Note

Analysis of Surface—Active Agents by Ion—Exchange Chromatography

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The discrimination of imported surface — active agents is necessary for classification in the Customs Tariff Schedule.

For that reason, application of the ion—exchange chromatography method for the separation of surface—active agents into its method was examined. It was found that this method was useful for the customs purpose

1 Introduction

The necessity of the surface—active agents are increasing in nearly every fields of manufacturing industries these days.

And various kinds of surface—active preparations have been developed and imported.

Sometimes ionic and nonionic surface — active agents are mixed to use. Acording to the「Interna tional Convention on the Harmonized Commodity Description and Coding System」which have been used as the Customs Tariff Schedule of Japan, organic surface—active agents are classified into 3402. 11, 3402. 12, 3402. 13, 3402. 19, 3402. 20 or 3402, 90 in its Sub—heading number, depending upon their ionic compositions.

Therefore it is necessary to discriminate between cationic and anionic characters of surface—active agents.

There were several typical of chemical separation methods. For example :

(1) thin—layer chromatography ;
(2) paper chromatography ;
(3) gel—permeation chromatography ;
(4) column chromatography ;
(5) ion—exchange chromatography ;

among these methods, ion—exchange chromatography is seemed to be convenient for the customs purpose.

Because it was easy and rapid analysis method.

More over, it's able to get sufficient amount of isolated substance for to measure infrared — absorption spectrum.

2 Experiments

2—1 Resin

The cation—exchange resin was DIAION SK#1, 100—200 mesh, quaternary ammonium base type, manufactured by MITUBISI KASEI KOGYO CO., LTD.

The anion－exchange resin was DIAION SK＃100, 100－200mesh, sulfonic acid type, manufactured by MITUBISI KASEI KOGYO CO., LTD.

2－2 Apparatus

Chromatography glass tube(inside diameter－15mm, length－30cm)equipped with stop cock was used as column.

2－3 Conditioning and Regeneration of resin

(1) Conditioning of resin

*cation－exchange resin

About 10g of cation－exchange resin into 100ml－beaker was washed with 30ml of 1N－HCl(3times), and was washed with water untill wash water becomes neutral, and with 30ml of Methanol(3 times).

After that chromaography glass tube was filled with the resin.

*anion－exchange resin

About 10g of anion－exchange resin into 100ml－beaker was washed with 30ml of 1N－NaOH(3 times), and with 30ml of 2.5 N－NaOH.

After that chromatography glass tube was filled with the resin, and was passed with 50ml of2.5 N－NaOH, and was with water untill the water becomes neutral, and with 50ml of Methanol.

(2) Regeneration of resin

*cation－exchange resin

After using, the chromatography glass tube that was filled with the cation－exchange resin was passed with 100ml of 2 N－HCl, and was passed with water untill the water becomes neutral, and with 50ml of Methanol.

After that it was used again.

*anion－exchange resin

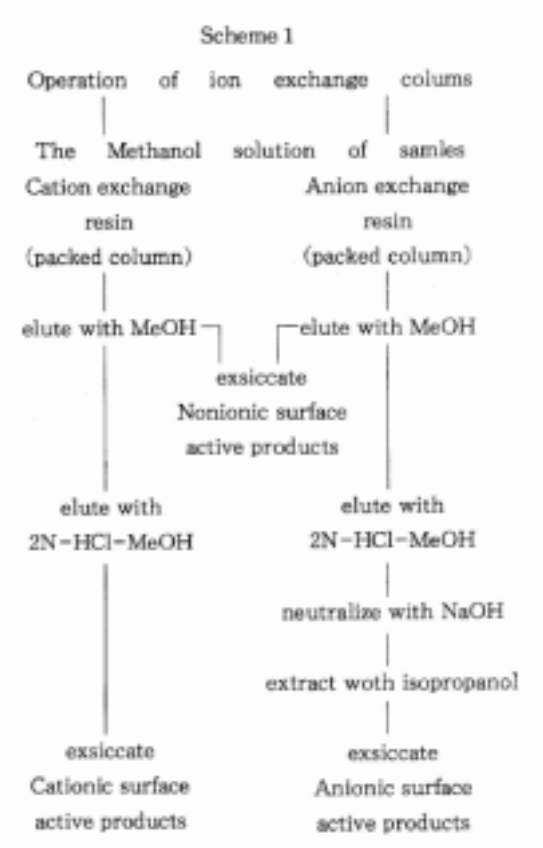
After using, the chromatography glass tube that was filled with the anion－exchange resin was passed with 50ml of 1 N－NaOH, and was passed with water untill the water becomes nautral, and was passed with 50ml of 2.5 N－NaOH, and was passed with water untill the water becomes neutral, and with 50ml of Methanol.

After that it was used again.

2－4 Sample

We used Benzyl dimethyl ammnonium chloride (BDAC), it was cationic surface－active product, and Sodium lauryl sulfate(SLS),it was anionic one, and Polyoxyethylene lauryl ether(POELE), it was nonionic one.

Mixed sample was the mixture of BDAC and POELE or SLS and POELE. Imported sample was 2 samples.



2－5 Procedure

The Methanol solution of samples were placed on the column packed with ion－exchange resin, and eluted with 100ml of Methanol, this elution gave us the nonionic surface－active products.

Next, eluted with 100ml of Methanol solution of

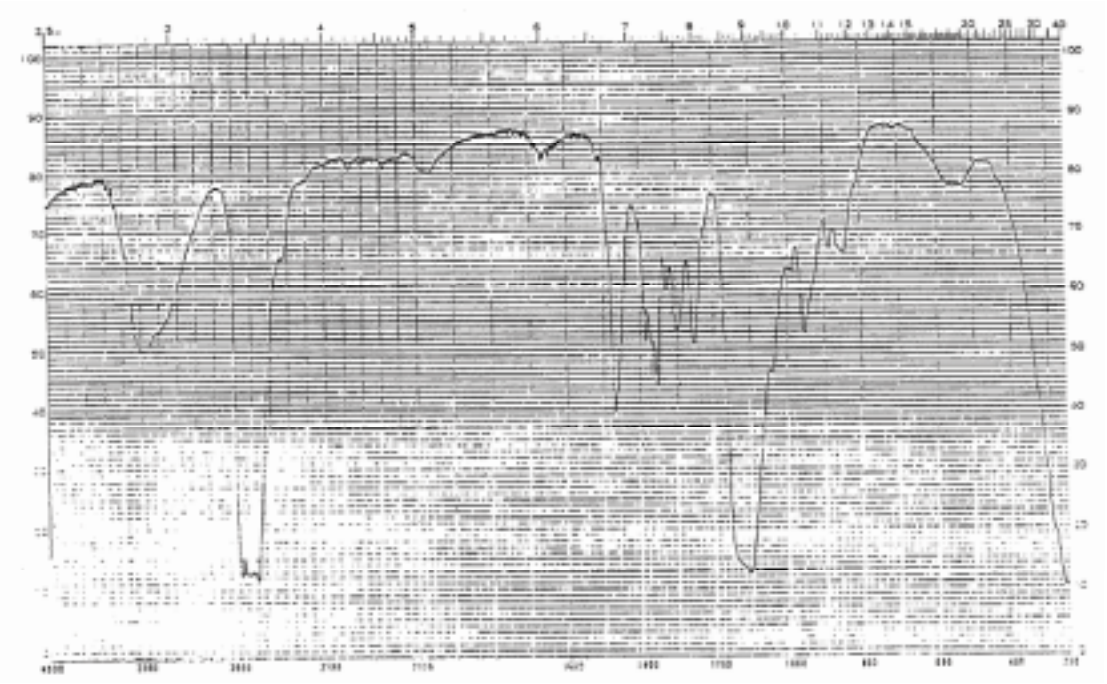


Fig.1 Infrared spectra of the methanol eluate at standard sample(POELE) by Cation exchange resin

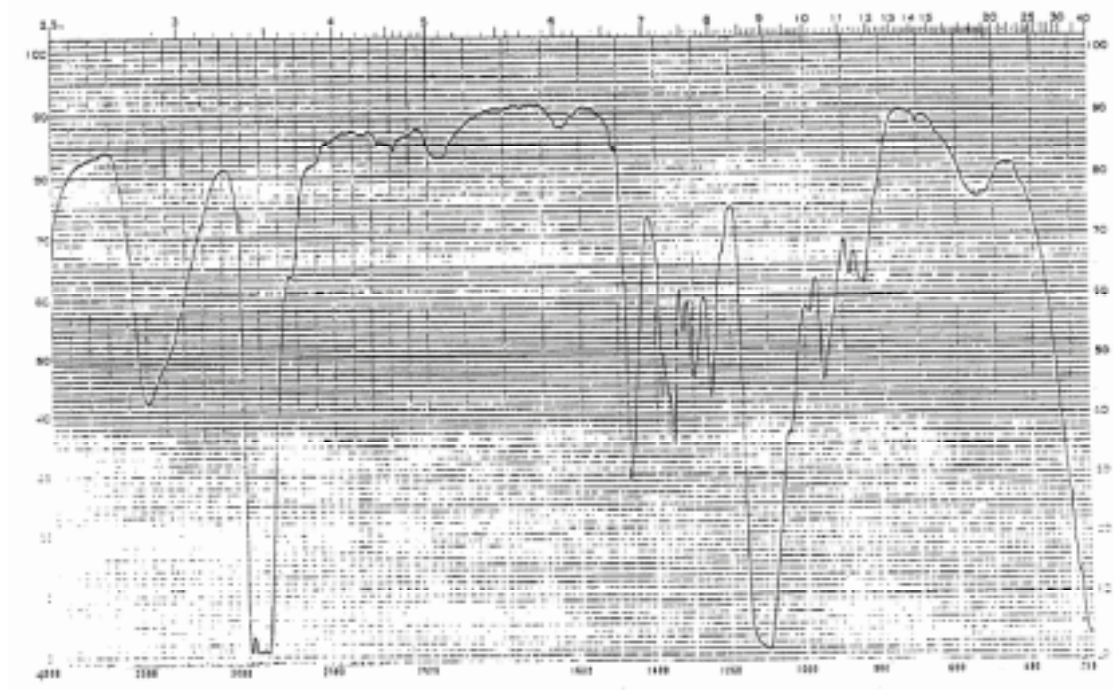


Fig.2 Infrared spectra of the methanol eluate at standard sample(POELE) by Anion exchange resin

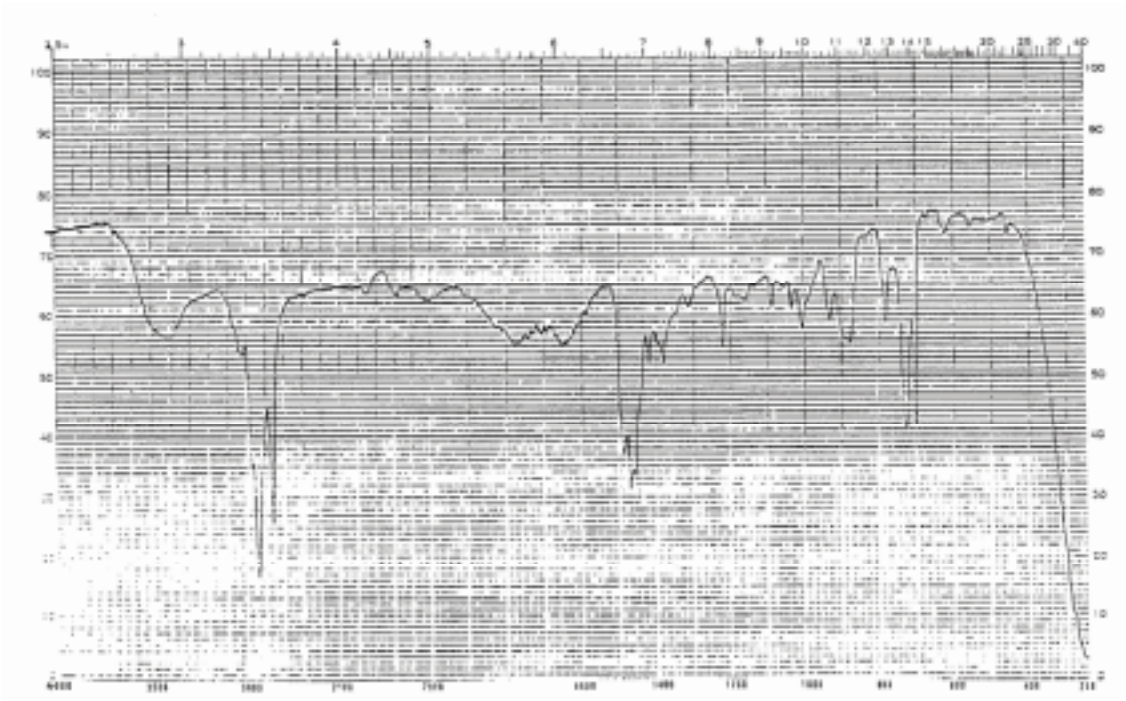


Fig.3　Infrared spectra of the 2 N—HCl—MeOH eluate at standard sample(BDAC)by Cation exchange resin

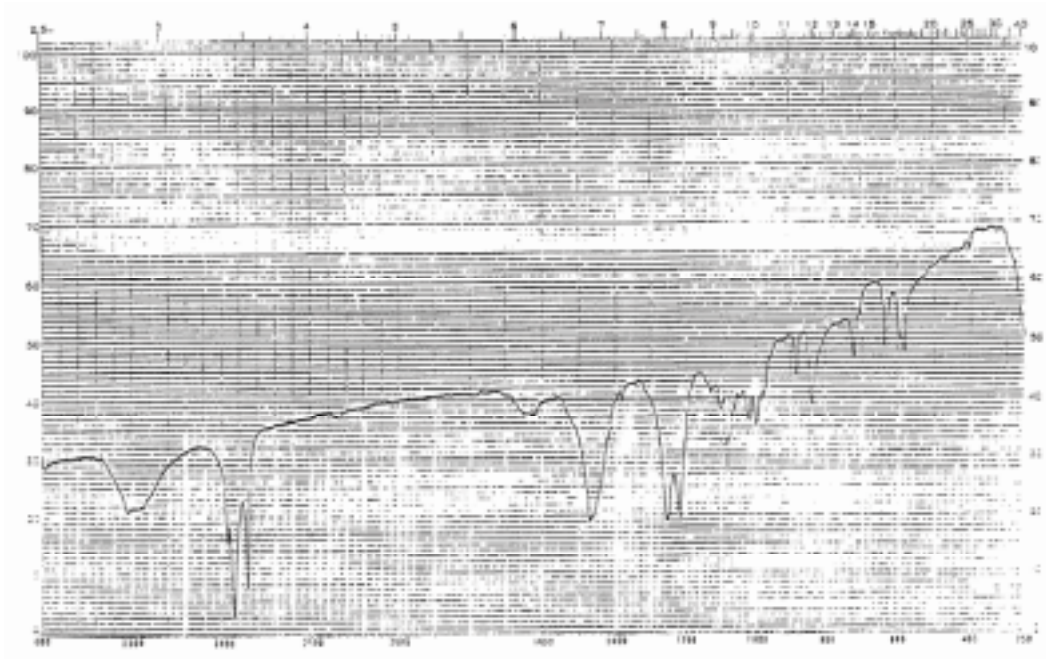


Fig.4　Infrared spectra of the 2 N—HCl—MeOH eluate at standard sample(SLS) by Anion exchange resin

2 N－ HCl (2 N－HCl－MeOH) , this elution gave us the ionic surface － active products as following Scheme 1.

3 Results and Discussion

3－1 Standard sample

(1) Nonionic surface－active product and ion－exchange resin

About 96% of POELE(2g) was recovered with 100ml of Methanol.

Its infrared－absorption spectrum(IRS)is shown in Fig.1 and Fig.2 that indicate POELE only.

(2) Cationic surface－active product and cation －exchange resin

BDAC(1g)was not eluted at all with Methanol, and was eluted in almost 95% yield with 100ml of 2 N－HCl－MeOH.

Its IRS is shown in Fig.3 that indicates BDAC only.

(3) Anionic surface－active product and anion －exchange resin

1g of SLS was used and around 0.25g of it was eluted with 100ml of Methanol, then about 65% of it was eluted with 100ml of 2 N－HCl－MeOH.

Its IRS is shown in Fig.4, it indicates that these are mixture of SLS and something unknown.

3－2 Mixture of standard samples

(1) Mixture of cationic and nonionic suerface－active product

The mixture(1g)of BDAC and POELE as 9 : 1, 7 : 3, 5 : 5, 3 : 7, 1 : 9 by weight was placed on the cation－exchange column and eluted.

As shown in Table.1, the recovery of them ranged 91% to 96% for the Methanol eluate and 91% to 93% for the 2 N－HCl－MeOH eluate.

Eluted samples were identified by comparing these IRS with standard one.

Table1 The recovery of BDAC and POELE by using Cation exchange resin

The mixture ratio (BDAC：P0ELE)	recovery % (BDAC／P0ELE)
9：1	92／92
7：3	91／93
5：5	96／91
3：7	93／93
1：9	95／92

(2) Mixture of anionic and nonionic surface－active product

The mixture(1g)of SLS and POELE as 6 : 4, 5 : 5, 4 : 6, 3 : 7, 2 : 8, 1 : 9 by weight, was treated in similar manner as above 3－2－(1)using anion－exchange resin instead of cation－exchange resin.

The recovery is shown in Table2.

Table2 The recovery of SLS and POELE by using Anion exchange resin

The mixture ratio (SLS：P0ELE)	recovery % (SLS/P0ELE)
6：5	67／93
5：5	48／95
4：6	63／92
3：7	58／93
2：8	75／96
1：9	0／94

It can be seen that POELE was always recovered more than 90% of it.

However the recovery of SLS was not as good as to be expected.

Fig.5 and Fig.6 show IRS of the eluate with 2 N－HCl－MeOH in the case of that the mixture ratio of SLS and POELE are 6：4 and 2：8

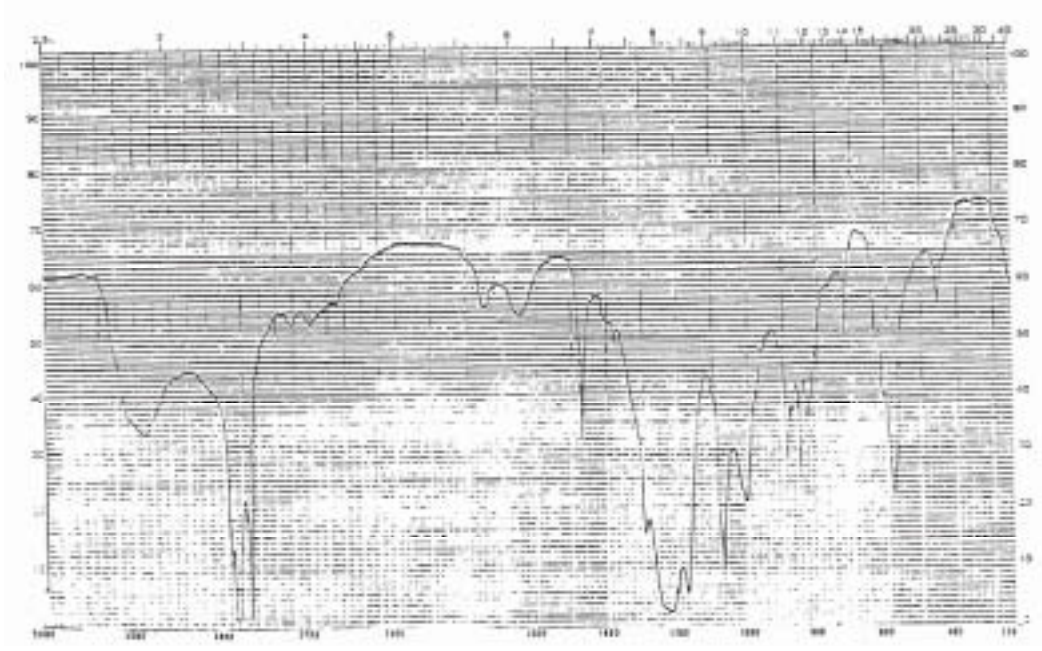


Fig. 5　Infrared spectra of the 2 N—HCl—MeOH eluate at mixture ratio of SLS and POELE are 6 : 4, by Anion exchange resin

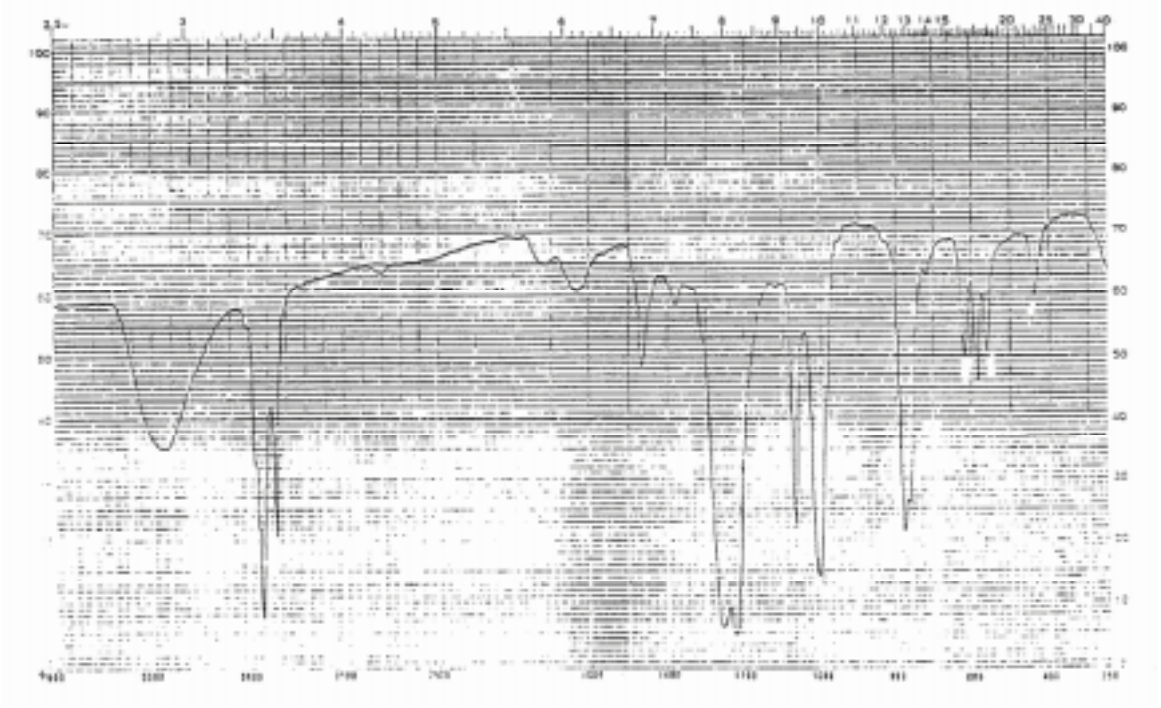


Fig .6　Infrared spectra of the　2 N—HCl—MeOH eluate at mixture ratio of SLS and POELE are 2 : 8, by Anion exchange resin

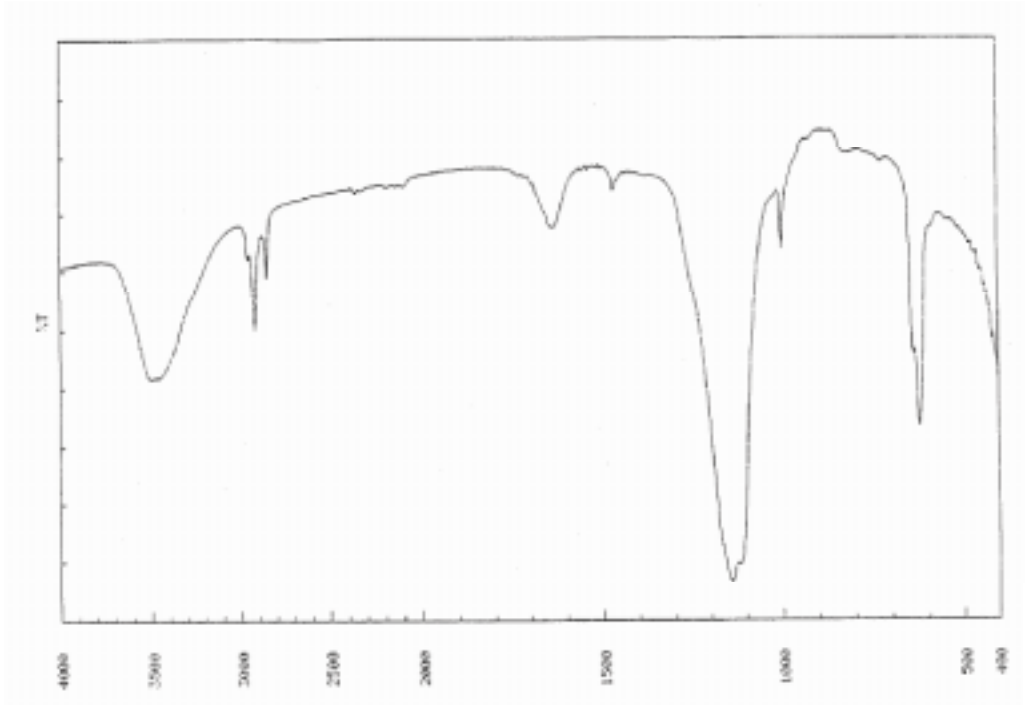


Fig.7 Infrared spectra of the residure that we separated SLS by Anion exchange resin

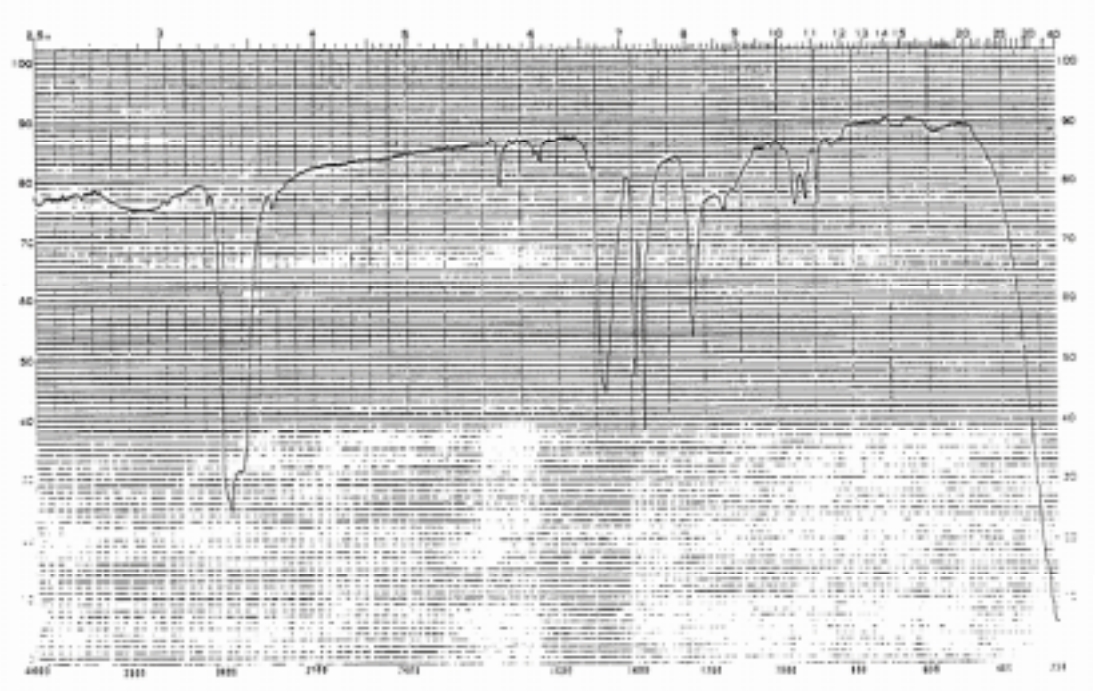


Fig.8 Infrared spectra of the insoluble matter in methanol at imported sample 1

respectively.

These spectra do not indicate SLS.

Another anionic surface—active product, Sodium laurylbenzene sulfonate was tested to compare SLS.

In this case, it was recovered more than 90% of it.

Measuring the IRS(Fig.7), the residue was confirmed Sodium sulfate.

It could be presumed that the residue was Sodium chloride but actually it was Sodium sulfate.

This was suggested that significant quantities of SLS was decomposed passing through the column.

SO^{2-}_4 of Sodium sulfate might derive from SLS.

By the reaction of Sodium alkyl sulfate and hot strong acid, the sulfuric ester was hydrolyzed to Fatty alcohol and Sodium hydrogen sulfate.

It is easy that Sodium hydrogen sulfate change into Sodium sulfate by neutralization.

Therefore it can be presumed that the Hydrolysis would be happened in the column.

Actually the eluting solution was strong acid and was accompanied by exothermic reaction passing through the column.

3—3 Imported samples

(1) Sample.1

Before on column, the sample was dissolved in Methanol, because this sample contained insoluble matter in Methanol.

IRS of insoluble matter is shown in Fig.8, that indicates Polyisobutylene.

The soluble material in Methanol was assumed as an anionic surface — active by active analysis (Methylene blue—chloroform test).

We tried to separate it using anion—exchange resin.

It was found that the Methanol eluate was Fatty acid ester of Polyoxyethylene alkyl phenyl ether from its IRS showing in Fig.9.

And 2 N—HCl—MeOH eluate was presumed Sodium alkyl benzene sulfonate, from its IRS is shown in Fig.10.

It might be concluded that this sample was consisted of Sodium alkyl benzene sulfonate, Fatty acid ester of Polyoxyethylene alkyl phenyl ether, and Polyisobutylene.

(2) Smaple.2

It was found that this sample contained Polyethylene glycol compound and Aromatic amine by measuring ^{13}C—NMR and ^{1}H—NMR, but no other components were detected and it cou1d not be separated by Gelpermeation chromatography.

So we applied the ion—exchange chromatography.

The IRS of eluate with Methanol by cation—exchange column is shown in Fig.11. It indicates Fatty acid.

As showing in Fig.12, the eluate with 0.1 N—H Cl—MeOH was presumed metallic oxide.

This results suggested us that it contained Fatty acid salt which was decomposed passing through the column.

Fig.13 shows IRS of the eluate with Methanol by anion — exchange column. It indicates Polyprop yleneglycol.

In conclusion, presented results suggested that this sample was consisted Polypropyleneglycol, Fatty acid salt, and Aromatic amine.

4 Conclusion

The above results show that the mixtures of nonionic and cationic surface—active agents are well separated by ion—exchange chromatography, while the mixtures of nonionic and anionic surface—active agents (especially SLS) are not separated efficientry.

Some of the anionic surface—active agents are decomposed passing through the column.

Usually the ion—exchange chromatography method is a very convenient way to separate surface —active products.

Nevertheless, in the case of anionic surface—active agents, we shall always call attention to the deco

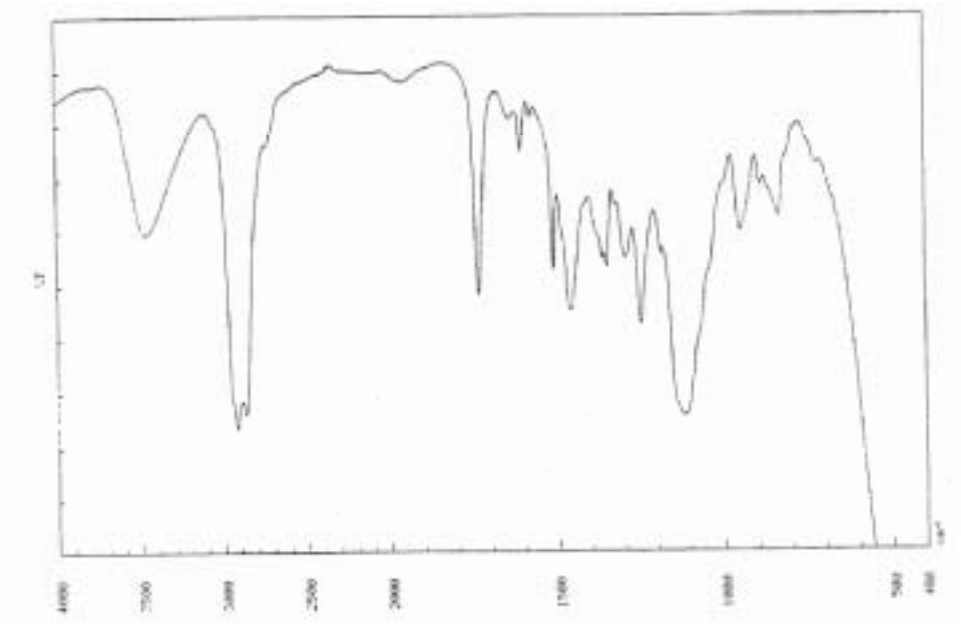


Fig.9 Infrared spectra of the methanol eluate at imported sample.1

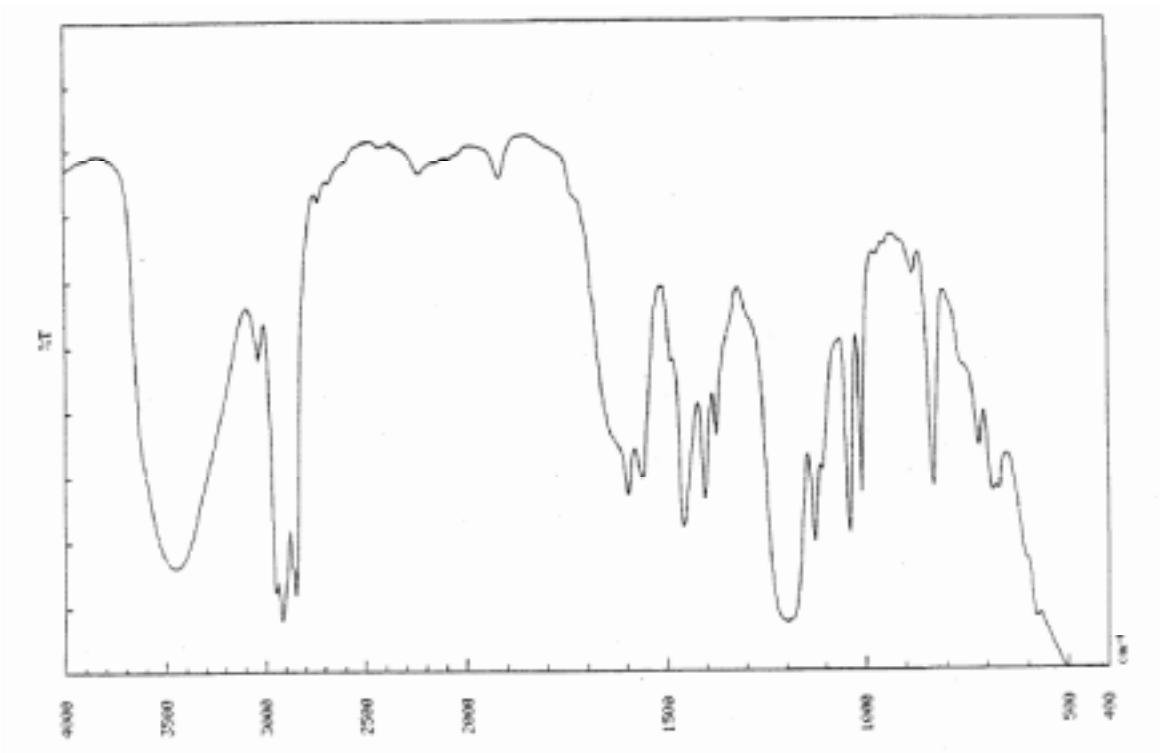


Fig.10 Infrared spectra of the 2 N—HCl—MeOH eluate at imported salmple.1, by Anion exchange resin

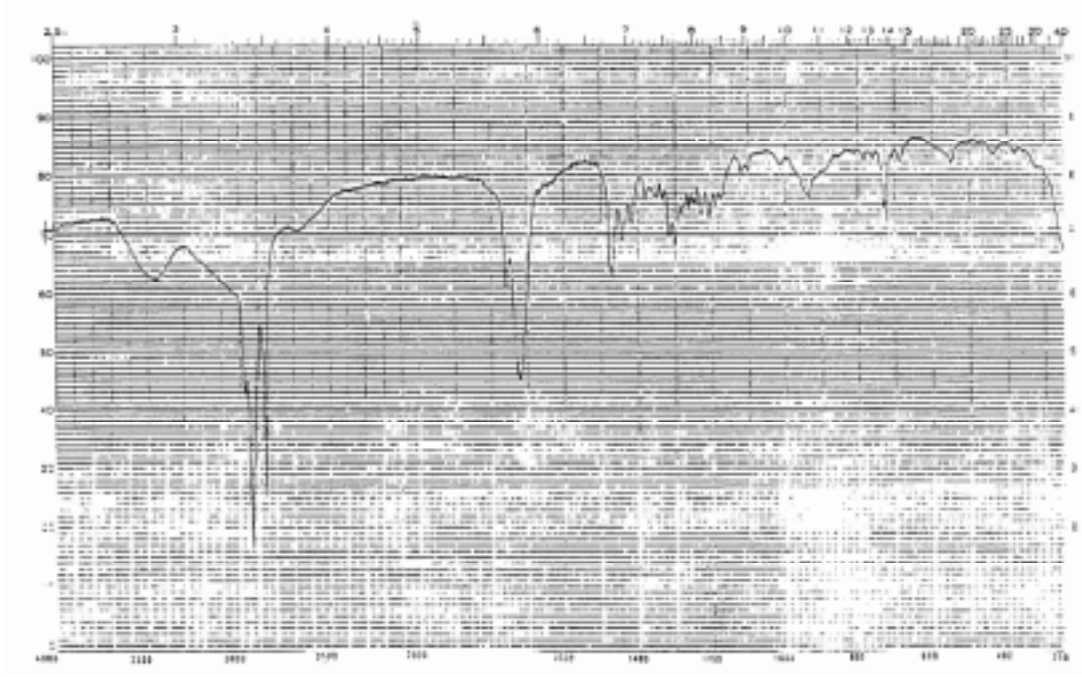


Fig.11　Infrared spectra of the methanol eluate at imported sample.2, by Cation exchange resin

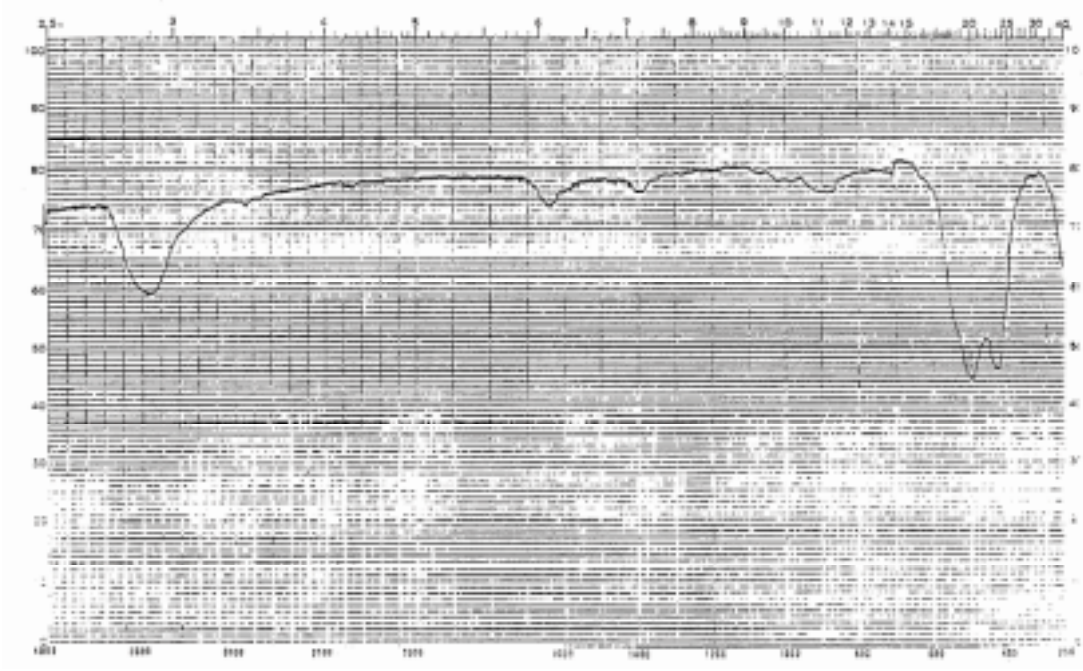


Fig.12　Infrared spectra of the 0.1 N—HCl—MeOH eluate at imported samle.2, by Cation exchange resin

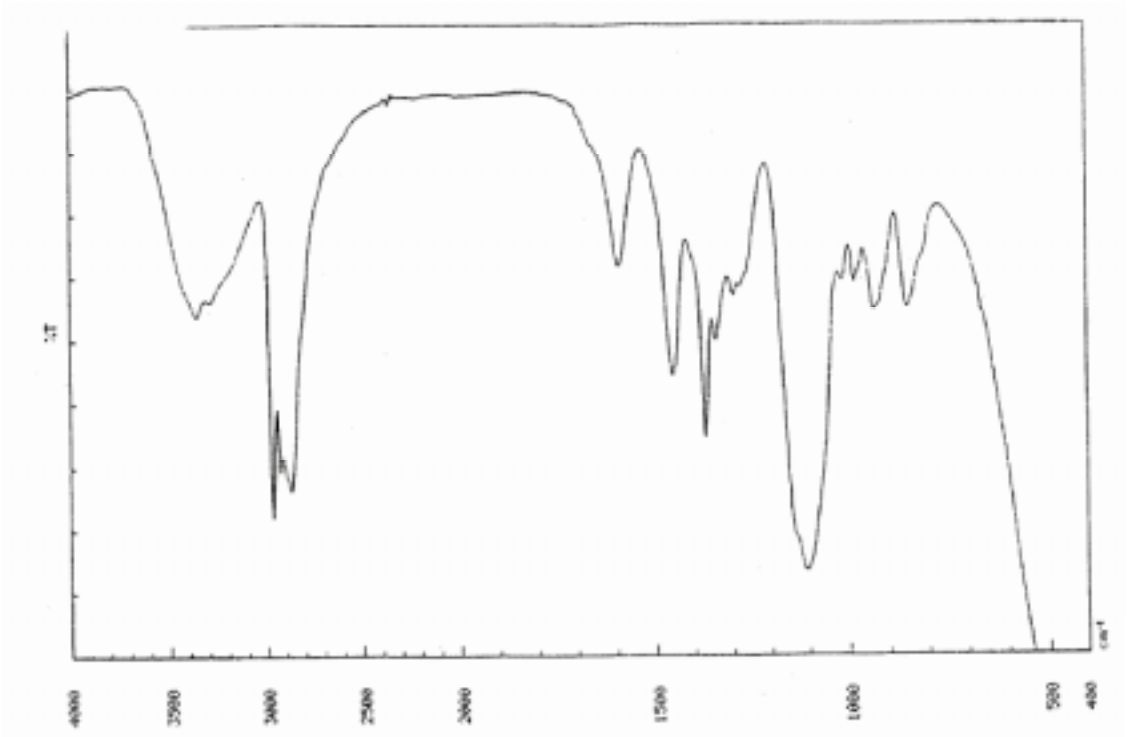


Fig.13 Infrared spectra of the methanol eluate at imported sample.2, by Anion exchange resin

mposition of them.

This work needs to be investigated further, using another materials and another ion—exchange resin.

5 References

1）H. Shimizu : 「Ion Exchange Resins」8 th edition (1962)
2）H. Kakibana k. Nalita : 「New Ion Exchanger」(1960)
3）S. Kuwata K. Matumoto : 「Report of the Central Customs Laboratory No.10」81 (1970)