SELECTIVE ION EXCHANGE RESIN

(II) *Physical chemistry of Chelate*
Reaction in Resins

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Annusual selectivity of chelate resins towards heavy metal ions was shown in the previous paper.[1] This paper deals with physical chemistry of chelating reactions in resins. In order to analyse the chelate reactions in polymer, many kinds of chemical properties of 3 Hydroxyphenyl thiourea–phenol resin have been considered in thermodynamical point of view. It is widely recognized that the increase in the stability of coordination compounds results from chelate ring formation.[2] This stability of chelate compounds is attributed not only to an increase in bond strength resulting from formation of the ring but also to a statistical or probability effect associated with chelation.

Since the enthalpy of chelate formation, ΔH, is considered a measure of the binding energy and the entropy of formation, ΔS, includes all stability factors of the controlling the stability of the chelate, measurment of these thermodynamic functions should provide the desired information. A determination of equilibrium constant in a chelate formation is very important not only for the study of chelate reaction but also for the purpose of understanding of the particular reactions which can be seen in proteins and other natural and artificial polymers. And this study will show us many beneficial uses and applications.

The determination of equilibrium constants will lead to a more comprehensive understanding of chelates and the relations which govern their formation and structure. The thermodynamic relations are;

$$\Delta F = -RT \ \ln K. \quad \cdots\cdots\cdots\cdots(1)$$

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \quad \cdots\cdots\cdots\cdots(2) \qquad \Delta F = \Delta H - T \Delta S \cdots\cdots\cdots\cdots(3)$$

These are important in a thorough study of any reaction. A number of factors offer serious limitations to the methods available for insoluble chelate resins. No systematic attempt to evaluate the relative contribution of each factor to chelate formation of low molecular compounds, to say nothing of high molecular compounds which are insoluble in any solvent. This paper deals with the chelation of Ag, Hg and Cu with 3-hydroxyphenylthiourea phenol–formaldehye resin and with 3-hydroxyphenythiourea (3HPTU) monomer in aqueous media.

From thermodynamical point of view, it is very important to determine.

the molar ratio of 3 HPTU to metal ion in the chelate. The more ring in chelate forms, the more stable it becomes, and it is very difficult to take away the metal ion from the chelate. There is no possibilty of knowing the structure of chelate bond in resin which is insoluble in any organic solvent through direct way, therefore the chelate formation of monomer from which polymer is produced is considered in various points of view and then the chelate formation in polymer were considered. Many methods may be applied for the determination of the molar ratio of chelate ligand to metal ion. Walter et al[3] determined the acid dissociation constants of thiourea and its analogs and the stability constants of severals of their metal complexes using the Calvin-Bjerrum potentiometric titration procedure. In their study values of n, the average number of reagent molecules bound to the metal, equalled four at the start of the titration in the case of each of the compounds studied with the metals Cu(I), Co(III) and Ni(II). This indicated that at even the lowest pH limit, complete complexing had occurred. This was not too surprising, however, since a comparison of the acid dissociation constants of the various ligands indicated that with the lack of ligand basicity, the competition between the metal and proton for the ligand was not very keen, so that the metal would tend to add to the ligand immediately upon combination. Acid dissociation constants should be at least 3.5—4.0 to enable the successful determination of stepwise formation constants. (Whether S or N atom is attached to Ag first in chelate formation is not obvious in this case.)
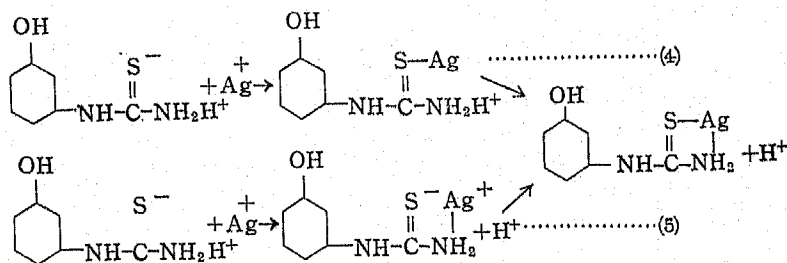
According to the reasons mentioned above, the combined 4 and 5 is applied to the calculation of equilibrium constant in this paper

$$K = \frac{[AgKe_2][H^+]}{[Ag][Ke]^2} \quad \cdots\cdots\cdots(6)$$

before applying this equation, the molar ratio of Ke to metal ion should be determined. The equilibrium constant may be calculated through the use of any combination measurements which allow calculation of activities of the four interaction substances. If the formula of the chelate is known and if the total amount of interacting substances may be calculated from the quantities introduced into the medium, then only a single measurement, unambiguously relate to the concentration of one of the substances involved, is needed to

determine the position of the equilibrium and to calculate Ke. Job[4] intro-
duced the simple calorimetric method for the determination of the composition
of chelate compounds in solution. For a constant total concentration of metal
and chelating agent, the concentration of chealte is greatest when the metal
and chelating agent are brought together in the same ratios in which they
exist in the chelates.   This technique was called the method of continuous
variation. Absorption spectra of 3HPTU, Ag, Hg, Cu respectively, and of
3HPTU–metal chelates have been determined in the wave length range 200—
700mμ. And the most favourable length range was decided and Job method
was applied.

EXPERIMENTAL

(I) Determination of the favourable wave length range[5]

A) Reagents : 3HPTU was purified by recrystallization from the hot.
aqueous solution for more than three times. The melting point of this compo-
und was found to be 183—184°C

Other reagents : Reagent grade KNO_3, $AgNO_3$, $Hg(NO_3)_2$ and $Cu(NO_3)_2$
were used without further purification.

Procedure : 5 ml of 0.005 M 3HPTU solution and 5 ml of 0.5 N HNO_3
were added to 100 ml measuring flask and filled up to 100 ml, the mixture
was held for 5 hr. to be constant for pH. Absorptimetric measurments in the
ultraviolet and the visible regions were made on the solutions prepared above
with Shimazu Model Q B 50 Spectrophotometer.

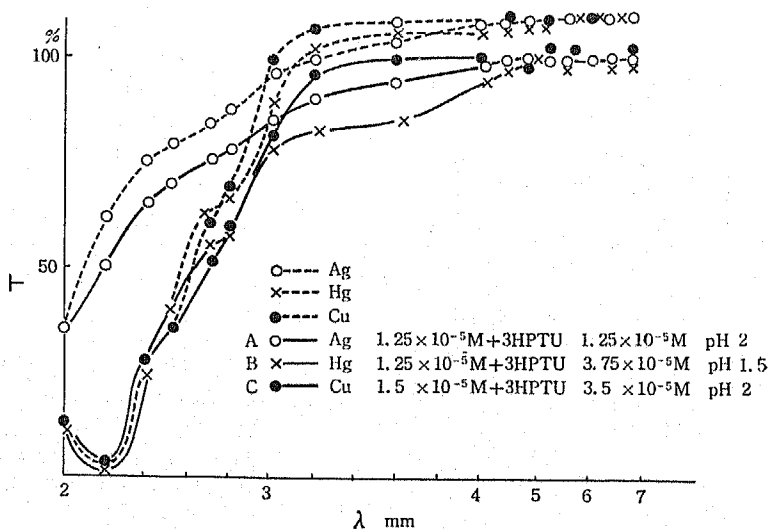B) Results; curve A, Fig. 1, shows the absorption curve of 3HPTU and

Fig. 1 Absorption spectra of 3HPTU and metal ions

Ag at pH 2. Curve B shows the absorption of 3HPTU and Hg at pH 1.5,
Curve C shows the absorption of 3HPTU and Cu at pH 2.

Chelate formation of 3HPTU with Ag, Hg and Cu may well be deter-
mined by absorption spectra at 300 mμ.

(II) Determination of molar ratio of 3HPTU to Ag Hg and Cu.

If substances are present which absorb light in the same region as does
the chelate, it is necessary to make allowance for this. In such a case the
difference in optical densities between the chelate and the estimated amounts
of unchelated colored substances present may be plotted as a function of the
concentration. Therefore the optical density that would have resulted if no
chelation had taken place is substracted from the observed optical density
and the difference ($\overline{D}$) is plotted against composition. Fig 3 shows the curves
obtained by plotting $\overline{D}$, the difference between the observed optical density
and that which would be obtained if no chelation had taken place, against
the ratio of Ag ion concentration [Ag], to total concentration of Ag ion and
3HPTU, [Ag]+[3HPTU].

The maximum definitely occurs at a ratio of 0.5, indicating a compound
in which molar ratio of metal to 3HPTU is I : I. This conclusion is further
supported by the dotted line, which represents the curve which would be
expected if the ratio were I : I. The result is consistent with that of expected
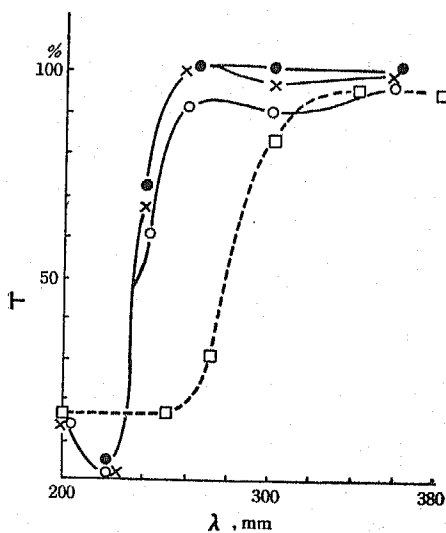

Fig.2 Absorption spectra of 3HPTU
    and metal ions
    □ 3HPTU 5×10⁻⁵M
    ○ Ag 3.5×10⁻⁵M   pH 1.9
    × Hg 2.5×10⁻⁵M   pH 2.2
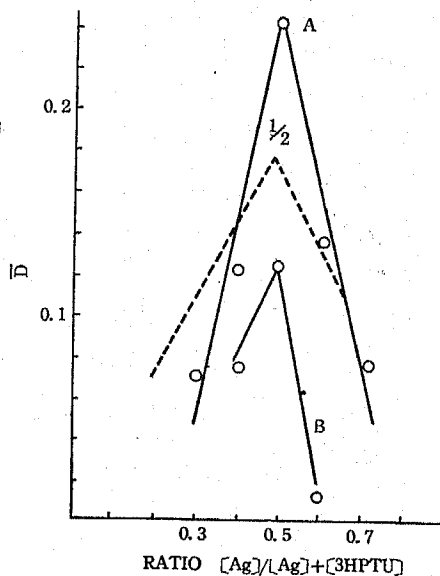   ○ Cu 2.5×10⁻⁵M   pH 1.8

Fig.3 Graphical determination of Com-
    position of Ag-3HPTU chelate
    $\overline{D}$ is optical density difference
    The dashed line is the relationships
    expected for 1 : 1
    The solide limes are the experime-
    ntal Curves A, λ=270; B, λ=300

from coordination number of Silver. Fig. 4 shows the curve obtained by plotting $\bar{D}$ against $[Cu] / [Cu] + [3HPTU]$. The maximum occurs at a ratio of about 0.2. This is much different from that of expected from coordination number of Cu. Hg has the same coordination number as Cu therefore much attention have been paid to get the more detailed results about this ratio. The results shown in Fig. 5 were the same as in the case of Cu. This phenomenon was explained as follows; Four membered chelate ring are relatively rare and there will be a considerable strain in bond angles of the atoms in chelate ring, and it is very difficult for a single Hg or Cu atom to form two chelate rings with two 3HPTU. Therefore only one of two ligands in thiourea group may be able to bond Cu atom which is already contained in a chelate ring. On account of this reason, two moles of 3HPTU are necessary to fill the coordination number of Cu after one complete chelate ring is formed with one mole of 3HPTU.
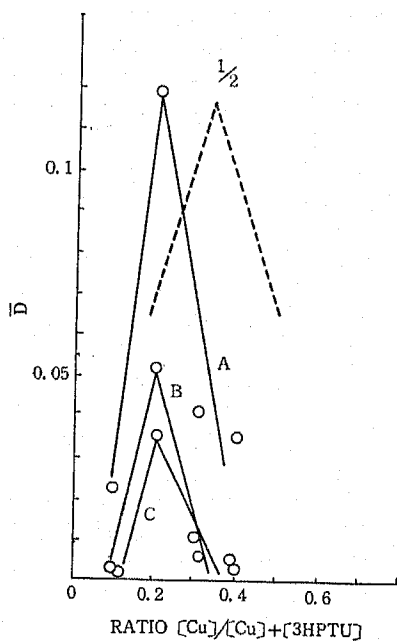

Fig. 4   Graphical determination of Composition of Cu-3HPTU. chelate
$\bar{D}$ is optical density difference
The dashed lines is the relationship expected for 1 : 1
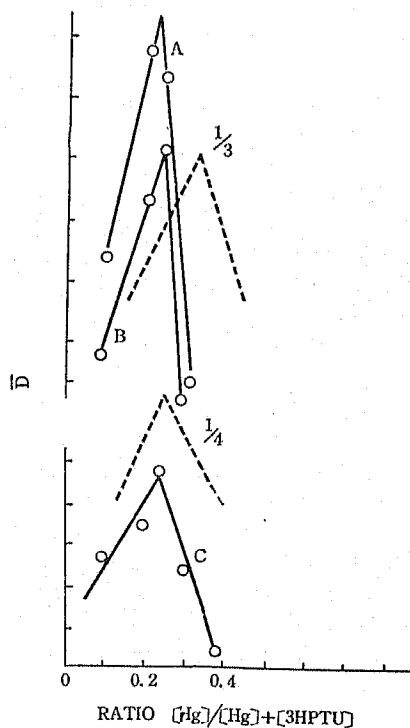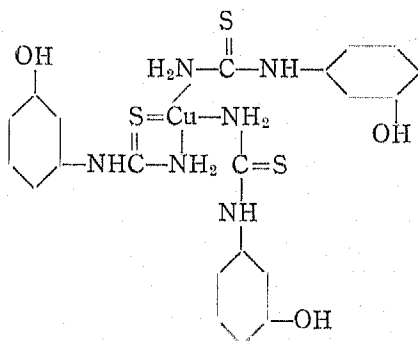The solide lines are the experimental Curves A, $\lambda=300$, B, $\lambda=320$, C, $\lambda=340$

Fig. 5   Graphical determination of Composition of Hg-3HPTU Chelate.
$\bar{D}$ is optical density difference
The dashed lines are the relationships expected for : 1 : 2, 1 : 3
A, $\lambda=340$, B, $\lambda=320$, C, $\lambda=300$

On the other hand, Ag will easily be filled up its coordination number "2" even with 3HPTU resin, because one thiourea group is enough to fill coordination number "2". In a cross linked resin phase, chelate ring can hardly be moved to other place for chelate formation, therefore, only one chelate group may bind with one metal ion in the cases of Hg and Cu.

(III) Determination of Equilibrium constant of Chelate formation in Resin.

Two methods were considered for this purpose.

(A) Calculation of K by the determination of Hydrogen ion concentration in solution :

The potentiometric measuremant of H ion concenration is the most accurate and reliable method for determination of chelate stability constants. The generalized method for this purpose has been thoroughly described by Bjerrum and various modifications of this method have been undertaken for each case. In order that this method may be apllied, Hydrogen ion should be produced stoichometrically in accordance with chelate formation of 3HPTU and metal ion. This means that the pH of a solution is directly affected by chelate formation since all chelating agents are also acids (or bases) and formation of the chelate is accompanied by the displacemant of a proton from the acid or by a decrease in concentration of the base. When the quantity of Ag added to the definite amonut of 3HPTU solution is samll, pH drop is negligible and pH drop proceeds abruptly as the quantity of Ag added to the 3HPTU becomes larger. Titration test were done by direct titration of 20 ml of 0.005 M 3HPTU solution with 0.02 N KOH in the presence of neutral salt KNO₃ · Then the same procedure was done with AgNO₃, HgCl₂ and Cu(NO₃)₂, The results were shown in Fig. 6-8. pH of the solution were determined with Shimazu Glass electrode pH meter Model GU2. As the quanitity of Cu added increases, the pH drop becomes greater, but beyond the point of 0.69 ml of solution, the breaks of the curves were seen in the same place as to the number of KOH solution, the ratio of 0.69 ml of the solution to 20 ml of 3HPTU solution means that the molar ratio of the chelate formed from 3HPTU and Cu is 3 : 1. Excess amount of Cu added to the definite amount of 3HPTU produces no more dissociable Hydrogen. As for number of KOH, the same fact was also seen. If one molecule of 3HPTU produces one Hxdrogen ion in accordance with chelate formation, a break should be

laid at the point of 5 ml of KOH in Fig. 6 but all breaks beyond the point of 0.69 ml of Cu (NO₃)₂ stand at the point of 1.6—1.7 ml of KOH : 1.6—1.7 ml is one third of 5 ml. These results are strictly the same as that of spectrometrical test. Two moleculs of 3HPTU bind the Cu ion which is contained in a complete chelate ring to fill the coordination number of Cu by giving one pair of electron per single 3HPTU molecule. Among three molecules, only one molecule which forms a complete chelate ring with Cu ion can give H ion to the solution, while other two can bind Cu without giving H ion to solution. Fig 7 shows the reaction of 3HPTU with Ag. No break was seen in the position expected from spectrophometrical determination. The more the amount of the Ag is, the more H ion in the solution is produced untill the

Fig. 6   pH titration of 3HPTU with KOH in the presence of Cu ion
×3HPTU; ◐3HPTU+0.5 ml Cu; ○3HPTU +0.69ml Cu, △3HPTU+1ml Cu; □3HPTU +1.5ml Cu; ◓3HPTU+2ml Cu
3HPTU=20ml of 0.005M 3HPTU solution+ 8ml of 2M KNO₃
Cu=0.05M Cu(NO₃)₂ solution

amount of Ag reaches 4 ml to 20 ml of 3HPTU solution. But more than 4 ml of Ag soltuion brought the breaks at the same place. The molar ratio of 4HPTU to Ag is 1 : 2. The same results as in the case of Ag were obtained in the case of Hg, Fig. 8, in Hg(NO₃)₂ region greater than 2 ml, all breaks are seen at the same quantity of KOH. In the cases of Ag and Hg, one 3HPTU molecule gives two H ion to the solution in accordance with chelate forma-tion and before reaching these points, no simple stoichiometrical relation is seen, Therefore it is not reasonable to deal with Cu Ag, and Hg under the same principle. From these reasons, the determination of equilibrium con-stants by potentiometric measurement of H ion in solution was put off to the next opportunity. The chelation of Cu with polyacrylic acid and polymeta-crylis acid has been investigated.

Wall and Gill[9] measured the ultraviolet spectra of partially neutralized polyacrylic acid (PAA) solutions containing Cu ion and found that single type of chelate was fromed over a wide range of conditions. They assumed that this chelate contained two caboxylates attached to the same polymer chain bound to Cu ion. The conclusion of Morawetz[10] indicated that four, rather than two, carboxylate groups of the polymer were participating in the
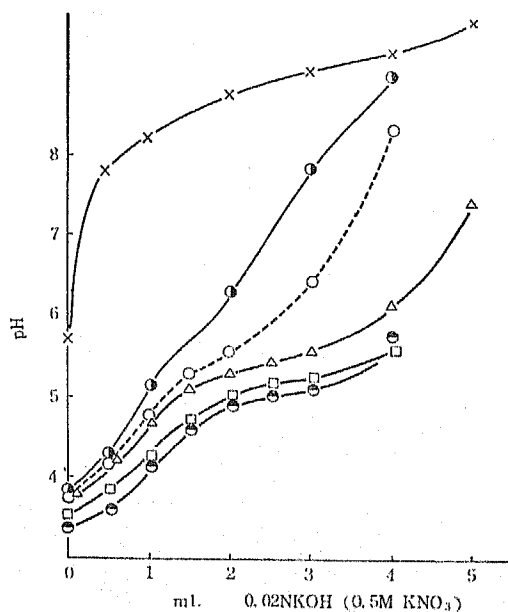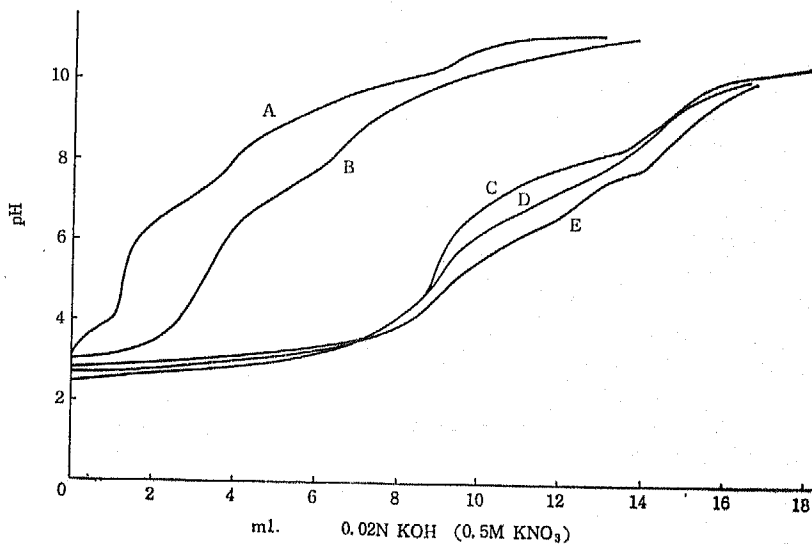
Fig. 7 pH titration of 3HPTU with KOH in the presence of Ag ion
0.05 M AgNO₃; A, 1 ml; B, 2 ml; C, 4 ml; D, 5 ml; E, 6 ml
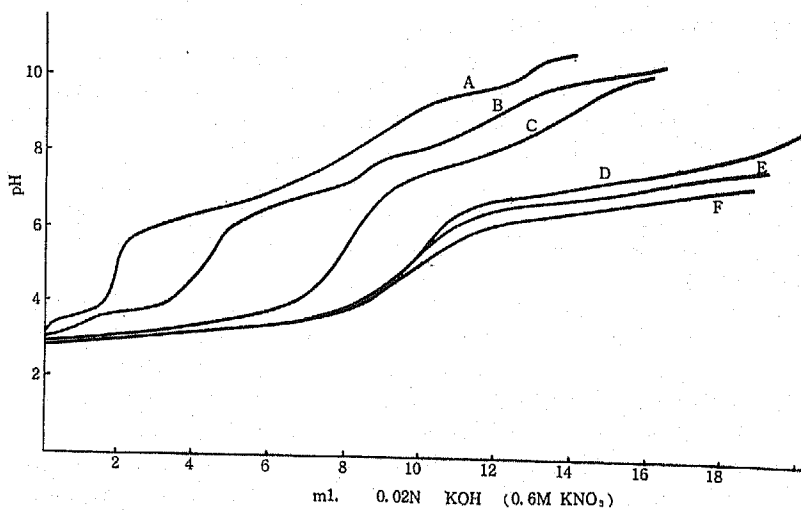0.005 M 3HPTU 20ml+2 MKNO₃ 8 ml

Fig. 8 pH titration of 3HPTU with KOH in the presence of Hg ion 20 ml
of 0.005 M 3HPTU+8 ml of 2 M KNO₃
0.05 M HgCl₂; A, 0.5ml; B, 0.7ml ; C, 1.0ml; D, 2.0 ml; E, 3ml; F, 5ml;

chelate, using dialysis equilibrium and spectroscopy in the visble region. It is
rather difficult to get an exact ratio of chelate ligand to metal ion by a single
method without combining others.

While Gregor et al[11] measured the shift in the titration curve of PAA
on addition of small concetrations of Cu salts, and analyzed their data by a
modification of the Bjerrum procedure, Wall and Gill investigated the intera-
ction of cupric ions with polyacrylic acid using spectroscopy, polarography
and by pH titration curves, and Kotliar and Morawetz[12] investigated the
binding of Cu ion by PAA and PMA by comparing titration data, absorp-
tionspectra and dialysis equilibrium.

(B) Calculation of K by the determination of Metal ion in solution

There are several difficulties to over come before the determination of K
from metal concentration in equilibrated soltuion. The first one is to know
the molar ratio of thiourea group to metal ion in 3HPTU resin, the second
one is the concetration of thiourea ligand in resin. Judging from the diffi-
culty of moving another thiourea group to the metal which is contained in a
chelate of having a single thiuorea group in three dimensional resin structure,
it may be expected that only a single chelate ring is formed for one metal
ion in resin phase, however large a coordination number a metal may have.
If all nitrogen and sulphur contained in 3HPTU resin react to the exact
same extent with metals which is adsorbable by this resin irrespective of
the kinds of metal ions, then the concentration of ligand (thiuorea group) can
be determined by elementary analysis. But adsorbablity of this resin towards
one metal ion is quite different from that to the other ion, therefor the inde-
finite values of the equilibrium constants of chelate reaction will be obtained
if it is derived from the analyzed values. Here, the concentration of ligand
in resin is expected to be the same as the maximum adsobability measured
under the definite condition.

Procedure : 3HPTU resin was prepared by the condensation of 3HPTU
which was purified by recrystallization from aqueous solution and vacuum
distillated phenol, and the resin so formed was washed with acid, base, and
the distillated water to remove soluble products. The size of resin used was
1.25――1.5 mm. Anal. Found C 55.46% H 5.85% S 8.9% N 5.77%
0.5g of 3HPTU resin was put into 100 ml Erlenmeyer flask, and 10 ml of
water, 10 ml of 2M KNO$_3$ and 20 ml of 0.05M AgNO$_3$ (or Hg$_2$(NO$_3$)$_2$, Cu(NO$_3$)$_2$),
were then added.

All experiments were carried out by shaking of the flask at room temper-
atur for 5 days, followed by analysis of an aliquot of the equilibrating solu-
tion. The chelate ligand Ke of this resin was calculated from the adsorbed
amount of metal ion by this resin, therefore Ke of the resin was different
in each case. If the Ke of this resin for a metal ion corresponds to x ml of
0.05M of the metallic solution, (30–x) ml of water and 10 ml of 2M KNO$_3$,
were added to the flask containing 0.5g of 3HPTU resin and the flask was
stood in the thermostat maintained at 20°C for more than five hours, then
x ml of 0.05M of the metal solution which was kept in the same thermostat
were added to it. The shaking of this flask was continued for seven days at.

the same temperature and the aliquot of the equilibrating solution was analized as before. Three or four flasks of the same content were used at one definite temperature.

Calculation of Equilibrium Constants: For easy understanding, an example in a case of Ag is shown as follows,

The 3HPTU resin of which x (Ke value for Ag) is 20 ml of KCNS solution and the aliquot of the equilibrated soluiotn contains Ag ion corresponding to 2.16 ml of KCNS solution. x ml of 0.05 M $AgNO_3$ corresponds to 54 ml of KCNS solution, then the concentration of Ag ion, $[Ag]$, is equal to $0.025 \times \frac{2.16}{54}$ M. 0.05M $AgNO_3$ solution was doubled with water and neutral salts solution. Before the reaction, $[Ke]$ is equal to $[Ag]$ and molar ratio of $[Ke]$ to $[Ag]$ is I : I in resin $[Ke]=[Ag]$

If one proton is produced when one Ag ion reacts with thiourea group in resin and forms one chelate ring, H ion in the solution is equal to the quantity of Ag consumed in chelate formation.

$$[H^+]=0.025 \times \frac{54-2.16}{54} \qquad [AgKe_2]=[H^+]$$

Introducing these valued, equilibrium constant K is obtained. Expermine-tal Results.

$$K_{Ag}=0.76 \sim 1.33 \times 10^5$$
$$K_{Hg}=1.63 \sim 5.00 \times 10^4$$
$$K_{Cu}=0.77 \sim 3.05 \times 10^3$$

Chelate stability constant Ks is represented in the following equation instead of the equation of (6)

$$K_S = \frac{[AgKe_2]}{[Ag][Ke]^2} \cdots\cdots\cdots\cdots (7)$$

The metal ion which is contained in a chelate can not easily be got rid of, therefore the reverse reaction of (4) is hardly occurred. In calculation of Ks from (7), H ion was omitted and following values were obtained.

	Ks
Ag	$3.31 \sim 5.72 \times 10^5$
Hg	$3.85 \sim 10.40 \times 10^5$
Cu	$2.01 \sim 6.90 \times 10^5$

(IV) **Determination of enthalpy of chelate reaction in resin phase**

If accurate values of the equilibrium constant at two controlled temperatures are known, the quantities $\Delta F, \Delta H,$ and ΔS may be calculated from those relationships (1~3). K defined in equation (6) was determined at the three different temperatures and introducing these values to (2), the enthalpy of this reaction will be obtained. The experimental details were essentially as described before. The chelate formation of 3HPTU resin were measured at
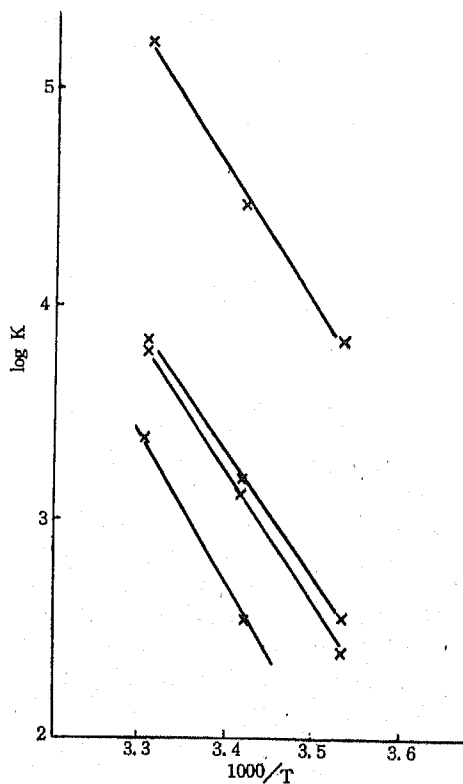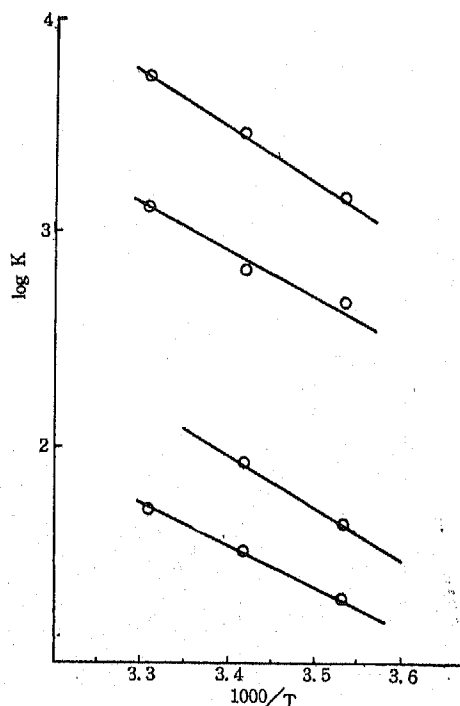
Fig. 9 Adsorption of Hg by 3HPTU Resin   Fig. 10 Adsorption of Cu by 3HPTU Resin

0, 10, 20, and 30°C. Intermittent shaking was perfomed manually on the samples at frequent intervals, between which they were kept at the temperature of choice. Figures were shown plotting log K against 1000/T, here T is absolute temperature. Fig. 9 shows the equilibrium constant of the reaction of 3HPTU with Hg. The curves were chosed from the results which show an extra-ordinary K value. The slopes of the curves from which enthalpy of this reaction can be derived are not different and all points measured at three different temperatures stand on the same straight line. This means that the enthalpy of this reaction is constant in this range of temperature and the equation (8) is applicable to the determination of enthalpy from the equilibrium constant of chelate reaction in resin. Fig. 10 shows the equilibrium constant of the reaction of 3HPTU resin with Cu. The same results as in the case of Hg were obtained. For Ag, the different results were obtained as shown in Fig. 11. The points measured at three different temperatures do not stand on the same straight line. This is probably because of being different of the reaction in chelate resin from that is expected. Chelation may occurr at the other position than thiourea in 3HPTU molecule.

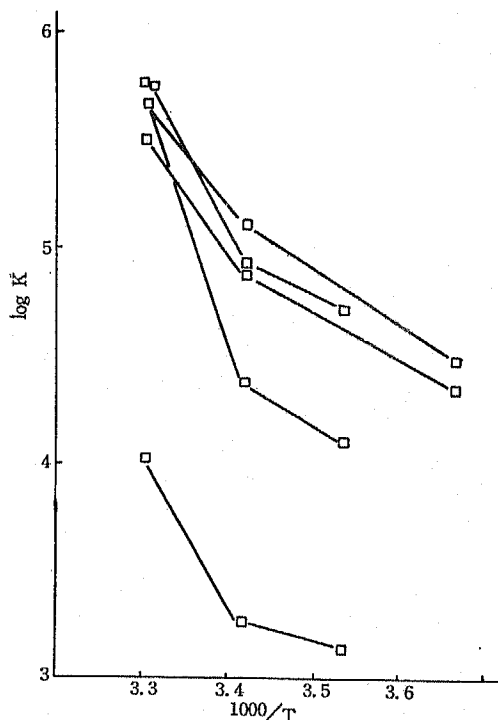   Calculation of Enthalpy from equilibrium constants :

Fig. 11 Adsorption of Ag by 3HPTU Resin

From equation (2), the following equation was derived.

$$\int \partial \ln K_2 = \int \frac{\Delta H}{R T_1^2} \partial T$$

$$\ln K = \frac{\Delta H}{R}\left(-\frac{I}{T}\right) + C$$

Equilibrium constants at the temperatures T_2 and T_1 are designed K_2 and K_1 respectively.

$$\ln K_2 - \ln K_1 = \frac{\Delta H}{R}\left(\frac{I}{T_1} - \frac{I}{T_2}\right)$$

$$\therefore \ \Delta H = R \ln K_2/K_1 \times \frac{T_2 T_1}{T_2 - T_1} \quad (8)$$

or

$$\ln K = -\Delta H/RT + C$$

Here enthalpy of this reaction can be determined directly from the gradiant of this curve. The results were shown in Table 1.

Table 1. Enthalpy of the chelate reaction in 3HPTU resin

	cal/mol
Hg	29,500
Ag	11,000
Cu	10,400

The Enthalpy of the reaction with Ag was calculated from K_{278} and K_{293}

(V) Determination of the Activation Energy in the chelate reaction[7][8]

Before the calculation of activation energy, reaction velocity must be considered. There is hardly any way to know chelate formation in resin directly. It was very difficult to take off the metal ion which was contained in chelate resin after adsorption, therefore it is supposed that all metal ions which were adsorbed by resin were hold in chelate rings and the reaction velocity of chelate formation would correspond to the adsorption velocity of metal ion by resin.

It is considered that only molecules possessing energy in excess of a certain amount of E, dependent on the nature of the reaction, can react on collision: All other collisions are fruitless. The quantity E is called the energy of activation. From the experiments, Arrhenius suggested that the following relation existed between a reaction velocity and a energy of activation.

$$K = A e^{-E/RT} \qquad\qquad\text{(a)}$$

$$\ln K = \ln A - E/RT \qquad\qquad\text{(b)}$$

These are (a) the Arrhenius equation and (b) its logarism form : The Arrhenius equation is widely applicable only to homogenous gas reations, but also to reactions in solution and to heterogeneous processes. Equation (a) and (b) require the plot of $\ln K$, logK, against I/T to be a straight line. If the velocity constant at two different temperatures T_1 and T_2 are determined, the energy of activation can be calculated from the following equation

$$E = \frac{R T_2 T_1}{T_2 - T_1} \ln K_2/K_1 \qquad\qquad\text{(9)}$$

The equation of reaction velocity of the chelate formation in resin and the factors affecting to this equation were considered, and the energy of activation were calculated.

Reaction Velocity of Chelate Formation in Chelate resins.

It is well Known that ion exchange velocity of ion exchange resin depends on the kinds of exchange group. The energy of activation computed from adsorption velocity contains not only pure energy of activation of chelate reaction in resin but also energy of diffusion of metal ion and other energy to carry out a chelate reaction in resin phase. If a definite amount of aliquot is taken away from reaction vessel in proceeding of the reaction, the ratio of reacting solution to resin will change with time, while the ratio of react-ants remains constant in the case of ester hydrolysis. As the chelate reaction proceeds, metal ion precipitates in the pore of resin, and the pore will become narrower, therefore it becomes gradually difficult to diffuse in resin for metal ion.

Two methods are considered for the determination of velocity of the chelate reaction.

  (A)   Continuous Method

  (B)   Discontinuous method.

       3HPTU–Phenol Resin was used for this purpose :

       Anal, C 55.46%, H 5.85%, S 8.9%, N 5.77%

  A)   Continuous method

Apparatus: The apparatus consisted of a 1000 ml three necked flask. A stirrer and a thermometer were inserted into the beaker, The last one hole was left for the insertion of the reagents. The flask was kept in a thermostst.

Procedure: I g of 3HPTU resin was put into the flask, then 10 ml of 0.5 N HNO_3 and 25 ml of 2 M KNO_2 were poured into it. The flask was stood for a day at room temperature, then it was moved to the thermostat which had been kept at the definte temperture. After the temperature becomes constant, 50 ml of 0.05 M $AgNO_2$ solution which had been kept at the same tempera-ture were added to the flask. 5 ml of the reacting solution were taken from it every thirty minutes.

Volhard method was applied for the volumetric determination of Ag and Hg. Potassium Iodate method was applied for the determination of Cu.
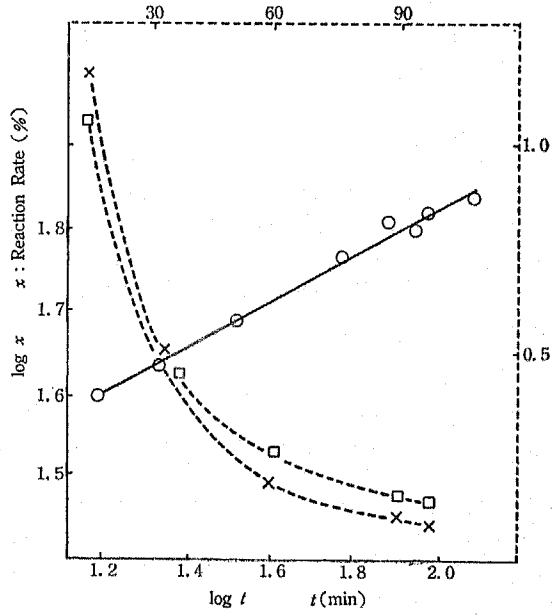
Fig. 12 Reaction velocity calculated from Continuous method
   × First order equation   □ Second order equation
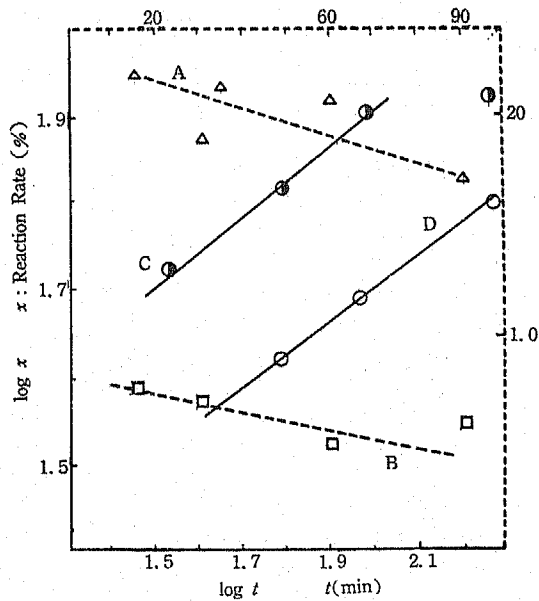   ○ The Equation derived from (13)

Fig. 13 Reaction Velocity calculated from discontinuous method
   A△ Second order equation: small resin size
   B□ Second order equation: large resin size
   C◐ The derived equation in stead of A
   D○ The derived equation in stead of B

B) Discontinuous method

Procedure; 0.3g of air dried 3HPTU resin was weighed in a 100 ml glass flask and 10 ml of water and 10 ml of 2 M KNO_3 were added to it and then they were stood for a day. 6 flasks of the same content were prepared. The flask was put in a thermostat and 10 ml of 0.05 M Ag NO_3 solution of the same temperature were added to it. A flask was taken out one by one every thirty minutes. Fig. 13 shows the relationship of velocity constnat K and time T. The value K measured by the method B is the mean value of K from the beginning till the solution was taken.

For calculation of velocity constant K, the following equations were applied. First order equation

$$K = \frac{1}{t} \times 2.303 \times \log\ c_0/c_0 - x \tag{10}$$

Second order equation

$$KC = \frac{x}{t} \times \frac{x}{1-x} \tag{11}$$

C   initial concentration; x. reaction rate

The results show that the above two equations are not suitable for this purpose. Diffusion of metal ion in resin phase is considered to be a serious factor for the determination of reaction velocity constant, so the following equation was considered and applied to the reaction velocity.

$$\frac{dx}{dt} = \frac{K}{x^n} \qquad (a)$$

K and n are the constant.

$$\int x^n\,dx = \int K\,dt, \quad \frac{x^{n+1}}{n+1} = Kt \tag{12}$$

Taking logarithms of equation (12)
It is seen that $(n+1)\log x = \log\,(n+1)K + \log t$

$$\log x = \frac{1}{n+1}\log K + \frac{1}{n+1}\log t + c \tag{13}$$

This requires the plot of $\log x$ against $\log t$ to be a straight line, so long as $\log K$ is constant. The curves which have been computed from equation (10)(11) were asymptotic to the time axis, while this curve turned to a straight line if the results were calculated from equation (13). Therefore the further experiments were done using equation (13). According to the preliminary experiments, the size of resin particle and the pH of the solution showed a close relation to results.

Calculation of the Energy of Activation

Constant at temperature T_2 is K_2 and at T_1 is K_1, then from equation (13) the following equations are obtained
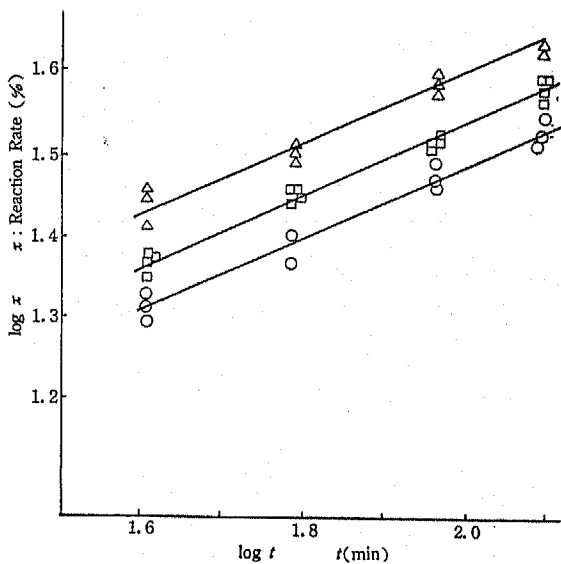
Fig. 14   Adsorption of Ag by 3HPTU Resin

$$\log x_2 = \frac{1}{n+1}\log t + \frac{1}{n+1}\log K_2 + C \tag{14}$$

$$\log x_1 = \frac{1}{n+1}\log t + \frac{1}{n+1}\log K_1 + C \tag{15}$$

(14)−(15) $\log x_2 - \log x_1 = \dfrac{1}{n+1}\log K_2/K_1$

$$\therefore \quad \log K_2/K_1 = (n+1)\{\log x_2 - \log x_1\} \tag{16}$$

n can be computed from the slope of the straignt line and log x_2−log x_1, corresponding to the vertical distance between two line at the same reaction time. Introducing $\log x_2 - \log x_1$ and n to equation (16), log K_2/K_1 is easily found. The results for Ag are shown in Fig. 14

Two groups of different sizes of resins were used; 1.25—1.5mm, 1.5—1.75 mm.

Constant k defined as before is not a true reaction velocity constant, so it is impossible to apply Arrhenius equation for the determination of activation energy

Assuming the equation (a) nearly correspond to the expression of Fick's law of diffusion, the activation energy was computed from the theory of activated diffusion.

The energy of activation of adsorbing Ag by 3HPTU resin was found to be 5,100 cal/mol between 15—20° C and 6,600 cal/mol between 25—35° C.

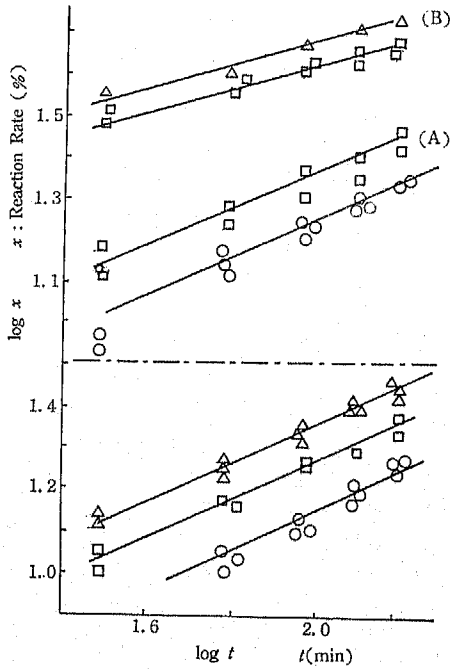According to Boyd,[13] the diffusion energy of Ag ion in desulfonated cation exchangers was 6,590—8,180 cal/mol.

Fig. 15 Adsorption of Hg by 3HPTU Resin
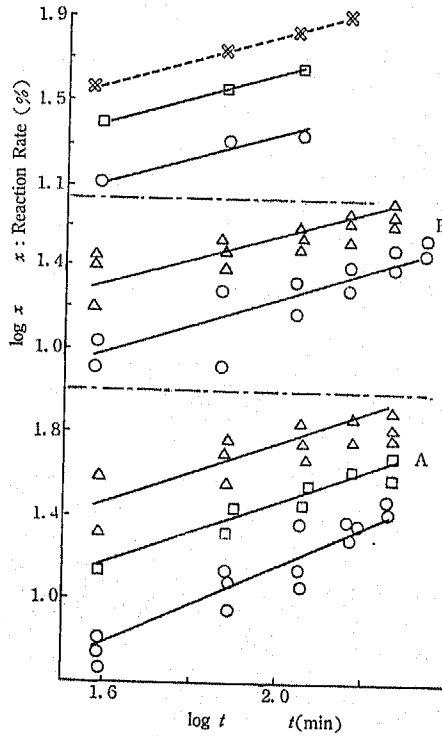A 1.5—1.75mm   B 1.25—1.5mm

Fig. 16 Adsorption of Cu by 3HPTU
Resin   A 1.5—1.75   B 1.25—1.5

Fig. 15 shows the energy of that with Hg. E was 6,300—7,500 cal/mol.
Fig 16 shows in the case of Cu. The activation energy was found to be 8,500—14,000 cal/mol.

Summary

The physical chemistry of chelating reactions in resin was discussed. The various factors which are necessary for the determination of Equilibrium constant of chelate reaction in resin were considered. Then enthalpy of chelate reaction in resin was calculated.

The diffusion of ion is resin phase was found to be a rate determining step in adsorption of metal ion by resin and activation energy of adsorption was considered.

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