

# Surface Active Properties of Simple Cyclic and Heterocyclic Amines in Water

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The surface tension of aqueous solutions of simple cyclic, heterocyclic and aromatic amines was measured with a Du Nöuy tensiometer at 25°C and the results discussed in terms of structure–aggregation relationships. The simple compounds used in this study were piperazine, piperidine, morpholine, 3-methylpyridine, cyclohexylamine and benzylamine, with carbon numbers ranging from four to seven.

Piperazine, piperidine and morpholine did not form micellar associations but cyclohexylamine, benzylamine and 3-methylpyridine did, indicating that more than six carbons are necessary to form micellar associations, at least for compounds having a six-membered ring.

**Key words** surface tension; self-association; simple ring compound; cyclic amine; heterocyclic compound; aqueous solution

It is generally known that compounds without any distinct hydrophobic and hydrophilic moieties do not easily form micelles. In contrast to a large number of studies on the surface activity of aliphatic compounds,<sup>1)</sup> only a few<sup>2–4)</sup> have been published on the surface activity of aromatic and/or cyclic compounds (especially simple compounds with a ring-structure). In 1995, we reported the self-association of cyclohexylamine in water.<sup>2)</sup> In the same year, Glinski *et al.* reported<sup>3)</sup> the surface tension of dilute aqueous solutions of cyclohexylamine and benzylamine, however the self-association of those compounds was not apparent because very dilute solutions were used.

On the other hand, the surface tension of some common surfactants in methylpyridine have been measured,<sup>5–7)</sup> although the surface active properties of methylpyridine were not discussed.

It would be interesting to know the degree of hydrophobicity necessary to form micelles, and it would also be of interest to investigate the surface activity of simple cyclic, heterocyclic and aromatic compounds in terms of structure–aggregation relationships. For systematic study of the surface activity of simple compounds with a ring-structure, we chose piperazine, piperidine, morpholine, 3-methylpyridine, cyclohexylamine and benzylamine, compounds with four to seven carbon atoms.

## Experimental

**Materials** Piperazine (hexahydropyrazine), piperidine (hexahydropyridine), morpholine (tetrahydro-2H-1,4-oxazine), cyclohexylamine, 3-methylpyridine and benzylamine purchased from Wako Pure Chemical Industries, Ltd. were of guaranteed reagent grade and were used without further purification. The structural formulas of those compounds are shown in Chart 1. Deionized and twice-distilled water were used throughout this study.

The  $pK_b$  values of piperazine,<sup>8)</sup> piperidine,<sup>8)</sup> morpholine,<sup>8)</sup> cyclohexylamine,<sup>9)</sup> 3-methylpyridine<sup>9)</sup> and benzylamine<sup>9)</sup> are 4.2, 2.8, 5.6, 3.34, 8.0 and 4.65, respectively. 3-Methylpyridine is a weak base and exists as ionic and non-ionic forms in water, while the other five amines are strong bases and exist almost entirely in ionic form in water. The solubility of piperazine in water is about 3 M, while the other five amines are freely soluble in water.<sup>8)</sup>

**Measurement of Surface Tension** The surface tension was measured with a Du Nöuy tensiometer. A platinum ring with a diameter of 19 mm was heated in an oxidizing flame before use. The thermostat temperature was maintained at 25±0.1°C. To calculate the surface tension of aqueous solutions, the value of 71.96 mN m<sup>−1</sup> was used as the surface tension of pure water at 25°C. The experimental determination of the surface tension was precise to ±0.1 mN m<sup>−1</sup>.

## Results and Discussion

**Surface Tension of Aqueous Solutions of Simple Amines with a Ring-Structure** The surface tension ( $\gamma$ ) of aqueous solutions of piperazine, piperidine, cyclohexylamine, morpholine, 3-methylpyridine and benzylamine are presented in Figs. 1 and 2.

The surface tension of an aqueous solution of morpholine fell continuously with increasing concentration of morpholine, and no inflection point in the surface tension curve was found, even above 10 M. Morpholine is unlikely to exhibit self-association. The surface tension of an aqueous solution of piperazine is higher than that of morpholine at the same concentration and so piperazine is also unlikely to exhibit self-association, although the surface tension of aqueous solutions of piperazine at concentrations above 4 M could not be measured because of the low solubility<sup>8)</sup> of piperazine. The surface activity of morpholine is slightly greater than that of piperazine, and so the substitution of –O– for –NH– seems to increase the surface activity of heterocyclic compounds.

In the case of cyclohexylamine, benzylamine and 3-methylpyridine, a marked decrease in  $\gamma$  and inflection points in the  $\gamma$  vs.  $\log C$  curves were found, suggesting that these compounds undergo self-association like micelles. If the critical micelle concentration (cmc) is estimated from the inflection point in the  $\gamma$  vs.  $\log C$  curve, cmcs are obtained as 0.54, 0.77 and 1.8 M for cyclohexylamine, benzylamine and 3-methylpyridine, respectively. In addition, the surface tension

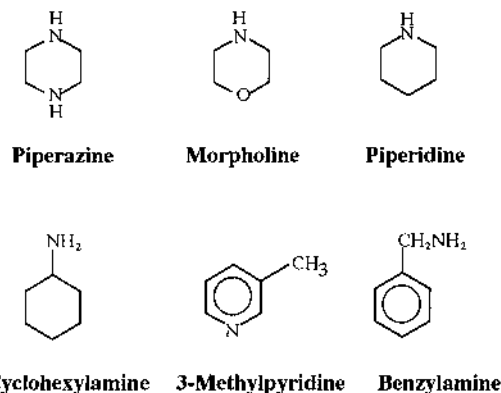


Chart 1. Structural Formulas of Simple Cyclic and Heterocyclic Compounds

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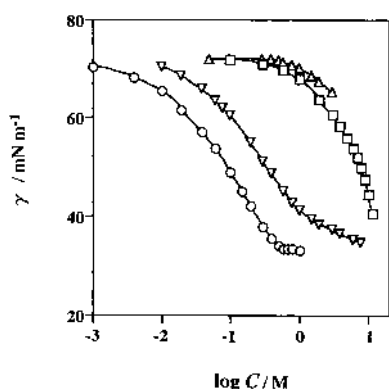


Fig. 1. Surface Tension of Simple Cyclic and Heterocyclic Amines in Water at 25 °C

○, cyclohexylamine; ▽, piperidine; □, morpholine; △, piperazine.

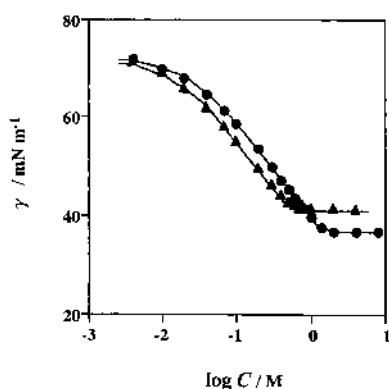


Fig. 2. Surface Tension of Benzylamine and 3-Methylpyridine in Water at 25 °C

▲, benzylamine; ●, 3-methylpyridine.

at the cmc ( $\gamma_{\text{cmc}}$ ) is 33.5, 41.5 and 36.7 mN m<sup>-1</sup> for cyclohexylamine, benzylamine, and 3-methylpyridine, respectively.

The change in surface tension just below the cmc is gradual. This is considered to be due to the fact<sup>10)</sup> that surface active compounds with aromatic hydrophobic groups are generally thought to undergo association by a process in which aggregate growth occurs by the continuous stepwise addition of monomers. We have obtained similar results for piperidolate hydrochloride,<sup>11)</sup> [*N*-ethyl-3-piperidyl diphenylacetate hydrochloride] (an anti-cholinergic drug) and dibucaine hydrochloride,<sup>12)</sup> [2-butoxy-*N*-[2-(diethylamine)ethyl]-4-quinolinecarboxamide] (a local anesthetic).

The aggregation numbers of 3-methylpyridine, benzylamine and cyclohexylamine are thought to be relatively small because of the six-membered ring-structure of those compounds and the large cmc value. In general, the micellar aggregation number of aromatic compounds is low: about equal to the micellar aggregation numbers of dibucaine hydrochloride<sup>13)</sup> and piperidolate hydrochloride<sup>14)</sup> which are 9 and 12, respectively.

The surface tension of aqueous solutions of piperidine decreased with increasing concentration of piperidine but a clear inflection point, as shown in the case of cyclohexylamine, benzylamine and 3-methylpyridine, was not found although the decrease in  $\gamma$  was gradual above 2 M. Therefore,

piperidine is unlikely to form a micellar association. Even if piperidine forms such associations, the aggregation number of the self-association would be much smaller than that of cyclohexylamine, benzylamine or 3-methylpyridine. The self-association of piperidine in water may result in a dimer or further dimerization of the dimer at the most. For a more detailed discussion, it is necessary to know the aggregation numbers of the self-associations of these cyclic and heterocyclic amines. Further measurement by light scattering or fluorescence quenching methods will be required to obtain the aggregation numbers of these compounds.

Piperidine has five methylene units, while cyclohexylamine and 3-methylpyridine have six carbons which suggests that more than six carbons are necessary to form micellar associations.

Regarding the surface activity of *ortho*-, *meta*- and *para*-isomers, it has been reported<sup>4)</sup> that *meta*-chlorobenzamide shows greater surface activity than *ortho*-chlorobenzamide under the same conditions and that the effect is related to the dipole moment of the molecule. So, the surface activity of 3-methylpyridine may differ from that of 2-methylpyridine and 4-methylpyridine. We intend to examine the surface active properties of 2-methylpyridine and 4-methylpyridine in the subsequent study.

The surface activity of cyclohexylamine with 6 carbons is greater than that of benzylamine with 7 carbons. This is because of the presence of unsaturated bonds in benzylamine. Regarding the effect of double-bonds, it has been reported<sup>15,16)</sup> that incorporation of a double-bond near the center of the hydrocarbon chain in long-chain surfactants has an effect on the cmc, equivalent to the removal of 1 to 1.5 CH<sub>2</sub> groups from a saturated chain. We have reported that the cmc of icosapolyenoic acid increased twofold on increasing the number of double-bonds.<sup>17)</sup> In the case of benzylamine, which has a benzene-ring, the surface activity of benzylamine is nearly equal to that of saturated cyclic compounds with a carbon number of 5.5.

In conclusion, piperidine did not form micellar associations but cyclohexylamine, benzylamine and 3-methylpyridine did (although the aggregation numbers of those associations are still unknown), indicating that more than six carbons in a molecule are needed to form micellar associations of compounds with a six-membered ring. Further measurement by light scattering or fluorescence quenching methods is necessary to obtain the aggregation numbers of these compounds. Nevertheless, the concentration of 3-methylpyridine, cyclohexylamine and benzylamine, when these compounds are used as a medium for synthesis or as a solvent, may be important.

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