Diverse applications of N-alkyl pyrrolidones

Dr Robert Gibbison of **ISP** looks at two surface-active N-alkyl pyrrolidones to show how their unique chemistry offers benefits in many applications

Pyrrolidone chemistry first became available in the 1930s, when W. Reppe developed a synthetic route by reacting acetylene with formaldehyde (Figure 1). The arising butynediol can be further reduced to the saturated butanediol form. This intermediate is dehydrogenated to form butyrolactone, the precursor to 2-pyrrolidone and the extensive family of alkyl pyrrolidones that is produced from a condensation reaction with ammonia or primary amines.

Surface activity

The range of N-substituted pyrrolidones is only limited by the ability of the primary amine to withstand the 200-300˚C temperatures necessary to dehydrate and cyclise the hydroxybutylamide intermediate. Variants where R = methyl, ethyl, 2-hydroxyethyl and cyclohexyl are all available.

The 2-pyrrolidone arising from the reaction with ammonia can be further reacted with acetylene to yield N-vinyl-2-pyrrolidone. The latter can be polymerised to form polyvinylpyrrolidone (PVP), which is widely used in hair care, dye transfer inhibition for laundry products, high quality paper coatings, pharmaceutical tablets and many other applications.

Increasing the chain length of N-alkyl pyrrolidones to C_8 results in a significant increase in surface activity. This reaches a maximum at C_{12} and drops off above C_{14}. Two surface-active variants are commercially available: N-octyl-2-pyrrolidone, or Surfadone LP-100, and N-dodecyl-2-pyrrolidone, or Surfadone LP-300 (see Figure 2).

Both are supplied as >99% active pale yellow, high boiling, low viscosity liquids, which are stable over a pH range of 2-10 and in the presence of hydrogen peroxide. Recent developments mean that both can be supplied as 30% active on a variety of carriers such as zeolite or soda ash for solid-state applications. N-alkyl pyrrolidones are non-ionic but exhibit pseudo-cationicity at a low pH. This is as a result of electron delocalisation in the lactam ring, which is stabilised by pye electron overlap in the planar structure.

This cationicity is of benefit when considering the solubilisation of N-alkyl pyrrolidones. As the R group chain length is increased, so the solubility in water decreases. The N-octyl-2-pyrrolidone variant, which has a hydrophilic lipophilic balance (HLB) of six, is soluble in water up to 0.124% and the N-dodecyl-2-pyrrolidone (HLB of 3) is soluble up to 0.002%.

For applications requiring solubilisation of higher concentrations this can easily be achieved by addition of small quantities of surfactants, especially anionics. Whilst neither has a critical micelle concentration (CMC) of its own in water, both have the ability to form mixed micelles with anionic surfactants. The small hydrophilic head is able to fit easily between the larger surfactant molecules. This allows for synergistic complexes to be formed (see below)[1].

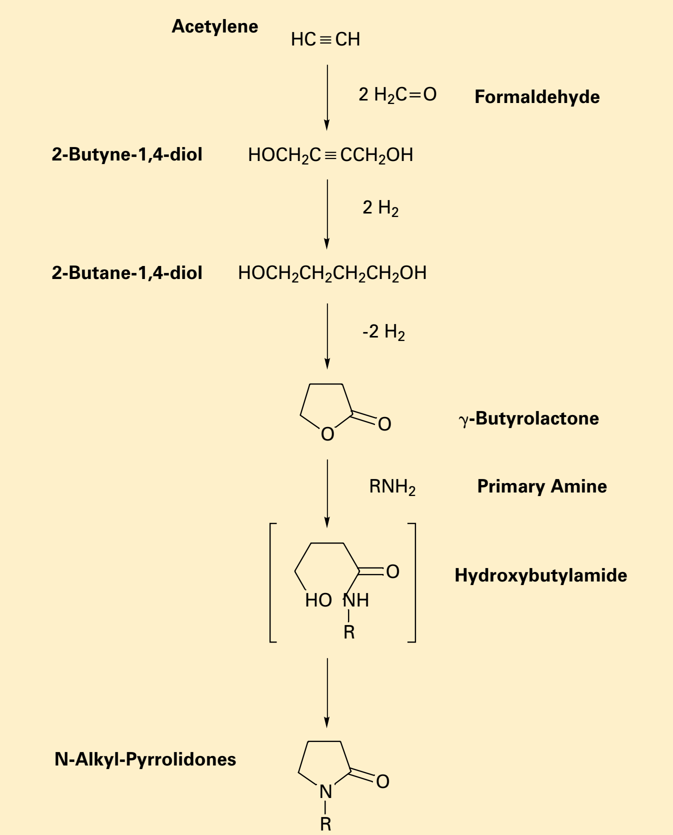

Figure 1 - Preparation of N-alkyl pyrrolidones

Surface tension & wetting

The ability of both pyrrolidones to act as efficient wetting agents is demonstrated well by the Draves Wetting Test. This measures the ability of the molecules to interact with a solid surface more strongly than with themselves. The faster the sinking time of a small cotton ball through a solution of the surfactant, the better the wetting agent.

At a concentration of 0.1% in water, the shorter chain pyrrolidone gives the best Draves Wetting Time (3.5 seconds). The longer chain dodecyl moiety gives a time of >300 seconds. This is probably a result of its reduced solubility in water. A dramatic improvement can be achieved by adding surfactant. For example, 0.018% sodium dodecyl sulphate (SDS) will improve the Draves Wetting time to just 4.4 seconds.

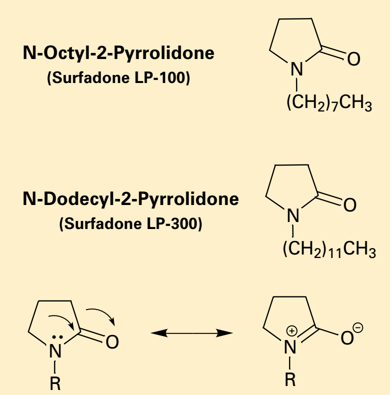

Figure 2 - Surface-active N-alkyl pyrrolidones and electron delocalisation of their surface

Further evidence of their ability to wet effectively comes from contact angle measurements, that is the equilibrium angle that the substrate makes with a drop of the liquid. The smaller the angle, the greater the wetting ability. Both can effectively wet high energy, hydrophilic surfaces like aluminium and low energy, hydrophobic surfaces, like Teflon. The contact angle for both is lower than 5˚ and 54˚ respectively.

Their ability to reduce static surface tension is best demonstrated in surface tension measurements (see Figure 3). Both products will lower surface tension to ~26 dynes/cm. This can best be achieved using a lower concentration of the more alkylated N-dodecyl-2-pyrrolidone. Some practical applications, however, do not reach equilibrium. This is why dynamic surface tension reduction is important in certain applications.

Figure 4 demonstrates the ability of N-octyl-2-pyrrolidone to reduce dynamic surface tension dramatically. These results were generated by the maximum bubble pressure method. A concentration of 0.12% N-octyl-2-pyrrolidone gives a surface tension measurement of 30 dynes/cm for a surface age of one second, close to the equilibrium value.

As the bubble rate is increased,

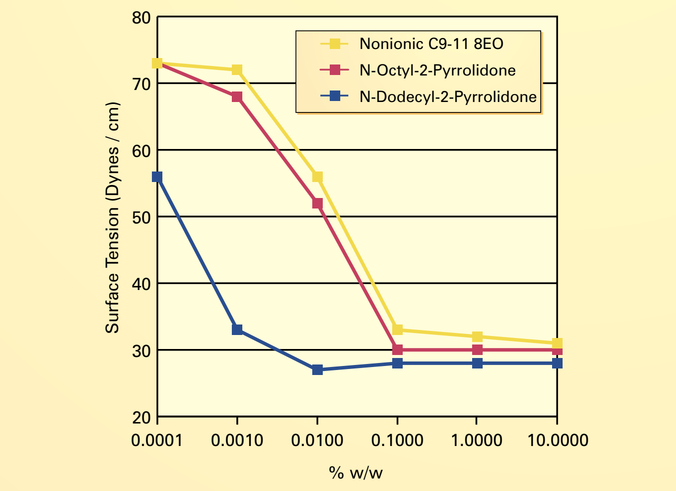

Figure 3 - Effect of N-octyl and N-dodecyl pyrrolidone on static surface tension reduction

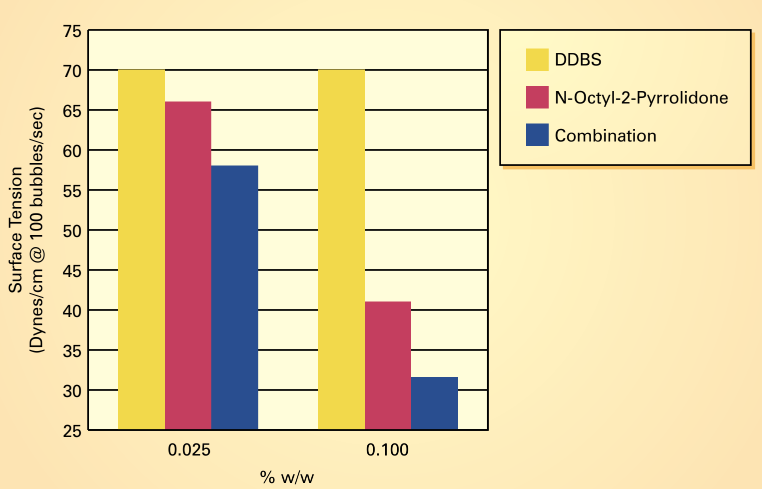

Figure 5 - Dynamic surface tension reduction of N-octyl-2-pyrrolidone in conjunction with 0.025% Sodium DoDecyl Benzene Sulphonate (DDBS)

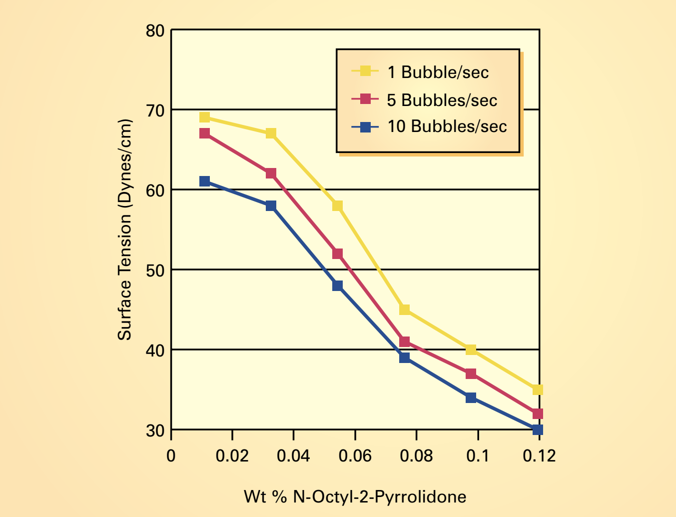

Figure 4 - Effect of N-octyl-2-pyrrolidone on dynamic surface tension reduction

so the surface age is decreased. There is only a slight loss in surface tension reduction at higher bubble rates. Even for a surface existing for only 0.1 seconds, surface tension is still significantly reduced, to 35 dynes/cm. This feature of N-alkyl pyrrolidones is due to the high mobility of the small hydrophilic pyrrolidone head group.

A further benefit of the small head group is seen in synergistic surface tension reduction when N-dodecyl- and N-octyl-2-pyrrolidones are used in conjunction with anionic surfactants (Figure 5).

The ability of the small hydrophilic head to fit between the larger surfactant molecules allows the resultant mixed micelles to reduce surface tension considerably. Addition of 0.025% N-octyl-2-pyrrolidone reduces surface tension of the DDBS from 70 to 58 dynes/cm. Increasing the level of the N-octyl-2-pyrrolidone to 0.1% reduces the dynamic surface tension further, to 32 dynes/cm.

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Applications

The addition of N-dodecyl-2-pyrrolidone to the **hair care** polymer vinyl caprolactam/vinyl pyrrolidone /dimethylaminoethylmethacrylate has been shown to alter the feel characteristics of the polymer on the hair dramatically. The chemistry of the polymer (that is, the hydrophobic caprolactam ring which improves humidity resistance, the vinyl pyrrolidone for film-forming ability and the pseudo-cationic dimethylaminoethylmethacrylate, which provides conditioning benefits and flexibility) combines to produce a highly effective styling polymer for aerosol hairsprays.

However, some consumers prefer a polymer with a stiffer feel and independent salon tests have shown that the addition of a small quantity of N-dodecyl-2-pyrrolidone can achieve this. The powerful wetting ability of the pyrrolidone significantly affects the spreading and drying characteristics of the polymer resulting in the desired stiffer, raspier feel. This product (Advantage LC-E) has been commercialised.

A recent trend in the household industrial and institutional market has been towards **wet wipes**. These provide a convenient means of cleaning a variety of hard surfaces. The shorter chain N-octyl-2-pyrrolidone has been successfully incorporated into these applications.

Used at up to 3% it can significantly boost cleaning efficacy when used in combination with anionic surfactants as a result of the formation of mixed micelles. Additional benefits are the low foaming characteristics whilst the dynamic surface tension reduction ensures reduction of smearing as well as high cleaning power. The pyrrolidone interacts effectively with the hard surface during the short contact time available.

N-dodecyl-2-pyrrolidone is well established in the personal care market as a thickener and foam booster, especially for shampoo systems for conditioning benefits and as a potential replacement for Cocamide DEA. The ability to tolerate hydrogen peroxide is a benefit in **oxidative hair dye** systems.

N-dodecyl-2-pyrrolidone may be used as an effective surfactant thickener in the alkaline colourant base. When this is mixed with the developer, the highly mobile surfactant is believed to help the dye to penetrate through the opened cuticle deep inside the cortex of the hair. As a result, the colouration of the hair achieves greater permanence.

Off-set **lithographic printing** is widely used for the production of books and magazines. The key requirement of this process is that the ink migrates only to those areas where it is desired and the remaining areas remain totally ink-free. In order to achieve this, a fountain solution is applied.

Traditionally fountain solutions have been comprised of water, iso-propyl alcohol (IPA) and a range of additives (biocides, corrosion inhibitors etc.). The key attribute is the ability of the fountain solution to wet the non-printing region of the paper - in other words, to have good surface coverage. Dynamic surface tension reduction is paramount, as printing is often at speeds of up to 15 metres/second.

Whilst traditional IPA systems are effective, tightening legislation on the use of VOCs has heightened interest in alternative processes. Replacing IPA with 2% of N-octyl-2-pyrrolidone has proved highly effective. The high mobility of the surfactant allows for effective spreading of the fountain solution and the necessary dynamic surface tension reduction can be achieved on the paper. As a result the non-printing region remains free from ink and high print quality can be achieved without the use of VOCs.

Reference

1. For a more detailed description of the chemistry of N-alkyl pyrrolidones including solubility, solvency ability, complexing ability and foaming, see J.C. Hornby & D. Jon, 'Surface Active Specialty Solvents' in *Soap/Cosmetics/Chemical Specialties*, September 1992.