

SEPARATION OF NONAROMATIC C₆ COMPOUNDS FROM NAPHTHA CRACKING RAFFINATE BY ADDUCTIVE CRYSTALLIZATION

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The separation of the nonaromatic raffinate found in naphtha crackers was studied using adductive crystallization with thiourea. Experimental results of the separation of cyclohexane from nonaromatic raffinate and on the separation capacity of three binary mixtures—methyl cyclopentane(MCP)-cyclohexane, MCP-*n*-hexane and cyclohexane-*n*-hexane—are presented in this study. Structure, habit and shape of adduct crystals were investigated to examine the adduction mechanism by SEM and X-ray diffraction. Separation factors as high as 92 and extent of separation up to 0.78 were observed for one adduction stage, and the separation by one stage is approximately 5.6 to 19.2 times greater than the maximum separation that could be obtained by one theoretical distillation stage. The tendency for adduction in thiourea was found to be cyclohexane > MCP >> *n*-hexane. Cyclohexane of a purity of 99.9 wt.% was obtained by 4-stage adductions from nonaromatic raffinate.

Introduction and Background

The separation of hydrocarbons from its isomers or multicomponent mixtures with close boiling points is a challenging task in the chemical industry. Although crystallization holds a number of advantages such as low thermal loads and high theoretical degrees of separation over other separation techniques, the yield of pure components from ordinary crystallization processes is limited by the eutectic, the molecular compound, and the low-melting impurities. Problems posed by such mixtures can be solved by adductive crystallization techniques. Thiourea ad-

ducts are a class of nonstoichiometric compounds in which guest molecules are trapped in two-dimensional channels formed by the thiourea molecules. Detailed reviews of this technique have been given by many authors^{5,12,13,14}. The adduct crystals form only in the presence of suitable guest compounds. Host compounds used in adductive crystallization are urea, thiourea, Werner complex, cyclodextrin, etc. They are selected by the restriction on shape and in some cases on polarity of the guests¹³. The best used adduct compounds are those of urea and thiourea. Urea forms adducts with straight-chain paraffins¹², but thiourea forms adducts with branched-chain paraffins or naphthenic hydrocarbon since the cage diameters of urea and thiourea are about 5.1 Å and 6.5 Å,

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respectively. The nonaromatic raffinate is a byproduct of ethylene production by naphtha cracking, and its production is about 0.14 tons per ton of ethylene production. This mixture is constituted of various kinds of naphthens, normal paraffins and isoparaffins, in which industrially useful components such as cyclohexane and methyl cyclopentane (MCP) are contained. Nonaromatic raffinate is composed of about 74 wt.% of C_6 nonaromatic hydrocarbons, about 16.8 wt.% of C_7 nonaromatic hydrocarbons, about 6.1 wt.% of C_8 nonaromatic hydrocarbons and about 2.1 wt.% of C_9 nonaromatic hydrocarbons.

Nonaromatic compounds heavier than C_6 nonaromatic hydrocarbons are easily eliminated from nonaromatic raffinate by distillation. But C_6 nonaromatic hydrocarbons cannot be economically separated by distillation or other conventional methods, as can be seen in the cyclohexane production plant, because of the closeness of physical properties of these components. Cyclohexane and MCP are separated by distillation from C_6 nonaromatic hydrocarbons as the following two streams: a cyclohexane-rich stream containing several impurities of which MCP is present in highest concentration (23.5 wt.%) and an MCP-rich stream containing *n*-hexane (17.8 wt.%) as a major impurity.

Therefore, the purpose of this study is to investigate the separation of cyclohexane and MCP from nonaromatic raffinate by an adductive crystallization technique using thiourea. In all cases, spectacular separations can be obtained compared with distillation.

1. Experimental

1.1 Materials and analysis

Methanol of a purity of 98.0 vol%, supplied by Waco Pure Chemical Ind. Co., Ltd., thiourea of a purity of 98.5 vol%, supplied by Fisher Scientific Co., and 1,2,4-trichlorobenzene (1,2,4-TCB) and CCl_4 , supplied by Junsei Kagaku Co., Ltd., were used as solvent, host molecule, and inductors, respectively.

Crystal structures were analyzed by X-ray diffraction measurement. The shape and habit change of the crystal were observed by SEM and optical microscope. Guest molecules in the residue and adduct were quantitatively analyzed by gas chromatography (Shimadzu GC-8A). Analysis was accomplished using a $30\text{ M} \times 0.53\text{ mm}$ capillary column (RSL-300) with the flame ionization detector at 40°C . Analysis of CCl_4 content was done using the same type of column with a thermal conductivity detector.

1.2 Apparatus and method

Figure 1 shows a schematic drawing of the crystallization apparatus used in this study. The crystallizer is placed, by means of a ground-glass joint, inside a triple-jacketed vessel. The outer one is under

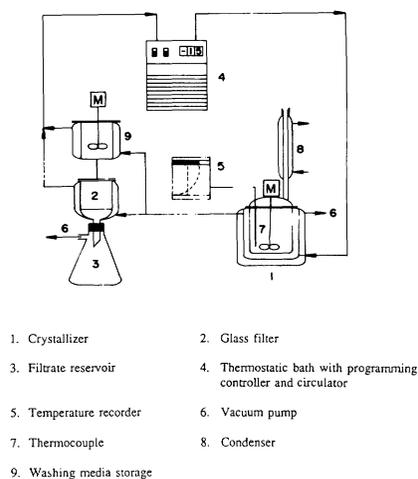


Fig. 1. Schematic diagram of experimental apparatus

vacuum and provides thermal insulation to allow visual observation of the mixtures. Through the middle passage, cooling and heating media are circulated from a refrigerated thermostat bath connected with an electrical heater and a controller (Eurotherm 808) with a control accuracy of 0.05 K. Mechanical agitation was provided by a turbine-type stainless steel impeller (38 mm diameter).

Experiments were carried out at optimum conditions of solvent ratio, feed ratio and crystallization temperature as established in a previous study⁶⁾ at this laboratory. In that study a temperature of -15.4°C , a thiourea-to-feed ratio of 0.94, a solvent-to-thiourea ratio of 2.73 and a cooling rate of $0.23^\circ\text{C}/\text{min}$ were chosen for the other separation test. This solvent-to-thiourea ratio results in a near-saturated solution at the boiling point of the mixture, and the thiourea-to-feed ratio chosen represents a compromise between more adduct formation and decreasing selectivity. All the experimental work was performed in a batch-operated and well-mixed cooling crystallizer. For a typical batch run 100 g of thiourea, 420 ml of methanol and 90 g of hydrocarbon mixture of varying composition were used to form the adducts. Initial and final temperatures of the crystallizer were set at 64.2°C and -15.4°C , respectively. The cooling rate of the crystallizer was set at $0.23^\circ\text{C}/\text{min}$ and the agitation rate was 400–500 rpm. Adducts are formed by mixing the feed (hydrocarbon mixtures) with thiourea solution saturated in methanol and then cooling. The feed was added dropwise to the saturated thiourea solution so that homogeneity was obtained. The adducts were separated from the nonadducted portion by filtration, the temperature of which was maintained equal to that of crystallization, and washed with 400 cc of *n*-pentane allowed to remain -15.4°C .

The adduct crystals were allowed to dry for approximately 12 hrs at 30°C before being dissolved

by adding hot water. The two phases obtained separated in a separating funnel. The nonadducted hydrocarbon is also liberated from the filtrate by the addition of water followed by phase separation.

2. Separation index

The extent of separation, ξ , defined as Eq. (1) by Rony,¹¹⁾ is an excellent indicator of the quantitative amount of separation being obtained from an equilibrium stage.

This index was used to characterize the separation capacity obtained by the adductive crystallization process. Assuming component 1 is the species selectively trapped in the adduct, the extent of separation is defined by

$$\xi = \text{abs} \left[\frac{1}{1 + K_1} - \frac{1}{1 + K_2} \right] \quad (1)$$

where the distribution ratio for compounds 1 and 2 is defined as

$$K_1 = (R/A)(x_1/y_1), \quad K_2 = (R/A)(x_2/y_2)$$

(R/A) is the ratio of the amount of hydrocarbons left in the residue to the amount trapped in adduct, and y and x are the mole fractions of the materials selectively trapped in the adduct and residue, respectively.

ξ varies between 0 (no separation) and 1 (perfect separation). The separation factor, α , which is closely analogous to relative volatility in distillation, is given by Eq. (2).

$$\alpha = \frac{K_2}{K_1} = \frac{y_1(1-x_1)}{x_1(1-y_1)} \quad (2)$$

This separation index was also used to compare adductive crystallization with distillation for some binary mixtures.

3. Results and Discussion

3.1 Preliminary test

Table 1 presents the approximate composition and physical properties of C_6 nonaromatic hydrocarbon which is obtained by elimination of nonaromatic compounds above C_7 from nonaromatic raffinate.

Separation by multistage thiourea adduction was investigated as a preliminary test using C_6 nonaromatic hydrocarbons as the feed shown in Table 1.

A feed with the approximate composition of the nonaromatics in naphtha raffinate was mixed with the thiourea solution saturated in the methanol. One-stage adduction was performed with 90 g of feed, 100 g of thiourea and 420 ml of methanol. Feed to each stage was the hydrocarbon entrapped in the adduct obtained in the previous stage.

The results of the preliminary test are shown in Table 2. As can be seen, MCP and cyclohexane are trapped significantly in thiourea as compared with 2-methylpentane (2-MP), 3-methylpentane (3-MP), *n*-hexane and *n*-heptane. Cyclohexane of a purity of 99.8 wt.% can be got by four successive adduction stages, and the major impurity was found to be MCP. On the other hand, to determine the effect of the inductor on separation capacity, the same experiments were performed using CCl_4 and 1,2,4-TCB as inductors, which had been introduced by McCandless⁹⁾. 85 g of inductor (CCl_4 or 1,2,4-TCB) was added to 90 g of the nonaromatic raffinate to enhance the selectivity. The results of the preliminary test by adductive crystallization using inductors are shown in Table 3.

As can be seen, cyclohexane of a purity of 99.9 wt.% is obtained with CCl_4 , while cyclohexane of a purity of 97.8 wt.% is obtained with 1,2,4-TCB in four successive adductions.

Table 1. Composition and physical properties of C_6 in nonaromatic raffinate stream

Compound	Composition (wt.%)	Normal BP (°C)	Normal FP (°C)
2-Methylpentane	19.0	60.3	-153.7
3-Methylpentane	5.8	63.3	—
<i>n</i> -Hexane	19.4	69.0	-95
Methylcyclopentane	37.8	71.8	-142.2
Cyclohexane	11.3	80.7	6.5
<i>n</i> -Heptane	5.5	98.4	-90.6
Others	0.6		

Total: 75% of nonaromatic raffinate.
Others: C_7 ; 16.8 wt.%, C_8 ; 6.1 wt.%, C_9 ; 2.1 wt.%.

Table 2. Multistage separation of nonaromatic raffinate by adductive crystallization with thiourea: 100 g of thiourea, 420 ml of methanol, 90 g of nonaromatics

Stage	Adduct composition							Yield (Cyclohexane (g) of adduct) Cyclohexane (g) of feed)
	2-MP	3-MP	<i>n</i> -Hexane	MCP	Cyclohexane	<i>n</i> -Heptane	Others	
1	1.45	0.34	1.0	20.5	75.4	0.8	0.5	0.440
2	0.4	0.0	0.1	9.6	89.7	0.0	0.2	0.432
3	0.0	0.0	0.0	1.3	98.7	0.0	trace	0.412
4	0.0	0.0	0.0	0.2	99.8	0.0	0.0	0.403

Table 3. Multistage separation of nonaromatic raffinate by adductive crystallization with thiourea and inductors; 100 g of thiourea, 420 ml of methanol, 90 g of nonaromatics, 84 g of inductor (CCl₄ or 1,2,4-TCB)
Inductor: CCl₄

Stage	Adduct composition							Yield (Cyclohexane (g) of adduct) Cyclohexane (g) of feed)
	2-MP	3-MP	<i>n</i> -Hexane	MCP	Cyclohexane	<i>n</i> -Heptane	Others	
1	1.20	0.35	0.9	18.7	78.2	0.4	0.3	0.452
2	0.1	0.0	0.0	5.2	94.6	0.0	0.2	0.433
3	0.0	0.0	0.0	0.7	99.3	0.0	0.0	0.412
4	0.0	0.0	0.0	0.01	99.9	0.0	0.0	0.408

Inductor: 1,2,4-TCB

Stage	Adduct composition							Yield (Cyclohexane (g) of adduct) Cyclohexane (g) of feed)
	2-MP	3-MP	<i>n</i> -Hexane	MCP	Cyclohexane	<i>n</i> -Heptane	Others	
1	2.2	0.9	0.8	21.3	74.1	0.3	0.4	0.433
2	0.3	0.0	0.0	12.6	87.0	0.0	0.1	0.421
3	0.0	0.0	0.0	4.2	95.8	0.0	trace	0.418
4	0.0	0.0	0.0	2.2	97.8	0.0	0.0	0.398

For these mixtures, adduct formation was very fast, requiring only a few seconds to obtain equilibrium. This compares with 2 to 24 hrs required to establish equilibrium for other systems using immiscible condition⁹). In these cases of slow adduction the crystallization rate appeared to be marked by a slow mass-transfer process such as diffusion within a solid, slow dissolution of solid thiourea or heterogeneous transport.

The fast adduction exposed in this study suggests that to mix rapidly the reactant, thiourea and hydrocarbon in a polar solvent minimizes mass transfer effects by dissolving them.

Inspection of the crystallized solids by microscope to show long, needlelike crystals confirmed adduct formation, and the crystal size increased as the temperature was reduced.

3.2 MCP-cyclohexane system

From the preliminary test of thiourea adduction it was concluded that the purity of cyclohexane was limited by trapping of MCP in thiourea. The difference in boiling point between these components is about 9°C. It is therefore obvious that a separation by fractional distillation can be performed. However, when it is desirable to recover either of the two components in a high degree of purity (above 97%), rather expensive and complicated fractional distillation will be necessary¹¹.

On the other hand, this mixture cannot be separated economically by melt crystallization because the mixture forms a solid solution³). Based on these results, further tests were made with cyclohexane-MCP binary mixture using CCl₄ and 1,2,4-TCB as inductors and also without inductor to determine the

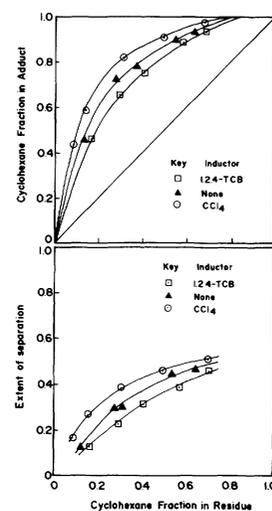


Fig. 2. Phase equilibrium and extent of separation for MCP-cyclohexane mixture

separation capacity of thiourea adduction. The binary separations were evaluated by the extent of separation and the separation factor presented in Eqs. (1) and (2), respectively.

Figure 2 shows the equilibrium and the extent of separation for binary mixtures of cyclohexane and MCP when using inductors and without their use.

In comparison of the separation factors obtained using inductors with those obtained without inductors for this system, CCl₄ has been shown to improve the selectivity of cyclohexane for thiourea adduction, while 1,2,4-TCB does not.

This suggests that CCl₄ is apt to be selective for cyclohexane and 1,2,4-TCB is apt to be selective for MCP. The average value of α was found to be 7.1 and

9.2 with 1,2,4-TCB and CCl_4 as inductors, respectively, and to be 7.9 without inductor.

Moreover, the extent of separation varied from 0.27 to 0.51 for CCl_4 , 0.13 to 0.46 without inductor, and 0.21 to 0.45 for 1,2,4-TCB.

Consequently, the tendency for adduction of cyclohexane in thiourea is found to be $\text{CCl}_4 >$ without inductor $>$ 1,2,4-TCB.

It is certain that inductors have an important effect upon the selectivity of thiourea adduction, but the mechanism is not understood. Probably, the inductor selectivity is related to the difference in the phase diagram between the inductor and guest.

3.3 MCP-*n*-hexane system

In the MCP-rich stream of the separation process for C_6 nonaromatic hydrocarbons, MCP is not separated in technical grade despite 120 stages of distillation column at a reflux ratio of 25:1, because of *n*-hexane.

But the thiourea adduction technique can be applied to the separation of MCP from MCP-*n*-hexane mixture effectively. Figure 3 shows the equilibrium MCP and the extent of separation for the binary mixture of MCP-*n*-hexane.

From the results depicted in Fig. 3, the average value of α was determined as 52 and the extent of separation was from 0.3 to 0.46. As can be seen in Fig. 3, thiourea adduction seems to be a promising method of separating MCP from MCP-*n*-hexane mixture.

These results suggest that the selectivity of thiourea is in some way based on molecular shape or size in the same order as the tendency for adduction, which can be expected from the difference in molecular size of these hydrocarbons¹³.

3.4 Cyclohexane-*n*-hexane system

Figure 4 presents the equilibrium and the extent of separation for the cyclohexane-*n*-hexane system. From Eqs. (1) and (2), the average value of α is determined to be 92 and the extent of separation varies from 0.58 to 0.78. As can be seen in Fig. 4, thiourea has a high selectivity for cyclohexane in these mixtures. Comparison of Fig. 3 with Fig. 4 suggests that the extent of separation of cyclohexane in thiourea is larger than that of MCP. Therefore, the tendency for thiourea adduction is found to be cyclohexane $>$ MCP \gg *n*-hexane.

Data determined experimentally show that the tendency for adduction is in the order cyclohexane $>$ MCP \gg branch-chain paraffin (2-MP, 3-MP) $>$ straight-chain paraffin (*n*-hexane, *n*-heptane). Naphthenic constituents can be removed from both straight-chain paraffins and branch-chain paraffins by thiourea adduction.

This coincides well with results reported by other workers for cyclohexane derivatives²⁾ and xylenes⁸⁾,

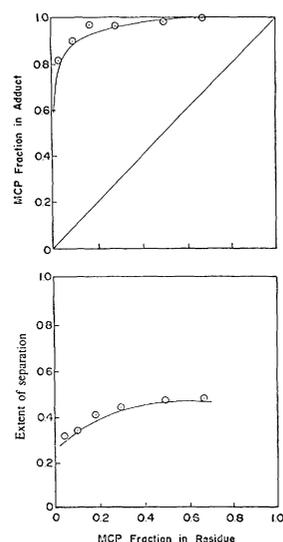


Fig. 3. Phase equilibrium and extent of separation for MCP-*n*-hexane mixture

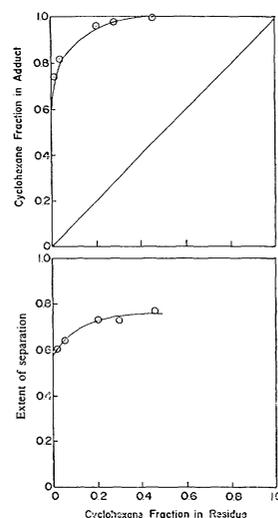


Fig. 4. Phase equilibrium and extent of separation for cyclohexane-*n*-hexane mixture

together with the study of molecular models of the different components, and suggests that the selectivity is based on molecular size.

McCandless⁷⁾ has suggested that electronic configuration, van der Waals force or hydrogen bonding must also be important factors.

Extensive research beyond the scope of this study would be required to examine further the basis for selectivity.

Table 4 compares some of the separation factors and the extent of separation obtained using adductive crystallization with relative volatility and the maximum extent of separation that is possible by distillation on one equilibrium plate at total reflux. The maximum extent of separation for one equilibrium stage is given as Eq. (3) by Rony¹¹⁾.

Table 4. Comparison of adductive crystallization with distillation

System	Inductor	α adduct	ξ adduct	α dist.	ξ_{\max} dist.	$\frac{\xi \text{ adduct}}{\xi \text{ dist.}}$
MCP-cyclohexane	CCl ₄	9.2	0.5	1.38	0.080	6.25
MCP-cyclohexane	1,2,4-TCB	7.1	0.45	1.38	0.080	5.63
MCP-cyclohexane	None	7.9	0.47	1.38	0.080	5.88
MCP- <i>n</i> -hexane	None	52.0	0.46	1.10	0.024	19.17
Cyclohexane- <i>n</i> -hexane	None	92.0	0.78	1.52	0.103	7.57

$$\xi_{\max} = \frac{\alpha^{1/2} - 1}{\alpha^{1/2} + 1} \quad (3)$$

As can be seen, the separation factor is much higher for separation by adductive crystallization than by distillation in all systems investigated in this study. Also, the separation obtained from one adduction stage is approximately 6 to 20 times greater than the maximum separation that could be obtained by one theoretical distillation stage.

Both the extent of separation and the amount of hydrocarbon included in the adduct increases in the order of increasing selectivity, as would be expected.

3.5 Structure of the adduct crystals

A further study was made in solving the problem that the mechanism for selectivity and the base for adduct stability of thiourea are still questionable.

It is reported that hydrogen bonds between the methyl group of guest and sulfur and N-H groups of the host thiourea may be important in adduct formation¹⁰.

Habits of thiourea with adduct and without adduct are extremely different, as shown in Fig. 5. The crystal of thiourea with adduct is needlelike, while that of thiourea without adduct shows a hexahedral shape.

This supports Hart's conclusion⁴) that the adduct and nonadduct complexes have different crystal structures. The X-ray diffraction patterns with adduct and without adduct are given in Fig. 6. The two patterns in this figure show a little different form. This means that when thiourea adduction with hydrocarbon occurs, a small change in crystal structures occurs. The lattice parameter calculated by computer program (KRICT software) from X-ray diffraction results for thiourea with adduct and for thiourea without adduct are shown in Table 5.

As shown in this table, it appears that the lattice parameters of thiourea adduct increase about 0.08% for a-axis, 0.04% for b-axis and 0.02% for c-axis owing to the adduction of hydrocarbon; thus the variation of lattice parameters for this systems can be neglected.

It is therefore concluded that the selectivity of thiourea is related not only to the interaction between host of thiourea and guest molecule (thus the stronger the host having interaction with hydrocarbon, the better is the adduct formation) but also to habit change

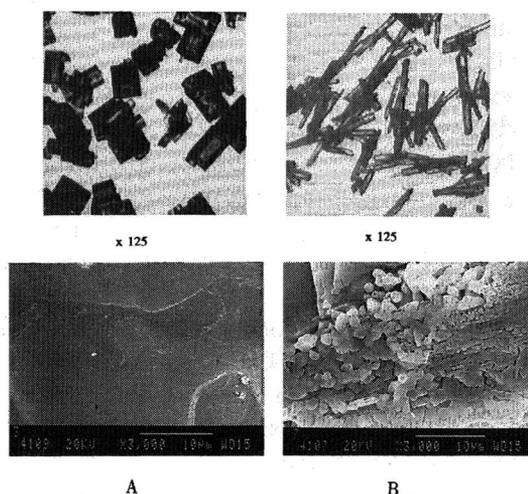


Fig. 5. SEM and microscopic photographs of samples A and B

A: Only thiourea was crystallized in methanol solution without hydrocarbon.

B: Adduct of thiourea and hydrocarbon is formed.

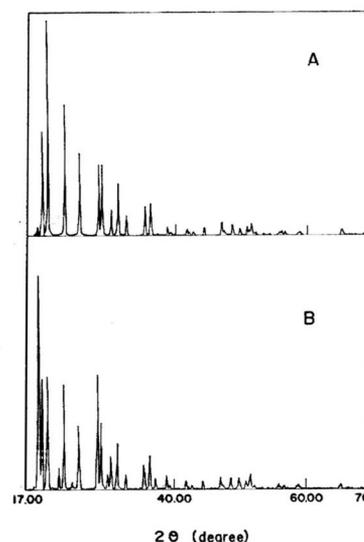


Fig. 6. X-ray diffraction patterns of crystal with adduct and without adduct at 2°C

A: Only thiourea was crystallized in methanol solution without hydrocarbon

B: Adduct of thiourea and hydrocarbon is formed.

by adduction of guest.

Conclusion

Adductive crystallization with thiourea has been

Table 5. X-ray diffraction results
(orthorhombic system)

Lattice parameter	Thiourea with adduct	Thiourea without adduct
a	7.665	7.659
b	8.560	8.556
c	5.492	5.489

successfully applied to separation of nonaromatic raffinates of naphtha crackers where a few stages are required.

Although the mechanism is not understood with accuracy, cyclohexane of a purity of 99.9 wt.% is separated by multistage adductive crystallization with thiourea from nonaromatic naphtha cracking raffinate and low-purity streams separated by distillation.

Therefore, it may be possible to make practical use of this technique for separation of nonaromatic raffinate as an alternative to the present process.

Nomenclature

A	= hydrocarbon amount trapped in adduct	[mole]
K_i	= distribution ratio for component i	
R	= hydrocarbon amount left in residue	[mole]
x	= mole fraction of residue	
y	= mole fraction of adduct	

α	= separation factor
ξ	= extent of separation
ξ_{\max}	= maximum extent of separation for one equilibrium stage

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