Steam chromatography with water—salt and water—acid inorganic phases

L. G. Berezkina,[a]* V. G. Berezkin,[b] E. N. Viktorova,[b] E. Yu. Sorokina,[b] and T. G. Andronikashvili[c]

[a]*Institute for Fertilizers, Insecticides and Fungicides,*
55 Leninsky prosp., 117333 Moscow, Russian Federation.
Fax: 007 (095) 135 8770
[b]*A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences,*
29 Leninsky prosp., 117912 Moscow, Russian Federation.
Fax: 007 (095) 230 2224. E-mail: tips@tips.rc.ac.ru
[c]*Institute of Physical and Organic Chemistry, Georgian Academy of Sciences,*
5 ul. Dzhikiya, 380086 Tbilisi, Georgia

Th peculiarities of steam chromatography with water—salt and water—acid stationary liquid phases have been studied. The effects of the nature of the salt, its concentration in the stationary liquid phase, and the temperature of the column on retention values have been studied using C_1—C_8 primary nonbranched alcohols as an example. The advantages and disadvantages of steam chromatography with aqueous electrolyte phases and challenges for the development of this method are discussed.

Key words: steam chromatography, water—salt and water—acid inorganic stationary liquid phases, retention values, inverse elution order of *n*-alcohols.

It is commonly accepted that in gas-liquid chromatography at low pressures the carrier-gas (mobile phase) mainly performs transport functions in the separation of compounds (*i.e.*, only moves zones of chromatographing-substances along a column). According to the concepts accepted presently, a real sorbent in gas-liquid chromatography is the layer of the stationary liquid phase (SLP), which can absorb components of the mobile phase, and the two interfaces (mobile phase—SLP and SLP—solid support), which can adsorb the same components. However, in steam chromatography the role of the mobile phase (water vapor) is more manifold. First, water can be dissolved in SLP to form an aqueous solution, *i.e.*, in fact a different, more polar phase. Second, water as a polar component can modify the interfaces of a sorbent to improve the symmetry of the chromatographic zones of the analyzed compounds and to decrease the retention times of the separated compounds. Third, water as a component of SLP can form hydrogen bonds with the separating compounds, which usually improves the selectivity of the water-containing stationary phase. Fourth, water-containing SLP can play the role of a fine solvent for some inorganic complex-forming agents, for example, silver nitrate, which also enlarges the range of the SLP used.

Steam chromatography was suggested more than thirty years ago. Pure water vapor has been primarily used as a mobile phase in packed columns by Japanese and French researchers;[1,2] although a mixed mobile phase containing water vapor had been described previously.[3,4] The systematic studies in the area of steam chromatography,[5—16] including capillary[17] and preparative steam chromatography,[18—20] show that this method is promising.

In the development of steam chromatography, researchers were mainly interested in the use of this method to modify solid surfaces in gas adsorption and gas-liquid chromatography.

The application of steam chromatography usually gives the following advantages: (1) it improves the symmetry of the chromatographic zones of polar compounds in gas adsorption and gas-liquid chromatography; (2) it enlarges the area of application of gas adsorption chromatography (for example, it makes it possible to analyze high-boiling and polar compounds); and (3) it makes possible the elution of aqueous samples without the disturbing effect of the main component (water). However, steam chromatography has certain limitations: (1) the possibility of chemical reactions between water and components of the analyzed samples and between water and SLP cannot be excluded and (2) there are no commercially accessible units (attachments) for the creation of water vapor flow in a standard chromatograph, which retards the development of steam chromatography.

The aforesaid makes it possible to conclude that steam chromatography is a promising method of analysis, which makes it possible to substantially improve the analytical and physicochemical parameters of the chromatographic process (see, *e.g.*, Refs. 12, 14—16, and 21—23). At the same time, it should be mentioned that one of the most intriguing potential possibilities of this method, the use of water as a polar SLP, has not been realized.

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The positive peculiarities of steam chromatography are associated with the unique properties of water as a chemical compound due to its unusual structure in the liquid state and its ability to form hydrogen bonds (see, *e.g.*, Refs. 24—26). Therefore, it is of unambiguous interest to use pure water as SLP in steam chromatography.[27—29] However, the practical significance of these works was limited due to the instability of water as SLP in a column and to the possibility of using it only at low temperatures. A novel type of phase, water—salt solutions, has been suggested to enlarge the area of application of water as SLP.[30,31]

The purpose of this work is to study the peculiarities of the variant of steam chromatography with aqueous solutions of inorganic electrolytes (salts and acids) as SLP.

Experimental

Studies in the area of steam chromatography were carried out on an LKhM-8MD (plant "Khromatograf," Moscow) chromatograph modified with a steam-generator for obtaining a water vapor flow[30] and a Biokhrom-1, model 21 (Central Designing Bureau of the N. D. Zelinsky Institute of Organic Chemistry, RAS, Moscow) chromatograph modified with a bubbling device for preparing a mixed mobile phase: nitrogen—water vapor. The saturator was described in detail in Ref. 32.

Sorbents with inorganic SLP were prepared by the method known for organic phases (see, *e.g.*, Ref. 33). Lithium, sodium, and potassium nitrates (reagent grade) and orthophosphoric acid (analytically pure grade) (10 and 20 % of the mass of the solid support, using bidistilled water as the solvent) were deposited on diatomite solid supports, Chromaton N-AW, Inerton AW (Chemapol, Czech Republic), and Celite C-22 (Ferac, Germany). A commercial sorbent with an organic SLP, 15 wt. % polydimethylsiloxane on Chromaton N-AW (Chemapol, Czech Republic), was used. Analytical columns of stainless steel or glass (2 m × 3 mm) were filled with the aforementioned sorbents using a vacuum pump. The ends of the column were closed with Teflon chips. Sorbents with an inorganic electrolyte were saturated with water under working conditions (at a specified temperature in a mobile phase flow containing water vapor for 3 to 6 h until the complete stabilization of the zero line of the detector).

Mixtures of aliphatic n-C_1—C_8 alcohols, aliphatic C_2—C_8 acids, and C_{10}—C_{13} olefins with *cis*- and *trans*-isomers were studied in steam chromatography. The following retention parameters were measured in the isothermic regime in the temperature range from 64 to 115 °C: the capacity coefficient of the column k and the relative retention α. The relative standard deviation for the measurements of the chromatographic parameters was not greater than 3 rel. % at a sample volume $\leq$ 0.1 mL. The "dead" time of the column was determined from the retention of the unsorbed gas (methane).

Retention values were also measured from time to time on a capillary column. The instrument used, an LKhM-8MD gas chromatograph, was modified for the work with capillary columns, provided with a modernized IMT-05 with a time constant of 0.15 sec and a standard TZ-21S recorder with the pen run of 0.25 sec. The carrier gas (helium), dry or moisturized at ~20 °C, was conveyed to a fused silica capillary column (25 m × 0.2 mm) with SLP SE-30 (film width 0.13 mm). Retention indices of various polar compounds (octanol-1, dimethylphenol, dimethylaniline, and naphthalene) were measured at 90 °C and at a sensitivity of $2 \cdot 10^{-11}$ A using a flame-ionization detector.

Results and Discussion

It is not difficult to separate substances on aqueous solutions of electrolytes used as SLP under steam chromatography conditions. Sorbents are prepared on the basis of white or pink diatomite solid supports with hydrophilic properties of the surface and a content of dry salt or acid from 5 to 20 wt. %. Sorbent particles do not adhere; therefore, no additional fractionation is needed, and analytical columns can be easily filled. A column is connected to an evaporator and a detector, a pure superheated steam is conveyed from a steam-generator, and a carrier gas saturated with water vapor is conveyed from a saturator. An electrolyte on the solid support surface contacts the water vapor and begins to absorb water, then spreads and forms a film of an aqueous solution, whose composition corresponds to the equilibrium:

$$\underset{\text{(SLP)}}{\text{Inorganic electrolyte—H}_2\text{O}} \rightleftarrows \underset{\text{(mobile phase)}}{\text{H}_2\text{O}} \qquad (1)$$

Thus, SLP is formed due to the interaction of a nonvolatile component of SLP (salt, acid) with a component of a mobile phase (water vapor).

Let us consider the regularities of the change in the partial pressure of the water vapor over aqueous solutions of nonvolatiles (for example, salts). For systems of this type (salt—water), the dependence of the pressure of the saturated water vapor P_{H_2O} over the solution on the salt concentration is described by the following function

$$P_{H_2O} = K(C_{MX}, T), \qquad (2)$$

where K is a constant (equilibrium constant) that is determined both by the salt concentration in the solution (C_{MX}) and the temperature of the system (T), and MX is salt.

Equation (2) describes the conditions of the equilibrium state (conditions of existence) of aqueous solutions of electrolytes as SLP in steam chromatography.

The isotherms of the saturated vapor pressure over aqueous solutions of some electrolytes are presented in Fig. 1 (the authors obtained these dependences from the reference data[34,35]). As follows from these dependences, the pressure of saturated water vapor over a solution determines unambiguously the equilibrium concentration of the solution of the electrolyte that is in equilibrium with the steam phase. The particular form of this dependence is determined by the nature of the salt used. A slight change in temperature results in a substantial change in these dependences (Fig. 1, curves *6* and *7* for sodium nitrate).

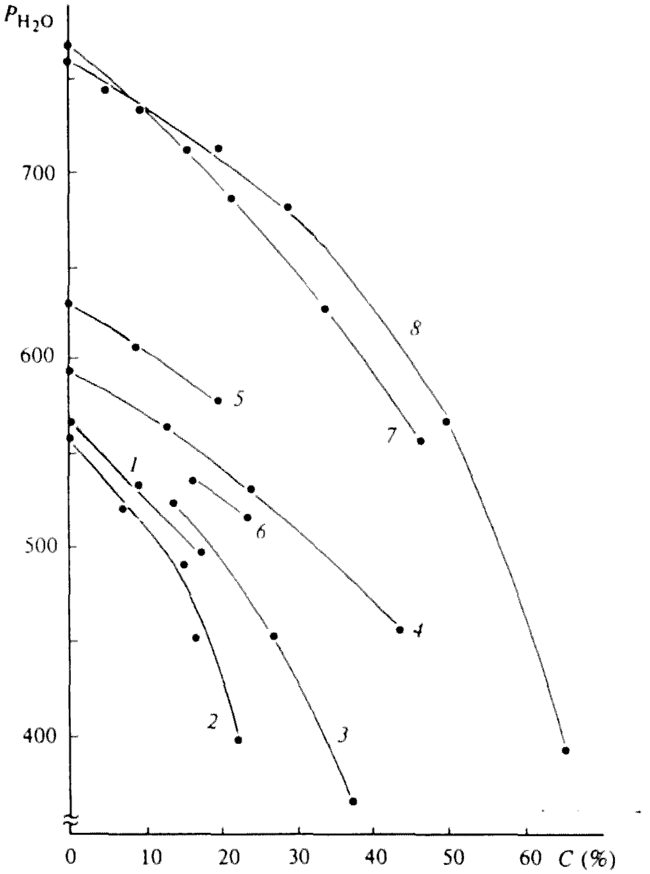

Fig. 1. Isotherms of the pressure of saturated water vapor (P_{H_2O}) over the solution of the electrolyte at various concentrations (*C*) of salt (from the reference data[34,35]): *1*, NaCl (92.0 °C); *2*, LiCl (91.6 °C); *3*, $LiNO_3$ (92.2 °C); *4*, RbCl (92.8 °C); *5*, KCl (94.2 °C); *6*, $NaNO_3$ (92.8 °C); *7*, $NaNO_3$ (100.3 °C); and *8*, *o*-H_3PO_4 (100 °C).

In steam chromatography, the retention of polar sorbates (for example, alcohols) can be a result of their interaction with water molecules existing both in the mobile and stationary phases. However, our experiments showed that the effect of water vapor in the mobile phase on the retention of alcohols likely can be neglected. It follows from the data presented in Table 1 that the retention indices of various compounds on a fused silica capillary column with SE-30 using the dry and moisturized carrier gas differ insignificantly. Therefore, the unusual retention of aliphatic alcohols on water-salt SLP in steam chromatography[30,31] is mainly associated with the unusual selectivity of phases of this type rather than with the effect of the water-containing mobile phase. Two chromatograms of a mixture of *n*-C_1—C_5 alcohols obtained on columns with water—salt ($LiNO_3$—H_2O) and organic (SE-30) phases (the mobile phase in both cases is nitrogen saturated with water vapor) are presented in Fig. 2. A sharp difference in the selectivities of the compared SLP is manifested in a quantitatively different elution orders of the *n*-alcohols.

Table 1. Effect of the moisture content of the carrier-gas (helium) on the retention indices (I) of polar compounds on a fused silica capillary column with the nonpolar stationary liquid phase SE-30

Sorbate	Dry carrier-gas, I_{dry}	Moist carrier-gas, I_{moist}	ΔI
Octan-1-ol	1052.32 ± 0.05	1053.14 ± 0.05	−0.82
Dimethylphenol	1079.18 ± 0.11	1079.97 ± 0.13	−0.79
Dimethylaniline	1132.33 ± 0.02	1132.84 ± 0.04	−0.51
Naphthalene	1154.92 ± 0.08	1155.21 ± 0.08	−0.32

Note. Experimental conditions: column length 25 m, diameter 0.2 mm, thickness of SLP films 0.13 mm, temperature of the column 90 °C, discharge 1 : 100, sensitivity $2 \cdot 10^{-11}$ A, flame-ionization detector. $\Delta I = I_{dry} - I_{moist}$.

On the column with SE-30 and a mobile phase containing 66 % water vapor, *n*-alcohols are eluted in order of increasing boiling point (and molecular weight): methanol (65 °C) < ethanol (78 °C) < propanol (97 °C) < butanol (118 °C) < pentanol (138 °C) (Fig. 2, *a*); while on the column with the water—salt phase ($LiNO_3$—H_2O) (Fig. 2, *b*) and a water-containing (17 % H_2O) mobile phase, the elution order of *n*-C_1—C_5 alcohols is inverse: pentanol < butanol < propanol < ethanol < methanol. This major change in the elution order of *n*-

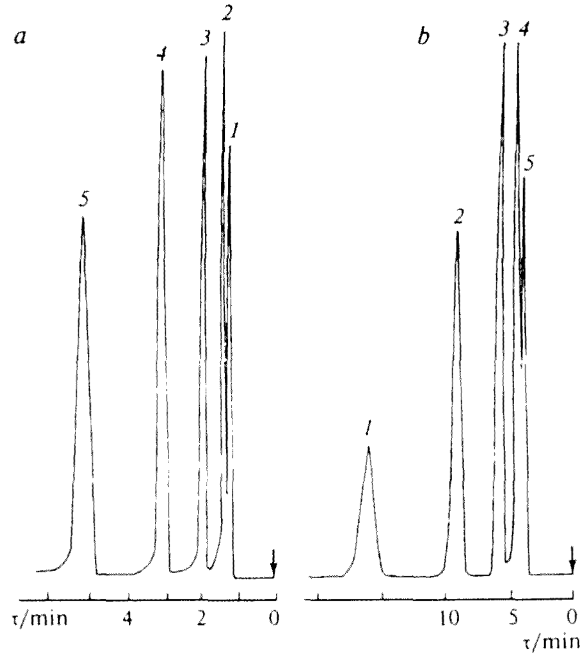

Fig. 2. Chromatograms of the separation of *n*-C_1—C_5 alcohols by steam chromatography on a sorbent with SE-30 (*a*) and on a sorbent with a $LiNO_3$—H_2O water—salt phase (*b*): *1*, methanol; *2*, ethanol; *3*, propanol; *4*, butanol; and *5*, pentanol. Experimental conditions: column 2 m × 3 mm (*a*, stainless steel; *b*, glass); sorbent 15 % SE-30 on Chromaton N-AW (*a*) and 10 % salt on Chromaton N-AW (*b*); temperature 90 (*a*) and 64 °C (*b*); mobile phase 66 % H_2O + 34 % N_2 (*a*); 17 % H_2O + 83 % N_2 (*b*).

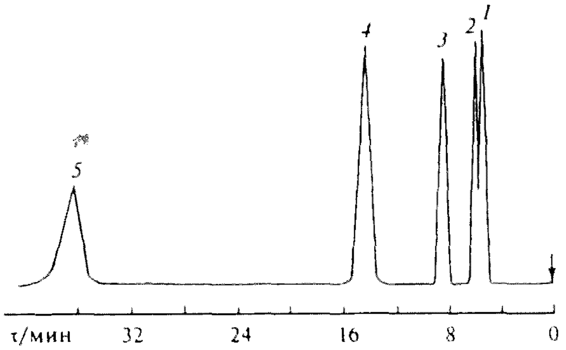

Fig. 3. Chromatograms of the separation of a mixture of aliphatic C_2—C_8 acids by steam chromatography: *1*, $C_7H_{15}COOH$; *2*, $C_5H_{11}COOH$; *3*, C_3H_7COOH; *4*, C_2H_5COOH; and *5*, CH_3COOH. Experimental conditions: column 2 m × 3 mm, stainless steel, sorbent 10 % H_3PO_4 on Inerton N-AW, temperature 115 °C, mobile phase water vapor.

Table 2. Dependence of the relative retention (α) of *n*-C_1—C_8 alcohols on the nature of the cation in the water—salt phase

Sorbate	Water-salt stationary liquid phase		
	$LiCl—H_2O$	$NaCl—H_2O$	$KCl—H_2O$
Methanol	1.00	1.00	1.00
Ethanol	0.45	0.46	0.49
Propanol	0.25	0.25	0.28
Butanol	0.16	0.15	0.23
Pentanol	0.08	0.12	0.22
Hexanol	0.05	0.11	0.33
Heptanol	0.04	0.16	0.54
Octanol	0.045	0.27	0.91

Note. Experimental conditions: column 2 m × 3 mm, sorbent 20 % salt on Celite C-22, temperature of the column 108—110 °C, mobile phase water vapor.

alcohols on the column with the water—salt phase can be explained by the different retention mechanism; in this case, retention occurs mainly due to the formation of hydrogen bonds between the functional group of alcohol and water-containing SLP.

The replacement of a metal ion with a hydroxonium ion in an aqueous solution does not basically change the regularities of the retention of polar compounds. For example, on a column with a water—acid SLP (a solution of orthophosphoric acid), the inverse elution order is typical for *n*-alcohols and aliphatic acids as well. As follows from the chromatogram presented in Fig. 3, aliphatic C_2—C_8 acids are eluted in this case in the following order: $C_7H_{15}COOH$ (b.p. 238 °C) < $C_5H_{11}COOH$ (b.p. 204 °C) < C_3H_7COOH (b.p. 162 °C) < C_2H_5COOH (b.p. 141 °C) < CH_3COOH (b.p. 118 °C). The results obtained attest that the regularities established for this variant of steam chromatography are general for sorbates of the RX type, where R is a hydrocarbon radical and X is a polar functional group.

In the study of water—salt phases, it seems reasonable to answer two questions: (1) what is the effect of the nature of the salt on the retention of sorbates and (2) what method can be used to study this effect? We decided to use the retention of *n*-C_1—C_8 alcohols to characterize the properties of water—salt SLP. This approach is explained, first, by the unusual retention of alcohols on phases of this type and, second, by a monotonic increase in the hydrophobicity of primary *n*-alcohols in the C_1—C_8 series. Therefore, we expected to obtain the most complete characteristics of the water—salt SLP studied using *n*-alcohols of different hydrophobic characters as a unique "molecular probe" for studying the structures of water—salt SLP. The retention values of the first eight members of the homologous alcohol series relative to methanol measured on aqueous solutions of lithium, sodium, and potassium chlorides at equal molar concentrations of the salt in these solutions (0.11±0.01 molar fractions) are presented in Table 2. Water vapor is the mobile phase. It follows from these data that for hydrophilic alcohols (methanol, ethanol, and propanol), which are highly water-soluble, the values of relative retention α are close, and, hence, the nature of the cation only slightly affects the chromatographic characteristics. However, the value of the capacitance coefficient of the column for the most strongly retained compound (methanol) decreases in the order: LiCl (k = 72.0) > NaCl (k = 11.5) > KCl (k = 3.3). Thus, the value of the salting-out effect decreases by ~22 times on going from lithium chloride to potassium chloride.

For *n*-C_4—C_8 alcohols with a longer hydrocarbon radical, the relative retention noticeably depends on the nature of the salt used in SLP. First, the nature of the salt determines at which of the studied *n*-alcohols the inversion of the elution order begins. Second, according to the direction of the increase in the inversion effect, the salts studied (SLP) can be arranged in the following order: lithium chloride (inversion at *n*-octanol) < sodium chloride (inversion at *n*-heptanol) < potassium chloride (inversion at *n*-hexanol).

It is noteworthy that qualitatively similar regularities for the relative retention values of the studied alcohols were also observed for lithium, sodium, and potassium nitrates. The values of the capacitance coefficient for methanol also decrease in the series: $LiNO_3$ (k = 32) < $NaNO_3$ (k = 14) < KNO_3 (k = 9). It is likely that the observed inversion of elution of *n*-C_4—C_8 alcohols is related to a change in the mechanism of their retention. The role of adsorption in the retention of heavier alcohols at the steam—aqueous salt solution interface increases substantially. Regarding the assumption made, it is noteworthy that the relative retention values of *n*-octanol/*n*-heptanol for sodium chloride and potassium chloride are equal and are 1.7 (these data follow from Table 2). The equal values of the relative retention testify to the validity of the assumption that the retention mechanism for alcohols with longer hydrocarbon radicals is the same.

The concentration of water vapor in the mobile phase also affects the inversion of the elution order of *n*-alcohols. However, a change in the salt concentration in the mobile phase affects in fact a change in the retention of sorbates rather than a change in the concentration of water vapor in the mobile phase, since, as shown above, the concentration of water vapor determines the concentration of salt in the water—salt phase. Using the data from the handbook,[34] the concentration of $NaNO_3$ in the water—salt SLP was tentatively calculated from the dependence of the salt concentration in an aqueous solution on the pressure of saturated water vapor over this solution. The retention values in the $NaNO_3$—H_2O system for two concentrations of the salt (19 and 51 %) in the stationary phase are presented in Table 3. As follows from the data in Table 3, for SLP with a less concentrated solution of the salt (19 % $NaNO_3$) inversion is manifested beginning at pentanol, while for SLP with a more concentrated solution of the salt, it is manifested beginning at butanol. Thus, a change in the concentration of water in the mobile phase (and in the concentration of the salt in SLP) dramatically affects the capacitance coefficients and can be an additional means for controlling the chromatographic process in this variant of steam chromatography.

It is noteworthy that the melt of the crystal hydrate $KF \cdot 2H_2O$ either as a component of a fairly polar organic phase (Triton X-305) or as SLP has been successfully used[36,37] for the analysis of aqueous solutions of polar organic compounds (alcohols, amines, and other). However, the elution order of the first members of the alcohol homologous series on the sorbent with crystal hydrate $KF \cdot 2H_2O$ did not differ from the traditional order (no inversion was observed). The retention of alcohols on an SLP that is a melt of crystal hydrate is mainly caused by van der Waals interactions, and hydrogen bonds with alcohols are not formed for these phases.[37]

The direct elution order of *n*-alcohols on the melt of the crystal hydrate does not contradict our results, because in steam chromatography on the water—salt SLP the elution order of *n*-alcohols exhibits a pronounced tendency to proceed in the traditional order (as on SE-30 SLP) as the salt concentration increases.

Changing the temperature of the column also affects the inversion of the elution order in the series of *n*-alcohols on water—salt SLP. As follows from the data in Table 4, in the chromatographic system with SLP ($NaNO_3$—H_2O) and a mobile phase containing 66 % water vapor, inversion is observed on *n*-pentanol and *n*-butanol at 90 and 100 °C, respectively. It should be emphasized that the main effect on the retention is caused not by the change in the temperature itself, but by the change in the concentration of the salt in the aqueous solution caused by the temperature change and, hence, by the change in SLP composition. Increasing the temperature results in an increase in the concentration of the salt in SLP and in the appearance of a new phase with new chromatographic parameters. Therefore, the methods that are used in gas chromatography for the determination of thermodynamic values are inappropriate in the case of water—salt SLP.

One difference between water—salt SLP and the known traditional SLP is also that for some sorbates, *e.g.*, for *n*-pentanol and *n*-hexanol, an increase in the capacitance of the column is observed as the temperature increases, rather than a decrease.

The regularities studied above are evidence that steam chromatography with water—salt phases in addition to traditional ways of controlling the chromatographic process (for example, by temperature) offers new possibilities for using such new optimization factors as the concentration of water in the mobile phase; however, the traditional factor, temperature, more substantially affects the selectivity of SLP of this type.

Based on the aforesaid, we can mention that steam chromatography on electrolyte—water SLP, unlike traditional chromatographic variants, has the following peculiarities: (1) the SLP is a binary (or multicomponent) solution, (2) the composition of SLP is determined by

Table 3. Effect of the concentration of salt ($NaNO_3$) in the water—salt stationary liquid phase on the retention of *n*-C_1—C_6 alcohols (capacitance coefficient *k* and relative retention α)

Sorbate	Concentration of $NaNO_3$ in SLP			
	19 %		51 %	
	k	α	*k*	α
Methanol	0.77	1.00	7.51	1.00
Ethanol	0.33	0.43	3.32	0.44
Propanol	0.20	0.26	1.90	0.25
Butanol	0.21	0.27	1.61	0.21
Pentanol	0.33	0.42	1.90	0.25
Hexanol	1.22	1.52	5.02	0.69

Note. Experimental conditions: column 2 m × 4 mm, sorbent 10 % salt on Chromaton N-AW (0.315—0.40 mm), temperature 90 °C, mobile phase nitrogen + water vapor (concentration of water vapor 50 and 66 %).

Table 4. Effect of the temperature of the column on the retention (capacitance coefficient *k* and relative retention α) of *n*-C_1—C_6 alcohols

Sorbate	Temperature of the column				$\Delta k/\Delta t$
	90 °C		100 °C		
	k	α	*k*	α	
Methanol	7.51	1.00	4.52	1.00	−0.30
Ethanol	3.32	0.44	2.24	0.50	−0.11
Propanol	1.90	0.25	1.50	0.33	−0.04
Butanol	1.61	0.21	1.50	0.33	−0.01
Pentanol	1.90	0.25	2.93	0.65	+0.10
Hexanol	5.02	0.69	8.25	1.83	+0.32

Note. Experimental conditions: column 2 m × 4 mm, sorbent 10 % $NaNO_3$ on Chromaton N-AW, Mobile phase 66 % water vapor and 34 % nitrogen.

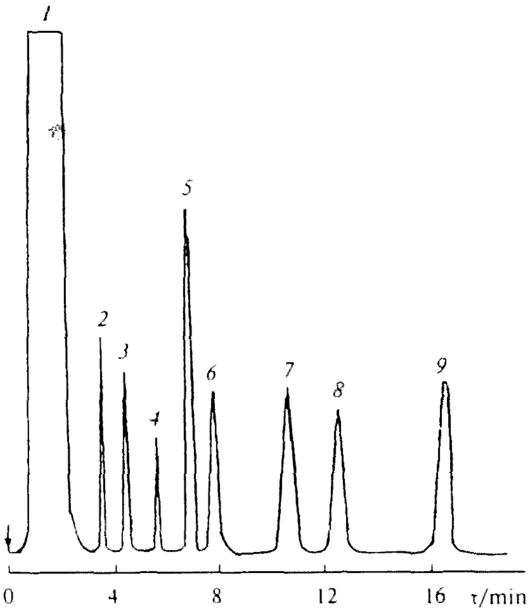

Fig. 4. Chromatograms of the separation of C_{10}—C_{13} olefins by steam chromatography on a sorbent with an $AgNO_3$—H_2O water—salt phase: *1*, hexane; *2*, *trans*-dec-5-ene; *3*, dec-1-ene; *4*, *cis*-dec-5-ene; *5*, *trans*-dodec-6-ene; *6*, dodecene; *7*, *cis*-dodec-6-ene; *8*, *trans*-tridec-5-ene; and *9*, *cis*-tridec-5-ene. Experimental conditions: column 2 m × 3 mm, sorbent 20 % $AgNO_3$ on Celite C-22; temperature 108 °C, mobile phase water vapor.

the pressure of the water vapor in the mobile phase; the composition of SLP can be controlled by changing the pressure of the water vapor in the mobile phase, (3) a change in the temperature of the column results in a change in the composition of SLP (the salt concentration increases); therefore, an increase in the temperature results in a sharper change in retention values on water—salt phases than on the usual phases, and (4) the chromatographic retention on water—salt phases is also determined by the nature of the salt used; the use of salts with complex forming properties makes it possible to substantially change the selectivity of phases. For example, the separation of several unsaturated hydrocarbons on a column with the water—salt phase ($AgNO_3$—H_2O) at 108 °C in water vapor is shown in Fig. 4. It is noteworthy that the use of aqueous solutions makes it possible to provide a higher stability of some complexing agents (including silver nitrate) than the use of organic solvents. For example, the limiting temperature silver nitrate is used in organic solvents[33] is not higher than 65 °C; in water—salt phases silver nitrate can be used at temperatures higher than 100 °C.

In conclusion, we list some challenges for the development of the new variant of steam chromatography: (1) the use of hydrophilic organic compounds (both ionogenic and nonionogenic) instead of inorganic salts; (2) the application of mixed organic and inorganic aqueous systems as SLP; (3) the use of water—electrolyte and water—organic SLP for concentrating admixtures from gas media; (4) the application of the described SLP to chemical technology for industrial separation and purification of gas and steam flows; and (5) the study of water—salt solutions by gas chromatography.

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