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Short communication

Ion chromatography of impurities in organic solvents

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Abstract

The capabilities of a determination of monohydric aliphatic carboxylic acids (C_1-C_7) $10^{-6}-10^{-4}$ g/l, chlorides, nitrates and carbonates impurities in 46 organic solvents, such as alcohols, ethers, ketones, acetonitrile, dimethyl sulphoxide, formamides, graded as 'pure for analytical purposes' and 'chemically pure' by ion chromatography with conductivity detection are reported. Data obtained allow to predict total content of carboxylic acids in the organic solvents starting from their empirical parameters of polarity (E_T , kcal/mol; 1 cal=4.184 J). © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Carboxylic acids; Alcohols; Ethers; Ketones; Acetonitrile; Dimethyl sulfoxide; Formamides; Inorganic ions

1. Introduction

Industrial synthesis, separations from reaction mixtures and storage of organic solvents usually yields an accumulation of monodentate carboxylic acids and inorganic salts, mostly chlorides, nitrates and carbonates. These accumulations of impurities of the first group are the product of the liquid-phase oxidation of the solvents by molecular oxygen, and the autooxidation of the aldehydes presented [1]. Chlorides, nitrates and carbonates are introduced from reagents practically under all methods of purification. On the other hand, the presence of nitrates and carbonates are explained by dissolving of atmospheric gases (NO_2 , CO_2 , etc.).

An application of these solvents for spectroscopy, extraction, absorption chromatography, acid–base titration and other research modern technologies requires extended demands to their purity. For instance, it is known that the application of organic solvents in microelectronics and optical fields de-

mands that the level of electrolyte impurities be less than $10^{-4}-10^{-3}$ g/l.

Therefore, the determination of low contents of acid impurities and inorganic salts in various organic solvents is important for application of the modern analytical chemistry. However, this information is known only for acetone [2] and several monohydric alcohols [3]. Systematic analysis of extensive set of organic solvents was not made. Therefore, the questions of interconnections between possible solvation mechanisms and impurity distribution are not considered. The latter is of special scientific interest.

The object of this report is the determination of carboxylic acids and inorganic salts in alcohols, ketones, ethers, acetonitrile, dimethyl sulphoxide and formamides (graded as 'pure for analytical purposes' and 'chemically pure') by anionic liquid chromatography [4] and correlation analysis recommended in [5,6].

2. Experimental

In the present work, a Tsvet 3006 ion-chromato-

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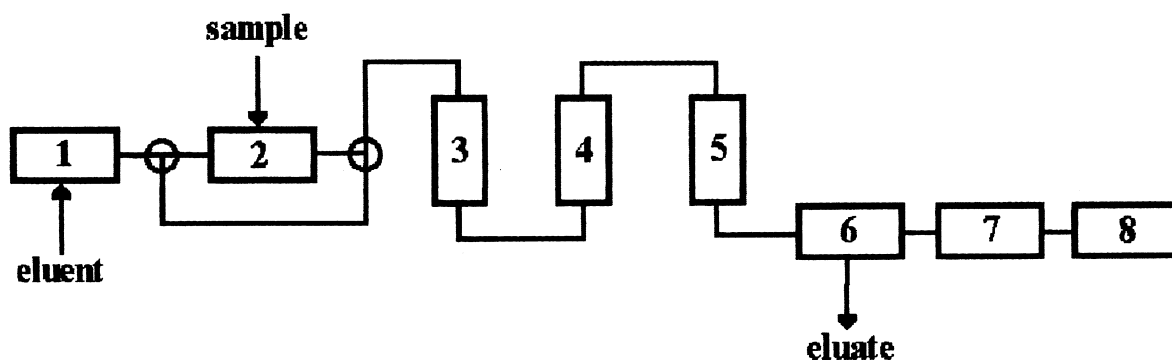


Fig. 1. Scheme of the liquid ion chromatograph Tsvet-3006. (1) Pump (6 ml/min); (2) input device of the sample (1 ml); (3) concentrating column (50×6 mm); (4) separating column (200×6 mm); (5) compensating column (50×6 mm); (6) conductivity cell; (7) conductivity detector; and (8) recorder.

graph with conductometric detector was used (Fig. 1). The chromatographic system consists of three columns: concentrating (existence of this column is explained by the relatively big sample volume), separating (in order to receive individual constituents of the analyzing mixture of anions) and compensating (working as a suppressor to reduce the level of conductivity).

The concentrating and separating columns were filled with the anion-exchange resin KANK-Ast with a small exchange capacity in the OH form. Anion exchanger beads were 16–20 μm . The feature of this resin is the presence of the strong base groups

$\text{N}^+(\text{CH}_3)_3$ that are bonded to the styrene–divinylbenzene matrix. The compensating column contained high-acidic cation exchanger KU-2-8 (50 μm) in the H form. The eluent was a mixture of $5 \times 10^{-4} \text{ M KOH}$ and $5 \times 10^{-4} \text{ M (C}_4\text{H}_9)_4\text{NOH}$. The flow-rate was 6 ml/min.

Forty-six different organic solvents (alcohols, ketones, ethers and others) graded as ‘pure for analytical purposes’ and ‘chemically pure’ were analyzed (Table 1). In all cases we used from eight to 10 samples from the same purity qualification, with variant production numbers (in general from Russian manufactures).

Table 1
Analyzed organic solvents

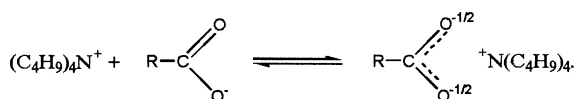
Class of organic solvents	Organic solvents (purity grade)
Aliphatic monohydric alcohols	
Normal structure	Methanol (c.p.), ethanol (c.p., rect.), propanol (c.p.), butanol (a.p.), amyl alcohol (a.p.), hexanol (a.p.), heptanol (a.p.)
Branched structure	Iso-propanol (c.p., a.p.), isobutanol (a.p.), <i>tert</i> -butanol (a.p.), isoamyl alcohol (c.p., a.p.), <i>tert</i> -amyl alcohol (a.p.)
Polyhydric alcohols	Ethylene glycol (a.p.), propylene glycol (a.p.), diethylene glycol (a.p.), triethylene glycol (a.p.), glycerin (c.p., a.p.)
Aliphatic and cyclic ethers	<i>n</i> -Propyl ether (a.p.), isopropyl ether (a.p.), diethyl ether (c.p.), <i>n</i> -butyl ether (a.p.), 1,4-dioxane (c.p., a.p.), tetrahydrofuran (c.p., a.p.), 2-ethoxyethanol (a.p.)
Formic, acetic and butanoic ethers	Methyl formate (c.p.), ethyl formate (a.p.), methyl acetate (a.p.), ethyl acetate (c.p., a.p.), <i>n</i> -propyl acetate (a.p.), <i>n</i> -butyl acetate (c.p., a.p.), <i>n</i> -amyl acetate (c.p.), ethyl butyrate (a.p.)
Aliphatic, aromatic and cyclic ketones	Acetone (c.p., a.p.), methyl ethyl ketone (a.p.), diethyl ketone (a.p.), methyl propyl ketone (a.p.), methyl isobutyl ketone (a.p.), acetyl acetone (a.p.), acetophenone (a.p.), cyclopentanone (a.p.), cyclohexanone (c.p., a.p.)
Nitriles, sulphoxides, formamides	Acetonitrile (c.p., a.p.), dimethyl sulphoxide (c.p., a.p.), formamide (a.p.), <i>N</i> -methylformamide (a.p.), <i>N,N</i> -dimethylformamide (c.p., a.p.)

c.p., chemically pure; rect., rectified product; a.p., for analytical purposes.

Before evaporating, the preparation of the sample consisted of exchanging the organic medium with aquatic matrix. Eluent (1–2 ml) was added to the sample of the solvent to convert volatile molecular constituents to salts. After that, an organic solvent (5–50 ml) was evaporated in vacuum ($\sim 3 \times 10^{-3}$ Pa, 40–60°C). The residue was dissolved in the fixed volume of deionizing water (50 $\mu\text{S}/\text{m}$) and 1 ml of the solution received was passed through the concentrating column.

3. Results and discussion

Retention time of carboxylates was found to depend on the two competing processes. The first one is explained by the possibility of complex formation between carboxylate ion and cation $(\text{C}_4\text{H}_9)_4\text{N}^+$ (from the eluent) [7,8]:



Reaction (1) predominates in the case of acetate ion, since the latter has an effective radius of 1.5 Å and does not produce space hindrance for complexing, the latter being less characteristic in the case of formic ion (Ref. [8], p. 530).

The second process involved is associated with adsorption of molecular forms of carboxylic acids on the cation exchanger matrix [9].

Thus, with the exception of formate and acetate, the retention time of carboxylates corresponds to the equation: $\tau_{\text{min}} = (2.3 \pm 0.1) \times 10^{-1} M - (6.1 \pm 0.3)$, where M is the carboxylate ion molecular mass.

The latter do not interfere in the determination of inorganic anions, such as Cl^- , HCO_3^- , NO_3^- . This is an essential advantage of our eluent and the proposed system of chromatographic columns with corresponding absorbers compared to that generally used.

The order of elution was as follows (min): Cl^- (1.8); HCO_3^- (5.0); NO_3^- (7.2); $\text{C}_2\text{H}_5\text{COO}^-$ (11.6); $\text{C}_3\text{H}_7\text{COO}^-$ (13.5); $\text{C}_4\text{H}_9\text{COO}^-$ (16.5); HCOO^- (18.0); $\text{C}_5\text{H}_{11}\text{COO}^-$ (20.0); $\text{C}_6\text{H}_{13}\text{COO}^-$ (23.0); $\text{C}_7\text{H}_{15}\text{COO}^-$ (26.2); CH_3COO^- (32.8); CO_3^{2-} (45.0). The detection limits of the determined contents ($\text{C}_H \times 10^6$, g/l) are: 3, 1, 2, 5, 10, 5, 1.5, 5, 5, 5, 0.04 and 10, respectively (these data are presented

with a correction for the concentration coefficient of 20 after sample preparation stage). Reproducibilities were 0.15–0.3 for concentrations between 10^{-2} – 10^{-4} g/l and 0.3–0.5 (10^{-5} – 10^{-6}) g/l.

A chromatogram of anion impurities in ethanol graded as ‘chemically pure’ is shown in Fig. 2.

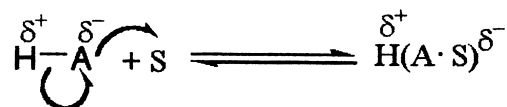
We were the first to determine the low concentrations of carbonates, chlorides, nitrates and carboxylate ions in alcohols, ethers, ketones and other dipolar organic solvents (Table 2) by ion chromatography (IC) using conductivity detection. Data presented for various samples of each solvent graded as ‘analytically pure’ and ‘chemically pure’ are convergent using Student’s t -criterion [10]. Received data allow to predict the impurity contents of the carboxylic acids in different classes of organic solvents.

The molecules of aliphatic alcohols which form homomolecular associates by means of hydrogen bonds are known to be largely associated and changing in the sequence n -butanol < n -propanol < ethylalcohol < ethylene glycol (Ref. [5], p. 29). Gildebrand’s solubility parameter (δ) can be measure of energy that is required to form holes situated in the solvent that can incorporate molecules of the solute in the course of solubility (Ref. [6], p. 551). Obviously carboxylic acids destroy H bond systems between alcohol molecules. Therefore, an increase of the δ_h (MJ/m^3)^{1/2} (Ref. [11], p. 51) (which estimates the role of the H bonds during solvation) is accompanied by an increase of the carboxylic acid contents.

Formation of H bonds between molecules of carboxylic acid (HA) and mono- or polyhydric alcohol (SH) increases with decrease of both the empirical parameter of polarity (E_T) and dielectric capacity (ϵ) of alcohols. The reason for this is a shielding of the anion charge by molecules of alcohol, so the charge delocalization occurs.



For ethers and esters, ketones, acetonitrile, dimethyl sulphoxide and formamides, the increase of ϵ and E_T is accompanied by a charge separation:



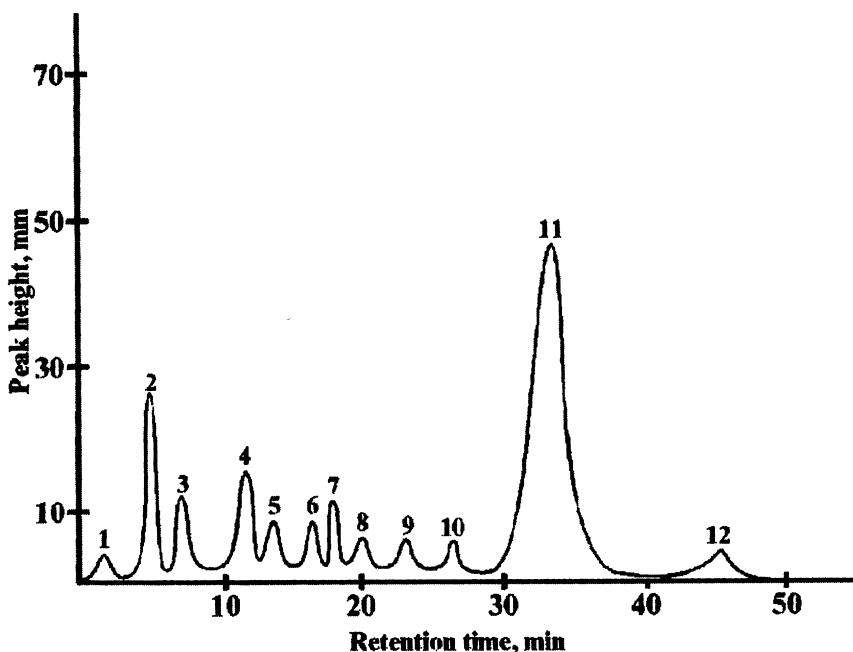


Fig. 2. Chromatogram of anionic impurities in ethanol, 'chemically pure' grade. (1) Cl^- (1.5×10^{-4} g/l); (2) HCO_3^- (6.5×10^{-4} g/l); (3) NO_3^- (3×10^{-4} g/l); (4) $\text{C}_2\text{H}_5\text{COO}^-$ (1.5×10^{-3} g/l); (5) $\text{C}_3\text{H}_7\text{COO}^-$ (9.0×10^{-4} g/l); (6) $\text{C}_4\text{H}_9\text{COO}^-$ (9.2×10^{-4} g/l); (7) HCOO^- (1.0×10^{-5} g/l); (8) $\text{C}_5\text{H}_{11}\text{COO}^-$ (8.0×10^{-6} g/l); (9) $\text{C}_6\text{H}_{13}\text{COO}^-$ (9.0×10^{-6} g/l); (10) $\text{C}_7\text{H}_{15}\text{COO}^-$ (8.0×10^{-6} g/l); (11) CH_3COO^- (2.5×10^{-5} g/l); (12) CO_3^{2-} (3.0×10^{-3} g/l).

Therefore, the total concentration of the carboxylic acid impurities increases.

Received correlation laws between concentrations

of carboxylic acid impurities and E_T or ϵ are characterized with a correlation coefficient between 0.97 and 0.99. These correlations allow to predict

Table 2

Content of inorganic salts and carboxylic acids impurities in different classes of organic solvents

Organic solvents (number of solvents)	Predominant impurities	
	Inorganic salts (g/l)	Carboxylic acids (g/l)
Aliphatic monohydric <i>n</i> - and isoalcohols (12): CH_3OH — $n\text{-C}_3\text{H}_7\text{OH}$ $n\text{-C}_4\text{H}_9\text{OH}$ — $n\text{-C}_5\text{H}_{11}\text{OH}$ $n\text{-C}_6\text{H}_{13}\text{OH}$ — $n\text{-C}_7\text{H}_{15}\text{OH}$ Iso- $\text{C}_3\text{H}_7\text{OH}$, iso- $\text{C}_4\text{H}_9\text{OH}$, <i>tert.</i> - $\text{C}_4\text{H}_9\text{OH}$, iso- $\text{C}_5\text{H}_{11}\text{OH}$, <i>tert.</i> - $\text{C}_5\text{H}_{11}\text{OH}$	HCO_3^- , Cl^- ($3\text{--}4$) $\times 10^{-3}$ HCO_3^- , Cl^- , NO_3^- ($3\text{--}4$) $\times 10^{-3}$ HCO_3^- , Cl^- ($4\text{--}5$) $\times 10^{-3}$ HCO_3^- , Cl^- ($3\text{--}6$) $\times 10^{-3}$	HCOOH — $\text{C}_4\text{H}_9\text{COOH}$ ($1\text{--}4$) $\times 10^{-3}$ $\text{C}_3\text{H}_7\text{COOH}$ — $\text{C}_4\text{H}_9\text{COOH}$ ($2\text{--}4$) $\times 10^{-2}$ $\text{C}_3\text{H}_7\text{COOH}$ — $\text{C}_7\text{H}_{15}\text{COOH}$ ($0.5\text{--}2$) $\times 10^{-1}$ $\text{C}_2\text{H}_5\text{COOH}$ — $\text{C}_4\text{H}_9\text{COOH}$ ($1\text{--}4$) $\times 10^{-3}$
Polyhydric alcohols (5)	NO_3^- , HCO_3^- ($0.5\text{--}10$)	HCOOH — $\text{C}_3\text{H}_7\text{COOH}$ ($0.6\text{--}4$) $\times 10^{-2}$
Aliphatic and cyclic ethers (7)	Cl^- , NO_3^- , HCO_3^- ($0.1\text{--}1$)	HCOOH — $\text{C}_5\text{H}_{11}\text{COOH}$ ($0.2\text{--}5$) $\times 10^{-3}$
Formic, acetic and butanoic ethers (8)	Cl^- , HCO_3^- ($4\text{--}8$) $\times 10^{-1}$	HCOOH — $\text{C}_3\text{H}_7\text{COOH}$ ($0.1\text{--}5$) $\times 10^{-3}$
Aliphatic ketones (without acetyl acetone) (5)	Cl^- , HCO_3^- ($2\text{--}6$) $\times 10^{-3}$	CH_3COOH — $\text{C}_4\text{H}_9\text{COOH}$ ($0.4\text{--}6$) $\times 10^{-2}$
Acetyl acetone	Cl^- , NO_3^- , HCO_3^- (5 ± 1) $\times 10^{-1}$	HCOOH — $\text{C}_2\text{H}_5\text{COOH}$ 0.7 ± 0.2
Aromatic and cyclic ketones (3)	Cl^- , HCO_3^- ($1\text{--}5$) $\times 10^{-3}$	$\text{C}_3\text{H}_7\text{COOH}$ — $\text{C}_6\text{H}_{13}\text{COOH}$ ($3\text{--}8$) $\times 10^{-3}$
Acetonitrile	Cl^- , NO_3^- ($3\text{--}5$) $\times 10^{-2}$	CH_3COOH — $\text{C}_4\text{H}_9\text{COOH}$ ($2\text{--}5$) $\times 10^{-2}$
Dimethylsulphoxide	Cl^- , NO_3^- ($2\text{--}7$) $\times 10^{-2}$	HCOOH ($0.2\text{--}1$) $\times 10^{-1}$
Formamides (3)	Cl^- , NO_3^- ($0.1\text{--}5$) $\times 10^{-1}$	HCOOH ($1\text{--}8$) $\times 10^{-1}$

Table 3

Correlation constants of equation $pC^a = a + b \times \lg E_T$

Organic solvents	<i>a</i>	<i>b</i>
Aliphatic monohydric		
<i>n</i> -Alcohols	−(95±1)	56.9±0.6
Isoalcohols	−(13.6±0.3)	9.7±0.2
Polyhydric alcohols	−(43.6±0.8)	26.0±0.3
Aliphatic and cyclic ethers	231±5	−(148.7±2.1)
Esters	30.1±0.6	−(16.9±0.2)
Aliphatic, aromatic and cyclic ketones		
Acetonitrile, dimethylsulphoxide, formamides	42.3±0.7	−(25.0±0.3)

^a $pC = -\lg \sum C_{\text{carb. acids}}$; *C*, g/l.

total carboxylic acid contents in organic solvents. Some of these are shown in Table 3.

Thus, the concentration levels of the carboxylic acids and inorganic salts impurities are determined by donor–acceptor properties of the organic solvent (specific solvation) and the dielectric capacity of the medium.

4. Conclusion

The regularities of the sorption and the elution of the monobasic aliphatic carboxylic acid (C_1 – C_7) anions by a solution containing 5×10^{-4} M KOH and 5×10^{-4} M $(C_4H_9)_4NOH$ in the chromatographic system containing anion exchanger KANK-Ast and cation exchanger KU-2-8 was studied.

The content (10^{-4} –10 g/l) of the aliphatic carboxylic acids (C_1 – C_7) and chlorides, nitrates and carbonates in 46 organic solvents of different classes (alcohols, ethers, ketones and others) graded as ‘analytically pure’ and ‘chemically pure’ is determined by an IC method with conductivity detection, after changing the organic matrix for an aqueous one. In all cases from eight to 10 samples from different manufactures were studied.

Data received allow to predict the total content of acids and inorganic salts impurities on the basis of the empirical polarity parameter (E_T) and dielectric capacity (ϵ) of organic solvents.

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