AN EQUILIBRIUM AND KINETIC INVESTIGATION OF SALT-CYCLOAMYLOSE COMPLEXES

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by

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The equilibrium constants and rate constants for the formation of inclusion complexes of cycloheptaamylose with small inorganic anions were measured by a spectrophotometric technique and an ultrasonic relaxation technique respectively. The stability of the complexes of anions with

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cycloheptaamylose decreased in the order $ClO_4^- > I^- > SCN^- > Br^- > NO_3^- > Cl^-$. Comparison is made between the equilibrium constants and the interaction of free anions with the solvent. Periodate and ClO_4^- exhibited a complexation rate constant 30 times greater than the remainder of the anions. A concentration independent relaxation was observed for aqueous cyclohexaamylose in the uncomplexed state. No like behavior was observed for cycloheptaamylose. A conformational change in the cycloheptaamylose may be the rate determining step in the complexation of the more slowly reacting anions.

Introduction

The cycloamyloses (cyclodextrins) are capable of forming inclusion complexes with a wide variety of guests ranging from hydrophobic to ionic character.[1,2,3] The mode of ionic complexation is the least studied and understood facet of cycloamylose chemistry. Recently, equilibrium constants for cyclohexaamylose, sometimes denoted by α-CD, with various inorganic salts were measured.[4] The complexes were determined to be anionic, and a correlation was observed between the logarithm of the measured equilibrium constant and the "structure breaking" properties of the free anions.

Explanations for the driving force for complexation have been as diverse as the guests which are complexed. Complexation has been attributed to hydrophobic interactions, hydrogen-bonding, and non-specific van der Waals forces.[1] Saenger and coworkers have postulated a driving force arising from the relaxation of the conformational strain in the cyclohexaamylose brought about by complexation.[5] Crystallographic evidence suggests that the cyclohexaamylose in the complexed state with both hydrophobic and ionic guests is in a slightly different conformation than in the uncomplexed state.[5,6,7,8]

In the present study of the mode of ionic complexation with cycloamylose, the kinetics and equilibrium constants of complexation were measured for cycloheptaamylose (β-CD) and various inorganic salts. The kinetics of an apparent conformational change in pure aqueous cycloheptaamylose and cyclohexaamylose were also studied by means of an ultrasonic absorption relaxation technique.

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Experimental

All solutions were prepared using deionized, redistilled water. Cyclohexaamylose and cycloheptaamylose were purchased from Sigma Chemicals and Aldrich Chemicals respectively. Both cycloamyloses were purified by literature methods.[9] All inorganic salts used were reagent grade sodium salts.

The equilibrium constants for the various salt-cycloheptaamylose systems were measured with a Cary 14 recording uv-vis spectrophotometer equipped with a thermostated cell compartment kept at 25.0±0.1°C. Equilibrium constants for the various salt-cycloamylose complexes were measured by a spectral competitive inhibition technique.[2] A 4-nitrophenylazo-2'-hydroxy,6'-sulfonaphthalene dye was used in this study and was prepared by standard azo dye coupling procedures.[10]

All spectroscopic measurements were made at 510 nm which corresponds to the largest difference in extinction coefficient between the free and complexed forms of the azo dye. Solutions were 0.1 M in salt and 2.0×10^{-5} M in azo dye while the cycloheptaamylose concentration varied from 0 to 10^{-2} M. All equilibrium constants were determined at a pH=5.7 and an ionic strength I=0.1 M. At least seven solutions varying in cycloheptaamylose concentration were used in obtaining the equilibrium constant for each anion. The equilibrium constant for the dye-cycloheptaamylose system was measured in the same manner as above but with Na_2SO_4, a salt which does not complex, establishing the I=0.1 M.[2]

The ultrasonic absorption kinetic measurements were made at a temperature of 25.0±0.1°C over the frequency range of 15-205 MHz using a laser acousto-optical technique.[11]

Results

Spectrophotometric titrations were made with 4-nitrophenylazo-2'-hydroxy, 6'-sulfonaphthalene and cycloheptaamylose in the presence of the sodium salts of (ClO_4^-, I^-, SCN^-, Br^-, NO_3^-, Cl^-, and SO_4^{2-} respectively. The equilibrium constant for the dye interacting with cycloheptaamylose was measured in the absence of added electrolyte and also with I=0.1 M (Na_2SO_4). The two measured equilibrium constants were the same within experimental error. Equation 1 describes the interaction of such hydrophobic guests with cycloheptaamylose.

$$CD + In \underset{\leftarrow}{\overset{K_D}{\rightarrow}} CD \cdot In \qquad (1)$$

Here In, CD, and CD·In represent the free dye, free cycloheptaamylose and complexed form of cycloheptaamylose respectively. In Figure 1, curve A represents the data obtained by plotting the change in absorbance, ΔA, versus the cycloheptaamylose concentration. In all cases the dye concentration was constant at 2.0×10^{-5} M and the cycloheptaamylose varied from $0\text{-}10^{-2}$ M. The data were plotted using the Hildebrand-Benesi relation.[12] The equilibrium constant as well as the extinction coefficient of the fully complexed form of the dye were obtained. Using molar units of concentration, a value $K_D = 7.7 \times 10^2$ was found for the stability constant of the cycloheptaamylose-dye system.

In the spectral competitive inhibition technique[2] for determining the equilibrium constants for the various salt-cycloheptaamylose systems a high concentration of inorganic salt is added to various solutions of cycloheptaamylose and dye. Assuming the lack of occupancy of the cycloheptaamylose binding site by both dye and salt, the equilibrium constants for the various salt-cycloheptaamylose systems are calculated from mass balance relations. The combination of eq 1 with

$$CD + X^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} CD \cdot X^- \qquad (2)$$

describes the interactions. The equilibrium constants are

$$K_D = \frac{[CD \cdot In]}{[CD]\ [In]} \tag{3}$$

$$K_{X^-} = \frac{[CD \cdot X^-]}{[CD]\ [X^-]} = \frac{k_f}{k_r} \tag{4}$$

The total concentrations of cycloheptaamylose and salt are conserved according to the mass balance equations:

$$CD_t = [CD] + [CD \cdot In] + [CD \cdot X^-]$$

$$X_t^- = [X^-] + [CD \cdot X^-] \tag{5}$$

The observed absorbance, A, is given by:

$$A = \varepsilon_{In}\ [In] + \varepsilon_{CD \cdot In}\ [CD \cdot In] \tag{6}$$

Since the initial concentrations of all reagents are known as well as K_D, ε_{In}, and $\varepsilon_{CD \cdot In}$ the equilibrium constant for the salt cycloheptaamylose system, K_{X^-}, can be readily obtained.

Figure 1 shows the effect of 0.1 M ClO_4^-, SCN^-, and I^- on the absorbance of the dye-cycloheptaamylose system. All the ions studied showed similar effects with the exception of Na_2SO_4. Perchlorate anion showed the largest effect. Cramer used this method to calculate a K_X^- value for the ClO_4^--cyclohexaamylose system.[2] The equilibrium constant calculated in this manner was in good agreement with that obtained by an independent conductometric technique.[4] Table I contains the cycloheptaamylose results along with earlier data[4] for the same ions with cyclohexaamylose.

The calculated K_{X^-} values for all anions except SCN^- are independent of the cycloheptaamylose concentration as an equilibrium constant should be. In the case of SCN^-, a concentration dependent K_{X^-} was observed, and a value of $K_{X^-} = 10.0$ was obtained at an extrapolated zero concentration of cycloheptaamylose. This is consistent with a value of $K_{X^-} = 9.9$ calculated by a conductometric technique.[4] Figure 1 shows that the asymptotic ΔA value in the case of SCN^- is significantly smaller than the asymptotic ΔA value measured for the dye-cycloheptaamylose system in the presence of other salts. Thiocyanate anion at 0.1 M showed no effect on

the absorption spectrum of the pure dye.

The ultrasonic absorption data, expressed as (α/f^2) neper sec^2 cm^{-1}, were analyzed in terms of a single relaxation using the following relation

$$(\alpha/f^2) = A\,[1 + (f/f_r)]^{-1} + B \qquad (7)$$

where A denotes the relaxation amplitude of the process, f is the experimental frequency, f_r is the relaxational frequency, and B is the solvent absorption. Table II shows the experimental ultrasonic absorption relaxation frequencies and the calculated parameters A and B that give the best fit to eq 7 for the pure aqueous cyclohexaamylose solutions at different concentrations. The raw ultrasonic absorption data appear as an appendix in the microfilm edition of the journal. (See paragraph at end of text regarding Supplementary Material.) The observed relaxation frequency is independent of the concentration of cyclohexaamylose and occurs at 12.3 MHz with an experimental error of ±0.5 MHz. As would be expected from solutions of increasing viscosity, the background absorption, B, at high frequencies was above that of pure water alone varying from an increase of 5×10^{-17} neper sec^2 cm^{-1} over water for the most concentrated solution, 0.102 M, to 1×10^{-17} neper sec^2 cm^{-1} over water for the 0.05 M solution.

A concentration independent relaxation in pure aqueous cyclohexaamylose can be described by eq 8

$$CD \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CD' \qquad (8)$$

for which

$$\tau^{-1} = k_1 + k_{-1} \qquad (9)$$

Since the reciprocal relaxation time equals the sum of two rate constants and is independent of concentration (eq 9), in the absence of relaxation amplitude data at several temperatures the values of k_1 and k_{-1} can be known only as the sum. Such first order processes as reaction 8 are generally the result of conformational changes that alter the solvation of the sound absorbing solute.

Aqueous cycloheptaamylose, at 0.016 M, showed no similar absorption over the accessible 15 to 205 MHz frequency range. In this case only the solvent absorption was observed. The fact that the cyclohexaamylose showed an absorption whereas the cycloheptaamylose did not may be attributable to the more limited solubility of cycloheptaamylose in water. Using the relaxation amplitude calculated for cyclohexaamylose, the absorption of cycloheptaamylose, if it were present, at 0.016 M would only be marginally above that of the solvent and would therefore be immeasurable.

Ultrasonic absorption relaxation frequencies for aqueous cycloheptaamylose complexing with ClO_4^-, SCN^-, NO_3^-, Cl^-, Br^-, and I^- are presented in Table III. Raw ultrasonic absorption data appear in an appendix in the microfilm edition of the journal. In these cases only one relaxation was detected which was concentration dependent on both cycloheptaamylose and salt. All the data are consistent with the complexation reaction of eq 2. When high concentrations of salt were employed (up to 2M) variable backgrounds were used to fit the ultrasonic absorption data. The B values decreased below that of pure water as the concentration of salt increased, being as low as 17×10^{-17} neper sec^2 cm^{-1} in the most concentrated solution of NaBr. This background absorption was consistent with the observed absorption of only the salt and water alone. This depression of the solvent ultrasonic absorption by simple electrolytes is attributable to several factors.[13]

The individual rate constants for anionic complexation, k_f and k_r, were calculated using the following equation.

$$\tau^{-1} = k_f ([CD] + [X^-] + K_X^{-1}) \qquad (10)$$

Table V contains the rate constants calculated in this manner.

Discussion

Anions bind to cycloheptaamylose as they do to cyclohexaamylose to varying degrees depending on the anion. It is evident from the new data that cycloheptaamylose binds anions roughly as well as does cyclohexaamylose and in the same general order of stability. Increasing the ring size by one glucose residue does not seem to affect the nature of anionic complexation although ring size does play a significant role in hydrophobic binding.[10,3] One would expect the relaxation of torsional angle strain to be greater in cyclohexaamylose than in cycloheptaamylose due to the smaller size and therefore more rigid structure of the former. Thus the equivalence of equilibrium constants for cyclohexa- and cycloheptaamylose introduces some doubt as to the importance of the conformational relaxation as the principal driving force for ionic guest-host complexation in the cycloamyloses.

A correlation exists between the order of stability of the complexes and "structure breaking" properties of the free anions as has been shown in previous work on salt-cyclohexaamylose complexes.[4] A parameter which correlates the "structure breaking" properties of the anions is the coefficient of the linear term of the concentration dependence of proton nuclear magnetic resonance relaxation rates in aqueous salt solutions, B^-.[14] If the logarithm of the equilibrium constant for the various salt-cycloheptaamylose systems is plotted against the B^- value for each anion a good correlation is observed (Fig.2). The line $\log K_{X^-} = -12.5B^- + 0.242$ is the linear least squares fit of the data with a correlation coefficient of 0.92. Table I contains the calculated equilibrium constants using the above relation. If one compares the similar correlation found[4] for cyclohexaamylose, $\log K_{X^-} = -26.5B^- - .75$, one finds that the magnitude of the slope term for cyclohexaamylose is significantly larger. This indicates that the salt-cycloamylose equilibrium constant for cyclohexaamylose is more sensitive to the B values or "structure breaking" effects of the free anions.

terizing free indicator to $\epsilon_{CD\cdot In}$ of the complex depending upon the depth of penetration of dye into the cycloamylose cavity, the SCN^- may be affecting this penetration depth. In other words, in the case of SCN^- the assumption of no simultaneous complexation of dye and anion by cycloheptaamylose may be invalid. Results of x-ray studies[7] of crystalline complexes of cyclohexaamylose suggest the anion is probably located in the hydrophilic plane defined by the primary hydroxyl groups. Hydrophobic guests such as the dye are generally believed to be located within the hydrophobic cavity.[1] Since the cavity may have these two distinct regions, dual occupancy by different guests could conceivably occur in some cases. Binding sites for hydrophobic guests and ionic guests would each have their own unique driving force responsible for complexation.

The rate constants calculated for complexation, k_f, (see Table IV) are strikingly similar. All the anions with the exception of ClO_4^- have roughly the same forward rate constant. The ClO_4^- has a k_f thirty times larger than that measured for the rest of the anions and approaches the diffusion controlled limit. The decomplexation rate constant, k_r, for all the ions increases with decreasing equilibrium constant, again with the exception of ClO_4^-.

Since ClO_4^- is anomalous with respect to k_f, the kinetics of complexation of IO_4^- were also studied. Periodate ion reacts oxidatively with such sugars, hence the kinetics were measured immediately after preparation of the solutions. A slow degradation process was indeed observed. However, this reaction was slower than the time necessary to measure the kinetics of complexation. Since an equilibrium constant could not be measured, the correlation between log K and B^- (Fig.2) was used to calculate an equilibrium constant for the IO_4^--cycloheptaamylose system, K_{X^-} (calc) = 15.5. The kinetic data obtained demonstrated that IO_4^- has a k_f similar to that obtained for ClO_4^-.

Since all the k_f's for the anions, with the exception of ClO_4^- and IO_4^-, are roughly equal and well below the diffusion controlled limit, some other process

is rate limiting. When log k_f is plotted versus reciprocal anionic radius for all these anions no systematic trend is found suggesting that anion desolvation is not rate determining for k_f. It should be added parenthetically that a linear correlation of log k_f with reciprocal ionic radius is well known for similarly charged cations, and the present range of anionic radii (3.19Å to 1.81Å) is quite comparable to that required in isovalent cations to convincingly demonstrate that cation desolvation is rate limiting in their complexation.

The conformational relaxation reported above for pure aqueous cyclohexaamylsoe could occur on the same time scale as a rate limiting conformational change in cycloheptaamylose in going from the uncomplexed to the complexed state[5,6,7,8] in all cases except ClO_4^- and IO_4^-. The complexation mechanism could then be described as

$$CD + X^- \underset{+}{\overset{K_o}{\rightleftharpoons}} CD \,||\, X^- \overset{k_1}{\underset{+}{\rightleftharpoons}} CD{\cdot}X^- \qquad (11)$$

where the first equilibrium is achieved very rapidly and may be described as the formation of a contact ion complex and the next step involves the slower rate determining conformational change of the cycloamylose complex. To compare the measured first order relaxation time of the conformational change of cyclohexaamylose to the overall second order complexation rate constant k_f, it is necessary to calculate the equilibrium constant K_o for contact ion formation since

$$k_f = K_o\, k_1 \qquad (12)$$

Theoretical expressions exist[15] for K_o from which a value $K_o = 1.51 \pm 0.15$ is calculated. From this and measured values of k_f it follows that $k_1 = 3.4 \pm 0.7 \times 10^7$ sec^{-1} which is of the same order of magnitude as the $\tau^{-1} = k_1 + k_{-1} = 7.7 \times 10^7$ sec^{-1} measured for a conformational change in aqueous cyclohexaamylose. This similarity favors the speculation that a conformational change is rate determining in the anion complexation process.

The ClO_4^- and IO_4^- ions may not show this rate limiting behavior because of their larger radii. They may be capable of forming a straddle type complex with either conformation of the cycloheptaamylose because these anions are too large to fit into

the primary (smaller) side of the cycloheptaamylose. In such a case a cycloamylose conformational change would not be rate limiting for anion complexation.

Acknowledgement

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TABLE I: Stability Constants for Anion-Cycloamylose Complexes

Anion	Cycloheptaamylose		Cyclohexaamylose
	K_X^-, M^{-1} (obs)[a]	(calc)[b]	K_X^-, M^{-1}[c]
ClO_4^-	26.7	20.2	28.9
SCN^-	9.9[c]	13.1	18.7
I^-	18.0	17.5	12.4
NO_3^-	5.5	7.4	1.4
Br^-	6.5	5.5	3.5
Cl^-	2.56	2.3	N.B.

[a]Determined by spectrophotometric competitive inhibition study.

[b]Calculated from the B^- structure breaking parameter correlation.

[c]Calculated from conductimetric data and originally reported in Reference 4.

TABLE II: Relaxation Parameters from Computer Analysis for Aqueous Cyclohexaamylose at 25°[a]

$[\alpha\text{-CD}]_o$, M.	f_R, MHz	10^{17} A Np cm^{-1} sec^2	10^{17} B Np cm^{-1} sec^2	10^{18} RMS[b]
0.102	12.01	52.1	26.8	0.71
0.0714	12.32	39.5	24.8	0.50
0.0500	12.66	36.9	23.0	0.51

[a] All symbols as defined in the text.

[b] Root mean square deviation.

TABLE III: Relaxation Parameters from Computer Analysis for Aqueous Complexation by Cycloheptaamylose[a]

[Anion]$_o$, [b] F.	[β-CD]$_o$, [b] M.	f_R, MHz	10^{17} A Np cm^{-1}sec^2	10^{17} B Np cm^{-1}sec^2	10^{18} RMS[c]
		PERCHLORATE			
0.010	0.0116	18.28	22.6	21.7	0.55
0.0191	0.0120	19.70	27.2	21.7	0.73
0.0252	0.0114	20.56	39.4	21.7	0.79
0.0101	0.0509	26.01	20.5	21.7	0.63
		IODIDE			
0.0197	0.297	3.46	334.1	22.4	1.0
0.00972	1.09	11.39	46.1	19.8	0.55
0.0108	1.48	16.61	35.5	19.5	1.0
		THIOCYANATE			
0.0116	0.560	4.62	192.	21.00	0.59
0.0240	1.51	11.20	41.3	21.00	1.0
0.0285	1.92	13.67	44.5	19.97	1.1
		BROMIDE			
0.0106	0.981	8.04	76.5	20.3	0.81
0.0100	1.52	12.03	38.5	19.6	0.60
0.0112	1.98	15.28	33.8	17.3	0.79
		NITRATE			
0.0102	1.02	8.25	84.8	20.4	0.76
0.00992	1.5.	12.15	44.8	21.0	0.63
0.0103	2.02	16.43	29.0	21.8	0.63
		CHLORIDE			
0.00971	1.0.	11.94	42.0	20.0	0.54
0.00917	1.49	16.24	22.3	19.6	0.52

[a] All symbols as defined in the text.

[b] The subscript zero on concentration denotes total initial concentrations.

[c] Root mean square deviation.

TABLE IV: Complexation Rate Constants, k_f, and Dissociation Rate Constants, k_r, for Several Anions and Aqueous Cycloheptaamylose at 25°

Anion	k_f, M^{-1} sec^{-1}	k_r, sec^{-1}
ClO_4^-	$(2.0\pm0.1)\times10^9$	$(7.4\pm2.)\times10^7$
I^-	$(6.5\pm0.3)\times10^7$	$(3.6\pm1.)\times10^6$
SCN^-	$(4.4\pm0.2)\times10^7$	$(4.4\pm1.)\times10^6$
Br^-	$(4.5\pm0.2)\times10^7$	$(6.9\pm1.)\times10^6$
NO_3^-	$(4.5\pm0.2)\times10^7$	$(8.2\pm2.)\times10^6$
Cl^-	$(5.4\pm0.3)\times10^7$	$(2.1\pm0.5)\times10^7$

Figure Captions:

Fig.1. Change in absorbance, ΔA, at a wavelength of 510nm plotted vs. aqueous cycloheptaamylose concentration in pH 5.7, 25° solutions that are 2×10^{-5} M in 4-nitrophenylazo-2'-hydroxy, 6'-sulfonaphthalene and 0.1 M in sodium salts of SO_4^{2-} (curve A), I^- (B), ClO_4^- (C), SCN^- (D). The hash mark identified by an ∞ sign is the ΔA at infinite cycloheptaamylose concentration determined from the Hildebrand-Benesi relation.

Fig.2. Logarithm of the stability constant K_X- for several aqueous cycloheptaamylose-salt solutions vs. values of the B^- "structure breaking" parameter for the several anions. A least squares straight line has been drawn with a correlation coefficient of 0.92. (The negative of B^- values have been plotted for convenience.)

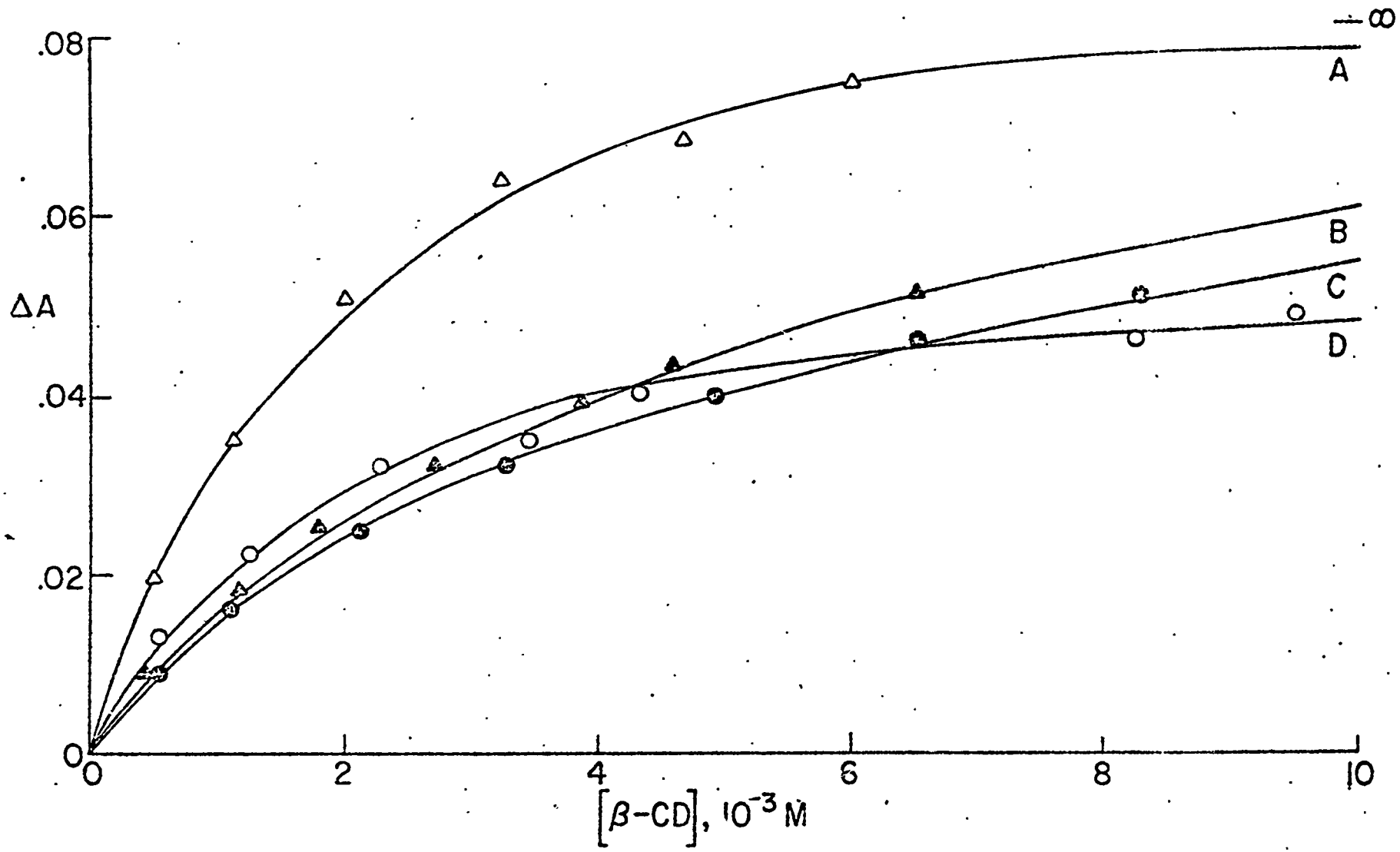

Fig. 1, Rohrbach et al.

APPENDIX I: Experimental Absorption as (α/f^2) in Np cm^{-1} sec^2 for Aqueous Cyclohexaamylose at 25°C.

$[\alpha\text{-CD}]_o$ = 0.102 M.		$[\alpha\text{-CD}]_o$ = 0.0714 M.		$[\alpha\text{-CD}]_o$ = 0.0500 M.	
$10^{17}(\alpha/f^2)$exptl., Np cm^{-1} sec^2	f,MHz	$10^{17}(\alpha/f^2)$exptl., Np cm^{-1} sec^2	f,MHz	$10^{17}(\alpha/f^2)$exptl., Np cm^{-1} sec^2	f,MHz
46.59	15.06	40.63	15.06	38.37	15.05
37.49	25.12	32.55	25.10	30.37	25.10
32.35	35.14	28.98	35.15	27.05	35.14
30.72	45.24	27.74	45.26	26.11	45.24
28.78	55.31	26.56	55.29	25.17	55.29
28.45	65.36	25.91	65.35	24.41	65.32
28.38	75.39	25.84	75.36	24.20	75.36
27.71	85.42	25.46	85.42	23.69	85.40
27.41	95.47	25.28	95.47	24.23	95.46
26.96	105.5	25.11	105.5	23.60	105.5
26.99	115.5	24.66	115.6	23.56	115.6
27.12	125.6	24.99	125.6	23.17	125.6
26.80	135.6	24.64	135.6	23.25	135.7
26.58	145.7	24.85	145.7	23.28	145.7

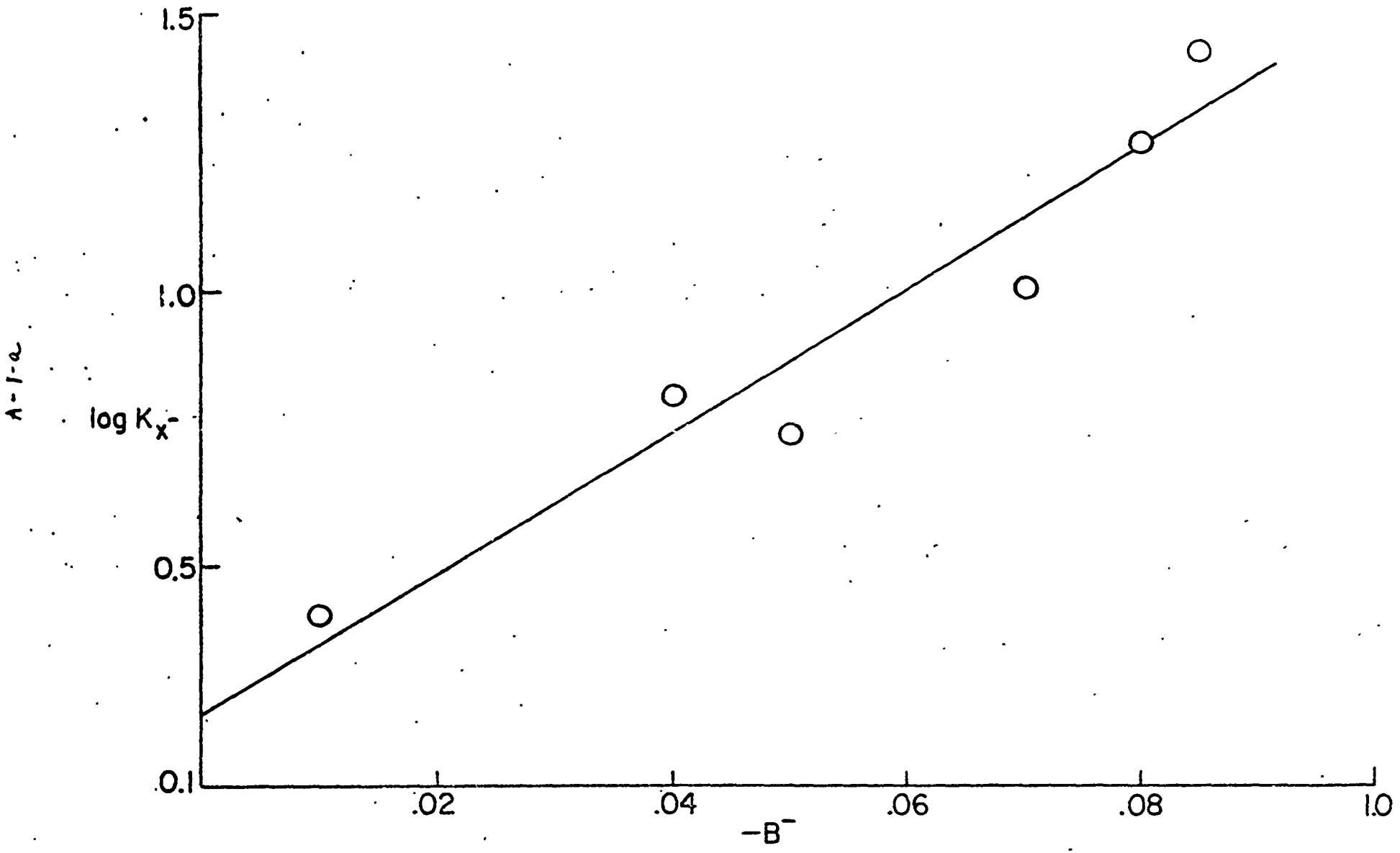

Fig. 2 Rahrbach et al.

APPENDIX II: Experimental Absorption as (α/f^2) in Np cm^{-1} sec^2 for Aqueous Sodium Perchlorate and Cycloheptaamylose at 25°C.

$[NaClO_4]_o$ = 0.0116 F.		$[NaClO_4]_o$ = 0.0120 F.		$[NaClO_4]_o$ = 0.0114 F.	
$[\beta\text{-CD}]_o$ = 0.0101 M.		$[\beta\text{-CD}]_o$ = 0.0191 M.		$[\beta\text{-CD}]_o$ = 0.0252 M.	
$10^{17}(\alpha/f^2)$exptl., Np cm^{-1} sec^2	f,MHz	$10^{17}(\alpha/f^2)$exptl., Np cm^{-1} sec^2	f,MHz	$10^{17}(\alpha/f^2)$exptl., Np cm^{-1} sec^2	f,MHz
35.43	15.21	38.82	15.21	47.75	15.05
29.25	25.37	31.65	25.37	37.56	25.10
26.49	35.53	28.95	35.53	31.08	35.16
25.23	45.77	26.18	45.73	28.44	45.22
23.97	55.89	25.10	55.91	26.93	55.28
23.46	66.04	24.05	66.08	25.51	65.30
22.83	76.21	23.84	76.30	24.24	75.35
22.47	86.38	22.99	96.64	23.65	85.40
22.23	96.54	22.65	106.8	23.51	95.43
22.09	106.7	22.38	117.0	23.21	105.5
21.85	116.9	23.98	127.2	22.90	115.5
21.86	127.0			22.21	125.6
21.63	137.2				

APPENDIX II (con't):

$[NaClO_4]_o$ = 0.0509 F.	
$[\beta\text{-CD}]_o$ = 0.0101 M.	
$10^{17}(\alpha/f^2)$expt1., Np cm^{-1} sec^2	f,MHz
36.88	15.08
32.84	25.11
28.44	35.15
27.01	45.24
25.43	55.30
24.36	65.32
23.93	75.37
23.25	85.41
23.07	95.45
22.67	105.5
22.50	115.5
22.35	125.6
22.08	135.6
21.84	145.7

APPENDIX II (con't):

$[NaClO_4]_o$ = 0.0509 F. $[\beta\text{-CD}]_o$ = 0.0101 M. $10^{17}(\alpha/f^2)$expt1., Np cm^{-1} sec^2	f,MHz
36.88	15.08
32.84	25.11
28.44	35.15
27.01	45.24
25.43	55.30
24.36	65.32
23.93	75.37
23.25	85.41
23.07	95.45
22.67	105.5
22.50	115.5
22.35	125.6
22.08	135.6
21.84	145.7

APPENDIX II (con't): Experimental Absorption as (α/f^2) in Np cm^{-1} sec^2 for Aqueous Sodium Thiocyanate and Cycloheptaamylose at 25°C.

$[NaSCN]_o$ = 0.560 F.		$[NaSCN]_o$ = 1.51 F.		$[NaSCN]_o$ = 1.92 F.	
$[\beta\text{-CD}]_o$ = 0.0116 M.		$[\beta\text{-CD}]_o$ - 0.240 M.		$[\beta\text{-CD}]_o$ = 0.0285 M.	
$10^{17}(\alpha/f^2)$exptl., Np cm^{-1} sec^2	f,MHz	$10^{17}(\alpha/f^2)$exptl., Np cm^{-1} sec^2	f,MHz	$10^{17}(\alpha/f^2)$exptl., Np cm^{-1} sec^2	f,MHz
37.54	15.07	43.67	15.07	39.13	15.06
27.30	25.12	28.61	25.10	29.89	25.10
24.11	35.14	25.49	35.15	25.21	35.14
23.12	45.25	23.50	45.25	23.62	45.24
22.38	55.27	22.69	55.28	22.36	55.28
21.88	65.31	22.16	65.30	21.72	65.33
21.77	75.36	21.86	75.36	21.09	75.42
21.53	85.40	21.21	85.41	21.12	95.46
21.45	95.44	21.20	95.45	20.32	105.5
		20.87	105.5	21.27	115.6
				20.49	125.6
				20.42	135.7
				19.72	145.7
				20.09	155.8
				20.22	165.8
				20.34	175.8

APPENDIX II (con't): Experimental Absorption as (α/f^2) in Np cm^{-1} sec^2 for Aqueous Sodium Iodide and Cycloheptaamylose at 25°C.

$[NaI]_o$ = 0.297 F.		$[NaI]_o$ = 1.09 F.		$[NaI]_o$ = 1.48 F.	
$[\beta\text{-CD}]_o$ = 0.0197 M.		$[\beta\text{-CD}]_o$ = 0.00972 M.		$[\beta\text{-CD}]_o$ = 0.0108 M.	
$10^{17}(\alpha/f^2)$exptl., Np cm^{-1} sec^2	f,MHz	$10^{17}(\alpha/f^2)$exptl., Np cm^{-1} sec^2	f,MHz	$10^{17}(\alpha/f^2)$exptl., Np cm^{-1} sec^2	f,MHz
39.23	15.05	36.52	15.06	38.55	15.06
28.28	25.09	27.44	25.10	30.55	25.12
25.58	35.13	24.47	35.14	25.53	35.15
25.53	45.24	22.52	45.20	23.68	45.17
24.14	55.26	21.39	55.26	22.70	55.21
23.69	65.32	20.64	65.29	22.40	65.27
23.52	75.37	20.79	75.35	20.89	75.32
23.04	95.43	20.58	85.32	21.81	85.36
23.15	95.43	20.27	95.37	19.90	95.41
22.53	105.5	20.30	105.4	18.34	105.5
22.25	115.5	20.50	115.4		
22.10	125.6	20.28	125.5		
22.03	135.6	20.15	135.6		
21.93	145.7	20.11	145.6		

APPENDIX II (con't): Experimental Absorption as (α/f^2) in Np cm^{-1} sec^2 for Aqueous Sodium Bromide and Cycloheptaamylose at 25°C.

$[NaBr]_o$ = 0.981 F.		$[NaBr]_o$ = 1.52 F.		$[NaBr]_o$ = 1.98 F.	
$[\beta\text{-CD}]_o$ = 0.0106 M.		$[\beta\text{-CD}]_o$ = 0.0100 M.		$[\beta\text{-CD}]_o$ = 0.0112 M.	
$10^{17}(\alpha/f^2)$exptl., Np cm^{-1} sec^2	f,MHz	$10^{17}(\alpha/f^2)$exptl., Np cm^{-1} sec^2	f,MHz	$10^{17}(\alpha/f^2)$exptl., Np cm^{-1} sec^2	f,MHz
37.91	15.04	34.54	15.05	34.65	15.03
27.50	25.08	26.67	25.10	26.41	25.11
24.21	35.13	23.51	35.13	21.79	35.11
23.11	45.23	22.62	45.24	20.87	45.23
22.05	55.29	21.55	55.28	20.07	55.29
21.76	65.31	20.72	65.33	19.31	65.31
21.38	75.36	20.58	75.36	19.04	75.37
21.27	85.41	20.40	85.41	18.23	85.42
20.85	95.47	20.31	95.45	17.95	95.47
20.83	105.5	20.08	105.5	17.56	105.5
20.56	115.6	19.95	115.6	17.46	115.6
20.54	125.6	19.66	125.6	16.95	125.6
20.57	135.7	19.75	135.7	17.09	135.7
20.42	145.7	19.57	145.7	16.82	145.7

APPENDIX II (con't): Experimental Absorption as (α/f^2) in Np cm^{-1} sec^2 for Aqueous Sodium Nitrate and Cycloheptaamylose at 25°C.

$[NaNO_3]_o$ = 1.02 F.		$[NaNO_3]_o$ = 1.51 F.		$[NaNO_3]_o$ = 2.02 F.	
$[\beta\text{-CD}]_o$ = 0.0102 M.		$[\beta\text{-CD}]_o$ = 0.00992 M.		$[\beta\text{-CD}]_o$ = 0.0103 M.	
$10^{17}(\alpha/f^2)$exptl., Np cm^{-1} sec^2	f,MHz	$10^{17}(\alpha/f^2)$exptl., Np cm^{-1} sec^2	f,MHz	$10^{17}(\alpha/f^2)$exptl., Np cm^{-1} sec^2	f,MHz
40.26	15.06	38.61	15.05	37.00	15.05
28.78	25.11	30.07	25.10	30.74	25.10
24.82	35.13	25.23	35.14	26.61	35.13
23.55	45.24	24.16	45.24	26.05	45.23
22.70	55.29	23.13	55.29	24.38	55.28
21.98	65.32	22.26	65.31	23.31	65.32
22.00	75.38	22.22	75.37	23.29	75.38
21.68	85.43	22.06	85.41	23.18	85.41
21.38	95.48	21.89	95.46	22.84	95.47
21.18	105.5	21.53	105.5	22.49	105.5
21.19	115.6	21.50	115.6	22.50	115.6
20.87	125.6	21.26	125.6	22.16	125.6
20.65	135.7	21.44	135.7	22.03	135.7
20.44	145.7	21.29	145.7	22.23	145.7
20.27	155.7				
20.12	165.8				
19.57	175.8				
19.48	185.9				

APPENDIX II (con't): Experimental Absorption as (α/f^2) in Np cm^{-1} sec^2 for Aqueous Sodium Chloride and Cycloheptaamylose at 25°C.

$[NaCl]_o$ = 1.01 F.		$[NaCl]_o$ = 1.49 F.	
$[\beta\text{-CD}]_o$ = 0.00971 M.		$[\beta\text{-CD}]_o$ = 0.00917 M.	
$10^{17}(\alpha/f^2)$exptl., Np cm^{-1} sec^2	f,MHz	$10^{17}(\alpha/f^2)$exptl., Np cm^{-1} sec^2	f,MHz
36.16	15.05	31.55	15.04
27.90	25.09	26.15	25.10
24.39	35.13	23.68	35.06
22.38	45.22	21.88	45.24
21.85	55.24	21.27	55.24
21.89	65.28	20.74	65.28
20.90	75.33	20.79	75.33
21.06	85.37	20.49	85.38
20.52	95.43	20.40	95.41
20.32	105.4	20.24	105.5
20.41	115.5	20.13	115.4
20.14	125.5	19.81	125.6
20.08	135.6	19.90	135.6
20.11	145.6	19.35	145.6