THE USE OF POLYETHERS IN THE TREATMENT OF ACIDIC HIGH ACTIVITY NUCLEAR WASTES

Second Progress Report

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Reporting Period: June 1, 1977 - May 31, 1978

Date Published - February 15, 1978

PREPARED FOR THE
DEPARTMENT OF ENERGY
OFFICE OF BASIC ENERGY SCIENCES
DIVISION OF CHEMICAL SCIENCES
UNDER CONTRACT E(38-1)-884

NOTICE

PERSONNEL

1. The principal investigator (Milton W. Davis, Jr.) devoted three full time summer months and 20% of each of the nine academic months during 1977-78.
2. Irene Gerow - Third year graduate student working for a Ph.D. has spent three full time summer months and twenty hours per week during each of the nine academic months during 1977-78.
3. James Rutland - With M.S. degree in chemical engineering spent three summer months in 1977 working on project before taking a job in Arabia at $35,000 per year.
4. Two undergraduate chemical engineering students are helping Miss Gerow with the analytical work.

In order to make graduate school more attractive it should be noted that in the budget for 1978-79 and 1979-80 I have raised the graduate student stipend from $425/month to $600/month. With starting salaries of at least $18,600 per year for B.S. students even this may not be enough to attract high quality graduate students. The University of Houston, for example, is paying some of their graduate students $800/month.

The 1977-78 Research Accomplishments Supported by DOE Contract No. E(38-1)-884

ABSTRACT

The objective of this work is to develop a solvent extraction process for treating acidic high activity nuclear wastes in order to remove 99.9% of the cesium and strontium. The removal of 99.9% will lower the relative toxicity(1) of 10 year old waste by a factor of 10^3. In order to accomplish this, a series of macrocyclic polyethers "crown" compounds which have the ability to form organic soluble complexes with the alkali metals (Cs^{+1}) and the alkaline earth metals (Sr^{+2}) are being screened. These "crown" compounds have been tested for solubility in both carbon tetrachloride (CCl_4) and kerosene, each solvent containing a range of tributyl phosphate (TBP) concentrations. Also distribution coefficients of both cesium and strontium have been measured between these organic phases with individual "crown" compounds dissolved in them and an aqueous phase containing no acid or an aqueous phase containing nitric acid with acid concentrations varying from .0125M to 3M. Other distribution coefficients for both metals have been measured in systems as above with di-2-ethylhexyl phosphoric acid (DEHPA) added as a source of organic soluble anions.

The results of these tests show very good extraction of the Cs^{+1} and Sr^{+2} into the organic phase when (DEHPA) is used to furnish organic soluble anions. The highest distribution coefficients obtained (organic/aqueous)(2) were .8 ± .05 for Cs^{+1} and 2000 for Sr^{+2}. The search for a more organic soluble "crown" compound continues as this would increase the amount of metal carried by the organic phase. For this reason, Parish Chemical Company in Provo, Utah is preparing a new "crown", 4, 4'(5') didecylcyclohexo 24-crown-8

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(1) Relative toxicity is the ratio of the concentration in the waste to maximum permissible concentration in public zone waste. See DP-MS-73-58 by R. F. Bradley, W. H. Hale and R. M. Wallace of the Savannah River Laboratory, E. I. du Pont de Nemours, Aiken, South Carolina 29801.

(2) Obtained by equilibrating equal volumes of aqueous and organic.

by hydrogenation of bis (4, 4'(5') decanoylbenzo) 24-crown-8.

This approach appears promising, and other compounds of this type will be tested in the future since it is unlikely that this is the one best suited to meet all of the requirements of nuclear processing.

RESEARCH RESULTS

The four "crown" compounds tested this past year for possible use in a solvent extraction process to extract cesium (Cs^{+1}) and strontium (Sr^{+2}) into an organic phase from an aqueous phase are named in Table I and their structures shown in Figure 1.

Table I
Names, Numbers and Melting Ranges for
Structures in Figure I

	Name and Number	Melting Ranges
I.	dibenzo 24-crown-8[a]	103° - 104°C
II.	4, 4'(5') di-tert-butylbenzo 24-crown-8 (BB)[a]	Waxy
IIIA.	Bis (4, 4'(5') decanoylbenzo) 24-crown-8 (BDB) (less soluble isomer)	85° - 95°C
IIIB.	Bis (4, 4'(5') decanoylbenzo) 24-crown-8 (more soluble isomer)	61°-70°C
IV.	Bis (4, 4'(5') [1-hydroxydecyl] benzo) 24-crown-8	90° - 94°C
V.	4, 4'(5') didecylcyclohexo 24-crown-8	In preparation
VI.	di-2-ethylhexyl phosphoric acid (DEHPA)	Liquid

a - melting range reported last year

Crown V is now being prepared by Parish Chemical Company in Provo, Utah. It is hoped that this "crown" compound will be more soluble in the organic phase and less soluble in the aqueous phase than the current "crown" compounds (See Figure 2 and Tables II and III). The choice of 24-crown-8 compounds resulted from previous work by Frensdorff[(3)] indicating that this size "crown" would be one of the best for Cs^{+1} complexation. Some 21-crown-7 compounds have been considered and may be used for Sr^{+2} complexation in the coming year as Parish Chemical Company can now supply two of these "crowns".

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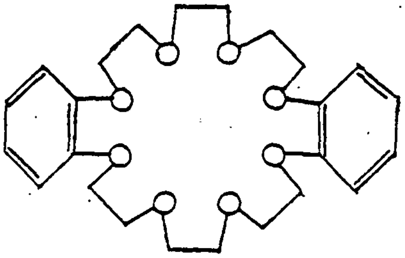
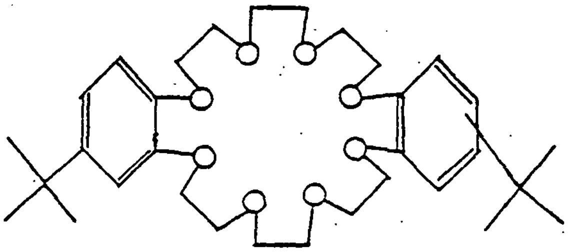
(3) H. K. Frensdoff, JACS, 93, 600 (1971)

FIGURE 1



I



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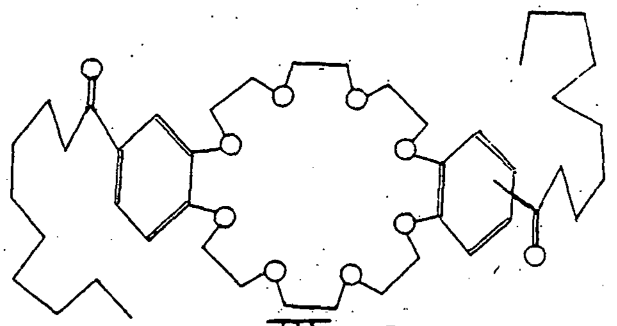
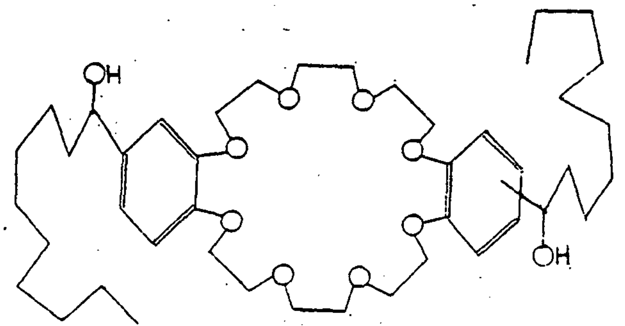
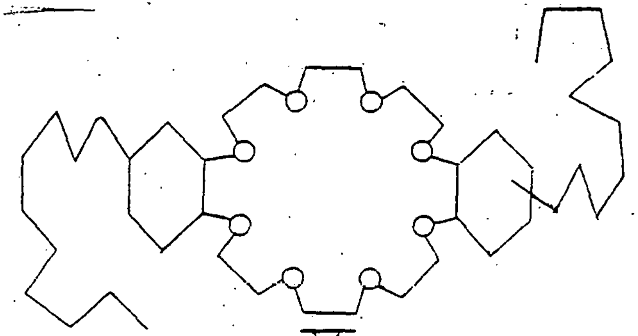


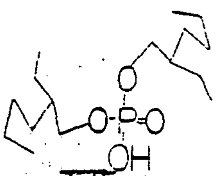
III A,B



IV



V



VI

Table II
Solubility of "Crown" Compounds in Organic Solvents at 25°C

Solvents	Solubility moles/liter	Compound[a]
100% TBP	.0130	I[b]
100% CCl_4	.0200	I[b]
50 vol% TBP in kerosene	.0229	II[b]
100% TBP	.0310	II[b]
100% CCl_4	.0500	II[b]
50 vol% TBP in kerosene	.0030	IIIA[b]
100% TBP	.0019	IIIA[b]
100% CCl_4	.0072	IIIA[b]
50 vol% TBP in kerosene	.0096	IIIB
100% TBP	.0139	IIIB
100% CCl_4	.0325	IIB
50 vol% TBP in kerosene	.0015	IV
100% TBP	.0085	IV
100% CCl_4	~0	IV

a - see figure I for Structures

b - solubilities reported last year

Table III
Solubility of "Crown" Compounds in HNO_3 at 25°C

Solubility moles/liter		
.10MHNO_3	2MHNO_3	Compound[a]
.00035	.0017	I[b]
.00009	.0054	II[b]
.00004	.00044	IIIA[b]
.00017	.00048	IIIB
.00019	.00018	IV
.00146	--	VI[c]

a - see figure I for structures

b - solubilities reported last year

c - di-2-ethylhexyl phosphoric acid

Better physical fit of the metal ion in the crown should provide better selectivity.

Compound VI in Table I and Figure 1 is the organic soluble anion supplier (DEHPA) which has been successfully used this past year. This compound is totally misible in the organic phase. It also has a rather higher solubility in the aqueous phase (Table III) and needs a very low aqueous phase acid concentration to ionize and shed a H+ into the aqueous phase allowing the remainder to be the organic soluble anion needed to allow substantial distribution of Cs^{+1} and Sr^{+2} into the organic phase. For these reasons, other compounds of this type need to be looked at.

The "crowns" are being dissolved in either CCl_4 or kerosene with varying concentrations of tributyl phosphate (TBP). Also as much as 50% DEHPA (VI) was added to the organic phase as an organic soluble anion supplier in some of the tests. The aqueous phases tested were distilled water or aqueous HNO_3 concentrations from .0125M to 3M containing .001M Cs^{+1} or Sr^{+2}. Also tests using .001M or .01M KNO_2 added to the aqueous phase have been made where the NO_2^- is used as an alternate anion to the NO_3^-. From a study of molecular models, the NO_2^- fits better with the "crowns" than the NO_3^- and therefore improves the metal distribution coefficient somewhat.

The best distribution coefficients for Cs^{+1} and Sr^{+2} with KNO_2 are .065 ± .02 and .08 ± .02 respectively. Since the K^{+1} competes with the Cs^{+1} and Sr^{+2} for the "crown" its distribution coefficients are also noted .10 ± .02 with Cs^{+1} and .16 ± .02 with Sr^{+2}. With DEHPA (VI), the best distribution coefficients for Cs^{+1} and Sr^{+2} are .8 ± .05 and 2000 respectively. Thus the use of DEHPA has resulted in a giant step toward a workable solvent extraction process. These data are displayed in the following graphs.

Explanation of Graphs:

All data was obtained by shaking equal volumes of aqueous and organic phases

Metal concentrations in the aqueous phase after shaking, were determined by using the Jarrell-Ash Atomic Absorption Spectrophotometer.

(1) Figures 3 and 5: Using Crown II (BB) and DEHPA (VI) in TBP with kerosene or CCl_4, the highest distribution coefficients, thus far, have been obtained. Lowering the concentration of DEHPA also lowers the distribution coefficient. Also using .10M HNO_3 in the aqueous phases causes the distribution coefficient of Cs^{+1} to go to zero. This indicates that the Cs^{+1} and Sr^{+2} can be moved from one phase to the other by changing the aqueous phase pH.

(2) Figures 4 and 6: There is no crown present in these tests to extract the metals; this shows the extraction of the metal due to the DEHPA alone.

(3) Figures 7 and 8: Variation of the ionic strength over the range of .002 to 3.00 using $Al(NO_3)_3$ showed no significant effect on the distribution coefficients of Cs^{+1} and Sr^{+2}. Variation of the ionic strength over the same range using HNO_3 showed no significant effect on the distribution coefficients. Variation of the ionic strength using HNO_3 and .001M KNO_2 does show some higher distribution coefficients.

(4) Figures 9 and 10: Distributions of Cs^{+1} and Sr^{+2} using .10M HNO_3 or .10M HNO_3 with .001M KNO_2 or .10M HCl in the aqueous phase and Crown II or IIIA in the organic phase. No significant extraction of Sr^{+2} or Cs^{+1} into the organic phase was obtained.

(5) Figures 11 and 12: Using KNO_2 and HNO_3 to vary the ionic strength in the aqueous phase and Crown II in varying volume percents of TBP in kerosene, the distributions of Cs^{+1} and Sr^{+2} were obtained, but are not especially significant.

The DEHPA type process is clearly the most promising lead thus far and will be pursued vigorously. A solvent extraction system compatible with the Purex process seems possible.

FIGURE 2

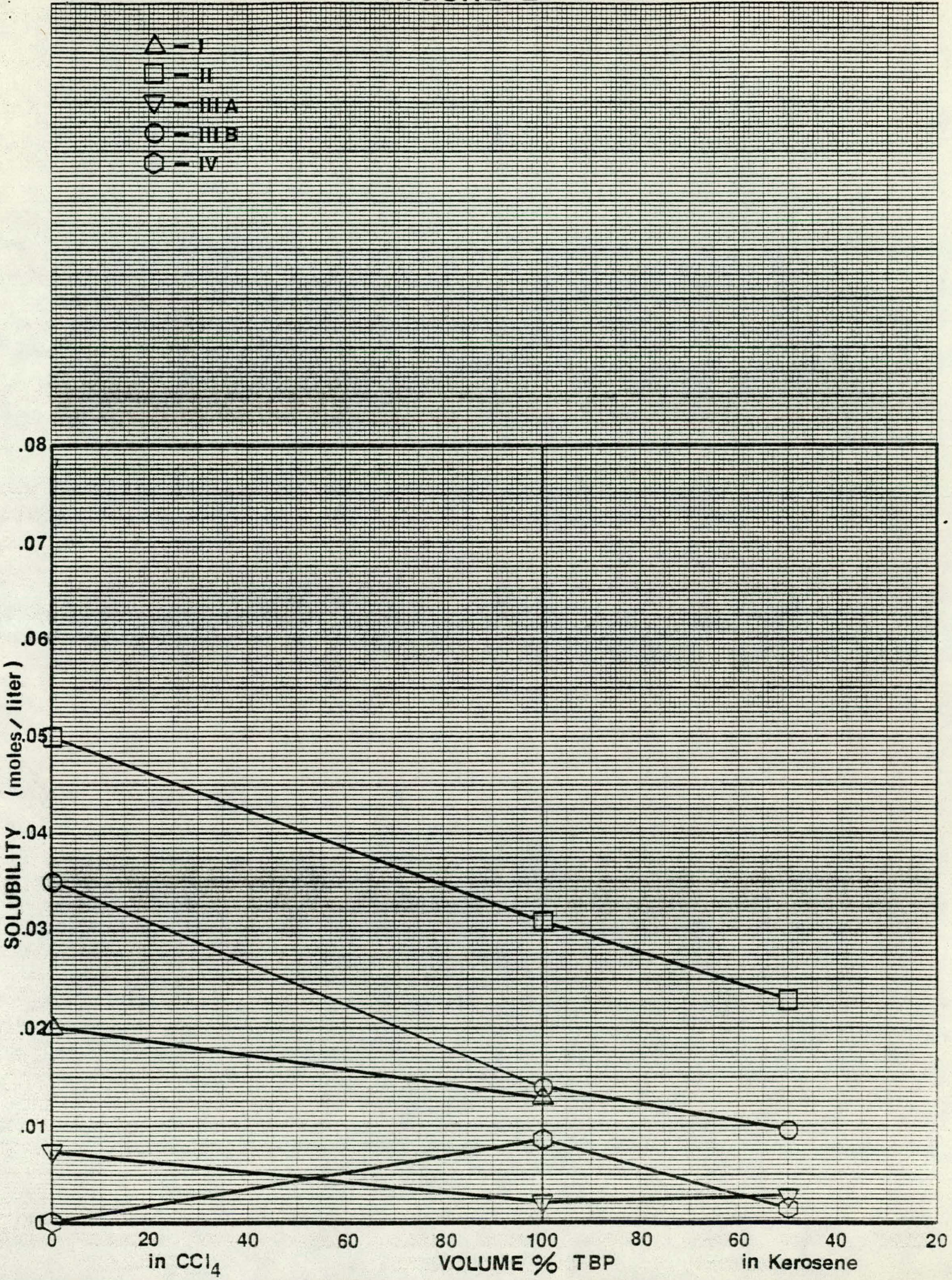

△ — I
□ — II
▽ — III A
○ — III B
⬡ — IV
SOLUBILITY (moles/ liter)
.08
.07
.06
.05
.04
.03
.02
.01
0
0
20
40
60
80
100
80
60
40
20
in CCl4
VOLUME % TBP
in Kerosene

FIGURE 3

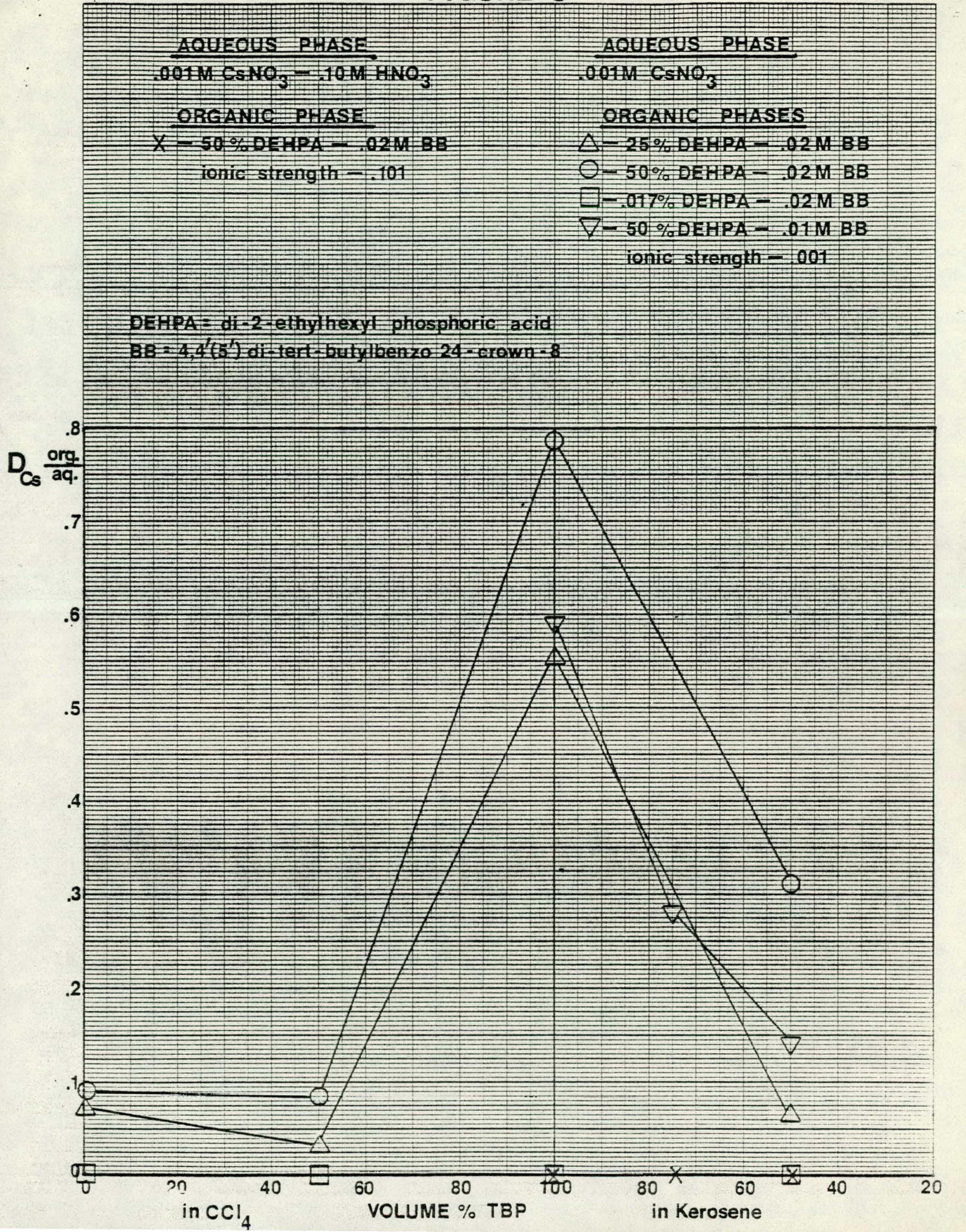

AQUEOUS PHASE
.001M CsNO$_3$ — .10M HNO$_3$
ORGANIC PHASE
X — 50 % DEHPA — .02M BB
ionic strength — .101
AQUEOUS PHASE
.001M CsNO$_3$
ORGANIC PHASES
△ — 25 % DEHPA — .02M BB
○ — 50 % DEHPA — .02M BB
□ — .017% DEHPA — .02M BB
▽ — 50 % DEHPA — .01M BB
ionic strength — .001
DEHPA = di-2-ethylhexyl phosphoric acid
BB = 4,4′(5′) di-tert-butylbenzo 24-crown-8
$D_{Cs} \frac{org.}{aq.}$
.8
.7
.6
.5
.4
.3
.2
.1
0
0
20
40
60
80
100
80
60
40
20
in CCl$_4$
VOLUME % TBP
in Kerosene

FIGURE 4

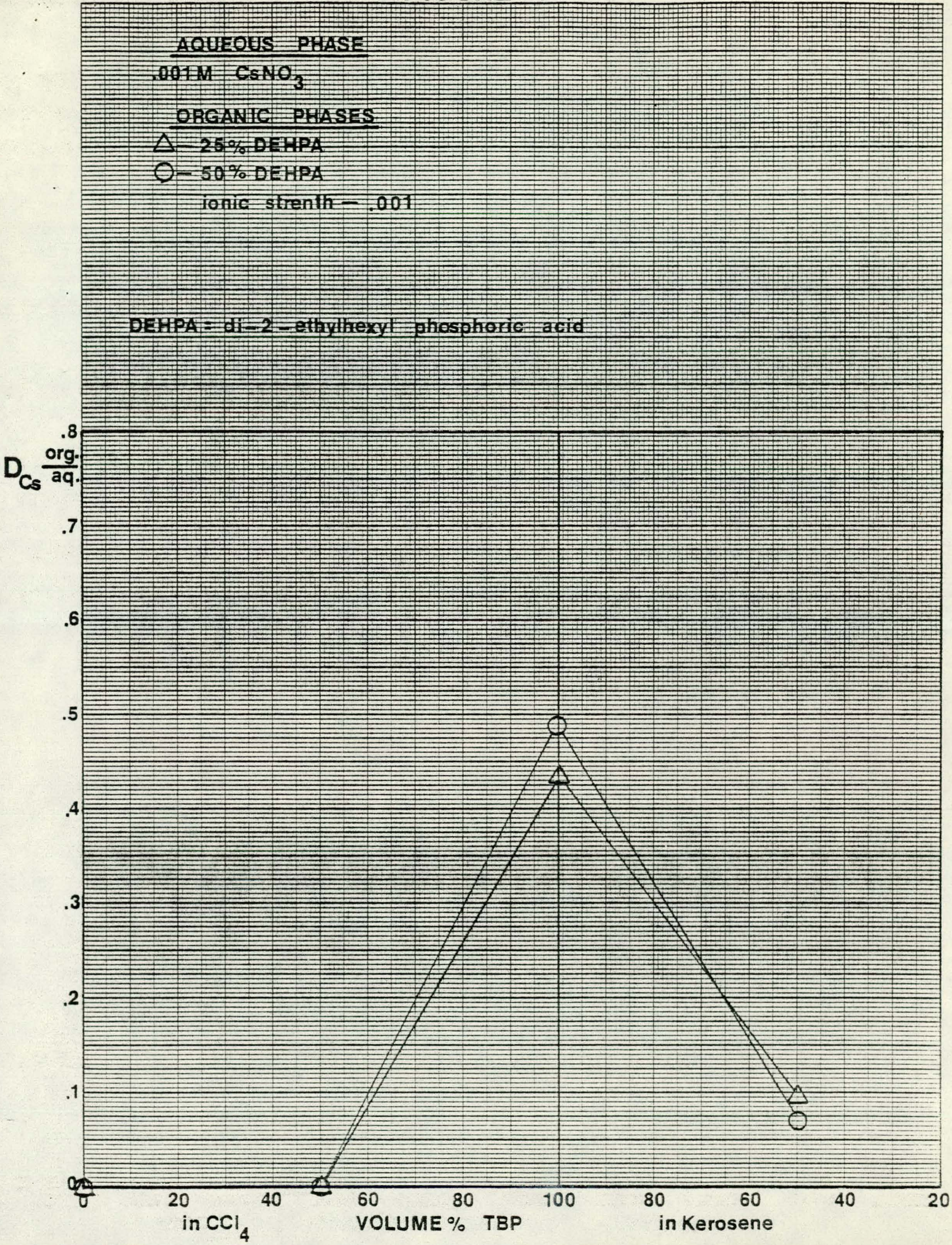

AQUEOUS PHASE
.001 M $CsNO_3$
ORGANIC PHASES
△ – 25% DEHPA
○ – 50% DEHPA
ionic strenth – .001
DEHPA = di–2–ethylhexyl phosphoric acid
$D_{Cs}\,\frac{org.}{aq.}$
.8
.7
.6
.5
.4
.3
.2
.1
0
0
20
40
60
80
100
80
60
40
20
in CCl_4
VOLUME % TBP
in Kerosene

FIGURE 5

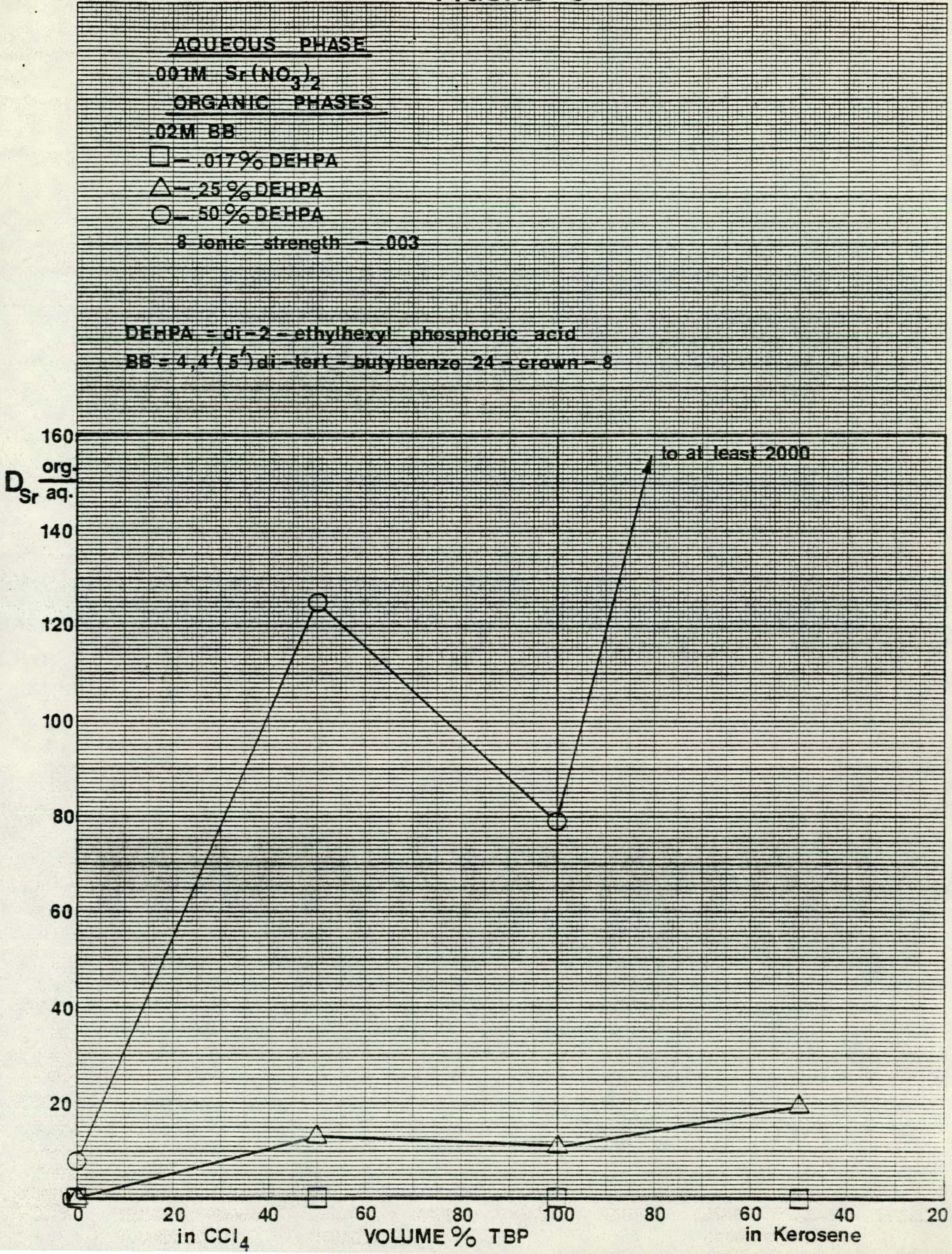

AQUEOUS PHASE
.001M $Sr(NO_3)_2$
ORGANIC PHASES
.02M BB
□ — .017% DEHPA
△ — .25% DEHPA
○ — 50% DEHPA
8 ionic strength — .003
DEHPA = di-2-ethylhexyl phosphoric acid
BB = 4,4′(5′)di-tert-butylbenzo 24-crown-8
to at least 2000
$D_{Sr}\ \frac{org.}{aq.}$
160
140
120
100
80
60
40
20
0
0
20
40
60
80
100
80
60
40
20
in CCl_4
VOLUME % TBP
in Kerosene

FIGURE 6

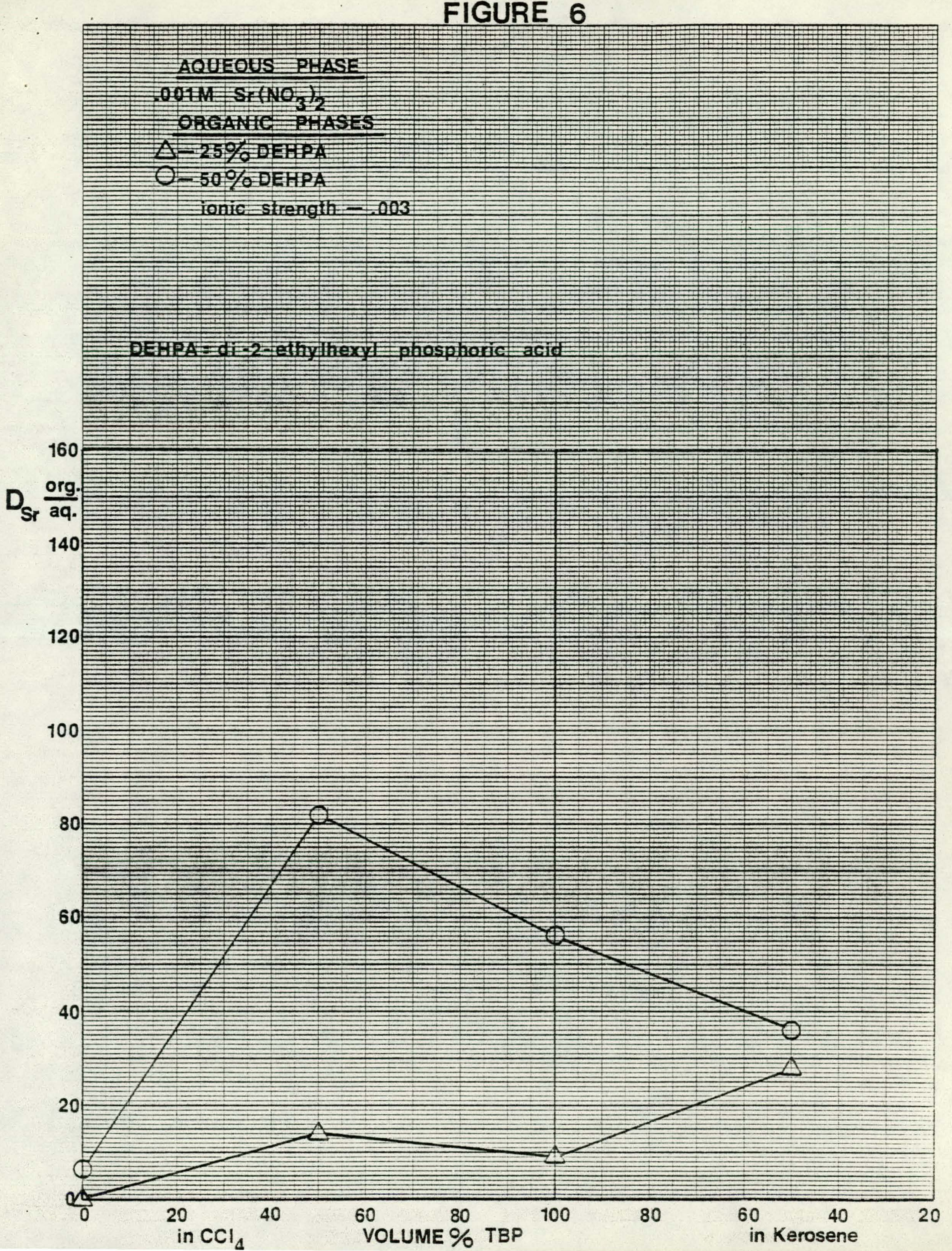

AQUEOUS PHASE
.001M $Sr(NO_3)_2$
ORGANIC PHASES
△ — 25% DEHPA
○ — 50% DEHPA
ionic strength — .003
DEHPA = di-2-ethylhexyl phosphoric acid
$D_{Sr}\ \frac{org.}{aq.}$
160
140
120
100
80
60
40
20
0
0
20
40
60
80
100
80
60
40
20
in CCl_4
VOLUME % TBP
in Kerosene

FIGURE 7

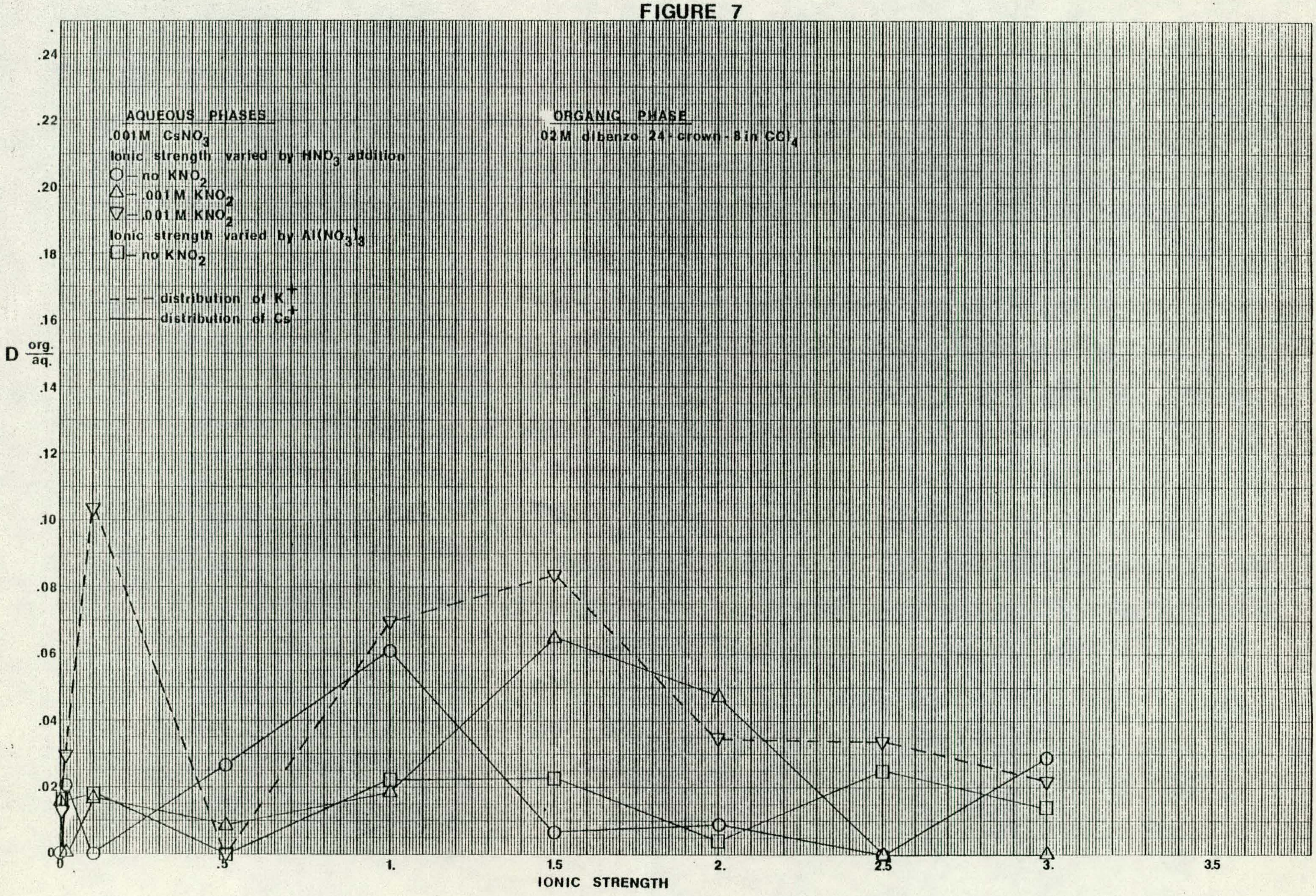

AQUEOUS PHASES
.001M CsNO3
Ionic strength varied by HNO3 addition
○ – no KNO2
△ – .001 M KNO2
▽ – .001 M KNO2
Ionic strength varied by Al(NO3)3
□ – no KNO2
– – – distribution of K+
—— distribution of Cs+
ORGANIC PHASE
.02M dibenzo 24-crown-8 in CCl4
D org./aq.
.24
.22
.20
.18
.16
.14
.12
.10
.08
.06
.04
.02
0
0
.5
1.
1.5
2.
2.5
3.
3.5
IONIC STRENGTH

FIGURE 8

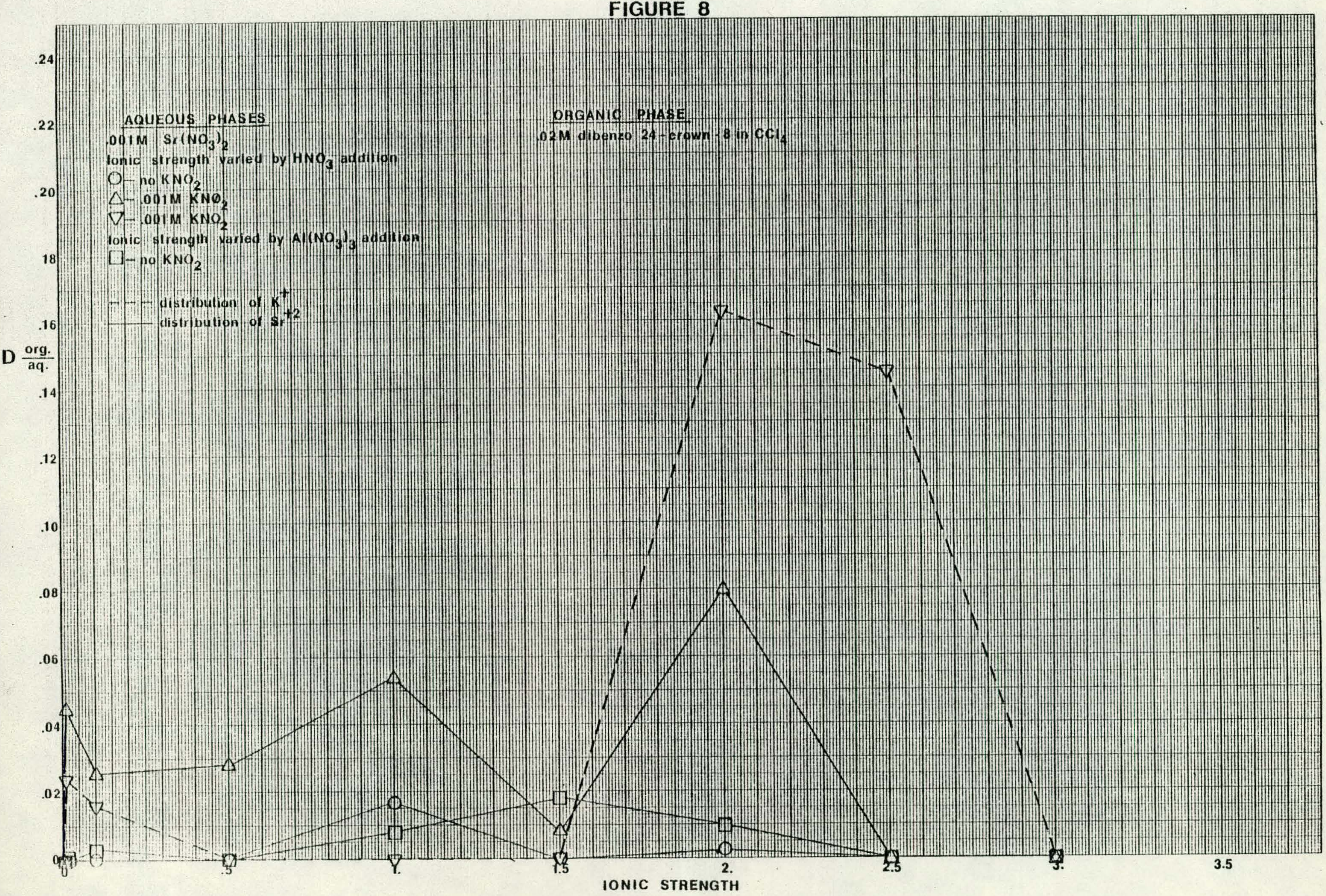

AQUEOUS PHASES
.001M $Sr(NO_3)_2$
Ionic strength varied by HNO_3 addition
○ – no KNO_2
△ – .001M KNO_2
▽ – .001M KNO_2
Ionic strength varied by $Al(NO_3)_3$ addition
□ – no KNO_2
- - - distribution of K^+
—— distribution of Sr^{+2}
ORGANIC PHASE
.02M dibenzo 24-crown-8 in CCl_4
.24
.22
.20
18
.16
.14
.12
.10
.08
.06
.04
.02
0
D $\frac{org.}{aq.}$
0
.5
1.
1.5
2.
2.5
3.
3.5
IONIC STRENGTH

FIGURE 9

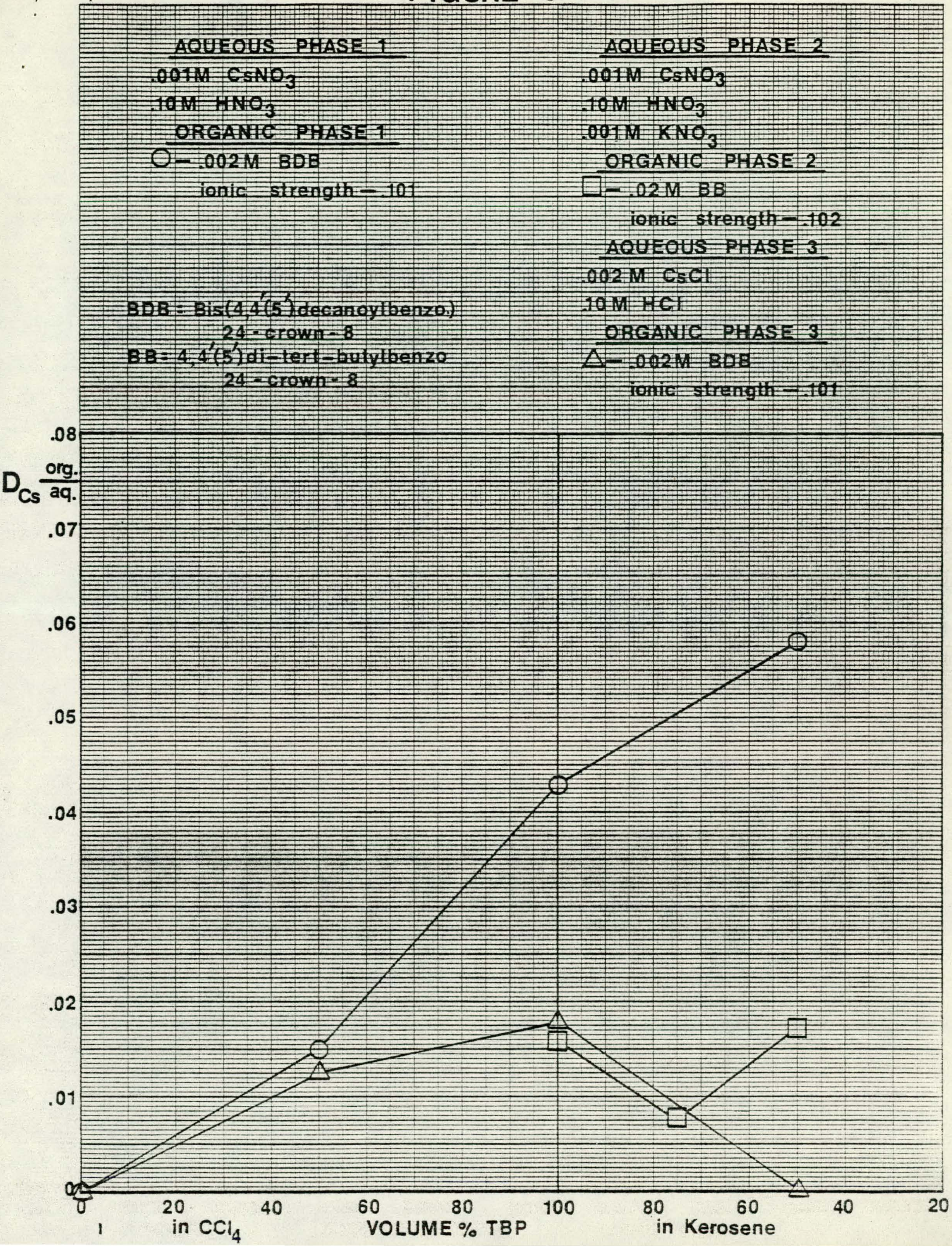

AQUEOUS PHASE 1
.001M CsNO3
.10M HNO3
ORGANIC PHASE 1
○ — .002M BDB
ionic strength — .101
AQUEOUS PHASE 2
.001M CsNO3
.10M HNO3
.001M KNO3
ORGANIC PHASE 2
□ — .02M BB
ionic strength — .102
AQUEOUS PHASE 3
.002M CsCl
.10M HCl
ORGANIC PHASE 3
△ — .002M BDB
ionic strength — .101
BDB = Bis(4,4'(5')decanoylbenzo)
24 - crown - 8
BB = 4,4'(5')di-tert-butylbenzo
24 - crown - 8
D Cs org./aq.
.08
.07
.06
.05
.04
.03
.02
.01
0
0
20
40
60
80
100
80
60
40
20
in CCl4
VOLUME % TBP
in Kerosene

FIGURE 10

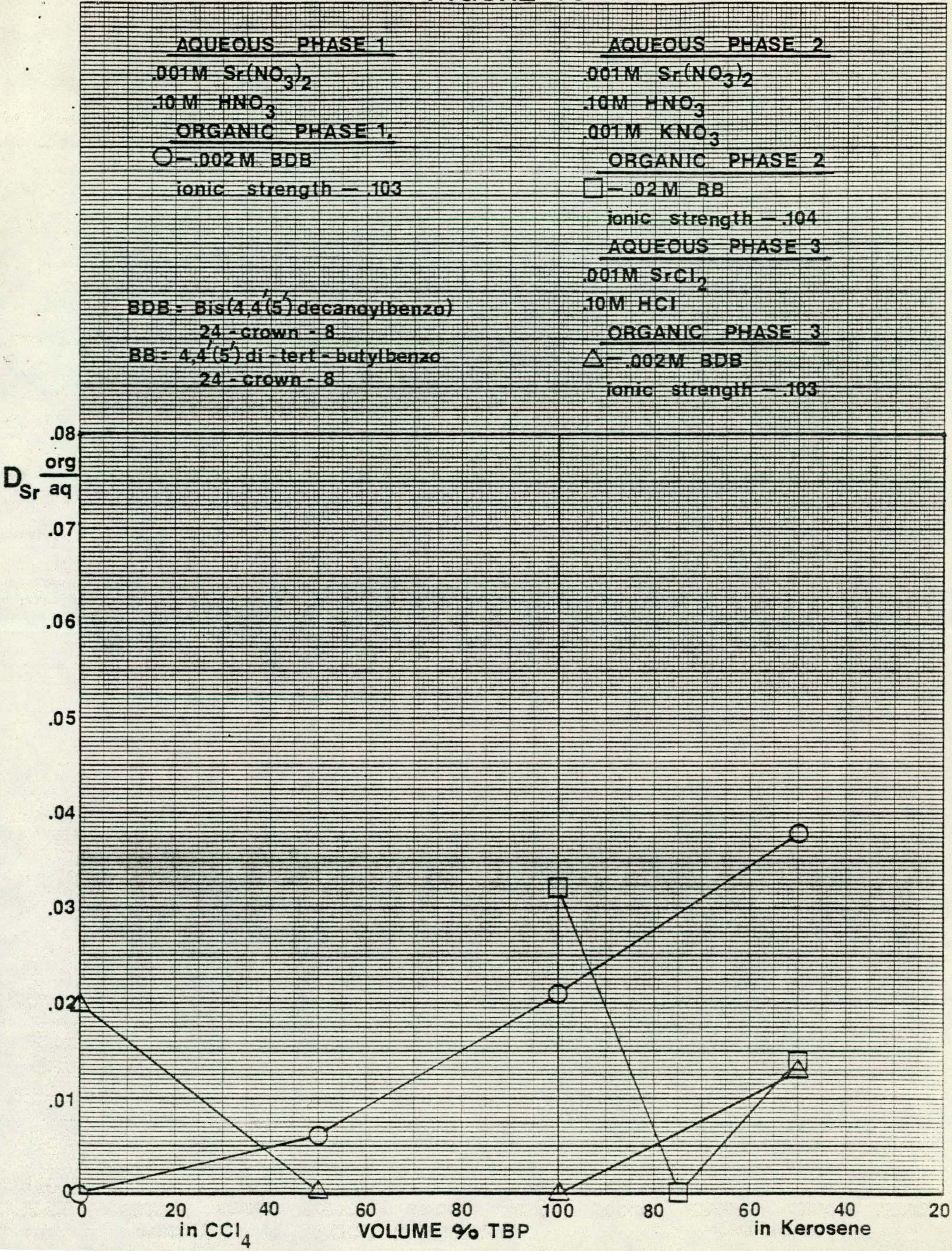

AQUEOUS PHASE 1
.001M $Sr(NO_3)_2$
.10M HNO_3
ORGANIC PHASE 1
○ — .002M BDB
ionic strength — .103
AQUEOUS PHASE 2
.001M $Sr(NO_3)_2$
.10M HNO_3
.001M KNO_3
ORGANIC PHASE 2
□ — .02M BB
ionic strength — .104
AQUEOUS PHASE 3
.001M $SrCl_2$
.10M HCl
ORGANIC PHASE 3
△ — .002M BDB
ionic strength — .103
BDB = Bis(4,4'(5')decanoylbenzo) 24 - crown - 8
BB = 4,4'(5') di - tert - butylbenzo 24 - crown - 8
$D_{Sr} \frac{org}{aq}$
.08
.07
.06
.05
.04
.03
.02
.01
0
0
20
40
60
80
100
80
60
40
20
in CCl_4
VOLUME % TBP
in Kerosene

FIGURE 11

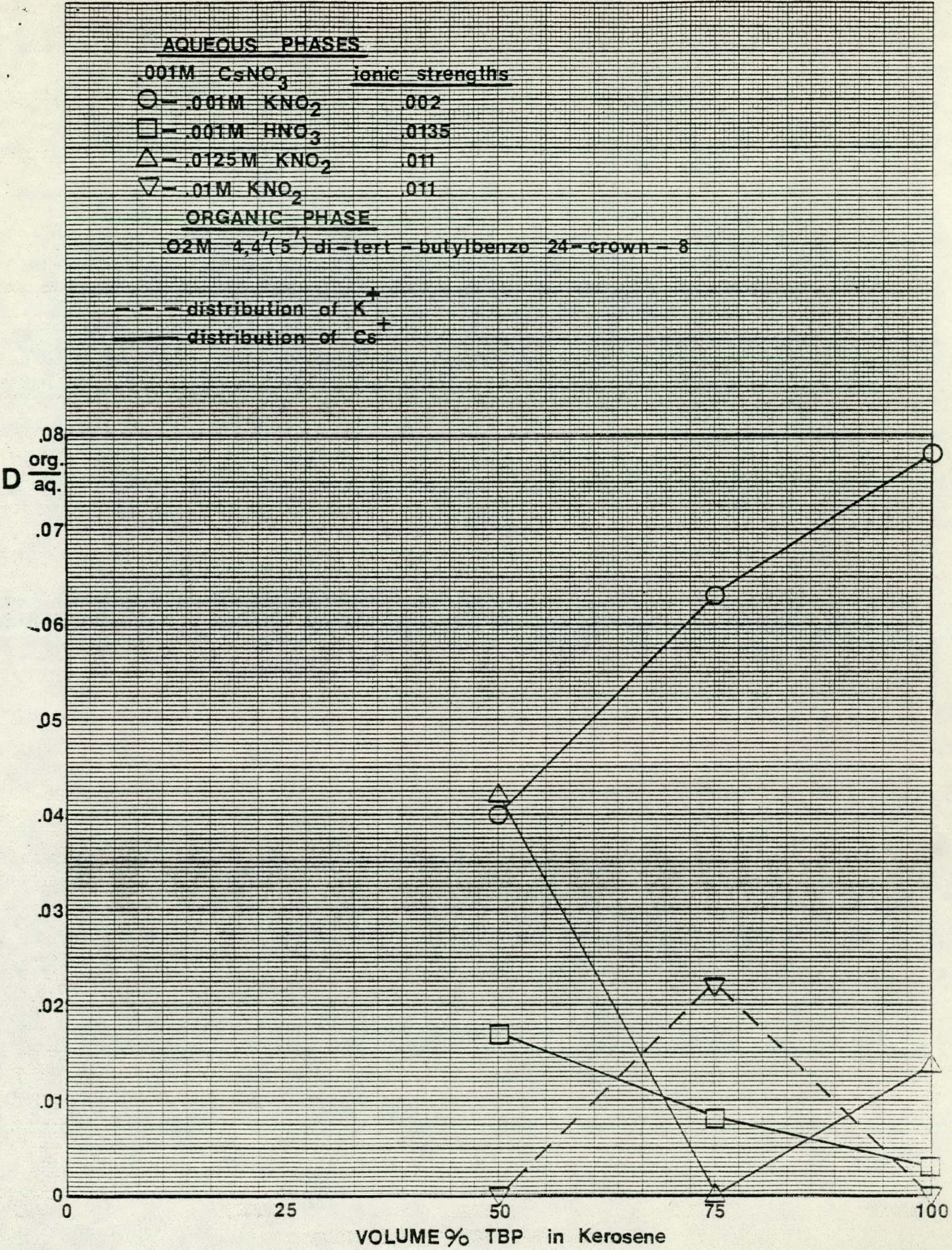
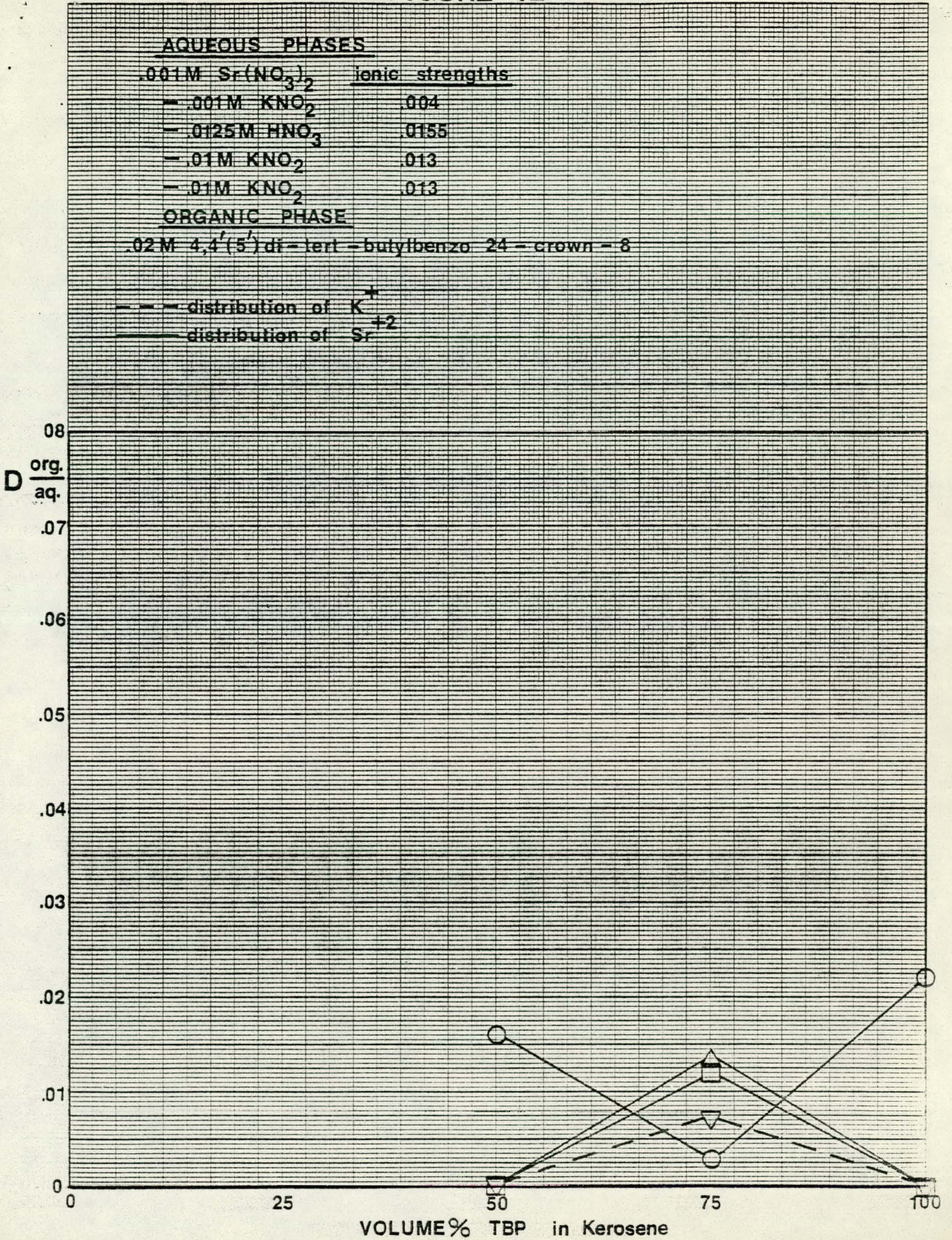

AQUEOUS PHASES
.001M CsNO3
ionic strengths
○ – .001M KNO2 .002
□ – .001M HNO3 .0135
△ – .0125M KNO2 .011
▽ – .01M KNO2 .011
ORGANIC PHASE
.02M 4,4'(5')di-tert-butylbenzo 24-crown-8
– – – distribution of K+
—— distribution of Cs+
D org./aq.
.08
.07
.06
.05
.04
.03
.02
.01
0
0
25
50
75
100
VOLUME % TBP in Kerosene

FIGURE 12


AQUEOUS PHASES
.001M Sr(NO3)2
ionic strengths
— .001M KNO2 .004
— .0125M HNO3 .0155
— .01M KNO2 .013
— .01M KNO2 .013
ORGANIC PHASE
.02M 4,4′(5′) di-tert-butylbenzo 24-crown-8
— — — distribution of K+
——— distribution of Sr+2
D org./aq.
08
.07
.06
.05
.04
.03
.02
.01
0
0
25
50
75
100
VOLUME % TBP in Kerosene

PUBLICATIONS

No publications have resulted from this work as yet but several should be forthcoming as soon as patent clearance is obtained.