutions by reversed-phase chromatography.

The main purpose of this review is to describe a new type of selective water-containing SLP and the prospects for their practical application.

Water as a selective SLP

Water was first used as an SLP in separating chloromethanes at ambient column temperature.[17] Although the results obtained indicated that water functioned as a polar SLP, it readily escaped the column in the stream of a dry carrier gas; therefore, the problem of extensive use of water as an SLP has not been discussed.

The next step in the application of water in gas-liquid chromatography is associated with the use[18] of pure water as the SLP under conditions of saturation of the mobile phase with water vapor. An inert gas saturated with water vapor at the temperature of the column was then used as the carrier gas. Despite the fact that this technique increased markedly the column stability and service life, the aqueous SLP still remained unstable and the content of water in the column rapidly decreased with time. Later, a study was published[19] in which the mechanism of evaporation of stationary liquid phases under gas chromatography conditions was considered for the first time. It was shown that the phase escapes over the whole length of the column even in the case where a gas saturated with the SLP vapor is used as the mobile phase. Obviously, as the carrier gas moves along the column, its volume increases and the concentration of the SLP vapor in it decreases. The additional evaporation of the volatile SLP immediately compensates this decrease.

Data indicating that water possesses a unique selectivity as an SLP have been reported.[18] As an example, Fig. 1 shows the chromatogram for the separation of *n*-alcohols on water at 70 °C. The order of elution of C_1—C_5 alcohols in the presence of water is opposite to the conventional sequence of their separation with known SLP, *i.e.*, the retention time increases in the series AllOH < BuOH < PrOH < EtOH < MeOH. The separation of diol isomers (Fig. 2) is an important practical achivement along this line.

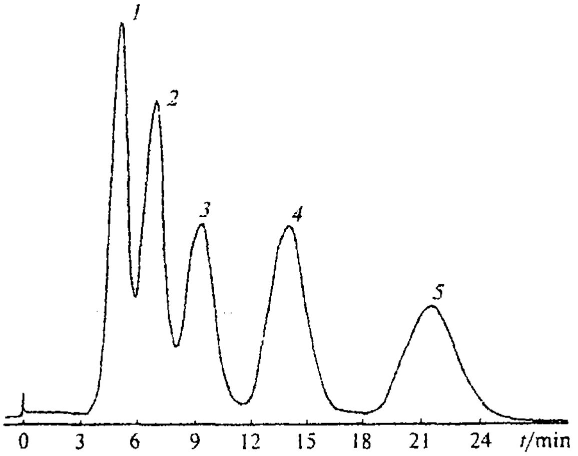

Fig. 1. Chromatogram for the separation of C_1—C_5 *n*-alcohols on an aqueous SLP[18]: *n*-pentanol (*1*), *n*-butanol (*2*), *n*-propanol (*3*), *n*-ethanol (*4*), methanol (*5*). Experimental conditions: water on the solid support Gas Chrom CLZ (80—100 mesh) as the sorbent, temperature 70 °C, water vapor (40 mL min^{-1}) + nitrogen (60 mL min^{-1}) as the carrier gas.

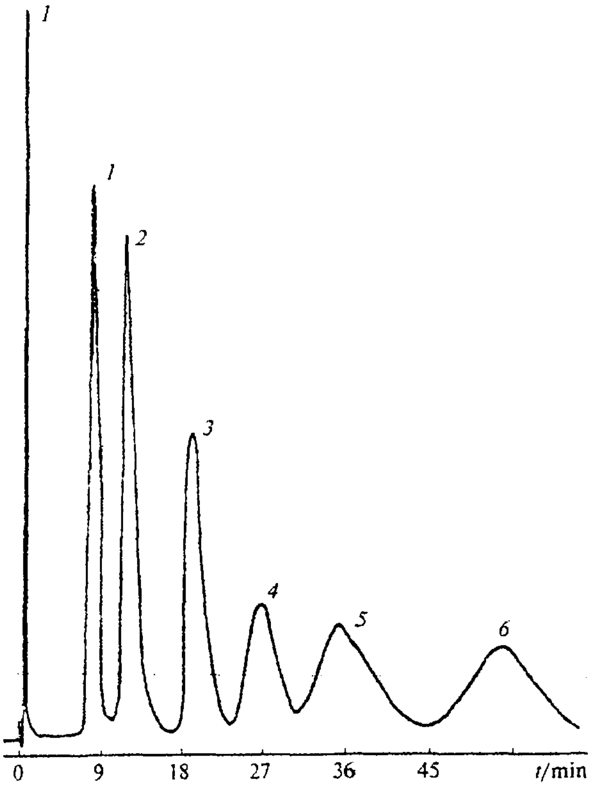

Fig. 2. Chromatogram for the separation of a mixture of diols on an aqueous SLP[18]: butane-2,3-diol (*1*), propane-1,2-diol (*2*), butane-1,3-diol (*3*), ethane-1,2-diol (*4*), propane-1,3-diol (*5*), butane-1,4-diol (*6*). Experimental conditions: water on the solid support Gas Chrom CLZ (80—100 mesh) as the sorbent, temperature 94 °C, water vapor (37 mL min^{-1}) + nitrogen (51 mL min^{-1}) as the mobile phase.

The behavior of water as an SLP has also been considered in other publications.[20,21] It was shown[20] that *n*-alkanes can be separated with water on a column kept at a temperature lower than the boiling points of the compounds under analysis by 200 °C. The retention times of *n*-alkanes (*e.g.*, *n*-decane) on the aqueous phase were substantially shorter than those for columns with conventional phases (Table 1). This is due to the fact that paraffins are virtually insoluble in water and are retained only due to adsorption on the gas—water interface, which is highly homogeneous and ensures good reproducibility of the adsorption characteristics. It was shown[21] that isooctanes can be efficiently separated on a column with water. Unfortunately, none of these studies was important for practical purposes because the retention times of compounds on these columns with water did not remain unchanged with time due to the evaporation of water.

More sucsessful and very interesting results have been obtained when water has been used to determine various physicochemical characteristics by reversed-phase chromatography, in particular, to determine[22—24] the absorption and adsorption characteristics of organic sorbates in gas—water system.

The above experiments were carried out under conditions of vapor-phase chromatography, in which steam was used as the mobile phase. Under these conditions, polar compounds come out as symmetrical zones and the use of large aqueous samples permits determination of trace impurities of organic compounds.[25,26] Therefore, the use of preparative vapor-phase chromatography in combination with aqueous solutions of salts as selective SLP provides this method with additional advantages over those using traditional stationary phases.

The use of mixed mobile phases containing an inert gas and water was first proposed for gas adsorption[27] and gas-liquid[28] chromatography. It has been shown that water vapor can be used as the mobile phase in capillary chromatography.[29]

Water-containing inorganic (salt) phases as stable analogs of the aqueous phase

The third step of the development of aqueous SLP in gas chromatography includes the use of aqueous inorganic (water—salt) phases under conditions of vapor-phase chromatography. Similar experimental approaches for the use of a water-containing vapor phase or a steam—inert carrier gas mixture as the mobile phase have been developed.[25,26] The general scheme of a vapor-phase chromatography experiment with a water-containing SLP is as follows. The mobile phase (pure steam or a steam-containing inert gas) moves along the column through a sorbent bed. The sorbent used is a solid support on whose surface a film of an aqueous solution of an inorganic salt (acid or alkali) is formed. Water contained in the SLP occurs in equilibrium with the steam of the mobile phase, *i.e.*,

$$\underset{\text{Steam in the mobile phase}}{H_2O} + \underset{\text{salt}}{MeX} \rightleftharpoons \underset{\text{Aqueous salt solution as the SLP}}{(MeX\text{—}H_2O)} \qquad (5)$$

At a constant temperature, the partial pressure of the water vapor in the mobile phase is related to the salt concentration in the water—salt SLP by the following equation:

$$p_{H_2O} = \varphi(C_{MeX}, T), \qquad (6)$$

where p_{H_2O} is the equilibrium water vapor pressure in the mobile phase, C_{MeX} is the equilibrium concentration of salt MeX in the aqueous solution (SLP), and T/K is temperature.

Table 1. Retention of *n*-decane at 50 °C with variois SLP

No.	Stationary liquid phase	t_R/min
1	2-Ethylhexyl sebacate	>1000
2	Apiezon L	>1000
3	Polyethylene glycol	20
4	Polyethylene glycol succinate	80
5	Water	<0.3

Note. Experimental conditions: *1—4*, organic phases as the SLP, 20% SLP on Chromosorb, 4-m long column[3]; *5*: water as the SLP, 46% water on Chromosorb P, a 1-m column.[20]

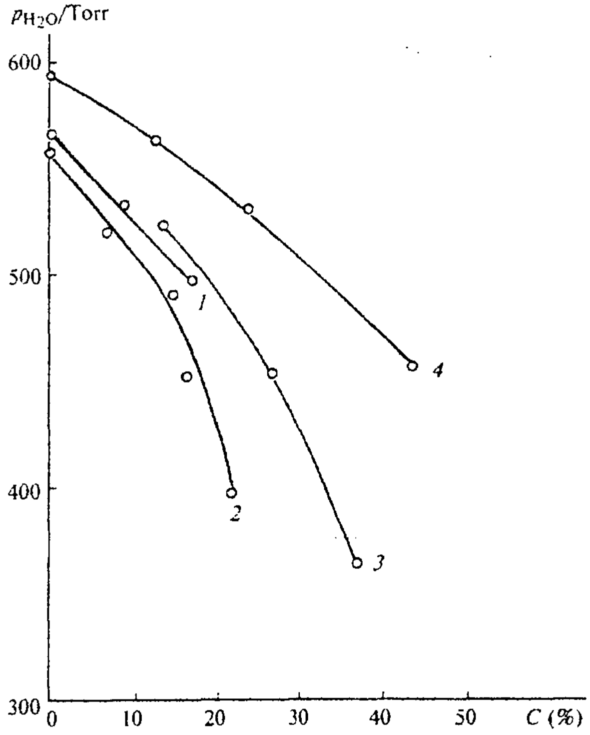

Fig. 3. The partial pressure (p) of water vapor in the mobile phase *vs* the concentration (C) of the salt in water—salt SLP: *1*, NaCl, 92.0 °C; *2*, LiCl, 91.6 °C; *3*, $LiNO_3$, 92.2 °C; *4*, RbCl, 91.6 °C.

This is exemplified in Fig. 3, which shows the plots for the equilibrium water vapor pressure *vs* the equilibrium salt concentration in the aqueous solution constructed using experimental data published previously.[30] It follows from Fig. 3 that an increase in the water vapor pressure results in a higher water content in the equilibrium solution, thus diluting the salt solution.

The aqueous salt SLP is formed upon contacting a salt located on the surface of a solid support with a water-containing mobile phase; the composition of the aqueous salt solution at a given temperature is determined by the water content in the mobile phase. Hence, the partial pressure of the water vapor in the mobile phase should be considered as an additional factor influencing the composition and the selectivity of the SLP. A mechanism for the formation of a solution upon interaction of water vapor with a solid salt has been proposed.[31]

Thus, the principle of action of a vaporized aqueous electrolyte is similar to that of the liquid phase in liquid chromatography, in which the nature and the composition of the mobile phase influence significantly the separating power of the chromatographic system as a whole.

Chromatographic selectivity of water—salt SLP

Aqueous solutions of salts were first used as SLP in the chromatographic laboratory at the Institute of Petrochemical Synthesis of the RAS.[32—42] They are highly selective and stable. The selectivity of aqueous salt solutions is unusual and presents obvious interest for application of many practically important separation procedures. The nature of this selectivity is due, first, to the unusual properties of water and water—salt solutions and, second, in some cases, to the formation of complexes, for example, in the aqueous phase between the salt cations and the compounds subjected to chromatography.[43]

Table 2. Selectivity of the separation of organic compounds of various classes on inorganic and organic polar SLP

Compound	Relative retention[a]			
	$MgNO_3$—H_2O[b]	$Al(NO_3)_3$—H_2O[b]	TCEP[c]	ODN[d]
n-Decane	0.04	0.08	0.25	—
n-Undecane	0.07	0.13	0.41	—
n-Dodecane	0.11	0.23	0.68	—
Benzene	0.04	—	0.70	0.60
Methanol	9.50	8.48	—	0.50
Ethanol	4.63	5.08	—	0.66
Propanol	2.04	3.53	—	1.17
Butanol	—	2.51	—	2.08
Pentanol	—	2.22	—	4.37
Acetone	1.79	1.68	0.71	0.66
Methyl ethyl ketone	1.0[e]	1.00[f]	1.00	1.00
Nitromethane	3.24	3.40	3.91	4.01
1-Nitropropane	0.84	1.07	—	—
2-Nitropropane	0.63	0.78	—	4.19

[a] Separation factor: k_i/k_{MEK}; MEK is methyl ethyl ketone.
[b] Separation temperature 120 °C.[35]
[c] TCEP is tri(β-cyanoethoxy)propane, separation temperature 100 °C.
[d] ODN is β,β′-oxydipropionitrile, separation temperature 100 °C.
[e] $k = 2.42$.
[f] $k = 2.62$

Water—salt phases exhibit very high selectivity to alcohols and some other organic compounds (Table 2). At a temperature of 120 °C, nonpolar hydrocarbons (C_{10}—C_{12}) are weakly retained on a water—salt SLP, the retention of nitromethane is relatively strong, and nitropropanes are retained weakly. However, the order of elution of light alcohols from a water—salt SLP is opposite to that observed for other known SLP; the retention of alcohols increases in the series AllOH < BuOH < PrOH < EtOH < MeOH. This reversed order of elution and the sharp difference between the retention of paraffins and polar compounds provides grounds for regarding water-containing phases as being superselective. The retention of C_1—C_3 alcohols on these phases is characterized by fairly high retention factors compared to those attained on traditional SLP.

The unusually high selectivity of aqueous salt SLP is clearly demonstrated by comparison of two chromato-

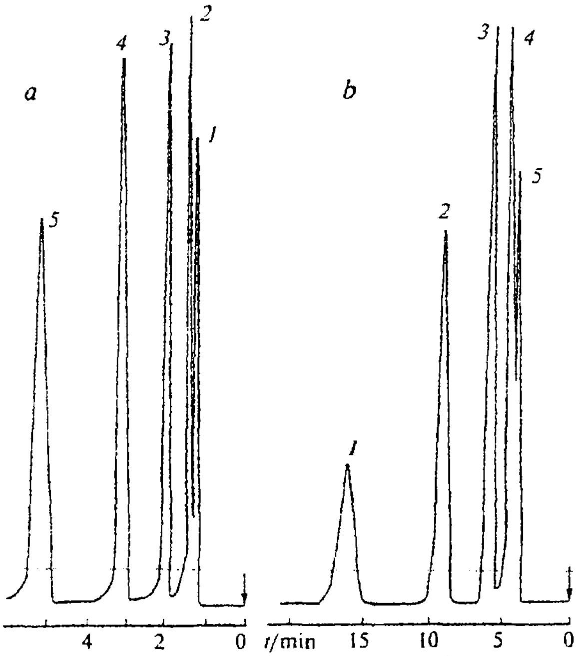

Fig. 4. Chromatogram for the separation of C_1—C_5 *n*-alcohols by vapor-phase chromatography on the following sorbents[46]: nonpolar SE-30 (*a*) and an aqueous solution of $LiNO_3$ (*b*): *1*, MeOH; *2*, EtOH; *3*, PrOH; *4*, Bu^nOH; *5*, All^nOH. Experimental conditions: a 2 m × 3 mm column; (*a*) 15% SE-30 on Chromaton N-AW as the sorbent, 90 °C, 66% H_2O + 34% N_2 as the mobile phase; (*b*) 10% $LiNO_3$ on Chromaton N-AW as the sorbent, 64 °C, 17% H_2O + 83% N_2 as the stationary phase.

grams of alcohols (Fig. 4), obtained with polydimethylsiloxane SE-30 and an aqueous solution of $LiNO_3$, respectively, as the SLP. It follows from the chromatograms that in the case of SE-30, methanol is the first and ethanol is the second to be eluted, while in the case of the water-containing salt phase, ethanol precedes methanol.

The use of water, which is the volatile component of water—salt SLP, imposes an upper temperature limit for aqueous salt systems. Nevertheless, water—salt phases still can be used at relatively high temperatures of the column (up to 150 °C),[42] which allows analysis of alcohols with boiling points of up to 350 °C.

Table 3 presents characteristics of the retention of hexadecanol isomers with the $CaCl_2—H_2O$ system (packed column) and PEG-20M (capillary column) being used as SLP.[42] The data listed in Table 3 indicate that the selectivity of separation of these alcohols is much higher when a packed column with a water—salt SLP is used.

Some other water—salt systems (*e.g.*, $KF \cdot 2H_2O$) have been successfully used to solve a number of important practical problems (see, *e.g.*, Refs. 47, 48). However, the order of elution of alcohols on this crystal hydrate is not reversed. Obviously, due to the high concentration of the salt, the properties of water are no longer manifested in this water—salt system.

Thus, water—salt systems in vapor-phase chromatography possess the following features:

1. The order of elution of $C_1—C_8$ alcohols in columns with aqueous salt phases differs from that observed with conventional SLP.

2. The dependence of the retention factor k of alcohols on the number of carbon atoms in the alcohol n (function $k = f(n)$) passes through a minimum at $n = 5$ to 8 depending on the nature of the salt system employed.

3. The ability of a water—salt phase to alter the traditional order of elution of alcohols depends on the nature of the salt used and decreases in the sequence LiX > NaX > KX (X = Cl, NO_3). This implies that the reversed order of elution of alcohols on an aqueous solution of LiCl is retained up to heptanol; in the case of NaCl, it is observed up to hexanol, and with KCl, it is retained up to butanol.

4. An increase in the concentration of water vapor in the mobile phase and a decrease in the column temperature results in a higher water content in the water—salt SLP and its higher selectivity.

The mechanism of retention of alcohols on water—salt phases is fairly complex; however, the features of retention of various molecules can be explained in the following way. As the hydrocarbon chain in the alcohol molecule becomes longer, *i.e.*, the number of carbon atoms in the molecule increases, the retention factor, the partition coefficient of the alcohol, and its solubility in the water—salt phase decrease. As the solubility of the alcohol in the water—salt SLP decreases, the bulk mechanism of retention changes to a surface mechanism, *i.e.*, to the retention of the sorbate at the interface between the mobile phase and the water—salt liquid phase. Therefore, the presence of a minimum on the plot of the k value *vs* the number of C atoms is apparently due to the transition from partition to adsorption mechanism of retention (Fig. 5). The Figure shows that this minimum is observed for all six of the water—salt systems studied and that lithium-based systems make the most selective SLP.[38] Indeed, the reversed order of elution of

Table 3. Retention of hexadecanol isomers on $CaCl_2—H_2O$ (water vapor as the mobile phase, packed column) and PEG-20M (helium as the mobile phase, capillary column)[42]

Chromatographed compound	$CaCl_2—H_2O$		PEG-20M	
	k	α	k	α
Hexadecan-1-ol	11.7	4.10	15.7	2.2
Hexadecan-2-ol	6.7	2.35	8.3	1.2
Hexadecan-3-ol	2.8	1.00	7.0	1.0

Note. α is relative retention; k is the retention factor.

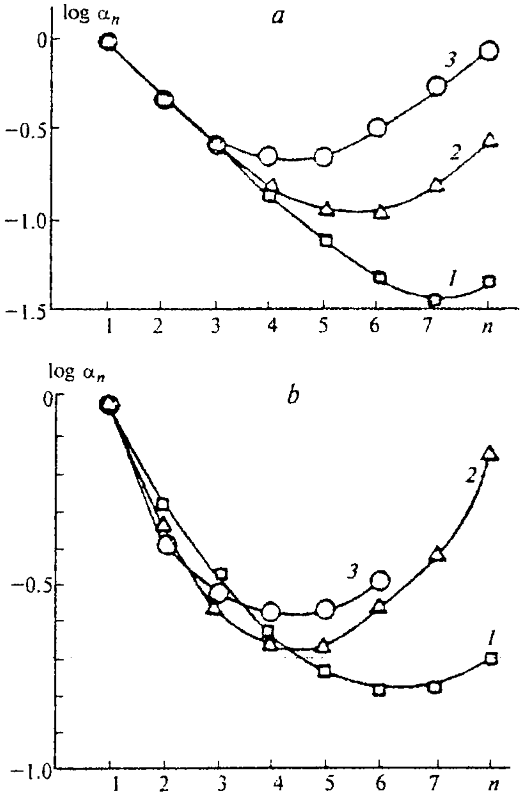

Fig. 5. Relative retention logarithms log α_n for $C_1—C_8$ alcohols *vs* the number of carbon atoms in the alcohol molecule for water—salt SLP[37]: (*a*) *1*, LiCl, *2*, NaCl, *3*, KCl; (*b*) *1*, $LiNO_3$, *2*, $NaNO_3$, *3*, KNO_3. Experimental conditions: a 2 m × 3 mm column, 20% salt on Celite C-22, temperature 108 °C, water vapor as the mobile phase.

n-alcohols is retained up to hexanol for an aqueous solution of $LiNO_3$ (SLP) and only to *n*-butanol for a solution of $NaNO_3$.

Selective separation of organic acids and amines on acidic and basic aqueous inorganic SLP

The results obtained for the separation of alcohols on water—salt phases can be used to analyze various organic acids and amines. In particular, it has been shown that organic acids can be separated on aqueous solutions of phosphoric acid under conditions of vapor-phase chromatography.[49] The results proved to be similar to those obtained for the separation of alcohols on water—salt SLP. Fig. 6 shows the chromatogram for the separation of C_2—C_8 fatty acids on a column packed with an acidic sorbent (20% H_3PO_4 on Chromaton). The order of elution of organic acids is opposite to that observed on traditional phases (Fig. 7). Thus, the unusual selectivity and the minimum on the $k = f(n)$ curve noted above for the separation of alcohols on water—salt phases are also visible in the separation of organic acids on an aqueous solution of H_3PO_4 under the conditions of vapor-phase chromatography.

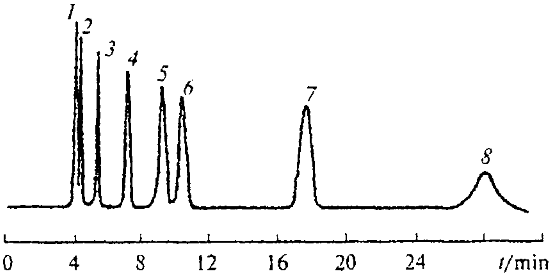

Fig. 6. Chromatogram for the separation of C_2—C_8 organic fatty acids on a packed column (initial sorbent 20% H_3PO_4 on Chromaton) at 115 °C[49]; acids: caprylic (*1*), enanthic (*2*), caproic (*3*), valeric (*4*), isobutyric (*5*), propionic (*7*), acetic (*8*).

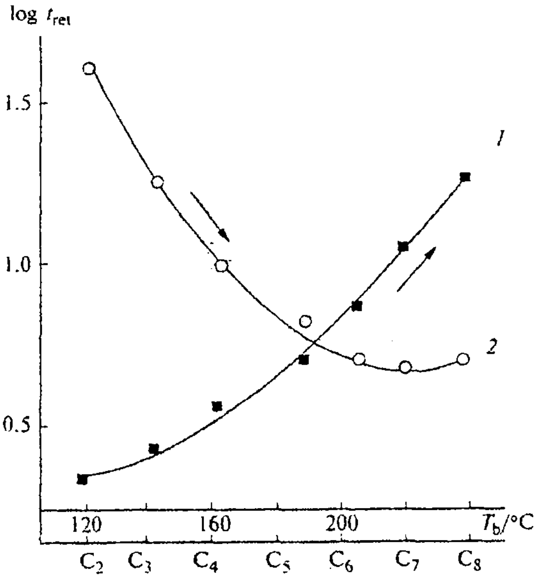

Fig. 7. Retention times (t_R) of C_2—C_8 fatty acids on polar phases *vs* their boiling points: *1*, trimeric organic acids[45]; *2*, water vapor, H_3PO_4.[49]

A similar regularity is also observed for the separation of amines on an aqueous solution of potassium hydroxide.[50] Thus in the presence of this solution, primary amines are eluted in the order *n*-amylamine < *n*-butylamine < *n*-propylamine, whereas elution on normal phases follows the series *n*-propylamine < *n*-butylamine < *n*-amylamine. In all experiments, the chromatographic zones of both acids and amines were symmetrical.

Aqueous solutions of complexing salts as SLP

The reversible formation of complexes between some complex-forming metal cations and organic compounds has long been used in gas-liquid chromatography to substantially increase the selectivity (see, for example, Ref. 51). Even the first studies[52—55] demonstrated the unusual selectivity of liquid phases prepared by dissolution of $AgNO_3$ in ethylene glycol. However, systems consisting of a polar organic solvent and $AgNO_3$ are relatively unstable, apparently, due to the slow reduction of the silver ion by the organic solvent. The relatively low upper temperature limit of using this type of phases (40—65 °C)[56] restricts the practical application of selective organic phases with $AgNO_3$. Therefore, it was of interest to extend the temperature range of using complex-forming SLP. It may be expected that the use of water instead of organic solvents for dissolution of $AgNO_3$ would extend the temperature range of applicability of complex-forming SLP and make it possible to determine the constants of complexation of organic compounds in water.

Unsaturated and aromatic compounds were separated at temperatures of 0 to 25 °C using aqueous solutions of silver salts as SLP.[57,58] Study of the com-

Table 4. Constants of complexation of gaseous unsaturated hydrocarbons with an aqueous solution of $AgNO_3$ at 25 °C

Hydrocarbon	Complexation constants	
	A	*B*
Ethylene	85	85*
Propylene	79	87*
Isobutene	51	71**
But-1-ene	110	118**
cis-But-2-ene	83	62**
trans-But-2-ene	27	25**

Note. *A* is the gas-chromatographic method[57]; *B* are independent physicochemical methods: * from Ref. 59; ** from Ref. 60.

plex-formation properties of the H_2O—$AgNO_3$ system[57] showed that the complexation constants for gaseous unsaturated hydrocarbons determined from gas chromatography experiments agree with those determined by independent physicochemical methods (Table 4).

Complexation in SLP composed of ethylene glycol solutions of silver nitrate has been studied.[53] The following scheme was proposed to describe the processes occurring in homogeneous SLP containing a complex-forming reagent[53]:

$$(\mathrm{Olf})_{\mathrm{gas}} \rightleftharpoons (\mathrm{Olf})_{\mathrm{water}}, \tag{7}$$

$$(\mathrm{Olf})_{\mathrm{water}} + (\mathrm{AgNO_3})_{\mathrm{water}} \rightleftharpoons$$
$$\rightleftharpoons (\mathrm{Olf{-}AgNO_3})_{\mathrm{water}}, \tag{8}$$

$$K_{\mathrm{s}} = (\mathrm{Olf})_{\mathrm{water}}/(\mathrm{Olf})_{\mathrm{gas}}, \tag{9}$$

$$K_{\mathrm{com}} = (\mathrm{Olf{-}AgNO_3})_{\mathrm{water}}/(\mathrm{Olf})_{\mathrm{water}}(\mathrm{AgNO_3})_{\mathrm{water}}, \tag{10}$$

$$K_{\mathrm{sum}} = [(\mathrm{Olf})_{\mathrm{water}} + (\mathrm{Olf{-}AgNO_3})_{\mathrm{water}}]/(\mathrm{Olf})_{\mathrm{gas}} =$$
$$= K_{\mathrm{s}} + K_{\mathrm{s}} \cdot K_{\mathrm{com}}[\mathrm{AgNO_3}], \tag{11}$$

where K_s is the olefin partition constant in the gas—H_2O system (see Eq. (9)); K_{com} is the olefin complexation constant in an aqueous solution of $AgNO_3$ (see Eq. (10)); and K_{sum} is the overall constant of the summary process (partition + complexation). The scheme shows the separation of unsaturated hydrocarbons[57] with different isotope compositions in aqueous solutions of $AgNO_3$ (Fig. 8). Thus, the use of aqueous solutions of $AgNO_3$ as SLP presents interest for the separation of unsaturated compounds with different hydrogen isotopes and for physicochemical measurements of the constants of complexation of organic compounds with different isotope compositions with complex-forming reagents.

The $AgNO_3$—H_2O system can be used as an SLP at a relatively high temperature (108 °C), which allows efficient separation of relatively high-boiling liquid olefins, C_{10}—C_{13} (Fig. 9).[61] The selectivity of this SLP can be illustrated by the difference between the retention indices of decene isomers, $\Delta I = I$ (*cis*-dec-5-ene) − I (*trans*-dec-5-ene) = 76 index units (iu). When squalane is used as the SLP, the ΔI value is 3 iu,[62] and that for dibutyl tetrachlorophthalate is 6 iu.[63]

Successful use of mixed SLP (for example, aqueous solutions of a mixture of $LiNO_3$ and $AgNO_3$) has been reported.[61,64] Selective separation of *cis*- and *trans*-isomers of unsaturated organic compounds was also attained in the $LiNO_3$—H_2O system.[61,64]

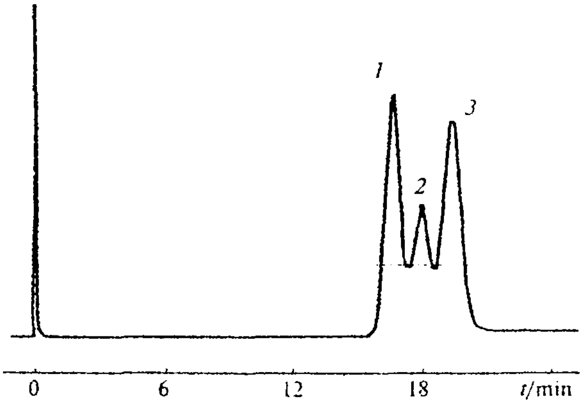

Fig. 8. Chromatogram for the separation of ethylenes differing in hydrogen isotope composition[57]: C_2H_4 (*1*), CHDCHD (*2*), C_2D_4 (*3*). Experimental conditions: a 3.6 m column, an aqueous solution of $AgNO_3$ as the SLP, temperature of the column 0 °C, flow rate of the carrier gas (helium) 60 cm^3 min^{-1}.

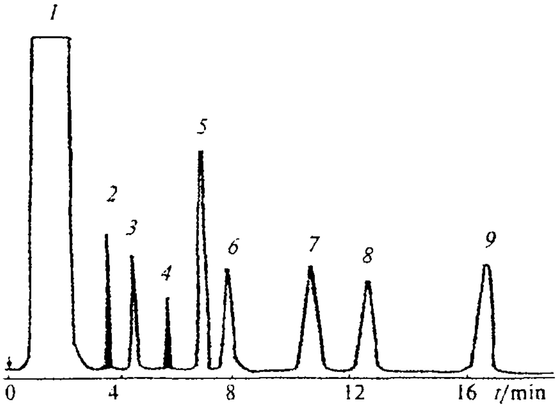

Fig. 9. Chromatogram for the separation of C_{10}—C_{13} olefins on the stationary phase under conditions of vapor-phase chromatography[61]: hexane (*1*), *trans*-dec-5-ene (*2*), dodec-1-ene (*3*), *cis*-dec-5-ene (*4*), *trans*-dodec-6-ene (*5*), dodec-1-ene (*6*), *cis*-dodec-6-ene (*7*), *trans*-tridec-5-ene (*8*), *cis*-tridec-5-ene (*9*). Experimental conditions: a 2 m × 3 mm column, 20% $AgNO_3$ on Celite C-22 as the sorbent, temperature 108 °C, water vapor as the mobile phase.

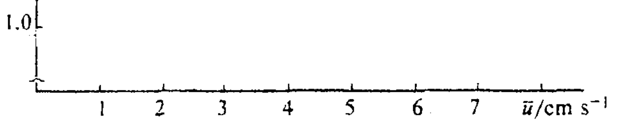

Fig. 10. HETP for *n*-alcohols *vs* linear velocity of the carrier gas ($\bar{u}$) for the SLP: $NaNO_3$—H_2O (curves *1* and *2*) and polydimethylsiloxane SE-30 (curve *3*).[37] Compounds subjected to chromatography: methanol (*1*), pentanol (*2*), and propanol (*3*). Experimental conditions: a 2 m × 4 mm column, 10% $NaNO_3$ on Chromaton N-AW as the sorbent, temperature of the column 90 °C (curves *1* and *2*) and 100 °C (curve *3*), 66% H_2O + 34% N_2 as the mobile phase.

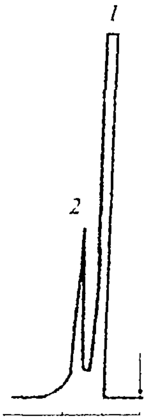

Fig. 11. Chromatogram of gasoline A-76 containing methanol[46]: gasoline A-76 (*1*), methanol (*2*). Experimental conditions: a 2 m × 4 mm column, 10% $NaNO_3$ on Chromaton N-AW as the sorbent, temperature 88 °C, 40% water vapor + 60% N_2 as the mobile phase.

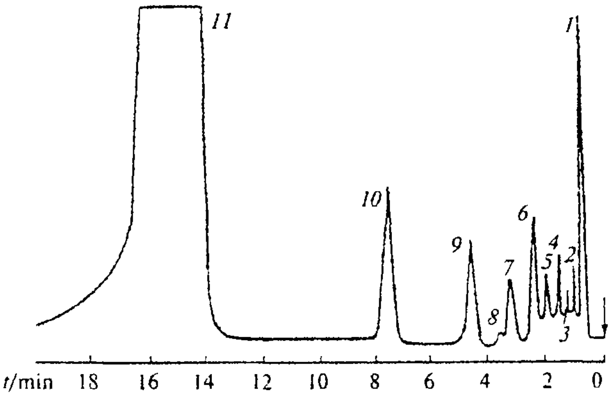

Fig. 12. Chromatogram of organic impurities in technical-grade methanol obtained under conditions of vapor-phase chromatography with water—salt SLP ($NaNO_3—H_2O$)[37]: dimethyl ether (*1*); methyl formate (*2*); methyl ethyl ketone (*3*); butan-2-ol (*4*); (*5*) and (*8*) were not identified; isobutyl alcohol (*6*), butan-1-ol (*7*); propan-1-ol (*9*); ethanol (*10*); methanol (*11*). Experimental conditions: a 2 m × 3 mm column, 20% $NaNO_3$ on Celite C-22 as the sorbent, temperature 110 °C, water vapor as the mobile phase.

Thus, aqueous salt solutions based on complex-forming salts possess unique selectivity for the separation of unsaturated organic compounds. These chromatographic phases can be advantageously used to separate relatively heavy unsaturated compounds (b.p. 250 °C or higher) and compounds with different isotope compositions. The gas-chromatographic method for determination of the constants of complexation of unsaturated compounds with complexing cations is relatively simple and highly productive, because the experiment is normally carried out for several (five to ten) compounds rather than for one compound.

The efficiency of packed columns with water—salt SLP

The separating capacity of a chromatographic column is known to be mainly determined by two parameters, namely, the selectivity of the SLP used and the efficiency of the column (or its specific HETP value) (see, for example, Refs. 65 and 66).

The HETP for water—salt SLP should not be higher than those for traditional phases because the diffusion coefficient for a sorbate in polydimethylsiloxane can be approximately estimated as $D_l \approx 5 \cdot 10^{-6}$ cm^2 s^{-1},[67] and that for water is $D_l \approx 10 \cdot 10^{-6}$ cm^2 s^{-1}.[68] Comparison of the diffusion coefficients leads to the assumption that broadening of chromatographic zones in water—salt phases would not exceed that for a traditional phase such as polydimethylsiloxane. Direct comparative measurements (Fig. 10) showed that the efficiency of columns with a water—salt phase virtually does not differ from that of columns with the traditional SE-30 phase. This allows one to take full advantage of selective water—salt phases in the separation.

Prospects for the practical use of water—organic SLP

The above-considered chromatographic characteristics of inorganic aqueous phases suggest that these phases can find practical application for the separation of complex mixtures and determination of impurities, preparation of pure compounds in preparative chromatography, and the determination of the complexation constants of compounds being chromatographed.

The practical merit of using the above-considered liquid inorganic aqueous phases is confirmed by the chromatograms shown to the left. Fig. 11 shows an effective separation of the components of gasoline A-76 and polar methanol and Fig. 12 demonstrates the possibility of determining the impurities present in technical-grade methanol. The prospects for using the new class of highly selective phases for determination of impurities in alcoholic drinks should also be noted (see, for example, Figs. 4, 5, 12).

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