Caking of KCl-NaCl Powder and its Prevention by Amino Acids

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Prevention of the caking of KCl-NaCl powder produced by a spray-dryer was investigated. The spray-dried powders of both a simple KCl-NaCl mixture and a mixture of KCl and NaCl with an amino acid that was less soluble than KCl and NaCl and that had hydrophobic functional groups were obtained in the form of particles that were hollow spheres. When stored in high humidity, the first powder soon caked, but the second did not. This difference could be explained by the solubility and polarity of the amino acid added. When the solubility of the amino acid added was higher than that of KCl or NaCl, the surface of the spray-dried particles was crystalline and porous. When the amino acid had hydrophobic functional groups and its solubility was lower than that of KCl or NaCl, the surface of the spray-dried powder was smooth and not porous; this result suggests that the surface of the spray-dried particles was covered with amino acid molecules. We concluded that the solubility and the functional groups of the amino acids that were added to a KCl-NaCl mixture could be used to control caking of the spray-dried powder.

The mean daily intake of NaCl in Japan is increasing year by year to 12.5 g/day in 1990¹⁾. The Ministry of Health and Welfare, Japan, is recommending to reduce NaCl intake to 10 g/day^{1)~3)}.

Food manufacturers are trying to formulate low-sodium or reduced-sodium foods^{4),5)}. Potassium chloride is the most popular substitute, and mixtures of NaCl and KCl have been used in a variety of processed foods⁶⁾. Powdering of NaCl or KCl, especially by spray-dryers, has been undertaken. However, the spray-dried powders of mixtures of KCl and NaCl cake so easily that it is difficult to store them. The caking of NaCl powder has been studied but the phenomenon cannot be prevented yet.

We studied the caking of KCl-NaCl powder, and a part of the caking phenomenon was elucidated.

Materials and Methods

Materials

KCl, NaCl and amino acids purchased from Nacalai Tesque, Inc., were all guaranteed reagents.

Spray-drying

A mixture of 24.5 g KCl, 24.5 g NaCl and 1.0 g amino acid in 500 ml of water was dried by a spray-dryer (Mobile Minor model, Rotary Atomizer Type, Niro Atomizer Ltd., Soeborg, Denmark). The temperatures of inlet and outlet were 140°C and 85°C, respectively. The rotational rate of rotary atomizer was ca. 32 500 r.p.m.

Preservation test

Spray-dried powder was put into a zippered polyethylene pouch at 30°C and 65% relative humidity in a chamber and kept at a constant temperature and humidity (LH-20-01 PRG-La, Nagano Science Equipment Mfg. Co., Ltd., Osaka, Japan) for two days.

Observation of spray-dried powder

Spray-dried powder was coated with Au by an Ion Coater (IB-3 model, Eiko Engineering Co., Ltd., Ibaraki, Japan) that was observed under a scanning electron microscope (SEM ; Hitachi model S-510, Tokyo, Japan) before and after the preservation test at the acceleration voltage of 15 KV ($\times 500$ and $\times 2000$) in the usual way.

Results and Discussion

Figure 1 shows SEM micrographs of spray-dried powders of KCl and NaCl. Both powders were obtained in a crystallized form as reported earlier⁷⁾. When a mixture of KCl and NaCl was spray-dried, a powder of spherical and hollow particles was formed (Fig. 2). The powder was found to cake during storage. The

particles were spherical hollow when KCl and NaCl were mixed at weight ratios of from 3 : 7 to 7 : 3 by weight. In further experiments, the ratio of KCl and NaCl was fixed at 1 : 1, because this ratio gave particles a suitable shape on spherical and hollow.

Figure 3 shows the spray-dried powder of a mixture of KCl, NaCl and monosodium glutamate. This powder also had particles that were spherical and hollow. In a mixture containing amino acid, the weight ratio of KCl, NaCl and the amino acid was fixed at 49 : 49 : 2, because this ratio gave particles a suitable shape on spherical and hollow.

Fig. 1 SEM micrographs of spray-dried powders of NaCl (A) and KCl (B) ($\times 2000$)

Fig. 2 SEM micrographs of spray-dried powder of a mixture of KCl and NaCl ($\times 2000$)

Fig. 3 SEM micrograph of spray-dried powder of a mixture of KCl, NaCl and monosodium glutamate ($\times 500$)

The powder were mixed with KCl, NaCl and one of 20 kinds of amino acid that were studied. The results suggested when the solubility of the amino acid was higher than that of KCl or NaCl, the surface of the spray-dried particles became crystalline and porous, and the powder caked. When the solubility of the amino acid was lower than that of KCl or NaCl, the surface of the particles became smooth and not porous.

For example, Fig. 4 shows SEM micrographs of spray-dried powders of KCl and NaCl mixtures to which L-proline or L-tryptophan was added. Because the solubility of L-proline is higher than that of KCl or NaCl, the surface

of the spray-dried particles was crystalline and porous. Because the solubility of L-tryptophan is lower than that of KCl or NaCl, the surface of the particles was smooth and not porous. During the preservation test, the powder with L-proline caked but the powder with L-tryptophan did not.

Diagrams of cross-sections of particles KCl, NaCl and L-proline mixture or KCl, NaCl and L-tryptophan mixture (Fig. 5) may help to explain the reason for this phenomenon. The surface of the former was covered with KCl and NaCl, and it caked easily. The surface of the latter was covered with L-tryptophan, and it did not cake.

Fig. 4 SEM micrographs of spray-dried powders of mixtures of KCl, NaCl and L-proline or L-tryptophan ($\times 500$)

- A, L-proline (before preservation test) ;
- B, L-proline (after preservation test) ;
- C, L-tryptophan (before preservation test) ;
- D, L-tryptophan (after preservation test)

Fig. 5 Diagrams of cross-sections of spray-dried particles

A, L-tryptophan ; B, L-proline

In general, the vapor pressure of water rises as the atmospheric temperature rises, and moisture escapes in vapor from the surface of particles⁸⁾. As a particle dries, the moisture moves from the inside to the surface^{9),10)}. van ARSDEL *et al.*¹¹⁾ reported that dissolved substances move from the outside to the inside as drying progresses. In addition, when a particle dries, a concentration gradient is generated between the outside and the center, which is still wet, and substances diffuse from the outside to the inside. For these reasons, in a spray-dried powder, the outer layer was probably made of the most insoluble substance and the inner layer was made of substances with higher solubility.

Figure 6 is a SEM micrograph of spray-dried

Fig. 6 Insides of spray-dried particles of a mixture of KCl, NaCl and L-tryptophan ($\times 2000$)

particles of a mixture of KCl, NaCl and L-tryptophan showing the inside of the particles. The surface of the particles was smooth and not porous, and the insides were crystalline which is evidence that our explanation of the differences in cabins is right. The inside of the particles of a mixture of KCl, NaCl and L-phenylalanine was crystalline, too.

The solubilities of KCl and of NaCl are about the same. In a mixture of KCl, NaCl and amino acid, the amino acid moves and diffuses if it is more soluble than KCl or NaCl.

The experimental results could not be interpreted simply by solubility. Fig. 7 shows SEM micrographs of particles of mixtures of KCl and NaCl with either L-alanine or L-phenylalanine. The solubilities of both L-alanine and L-phenylalanine are lower than those of KCl and NaCl. The surface of the particles with L-alanine was smooth but porous. That of particles with L-phenylalanine was not porous or smooth. During the preservation test, the powder with L-alanine caked slightly, but that with L-phenylalanine did not cake at all. Fig. 8 shows a diagram to explain this phenomenon. The surface of the latter was covered with L-phenylalanine and the powder did not readily cake.

On the other hand, there were KCl, NaCl and L-alanine on the surface of the particles, the

Fig. 7 SEM micrographs of spray-dried particles of mixtures of KCl and NaCl with L-alanine or L-phenylalanine ($\times 500$)

- A, L-alanine (before preservation test) ;
- B, L-alanine (after preservation test) ;
- C, L-phenylalanine (before preservation test) ;
- D, L-phenylalanine (after preservation test).

powder would cake readily.

Figure 9 shows SEM micrographs of particles of a mixture of KCl, NaCl and L-asparagine before and after the preservation test. The solubility of L-asparagine is lower than that of KCl and NaCl. If the particles were covered with L-asparagine, their surface not be porous or smooth. However, the particles were of several different shapes. During the preservation test, this powder caked, probably because L-asparagine has hydrophilic functional groups. Powder with L-glutamic acid caked, too. In short, functional groups of amino acids affected the caking phenomenon.

Based on the results described above, we

classified in our eyes amino acids into four groups (Table 1)¹²⁾. Amino acids of group A were more soluble than KCl and NaCl. They did not prevent caking. Groups B and C were intermediate in effect between groups A and D. Amino acids of group D were more insoluble than KCl and NaCl and had hydrophobic functional groups. When added to a mixture of KCl and NaCl and spray-dried, they were most effective in preventing caking in high humidity.

Thus, it was possible to prepare a stable KCl-NaCl powder by the addition of an amino acid that was less soluble than KCl and NaCl and that had hydrophobic functional groups. Such a powder would be useful in the food

Fig. 8 Diagrams of cross-sections of spray-dried particles

A, L-phenylalanine ; B, L-alanine

Fig. 9 SEM micrographs of spray-dried powders of mixtures of KCl, NaCl and L-asparagine ($\times 500$)

A, L-asparagine (before preservation test) ;
B, L-asparagine (after preservation test)

industry.

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Table 1 Grades of caking

Substance	Group	Solubility (g) (25°C)
Proline	A	162.3
Serine	A	38.0
NaCl	—	36.1
KCl	—	35.5
Glycine	B	25.0
Alanine	B	16.5
Threonine	C	14.1 (52°C)
Valine	C	8.9
Methionine	C	5.6 (30°C)
Glutamine	C	4.3
Histidine	C	4.3
Isoleucine	C	4.1
Asparagine	C	3.0
Phenylalanine	D	3.0
Leucine	D	2.2
Tryptophan	D	1.1
Glutamic acid	D	0.8
Aspartic acid	D	0.6

A, Did not prevent caking.

B and C, Helped to prevent caking (B more than C).

D, Prevented caking

KCl-NaCl 系粉末の固結性防止効果について

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KCl および NaCl の混合物にある種のアミノ酸を添加溶解後噴霧乾燥すると、極めて耐固結性の高い中空粉末が得られることが分かった。KCl および NaCl の混合物と比較して溶解度の高いアミノ酸を添加溶解後噴霧乾燥した粉末の表面は、KCl および NaCl の結晶で覆われていた。逆に溶解度の低いアミノ酸を添加混合噴霧乾燥した場合、添加したアミノ酸が粉末の表面を覆っていた。さらにこの場合、表面に被覆したアミノ酸の官能基の物性（親水性、疎水性）が粉末の固結性を支配していることが分かった。したがって、KCl および NaCl 系粉末の耐固結性能を向上させるために必要な条件は、添加するアミノ酸の溶解度が KCl および NaCl よりも低く、疎水性基を有する事である。