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Sorption of 4-Carboxyquinoline Derivatives from Aqueous Acetonitrile Solutions on the Surface of Porous Graphitized Carbon

A. S. Savchenkova^a, A. K. Buryak^b, and S. V. Kurbatova^a

^a Samara State University, Samara, Russia

^b Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, Russia

e-mail: curbatsv@gmail.com

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Abstract—The sorption of 4-carboxyquinoline derivatives from aqueous acetonitrile solutions on porous graphitized carbon was studied. The effect of the structure of analyte molecules and the eluent composition on the characteristics of retention under the conditions of RP HPLC was analyzed. The effect of pH of the eluent on the shift of equilibrium in aqueous acetonitrile solutions was investigated.

Keywords: reversed-phase high-performance liquid chromatography, acetonitrile, composition of the mobile phase, quinolines, porous graphitized carbon, pH of eluent.

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INTRODUCTION

In high-performance liquid chromatography, the selectivity of separation can be regulated by varying the composition of the mobile phase by replacing the organic modifier or by varying the eluent or the quantitative ratio between its components. Another method for optimizing the selectivity of the system in chromatography of acidic or basic analytes is variation of pH of the eluent, which can change either when the concentration of the organic component of the mobile phase changes or when appropriate buffer mixtures are added [1]. In the mobile phase solution and on the sorbent surface, ionogen substances exist in the form of both neutral molecules and ions. Variation of pH of the mobile phase changes the p*K* of these analytes, which, in turn, leads to a change in the ratio between their ionized and molecular forms, whose chromatographic retention can differ significantly [2, 3]. Therefore, these substances are usually recommended to be chromatographed in the presence of a buffer with suitable buffer capacity, which allows pH control of the eluent, reproducible characteristics of retention, and chromatograms with well discernible peaks [4, 5]. It should be noted, however, that addition of a buffer mixture to the aqueous organic mobile phase leads to more complex intermolecular interactions in the system and, occasionally, to possible sorption of the components of the buffer system on the surface of the stationary phase.

The pH effect on the chromatographic retention of organic analytes was described and methods for calculating the pH of sorbate solutions in the eluent in the presence of a buffer based on the characteristics of all components of the chromatographic system were

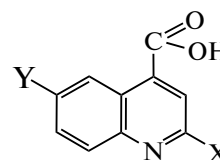
reported in [6, 7]. In practice, however, these calculations are complicated by many factors; therefore, the type of buffer solution in chromatographic analysis of acids is selected mainly experimentally. (Note that if chromatography is performed with a modified silica gel column, the shift of the acid–base equilibrium in the eluent may be affected by the residual (unmodified) hydroxyl groups of the sorbent, which contribute to the change in pH of the mobile phase.)

Therefore, the goal of this study was to investigate the effect of pH of the eluent on chromatographic retention of 4-carboxyquinolines under the conditions of reversed-phase high-performance liquid chromatography (RP HPLC) using porous graphitized carbon (Hypercarb) as a sorbent, whose direct involvement in the acid–base equilibrium should be minimum.

Previously, the chromatographic behavior of 4-carboxyquinolines with a substituted carboxyl group (esters, amides, hydrazides, etc.) was studied [8, 9]. Data on chromatographic studies of acids were not found in the literature.

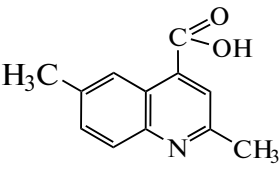
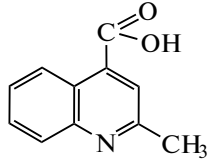
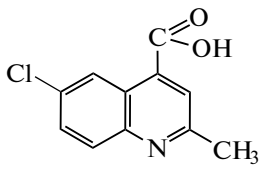
EXPERIMENTAL

The objects of this study were the derivatives of 4-carboxyquinolines with the general formula



where Y: –H, –CH₃, –Cl; X: –CH₃, –OH, =O.

Table 1. pK_a Values for several 4-carboxyquinolines in aqueous acetonitrile solutions with different acetonitrile concentrations

Substance	pK_a at different acetonitrile : water ratios			
	4 : 6	1 : 1	6 : 4	7 : 3
	8.03	7.95	8.59	8.54
	8.59	8.45	8.15	8.17
	7.93	8.75	9.02	7.91

The chromatographic study was performed on a Varian ProStar liquid chromatograph with a ProStar UV spectrophotometric detector at a wavelength of 254 nm. Porous graphitized carbon (Hypercarb) was the adsorbent. As an eluent, we used an acetonitrile–water mixture with different acetonitrile contents (20–80 vol %). The eluent rate was 0.5 mL/min. The sorbate sample was prepared by dissolving the crystalline substance in acetonitrile. The retention of the compounds under study was characterized by the retention factor (k) calculated by the formula

$$k = (t_R - t_h)/t_h,$$

where t_R is the retention time of the substance under study, and t_h is the retention time of the non-sorbing substance (nitromethane).

To maintain definite pH values of the eluent, we used buffer solutions of sodium tetraborate (pH of the aqueous solution is 9.18) and sodium hydrogen tartrate (pH 3.56). For potentiometric studies, we used a pH 211 HANNA laboratory pH-meter (the measurement error was ± 0.03 pH units) with a composite glass electrode (HI 1131B). The pH-meter was calibrated against the standard buffer solutions. The pH of the control solutions was determined by the procedure of [10–12].

The mass spectra of the compounds were recorded by the MALDI method on a Bruker Daltonics Ultraflex II MALDI mass spectrometer with nitrogen laser ionization with a working wavelength of 337 nm. The laser energy was varied from 10 to 150 μ J/pulse. The pulse frequency was 20 Hz. The number of pulses was varied from 1 to 100 for optimization of the intensity of the obtained spectra. The samples were deposited on

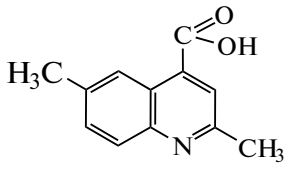
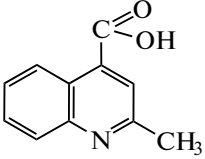
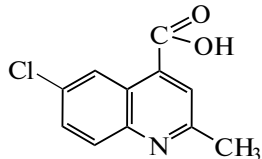
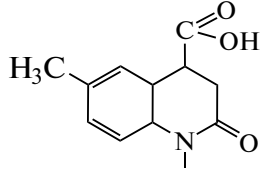
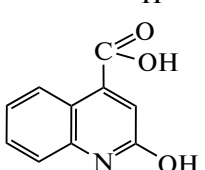
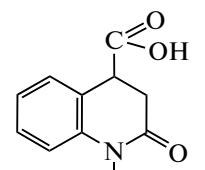
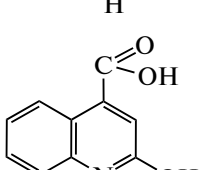
the surface of polished stainless steel, which was a standard target for samples and was purchased from Bruker.

RESULTS AND DISCUSSION

4-Carboxyquinolines are aromatic heterocycles, whose major structural fragment is a quinoline nucleus with a carboxyl group in the fourth position. These are weak acids, whose pK values for various solvents are given in [11]. In the aqueous acetonitrile solutions of 4-carboxyquinoline, the molecular and ionized forms equilibrate due to the high differentiating ability of acetonitrile. According to the data of Table 1, variation of the acetonitrile concentration leads to a change in pK of these compounds, which corresponds to the literature data obtained for aqueous acetonitrile solutions of other acids [13]. These changes are associated with the peculiarities of aqueous acetonitrile solutions, which have recently attracted considerable attention of researchers [14, 15]. It was shown that homo- and heteroassociates can form in them due to the relatively high donor–acceptor ability of acetonitrile [3–5] and the ensuing change in pH of aqueous acetonitrile solutions [15].

We analyzed the effect of acetonitrile concentration on pH of the water–acetonitrile mixture and aqueous acetonitrile solutions of 4-carboxyquinolines. Figure 1 presents the plots of the corresponding dependence obtained from the experimental and literature data. According to these plots, pH of the water–acetonitrile mixture increases almost linearly with the acetonitrile concentration. Variation of the initial pH value of the solution through addition of the corre-

Table 2. Retention factors of 4-carboxyquinolines in the absence and in presence of buffer additions in the eluent

No.	Substance	Retention factor (<i>k</i>) at different acetonitrile concentrations in the eluent (vol %)									
		30	40	50	60	40	50	60	30	40	
		no buffer				acid buffer (pH 3.54)			alkaline buffer (pH 9.18)		
1		2.77	1.61	0.48	0.73	7.59	6.79	5.09	1.95	1.10	
2		7.15	2.46	1.15	1.08	3.32	3.25	2.11	0.73	0.63	
3		17.52	4.44	1.91	1.38	8.99	8.51	4.2	1.09	0.82	
4		2.60	1.15	0.55	0.42	3.45	2.43	0.93	1.38	0.81	
5		2.97	0.85	0.45	0.48	2.82	3.47	0.67	0.45	0.44	
6		1.40	0.81	0.48	0.35	1.18	1.23	0.6	0.42	0.47	
7		1.40	0.81	0.48	0.35	1.18	1.23	0.60	0.42	0.47	

sponding buffer does not affect the form of the dependence, except the shift of the intersection point between the plot and the ordinate axis in accordance with the initial pH value.

For solutions of 4-carboxyquinolines, the dependence of pH on the acetonitrile concentration is dif-

ferent, as illustrated by the plots given in Fig. 2. The authors of [16] suggested that this form of the dependence points to the existence of various forms of analyte in solutions, and the presence of inflection points on the plots of pH corresponds to the equality of the concentrations of the molecular and ionized forms. An analysis of the mass spectra of the aqueous aceto-

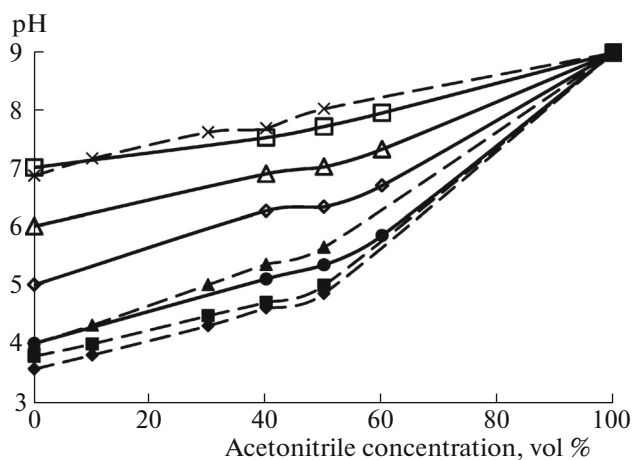


Fig. 1. Dependences of pH of aqueous acetonitrile solutions on the acetonitrile concentration (solid lines: experimental data, dashed lines: literature data [15]).

nitrile solutions of 4-carboxyquinolines showed that for compounds 4 and 6, the dominant signals were those that correspond to the salts of these acids. For other substances, the signals corresponding mainly to the molecular ions were found (the numbering of substances corresponds to that in Table 2). The intensity ratio between the protonated and cationized molecular ions correlates with the dissociation constants.

Thus, we can state that in aqueous acetonitrile solutions of 4-carboxyquinolines, the molecular and ionized forms can exist in equilibrium, which shifts when the composition of the eluent changes. This shift, in turn, presumably affects the sorption characteristics of substances, the retention factor being the sum of the retention factors of the protonated and deprotonated forms.

Table 2 lists the retention factors of 4-carboxyquinolines obtained in studies of sorption on the surface of porous graphitized carbon (PGC) from aqueous ace-

tonitrile solutions with different acetonitrile concentrations with additions of buffer solutions or in the absence of buffer solutions. It follows from these data that the retention factors of the compounds depend substantially on the structure of the analyte molecules and the content of the organic component: as the acetonitrile concentration decreases, the retention factor increases, which conforms with the laws of RP HPLC [17]. For several compounds, the retention factor increased approximately tenfold and more.

Significant retention of polar compounds is generally characteristic of hypercarb (the so-called polar retention effect) and is due to the interaction of the analyte molecules having a free electron pair or an aromatic system with the free electrons (conduction electrons) of PGC [18]. When the acetonitrile content in the mobile phase increases, this interaction is more or less compensated by the polar interactions of the analyte with the eluent, which decreases the retention considerably. At the same time, the significant differences in the retention characteristics of the analytes at different acetonitrile concentrations may be due, inter alia, to the shift of the acid–base equilibrium in solution, leading to a change in the ratio between the ionized and molecular forms of the analyzed acids.

The addition of an acid buffer solution considerably increased the retention factor relative to the values of the factor in the absence of a buffer. The addition of an alkaline buffer, however, decreased the retention; the retention factor was almost independent of the structure of the analyte molecules and the acetonitrile content in the eluent. Since the decrease in pH after the addition of an acid buffer and the increase after the addition of an alkaline buffer should lead to a shift of equilibrium in solution toward the molecular or ionized forms of the analyte, respectively, we can assume that the difference in the retention factor in the instances under study is explained by the presence of different forms (molecular and ionized forms in the presence of an acid and alkaline buffer, respectively)

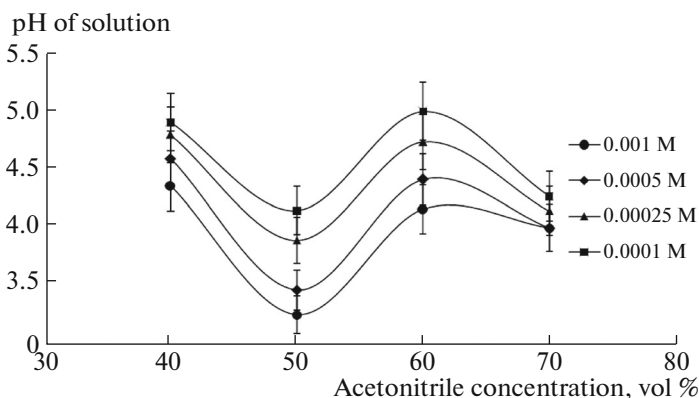


Fig. 2. Dependences of pH of aqueous acetonitrile solutions of 4-carboxy-2,6-dimethylquinoline on the acetonitrile concentration at different analyte concentrations.

and both forms in the absence of a buffer. An argument in favor of this assumption are the data published by Roses and Bosch in the series of papers [1–4] devoted to a study of the pH effect on chromatographic retention of ionogen analytes; they gave strong evidence that under the conditions of RP HPLC, the nonionized (neutral) molecules are characterized by longer retention than the ionized ones, and in any case, retention decreases at higher acetonitrile concentrations in the eluent.

CONCLUSIONS

Thus, we can conclude that the role of pH of the mobile phase in a definite mechanism of retention in liquid chromatography can be significant, but has not yet been clearly defined [16, 18]. The reason for this is the lack of a universal theory of aqueous organic solutions. The development of this theory would stimulate the development of the theory of liquid chromatography, whose potential as a physicochemical method has not yet been exhausted.

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