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Spectroscopic Evidence for the Presence of an Inclusion Structure of Urea in Solution

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Synopsis. The FT-IR spectra of a valeric acid–urea–water system and a 1-butanol–urea–water system were measured. By comparing the spectra with those of related systems, an inclusion structure of urea molecules was found to exist in the solution state; the interpretation that the increase in the solubility of valeric acid or 1-butanol into water by the addition of urea is due to the existence of an inclusion structure was verified.

It has been well-known since the discovery by Schlenk$^{1)}$ that the solubility of valeric acid into water increases upon the addition of urea. The increase in the solubility has been interpreted as being due to urea molecules occluding valeric acid molecules in solution. However, until now, no experimental evidence has been given concerning the presence of an inclusion structure formed by urea molecules in solution. The present study was carried out for the purpose of determining whether the inclusion structure exists in solution or not.

Experimental

The infrared spectra of a valeric acid–urea–water system and a 1-butanol–urea–water system were measured. Those comprising aqueous solutions of urea, valeric acid, and 1-butanol were also measured in order to compare the spectra. The spectra were obtained for capillary films of samples between two KRS-5 plates, using a Bruker IFS66v FT-IR spectrometer. The results are shown in Figs. 1 and 2.

Results and Discussion

The band of an aqueous solution of urea at about 1650 cm^{-1} in Fig. 1(a) was found to comprise four bands (1665 (shoulder), 1652 (shoulder), 1639 (vs), and 1604 (shoulder) cm^{-1}), among which that at 1652 cm^{-1} was assigned to water. The other three bands are the C=O stretching band, or the NH_2 bending band of urea. In the spectrum of the valeric acid–urea–water system, a new band appeared at 1685 cm^{-1} in addition to those at 1656, 1637, and 1602 cm^{-1} (refer to Fig. 1(b)). Though valeric acid, itself, has a strong band at 1712 cm^{-1} (Fig. 1(d)), no band exists at 1685 cm^{-1} in the spectra of either the valeric acid–water system or valeric acid, as shown in Fig. 1(c and d). Therefore, the above-mentioned band at 1685 cm^{-1} can not be attributed to valeric acid, but is assigned to urea in the valeric acid–urea–water system. Similar, but more definite, situations were found for the 1-butanol–urea–water system and related compounds, as shown in Fig. 2 (a, b, and c). In the case of this system, a new band appeared at 1677 cm^{-1}, corresponding to the band at 1685 cm^{-1} in the case of valeric acid–urea–water system; it must be emphasized that no strong band exists at about 1680 cm^{-1}, or in the region above for the 1-butanol–water system and 1-butanol, itself. It has been established by many investigators$^{2—9)}$ that urea inclusion adducts have a characteristic infrared absorption band in the 1650—1700 cm^{-1} region, which is due to an inclusion structure formed by urea molecules.$^{1,10)}$ The presence of the above-mentioned bands at 1685 cm^{-1} and 1677 cm^{-1} for the (valeric acid or 1-butanol)–urea–water system, which correspond to the band of urea inclusion adducts in the 1650—1700 cm^{-1} region, may be proof of the presence of an inclusion structure in solution. Other proof is also given by the following spectral changes. Corresponding to the appearance of the above-

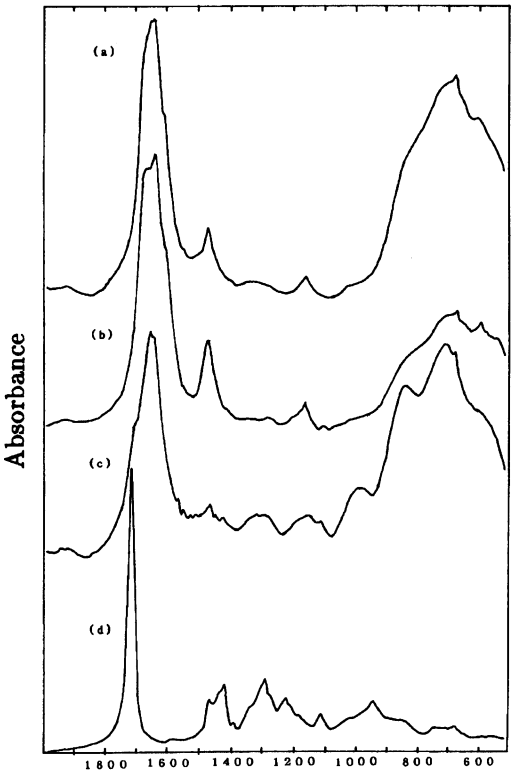

Fig. 1. IR spectra of the valeric acid–urea–water system and its related system. (a) aqueous solution of urea (mol fraction: urea, 0.034; water, 0.966). (b) valeric acid–urea–water system (mol fraction: valeric acid, 0.014; urea, 0.110; water, 0.876). (c) aqueous solution of valeric acid (mol fraction: valeric acid, 0.008; water 0.992). (d) valeric acid.

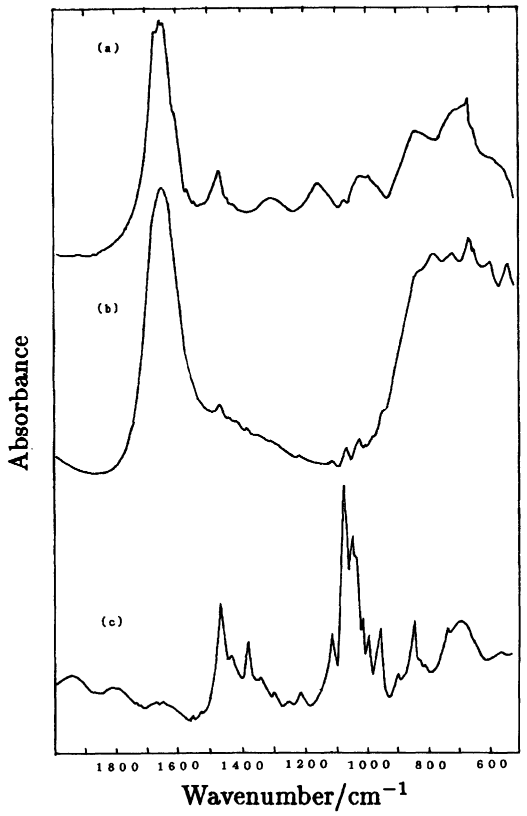

Fig. 2. IR spectra of the 1-butanol–urea–water system and its related systems. (a) 1-butanol–urea–water system (mol fraction: 1-butanol, 0.020; urea, 0.033; water, 0.948). (b) aqueous solution of 1-butanol (mol fraction: 1-butanol, 0.017; water, 0.983). (c) 1-butanol.

mentioned bands at 1685 cm^{-1}, several bands at 1264, 1195, and 1092 cm^{-1}, which are not found in the spectrum of the urea–water system, but exist as shoulder bands in the spectrum of the valeric acid–water system, remarkably increase in intensity, showing a conformational change of the valeric acid due to occlusion by urea molecules, as shown in Fig. 1(b). Regarding the case of the 1-butanol–urea–water system, the change is not as remarkable as in the case of the valeric acid–urea–water system, since the solubility of 1-butanol is small compared with that of valeric acid, and the bands of 1-butanol are weak.

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