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SINGLE-STAGE AND TWO-STAGE SOLVENT EXTRACTION OF Tl(III) IN HOLLOW-FIBER CONTACTORS UNDER RECIRCULATION MODE OF OPERATION

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SINGLE-STAGE AND TWO-STAGE SOLVENT EXTRACTION OF Tl(III) IN HOLLOW-FIBER CONTACTORS UNDER RECIRCULATION MODE OF OPERATION

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ABSTRACT

This paper presents the experimental results of thallium (III) extraction from NaCl/H_2SO_4 solution with butyl acetate in hollow-fiber membrane contactors. The experiments were performed using laboratory made modules consisting of hydrophobic polypropylene or polyvinylidene fluoride fibers of different effective membrane areas. The aqueous phase was recirculated between the module and a mixed reservoir, and the organic phase was fed at the shell side in once-through mode. The influences of the aqueous and organic phase flow rate on the overall mass transfer coefficient were investigated. The experimental results are discussed in terms of the

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fraction of Tl(III) removed from the aqueous phase reservoir and the mean Tl(III) flux through the interfacial area. The results can be used for the design of a hollow-fiber contractor based extraction process that can be utilized in production of the radiopharmaceutical ^{201}TlCl.

Key Words: Thallium; Nondispersive solvent extraction; Hollow-fiber membrane; Production of radiopharmaceuticals; ^{201}TlCl

INTRODUCTION

The application of hollow-fiber contactors for solvent extraction processes using different kinds of microporous membranes has been studied extensively. Their success has been confirmed in the extraction of different compounds including metals (1,2), phenols (3), organic acids (4,5), proteins (6), and pharmaceutical products (7).

Membrane contactors for solvent extraction processes can be operated in a batch recirculation or a continuous contact mode of operation (8). It is very often that a prescribed degree of solute extraction cannot be achieved in a hollow-fiber module with single-pass continuous contact feed flow. In that case, the solute-containing feed stream should recycle between the module and a mixed liquid tank. This mode of operation is primarily used to achieve high degrees of solute extraction in small contacting devices.

Membrane contactors in recirculation mode of operation were first studied by Qi and Cussler (9,10) for dispersion-free gas absorption of H_2S, NH_3, SO_2, and CO_2 in water and aqueous sodium hydroxide solutions. They derived expressions for calculation of the overall mass transfer coefficient in membrane contactors from the concentration change in the holding reservoirs (gas or liquid). The recirculation mode of operation was also used for the separation of alcohols from an aqueous solution by pervaporation (11), for the removal of NH_3 from aqueous solutions containing both NH_3 and CO_2 by hollow-fiber gas-membrane process (12,13), for ternary gas mixture separation with mobile liquid extractants (selective membrane valve) (14), and for dispersion-free membrane aeration of water in modules with sealed-end hollow fibers (15). The membrane-based extractors in recirculation mode of operation were investigated for the separation of gold (16), proteins (6), chromium (VI) (17), and acetic acid (18).

The aim of this study is to investigate the applicability of recirculation hollow-fiber contactors for the separation of Tl(III) from Pb(II) in the radiopharmaceutical ^{201}TlCl production. ^{201}TlCl is a well-known radiopharmaceutical for myocardial and tumor imaging (19,20). The radioisotope ^{201}Tl is usually produced by the indirect nuclear reaction $^{203}\mathrm{Tl}(\mathrm{p}, 3\mathrm{n})^{201}\mathrm{Pb} \rightarrow {}^{201}\mathrm{Tl}$, followed by subsequent

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target processing. The first step in the production of ^{201}TlCl is the separation of trace amounts of ^{201}Pb (the parent of ^{201}Tl) from the irradiated target material, metallic ^{203}Tl. The second step is the separation of trace amounts of ^{201}Tl from trace amounts of ^{201}Pb. One of the most suitable techniques for the separation of thallium from lead is solvent extraction using butyl acetate (BuAc) (21). The distribution coefficient of Tl(III) between butyl acetate and aqueous phase is about 1000 when the extraction is carried out from 5 $\text{mol} \cdot \text{dm}^{-3}$ H_2SO_4 solution containing NaCl, providing molar ratios between Tl(III) and Cl^- not less than 1:4. From this solution, Tl(III) will be extracted in the form of $HTlCl_4$ complex (21).

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EXPERIMENTAL

Chemicals and Materials

The experiments were performed with aqueous solutions initially containing between 0.015 and 0.06 $\text{mol} \cdot \text{dm}^{-3}$ Tl_2SO_4 (Fluka, p.a. grade), 5.0 $\text{mol} \cdot \text{dm}^{-3}$ H_2SO_4 (Merck, p.a. grade), and 0.3 $\text{mol} \cdot \text{dm}^{-3}$ NaCl (Merck, p.a. grade). Trivalent thallium, which is appropriate for the extraction with butyl acetate (Fluka, p.a. grade), was obtained by oxidation with excess of $KBrO_3$ (Merck, p.a. grade). The concentration of Tl(III) in the aqueous and organic phase was determined by labeling the initial feed solution with ^{201}TlCl (CIS bio international) followed by subsequent determination of the activities of both phases using an automated γ-counter (LKB WalLac, CompuGama Model 1282-001) (21).

Experimental Setup and Procedures

Four microporous hollow-fiber modules were constructed and used in this study (Tab. 1). The modules were made of hydrophobic polypropylene (Celgrad X-20) or polyvinylidene fluoride (Akzo Enka) fibers. In order to obtain regular fiber packing and thus to minimize shell side bypassing, perforated Teflon disks were placed close to the end of the modules. The fiber bundle was aligned and potted with epoxy resin in an open glass tube of 1 cm inner diameter.

The membrane-based solvent extraction system used for our experiments (Fig. 1) consisted of a hollow-fiber module (C), three reservoirs of 100 cm^3 volume for the aqueous solution (R1), organic solvent (R2) and extract (R3), two peristaltic pumps (P1 and P2), and tubes. The aqueous phase with a total volume of 3.5 cm^3 was recirculated between the module and the reservoir R1 by the peristaltic pump P1 at a flow rate of 0.65–8 $\text{cm}^3 \cdot \text{min}^{-1}$. The total holdup volume of the tubing

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Table 1. Specifications of Hollow-Fiber Modules

Module Code	1	2	3	4
Membrane material	PVDF	PVDF	PP	PP
Length of module (m)	0.103	0.14	0.09	0.14
No. of fibers in a module, N	31	30	30	31
Effective fiber length, L (m)	0.068	0.122	0.065	0.120
Total volume in the lumen of fibers (cm^3)	0.106	0.185	0.120	0.229
Total volume on the shell side of fibers (cm^3)	4.65	8.48	4.42	8.15
Void fraction	0.87	0.87	0.87	0.86
Effective membrane area, A (cm^2)‡	16.8	29.2	17.2	32.7
Membrane area per volume (cm^{-1})	3.1	3.0	3.4	3.5
Inner fiber diameter, d_i^* (μm)	254	254	280	280
Outer fiber diameter, d_o^* (μm)	648	648	660	660
Membrane wall porosity, ε^{**}(%)	35	35	28	28

*Diameters of hollow fibers, previously saturated with butyl acetate, were determined under a microscope (Zeiss, FRG) using polarized light.

**The porosity of membrane wall was experimentally determined using a procedure suggested by Prasad and Sirkar (5).

‡Effective membrane area was calculated as inner surface area of hollow fibers.

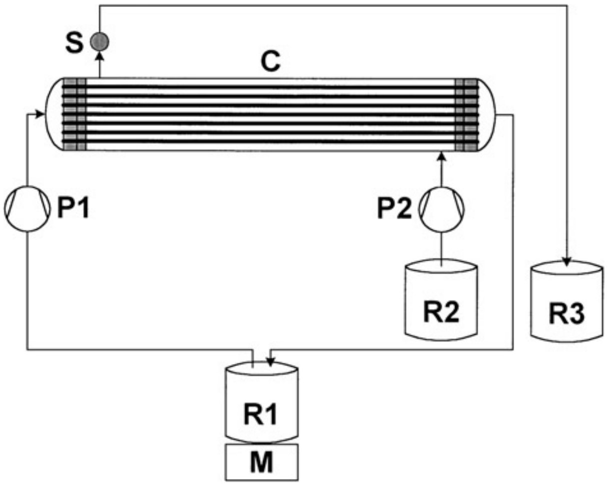

Figure 1. Schematic of the experimental set-up showing a section through the contactor housing: C—contactor, P1–P2—peristaltic pumps, S—sample port, R1–R3—reservoirs, M—magnetic stirrer.

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used for the aqueous phase recirculation was 0.9 cm^3. The aqueous phase in the reservoir R1 was vigorously mixed by a magnetic stirring bar to obtain nearly ideal mixing conditions. The organic solvent flowed through the module in once-through mode at a flow rate of 0.65 $cm^3 \cdot min^{-1}$. All experiments were carried out at a constant temperature of 291 K. During the extraction 10 μl aliquots of aqueous and organic phase were taken every 5 min and used for the determination of Tl concentration.

After each set of experiments the contactors were cleaned from the process solutions by the following procedure: the lumen side of the fibers was washed by 3 cm^3 of 5 $mol \cdot dm^{-3}$ H_2SO_4, then the lumen and pores of hollow fibers were washed with 10 cm^3 of butyl acetate, then with 10 cm^3 of 70% ethanol, and finally with 30 cm^3 of water. The concentration of Tl in these wastes was measured by the same technique as in the experiments.

It is known that a significant portion of the shell side fluid may flow along the outside of the tube bundle, and not within the tube bundle (22,23). Seibert et al. (22) have shown that the actual residence time of the shell side fluid in a commercial unbaffled hollow-fiber extractor was three to four times shorter than the ideal residence time and as a result, only 10–30% of the membrane surface area was effective for the mass transfer. In order to avoid the detrimental effect of shell side bypassing on the mass transfer performance, the feed solution was always sent through the tube side, whereas the organic phase was pumped countercurrently through the shell side. Because the fibers are hydrophobic, the pores of the membrane were filled with organic phase. Therefore, the aqueous phase pressure was maintained slightly higher than the organic phase pressure to prevent leakage of the organic phase from the pores into the aqueous phase.

The time-dependent Tl(III) concentration in the aqueous phase C_w^{in} was used to calculate the overall mass transfer coefficient, K_w, according to the following equation:

$$K_w = -\frac{Q_w}{\pi d_i N L} \ln\left[1 - \frac{V_w}{Q_w} \frac{d \ln\left[\left(C_{w,t=0}^{in} / C_w^{in}\right)\right]}{dt}\right] \tag{1}$$

where the symbols are defined in the List of symbols. Equation (1) is the simplified form of the general solution (6), which is valid for high solute distribution coefficients ($m_i \gg 1$). In our case, the distribution coefficient m_i defined as the equilibrium concentration of $HTlCl_4$ in the organic phase (butyl acetate) divided by that in the aqueous phase (5 $mol \cdot dm^{-3}$ H_2SO_4 and 1 $mol \cdot dm^{-3}$ NaCl) was found to be 1180 at 291 K (21). It must be noted here that the overall mass transfer resistance for $HTlCl_4$ transfer is given by:

$$\frac{1}{K_w} = \frac{1}{k_w} + \frac{d_i}{m_i d_{lm} k_{mo}} + \frac{d_i}{m_i d_o k_o} \tag{2}$$

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RESULTS AND DISCUSSION

Single-Stage Tl(III) Extraction Process

The influence of the organic phase flow rate on the time variations of Tl(III) concentration in the aqueous phase reservoir at a constant aqueous flow rate of 0.65 $\mathrm{cm}^3 \cdot \mathrm{min}^{-1}$ is given in Figure 2. It is clear that the organic phase flow rate has no significant influence on the Tl(III) extraction, indicating that the major mass transfer resistance is in the aqueous phase. This fact can be explained by a very high distribution coefficient. Thus, in the subsequent experiments the organic phase flow rate was kept constant at 0.65 $\mathrm{cm}^3 \cdot \mathrm{min}^{-1}$, which is the minimum flow rate the pump P2 could achieve.

The time variation of Tl(III) concentration in the aqueous phase reservoir can be calculated by solving the differential Equation (1):

$$C_{\mathrm{w}}^{\mathrm{in}} = C_{\mathrm{w,t=0}}^{\mathrm{in}} \cdot \exp\left\{-\frac{Q_{\mathrm{w}}}{V_{\mathrm{w}}}\left[1-\exp\left(-\frac{K_{\mathrm{w}}\pi d_{\mathrm{i}} N L}{Q_{\mathrm{w}}}\right)\right] \cdot t\right\} \tag{3}$$

Thus, one would expect that the experimentally measured concentration in the reservoir decreases exponentially with time. The measured time dependencies

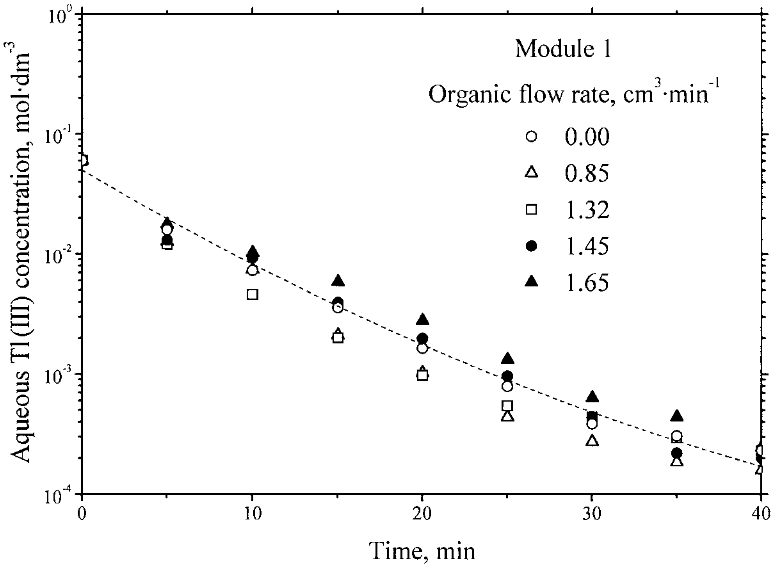

Figure 2. The influence of the organic phase flow rate on the time variation of Tl(III) concentration in the aqueous phase reservoir in module 1. The aqueous flow rate was constant (1.8 $\mathrm{cm}^3 \cdot \mathrm{min}^{-1}$).

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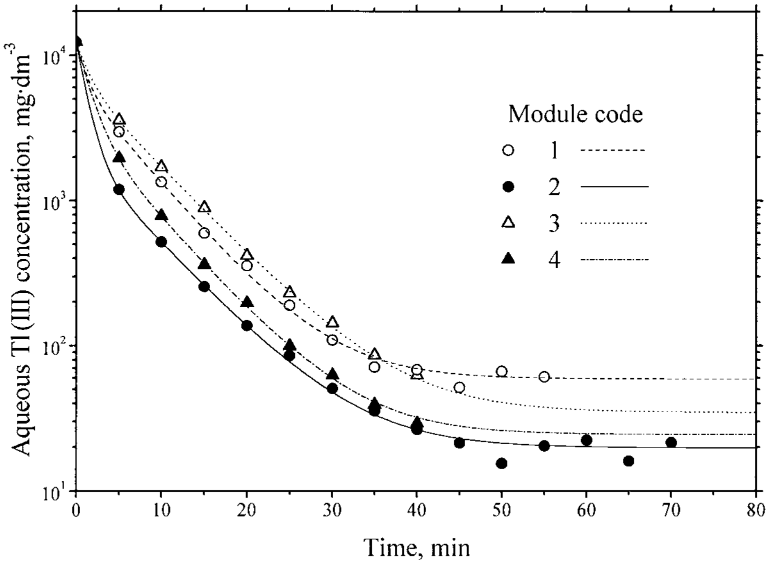

Figure 3. The time variations of Tl(III) concentration in the aqueous phase reservoir for different modules. The aqueous flow rate was 3.8 $cm^3 \cdot min^{-1}$ and organic flow rate was 0.65 $cm^3 \cdot min^{-1}$.

for different modules and aqueous phase flow rates are given in Figures 3 and 4. Apparently, the Tl(III) concentration in the aqueous phase reservoir, C_w^{in}, decreased with time, t, according to the following empirical equation:

$$C_w^{in} = a + b\exp(-ct) + d\exp(-et) \tag{4}$$

where a, b, c, d, and e are the coefficients depending on the experimental conditions. The Tl(III) concentration decreases with time; however, it tends to a finite limiting value as time approaches infinity. The coefficient **a** in Equation (4) gives the minimum Tl(III) concentration in the aqueous phase, which can be achieved in a single-stage, extraction process irrespective of time. In the first part of each curve, the rate of Tl(III) transfer is limited by the mass-transfer resistance in the aqueous phase and the exponential terms in Equation (4) are much more important than the coefficient **a**. In the final part of the curves the rate of Tl(III) transfer is limited by some process(es) other than the mass-transfer resistance, probably by the adsorption/desorption of Tl(III) on the surface of the membrane pores.

The adsorption of Tl in the pores of the fibers is also evident from the overall mass balance, determined after the final decontamination of the contactors. In average, around 75% of Tl was in the bulk of the organic phase at the end of the extraction procedure. 10% of Tl was usually in the organic phase entrapped in the pores of

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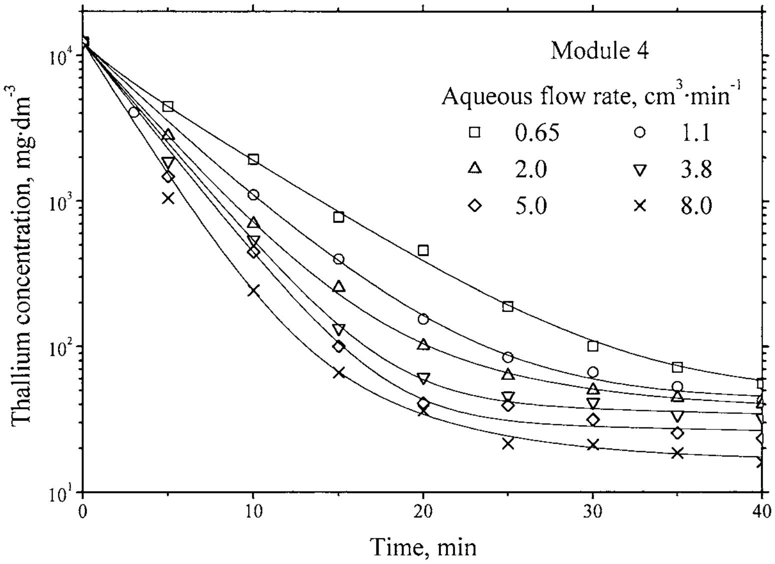

Figure 4. Effect of the aqueous flow rate variation on the Tl(III) concentration in the aqueous phase reservoir in module 4. The organic flow rate was constant (0.65 cm^3 · min^{-1}).

the fibers, which could be easily washed out by butyl acetate. The remaining 8–10% of Tl could not be removed by further washing with butyl acetate, however washing with 70% ethanol resulted in a complete decontamination of the contactors.

After 40 min of operation the Tl(III) concentration in the aqueous phase reservoir was less than 1% of its initial value even for the lowest aqueous phase flow rate of 0.65 cm^3 · min^{-1}. PVDF hollow fibers were more efficient in removing Tl(III) from the aqueous phase than PP fibers. This can be explained by the fact that PVDF fibers have smaller inner diameters than PP fibers enabling higher velocities in the fiber lumen and therefore higher K_w values at the same aqueous phase flow rates. As expected, the longer modules 2 and 4, with higher interfacial contact areas, were more efficient in removing Tl(III) than shorter modules 1 and 3. In Figure 4, the Tl(III) concentration in the aqueous phase reservoir is shown as a function of the aqueous phase flow rate for module 4. The Tl(III) concentration in the aqueous phase decreased with increasing the aqueous phase flow rate, which is a type of behavior opposite to the continuous contact mode of operation (24).

For our operating conditions, the minimum Tl(III) concentration in the aqueous phase ranged between 15 and 190 mg · dm^{-3} (Tab. 2) and was established within 40–60 min of operation. At higher aqueous flow rate and for longer modules, the Tl(III) concentration decreased more rapidly and lower amount of thallium was adsorbed on the membrane surface. Therefore, the minimum Tl(III) concentration

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Table 2. The Limiting Tl(III) Concentration in the Aqueous Phase Reservoir That Can Be Achieved in a Single-Stage Process, That Is, the Coefficient **a** in Equation (4) as a Function of Aqueous Phase Flow Rate for Different Modules

Aqueous Flow Rate, $cm^3 \cdot min^{-1}$	**a**, $mg \cdot dm^{-3}$			
	Module 1	Module 2	Module 3	Module 4
0.65	90.1	47.2	189	56.6
1.1	59.3	43.5	99.7	43.9
2.0	54.6	39.4	109	45.8
3.8	53.3	37.4	63.8	35.6
5.0	36.0	28.6	53.3	31.3
8.0	—	15.5	—	—

in the aqueous phase decreased with increasing aqueous flow rate and module length (Tab. 2).

The typical plots for the determination of the overall mass transfer coefficient, K_w, are given in Figure 5. There is a clear linear relation between $\ln(C^{in}_{w,t=0}/C^{in}_{w})$ and t with correlation coefficients exceeding 0.99 in all cases, except for the highest

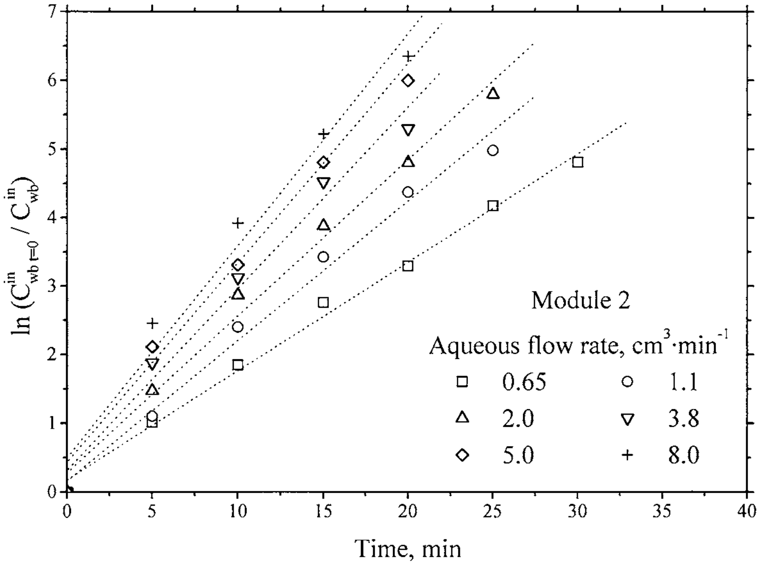

Figure 5. The plot for the determination of the overall mass transfer coefficient for module 4.

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Q_w value of 5 $cm^3 \cdot min^{-1}$. The K_w values were determined from the slopes of these lines according to Equation (1) and listed in Table 2. Obviously, K_w increases with increasing the aqueous phase flow rate, which is generally observed behavior (6,17). For the range of aqueous phase flow rates of 0.6–5 $cm^3 \cdot min^{-1}$ the K_w values varied from 2.68 to 5.96×10^{-6} $m \cdot s^{-1}$, which is 9–16% lower than those obtained using the same modules in a continuous contact mode (25). The deviations are higher at higher aqueous phase flow rates. The discrepancy between the K_w values obtained in a batch and a continuous contact mode is a consequence of the fact that a quasi steady-state, for which Equation (1) holds, was not fully established in our experiments due to relatively small aqueous phase volume.

At the same aqueous flow rate and membrane type, K_w decreases with increasing L, which is in agreement with laminar flow correlations developed by Lévêque (26), Sieder and Tate (27), and Dahuron and Cussler (28). In our experiments the Reynolds number in aqueous phase flow was in the range of 10–100, which is an indication of laminar regime (29). The membrane polymer plays no important role in the Tl(III) permeation, as the membrane resistance is negligible, and as shown by the effectiveness of final decontamination of the contactors, the adsorption of Tl is approximately the same on both materials. The membrane mass-transfer coefficient, k_{mo}, depends on the porosity ε, thickness δ, and tortuosity τ of the hollow fiber wall, according to the equation: $k_{mo} = D_o\varepsilon/(\delta\tau)$, where $D_o = 1.65 \times 10^{-9}$ $m^2 \cdot s^{-1}$ is the $HTlCl_4$ diffusivity in butyl acetate at 291 K calculated from the Wilke-Chang correlation (30). For PP hollow fibers $\varepsilon = 0.28$, $\delta = 1.9 \times 10^{-4}$ m, and $\tau = 2.5$ according to Prasad and Sirkar (5), from which one obtains $k_{mo} = 9.72 \times 10^{-7}$ $m \cdot s^{-1}$. The substitution of this k_{mo} value into the second right-hand term of Equation (2) gives a membrane resistance value of around 550 $s \cdot m^{-1}$. It is three orders of magnitude lower than 1.7×10^5 $s \cdot m^{-1}$, which is the minimum value of the overall mass-transfer resistance $1/K_w$ for the data in Table 3.

Table 3. The Overall Mass Transfer Coefficient, K_w, as a Function of Aqueous Phase Flow Rate for Different Modules

Aqueous Flow Rate, $cm^3 \cdot min^{-1}$	$K_w \times 10^{-6}$, $m \cdot s^{-1}$			
	Module 1	Module 2	Module 3	Module 4
0.65	4.74	3.05	3.91	2.68
1.1	4.89	3.50	3.96	2.74
2.0	5.01	3.48	4.45	2.69
3.8	5.60	3.80	4.94	2.94
5.0	5.96	4.11	5.36	3.47
8.0	—	4.26	—	—

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Table 4. The Amount of Tl(III) Extracted in a Single Pass through the Module, E, as a Function of Aqueous Phase Flow Rate for Different Modules

Aqueous Flow Rate, $cm^3 \cdot min^{-1}$	E, %			
	Module 1	Module 2	Module 3	Module 4
0.65	49.4	56.0	46.2	55.5
1.1	34.0	42.7	31.0	38.7
2.0	20.9	26.2	20.5	23.2
3.8	12.9	16.0	12.5	14.1
5.0	10.5	13.4	10.4	12.7
8.0	—	8.9	—	—

The fraction of Tl(III) removed from the aqueous phase reservoir in time interval from $t = 0$ to $t = t$ can be calculated as:

$$E_w = 1 - \frac{C_w^{in}}{C_{w,t=0}^{in}} = 1 - \exp\left(-\frac{EQ_w t}{V_w}\right) \tag{5}$$

where E is the fraction of Tl(III) extracted along the module in a single aqueous phase pass given by:

$$E = 1 - \frac{C_w^{out}}{C_w^{in}} = 1 - \exp\left(-\frac{K_w \pi d_i N L}{Q_w}\right) \tag{6}$$

The E values listed in Table 4 are somewhat lower than the E values obtained in a continuous contact mode (25), which is due to the lower K_w values. The time variation of the amount of extracted Tl(III), E_w, for different modules and aqueous flow rates are given in Figures 6 and 7. It must be noted here that after 30 min of operation, E_w is virtually 100% and is independent of the aqueous phase flow rate. These high E_w values compared to E are obtained at the expense of lower overall capacity. As an example, if a feed solution of 3.5 cm^3 is recycled for 30 min, the overall capacity is 0.12 $cm^3 \cdot min^{-1}$, which is much lower than the lowest Q_w value of 0.65 $cm^3 \cdot min^{-1}$. Figure 8 presents the influence of the initial concentration of Tl(III) in aqueous phase on the amount of extracted Tl(III), E_w. It is clear that the initial concentration of thallium (6.16–24.63 $g \cdot dm^{-3}$) has no influence on the fraction of Tl(III) removed from the aqueous phase reservoir.

The mean Tl(III) flux through the interfacial area in time interval from $t = 0$ to $t = t$ can be calculated from the equation:

$$\bar{J} = \frac{Q_w E}{\pi d_i N L} C_w^{in} = \frac{Q_w E}{\pi d_i N L} C_{w,t=0}^{in} \exp\left(-\frac{Q_w E}{V_w} t\right) \tag{7}$$

The time variations of the mean Tl(III) flux through the interfacial area are presented in Figures 9 and 10. Obviously, there is a linear relation between ln $\bar{J}$

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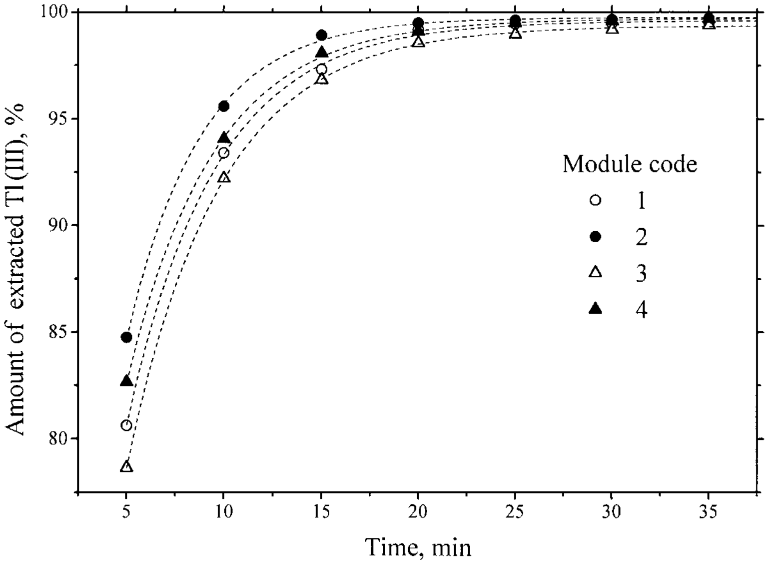

Figure 6. The percent of Tl(III) extracted as a function of the different modules. The aqueous flow rate was 3.8 $cm^3 \cdot min^{-1}$ and organic flow rate was 0.65 $cm^3 \cdot min^{-1}$.

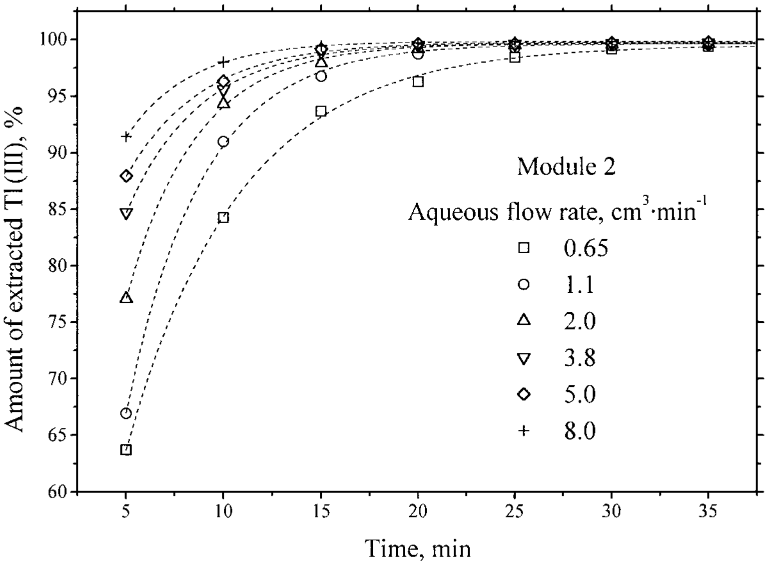

Figure 7. The percent of Tl(III) extracted as a function of the aqueous flow rate for module 2.

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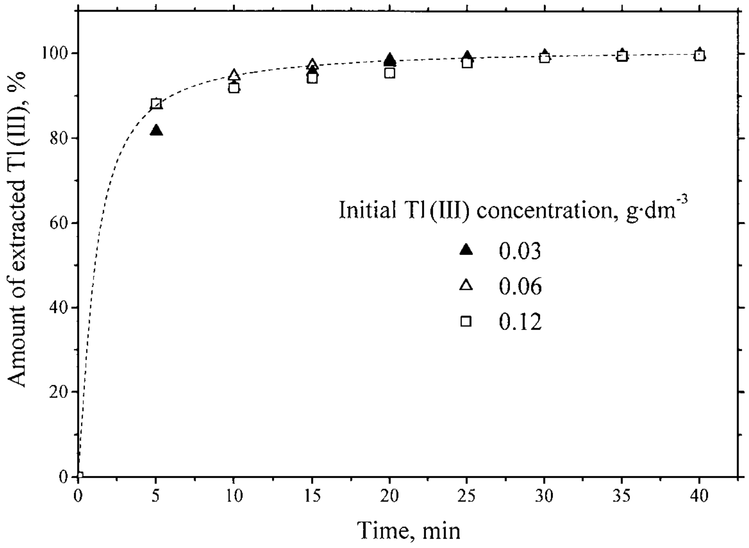

Figure 8. The influence of the initial thallium concentration (6.16– 24.63 g · dm^{-3}) on the amount of extracted Tl(III) for module 2. The aqueous flow rate was 3.8 cm^3 · min^{-1} and the organic flow rate was 0.65 cm^3 · min^{-1}.

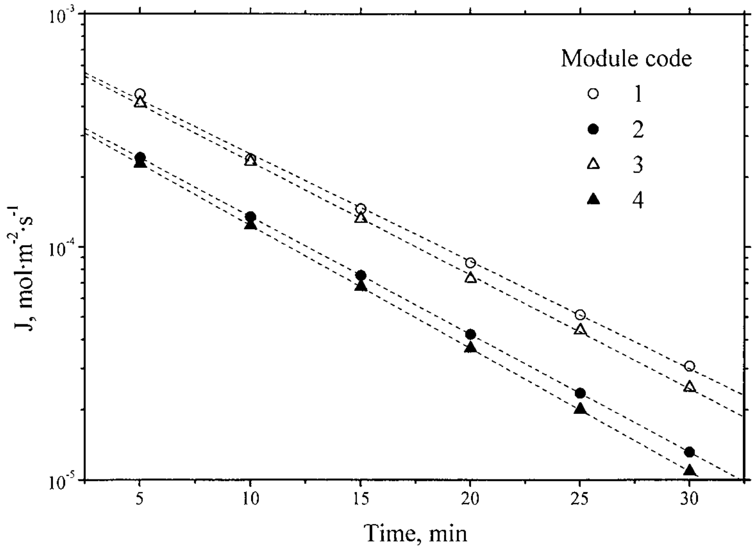

Figure 9. The variation of the mean thallium (III) flux through the interfacial area with the time of extraction for different modules.

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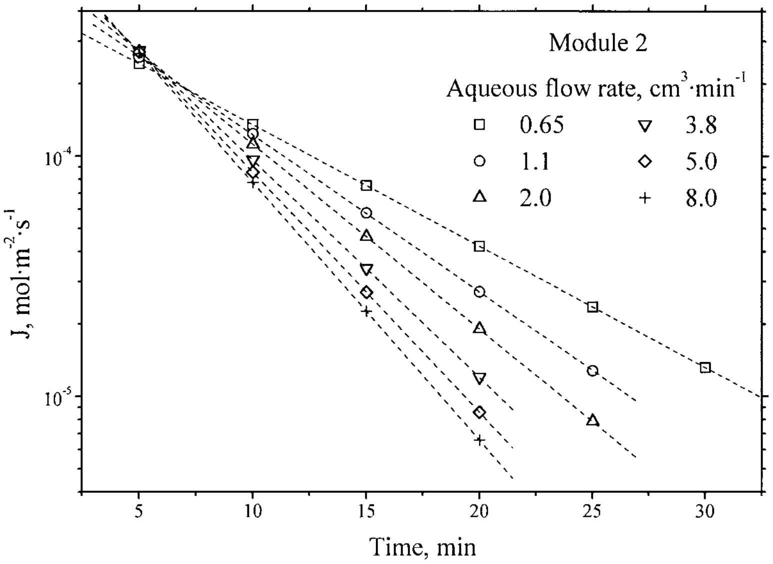

Figure 10. The variation of the mean thallium (III) flux through the interfacial area with the aqueous feed flow rate for module 2.

and t, as predicted by Equation (7). The mean Tl(III) flux decreases with time due to a decrease in the concentration driving force. The rate of Tl(III) flux decrease is higher at the higher aqueous flow rate which is in accordance with Equation (7). At the same aqueous phase flow rate the Tl(III) flux is higher for smaller modules (1 and 3).

Two-Stage Tl(III) Extraction Process

For a single-stage extraction process the minimum Tl(III) concentration in the aqueous phase given in Table 2 is higher than the maximum tolerable concentration of thallium in the radiopharmaceutical ^{201}TlCl of 10 and 2 $mg \cdot dm^{-3}$ prescribed in European (31) and U.S. (32) pharmacopoeia, respectively. It means that the single-step extraction is not sufficient. Therefore, the extraction was repeated in a second identical module using the raffinate from the first extraction process as a feed solution. The experimental procedure and conditions were the same as in the first set of experiments.

The measured time dependencies of Tl(III) concentration in the aqueous phase reservoir during the second extraction stage are shown in Figure 11. The four lines in the upper part (a) of Figure 11 show the anticipated Tl(III) concentrations in

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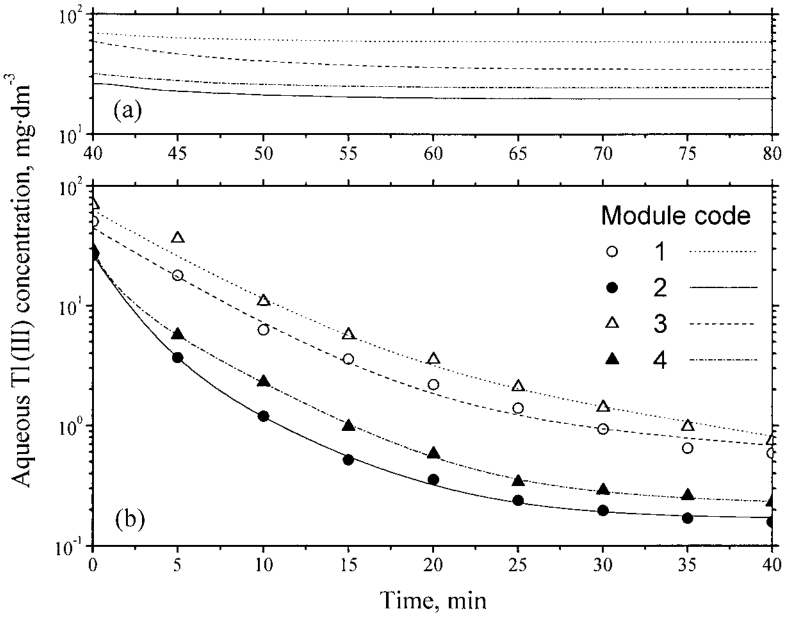

Figure 11. a) Extrapolation of Tl(III) concentration in the first stage of extraction. b) The second-stage Tl(III) extraction process. The raffinate from the first extraction was used as a feed solution. The aqueous flow rate was 3.8 $cm^3 \cdot min^{-1}$ and organic flow rate was 0.65 $cm^3 \cdot min^{-1}$.

a prolonged single-stage extraction process. After 40 min of operation in a second stage, the aqueous phase contained only 0.59–0.75 and 0.16–0.23 $mg \cdot dm^{-3}$ of Tl(III) in shorter and longer modules, respectively. After only 10 min of operation in a second stage, the Tl(III) concentration decreased to below 2 $mg \cdot dm^{-3}$ in longer modules (2 and 4). Therefore, the concentration of inactive thallium in the radiopharmaceutical can be decreased below the required value for an overall time of 50 min using a two-step process. On the other hand, in a single-stage extraction process the concentration of inactive thallium in the radiopharmaceutical cannot be decreased below 20 $mg \cdot dm^{-3}$ even after 80 min.

CONCLUSIONS

The solvent extraction of trivalent thallium from NaCl/H_2SO_4 solutions into butyl acetate was successfully achieved using microporous PVDF and PP hollow fibers. In a single-stage process, due to thallium interactions with the membrane polymer, the minimum Tl(III) concentration in the aqueous phase was higher

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than the maximum tolerable concentration of thallium in the radiopharmaceutical ^{201}TlCl. However, in a two-stage process in which raffinate from the first extraction stage was used as a feed solution in a second stage, the Tl(III) concentration in the aqueous phase was far below the required value prescribed by pharmacopoeia. The mass-transfer efficiency increased with increasing the module length and aqueous flow rate.

SYMBOLS

C_w	concentration of Tl(III) in aqueous phase, $\text{mol} \cdot \text{dm}^{-3}$ or $\text{mg} \cdot \text{dm}^{-3}$
D_o	diffusivity of $HTlCl_4$ in organic phase, $\text{m}^2 \cdot \text{s}^{-1}$
d_i	inner diameter of a hollow fiber, m
d_o	outer diameter of a hollow fiber, m
d_{lm}	log mean diameter of a hollow fiber, $(d_o – d_i)/\ln(d_o/d_i)$, m
E	fraction of Tl(III) extracted in a single aqueous pass, (%)
E_w	fraction of Tl(III) removed from the aqueous phase reservoir, (%)
$\bar{J}$	mean flux of Tl(III) through interfacial area from $t = 0$ to $t = t$, $\text{kmol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$
K_w	overall mass-transfer coefficient based on aqueous phase, $\text{m} \cdot \text{s}^{-1}$
k_{mo}	membrane mass-transfer coefficient for hydrophobic membrane, $\text{m} \cdot \text{s}^{-1}$
k_o	organic phase mass-transfer coefficient, $\text{m} \cdot \text{s}^{-1}$
k_w	aqueous phase mass-transfer coefficient, $\text{m} \cdot \text{s}^{-1}$
L	effective length of a hollow fiber, m
m_i	distribution coefficient of Tl(III) between organic and aqueous phases, C_o/C_w
N	number of hollow fibers in a module
Q_w	aqueous flow rate, $\text{m}^3 \cdot \text{s}^{-1}$
PP	polypropylene
PVDF	polyvinylidene fluoride
t	time, s
V_w	volume of aqueous phase in the reservoir, cm^3
δ	thickness of membrane, m
ε	porosity of membrane, (-)
τ	tortuosity of membrane, (-)

Subscripts and Superscripts

in	denotes value of C_w at module inlet, i.e., in aqueous phase reservoir
out	denotes value of C_w at module outlet
$t = 0$	denotes value of C_w at time $t = 0$

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