Korean J. Chem. Eng., **24**(2), 282-287 (2007)

SHORT COMMUNICATION

Purification of 2-mercaptobenzothiazole by solvent extraction

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(*Received 16 September 2006 • accepted 19 October 2006*)

Abstract−Purification of 2-mercaptobenzothiazole (91.9% purity) by solvent extraction was studied. The extraction of impurities present in crude 2-MBT (e.g. benzothiazole, sulfides and sulfur containing compounds) was carried out at temperatures between 70-180 °C using various solvents and their mixtures of different polarity. The highest purity of 2-MBT, above 99% was obtained using nitrobenzene, toluene and ethanol, even at a concentration of 2-MBT above 50 wt%. Increasing temperature and decreasing concentration of the raw material have a positive influence on the purification process. A comparable efficiency of purification was observed also with mixed solvents, (toluene with ethanol, acetone and aniline) possessing the same polarities. A correlation between the polarity indexes (PI) of mixed solvents and experimentally obtained purity of 2-MBT was found. The highest purity of 2-MBT provides extraction of the raw material with mixed solvents having PI 3.8-4.4

Key words: Purification, Impurities, 2-Mercaptobenzothiazole, Solvent Extraction, Polarity

INTRODUCTION

2-Mercaptobenzothiazole (2-MBT) has been commercially utilized in elastomer conversion as a vulcanization accelerator [1]. It is also employed for the syntheses of plant-protection or pharmaceutical compounds and is also included as an anti-corrosive agent in metal protection preparations.

Most manufacturing processes for 2-MBT make use of the reaction of aniline, sulfur and carbon disulfide at high temperature and high pressure. It produces unreacted starting materials, for example aniline, by-products and intermediates such as benzothiazole and anilinobenzothiazole [2]. Therefore, purification of the crude 2-MBT is necessary.

Numerous processes for purification of 2-MBT have been proposed: purification based on the formation of water soluble salts with alkali metals or ammonia [3,4], extraction with aliphatic and cycloaliphatic alcohols [5], washing with aromatic hydrocarbons selected from benzene, toluene, xylene and ethylbenzene [6], extraction with nitrobenzene [7,8], purification by steam distillation of by-products at molten conditions and removing of impurities in the vapors [9], extraction for the impurities by treatment of the reaction product with carbon disulfide or an emulsion of carbon disulfide and water [10,11].

Although they may actually be industrialized, these processes are not satisfactory and each shows wholly or in part the following disadvantages [12]:

1. Difficult recovery of the unreacted starting materials, which it is of great economic interest to recycle (aniline).
2. The need to operate at less than high concentration in order to favor the precipitation of the impurities.
3. Losses by chemical degradation of 2-MBT during the oxidation reactions intended to insolubilize the soluble impurities in alkaline medium.
4. The necessity of having to treat before their injection large volumes of aqueous effluents containing strong polluting charges. These treatments are difficult and costly.

The technique of the present work takes into account the properties of certain solvents to solubilize the impurities contained in the crude reaction product 2-MBT being itself less soluble in these solvents. 91.9% of 2-MBT was used as raw material to be purified by the solvent extraction process. This technique has proved very advantageous compared to the preceding techniques because of its simplicity and the yield from purification which can thus be attained [12]. The extraction processes without extractant [13] were studied as a function of several variables: concentration of 2-MBT, types of the solvent, ratio of the component to the solvent mixture, polarity of the solvent and temperature.

EXPERIMENTAL

1. Materials

The crude 2-MBT was a product produced by Istrochem a.s. Bratislava, Slovakia. The ground and homogenized sample contained 91.9% of 2-MBT and was stored in a closed box. The solvents were reagent grade purity and were used without purification. Ethanol was an azeotropic mixture with water (96%).

2. Procedure

The purification of crude 2-MBT with solvents was performed in 250 ml stainless steel vessels placed in an oven heated at the desired temperature for 3 hours. The mixing of components was ensured by rocking the vessels (35 swings per minute). Into the vessel was weighed about 60 g of a solvent and 80 grams of crude 2-MBT. After extraction at the desired temperature, the vessel was cooled,

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and the purified solid 2-MBT was separated by filtration, washed with the same solvent (2×50 ml), dried at 100 °C for 12 hours and weighed. From the weight of the solid product, the percentage of 2-MBT recovery (recovery %) was determined.

3. Analysis

The content of 2-MBT in the dried samples (purity%) was determined by titration and in some very pure samples controlled by HPLC analysis. About one gram of the sample of 2-MBT was dissolved in 100 ml of ethanol at about 60 °C. 10 ml of this solution was titrated with 0.1 M sodium hydroxide by using a phenolphthalein indicator. High pressure liquid chromatography (HPLC) analyses were performed using LC10AD delivery system, SPD M6A photodiode-array detector (Shimadzu) and column of 150×3.6 (I.D.) mm filled with Separon SGX C18, 5 μm (Tessek) at ambient temperature. About 2 mg of samples was dissolved in 15 ml of acetone. For the elution of the compounds, methanol - water mobile phase composition was employed under high pressure gradient conditions. From the monitored whole UV VIS region the wavelength 230 nm was chosen for comparison.

RESULTS AND DISCUSSION

1. Effect of the Type of Solvents

It is well known that the type of solvent has a dominant influence on the extraction process. For the studied purification of crude 2-MBT, solvents with different polarity were chosen. The efficiency of purification was followed on the basis of (i) the percentage of 2-MBT recovered after extraction and (ii) its purity (in %) In Fig. 1 is depicted the effect of solvents on the purity of 2-MBT obtained after extraction of the raw material at 130, 150 and 180 °C. As seen from the figure, the highest purity of 2-MBT (above 98%) was obtained by extraction with toluene, nitrobenzene and ethanol. Besides water, in all solvents the purity increases with the temperature of extraction. This increase is the highest in decanol.

In these experiments the concentration of crude 2-MBT in the solvent was 57 wt%. A very high purity of 2-MBT obtained by extraction with toluene, nitrobenzene and ethanol was reached at 65-80% recovery of purified 2-MBT (Fig. 2). The percentage of 2-MBT

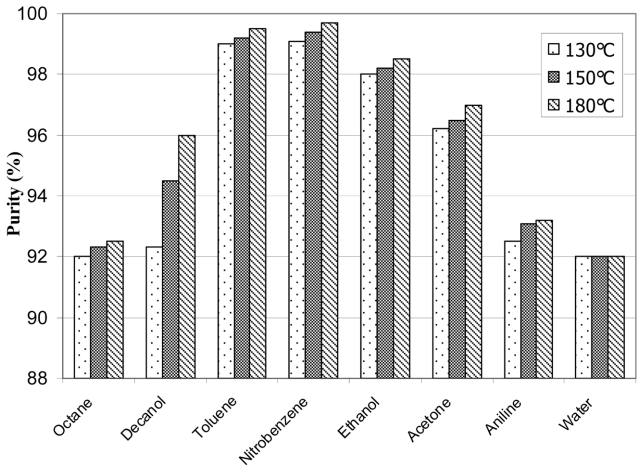

Fig. 1. Effect of solvent on the purification of crude-2-MBT at different temperatures.

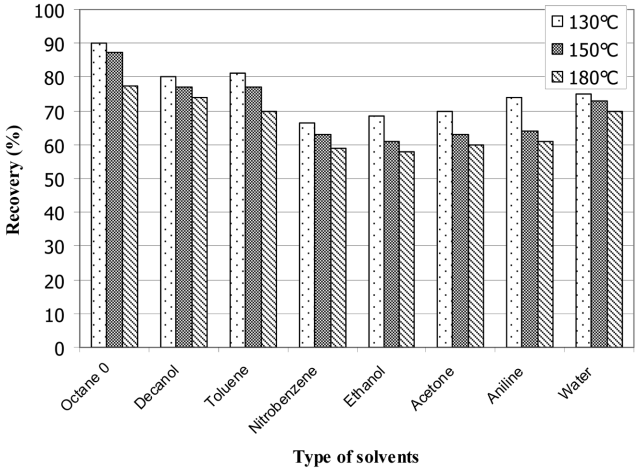

Fig. 2. Percentage of 2-MBT recovery after extraction with different solvents at various temperatures.

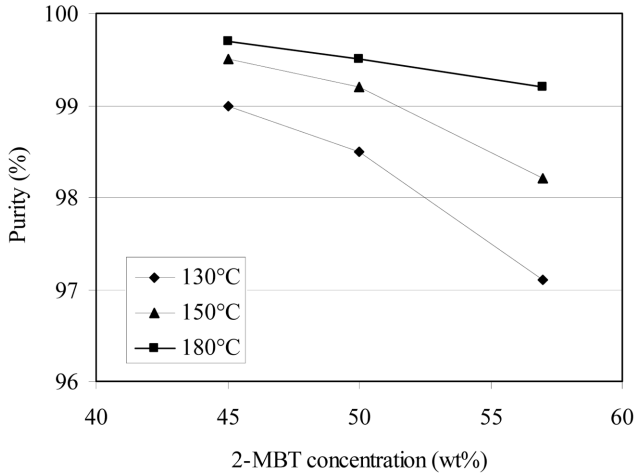

Fig. 3. Effect of concentration of the crude 2-MBT in toluene at different temperatures on the purity of the final product.

recovery in all tested solvents is higher at lower temperatures of extraction and is only partly dependent on the polarity of the solvent used.

2. Effect of Concentration of the Raw Material

In these experiments, toluene was selected to be the representative for all of the solvents. The effect of concentration of the raw material in toluene on the purity of the final product at temperatures of 130 °C, 150 °C and 180 °C is shown in Fig. 3. From the results, it is clear that the purity of 2-MBT decreases with increasing concentration of the raw material. This decrease is more significant if the extraction proceeds at lower temperature. Probably, the impurities present in the raw material are at lower temperature more difficult to extract by toluene. Nevertheless, if the extraction is performed at 180 °C the increase of concentration of 2-MBT in toluene by 25-30% only slightly decreases the purity of the recovered 2-MBT(about 1%).

An opposite influence has the increasing 2-MBT concentration and higher temperature of extraction on the percentage of recovery of the final product from toluene (Fig. 4). At temperatures 130-150 °C

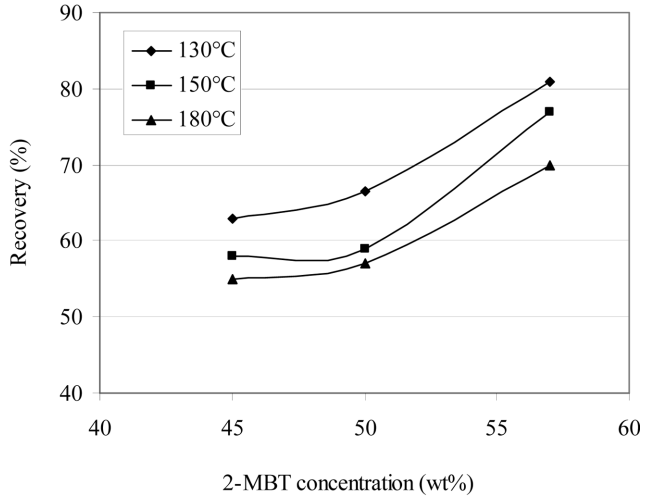

Fig. 4. Influence of 2-MBT concentration in toluene on percentages of 2-MBT recovery measured at various temperatures.

and concentration of crude 2-MBT in toluene (57 wt%), about 77-81.5% of 2-MBT with a purity of about 98.2-99.2% was recovered after one-step purification procedure.

3. Effect of Temperature

As was shown above, the temperature of extraction of crude 2-MBT significantly influences the purification process. This influence was investigated in a broader range using toluene, nitrobenzene and ethanol as solvents. The concentration of 2-MBT was constant, i.e., 57 wt%. As is evident from the results depicted in Fig. 5, in toluene and nitrobenzene it is possible to obtain 2-MBT with purity above 98% even at 70 °C. In ethanol such purity is reached only at temperatures above 130 °C. Since for extraction of impurities from crude 2-MBT 57 wt% concentration of 2-MBT in the solvents was used, it is clear that at lower temperatures only a part of 2-MBT is dissolved. Despite this, impurities present in the solid part of 2-MBT were extracted into the studied solvents, in which they are probably very soluble.

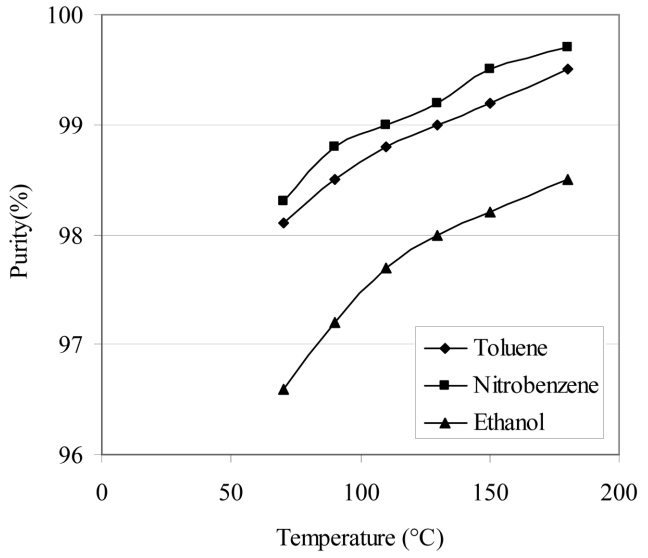

Fig. 5. Effect of temperature on purification of crude 2-MBT in selected solvents.

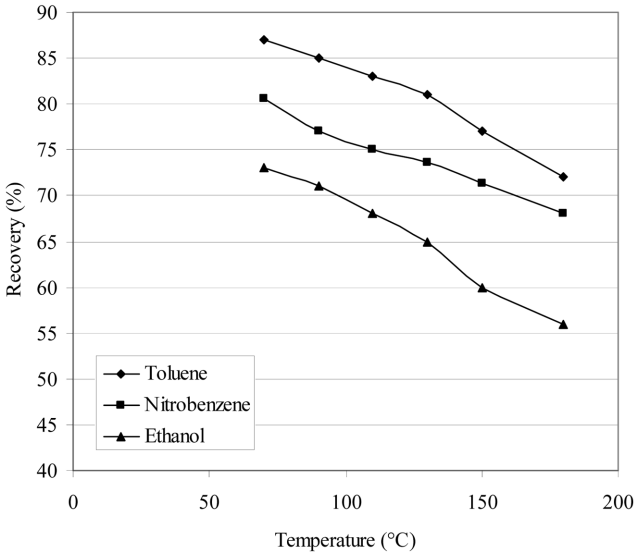

Fig. 6. Effect of temperature on the recovery of 2-MBT after extraction.

A lower temperature of extraction has a highly positive effect on the percentage of recovery of 2-MBT (Fig. 6). For example, after extraction of crude 2-MBT with toluene at 70 °C about 87% of 2-MBT was recovered.

4. Effect of Mixed Solvents

As was discovered, a very high purity of 2-MBT can be obtained not only by using pure solvents for the extraction, like toluene or nitrobenzene, but also mixed solvents.

When solvents are mixed together, the properties of the solvent mixtures are changed. This technique was used in our experiments to change the polarity of the solvents. Ethanol, acetone and aniline were used in the mixture with toluene in different concentrations. The concentration of crude 2-MBT in the mixture of solvents was always 57 wt%.The results of these studies are shown in Figs. 7-9.

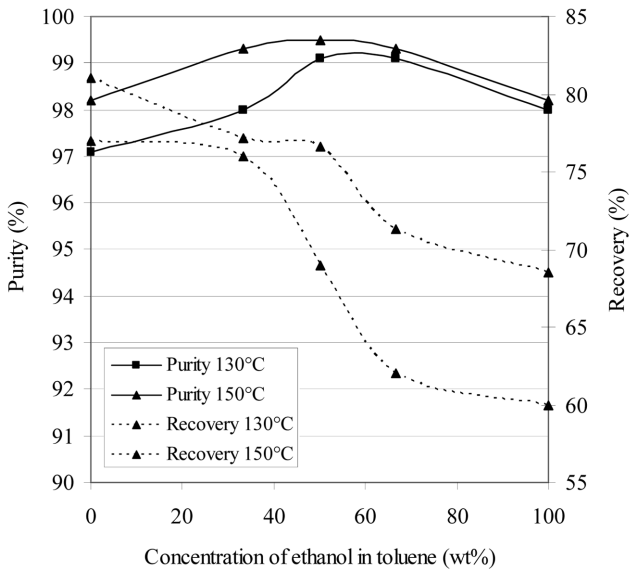

Fig. 7. Effect of ethanol concentration in toluene.

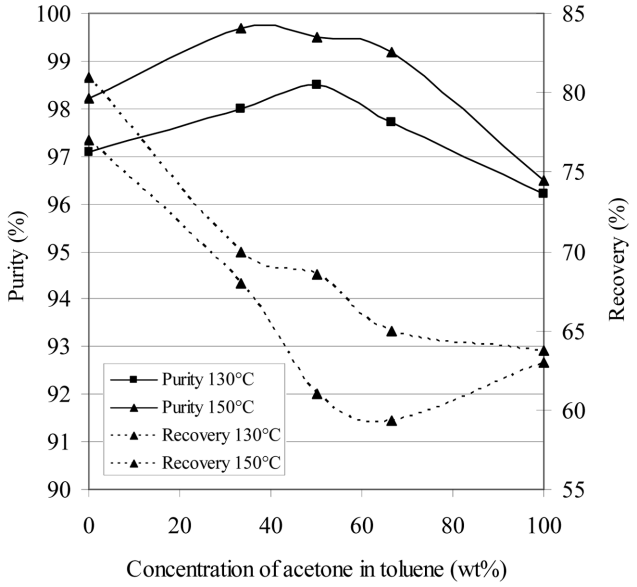

Fig. 8. Effect of acetone concentration in toluene.

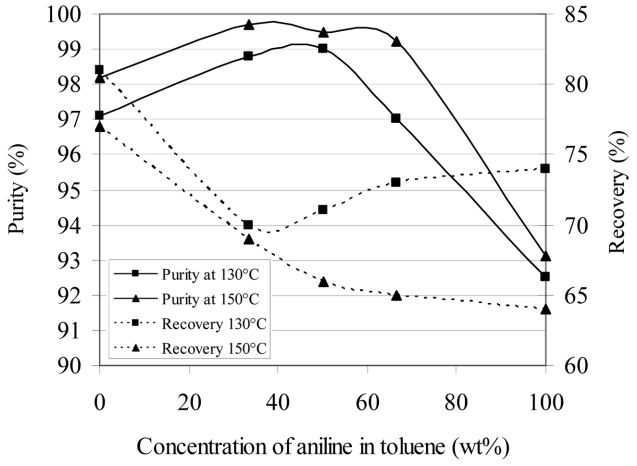

Fig. 9. Effect of aniline concentration in toluene.

When the additives were mixed with toluene, the purity rose up to about 99.5%. The concentration of additives in toluene was 50%, 33% and 50% for ethanol, acetone and aniline, respectively, in the case of reaching the maximum purity of 2-MBT. However, the percentage of recovery of 2-MBT decreases when the additives were added. The lowest decrease was registered for the mixture of ethanol-toluene, containing maximal 30-40 wt% of ethanol (Fig. 7). Acetone and aniline in the mixture with toluene significantly decreases the recovery of 2-MBT already at concentrations below 35% (Figs. 8 and 9).

5. Correlation between the Polarity of Solvents and Product Purity

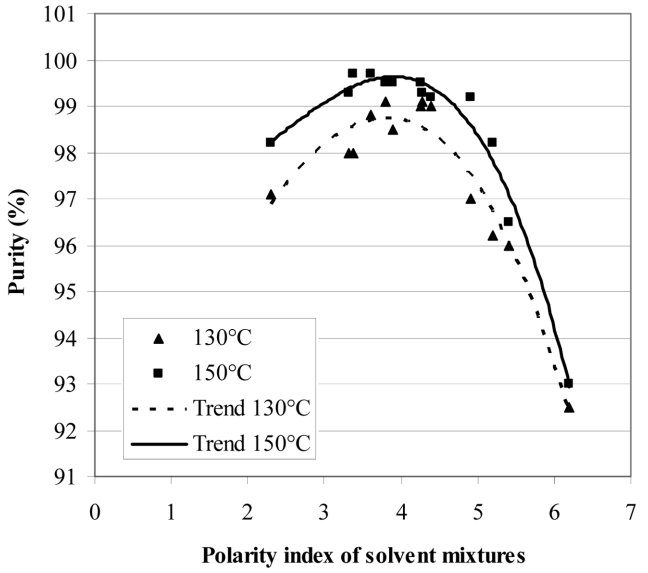

Fig. 10. Dependence of the purity of 2-MBT on the polarity indexes of solvent mixtures. The data were obtained at temperature of 130 °C and 150 °C at the concentration of crude 2-MBT 57 wt%.

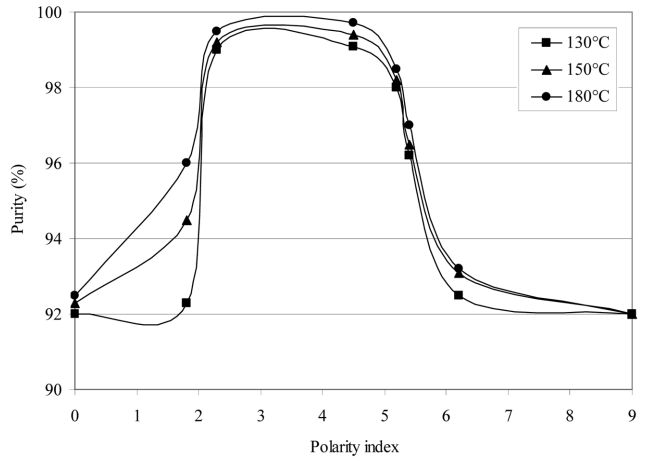

Fig. 11. Dependence of purity of 2-MBT on the polarity indexes of pure solvents obtained at different temperatures (data see Fig. 1).

When the solvents are mixed together, the polarity of the solvent mixtures is being changed. The changes of the polarity can be determined with sufficient accuracy by using the composition of solvent mixtures which have approximately the same polarity [14].

$$PI_{mixture}=\%SOL_A\times PI_A+\%SOL_B\times PI_B \quad (1)$$

where $PI_{mixture}$=polarity index of the solvent mixture, PI_A=polarity index of solvent A and PI_B=polarity index of solvent B.

Table 1. The polarity index of the mixture of toluene and other solvents at different ratio

	Ethanol					Acetone					Aniline				
wt%	0	33	50	66	100	0	33	50	66	100	0	33	50	66	100
PI	2.30	3.31	3.80	4.27	5.20	2.30	3.37	3.89	4.4	5.4	2.30	3.60	4.25	4.90	6.20

The experimental data obtained at temperatures of 130 °C and 150 °C in the solvent mixtures (Figs. 7-9) were re-arranged by Eq. (1). They are depicted in Fig. 10 and Fig. 11. The polarity index of the mixture between toluene and other solvents in different concentrations is shown in Table 1.

As is seen from Fig. 10, with increasing polarity indexes of solvent mixtures up to 3.3-3.5, the purity of 2-MBT significantly increases. The maximum value of the purity, about 99.5%, was obtained by extraction with mixed solvents having polarity indexes of 3.6-4.4. When for the purification of crude 2-MBT mixed solvents with polarity indexes above 3.8 were used, the purity of the desired product sharply decreased. Probably, in these solvent mixtures the solubilities of 2-MBT and its impurities are very similar.

By using Eq. (1) were treated also the data summarized in Fig. 1, where pure solvents were used for purification of crude 2-MBT. According to the literature [10], the polarity indexes of these solvents are: octane 0.0; decanol 1.8; toluene 2.3; nitrobenzene 4.5; ethanol 5.2; acetone 5.4; aniline 6.2 and water 9.0. The dependence of the purity of 2-MBT on the polarity indexes of these solvents is depicted in Fig. 11. As seen from the figure, the highest purity was reached in solvents with polarity indexes 2.2-4.5. Very interesting is the finding that the maximum purity of 2-MBT can be obtained by extraction with pure solvents or with mixed solvents which have similar polarity indexes. Therefore, the main effect influencing the purification of crude 2-MBT is the polarity of the solvent used.

Some selected samples of 2-MBT with a purity above 99% obtained in solvents and solvent mixtures with suitable polarity were checked by HPLC analysis. In Fig. 12 is analysis of crude 2-MBT and 2-MBT purified in nitrobenzene at a temperature of 150 °C. As seen from the HPLC analysis, nitrobenzene used as a solvent removes by-products present in the crude 2-MBT which evaluate between 5 and 12 min.

These studies confirmed that by using solvents with suitable polarity indexes it is possible to prepare 2-MBT with a purity above 99% by one-step extraction of crude 2-mercaptobenzothiazole.

CONCLUSIONS

Commercial crude 2-mercaptobenzothiazole (91.9% assay of 2-MBT) was purified by solvent extraction at different temperatures. The highest purity of 2-MBT (above 99%) was obtained by extraction with pure solvents, nitrobenzene and toluene and with some mixtures of toluene with ethanol, acetone or aniline. These data were confirmed by HPLC analysis of selected samples. It was found that the purification efficiency of pure solvents and their mixtures correlates with their polarity indexes. The extraction of impurities from crude 2-MBT is highly efficient with solvents having polarity indexes 2.3-4.4. In such solvents the solubility of the main impurities is probably much higher than the solubility of 2-MBT.

ACKNOWLEDGMENTS

The authors greatly appreciate the VEGA grant No.1/2459/05 for the financial support and also The Royal Golden Jubilee Ph.D. Program (Grant No. PHD/0043/2547) supported by the Thailand Research Fund.

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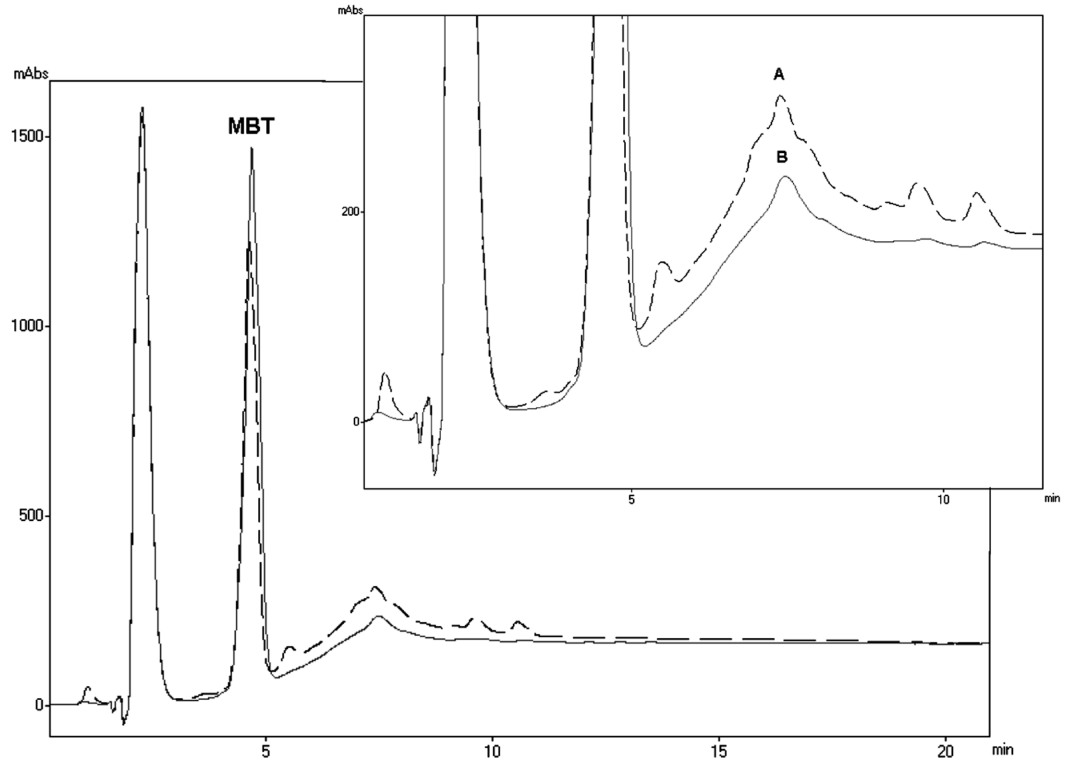

Fig. 12. Analysis of crude 2-MBT (A) and 2-MBT purified in nitrobenzene at 150 °C (B).

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