The Effect of pH on Flux and Rejection of Coloring Matters on Ultrafiltration of Caramel Color*

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The effect was examined on ultrafiltrability of caramel solution of the change in pH due to addition of sulfuric acid or sodium hydroxide. Ten % caramel solution of which pH was adjusted to the range from 1 to 13 was ultrafiltered to measure the flux and the rejection of coloring matters. The flux was almost constant over the pH range from 3 to 12, and progressively decreased below pH 3 and above pH 12. The rejection of coloring matters was varied little within the pH range from about 2.5 to 7, progressively increased below pH about 2.5, and progressively decreased above pH 7. These results showed that for releasing the bound imidazole compounds addition of an adequate amount of sulfuric acid is desirable to avoid the excessive reduction of flux and rejection of coloring matters.

Caramel color prepared by the ammonia-sulfite process contains several imidazole compounds¹⁾ including 4-methylimidazole which is recognized as a convulsant compound²⁾. We have examined the elimination of imidazole compounds in order to improve its quality by ultrafiltration³⁾⁻⁷⁾. On ultrafiltration of caramel solution, much imidazole compounds were eliminated from the solution to the permeate but those which were bound to high-molecular-weight coloring matters were retained in the concentrate³⁾⁴⁾. These bound imidazole compounds could be released from the coloring matters by addition of sulfuric acid or sodium hydroxide⁸⁾. By a combination of ultrafiltration and addition of sulfuric acid caramel color free from the imidazole compounds could be prepared⁷⁾.

In the course of the above studies we have experienced decrease of flux by the addition of sulfuric acid to caramel solution. Since a change in pH of protein solutions such as cheese whey⁹⁾, soybean water extracts⁹⁾, cottonseed protein solution¹⁰⁾ and waste water from Miso

factory¹¹⁾ produces significant effect on the property of protein and the ultrafiltration flux, that of the caramel solution may also produces some effects on the ultrafiltrability. In this paper, the effect of addition of sulfuric acid or sodium hydroxide to the caramel solution on the ultrafiltration flux and the rejection of coloring matters was examined.

Experimental Methods

A commercial caramel color prepared by the ammonia-sulfite process was used as the sample. The original pH of 10% caramel solution was 3.1. The pH of caramel solution was adjusted to the range from 1 to 13 with sulfuric acid or sodium hydroxide, and the solution was diluted to 10% concentration. The caramel solution was ultrafiltered by using the apparatus shown in Fig. 1. The membranes used were Amicon PM-10 (aromatic polymer; molecular weight cut-off, 10,000) and Asahi-Kasei PAN (polyacrylonitrile; molecular weight cut-off, 13,000) membrane. It has been insured that

* Ultrafiltration of Caramel Color (Part VI)

Fig. 1 Schematic diagram of ultrafiltration system

1=Filtration cell	2=Feed tank
3=Permeate port	4=Accumulator
5=Pressure switch	6=Pressure gauge
7=Valve	8=Back pressure regulator
9=Pump	10=Magnetic stirrer
11=Const. temp. bath	

both PM-10¹²⁾ and PAN¹³⁾ membranes can be used over pH range from 1 to 13. The operating pressure were 4 kg/cm² and 1 kg/cm² for PM-10 and PAN membrane, respectively. The temperature was 30°C and the stirring speed was 1,100 r.p.m. Both the concentrate and the permeate were recycled back to the feed tank. After the ultrafiltration attained to steady state, the flux and the rejection of coloring matters (1—color intensity of permeate/color intensity of feed) were measured. The optical density at 460nm was used as the color intensity. The viscosity of caramel solution was measured with an Ostwald's viscometer.

Results and Discussion

The relationship between pH and flux is shown in Fig. 2. The fluxes for both PM-10 and PAN membranes were almost constant over the pH range from 3 to 12, and progressively

Fig. 2 Relationship between pH and flux for 10% caramel solution at 30°C

.....flux corresponding to viscosity of original caramel solution

decreased below pH 3 and above pH12, although PM-10 membrane showed smaller fluxes per unit operating pressure than those of PAN membrane.

As the viscosity of caramel solution had a large influence on the ultrafiltration flux¹⁴⁾, the relationship between pH and viscosity was examined for 10% caramel solution. As shown in Fig. 3., the viscosity was constant over the pH range from 2 to 12 and became larger below pH 2 and above pH 12. For adjusting extreme pHs of the caramel solution, a larger amount of sulfuric acid or sodium hydroxide was needed due to the probable buffer action. For example, the concentration of sulfuric acid or sodium

Fig. 3 Relationship between pH and viscosity of 10% caramel solution at 30°C

hydroxide in 10% caramel solution of which pH was adjusted to 1 or 13 was 0.4 N (2%) or 0.2N (0.8%), respectively. The viscosity of 0.4 N sulfuric acid solution or 0.2N sodium hydroxide solution was 0.831 c. p. or 0.832 c. p. at 30°C, respectively, and it was slightly higher than that (0.800 c. p.) of water. It seemed, therefore, that the elevation in viscosity of caramel solution at low or high pH was mainly caused by a change in properties of caramel color.

By using the previously reported relationship¹⁴⁾ between flux and viscosity, the fluxes of caramel solution at low or high pH were corrected to those corresponding to the viscosity of original solution, and the corrected values are shown with dotted lines in Fig. 2. These corrected fluxes at high pH were not significantly affected by pH changes, whereas at low pH it remained a quite significant effect of pH changes, although its effect was reduced somewhat by the correction. These results revealed that the flux was affected not only by viscosity but also by pH.

FORBES⁸⁾ reported that in ultrafiltration of Cheshire cheese whey the flux became minimum at the isoelectric point because the solubility of protein was reduced and a gel layer might be formed on the membrane surface. On the contrary, MOCHIZUKI¹¹⁾ reported that in ultrafiltration of waste water from Miso factory the flux became maximum at the isoelectric point because particle of protein formed due to its coagulation might avoid the plugging of membrane pores. On the other hand, OMOSAIYE et al.⁹⁾ have mentioned that it is doubtful in ultrafiltration of soybean water extracts if differences in solubility could be accounted for the effect of pH on flux. At present, explanation for these phenomena have not well established. In the case of caramel solution, the reduced flux

Fig. 4 Relationship between pH and rejection of coloring matters for 10% caramel solution at 30°C

in the low pH range may have relation with the isoelectric point which is pH 1~3.5.

The relationship between pH and rejection of coloring matters is shown in Fig. 4. The color intensity of caramel solution was measured after its pH was brought to the range from 3 to 4, because the color intensity was increased hardly in acidic environments and largely in alkaline ones as the pH was increased, and when the pH was readjusted to that of the original caramel solution the color intensity was also brought back to the original. The rejection of coloring matters for the membranes were varied little within the pH range from about 2.5 to 7, progressively increased below pH about 2.5, and progressively decreased above pH 7, especially deeply above pH 12.

It was considered that the decrease in flux and the increase in rejection of coloring matters at low pH were caused by a change in the shape of color molecules and/or the easier formation of gel layer. Plugging of the membrane pores, moreover, may occur. It seemed that the decrease in rejection of coloring matters at high pH was ascribed to the change in properties of caramel color.

In the ultrafiltration of caramel solution for

the elimination of imidazole compounds, a large loss of coloring matters must be avoided. From this point of view, it is undesirable to add sodium hydroxide to release the bound imidazole compounds from the coloring matters. Addition of sulfuric acid, hence, is desirable for releasing the bound imidazole compounds. In this case, an adequate amount of sulfuric acid must be added to the caramel solution, since high concentration of the acid produces a large decrease of flux and probable fouling of membrane. As mentioned in a previous paper⁹⁾, partial elimination of permeable imidazole compounds before addition of sulfuric acid enhances the effect of its addition and reduces the amount to be added.

Conclusions

The effect of pH was studied on ultrafiltrability of caramel solution. At low pH the flux was decreased and the rejection of coloring matters was increased, and in alkaline environments the rejection of coloring matters was decreased. From the above reasons, it was concluded that the amount of sulfuric acid to be added for releasing the bound imidazole have to be as minimal as possible.

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カラメルの限外濾過における透過流束と色素の阻止率に及ぼす pH の影響 カラメル限外濾過 (第6報)

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カラメル中の高分子色素と結合しているイミダゾール化合物を遊離させるために添加した硫酸または水酸化ナトリウムによる溶液の pH 変化が限外濾過性に及ぼす影響について調べた。透過流束は pH 3-12 においては pH 変化に影響されず、pH 3 以下または pH 12 以上においては徐々に減少した。色素の阻止率は pH 約 2.5~7 に

おいてはほとんど変化しなかったが、pH 約 2.5 以下においては徐々に増加し、アルカリ性下においては徐々に減少した。とくに、高 pH において、阻止率は大きく低下した。これらのことから、結合性イミダゾール化合物の遊離には、必要最少量の硫酸の添加が望ましいことがわかった。