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= 단신 =

암모니움 이온을 가진 카드뮴 호스트 착물의 방향족 게스트 분자에 대한 포접선택성 변화

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Variation of Inclusion Selectivities of the Cadmium Host Complexes with Ammonium Oniums for Aromatic Guest Molecules

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Abstract : Inclusion selectivities of the cyanocadmate host complexes with ammonium oniums, $[Cd_x(CN)_{2x}][onium \cdot zG]$ (onium = NMe_3Et^+, $NMeEt_3^+$ and NEt_4^+, G = guest), have been investigated for C_6H_6 (B), PhMe (T), PhEt (E), ortho (O), meta (M), and para (P) isomers of $C_6H_4Me_2$ as the aromatic guest molecules. From the binary, ternary, quaternary and quinary mixed guests of B, T, E, O, M and P, the order of preference in the NMe_3Et+-host is B≫T＞P≒O≒M and E＞O≫P≒M; in the $NMeEt_3^+$-host is T＞B＞P≫O≒M and E＞P≫M＞O; in the NEt_4^+-host is B≫T≒O≒M≒P. However, the NEt_4^+-host complexes of E, O, M and P mixed-guests were not obtained. These inclusion selectivities were compared to our previous results of the NMe_4^+-host; T＞B＞P≫M＞O and E＞P≫M＞O.

Key words : inclusion selectivities, cyanocadmate host complexes, ammonium oniums, aromatic guest molecules

1. Introduction

Supramolecular chemistry has been of great interest to chemists because of the potential applicabilities such as the media of molecular recognition, separation, self-assembly and self-organization, *etc*.[1] Especially, the application of molecular inclusion phenomena is one of the most important strategies to develop novel separation technologies. Examples of applications using the organic inclusion compounds such as crown ethers, cyclodextrins, calixarenes, cryptands, cyclophanes, *etc*, have been reported by many investigators.[2,3] However, the use of artificially-designed inorganic metal complexes has been unexplored in detail compared to the application of designed organic macrocyclic hosts.

Recently Iwamoto group and we have prepared and characterized the zeolite-like host complexes of $[Cd_x(CN)_y]^{2x-y}$ enclathrating organic onium cations and neutral organic molecules along with the well-defined X-ray single crystal structures.[4,5] In general, zeolites and clay minerals attract wide interest both in academic and in

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industrial research since they are able to serve as ion exchangers, as molecular sieves, as shape-selective catalysts, *etc*. providing a great number of different applications.[6,7] Therefore, the zeolite-like host complexes of $[Cd_x(CN)_y]^{2x-y}$ have applied to the studies concerning the inclusion selectivities of aromatic guest mixtures and some preliminary results have been reported previously.[5,8-10] Other investigations related to the zeolite-like adsorption properties of the cyanometallates with the general formular $M_x[M(CN)_6]_y$ have been reported.[11,12]

On the other hand, the separation of benzene, toluene, ethylbenzene and xylenes from the BTX mixture has been an important subject of chemistry. Pure ethylbenzene, *p*-xylene and *m*-xylene is very useful for production of styrene monomer, terephthalic acid and isophthalic acid, respectively. However, there are many problems in the separation of isomers, especially the boiling points of ethylbenzene and *o*-, *m*-, *p*-xylene isomers are too close to separate by distillation.

Our research aims to investigate the inclusion selectivity of cyanometallate host complex and to develop novel materials with functions such as molecular recognition and separation. As a continuation of this application research using molecular inclusion phenomena, we now report the relative inclusion selectivities of cyanocadmate host complexes with ammonium oniums such as NMe_3Et^+, $NMeEt_3^+$ and NEt_4^+, $[Cd_x(CN)_{2x}][onium \cdot zG]$, for aromatic guest molecules.

2. Experimental

2.1. Preparation and identification

The single- and mixed-guest complexes were prepared by a method based on our previous papers.[5,8-10] An aqueous solution containing the host moieties, $CdCl_2 \cdot 2.5H_2O$, $K_2[Cd(CN)_4]$, and oniums (NMe_3Et^+, $NMeEt_3^+$ and NEt_4^+) were respectively mixed with the single-guest species or with the mixed-guest liquid phase of the equimolar binary, ternary, quaternary, and quinary mixtures of B-T-O-M-P or E-O-M-P systems. This sample solution kept standing in a refrigerator at 5 ℃ for a few days to obtain crystalline products grown at the interface between the aqueous and the organic phases and/or the bottom of the aqueous phase.

In order to identify compositions of the obtained complexes, infrared spectra of the products were recorded on a BioRad Digilab FTS-165 FT-IR spectrometer as the nujol mulls to prevent spontaneous liberation of guest molecules from the complexes. Bridging CN groups were ascertained from the strong peak at 2150 cm^{-1}, and guests were assigned by the characteristic bands of guest molecules. Carbon, hydrogen and nitrogen contents in single-guest complexes were determined by CE instruments EA-1110 elemental analyzer.

2.2. Gas chromatography

The qualitative and quantitative analyses of the aromatic guest species in the mixed-guest complexes were carried out on a Hewlett-Packard 5890 series II gas chromatograph. Optimum separation and analysis conditions are as follows:

Column : Nukol capillary (30 m × 0.25 mm)
Oven temp. : 50 ℃ (3 min) to 110 ℃ (5 min), rate ; 6 ℃/min.
Detector : flame ionization detector
Injector temp. : 220 ℃
Detector temp. : 270 ℃.

Compositions of the guests in mixed-guest complexes were determined by gas chromatography through the following procedures. The crystals of the mixed-guest complexes were filtered out on a sintered glass, washed with small amounts of ethanol and acetone quickly, and air-dried for a short while. The washed crystals were immersed in a small amounts of carbon tetrachloride on an agate mortar, and powdered more finely to extract the aromatic guests at ambient temperature. The carbon tetrachloride solution containing the extracted aromatic species was filtered through the plastic membrane and subjected to the gas chromatographic measurement.

Although there is no guarantee of the complete extraction of the guest species from the complexes, the determined values were read as the mole fractions of the guests enclathrated assuming that the ratio had been

kept unchanged. Reproducibilities of the results were within ±1% in a batch but *ca.* ±3% for a set of several batches of the mixed-guest complexes prepared under similar experimental conditions.

3. Results and Discussion

The compositions of the guests in the formed mixed-guest complexes obtained from the feed mixtures and the feed mixtures with equimolar mixing ratio in mole fraction were compared to evaluate the inclusion selectivity; the results of the host complexes with NMe_3Et^+, $NMeEt_3^+$ and NEt_4^+ for the guest feed mixtures, benzene, toluene, ethylbenzene and xylene isomer are shown in *Tables* 1～3, respectively. The enrichment factor Q in *Tables* 1～3 are defined as $Q_X = N_X/n_X$ for guest X species where N_X and n_X are mole fractions of guest X in the complex and in the feed mixture, respectively. Although Q values are independent in a given feed mixture, they may be usable as relative figures.

As listed in *Table* 1, the inclusion selectivity of the host complex with NMe_3Et^+ onium for BTX guest mixtures showed that benzene guest molecule give the highest selectivity from the mixed feeds throughout the binary to quinary mixtures; toluene was the second, and *p*-xylene in the third. The inclusion selectivity for ethylbenzene and xylene isomer mixtures showed that ethylbenzene guest molecule give the highest selectivity from the mixed feeds throughout the binary to quaternary mixtures; *o*-xylene was the second. For example, from the quinary feed mixture of B-T-O-M-P, benzene is the most enriched with Q_B = 0.81/0.20 = 4.05, toluene is the second enriched with Q_T = 0.14/0.20 = 0.70, Q_P = 0.05/0.20 = 0.25, $Q_O = Q_M$ = 0.00/0.20 = 0.00. As for the quaternary feed mixture of E-O-M-P, Q_E = 0.45/0.25 = 1.80, Q_O = 0.35/0.25 = 1.40, Q_P = 0.10/0.25 = 0.40, Q_M = 0.10/0.25 = 0.40. From those results, the order of the priority in the host complexes is B≫T>P≒O≒M and E>O≫P≒M.

The results of inclusion selectivities of the host complex with $NMeEt_3^+$ onium for guest mixtures are listed in *Table* 2. As shown in results, toluene guest molecule is always the most enriched in the complex phase from the equimolar binary, ternary, quaternary and quinary BTX feed mixtures. Benzene has the second priority, and *p*-xylene the third. However, in case of the feed mixture of B-P, B-O-P, B-M-P and B-O-M-P give the *p*-xylene selectivity. The inclusion selectivity for ethylbenzene and xylene isomer mixtures showed that ethylbenzene guest molecule give the highest selectivity from the mixed feeds throughout the binary to quaternary mixtures; *p*-xylene was the second. From those results, the order of the priority in the host complexes is T>B>P≫O≒M and E>P≫M>O.

As listed in *Table* 3, the inclusion selectivity of the host complex with NEt_4^+ onium for BTX guest mixtures showed that benzene guest molecule give the highest selectivity from the mixed feeds throughout the binary to quinary mixtures. The crystalline inclusion compounds of toluene, ethylbenzene, *o*-xylene, *m*-xylene and *p*-xylene single-guest were not obtained: accommodation of other guest molecule were only possible when it was mixed with other guest species which could be enclathrated. Therefore, the inclusion selectivity of the host complex with NEt_4^+ onium for ethylbenzene and xylene isomer guest mixtures give no results under similar conditions. From those results, the order of the priority in the host complexes is B≫T≒O≒M≒P.

In previous papers[5,8-10] we reported that inclusion selectivity of the zeolite-like host complexes of $[Cd_3(CN)_7][onium \cdot zG]$; in case of $N(CH_3)_4^+$ onium, the selectivity order of aromatic guest is T>B>P≫M>O and E>P≫M>O; in case of $S(CH_3)_3^+$ onium, that is P>T>B ≫M>O and P>E≫M>O; in case of imidazole-ligated cyanocadmate complex is B>T>P≫M>O and P>E≫ M>O. In comparison with our present results, inclusion selectivity of cyanocadmate host complex for guest mixtures were changed by onium cation guests and/or by secondary ligand. It is noticeable observation in comparison with earlier results;[13,14] in fact the priority of the *p*-xylene has been pointed out earlier paper dealing with the selectivity of aromatic isomers by inclusion into the $[Ni(SCN)_2(4\text{-methylpyridine})_4]$ host complex.

Table 1. Relative inclusion selectivities of the host complex with NMe_3Et^+ onium for the guest feed mixtures, benzene, toluene, ethylbenzene and xylene isomer

Mixed guest	Feed mixture					Complex					Enrichment factor				
	n_B	n_T	n_O	n_M	n_P	N_B	N_T	N_O	N_M	N_P	Q_B	Q_T	Q_O	Q_M	Q_P
BT	0.50	0.50				0.72	0.28				1.44	0.56			
BO	0.50		0.50			1.00		0.00			2.00		0.00		
BM	0.50			0.50		1.00			0.00		2.00			0.00	
BP	0.50				0.50	0.96				0.04	1.92				0.08
TO		0.50	0.50				0.98	0.02				1.96	0.04		
TM		0.50		0.50			0.98		0.02			1.96		0.04	
TP		0.50			0.50		0.93			0.07		1.86			0.14
BTO	0.34	0.33	0.33			0.84	0.08	0.08			2.47	0.24	0.24		
BTM	0.34	0.33		0.33		0.91	0.06		0.03		2.68	0.18		0.09	
BTP	0.34	0.33			0.33	0.84	0.09			0.07	2.47	0.27			0.21
BOM	0.34		0.33	0.33		1.00		0.00	0.00		2.94		0.00	0.00	
BOP	0.34		0.33		0.33	0.95		0.00		0.05	2.79		0.00		0.15
BMP	0.34			0.33	0.33	1.00			0.00	0.00	2.94			0.00	0.00
TOM		0.34	0.33	0.33			0.95	0.03	0.02			2.79	0.09	0.06	
TOP		0.34	0.33		0.33		0.93	0.04		0.03		2.73	0.12		0.09
TMP		0.34		0.33	0.33		0.90		0.05	0.05		2.65		0.15	0.15
BTOM	0.25	0.25	0.25	0.25		0.95	0.05	0.00	0.00		3.80	0.20	0.00	0.00	
BTOP	0.25	0.25	0.25		0.25	0.95	0.05	0.00		0.00	3.80	0.20	0.00		0.00
BTMP	0.25	0.25		0.25	0.25	0.95	0.05		0.00	0.00	3.80	0.20		0.00	0.00
BOMP	0.25		0.25	0.25	0.25	1.00		0.00	0.00	0.00	4.00		0.00	0.00	0.00
TOMP		0.25	0.25	0.25	0.25		0.95	0.03	0.00	0.02		3.80	0.12	0.00	0.08
BTOMP	0.20	0.20	0.20	0.20	0.20	0.81	0.14	0.00	0.00	0.05	4.05	0.70	0.00	0.00	0.25

Mixed guest	Feed mixture				Complex				Enrichment factor			
	n_E	n_O	n_M	n_P	N_E	N_O	N_M	N_P	Q_E	Q_O	Q_M	Q_P
EO	0.50	0.50			0.94	0.06			1.88	0.12		
EM	0.50		0.50		0.98		0.02		1.96		0.04	
EP	0.50			0.50	0.95			0.05	1.90			0.10
OM		0.50	0.50			1.00	0.00			2.00	0.00	
OP		0.50		0.50		0.68		0.32		1.36		0.64
MP			0.50	0.50			0.41	0.59			0.82	1.18
EOM	0.34	0.33	0.33		0.94	0.02	0.04		2.76	0.06	0.12	
EOP	0.34	0.33		0.33	0.81	0.12		0.07	2.38	0.36		0.21
EMP	0.34		0.33	0.33	0.90		0.04	0.06	2.65		0.12	0.18
OMP		0.34	0.33	0.33		0.60	0.20	0.20		1.76	0.61	0.61
EOMP	0.25	0.25	0.25	0.25	0.45	0.35	0.10	0.10	1.80	1.40	0.40	0.40

* *n*, *N* and *Q* have been defined in text.

Table 2. Relative inclusion selectivities of the host complex with $NMeEt_3^+$ onium for the guest feed mixtures, benzene, toluene, ethylbenzene and xylene isomer

Mixed guest	Feed mixture					Complex					Enrichment factor				
	n_B	n_T	n_O	n_M	n_P	N_B	N_T	N_O	N_M	N_P	Q_B	Q_T	Q_O	Q_M	Q_P
BT	0.50	0.50				0.30	0.70				0.60	1.40			
BO	0.50		0.50			0.93		0.07			1.86		0.14		
BM	0.50			0.50		0.99			0.01		1.98			0.02	
BP	0.50				0.50	0.22				0.78	0.44				1.56
TO		0.50	0.50				0.81	0.19				1.62	0.38		
TM		0.50		0.50			0.97		0.03			1.94		0.06	
TP		0.50			0.50		0.61			0.39		1.22			0.78
BTO	0.34	0.33	0.33			0.34	0.63	0.03			1.00	1.91	0.09		
BTM	0.34	0.33		0.33		0.34	0.64		0.02		1.00	1.94		0.06	
BTP	0.34	0.33			0.33	0.36	0.61			0.03	1.06	1.85			0.09
BOM	0.34		0.33	0.33		0.86		0.09	0.05		2.53		0.27	0.15	
BOP	0.34		0.33		0.33	0.18		0.02		0.80	0.53		0.06		2.42
BMP	0.34			0.33	0.33	0.20			0.28	0.52	0.59			0.85	1.58
TOM		0.34	0.33	0.33			0.88	0.07	0.05			2.59	0.21	0.15	
TOP		0.34	0.33		0.33		0.56	0.05		0.39		1.65	0.15		1.18
TMP		0.34		0.33	0.33		0.57		0.12	0.31		1.68		0.36	0.94
BTOM	0.25	0.25	0.25	0.25		0.32	0.59	0.06	0.03		1.28	2.36	0.24	0.12	
BTOP	0.25	0.25	0.25		0.25	0.40	0.43	0.04		0.13	1.60	1.72	0.16		0.52
BTMP	0.25	0.25		0.25	0.25	0.33	0.36		0.15	0.16	1.32	1.44		0.60	0.64
BOMP	0.25		0.25	0.25	0.25	0.24		0.03	0.26	0.47	0.96		0.12	1.04	1.88
TOMP		0.25	0.25	0.25	0.25		0.54	0.05	0.15	0.26		2.16	0.20	0.60	1.04
BTOMP	0.20	0.20	0.20	0.20	0.20	0.29	0.54	0.04	0.03	0.09	1.45	2.70	0.20	0.15	0.45

Mixed guest	Feed mixture				Complex				Enrichment factor			
	n_E	n_O	n_M	n_P	N_E	N_O	N_M	N_P	Q_E	Q_O	Q_M	Q_P
EO	0.50	0.50			0.90	0.10			1.80	0.20		
EM	0.50		0.50		0.76		0.24		1.52		0.48	
EP	0.50			0.50	0.58			0.42	1.16			0.84
OM		0.50	0.50			0.18	0.82			0.36	1.64	
OP		0.50		0.50		0.03		0.97		0.06		1.94
MP			0.50	0.50			0.34	0.66			0.68	1.32
EOM	0.34	0.33	0.33		0.71	0.08	0.21		2.09	0.24	0.64	
EOP	0.34	0.33		0.33	0.54	0.16		0.30	1.59	0.48		0.91
EMP	0.34		0.33	0.33	0.53		0.15	0.32	1.56		0.45	0.97
OMP		0.34	0.33	0.33		0.06	0.35	0.59		0.20	1.05	1.78
EOMP	0.25	0.25	0.25	0.25	0.57	0.03	0.10	0.30	2.28	0.12	0.40	1.20

* n, N and Q have been defined in text.

Table 3. Relative inclusion selectivities of the host complex with NEt_4^+ onium for the guest feed mixtures, benzene, toluene and xylene isomer

Mixed guest	Feed mixture					Complex					Enrichment factor				
	n_B	n_T	n_O	n_M	n_P	N_B	N_T	N_O	N_M	N_P	Q_B	Q_T	Q_O	Q_M	Q_P
BT	0.50	0.50				0.99	0.01				1.98	0.02			
BO	0.50		0.50			1.00		0.00			2.00		0.00		
BM	0.50			0.50		1.00			0.00		2.00			0.00	
BP	0.50				0.50	0.84				0.16	1.68				0.32
TO		0.50	0.50				-	-				-	-		
TM		0.50		0.50			-		-			-		-	
TP		0.50			0.50		-			-		-			-
BTO	0.34	0.33	0.33			0.95	0.05	0.00			2.79	0.15	0.00		
BTM	0.34	0.33		0.33		1.00	0.00		0.00		2.94	0.00		0.00	
BTP	0.34	0.33			0.33	0.93	0.00			0.07	2.74	0.00			0.21
BOM	0.34		0.33	0.33		1.00		0.00	0.00		2.94		0.00	0.00	
BOP	0.34		0.33		0.33	1.00		0.00		0.00	2.94		0.00		0.00
BMP	0.34			0.33	0.33	0.90			0.00	0.10	2.64			0.00	0.30
TOM		0.34	0.33	0.33			-	-	-			-	-	-	
TOP		0.34	0.33		0.33		-	-		-		-	-		-
TMP		0.34		0.33	0.33		-		-	-		-		-	-
BTOM	0.25	0.25	0.25	0.25		0.83	0.00	0.00	0.17		3.32	0.00	0.00	0.68	
BTOP	0.25	0.25	0.25		0.25	1.00	0.00	0.00		0.00	4.00	0.00	0.00		0.00
BTMP	0.25	0.25		0.25	0.25	1.00	0.00		0.00	0.00	4.00	0.00		0.00	0.00
BOMP	0.25		0.25	0.25	0.25	1.00		0.00	0.00	0.00	4.00		0.00	0.00	0.00
TOMP		0.25	0.25	0.25	0.25		-	-	-	-		-	-	-	-
BTOMP	0.20	0.20	0.20	0.20	0.20	0.94	0.00	0.00	0.00	0.06	4.70	0.00	0.00	0.00	0.30

* *n*, *N* and *Q* have been defined in text.

In order to attempt to explain the results obtained we have looked in detail at a number of parameters: dimensions of guest molecules, vapor pressures, guest solubility, boiling points and calculated dipole moments of the guest obtained from molecular graphics. No correlation is found between the physical property and the experimentally observed inclusion selectivity. The variation of the inclusion selectivity suggests that inclusion process would be selective as regards the shape and size rather than the chemical properties of molecules (Fisher-Hirschfelder-Talor's dimension: benzene = 2.5×6.5×7.2, toluene = 3.6×6.5×8.1, *o*-xylene = 3.6×7.1×8.1, *m*-xylene = 3.6×7.2×8.6, *p*-xylene = 3.6×6.5×8.9, ethylbenzene = 3.6×6.5×8.9 Å).

4. Conclusion

Variation of inclusion selectivities of the cyanocadmate host complexes with ammonium oniums, $[Cd_x(CN)_{2x}]$[onium · zG], for benzene, toluene, ethylbenzene and xylene isomer guests are as follows. The order of preference in the NMe_4^+-host is T>B>P≫M>O and E>P≫M>O; in the NMe_3Et^+-host is B≫T>P≒O≒M and E>O≫P≒M; in the $NMeEt_3^+$-host is T>B>P≫O≒M and E>P≫M>O; in the NEt_4^+-host is B≫T≒O≒M≒P. Inclusion selectivity of host complex for guest

mixtures were changed by ammonium oniums. These results may be very effective for the separation of isomers which have boiling points too close to separate by distillation such as ethylbenzene and *o*-, *m*-, *p*-xylene. Further studies, which will be the relationships between the selectivity for the aromatic guest molecules and the host structure, are in progress.

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