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Extraction of Vanillin by Aliphatic Alcohols

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Vanillin extraction from alkaline solutions by means of higher-homologues alcohols was studied. Effects of pH as well as vanillin concentration and ion strength on vanillin–aqua–alcohol equilibrium were studied. The data on distribution ratios (D) of vanillin were obtained. The values of distribution ratios at technological pH (about 9–10) are shown to be equal to 1 – 10, that approaches for multistage reverse-flow extraction. If pH values is 11–14 then the distribution ratios values less then 0.2, that makes easy the vanillin stripping process to aqueous phase.

Keywords: vanillin, lignosulfonates, lignin, extraction, aliphatic C₆–C₈ alcohols, stripping vanillin, bisulfitation.

Vanillin is one of the most valuable products obtained from waste materials of chemical processing of wood. A very important stage in vanillin production is the product extraction from the reaction solutions that contain about 10 g/l of vanillin and an order of magnitude greater amount of organic byproducts.

In laboratory practice a sequence of extraction – distillation of solvent is commonly used for recovering organic compounds, but in industry a technology of extraction – stripping is more desirable. An overview of possible methods of vanillin extraction and of corresponding extractants has been published in [1–3]. Table 1 summarizes the data on different methods of vanillin extraction.

Despite the large number of works devoted to the problem of vanillin extraction, all of them have serious disadvantages: low selectivity or

efficiency of extraction (high content of tar and low distribution ratio respectively) by simple and affordable extractants like esters or paraffin hydrocarbons; complicated or even impossible vanillin stripping or extractant recovery (alkylamines); extractant toxicity (benzene), solubility of extractants in water (butanol, butyl acetate, benzene). A serious obstacle to the choice of an extractant can be its price, as vanillin is not a very expensive product (about 10 USD/kg).

Two principal ways of vanillin stripping are known: by sodium bisulphite or by alkaline solutions. The former method yields high selectivity, as extractant reacts with vanillin's carbonyl group. The formation constant of the sodium bisulphite derivative of benzaldehyde is quite high ($K = 6.4 \cdot 10^3$ at 21°C and pH 3.5 – 6.8 [8]), but for vanillin this constant is much less, K

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Table 1. Characteristics of methods of vanillin extraction

Extractant	D	Advantages	Disadvantages	Reference
Benzene	6.3	Industrially used	Toxicity of extractant, phase – separation difficulties	4
Toluene	4.1	Moderate toxicity	Low D	4
Hexane	0.2	High extraction selectivity	Very low D	4
Chloroform	26.5	High D value, quick phase separation	Low extraction selectivity	4
Butyl acetate	28.2	High D value	Low extraction selectivity, stripping difficulties	5
Butanol	27	High D value	Solubility of extractant in water	6
Octanol	20.5	High D value	Low extraction selectivity, stripping difficulties	4
Octylamine	Up to 600	High extraction selectivity and distribution ratio	Stripping difficulties	2
Tetraalkyl-ammonium chloride	50 – 100	Possibility of extraction from alkaline media	Difficulties with extractant recovery	6, 7

≈ 350 [9,10]. According to reported data [11,12] for vanillin stripping in the form of sodium bisulphite derivative from industrial extracts, a triple treatment with sodium bisulphite solution is used; thus the bisulphite derivative of vanillin is not sufficiently stable to carry out one-stage stripping.

For most solvents used for extraction, stripping with alkaline solutions allows very high distribution into the water phase, thus concentrating vanillin on stripping. This is due to the fact that, except for alcohols and alkylamines, hydrophilic vanillate-ion only slightly distributes into the organic phase. Esters are unstable in aqueous alkaline media, and so they unsuitable for such stripping processes. Thus, for creating an effective extraction–stripping process, aliphatic alcohols as extractant and aqueous alkaline solutions for stripping is a prospective combination. Data for vanillin stripping from aliphatic alcohol solutions lack, and in the case of butanol are ineffective, as the sodium vanillate distribution ratio in the system butanol – water is close to unity ($D = 0.7 – 0.8$) [6].

The goal of the present work is to study vanillin extraction with the aliphatic $C_6 – C_8$ alcohols for a conceptual vanillin separation process.

Experimental

Extractants were purified according to commonly used methods.

The batch of vanillin was dissolved in water in a 100 ml volumetric flask and the calculated amounts of sodium sulphate, hydrochloric acid or sodium hydroxide were added to provide required pH values and ionic strength.

Aqueous phase (2 ml) and extractant were put into a glass tube, which was then shaken for 300 – 450 seconds. Phases were separated by centrifugation. The total time of phase contact is 1200-1500 seconds. Preliminary experiments had shown that extraction equilibrium is attained after 250 – 300 s. Then a sample of 1.0 ml was removed from each phase and diluted to 10.0 ml by solution of neutralizing agent in aqueous ethanol. The concentration of vanillin in resulting solution was determined by the spectrophotometric method.

Results and discussion

Fig. 1 shows the dependency of observed vanillin distribution ratio versus the pH of the aqueous phase in the water – alcohol system.

Distribution ratios obtained at $\text{pH} < 7$ (30.5 for hexan-1-ol, 24.6 for heptan-1-ol and 20.3 for octan-1-ol) coincide with known data (Table 2).

Distribution ratios in the pH range 11-14 (0.21 ± 0.02 for hexan-1-ol, 0.18 ± 0.02 for heptan-1-ol, 0.15 ± 0.03 for octan-1-ol) characterize the efficiency of vanillate-anion extraction. Residual concentrations of molecular vanillin in the aqueous phase at pH 11 and above are less than 10^{-5} M in correspondence with the acid dissociation constant of vanillin ($\text{pK} 7.2$ [13]), thus they can't explain the observed vanillin concentration in the organic phase in alkaline media.

In an extraction – stripping process, the possibility of concentrating the product is determined by the change of distribution ratios in going from acid to alkaline media (table 2). Except

for hydrophilic butanol, for higher alcohols, these values are close to each other and range from 135 to 145. An order-of-magnitude greater values of this ratio are obtained for octane-1-ol solutions in heptane (Table 2). These data indicate high efficiency of vanillin extraction (from acid media) and stripping (into alkaline media) with higher alcohols and their solutions.

In pH range close to the pK of vanillin, the observed distribution ratio decreases with increasing pH, from values equal to the distribution ratio of molecular vanillin to distribution ratio of vanillate-ion. Reaction solutions of vanillin production have a pH of about 9, at which the apparent vanillin distribution ratio values are 5, 3 and 1.5 for hexan-1-ol, heptan-1-ol and octan-1-ol, respectively. These values are close to the vanillin distribution ratio in the water – benzene system in acid media ($D = 6.3$ [4]). That is, $\text{C}_6 - \text{C}_8$ alcohols can be used to extract vanillin from reaction solutions without acidification with expenses similar to that in the technology

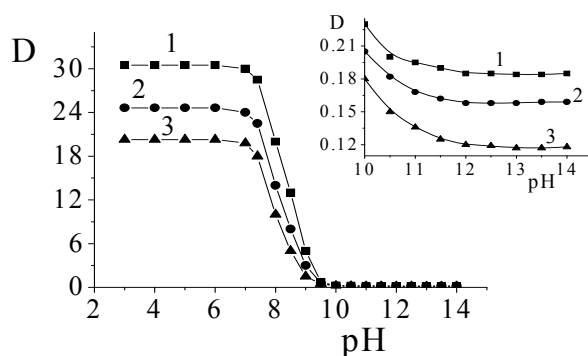


Fig. 1. Dependency of vanillin distribution ratio D versus pH . Extractant: 1 – hexan-1-ol, 2 – heptan-1-ol, 3 – octan-1-ol (initial vanillin concentration in aqueous phase 0.01 mol/l , ionic force 0.1 mol/l)

Table 2. Influence of alcohol's nature and concentration on vanillin distribution ratios from acid and alkaline media [4]

Extractant	Butan-1-ol	Hexan-1-ol	Heptan-1-ol	Octan-1-ol
$D(\text{pH } 1 - 4)$	27	30.5	24.6	20.3
$D(\text{pH } 11 - 14)$	0.75	0.21	0.18	0.15
$D(\text{pH } 1 - 4) / D(\text{pH } 11 - 14)$	36	145	136	135

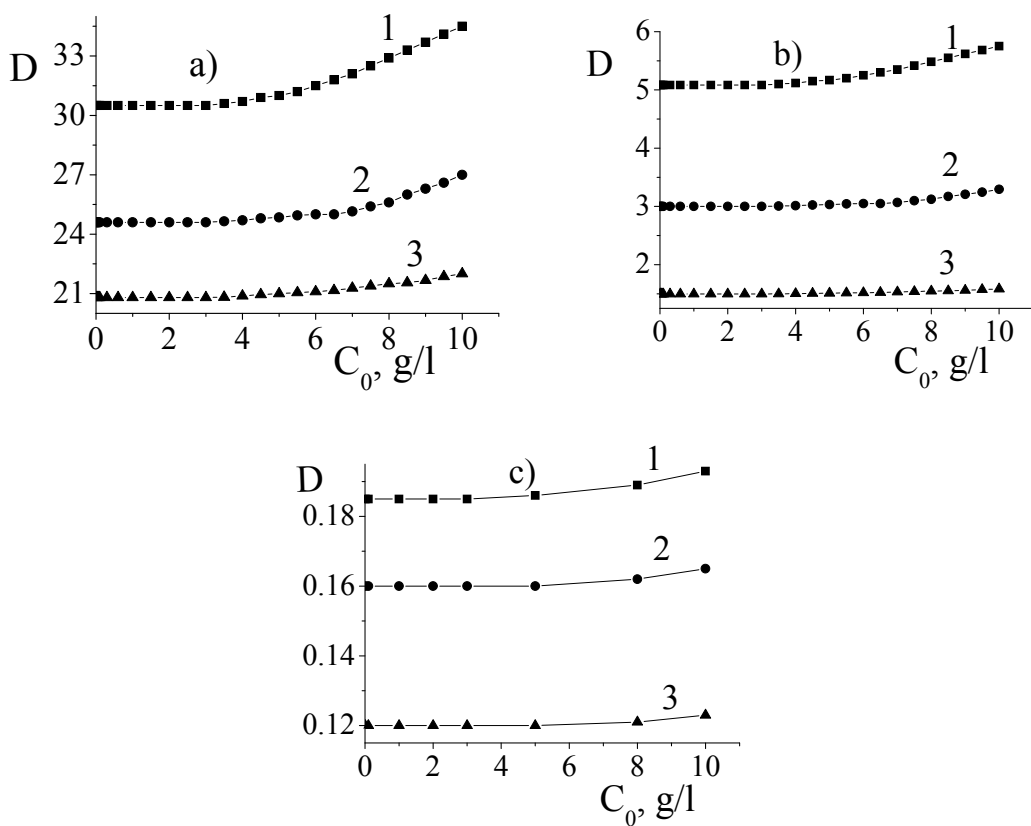


Fig. 2. Dependency of distribution ratio D versus initial vanillin concentration in aqueous phase, a) pH 5, b) pH 9, c) pH 11. Extractant: 1 – hexan-1-ol, 2 – heptan-1-ol, 3 – octan-1-ol

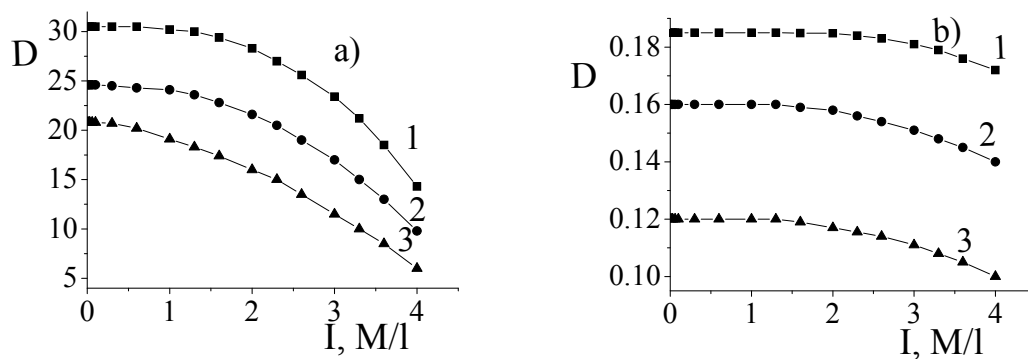


Fig. 3. Dependency of vanillin distribution ratio D versus ionic force in aqueous phase, a) pH 6, b) pH 12. Extractant: 1 – hexan-1-ol, 2 – heptan-1-ol, 3 – octan-1-ol

of vanillin extraction by benzene from acidified liquors.

Observed vanillin distribution ratios increase slightly (by 10–20 %) within the studied pH range with increase of initial vanillin concentration from $6.5 \cdot 10^{-5}$ to $6.5 \cdot 10^{-2}$ mol/l (Fig. 2). This is probably due to vanillin's association in organic phase and formation of extraction complexes containing several molecules of vanillin.

Increase of ionic force in aqueous phase leads to decrease of vanillin distribution ratios 2 to 4 fold (Fig. 3). Such effects were not previously described in literature and they can describe low observed distribution ratios in industrial reaction solutions in which concentration of sodium sulphate can exceed 1 mol/l [8]. Ionic force value doesn't have a strong effect on vanillate-ion distribution in alkaline media (Fig. 3b)

The results obtained indicate that aliphatic alcohols $C_6 - C_8$ have substantial advantages over benzene, butanol and many other vanillin extractants. Unlike benzene, these alcohols can be used to extract vanillin from weakly alkaline media, that is, from industrial reaction solutions of lignin oxidation without their acidification. This eliminates the serious technological problems related to lignoacids precipitation that follows the solution acidification (emulsifying the extraction system and vanillin sorption by the tar phase). In comparison to butanol the studied alcohols are practically insoluble in water and are characterized by 4–5 times weaker distribution ratio of vanillate-ion, which allows to effective stripping of vanillin from alcohol extracts into aqueous alkaline solutions.

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Экстракция ванилина алифатическими спиртами

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Исследованы экстракционные равновесия в системе вода – высший алифатический спирт – ванилин в зависимости от рН среды, ионной силы и начальной концентрации ванилина в растворах. Определены коэффициенты распределения ванилина. Показано, что значения коэффициентов распределения ванилина (рН 9-10) между водой и спиртами изменяются в пределах 1-10, что позволяет применять их для многоступенчатой противоточной экстракции в промышленности. При значениях рН 11-14 коэффициенты распределения составляют 0.1-0.2, что позволяет реэкстрагировать ванилин водно-щелочным раствором.

Ключевые слова: ванилин, лигносульфонаты, лигнин, экстракция, алифатические C₆-C₈ спирты, реэкстракция, бисульфитирование.
