A Theoretical Consideration on Uranium Isotope Effects Observed in Chemical Uranium-235 Enrichment Processes *

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This paper is dedicated to Professor J. Bigeleisen on the occasion of his 70th birthday

Theoretical consideration on the uranium isotope effects in chemical chromatographic uranium isotope enrichment processes are presented, making use of up-to-date spectroscopic, solution chemical and separation factor data. It is shown that hydration of the uranyl (UO_2^{2+}) and uranous (U^{4+}) ions has a profound effect on the reduced partition function ratios (RPFR's) of these ions and that, in accordance with experiment, the RPFR of the uranous ion is larger than that of the uranyl ion. Future prospects concerning the separation factors in chemical processes are mentioned.

Key words: Chemical processes for uranium isotope enrichment, Uranium isotope effects, Reduced partition function ratio, Separation factor, Uranyl and uranous ions

Introduction

Chemical chromatographic processes for uranium isotope enrichment have a high nuclear proliferation resistance [1] and may become economically superior to the gaseous diffusion and gas centrifuge processes that are presently in operation [2].

Four kinds of chemical processes have been considered; **1** U(VI) (UO_2^{2+}; uranyl ion) complex formation [3], **2** U(IV) (U^{4+}; uranous ion) complex formation [4], **3** redox process between U(IV) and U(VI) [5], and **4** redox process between U(III) and U(IV) [6]. Processes **1**, **2** and **3** have been intensively studied by us and our colleagues. A pilot plant based on process **3** has been built by Asahi Chemical Industry Co. Process **4** has been developed in France [6].

Compared to the experimental and technological aspect of the chemical processes, theoretical elucidation of the uranium isotope effects on which they are based is underdeveloped. This is because the chemical and isotope exchange reactions occurring in these processes are very complicated and, in addition, spectroscopic and solution chemical data on the chemical species involved in those reactions are very limited.

Yet, there has been a steady accumulation of separation factor data, and spectroscopic and solution chemical studies on some uranyl and uranous species in aqueous systems have scatteringly been published in recent years.

In this paper, we discuss the fundamental uranium isotope effects that underlie Processes **1**, **2** and **3**, making use of the most up-to-data information on these processes.

Brief Description of the Chemical Processes

Uranyl Complex Formation

The uranium isotope separation effect in this process originates from the fact that the equilibrium constant, K, of the isotope exchange reactions expressed as

$$^{235}UO_2^{2+} + {}^{238}UO_2^{2+}L_n = {}^{238}UO_2^{2+} + {}^{235}UO_2^{2+}L_n \tag{1}$$

or more accurately as

$$^{235}UO_2^{2+}(H_2O)_m + {}^{238}UO_2^{2+}(H_2O)_{m'}L_n = {}^{238}UO_2^{2+}(H_2O)_m + {}^{235}UO_2^{2+}(H_2O)_{m'}L_n\,, \tag{1'}$$

is different from unity, where L is a ligand, n the number of ligands coordinating a uranyl ion, and m and m' are the hydration numbers of the uranyl ion and the uranyl complex, respectively. Ligands so far investi-

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gated are some halide ions and carboxylates. Although both anion [7] and cation [3] exchange resin systems have been studied, in this paper we limit our consideration to systems of strongly acidic cation exchange resins. This is because these systems are most extensively and most systematically studied among the systems utilizing uranyl complex formation.

In the strongly acidic cation exchange resin systems, $UO_2^{2+}L_n$ exists in the solution and UO_2^{2+} in the resin phase, both being hydrated. The uranyl ion in the resin phase can be well approximated by the uranyl ion in aqueous perchlorate solutions [3], that is, it is not ligand-coordinated. The experimental fact that the lighter isotope ^{235}U is enriched at the front of uranium adsorption bands in band displacement chromatography means that ^{235}U is preferentially fractionated into the complex species.

The relationship between K for reaction (1′), in which the symmetry numbers cancel each other, and the single stage separation factor, S, of a separating system based on (1′) can be stated, by a theory of the two phase distribution of isotopes [8], as follows. When only one species of uranyl complex exists in the solution phase and only the simple hydrated species in the resin phase, S is equal to K. The higher the concentration of the complex species in the resin phase and the higher the concentration of the simple hydrated species in the solution phase, the more deviates S from K and the closer to unity it is. Under the conditions of the experiments actually carried out, $S = K$ is a good approximation.

The S values so far obtained vary from 1.000025 for the chloride complex system to 1.000218 for the malate complex systems at 25 °C [3]. The temperature dependence of S in this process seems small at temperatures between 25 and 60 °C [9].

Uranous Complex Formation

Analogously to the uranyl process, the basic isotope exchange reaction in this process is expressed as

$$^{238}U^{4+} + {}^{235}U^{4+}L_q = {}^{235}U^{4+} + {}^{238}U^{4+}L_q \qquad (2)$$

or more accurately as

$$^{238}U^{4+}(H_2O)_p + {}^{235}U^{4+}(H_2O)_{p'}L_q = {}^{235}U^{4+}(H_2O)_p + {}^{238}U^{4+}(H_2O)_{p'}L_q\,, \qquad (2')$$

where q is the number of ligands coordinating a uranous ion and p and p' are the hydration numbers of the uranous ion and the uranous complex, respectively. Up to now, studies on strongly acidic cation exchange resin systems have only been reported in [4], and only three carboxylates and the sulfate ion have been used as ligands. In these systems, $U^{4+}L_q$ exists in the solution and U^{4+} in the resin phase, both being hydrated. The heavier isotope ^{238}U is enriched at the front of the uranium bands in band displacement chromatography, which means that ^{238}U is preferentially fractionated into the complex species. That is, K for the reaction (2′) is larger than unity. This tendency is just opposite to the tendency observed in the uranyl complex formation process.

The S value, which is $\leqslant K$ for reaction (2′) according to the two-phase distribution theory of isotopes [8], seems little affected by the kind of ligand. The temperature dependence of S, however, is very clear; for instance, for the uranous-lactic acid system, $S =$ 1.000120, 1.000082, 1.000067 and 1.000046 at 11, 30, 50 and 70 °C, respectively [4]. The q value in (2′) for this system is unkown (presumably 2). As for the p and p' values, see the next section.

Redox Process between Uranous and Uranyl Ions

This process makes use of the uranium isotope effect in the following isotope exchange reaction between the two different oxidation states of uranium,

$$^{235}U^{4+}L_q + {}^{238}UO_2^{2+}L_n = {}^{238}U^{4+}L_q + {}^{235}UO_2^{2+}L_n \qquad (3)$$

or

$$^{235}U^{4+}(H_2O)_{p'}L_q + {}^{238}UO_2^{2+}(H_2O)_{m'}L_n = {}^{238}U^{4+}(H_2O)_{p'}L_q + {}^{235}UO_2^{2+}(H_2O)_{m'}L_n\,. \qquad (3')$$

This isotope effect can be regarded as a combination of the effect in the pure redox reaction expressed by

$$^{235}U^{4+} + {}^{238}UO_2^{2+} = {}^{238}U^{4+} + {}^{235}UO_2^{2+} \qquad (4)$$

or

$$^{235}U^{4+}(H_2O)_p + {}^{238}UO_2^{2+}(H_2O)_m = {}^{238}U^{4+}(H_2O)_p + {}^{235}UO_2^{2+}(H_2O)_m \qquad (4')$$

and those in Reactions (1) and (2) (more accurately, (1′) and (2′)).

Both anion [5] and cation [10] exchange resin systems have been studied. In this paper, we consider only systems with anion exchange resins; they are closest to industrialization among the various chromatographic systems for ^{235}U enrichment [11].

In the anion exchange resin systems the ligand used by most of the authors is the chloride ion, the uranyl ions being preferentially adsorbed in the resin while the uranous ions stay in the solution, both being ligand-coordinated and hydrated. As for the uranium isotope fractionation, the lighter isotope ^{235}U is always enriched at rear parts of uranium bands, that is, ^{235}U is preferentially fractionated into the resin phase, and hence, ^{235}U is preferentially fractionated into uranyl ions and ^{238}U is preferentially fractionated into uranous ions.

The S value of this process seems affected by the chemical composition and the temperature of the system and is about 1.0007 or larger. Considering the marked difference in S values between this process and the uranyl and uranous complex formation processes, the uranium isotope separation effect of this process originates mostly from the fact that the K value of Reaction (4') is larger than unity. The isotope effects in (1') and (2') play subsidiary roles in the redox process. As for the temperature dependence of K for (3'), there are conflicting results. One study claims that the K in the systems of $L = Cl^-$ is little influenced by the temperature [12] while another says that it is temperature dependent [5]. Both agree that the K value is about 1.00138 at 25 °C. In this case, q and n in (3') are presumably both 4. As for the values of p' and m', see the next section.

The ranges of S values obtained so far in chemical chromatographic processes are summarized in Table 1.

Table 1. Separation factors, S, for uranium isotopes obtained in the chemical chromatographic processes for ^{235}U enrichment.

Process	Range of ln S value	Temp. °C	Comments
U(VI) complex formation	0.000025 ∼0.000218	25	^{235}U preferentially fractionated into complex species
U(IV) complex formation	0.000066 ∼0.000083	30	^{238}U preferentially fractionated into complex species
U(IV)-U(VI) redox	0.00067 ∼0.0014	30 ∼80	^{235}U preferentially fractionated into U(VI)

Estimation of the Isotopic Reduced Partition Function Ratios of Some Uranyl and Uranous Species in Aqueous Solution

In principle, the theoretical consideration of a chemical exchange isotope effect is reduced to the estimation of the isotopic reduced partition function ratios (RPFR), $(s/s')f$, of the chemical species involved in the isotope exchange reaction concerned [13]. For free molecules it can be calculated if all the frequency data of the species are available. The estimate of the RPFR of species in solution, however, is not easy since the interaction between the chemical species and its surroundings must be taken into consideration. In a first attempt ot explain the uranium isotope effect observed in the redox process between U(IV) and U(VI), Yato and Kakihana [14] considered unsuccessfully the hydration effect of the uranous ion in the calculation of the RPFR of the uranous ion in aqueous solution. However, a steady accumulation of separation factor data as well as spectroscopic and solution chemical data on the uranyl and uranous ions in aqueous systems has reached a point which makes it possible to estimate the RPFR's of some uranyl and uranous species under some reasonable assumptions.

In the following, we discuss the RPFR values of some forms of the uranyl and uranous ions in aqueous solutions.

Free Uranyl Ion (Hypothetical Uranyl Ion Isolated from its Surroundings)

Recently, all of the (three) uranyl mode frequencies were observed in aqueous solutions [15]. In a previous paper [16], we constructed the F matrices of UO_2^{2+} that best reproduce the observed frequencies. The $\ln(s/s')f$ value of UO_2^{2+} was calculated to be 0.001220 at 25 °C. The theoretically calculated S value for the chloride complex system [16] was much smaller than the value experimentally obtained [3]. It was thus shown that the consideration of the uranyl mode frequencies alone is quite insufficient to explain the observed uranium isotope effects in uranyl systems. This suggests that the hydration and ligand coordination effects have to be taken into consideration.

Hydrated Uranyl Ion

In ref. [17], we carried out the normal coordinate analysis of the hydrated uranyl ion assuming the hydration number $m = 5$, which seems most probable [18], assuming that 5 hydrating water molecules are symmetrically surrounding the uranyl ion on the equatorial plane [18], and regarding a hydrating water molecule as a point mass with the weight of 18.0153 (The U – O bond length is 177 pm and the $U-H_2O$ distance is 240 pm [17].). The value of the U – O stretching force constant obtained was 744.435 Nm^{-1} and was very close to 744.865 Nm^{-1} obtained for the hypothetical free uranyl ion [16]. Using the calculated frequencies of the ^{235}U and ^{238}U species, the $\ln(s/s')f$ value of $UO_2^{2+}(H_2O)_5$ was calculated to be 0.002003 at 25 °C. This value should be compared with 0.001220 for the hypothetical free uranyl ion. The large difference between the two values is due to the hydration and indicates that the hydration plays a very important role in the uranium isotope effect in aqueous systems involving the uranyl ion.

Uranyl Complexes

At present, the normal coordinate analysis of ligand-coordinated uranyl ions in aqueous solution is impossible because of lack of spectroscopic and structural data on these species. However, it is possible to estimate the RPFR values of a few uranyl complexes from the RPFR values of the hydrated uranyl ion and experimental S values. Experimental result that ^{235}U is preferentially enriched into the complex species shows that the RPFR of $UO_2^{2+}(H_2O)_m$ is larger than that of $UO_2^{2+}(H_2O)_mL_n$ in the case of the outer sphere complex formation or that it is larger than that of $UO_2^{2+}(H_2O)_{m-n}L_n$ in the case of the inner sphere complex formation. If the effects of the hydration and the outer sphere complex formation are additive, an assumption which is reasonable as a first approximation, the RPFR of $UO_2^{2+}(H_2O)_mL_n$ should be larger than that of $UO_2^{2+}(H_2O)_m$. The experimental fact that ^{235}U is enriched into the complex species means that the RPFR of the complex species is smaller than that of $UO_2^{2+}(H_2O)_m$, which is consistent with the formation of inner sphere complexes. This is also supported by a recent IR and ^{13}C-NMR spectroscopic study on some uranyl-carboxylate species [19]. Based on the above discussion and the two-phase isotope distribution theory [8], and using the RPFR value of $UO_2^{2+}(H_2O)_5$ and experimental separation factor data [3], the maximum RPFR values of the uranyl complexes are calculated for several uranyl complex formation systems at 25 °C and are listed in Table 2.

Table 2. Maximum $\ln(s/s')f$ values of some uranyl complexes in aqueous solution at 25 °C.

Uranyl complex system	$\ln(s/s')f$
uranyl chloride	0.001978
uranyl acetate	0.001915
uranyl lactate	0.001861
uranyl citrate	0.001823
uranyl malate	0.001785

Hydrated Uranous Ion and Uranous Complexes

Very little is known about the uranous species in aqueous solution. The hydration number of the uranous ion in aqueous solutions is said to be $p=8$ [20]. Not a single frequency datum is reported for this species, and consequently neither the normal coordinate analysis is possible nor the simplifying formula for the RPFR calculations [13] can be used. The experimental facts that ^{238}U is enriched into the complex species and that the separation factors obtained in uranous complex formation systems are rather small and seem to be independent of the kind of ligand [4] appear to be consistent with the formation of the outer sphere complexes. An X-ray investigation of an aqueous uranous perchlorate solution [20] showed that the perchlorate groups do not enter the inner coordination sphere but seem to form outer sphere complexes.

As was briefly mentioned for uranyl complexes, the RPFR of an outer sphere complex of the uranous ion may be divided into two parts; one is that of the hydrated uranous ion and the other one is due to the effect of ligand coordination to the hydrated uranous ion. Thus, denoting the RPFR of the hydrated uranous ion as $(s/s')f_{4h}$ and the RPFR change due to the coordination effect as Δf_{4c-4h}, the RPFR of the uranous complex, $(s/s')f_{4c}$, is related to $(s/s')f_{4h}$ and Δf_{4c-4h} by

$$\ln(s/s')f_{4c} = \ln(s/s')f_{4h} + \ln \Delta f_{4c-4h}\,. \tag{5}$$

Δf_{4c-4h} is nothing but the separation factor, S, in uranous systems (more accurately, K for (2′) with $p'=p$).

It is possible to estimate the RPFR values of the hydrated uranous ion and uranous complexes from the separation factor data of uranous-uranyl redox systems (more accurately, the K values for (3′) and (4′)), the RPFR value of the uranyl complex, $UO_2^{2+}(H_2O)_{5-n}L_n$, and the separation factor values of the uranous systems. Let the K for (3′) with $L=Cl^-$ be K_{4-6} and the RPFR of the $UO_2^{2+}(H_2O)_{5-n}L_n$ be $(s/s')f_{6c}$. Then the RPFR of the uranous complex

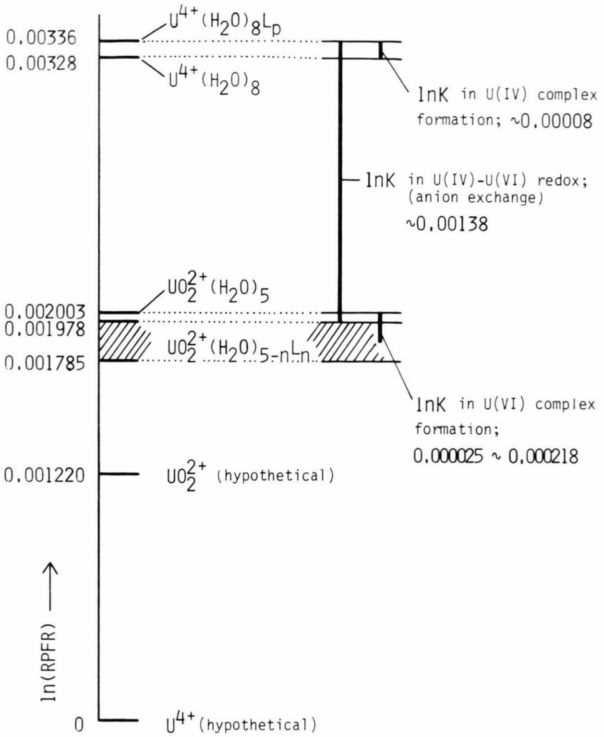

Fig. 1. Schematic relationship among the RPFR's of uranous and uranyl species in aqueous systems.

($(s/s')\,f_{4c}$) is related to K_{4-6} and $(s/s')\,f_{6c}$ by the equation

$$\ln (s/s')\,f_{4c} = \ln K_{4-6} + \ln (s/s')\,f_{6c}. \qquad (6)$$

Thus, at 25 °C, the ln (RPFR) value of the uranous complex is $\ln (s/s')\,f_{4c} = 0.00138 + 0.001978 = 0.00336$, in which 0.001978 is for the Cl^- complex of uranyl ion from Table 2. Then, from (5) and the experimental result that the S value in the uranous process seems ligand-independent, the ln (RFPR) value of the hydrated uranous ion is $\ln (s/s')\,f_{4h} = 0.00336 - 0.00008 = 0.00328$ at 25 °C (see Table 1 for the value of 0.00008).

Relationship among the RPFR's of Uranous and Uranyl Species in Aqueous Systems

As a summary of this section, a schematic presentation of the relationship among the RPFR's of uranous and uranyl species in aqueous systems at 25 °C is given in Figure 1. In any combination of two species, the heavier isotope ^{238}U is always enriched in the species whose RPFR value is larger. The equilibrium constant of the uranium isotope exchange reaction of a system involving the two species is given as the ratio of the RPFR's of the two species. Thus, it is seen that the direction of the uranium isotope effect in the uranyl complex formation process is just opposite to that of the uranous complex formation process; the lighter isotope ^{235}U is enriched in the complex species in the uranyl process while the same isotope is enriched in the simple hydrated species in the uranous process. Also it is easily understood from the Figure that the separation factors of the U(IV)-U(VI) redox systems using the anion exchange [cf. (3')] are larger than the separation factors of the U(IV)-U(VI) redox systems using the cation exchange [cf. (4')].

The average ln (RPFR) increase per water molecule added in the case of the hydrated uranous ion is $0.00328/8 = 0.00041$, which is much larger than that for the case of the hydrated uranyl ion ($(0.002003 - 0.001220)/5 = 0.00016$). However, if one considers that the uranous ion is coordinated by hydrating water molecules more tightly than the uranyl ion is due to the high ionic charge (4+) and the small ionic volume of the former ion [21] compared with those of the latter, this large increase is not unreasonable.

Separation Factors: Present Status and Future Prospect

In terms of the separation factors that so far have been obtained experimentally, the redox process between U(IV) and U(VI) is by far the best, the uranous complex formation process is the least favorable and the uranyl complex formation process is in between. This is why the uranous-uranyl redox process is being most intensively and most extensively investigated for the purpose of the industrial production of fuel-grade uranium [11].

Confining our attention to separation factors, we will discuss the present status and future prospect of each uranium isotope enrichment process in the following. Theoretically, separation factors can be estimated when knowing the involved RPFR values [13] and the isotope distribution between two phases [8].

Uranyl Complex Formation Process

In Table 3 we summarize the effect of the number of atoms in a chelate ring on the separation factor observed in some uranyl-carboxylate systems using strongly acidic cation exchange resins. Separation factor data have been taken from [3] and the structure of

Table 3. Separation factors, S, obtained in the uranyl complex formation process at 25 °C and the effect of chelate ring size on S value.

Ligand	ln S	Average experimental uranium isotope effect per			
		one $UO_2 \cdots O$ bond	one 4-membered chelate ring	one 5-membered chelate ring	two fused 5- and 6-membered chelate rings
acetate	0.000088	0.000022	0.000044	–	–
glycolate	0.000103	0.000026	–	0.000052	–
lactate	0.000142	0.000036	–	0.000071	–
malate	0.000218	0.000054	–	–	0.000109

each carboxylate species is taken from [19]. From the very limited data in this table we may extract the trend that the larger the number of atoms in a ring, the larger the separation factor, and that when the structural arrangements and the potential energies are similar around the coordination site (cf. glycolate and lactate), the heavier or bulkier ligand gives the larger separation factor. The former is explainable by reasonably assuming that the larger chelate ring expels a larger number of water molecules from the hydration sphere around the uranyl ion, thus enhancing the difference in RPFR value between the simple hydrated uranyl ion and the uranyl complex. The latter is attributable to two effects. One is the kinetic energy difference between the $-C-CH_3$ moiety in the lactate and the $-CH_2$ group in the glycolate. However, this effect is too small to explain alone the large isotope separation effect for the uranyl-lactate system as compared with that for uranyl-glycolate system. Consequently, the second trend will be mostly due to the other effect, i.e., due to the difference in the two-phase distribution of isotopes [8] between the two systems; more glycolate complex will be in the resin phase than lactate complex.

To sum up, one can expect a larger separation factor by introducing larger and/or heavier functional groups into the ligand that forms a larger chelate ring with the uranyl ion, unless other effects such as steric effect set in. The above discussion is limited to carboxylate complexes, to which most works so far have been directed. In uranyl-carboxylate systems, the uranium isotope effect comes basically from the difference between the U – O (O in H_2O) bond and U – O (O in COO^-) bond, anyway. Thus, in spite of the above discussion, one may not expect a substantial increase in separation factor value as long as one sticks to carboxylates or other ligands that coordinate the uranyl ion through their oxygens.

Studies of the uranyl complex formation process are still very limited, and many fundamental studies have to be done before discussing its application to industrial-scale uranium isotope enrichment.

Uranous Complex Formation Process

Due to the quite large RPFR value of the hydrated uranous ion, the uranous complex formation process has potentially high separation factors, although in reality only the smallest separation factors are obtained among the three processes. This means that it is extremely difficult to deprive hydrating water molecules of the uranous ion due to the strong $U-H_2O$ bond, and that in the experiments so far carried out, the structure of the hydration sphere around the uranous ion has been little affected by ligand coordination. However, if one *does* strip the hydrating water molecules of the uranous ion in some way, then one can expect a larger separation factor in the uranous process, and in that case the heavier isotope ^{238}U will preferentially be fractionated into the hydrated uranous ion and ^{235}U will be enriched in the dehydrated species.

Redox Process between Uranous and Uranyl Ions

For this process, one can not expect a substantial increase in separation factor, since the uranium isotope separation effect in this process depends mostly on the uranium isotope effect in the uranous-uranyl redox reaction and subsidiary isotope effects of uranous and uranyl complex formations are small compared to that of the redox reaction. Thus, different systems that differ from each other in the kind of ligands will show similar separation factors at a given temperature. Improvement of distribution of uranyl and uranous species between the resin and external solution phases [8] by introducing a new and improved ion exchange resin and/or changing the chemical composition of the solution phase may moderately increase the separation factor.

Conclusion

In this paper, as an effort toward the theoretical elucidation of the uranium isotope effects observed in aqueous systems, we attempted to estimate the ^{238}U-to-^{235}U isotopic reduced partition function ratios of some forms of uranyl and uranous ions in aqueous solution, and we believe that we were able to achieve the purpose to some extent.

The $\ln(s/s')f$ values of the hydrated uranyl and uranous ions are 0.002003 and 0.00328, respectively, both at 25 °C. These values are considerably larger than the $\ln(s/s')f$ values of uranyl and uranous ions calculated without consideration of hydration. Thus, hydration of the uranyl and uranous ions has a profound effect on the uranium isotope effects in aqueous uranium systems.

From a limited number of data on the uranyl complex formation process it is concluded that a larger chelate ring gives a larger separation factor. The uranous process has potentially larger separation factors due to the large RPFR value of the hydrated uranous ion. At present the redox process between U(IV)-U(VI), which is closest to industrialization among the three chemical chromatographic processes, shows the largest separation factor.

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