Blue Solutions of Sulphur in Hexamethylphosphoramide

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Summary Elemental sulphur is sparingly soluble in hexamethylphosphoramide (HMPA) to give blue solutions attributed to the formation of a negatively charged species, probably S_3^-.

ELEMENTAL sulphur dissolves in anhydrous HMPA at 25° to give intense blue-green solutions which do not obey Beer's law. The structured peak at 620 nm suggests the presence of the same species as that formed by alkali tetrasulphides in dimethylformamide (λ_{max} 618 nm) and previously attributed to neutral molecules S_x ($x = 2$—4).[1,2] Transference experiments show that the blue species is anionic and dilute solutions (*ca.* 10^{-3}M in g atoms of sulphur in HMPA) behave as moderately strong electrolytes with Λ_0 *ca.* 6·6 ohms^{-1} cm^2/g atom of sulphur (*cf.* $\Lambda_0 = 20$—30 ohms^{-1} cm^2 moles^{-1} for 1:1 electrolytes in HMPA)[3,4] suggesting the composition S_3^-. In support of this assignment, Raman spectra of alkali halide crystals heated in the presence of sulphur[5] have shown that the broad visible absorption band at 610 nm can be attributed to S_3^- and that at 400 nm to S_2^-, although Giggenbach has suggested that the blue species is S_2^-.[6]

HMPA is a useful catalyst for preparative reactions involving elemental sulphur. For example, the phosphine sulphides $(C_6H_5)_3PS$, $(C_6H_5)_2P(S)CH_2CH_2(S)P(C_6H_5)_2$ and $(C_6H_{11})_3PS$[7] can readily be prepared in good yields *at room temperature* by addition of the appropriate phosphine to a solution of sulphur in carbon disulphide/HMPA (70:30; v/v).

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