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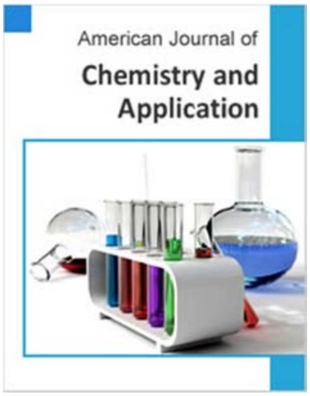

Modeling of Separation of Platinum Metals by Counter-Current Chromatography

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Abstract

A possibility of application of the calculation program for numerical researches and modeling of metal separation by the combined method of liquid chromatography and counter-current extraction (dynamic counter-current extraction) has been examined. The experimental data on the distribution of chlorides of platinum metals from 2 M HCl solutions with methyltrioctylammonium dinonylnaphthalene sulphonate in toluene were used for calculation researches and simulation of separation processes of metals. Numerical studies on the dynamic counter-current extraction have shown that with increasing values of dimensionless sample loading time the separation of metals decreases, whereas with increasing number of extraction stages fewer cycles are required for metal separation. In the last case, increase in yield and purity of the separated metals is observed.

1. Introduction

Counter-current chromatography (CCC) is a liquid chromatography technique that uses two immiscible liquid phases without solid support. This technique combines the features of liquid-liquid extraction and partition chromatography [1]. Unlike to the classical chromatography, one liquid acts as the stationary phase and the other as the mobile phase. The so-called stationary phase is mobile, because is unfixed on the stationary solid support and it is held in place by gravity or centrifugal forces [1-3]. Intermittent dual (cyclic dual-mode) counter-current chromatography has been extensively studied [3, 4-9]. The cyclic dual-mode CCC separation consists of a succession of two isocratic counter-current steps and is carried out in series alternating between the upper and the lower phase flow periods [10-12]. In this case the processes of liquid chromatography are combined with counter-current extraction that allows developing novel high efficiency separation processes, which can be called dynamic counter-current extraction. Each cycle of such counter-current processes consists of two half-periods: 1 - a half-period of the flow of an initial solution (aqueous phase) and 2 - a half-period of the flow of an extractant (organic phase). Kostanyan et al. [13, 14] studied the cyclic mode process with variable duration of the periods of the phase flows. The sample dissolved in the aqueous phase is continuously fed into a CCC column at the beginning of the first half-period of every cycle over a constant time, not exceeding the run time of the first half-period. In conducting such a cyclic process, the phase flow in the extraction-chromatographic unit is repeatedly switched back and forth at given intervals to retain the solutes inside the column as long as a separation of the components is reached. Consequently, it increases the way of sample movement in the column, which increases the efficiency of the separation of components. To hold the sample in the column for a predetermined number of cycles a decrease in the duration of the flow of the phases is needed from cycle to cycle. In [14] equations were developed allowing the simulation of the chromatograms eluted from the column with the phases during each half-period of the cycles.

The aim of this study is to analyze the possibilities of using the calculation program for the separation of platinum metals by the dynamic counter-current extraction. Earlier the systems involving ionic liquids, which were called binary extractants (salts of organic acids with organic bases) for the extraction and separation of platinum metals have been examined [15, 16]. It has been found that binary extractant systems are characterized by reversibility of extraction and stripping processes because of the high thermodynamic stability of binary extractants in the heterogeneous systems [15]. For practical purposes, ionic liquids involving strong organic acids (for example, dinonylnaphthalene sulphonic acid) are of the most interest, since stripping processes in these systems can be performed by more simple way. At first, the distribution of platinum metal chlorides from 2 M HCl solutions with the ionic liquid such as methyltrioctylammonium dinonylnaphthalene sulphonate was investigated. The experimental data were used for calculation studies of separation of platinum metals by dynamic counter-current extraction.

2. Materials and Methods

2.1. Chemicals and Reagents

Dinonylnaphthalene sulphonic acid was obtained from Sigma-Aldrich and methyltrioctylammonium chloride was obtained from Acros Organics, and the extractants were used without further purification.

Solutions of ionic liquid (methyltrioctylammonium dinonylnaphthalene sulphonate) in toluene were employed as the extractants. Ionic liquid was prepared by dissolving equimolar amounts of methyltrioctylammonium chloride and dinonylnaphthalene sulphonic acid in toluene, followed by shaking the organic solution with an equal volume of 1 M NaOH solution for 10 min and followed by washing the organic phase with water [17].

Stock solutions of platinum metal chlorides were prepared by dissolving hydrated hydrogen hexachloroplatinate (IV) and palladium (II) chloride in 6 M HCl solution. Before experiments, platinum metal stock solutions were diluted by distilled water to the required concentration of the acid and metal. All chemicals used were of analytical grade.

2.2. Solvent Extraction Procedure

The metal extraction with equal volumes of the aqueous and organic phases was carried out at 20°C. Samples in test tubes with ground-in stoppers were shaken mechanically. The duration of phase mixing was 15 min, which was sufficient to establish the equilibrium values of the distribution coefficients of the platinum metals.

After separation of the layers, a suitable aliquot of the aqueous phase was analyzed by the corresponding method. The platinum metal concentrations in aqueous solutions were determined by the photometric methods with $SnCl_2$ for platinum, KI and Na_2SO_3 for palladium. The concentrations of metals in the organic phase were determined by the differences between the concentrations in the initial solutions and the aqueous phases after extraction.

Experimental data on the extraction of platinum metals from 2 M HCl solutions with solutions of methyltrioctylammonium dinonylnaphthalene sulphonate in toluene under various conditions are given in Table 1.

Table 1. *Experimental data on the extraction of platinum metals from 2 M HCl with solutions of methyltrioctylammonium dinonylnaphthalene sulphonate in toluene.*

Concentration of extractant, M	**Initial metal concentration, M**	**Distribution coefficients of metals, K_D**	
		Pt	**Pd**
0.025	0.003	2.07	1.15
0.01	0.003	0.52	0.28

3. Numerical Studies of Separation of Platinum Metals

To verify the possibility of using the calculation program [14] for metal separation numerical researches with using the experimental values of distribution coefficients of platinum metal chlorides in the ionic liquid system (Table 1) were carried out. The calculating machine is presented in the online version of the paper [14] and allows simulating distribution of solutes in the column after both steps (half periods) for any cycle and the chromatograms of solutes eluted from the column with both phases during each step and cycle for given elution periods. Using this program it is possible to calculate the retained (In) and eluted (Out) portions of each solute in the mixture to be separated for each cycle of the process. The numerical researches of separation of metal mixtures depending on various parameters were conducted. It was assumed that the process starts with feeding the first (aqueous) phase, which is a mixture of metal salts. The distribution coefficient (K_D) is the ratio of metal concentration in the organic phase to metal concentration in the aqueous phase. In calculations, following parameters such as values of extraction stages (N), the dimensionless sample loading time (t_s), variable values of dimensionless time of phase movements (t_x and t_y) to achieve the best possible separation of metal mixtures were set. It should be noted that after feeding a metal mixture in the first half period of one cycle at first the metal with less distribution coefficients is coming out of an extraction system and in the second half period of cycle the reverse order of output of metals is observed.

4. Results and Discussions

The results of numerical studies on the effect of dimensionless sample loading time, t_s, on the separation of platinum and palladium are presented in Fig. 1 and Table 2.

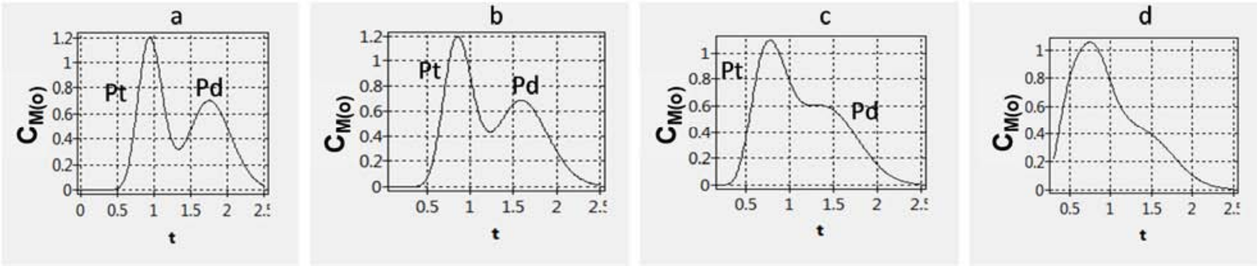

Figure 1. *Calculated chromatograms (organic phase) of the palladium and platinum mixtures separation ($K_{D(Pd)}$ = 0.28, $K_{D(Pt)}$ = 0.52) for the first cycle of counter-current process for different sample loading time (t_s: 0.01 (a), 0.1 (b), 0.2 (c), 0.3 (d) at N = 100, t_x = 0.5, t_y = 0.4).*

Table 2. *The calculation results of the separation of palladium and platinum by varying the values of dimensionless sample loading time for N = 100 ($K_{D(Pd)}$ = 0.28, $K_{D(Pt)}$ = 0.52).*

Cycle	t_x	t_y	t_s	Relative proportions of Pd and Pt							
				1 half period (aqueous phase)				2 half period (organic phase)			
				Pd		Pt		Pd		Pt	
				In	Out	In	Out	In	Out	In	Out
1	0.5	0.6	0.1	0.9926	0.0074	1	0	0.9926	0	0.9920	0.0079
2	0.12	1		0.9905	0.0021	0.992	0	0.9717	0.0188	0.0202	0.9718
		2.8						0	0.9717	0	0.0202
Yield, %									97.2		98.0
Purity, %									99.0		98.1
1	0.5	0.6	0.2	0.9926	0.0074	1	0	0.9926	0	0.9920	0.0079
2	0.15	1.1		0.9822	0.0104	0.992	0	0.9619	0.0203	0.0139	0.9781
		2.8						0	0.9619	0	0.0139
Yield, %									96.2		98.6
Purity, %									98.6		98.0
1	0.5	0.2	0.3	0.9994	0.0006	1	0	0.9994	0	0.9988	0.0012
2	0.11	0.25		0.9900	0.0094	0.9988	0	0.9900	0	0.9876	0.0111
3	0.08	0.8		0.9799	0.0101	0.9876	0	0.9405	0	0.2104	0.7712
4	0.08	0.4		0.9405	0	0.2104	0	0.8883	0.0523	0.0445	0.1659
		3						0	0.8883	0	0.0445
Yield, %									88.8		94.9
Purity, %									95.2		94.8
1	0.55	0.15	0.5	0.9963	0.0037	1	0	0.9842	0.0121	0.9380	0.0620
2	0.2	0.6		0.8396	0.1446	0.9270	0.0109	0.8296	0.01	0.7070	0.2201
3	0.3	1		0.5770	0.2526	0.6949	0.0121	0.5643	0.0127	0.2718	0.4231
4	0.5	1.7		0.1509	0.4134	0.2559	0.0159	0.1355	0.0155	0.0009	0.2550
5	0.8	1		0.0001	0.1354	0.0002	0.0007	0.0001	0	0.0002	0
Yield, %					94.5						96.0
Purity, %					96.0						95.0

Data presented in Fig. 1 and Table 2 indicate that with increasing values of dimensionless sample loading time the separation of metals significantly decreases. For example, at t_s equal to 0.01 (Table 2) Pd and Pt separation can be achieved producing Pd with a purity of 98.0% and Pt with a purity of 98.1% after two cycles of counter-current extraction process. With increasing the value of t_s to 0.5 the implementation of 5 cycles of counter-current process is required for satisfactory separation of metals with obtaining Pd and Pt of 96.0% and 95.0% purity respectively (Table 2). Unlike to previous separation conditions, in this case, the process proceeds with forming the aqueous phase containing palladium and the organic phase containing better extractable platinum.

The results of numerical studies on the separation of palladium and platinum at values of N equal to 50 and 30 and various values of t_s are shown in Tables 3 and 4. With N equal to 50 and a variation of t_s within 0.1-0.5 for the separation of palladium and platinum it is necessary to conduct four extraction cycles wherein the output of palladium proceeds with the aqueous phase and platinum with the organic phase (Table 3) as in the case of separation of these metals at N equal 100 and t_s equal to 0.5 (Table 2). For the separation of palladium and platinum at a value of N equal to 30 and t_s varying in the range of 0.01-0.4 it is also necessary to carry out 4-5 cycles of counter-current extraction process (Table 4). As it follows from Tables 2-4 increase in values of dimensionless sample loading time not only leads to a drop of the Pd and Pt separation, but generally to a decrease in yields of these metals.

Table 3. *The calculation results of the separation of palladium and platinum for N = 50 ($K_{D(Pd)} = 0.28$, $K_{D(Pt)} = 0.52$).*

Cycle	t_x	t_y	t_s	**Relative proportions of Pd and Pt**							
				1 half period (aqueous phase)				**2 half period (organic phase)**			
				Pd		**Pt**		**Pd**		**Pt**	
				In	**Out**	**In**	**Out**	**In**	**Out**	**In**	**Out**
1	0.48	0.4	0.1	0.9924	0.0076	0.9997	0.0003	0.9924	0	0.9894	0.0103
2	0.28	1		0.6384	0.3540	0.9688	0.0206	0.6352	0.0032	0.4501	0.5186
3	0.45	1.5		0.1659	0.4693	0.4285	0.0216	0.1548	0.0111	0.0227	0.4058
4	1	1		0	0.1548	0.0002	0.0225	0	0	0.0002	0
Yield, %					98.6						93.5
Purity, %					93.8						98.5
1	0.45	0.2	0.3	0.9992	0.0008	1	0	0.9975	0.0017	0.9737	0.0263
2	0.27	0.8		0.8240	0.1735	0.9556	0.0181	0.8156	0.0084	0.6179	0.3377
3	0.4	1.5		0.3540	0.4616	0.5868	0.0311	0.3125	0.0415	0.0280	0.5588
4	1	1		0	0.3125	0.0002	0.0277	0	0	0.0002	0
Yield, %					94.8						92.3
Purity, %					92.5						94.7
1	0.45	0.1	0.4	0.9994	0.0006	1	0	0.9891	0.0104	0.9593	0.0407
2	0.3	0.8		0.7577	0.2313	0.9098	0.0495	0.7463	0.0115	0.6342	0.2756
3	0.38	1.5		0.3867	0.3595	0.6006	0.0335	0.3282	0.0585	0.0294	0.5713
4	1	1		0	0.3282	0.0002	0.0029	0	0	0.0002	0
Yield, %					91.9						84.7
Purity, %					91.5						92.4
1	0.7	0.5	0.5	0.8514	0.1486	0.9640	0.0360	0.8390	0.0124	0.8216	0.1424
2	0.25	1		0.6386	0.2004	0.7941	0.0275	0.5914	0.0472	0.300	0.4941
3	0.5	1.6		0.1902	0.4012	0.2636	0.0364	0.1648	0.0254	0.0109	0.2527
4	0.8	1.5		0.001	0.1638	0.0024	0.0085	0.001	0	0.0006	0.0018
Yield, %					91.4						89.1
Purity, %					89.4						91.3

Table 4. *The calculation results of the separation of palladium and platinum for N = 30 ($K_{D(Pd)} = 0.28$, $K_{D(Pt)} = 0.52$).*

Cycle	t_x	t_y	t_s	**Relative proportions of Pd and Pt**							
				1 half period (aqueous phase)				**2 half period (organic phase)**			
				Pd		**Pt**		**Pd**		**Pt**	
				In	**Out**	**In**	**Out**	**In**	**Out**	**In**	**Out**
1	0.27	1	0.1	0.9877	0.0123	0.9988	0.0012	0.9874	0.0003	0.9851	0.0137
2	0.4	1.3		0.6412	0.3461	0.9294	0.0557	0.6259	0.0153	0.4563	0.4731
3	0.4	1.3		0.2973	0.3286	0.4313	0.0250	0.2719	0.0254	0.0764	0.3549
4	0.8	1.5		0.0030	0.2688	0.0160	0.0603	0.0029	0.0002	0.0042	0.0118
Yield, %					95.6						85.3
Purity, %					87.0						95.4
1	0.45	0.55	0.2	0.9937	0.0063	0.9994	0.0006	0.9611	0.0326	0.7057	0.2937
2	0.28	0.8		0.8301	0.1310	0.6984	0.0072	0.8016	0.0285	0.3481	0.3504
3	0.4	1.3		0.3941	0.4076	0.3268	0.0213	0.3555	0.0386	0.0576	0.2692
4	0.8	2		0.0042	0.3512	0.0121	0.0455	0.0027	0.0016	0.0002	0.0119
Yield, %					89.6						92.5
Purity, %					92.3						90.2
1	0. 5	0.35	0.4	0.9886	0.0114	0.9985	0.0015	0.9281	0.0604	0.7774	0.2211
2	0.27	0.7		0.7631	0.1650	0.7525	0.0249	0.7405	0.0226	0.5107	0.2418
3	0.4	1.2		0.3392	0.4013	0.4527	0.0580	0.3174	0.0218	0.1401	0.3126
4	0.5	1.5		0.1042	0.2132	0.1218	0.0183	0.0902	0.0140	0.0136	0.1082
5	0.8	2		0.0014	0.0888	0.0031	0.0105	0.0009	0.0005	0	0.0031
Yield, %					87.9						88.7
Purity, %					88.6						88.1

In the previous examples (Tables 2-4) the separation of metals with their low values of distribution coefficients was considered. In Table 5 the data for the separation of palladium and platinum when their distribution coefficients are significantly higher (Table 1) are given. The calculated data (Table 5) indicate that at N equal to 100 after 3 cycles of counter-current process 92.7% of platinum (93.0% purity) and 93.0% of palladium (92.8% purity) flow out the column successively in the second half period (organic phase). By using 150 extraction stages of the extraction, the separation of platinum and palladium with yields of these metals in the second half period (organic phase) equal to 93.0% (96.1% purity) for platinum and 96.2% (93.2% purity) for palladium is reached after 2 cycles of the counter-current extraction process. It can be concluded that with increasing number of the extraction stages fewer cycles are required, thus increasing the yield and purity of the separated metals.

Table 5. *The calculation results of the separation of palladium and platinum with high distribution coefficients ($K_{D(Pd)} = 1.15$, $K_{D(Pt)} = 2.07$; $t_s = 0.01$).*

Cycle	t_x	t_y	*N*	**Relative proportions of Pd and Pt**							
				1 half period (aqueous phase)				**2 half period (organic phase)**			
				Pd		**Pt**		**Pd**		**Pt**	
				In	**Out**	**In**	**Out**	**In**	**Out**	**In**	**Out**
1	0.26	0.11	100	1	0	1	0	0.9835	0.0165	0.6583	0.3417
2	0.2	0.13		0.9835	0	0.6583	0	0.9713	0.0122	0.3574	0.3009
3	0.21	0.19		0.9713	0	0.3574	0	0.9302	0.041	0.0725	0.2849
		1						0	0.9302	0	0.0725
Yield, %									93.0		92.7
Purity, %									92.8		93.0
1	0.27	0.12	150	1	0	1	0	0.9932	0.0068	0.6179	0.3821
2	0.27	0.22		0.9932	0	0.6179	0	0.9624	0.0308	0.070	0.5479
		1						0	0.9624	0	0.070
Yield, %									96.2		93.0
Purity, %									93.2		96.1

5. Conclusion

The results presented in this paper showed the possibility of the application of the calculation program for numerical researches for modeling of metal separation by the method of dynamic counter-current liquid-liquid extraction. Numerical researches with using the experimental data on metal distribution coefficients indicated that increase in values of dimensionless sample loading time leads to a drop of the metal separation, and with increasing a number of the extraction stages fewer cycles are required, thus increasing the yield and purity of the separated metals.

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