

Extractive freezing-out in the determination of organic compounds in aqueous media

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A method and mechanism of extractive freezing-out for the isolation of organic compounds from aqueous solutions are presented.

Extraction is the most commonly used method for the separation of organic substances from water.^{1,2} The principle of selective isolation from one phase into another is underlying in the extraction. In vapour phase extraction,³ the allocation of organic substances from water in the vapour of an added extractant takes place during the formation of a liquid–vapour interface directly in the test sample. The vapour phase extraction allows one to use hydrophilic organic liquids. Here, a method of extraction coupled with freezing-out is offered.^{4,5} The target components are allocated in previously added soluble or limitedly soluble organic liquid (acetonitrile, acetone, ethoxyethane, etc.) by crystallization of a water part of subsample. In this case, the repartition of the dissolved organic compounds between water and extractant also occurs under conditions of formation of an interface between a liquid phase of the added organic extractant and ice crystals.

It is known⁶ that, in the crystallization of water solutions, the dissolved substances concentrate in liquid microinclusions in the volume of a sample; the total amount depends on the composition and temperature of a test sample.

The test substances were aqueous solutions of one-basic carboxylic acids C₂–C₆. The partition coefficient in this homologous series is maximal for a hexanoic acid and even in the most successful water–extractant systems does not exceed 120.⁷

The research of the phase diagram of a multicomponent aqueous solution of a mix of the organic acids with a hydrophilic extractant is a difficult task. In this work, at an atmospheric pressure of 100.4±0.7 kPa, a test sample was cooled to –12±2 °C, which is characteristic of fridge-freezer of a household refrigerator. The speed of cooling did not exceed 0.04 K s^{–1}. It corresponds to equilibrium conditions of formation of a solid phase.⁶

Under these conditions, the mix of water with acetonitrile (freezing point of –45.7 °C) under cooling from +20 to –12 °C is flaked with formation of a layer of the added organic solvent

in the upper part of a test sample with postcrystallization of water in a range of water–acetonitrile ratios from 3.3 to 0.5 (by volume). In the field of the volumetric relations water–acetonitrile lower than 0.5, the water part of a sample does not crystallize, the sample remains liquid at cooling up to –12 °C. At a water–acetonitrile ratio more than 3.3 mixes freeze without allocation acetonitrile as a separate liquid phase on a surface of the solid test sample.

It was found that with increasing the acetonitrile portion, added in initial test sample, the weight (volume) of the extract, forming during the extractive freezing-out process, increases (Table 1). Besides on a background of this tendency it was wide spread of volume of the formed extract in parallel determinations. However, this fact practically had not an effect on the contents of acids in the extract. From the results presented in Table 1 it is also visible that the increase of volume of test sample, taken for extractive freezing-out, is accompanied by growth of concentration of acids in the forming extract.

Partition factors of acids between a crystal phase of ice and liquid acetonitrile extract cannot be determined, as it is impossible to determine precisely volume of the extract. The part of the extract can exist as microinclusions in the volume of ice crystals. At the same time, thermodynamically, it is more advantageous to allocate the dissolved substances outside of the crystal in comparison with inclusion them in a crystal lattice.⁶ It is possible to assume that the mechanism of a process combining extraction with freezing is similar to the phenomenon of adsorption. But in this case, the process goes in the reverse direction. During the cooling of the sample, the molecules of the dissolved acids are pushed out on a surface of forming ice crystals and desorbed in volume of an organic liquid phase. Hence, as a first approximation for the description of the extractive freezing-out phenomenon, it would be possible to apply the Langmuir model of located monomolecular adsorption on a homogeneous surface. The equilibrium constant of this phenomenon

$$\text{Molecule in the liquid phase} + \text{Free adsorption centre} = \text{Occupied adsorption centre}$$

is determined by the equation:

$$K_{\text{eq}} = c_{\text{org}} \frac{[\text{concentration of the free adsorption centres}]}{[\text{concentration of the occupied adsorption centres}]}, \quad (1)$$

where c_{org} is the concentration of the target component in the liquid phase, extract, $\mu\text{g cm}^{-3}$.

On the other hand, it is clear that, with increase of the volume of the liquid phase, i.e., with reduction of c_{org} , according

Table 1 The results of extractive freezing-out of C₂–C₆ acids from aqueous solutions into acetonitrile, pH 3–4.^a

Volume/cm ³		Mass of the extract/g	Concentration of organic acids in an extract/ $\mu\text{g cm}^{-3}$				
Test sample	Acetonitrile		C ₂	C ₃	C ₄	C ₅	C ₆
5	5	1.4±0.7	131±8	160±9	190±11	210±13	230±14
10	10	3.0±0.4	114±7	160±10	190±10	220±13	230±13
10	5	0.12±0.07	350±20	340±20	340±21	350±21	350±24
20	5	0.04±0.03	610±37	610±35	640±37	680±40	690±41

^aThe replicate analysis is 6. The concentration of organic acids in the initial aqueous solution was: acetic (C₂), 201; propionic (C₃), 196; butyric (C₄), 190; pentanoic (C₅), 193 and hexanoic (C₆), 192 $\mu\text{g cm}^{-3}$.

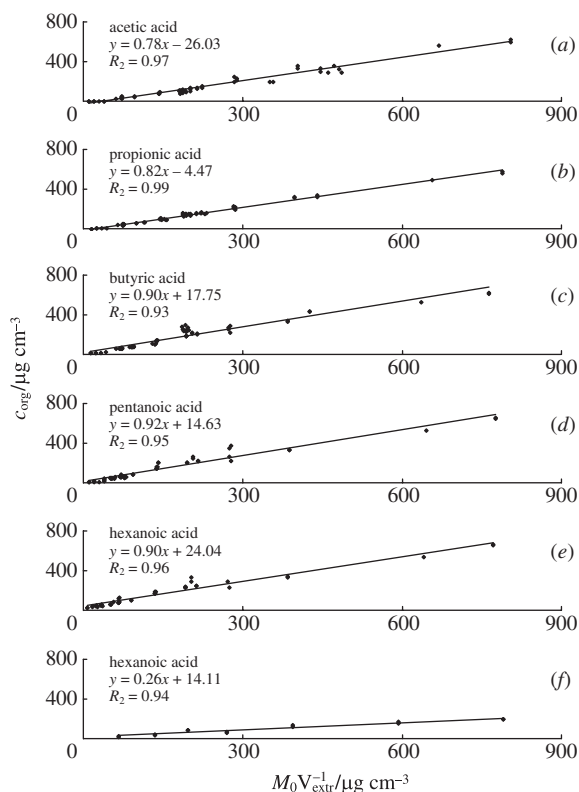


Figure 1 Dependence of concentration of the organic acid in the obtained extract on initial mass in test sample and volume of extractant, taken for extractive freezing-out: (a)–(e) acetonitrile and (f) hexane.

to (1) the number of acid molecules desorbing from a surface of the ice crystals should rise. It corresponds to an increase of the concentration of the free adsorption centres, *i.e.*, their concentration is proportional to the extractant volume taken for the extractive freezing-out:

$$[\text{concentration of the free adsorption centres}/\text{cm}^{-2}] = \alpha V_{\text{extr}} \quad (2)$$

where α is a coefficient of proportionality, cm^{-5} ; V_{extr} is the extractant volume, volume of the added acetonitrile, cm^3 .

Analogously, the concentration of the occupied adsorption centres increased proportionally to the total amount of the acid in a sample, *i.e.*, its initial quantity in the test sample $M_0/\mu\text{g}$:

$$[\text{concentration of the occupied adsorption centres}/\text{cm}^{-2}] = \beta M_0 \quad (3)$$

where β is a coefficient of proportionality, $\mu\text{g}^{-1} \text{cm}^{-2}$.

Taking into account (2) and (3), the equation for equilibrium constant K_{eq} (1) is

$$K_{\text{eq}} = c_{\text{org}} \alpha V_{\text{extr}} / \beta M_0 \quad (4)$$

or

$$c_{\text{org}} = \frac{\beta K_{\text{eq}}}{\alpha} \frac{M_0}{V_{\text{extr}}} \quad (5)$$

Therefore, if the offered model of the phenomenon of the extractive freezing-out of organic compounds from water is realized, a linear dependence of their concentration c_{org} in a formed extract on the quantity M_0/V_{extr} would be expected. The large file of the obtained experimental data on an example of the low-molecular acids C_2 – C_6 testifies for the benefit of it. As follows from Figure 1(a)–(e), such a linear dependence of the acid concentration in the acetonitrile extract from quantitative relation ‘initial quantity in test sample/volume of the added acetonitrile’ is established.

From the obtained results (Table 1), it follows that with increase of molecular weight of an acid the efficiency of the

Table 2 The results of extraction of C_2 – C_6 acids by hexane at combination with freezing from aqueous solutions, pH 3–4.^a

Test sample	Volume/ cm^3	Mass of the extract/g	Concentration of organic acids in an extract/ $\mu\text{g cm}^{-3}$				
			C_2	C_3	C_4	C_5	C_6
5	5	3.183±0.008	2.1±0.5	7±2	19±2	45±3	87±6
10	5	3.15±0.01	2.0±0.6	8±2	20±2	55±4	130±11
20	5	3.14±0.02	3.9±0.9	13±3	32±2	90±8	210±15

^aThe replicate analysis is 4. The concentration of organic acids in the initial aqueous solution was: acetic (C_2), 197; propionic (C_3), 201; butyric (C_4), 201; pentanoic (C_5), 195 and hexanoic (C_6), 197 $\mu\text{g cm}^{-3}$.

extraction rises, that is shown in increase of a corner of an inclination of the graph [Figure 1(a)–(e)]. It is explained by the common tendency of the increased hydrophobicity of acids in this homologous series. The same dependence of partition coefficient, and accordingly the efficiency of extraction, is known in traditional liquid extraction.

According to equation (5) at $M_0 = 0$, *i.e.*, absence of the acid in the initial test sample, its concentration in the extract $c_{\text{org}} = 0$. As follows from comparison of the graphs of c_{org} from M_0/V_{extr} in Figure 1(a)–(e) at $M_0 \rightarrow 0$ the character of this dependence for acetic acid differs from those, obtained for C_3 – C_6 . At approximation trend of its linear dependence assumes a point of intersection of the graph with an ordinate axis in a negative area. Angular factor $\beta K_{\text{eq}}/\alpha$ of its graph at aspiration $M_0 \rightarrow 0$, *i.e.*, at small acid concentration in initial test, sharply reduces. It was determined that in a range of concentration of acetic acid 0–10 $\mu\text{g cm}^{-3}$ angular factor of its linear approximation does not exceed 0.15. This does not take place in case of acids C_3 – C_6 , and their angular factors of the linear approximations in this area of concentration in an initial aqueous solution reduce only 2–2.5 times. This fact opens the possibility of the use of the considered method of extractive freezing-out for purifying C_3 – C_6 acids from acetic acid.

The efficiency of the extraction of organic acids from water under conditions of extraction in combination with freezing depends on nature of the extractant. Experimental data (Table 2) show that, if hexane was used as the extractant, at the repartition of organic acids between ice crystals and liquid hexane their concentration in the extract remains unchanged. In this case, the concentration of C_2 – C_6 acids in the obtained extract is lower than their initial concentration in water. At the same time, as the dependence of acid concentration in the hexane extract c_{org} on quantity M_0/V_{extr} , *e.g.*, for hexanoic acid [Figure 1(f)] is practically linear. It serves as an additional argument for the benefit of the above model of the mechanism of the extractive freezing-out.

Thus, the use of hydrophilic solvents in the extraction by freezing-out a water part of test sample after addition of the extractant is offered. The obtained results of C_2 – C_6 acids isolation allowed us to offer model of the mechanism of the phenomenon.

On the basis of this easy operating method the procedures for the analysis of drugs in biological liquids were developed.^{4,8} In comparison with other methods⁹ of the drug analysis, the developed method demands considerably smaller amount of chemicals. The realization of the extraction in a mode of negative temperatures also reduces volatility of used organic solvents.

In addition, compared with other known procedures,^{1,9} this method practically does not demand any chemical ware (*e.g.*, support, funnels, *etc.*) and specified expendables (sorbents for an extraction, filters, *etc.*).

References

- 1 D. E. Raynie, *Anal. Chem.*, 2006, 3997.
- 2 D. Harvey, *Modern Analytical Chemistry*, McGraw-Hill Higher Education, USA, 2000.

- 3 V. N. Bekhterev and E. A. Kabina, *Mendeleev Commun.*, 2007, **17**, 45.
- 4 V. N. Bekhterev, *Book of Abstracts of the International Congress on Analytical Sciences, ICAS-2006*, Moscow, vol. 2, p. 592.
- 5 V. N. Bekhterev, *Patent Application on Invention*, 2005112810/15(014779), 27.04.2005 (in Russian).
- 6 G. B. Sergeev and V. A. Batyuk, *Kriokhimiya (Cryochemistry)*, Khimiya, Moscow, 1978, p. 178 (in Russian).
- 7 Ya. I. Korenman, *Koeffitsienty raspredeleniya organicheskikh soedinenii. Spravochnik (Partition Coefficients of Organic Compounds. Handbook)*, VGU, Voronezh, 1992 (in Russian).
- 8 V. N. Bekhterev, S. N. Gavrilova and I. V. Maslakov, *Sudebno-Meditsinskaya Ekspertiza*, 2007, no. 2, 32 (in Russian).
- 9 S. K. Eremin, B. N. Izotov and N. V. Veselovskaya, *Analiz narkoticheskikh sredstv. Rukovodstvo po khimiko-toksikologicheskomu analizu narkoticheskikh i drugikh odurmanivayushchikh sredstv (Analysis of Drugs. Manual for Chemical-Toxicological Analysis of Narcotic and Dopy Compounds)*, Mysl, Moscow, 1993 (in Russian).

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