Ammonia as a carrier gas for acidic–basic chromatography

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Abstract

The influence of ammonia as a basic carrier gas on the retention of acidic and basic solutes was experimentally studied. Use of the basic carrier gas (ammonia) leads to an increase in retention of acidic solutes. A simplified theory on the influence of carrier gas basicity influence on the retention of acidic and basic solutes was developed. Contact of an inert gas with ammonia water at ambient temperature can be used to obtain basic humid carrier gas and to improve the chromatographic characteristics of amine's zones. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Carrier gas; Ammonia

1. Introduction

Recently we showed (see, e.g., Ref. [1]) that contrary to conventional opinion (see Refs. [2,3]) traditionally used carrier gases (He, H_2, N_2, CO_2, etc.) have a significant influence on the retention factor k and, therefore, on the separation of chromatographed compounds. We studied the possible mechanism of carrier gas influence on the chromatographic characteristics of solutes and draw the conclusion that it is possible and reasonable to study a chromatographic system where the interactions between the carrier gas and solute are of chemical and physical nature. Such a system is of practical importance as well. It was shown earlier (see, e.g., Ref. [4]) that the application of the chemical factor in the interactions allows realisation of a high selectivity in chromatographic separations. The realisation of the idea showed promise [5,6], but in the

literature the main attention was paid to the application of an acidic carrier gas (CO_2).

Hence, the main goals of the present research were: (1) to study theoretically and experimentally the retention of organic compounds using a basic carrier gas (NH_3); (2) to search for a simple technique for acidic–basic chromatography with a basic carrier gas on the basis of a standard gas chromatograph.

Note that recently Abdel-Rehim performed a number of studies on the application of NH_3 as a carrier gas. These studies are mentioned in the recently published review [7]. Abdel-Rehim noted that the ammonia effect on the retention factors was more pronounced using polar liquid phase compared to nonpolar one.

It has been suggested that NH_3 application as a carrier gas for the separation of acidic solutes (for example, low-molecular-mass organic acids) can cause formation of ammonium salts of acids under the given conditions in the gas phase (i.e., in the carrier gas). According to Bielstein [8] vapours of

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NH_4COOCH_3 (salt) completely dissociate at 208°C. According to later data [9], in the gas phase NH_3 weakly interacts with weak acids forming complexes on the basis of hydrogen bonding (energy of complex formation is less than 2.8 kcal/mol). However, NH_3 shows no evidence for hydrogen-bond donation in its gas phase interactions with Lewis bases.

2. Experimental

Experiments were carried out on a modified LKhM-8MD gas chromatograph (Model 5, Khromatograf, Moscow, Russia) equipped with a flame ionisation detection (FID) system. The chromatographic separations were performed on a fused-silica capillary column of 30 m×0.25 mm I.D. coated with polyethylene glycol, film thickness 0.25 μm. Carrier gases were pure helium; pure ammonia and helium containing water vapour and ammonia after contact (bubbling) with ammonia water. The split ration was 1:20–1:100. Note that the used ammonia contained 0.6% water vapour. In several experiments carrier gas containing NH_3 and water was used instead of NH_3. In this case the carrier gas was bubbled through ammonia water and the bubbler was placed before the injector. The initial content of ammonia in ammonia water was 30%, but after a series of experiments it was 20%. Note, from the data of Ref. [10], the partial pressure of ammonia is 216 mmHg and that of water is 12.3 mmHg at 19.9°C at 19.4% ammonia content in ammonia water (1 mmHg=133.322 Pa). At 30% ammonia content the partial pressure of ammonia is 435 mmHg and that of water is 8.5 mmHg.

3. Results and discussion

3.1. Theoretical approach to the retention of acidic solutes using basic carrier gas

The processes taking place in the chromatographic system with the basic carrier gas (NH_3) and acidic solute (for example, $CH_3COOH=AcH$) are shown in Fig. 1.

At first we studied the influence of carrier gas nature on the retention of neutral and acidic solutes.
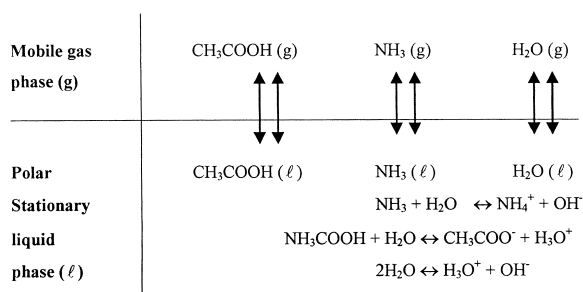

Fig. 1. Scheme of equilibrium process in gas–liquid chromatography (GLC) using basic humid carrier gas (NH_3, H_2O), acidic solute (CH_3COOH or AcH) and polar SLP.

Table 1 shows the retention factors (k) and relative retention (r) values, Δk_r for organic solutes using two types of carrier gas: neutral helium and basic ammonia at 100°C and 140°C, respectively. To evaluate the influence of the basic carrier gas on the retention factor we used the following relative value:

$$\Delta k_r = \frac{[k(NH_3) - k(He)] \cdot 100}{k(He)};$$

$$\Delta r_r = \frac{[r(NH_3) - r(He)] \cdot 100}{r(He)}$$

As follows from Table 1, in the chromatographic system replacing neutral carrier gas for basic leads to a significant increase in retention (30–40%) for acetic and propionic acids without considerable variation in retention for other solutes.

Fig. 2 presents the following dependence for some solutes using various carrier gases:

$$k_i(NH_3) = \psi[k_i(He)] \tag{1}$$

As can be seen the points corresponding to acetic and propionic acids deflect from the linear dependence (Eq. (1)) for neutral organic solutes. This means considerable changes in the retention mechanism of organic acids when neutral helium is exchanged for basic ammonia. An analogous dependence is also observed at a higher temperature, 140°C (see Table 2).

The new phenomenon we observed (i.e., a considerable increase in the retention of acidic solutes with basic carrier gas) can be explained by the known ionisation concept for chemical compounds (solute

Table 1
Influence of ammonia as basic carrier gas on the retention of organic compounds on the column coated with polyethylene glycol at 100°C

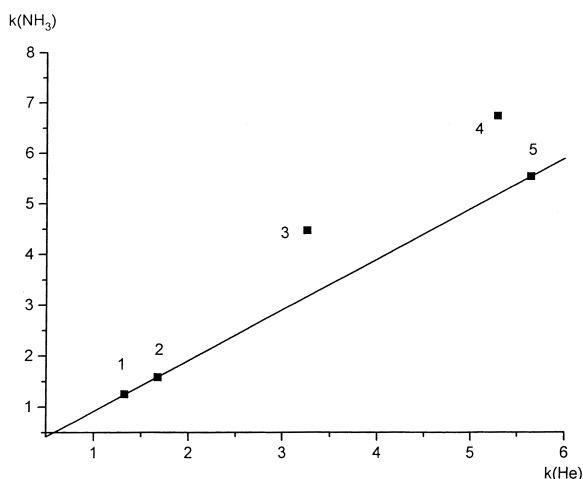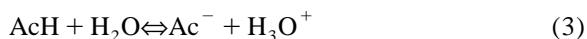| Solute	Retention factor			Relative retention		
	He	NH$_3$	Δk_r (%)	He	NH$_3$	Δr_r (%)
Pseudocumene	1.328	1.253	−5.7	0.235	0.226	−3.8
Hexylpropionate	1.676	1.582	−5.6	0.297	0.286	−3.7
Acetic acid	3.263	4.469	37.0	0.578	0.808	39.8
Propionic acid	5.289	6.738	27.4	0.937	1.214	29.6
Octanol-1	5.645	5.540	−1.9	1.000	1.000	–

Fig. 2. Dependence of the retention factor of solutes with basic carrier gas $k_i(NH_3)$ on that with inert carrier gas $k_i(He)$. Solutes: 1=pseudocumene, 2=hexylpropionate, 3=acetic acid, 4= propionic acid.

and carrier gas) in a stationary liquid phase (SLP) containing water vapour.

When dissolved in a water-containing SLP, the basic carrier gas (NH$_3$) is partially ionised (Eq. (2)) resulting in the SLP becoming a basic medium. So,

an additional ionisation of organic acid occurs at the solute dissolution in the basic SLP and equilibrium (Eq. (3)) shifts to the right. As a result, the effective partition constant of the acidic solute in the system (basic SLP)/gas increases and leads to an increase in the retention of the solute.

The processes considered above can be quantitatively presented as following equilibrium chemical reactions and corresponding equilibrium constants of these processes:

$$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^- \tag{2}$$

$$AcH + H_2O \Leftrightarrow Ac^- + H_3O^+ \tag{3}$$

$$H_3O^+ + OH^- \Leftrightarrow 2H_2O \tag{4}$$

Combination of Eqs. (2) and (3) gives the following relationship:

$$NH_3 + AcH \Leftrightarrow NH_4^+ + Ac^- \tag{5}$$
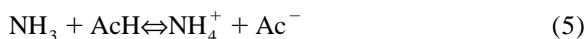
The equilibrium constants of the above-discussed processes are as follows:

Table 2
Influence of ammonia as basic carrier gas on the retention of organic compounds on the column coated with polyethylene glycol at 140°C

Solute	Retention factor			Relative retention		
	He	NH$_3$	Δk_r (%)	He	NH$_3$	Δr_r (%)
Hexylpropionate	0.439	0.432	−1.6	0.294	0.292	−0.7
Acetic acid	0.747	0.818	9.5	0.501	0.553	10.4
Decanol-2	1.490	1.479	−0.7	1.000	1.000	0
Butyric acid	1.664	1.769	6.3	1.117	1.195	7.0
Valeric acid	2.719	2.866	5.4	1.824	1.936	6.1
Naphthalene	2.974	2.897	−2.6	1.995	1.958	−1.9

$$K_2 = \frac{[\text{OH}^-][\text{NH}_4^+]}{[\text{NH}_3]_{(\ell)}[\text{H}_2\text{O}]_{(\ell)}} \tag{6}$$

$$K_3 = \frac{[\text{Ac}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]_{(\ell)}[\text{AcH}]_{(\ell)}} \tag{7}$$

$$K_{\text{weff}} = [\text{H}_3\text{O}^+][\text{OH}^-] \tag{8}$$

The product of the concentration of $[\text{OH}^-]$ and $[\text{H}_3\text{O}^+]$ ions in a water-containing SLP can be considered as a quasi-constant (see Eq. (8)). With the above listed equations the following expressions for the concentration of $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ can be obtained:

$$[\text{OH}^-] = \frac{K_2[\text{NH}_3]_{(\ell)}[\text{H}_2\text{O}]_{(\ell)}}{[\text{NH}_4^+]} \tag{9}$$

$$[\text{H}_3\text{O}^+] = \frac{K_{\text{weff}}[\text{NH}_4^+]}{K_2[\text{NH}_3]_{(\ell)}[\text{H}_2\text{O}]_{(\ell)}} \tag{10}$$

It is of interest to consider the expressions for $\lambda = [\text{Ac}^-]/[\text{AcH}]_{(\ell)}$ and $[\text{Ac}^-]$ to estimate the ionisation degree of $\text{AcH}_{(\ell)}$:

$$\lambda = \frac{K_2 K_3}{K_{\text{weff}}} \cdot \frac{[\text{NH}_3]_{(\ell)}[\text{H}_2\text{O}]_{(\ell)}^2}{[\text{NH}_4^+]} \tag{11}$$

$$[\text{Ac}^-] = \frac{K_3}{K K_{\text{weff}}} \cdot [\text{AcH}]_{(\ell)} \cdot [\text{H}_2\text{O}]_{(\ell)} \cdot [\text{OH}^-] \tag{12}$$

The observed (general) partition constant of an organic acid (e.g., AcH) K_{m} can be presented as follows:

$$
\begin{aligned}
K_{\text{m}} &= \frac{[\text{HAc}]_{(\ell)} + [\text{Ac}^-]}{[\text{HAc}]_{(g)}} \\
&= \frac{[\text{AcH}]_{(\ell)}}{[\text{AcH}]_{(g)}} + \frac{[\text{Ac}^-]}{[\text{AcH}]_{(g)}}
\end{aligned} \tag{13a}
$$

$$K_{\text{m}} = K_{\ell\text{AcH}} \cdot \left\{ 1 + \frac{K_3}{K_{\text{weff}}} \cdot [\text{H}_2\text{O}]_{(\ell)} \cdot [\text{OH}^-] \right\} \tag{13b}$$

$$K_{\text{m}} = K_{\ell\text{AcH}} \cdot \left\{ 1 + \frac{K_2 K_3}{K_{\text{weff}}} \cdot \frac{[\text{NH}_3]_{(\ell)}[\text{H}_2\text{O}]_{(\ell)}}{[\text{NH}_4^+]} \right\} \tag{14a}$$

$$K_{\text{m}} = K_{\ell\text{AcH}} \cdot \left\{ 1 + \frac{K_3[\text{H}_2\text{O}]_{(\ell)}}{[\text{H}_3\text{O}^+]} \right\} \tag{14b}$$

where

$$K_{\ell\text{AcH}} = \frac{[\text{AcH}]_{(\ell)}}{[\text{AcH}]_{(g)}} \tag{15}$$

The following equations can be written for the description of adsorption of ammonia and water vapours by an SLP:

$$K_{\ell\text{NH}_3} = \frac{[\text{NH}_3]_{(\ell)}}{[\text{NH}_3]_{(g)}} \tag{16}$$

$$K_{\ell\text{H}_2\text{O}} = \frac{[\text{H}_2\text{O}]_{(\ell)}}{[\text{H}_2\text{O}]_{(g)}} \tag{17}$$

With Eqs. (16) and (17), Eqs. (13a), (13b), (14a) and (14b) give:

$$K_{\text{m}} = K_{\ell\text{AcH}} \cdot \left\{ 1 + \frac{K_3 K_{\ell\text{H}_2\text{O}}}{K_{\text{weff}}} \cdot [\text{H}_2\text{O}]_{(g)} \cdot [\text{OH}^-] \right\} \tag{18a}$$

$$K_{\text{m}} = K_{\ell\text{AcH}} \cdot \left\{ 1 + \frac{K_3 K_{\ell\text{H}_2\text{O}}[\text{H}_2\text{O}]_{(g)}}{[\text{H}_3\text{O}^+]} \right\} \tag{18b}$$

or

$$K_{\text{m}} = K_{\ell\text{AcH}} \cdot \left\{ 1 + \frac{K_2 K_3 K_{\ell\text{NH}_3} K_{\ell\text{H}_2\text{O}}}{K_{\text{weff}}} \cdot \frac{[\text{NH}_3]_{(g)}[\text{H}_2\text{O}]_{(g)}^2}{[\text{NH}_4^+]} \right\} \tag{19}$$

When analysing Eq. (18b) let us note that the K_{m} value is inversely related to the concentration of the hydrogen ions H_3O^+ in the polar SLP. If the SLP acidity increases, the K_{m} value decreases, and conversely if the acidity decreases the K_{m} value increases. This effect can be qualitatively observed experimentally.

When analysing Eq. (19) let us note, first, at zero ammonia concentration: $K_{\text{m}} = K_{\ell\text{AcH}}$, i.e., Eq. (19) describes a specific chromatographic process with an inert carrier gas and, second, K_{m} increases as the concentration of ammonia and water vapours in the carrier gas increases. Hence, Eqs. (18a), (18b) and (19) allow qualitative explanation of the observed

regularities and, in particular, the effects of exchanging the inert carrier gas for a basic carrier gas.

Note that the retention (for example, retention factor k) is in direct proportion to the partition constant (e.g., K_m). With this statement and Eq. (19) the retention factor can be presented as:

$$k = bK_{\ell AcH}$$

$$+ \frac{bK_{\ell AcH} K_2 K_3 K_{\ell NH_3} K_{\ell H_2O} [NH_3]_{(g)} [H_2O]^2_{(g)}}{K_{weff} [NH_4^+]}$$

$$= bK_{\ell AcH}$$

$$\cdot \left\{ 1 + \frac{K_2 K_3 K_{\ell NH_3} K_{\ell H_2O} [NH_3]_{(g)} [H_2O]^2_{(g)}}{K_{weff} [NH_4^+]} \right\}$$

$$(20a)$$

or

$$k = bK_{\ell AcH} \cdot \left\{ 1 + \frac{K_3 K_{\ell H_2O} [H_2O]_{(g)}}{[H_3O^+]} \right\} \qquad (20b)$$

where $b = (1/\beta)$, β is the phase ratio (note that $k = bK_m$).

3.2. Temperature dependence of solute retention

In acidic–basic chromatography the physicochemical nature of the retention mechanism of acidic solutes with basic carrier gas is dualistic. Hence, the temperature dependence of retention for acidic solutes is expected to be more pronounced than that for neutral solutes whose retention is based on physical distribution processes in a definite chromatographic system (stationary liquid phase)/(mobile gas phase).

All expected regularities can be observed experimentally.

Hence, first, as temperature increases the observed effect for acidic solutes decreases (approx. threefold) and, second, the discussed effect is less for higher-molecular-mass (butyric and valeric) acids. The contribution of the functional group to retention for the higher-molecular-mass organic acids is much lower.

As is known, the heat of sorption of solutes is an important characteristic of the sorption process which allows all chemical and physical characteristics of compounds considered to reflect the nature of the chemical compound. Hence, we estimated the

Table 3
Heat of sorption (Q) for organic solutes in polyethylene glycol using inert (helium) and basic (ammonia) carrier gases

Solute	Q (kcal/mol)		ΔQ[a] (kcal/mol)
	He	NH$_3$	
Hexylpropionate	10	10	0
Acetic acid	11	13	2

[a] $\Delta Q = Q(NH_3) - Q(He)$.

heats of sorption for hexylpropionate (neutral solute) and acetic acid (see Table 3). As can be seen from the listed data the changing of inert helium for basic ammonia does not influence the heat of sorption for neutral hexylpropionate. But for the acidic solute (acetic acid) the change leads to an increase in the heat of sorption, probably, because of a new chemical constituent of the sorption process (see Table 3).

For temperature programming the influence of the carrier gas basicity on the retention of acidic solutes is more pronounced than that at isothermal conditions.

For example, the separation number SN (or TZ) for the propionic acid/acetic acid pair is 6.0 at 150°C, but SN is 8.5 for the butyric acid/propionic acid pair. For temperature programming (isothermal mode at 110°C during 15 s, then temperature programming from 110°C at 8°C/min until elution of the last component) for the propionic acid/acetic acid pair SN is 11.1.

Thus an increase in the separation number of 50–30% is observed when changing the isothermal mode for temperature programming for acidic solutes.

3.3. Influence of basic carrier gas (ammonia) on retention of basic solutes

The main equilibrium processes occurring in the gas chromatographic system with a basic carrier gas (NH$_3$) and basic solutes (amines) are listed in Fig. 3.

In chromatography the application of ammonia as a carrier gas was suggested earlier for the improvement of the symmetry of amine's zones, stability of chromatograms and for obtaining reliable, quantitative results [11–17]. Unfortunately, interpretation of the results obtained was qualitative only. Hence, we made an attempt to describe the equilibrium pro-
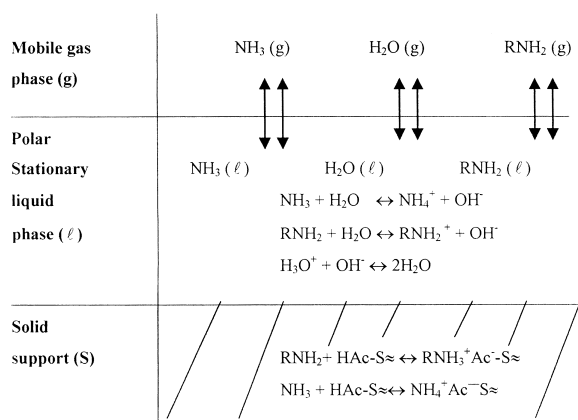
Fig. 3. Scheme of equilibrium process in GLC using basic humid carrier gas (NH_3, H_2O), basic solute (RNH_2), polar SLP and acidic sorption centres ($HAcS\approx$).

cesses in the chromatographic column to explain the improvement of analytical results of amine chromatography with basic carrier gas.
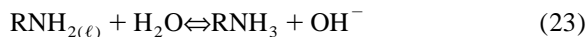
For example, when the primary amine contacts with the SLP, the equilibrium of its molecular form between the gas phase and SLP is established:

$$RNH_{2(g)} \Leftrightarrow RNH_{2(\ell)} \qquad (21)$$

This process is characterised by the following interface equilibrium constant:

$$K_{\ell RNH_2} = \frac{[RNH_2]_{(\ell)}}{[RNH_2]_{(g)}} \qquad (22)$$

But the primary amine dissolved in the water-containing SLP is partially ionised:

$$RNH_{2(\ell)} + H_2O \Leftrightarrow RNH_3 + OH^- \qquad (23)$$

The constant of the process can be described as follows:

$$K_{RNH_2} = \frac{[RNH_3^+][OH^-]}{[RNH_2]_{(\ell)}[H_2O]_{(\ell)}} \qquad (24)$$

Hence, a general interface equilibrium constant K_m for amine can increase (in comparison with $K_{\ell RNH_2}$) as a result of the above mentioned processes (partition and ionisation):

$$K_m = \frac{[RNH_{2(\ell)}] + [RNH_3^+]}{[RNH_{2(g)}]} \qquad (25)$$

or

$$K_m = K_{\ell RNH_2} \cdot \left\{ 1 + [RNH_3^+]/[RNH_{2(\ell)}] \right\} \qquad (26a)$$

$$K_m = K_{\ell RNH_2} \cdot \left\{ 1 + K_{RNH_2} \cdot \frac{[H_2O]_{(\ell)}}{[OH^-]} \right\} \qquad (26b)$$

$$K_m = K_{\ell RNH_2} \cdot \left\{ 1 + \frac{K_{RNH_2} K_{\ell H_2O} [H_2O]_{(g)} [H_3O^+]}{K_{weff}} \right\} \qquad (26c)$$

The effect established by Abdel-Rehim [7] that the basic carrier gas (NH_3) has a significant influence on the retention of the basic compounds to be chromatographed (e.g., amines) on a more polar phase is in agreement with Eq. (26c). In fact, when using more polar phase constants, $K_{\ell RNH_2}$ and $K_{\ell RH_2O}$ increase and, consequently, the general distribution constant K_m for a compound to be chromatographed in the SLP–gas system increases as well (see Eq. (26c)). Note that:

$$\frac{K_m}{K_{\ell RNH_2}} = 1 + \frac{[RNH_3^+]}{[RNH_2]_{(\ell)}} \qquad (27)$$

When $K_m / K_{\ell RNH_2} >> 1$ practically all the amine is ionised, i.e., at the given experimental conditions amine is non-volatile and does not elute from a column ($[RNH_3^+] >> [RNH_{2(\ell)}]$).

With Eqs. (22) and (23), the following ratio can be obtained:

$$\frac{[RNH_3^+]}{[RNH_{2(\ell)}]} = \frac{K_{RNH_2}}{K_{NH_3}} \cdot \frac{[NH_4^+]}{NH_{3(\ell)}} \qquad (28)$$

With Eq. (28) it can be shown that $[RNH_3^+]/[RNH_{2(\ell)}]$, i.e., ionisation of amines in the SLP can be neglected at high concentrations of NH_3 since $[RNH_4^+]/[NH_{3(\ell)}] << 1$ and $K_{RNH_2}/K_{NH_3} << 1$ (see Table 4).

Chemical sorption (chemical interaction) of amines on acidic centres of solid supports $\approx$S-AcH or on acidic contamination centres of SLPs (for example, such centres can be formed as a result of introduction of acidic cross-linking reagents into the SLP) are the most probable reasons for the signifi-

Table 4
Comparison of the ionisation constants for ammonia and some primary amines in aqueous media at 25°C [19]

Compound	Ionisation constant (K, $\cdot 10^{11}$)	Ratio of ionisation constants of amine and ammonia
Ammonia	56.20	1.00
Methylamine	2.34	0.0042
Ethylamine	1.99	0.035
Butylamine[a]	1.70[a]	0.03
Amylamine	2.34	0.042

[a] The data at 20°C.

cant increase in amine retention. Amines can be chemically adsorbed on the surface acidic centres:

$$RNH_2 + HAcS \approx \Leftrightarrow RNH_3^+ (Ac^-)\text{-}S \approx \qquad (29)$$
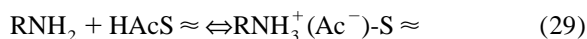
Since acidic centres of various nature (and various "power") are often in a real column, the formation of product with various stability is possible as a result of the interactions between such centres and amines. This has lead to the "disappearance" of the amine peak on the chromatogram or to the formation of very broadened asymmetry zones of amines (e.g., see Ref. [18]).

Two main methods to overcome these difficulties in the analysis of amines are described in the literature (see Ref. [18]). The first method is an introduction of basic non-volatile components into the SLP. The interaction between ammonia and the acidic centres of the SLP (and solid support) is more strong than that of the amines. The second method is application of basic carrier gas, the poisoning acidic centres in the chromatographic system.

The acidic centre takes part in two competitive reactions (Eqs. (28) and (30)):

$$NH_3 + HAcS \approx \Leftrightarrow NH_4^+ [Ac^-]\text{-}S \approx \qquad (30)$$

The equilibrium constants of the reactions (28) and (30) are listed below:

$$K_{RNH_2S} = \frac{[RNH_3^+ - (Ac^-)S \approx]}{[HAcS_{(S)} \approx][RNH_{2(\ell)}]} \qquad (31)$$

$$K_{NH_3S} = \frac{[NH_4^+ - (Ac^-)S \approx]}{[HAcS_{(S)} \approx][NH_{3(\ell)}]} \qquad (32)$$

The ratio λ_S is of interest for estimation of the predominant process:

$$\frac{K_{RNH_2S}}{K_{NH_3S}} = \frac{[RNH_3^+ - (Ac^-)S \approx]}{[NH_4^+ - (Ac^-)S \approx]} \cdot \frac{[NH_3]_{(\ell)}}{[RNH_2]_{(\ell)}} \qquad (33)$$

$$\lambda_S = \frac{[RNH_3^+ - (Ac^-)S \approx]}{[NH_4^+ - (Ac^-)S \approx]}$$

$$= \frac{K_{RNH_2S}}{K_{NH_3S}} \cdot \frac{[RNH_2]_{(\ell)}}{[NH_3]_{(\ell)}} \qquad (34)$$

Applying the general ionisation regularities of ion exchangers for ammonia and amines and $[RNH_{2(\ell)}]/[NH_{3(\ell)}] \ll 1$ as well, then $\lambda_S \ll 1$.

3.4. Ammonia water as a source for humid basic carrier gas

Conventional columns with traditional carrier gases (e.g., He) cannot be used for amines separation. Only special (more expensive) columns are in common use for analysis of amines. Hence, we suggest a simple and inexpensive technique for obtaining symmetric peaks for the amines to be analysed. We recommend the application of an inert carrier gas saturated with water and ammonia vapours by bubbling the inert carrier gas through ammonia water. In this way, the acidic centres in the chromatographic system are neutralised by ammonia on the capillary column coated with polar polyethylene glycol. In the humid system modified by ammonia, amines are eluted from the column as symmetric peaks.

We suggest using a flow of inert carrier gas (e.g., nitrogen or helium) passing through a bubbler with ammonia water at ambient temperature to simplify obtaining of the humid basic carrier gas. After the bubbler inert gas contains 200–400 mm NH_3.

Note that application of the humid basic carrier gas by the above technique allows one to obtain

symmetric peaks of amines and other polar solutes. Chromatograms of solute mixtures with helium and helium containing ammonia and water vapours are presented in Fig. 4.

As can be seen from chromatograms, application of ammonia water as a humid basic carrier gas allows an essential improvement of separation and peak symmetry for amines.

To estimate the application of a carrier gas containing ammonia for amines separation it is necessary to compare the efficiency of the column used for two types of solutes: amines and neutral compounds. If the column is characterised by the same efficiency, then ammonia application allows one to completely eliminate the influence of adsorption phenomena on the amines zones. The estimation we performed showed that the column

efficiency for both amines and neutral compounds is practically the same.

Hence, ammonia as a carrier gas allows improvement of amines separation.

4. Conclusion

The partition of acidic and basic solutes in the (SLP)/carrier gas system was considered taking into account acidic–basic reactions in the polar SLP using ammonia as the basic carrier gas.

A simple retention theory for acidic and basic solutes using a basic carrier gas was developed for the given chromatography variant.

It was shown that acidic–basic chromatography suggested recently allows improvement of separation selectivity and other separation characteristics as well.

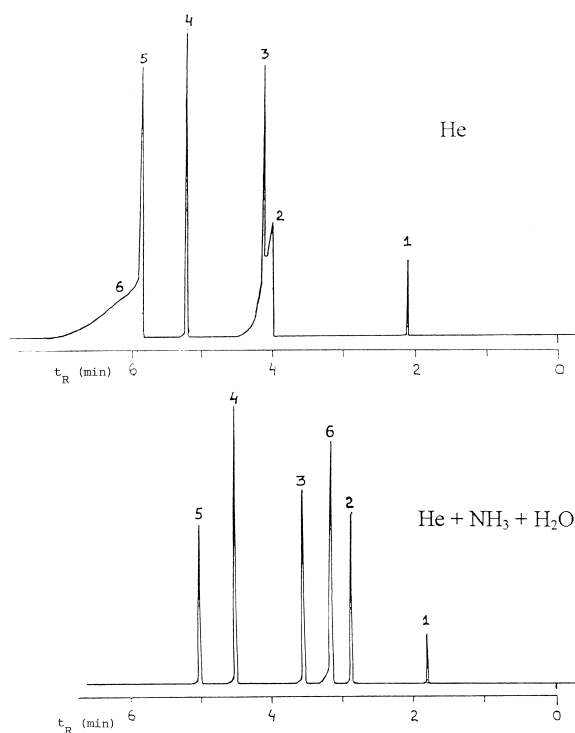A simplified technique using ammonia water was suggested for acidic–basic chromatography.

Fig. 4. Influence of an admixture of ammonia and water vapours in helium as inert carrier gas on the retention and zone symmetry of polar solutes. Experimental conditions: column 30 m×0.25 mm I.D. (J&W Scientific, USA) coated with polyethylene glycol as SLP, temperature 90°C. Solutes: 1=methane, 2=dibutylamine, 3=*n*-dodecane, 4=pentanol, 5=pseudocumene, 6=hexylamine.

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