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THE EFFECTIVE APPROACH FOR RECOVERY OF METHYL-SUBSTITUTED 1,3-DIOXANE FROM AQUEOUS MEDIA

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ABSTRACT

The solvent extraction has been successfully applied to the recovery of methyl-substituted 1,3-dioxane from the aqueous reaction media. Aromatic hydrocarbons used as extractants allowed the removal, from the aqueous phase, of up to 75% of dioxane formed in the one stage reactor–extractor. The concept could be included in a downstream separation scheme for the isolation of 1,3-propanediol from a dilute aqueous solution using reversible reaction of the diol with acetalaldehyde.

INTRODUCTION

Acetals can be obtained mainly in the acid-catalyzed reaction of an aldehyde with an alcohol. They are frequently used in preparative chemistry to protect aldehyde function, in polymer chemistry (1–3), in the synthesis of pharmaceuticals

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(4). Substituted 1,3-dioxanes, cyclic acetals, are intermediates in the synthesis of conjugated dienes, isoprene being the most important example (5).

Most recently, the application of a cyclic acetalization reaction as a part of the downstream separation of trimethylene glycol (1,3-propanediol) from the aqueous solution has been proposed (6). The reversible reaction of 1,3-propanediol with acetaldehyde leads to 2-methyl-1,3-dioxane that has to be separated from the reaction media. 1,3-propanediol finds applications in the synthesis of heterocycles and polyesters. This diol has recently received considerable attention due to the possibility of its production by a biological route from glycerol and/or glucose (7,8), and the commercialization of poly(propylene terephthalate), 1,3-propanediol-based polyesters (9,10). However, the product made by biotechnology, usually appears in a dilute and complex aqueous media, making its recovery and purification costly. Attempts to identify a biocompatible extractant suitable for in situ separation of 1,3-propanediol from the fermentation broth proved unsuccessful (11). On the whole, the conversion of 1,3-propanediol to 2-methyl-1,3-dioxane seems to be a promising way to make the separation of the diol more effective.

In this article, the application of solvent extraction for the recovery of 2-methyl-1,3-dioxane from the aqueous solution is discussed. The problem is closely related but not restricted solely to the downstream separation of 1,3-propanediol from the fermentation broths. The same approach can also be applied to the separation of other acetals.

MATERIALS AND METHODS

Materials

Acetaldehyde (99%), 1,3-propanediol (98%), ethyl benzene (99%), *o*-xylene (97%), toluene (99.5% +), and Dowex, 50-WX4-200 ion-exchange resin were obtained from Aldrich (Sigma-Aldrich Sp. z o.o., Poznań, Poland). Amberlite IR-120 (H^+), a strongly acidic cation-exchange resin was provided by Fluka (Sigma-Aldrich Sp. z o.o., Poznań, Poland).

Solvent Selection

Potential extractants were screened using a computer program based on the UNIFAC group contribution method to calculate multicomponent liquid–liquid equilibria (12). This program has been found to be a useful tool for preliminary selection of solvents for liquid extraction in different applications, including extractive fermentation (11,13–15). The ranking focused on the mass

distribution coefficient, which is crucial for the development for any liquid extraction process. The solvent's toxicity also requires special attention, if it is applied for in situ bioseparation process. The estimation of the solvent biocompatibility can be made using another parameter like log P value, where P is the partition coefficient of a given compound in the standard octanol–water system (16).

The solvents search strategy, using predictions from the UNIFAC, is widely accepted (17–19) and experimental work is focused on the solvents with the most promising properties as extractants.

Extraction of Dioxane

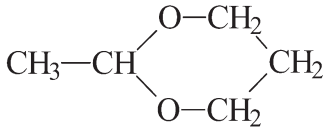
Equal volumes (50 mL) of a reaction mixture containing an aqueous solution of 1,3-propanediol and acetaldehyde together with a cation-exchange resin as a catalyst, and an appropriate organic extractant were stirred vigorously in the one-step glass reactor–extractor. The initial concentrations of reagents were as follows: 1,3-propanediol—39.95 or 59.60 g/L, acetaldehyde—235 or 352 g/L, and catalyst—20, 50 or 100 g/L. The lower concentration of 1,3-propanediol was chosen to represent a typical composition of the fermentation broth from the bioconversion of glycerol (20).

Analysis of 2-methyl-1,3-dioxane in both, aqueous and organic phases, were performed on a HP 5890 gas chromatograph equipped with TCD detector and a 30-m HP-1 column (0.53 mm diameter, 0.88 μm film thickness) (Hewlett-Packard, USA) using helium as a carrier gas. The injector and detector were set at 250 and 300° C, respectively. The oven temperature was programmed from 70 to 200°C.

RESULTS AND DISCUSSION

Procedure of Solvent Selection

The structural formula of 2-methyl-1,3-dioxane is given below:



It can be seen that 2-methyl-1,3-dioxane molecule can be "broken down" in two different ways into UNIFAC functional groups. Two possible UNIFAC group

assignments for this compound are:

Type 1 : $1 \times CH_3$; $1 \times CH_2$; $1 \times CH$; $2 \times CH{-}O$,

Type 2 : $1 \times CH_3$; $2 \times CH_2$; $1 \times CH{-}O$; $1 \times CH_2O$.

The initial screening of extractants has been performed using these two sets of functional groups. As expected, the predicted values of mass distribution ratio were quantitatively different in the two printouts generated by the UNIFAC-based computer program. However, the printouts still suggested more or less the same extractants in much the same order. It is not surprising since any group contribution method is approximate.

Table 1 lists the top ranked extractants as selected by the UNIFAC-based program. Taking into account the chemical functionality, esters and chlorinated hydrocarbons have been excluded. The former compounds are unstable under acidic conditions existing in the reactor where the extraction of dioxane has to be made and

Table 1. List of Top Ranked Extractants Based on Predicted Mass Partition Coefficient D_{mass}

Extractant	D_{mass}	r_{sol}
Ethane,1,1,2,2-tetrachloro	493.4209	0.000087
Ethene, tetrachloro	467.7274	0.000224
Butane,1,1,2,2,3,4,4-heptachloro	206.2686	4.20×10^{-7}
Acetic acid, ethenyl ester	193.319	0.003432
2-Butene,1,1,2,3,4,4-hexachloro	152.538	0.000038
Acetic acid, benzyl ester	106.287	0.00009
Acetic acid,2-propenyl ester	98.47053	0.000819
Benzene, chloro	74.48469	0.000102
Ethane,1,1,1,2-tetrachloro	69.68855	0.000139
Benzaldehyde	68.73491	0.001182
Toluene	60.73829	5.40×10^{-4}
Acetic acid, chloromethyl ester	56.77687	0.007784
Acetaldehyde,diacetate	54.95015	0.002304
Diphenylacetaldehyde	52.33553	0.000002
Benzene, bromo	52.1105	0.000614
Triacetin	51.81328	0.000337
Aniline, *n*-methyl	50.44604	0.000445
Acetic acid, phenyl, ethyl ester	48.85482	0.000011
Benzene,1,2-dimethyl (*o*-xylene)	47.16833	0.000054

D_{mass}—predicted mass partition coefficient.
r_{sol}—predicted aqueous solubility (wt.%).

the latter ones are known environment pollutants. After detailed analysis of the ranking, aromatic hydrocarbons, toluene, *o*-xylene, and ethyl benzene were selected for experimental verification in the 2-methyl-1,3-dioxane recovery process. The predicted mass distribution ratio for toluene, *o*-xylene, and ethyl benzene were 61, 47, and 19, respectively. They have low water solubility and are inert, hence, do not hamper the acetalization reaction course. Moreover, predicted mass distribution ratios for 1,3-propanediol were in the range of 0.001–0.003 while for acetaldehyde 0.49, 0.29, and 0.88 for toluene, *o*-xylene, and ethyl benzene, respectively. These properties allow as many reagents, i.e., acetaldehyde and 1,3-propanediol, as possible in the aqueous reaction phase. However, as the UNIFAC model prediction provides only an approximation of the real properties, one cannot rule out that there are superior solvents for 2-methyl-1,3-dioxane extraction that were not identified in the screening procedure.

In Situ Extraction of 2-Methyl-1,3-Dioxane

A series of experiments of the cyclic acetalization of 1,3-propanediol reaction with the simultaneous extraction of dioxane have been performed. The process was carried out at different temperatures using different initial substrate concentrations and the catalyst load. The preliminary data on the kinetics of the reaction have been presented elsewhere (6).

As could be expected, the improvement in the conversion of glycol was observed. In all the cases, conversion was as high as 98–99% while it never exceeded 95% in the runs without the extraction of dioxane. This is attributed to the shift of the reaction equilibrium due to the in situ product removal from the aqueous phase.

In Figs. 1–3, the time evolution of the distribution ratio D during the reaction–extraction process is presented. It may be seen that the distribution ratio for the investigated extractants reached values in the range of 2.5–3.3. Closer inspection of the data revealed that the slopes of the initial fragments of curves in Fig. 1 are higher than those presented in Figs. 2 and 3. It reflects the difference in the reaction rates offered by two different ion-exchange resins with that offered by Dowex resin (Fig. 1) being higher than that by Amberlite. The results also demonstrate that toluene shows the best extraction potential among the solvents tested in good agreement with the prediction by the UNIFAC method. However, the extraction behavior of all solvents is quite similar. Extraction efficiency, calculated as a ratio of the mass of dioxane recovered by the organic solvent to the total mass of dioxane formed, was in the range of 71–75%, depending on the process conditions. Apparently, the contact of aqueous and organic phases in the countercurrent arrangement composed of a series of the mixers–settlers will lead to the better recovery than that achieved in the one stage reactor–extractor.

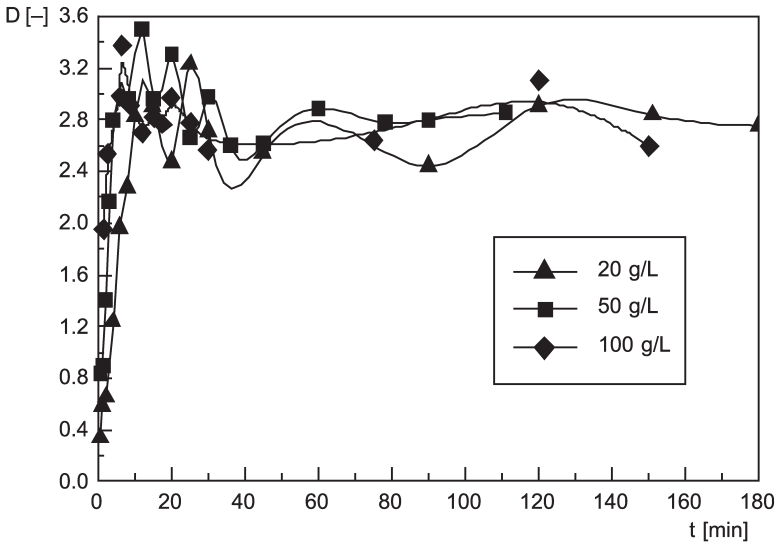


Figure 1. Effect of catalyst loading on the in situ extraction of 2-methyl-1,3-dioxane from the reaction media by *o*-xylene. Conditions: catalyst—Dowex, $T = 40$°C, initial 1,3-propanediol concentration—59.6 g/L.

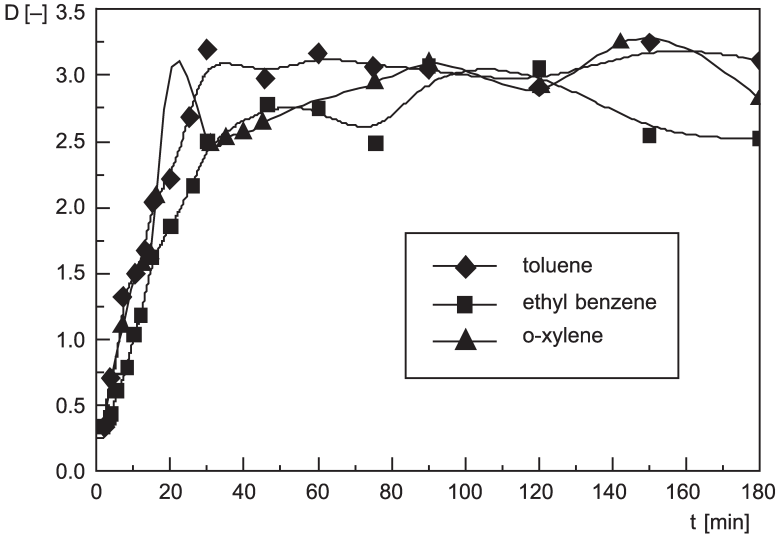


Figure 2. Time plots of distribution ratio of 2-methyl-1,3-dioxane in the reaction–extraction process using different extractants. Conditions: catalyst is Amberlite—20 g/L, $T = 40$°C, initial 1,3-propanediol concentration—59.6 g/L.

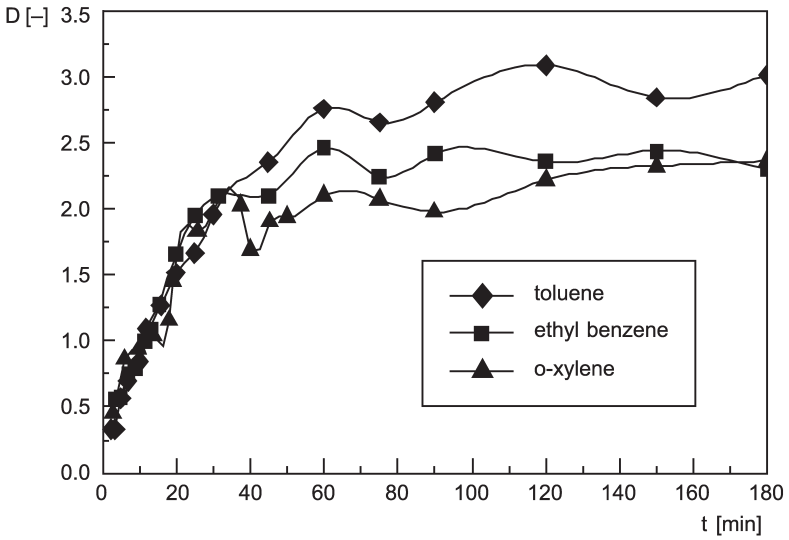


Figure 3. Time plots of distribution ratio of 2-methyl-1,3-dioxane in the reaction–extraction process using different extractants. Conditions: catalyst is Amberlite—20 g/L, $T = 31$°C, initial 1,3-propanediol concentration—39.95 g/L.

Finally, an evaporation process should be used to strip dioxane out of the organic phase. Toulene, despite the best extraction performance, has the boiling point (110.6°C) too close to that of 2-methyl-1,3-dioxane (111°C), thus the choice of a higher boiling extractant, *o*-xylene or ethyl benzene would be advantageous.

CONCLUDING REMARKS

The solvent extraction proved to be the effective method for the separation of 2-methyl-1,3-dioxane from the aqueous solution. The aromatic hydrocarbons selected based on the UNIFAC method predictions are well suited as extractants of dioxane. The application of this approach allowed the in situ recovery from the reaction mixture of about 75% of dioxane formed during the acetalization of acetaldehyde with 1,3-propanediol. As this reaction is reversible, it is possible to hydrolyze the dioxane separated from the organic solvent to 1,3-propanediol, and to apply this procedure to recover this hydrophilic diol from the fermentation broth. It seems that the proposed treatment of spent fermentation broth is technically feasible and more attractive in terms of energy input requirements than a direct evaporation of the diol. The concept presented can also be extended to the separation of other dioxanes.

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