

FEATURES OF THE EXTRACTION OF ESSENTIAL OILS FROM PLANT RAW MATERIAL IN THE PRESENCE OF SURFACE-ACTIVE AGENTS

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It has been established that the influence of surface-active agents (SAAs) on the extraction of essential oils (EOs) is connected with a fall in the surface tension of water, which facilitates the process of steeping, wetting, and swelling of plant raw material and also the solubilization of the EOs in micellar solutions of SAAs.

The main method of isolating essential oils (EOs) from plant raw materials is steam distillation. In view of this, it is necessary to develop scientific principles of regulation of the processes at the phase-separation boundaries of dispersions of medicinal plants and solvents. Nontraditional methods based on the use of liquefied gases [1, 2], wide-range frequency vibrations, electric and magnetic fields, impulses, etc. [3, 4] are being used to solve this problem. In the present paper we give results on the possibility regulating the properties of the surface of a dispersion of plant origin and the structure of a solvent (water) with the aid of additions of surface-active agents (SAAs) in order to intensify the extraction of EOs.

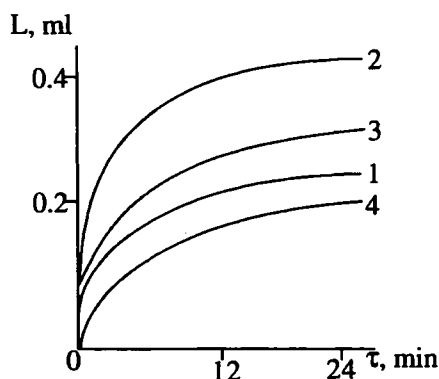


Fig. 1. Dependence of the depth of dispersion of *Origanum tyttanthum* on the time of steeping: 1) 0.05% of alkylarylsulfonate (AAS); 2) 0.1% of AAS; 3) 0.2% of AAS; 4) water.

Figure 1 shows the time dependence of the depth of penetration (L) of a powder of the raw material *O. tyttanthum* with solutions of an SAA. For each concentration of the SAA we used separate samples of one and the same batch of raw material. The value of L was obtained from the equation:

$$L = \frac{\Delta X_0 D^2}{D_0^2} n,$$

where ΔX is the displacement of the meniscus in a calibrated capillary; D is the diameter of the calibrated capillary (1.18–2.28 mm); $D_0 = 37$ mm is the diameter of the tube into which the sample powder was charged; and n is the porosity of the raw material.

It can be seen that with a rise in the concentration of the SAA the depth of penetration of the raw material increased.

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When 0.2% solutions of the SAA were used the rate of capillary penetration of the plant raw material doubled, as compared with water. A further increase in the concentration of the SAA did not appreciably affect the depth of penetration.

The swelling of the raw material takes place simultaneously with the penetration of the extractant. The rate of swelling is determined by the rate of absorption of the extractant.

To determine the absorbability of an SAA, raw materials with different degrees of grinding (0.1—0.2 mm) were wetted in the SAA solutions and were steeped from 10 to 80 min. The increase in weight was determined after drying with filter paper. The absorption coefficient was determined from the ratio of the weights of the raw material before and after swelling.

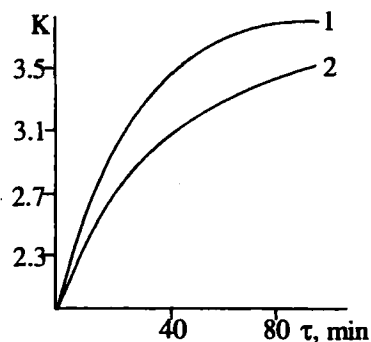


Fig. 2. Time dependence of the absorption coefficient of the raw material *Ziziphora pedicellata*: 1) AAS; 2) water.

Figure 2 shows the dependence of the absorption coefficient on the time (τ). The extractant was absorbed most rapidly during the first hour, when the wetting of the ground raw material took place. The time of absorption in a solution of an alkylarylsulfonate (AAS) was half that for water.

An important characteristic of the swelling process is contraction — a decrease in the total volume of the system. The kinetics of the swelling of plant raw material in water and in aqueous SAA solutions has been studied by measuring the contraction at various moments.

The dependence of contraction (ΔV_t) on the time (τ) in aqueous solutions of a SAA and in water is shown in Fig. 3, a. It has the form that is characteristic for limited swelling. The swellability of the raw material in aqueous solutions of a SAA was greater than in water. The experimental results are described by the following equation:

$$\Delta V_t = \frac{\Delta V_e K t}{1 + K t}$$

From a graph in reciprocal coordinates we calculated the change in volume at the equilibrium state (ΔV_e) and the equilibrium constant (K). Fig. 3, b, shows the relationship plotted in the coordinates $1/\Delta V_t - 1/t$. It has a linear nature. The parameter K , calculated from the tangent of the angle of slope of the straight lines is $4.10 \cdot 10^{-3} \text{ min}^{-1}$ for water and 15.0 for the AAS solution. Consequently, a correlation exists between the coefficient of equilibrium swelling of the plant raw material and the efficacy of the SAA.

The degree of swelling (α_t) of the raw material was determined by measuring the final weight of the swollen raw material after the cessation of contraction. For the systems with water and with aqueous AAS solutions it was 1.20 and 1.60, respectively. The value of α_t was calculated from the equation:

$$\frac{\alpha_t}{\alpha_e} = \frac{\Delta V_e}{\Delta V_t}$$

where α_t and α_e are the degrees of swelling at the given time and at equilibrium, respectively, and ΔV_t and ΔV_e are the changes in volume at the given time and at equilibrium, respectively. The results of the calculation are given in Table 1. As follows from this table, the SAA solutions had a favorable influence on the swelling of the plant raw material, and from the equilibrium swelling constants it is possible to predict the efficiency of the extraction of an EO.

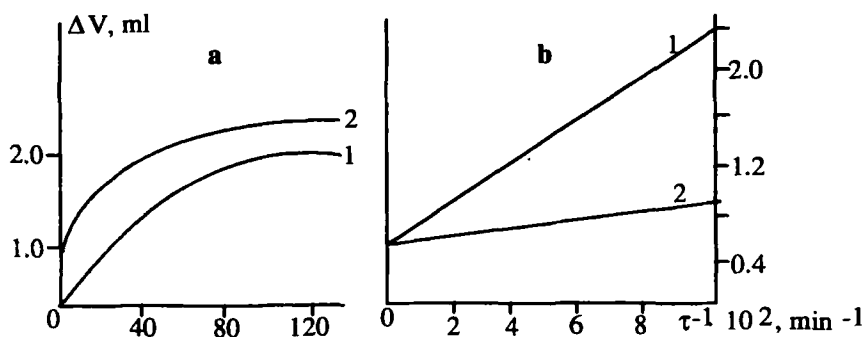


Fig. 3. Change in the volume of the system with time in the swelling of a dispersion of *O. tyttanthum* in direct (a) and reciprocal (b) coordinates: 1) in water; 2) in AAS solution.

TABLE 1. Change in Volume (ΔV_t , ml) and in the Degree of Swelling (α_t , %) of a Powder of *O. tyttanthum* in Water and in Aqueous SAA Solutions ($\tau = 1$ h; $T = 301K$)

Time, min	Water		SAA	
	V_t , ml	α_t	V_t , ml	α_t
10	0.36	0.23	1.12	0.78
30	0.90	0.58	1.72	1.20
50	1.34	0.86	2.00	1.40
80	1.76	1.13	2.20	1.54
120	1.84	1.18	2.25	1.57
At equilibrium	1.86	1.20	2.28	1.60

We measured the heat of wetting of the *Origanum* raw material with water. The total heat effect amounted to 3.04 J/g. It was found that with a rise in the concentration of the SAA up to the critical micelle concentration (CMC) the heat of wetting and the heat effect of swelling decreased. The heat effect of swelling in water amounted to 4.50—3.25 J/g, and in a micellar solution of AAS to 0.35—4.50 J/g.

The efficacy of the extraction of EOs depends substantially on the concentration of the SAA solution. The yields of EOs from the *Ziziphora* and the *Origanum* without the use of a SAA were 78.4 and 77%, respectively, and in the presence of a 0.2% aqueous solution of the AAS they increased by 25—30% and for both plants amounted to 98% of the total amount of EOs present.

It is interesting to note that in the EO extraction process SAAs have the most favorable influence at the critical micelle concentration, when the depth of penetration, the degree of swelling, and the swelling constant have their maximum values.

In order to determine the influence of SAAs on the time of the extraction process, we performed a series of experiments in which the yields of EOs were determined every 20 min. The results show that the time of the extraction process is almost halved in the presence of a SAA (Fig. 4).

The influence of SAAs on the quality and the component composition of the EOs was determined. The results of analysis of EOs according to GF-XI [State Pharmacopeia, XIth edn.] showed that the constants characterizing such qualitative indices as the density, refractive index, and acid and ester Nos., and also the composition of EOs obtained by steam distillation and in the presence of an SAA agreed. The EO of the *Ziziphora pedicellata*: d_{20}^{20} 0.9882; n_D^{20} 1.4856; acid No. 4.62; ester No. 13.54. The EO of the *Origanum tyttanthum*: d_{20}^{20} 0.9492; n_D^{20} 1.5015; acid No. 2.40; ester No. 18.60.

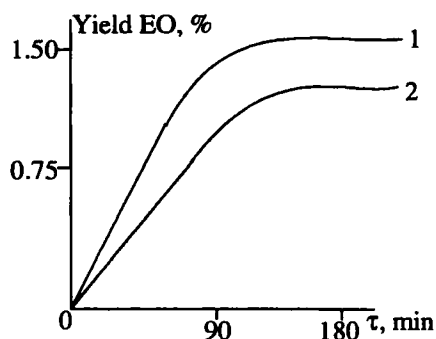


Fig. 4. Dependence of the yield of essential oils (100 g of raw material) on the time of distillation: 1) in the presence of a SAA; 2) with water.

The volume fractions of aldehydes, ketones, and phenols in the EOs of the *Origanum tyttanthum* and the *Ziziphora pedicellata* obtained by the two methods were determined by a standard method [8], and their compositions were found to be identical [9], as was confirmed by the GLC of the *Ziziphora* EO (pulegone — 52%; menthone — 22.4%; menthol — 9.6%; thymol — 10.2%, and of the *Origanum* EO (carvacrol — 49.5%; thymol — 16.3%, η -cymene — 4.8%).

Thus, it can be stated that the use of SAAs in the extraction process raises the yield of essential oils without affecting their qualitative and quantitative compositions.

EXPERIMENTAL

The EOs were extracted from the epigeal parts of *Ziziphora pedicellata* and *Origanum tyttanthum* gathered in the Bostanlykskii region. The particle size of the raw material was 1.0–0.2 mm. Alkylarylsulfonates were used as the SAAs.

In the study of the kinetics of swelling, the vessel of the apparatus [9] was charged with 1.0 g of raw material, and then water or a SAA solution was added from the top.

To determine the compositions of the EOs we used the GLC method (Chrom-5 chromatograph, flame-ionization detector), evaporator temperature 250°C, temperature of the column thermostat 36–100°C with programming of the temperature at 4°C/min. Rate of flow of the carrier gas (nitrogen or helium) 30 ml/min; rate of flow of air 300 ml/min. Column, 3 × 1300 mm, with 1% of Chromosorb OV-17 on Chromaton. The heat of wetting of the raw material in the SAA solutions was determined with a microcalorimeter of the Schottky type at a temperature of 285±1 K [5].

The influence of additions of SAAs on the rate of absorption by the plant material was studied by the method of Lishtvan et al. [6], and the kinetics of swelling according to [7].

The extraction of the EOs from the plant material was conducted in a round-bottomed flask fitted with a reflux condenser and a Ginzburg device. The experiments were conducted in five repetitions and the mean value of the yield of EO was obtained.

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