are the average and maximum deviations from the average value, respectively.
(5) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed, Wiley, New York, N.Y., 1972, p 951.
(6) Reference 2, p 304.
(7) W. G. Klemperer and W. Shum, *J. Am. Chem. Soc.*, **98**, 8291, (1976).
(8) Camille and Henry Dreyfus Teacher-Scholar.
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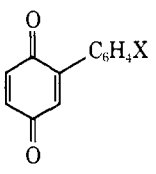
Crystal Growth by Nonaqueous Gel Diffusion[1]

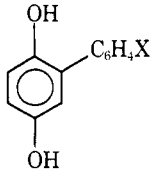
Sir:

Aqueous gel diffusion has been known since the end of the last century to be a superior method of crystal growth. It consists of the controlled growth of product crystals by diffusion of reactants together in a gel such as aqueous sodium silicate.[2] Since the method used *aqueous* gels, the low solubility in water of most organic compounds has excluded general applicability to such compounds.

In the course of an investigation[3] of 1:1 complexes (quinhydrones) of quinones such as **1** with hydroquinones such



1a, X = H
b, X = Cl



2a, X = H
b, X = Cl

as **2**, we encountered much difficulty in obtaining single crystals because of a great tendency of the complexes to crystallize as fine powders or, alternatively, to form twinned crystals.[4]

This communication reports a method of preparing *nonaqueous* gels that permits the extension of crystallization by gel diffusion to a much wider range of compounds and which gives good results when other methods fail. The basis is the demonstration that Sephadex LH-20, an alkylated cross-linked dextran, forms suitable gels with aromatic hydrocarbons provided small amounts of an alcohol are present. The details of the procedure[5] are of great importance since the relative amounts of Sephadex and the other components must be so chosen that on mixing a satisfactory gel is obtained directly; otherwise the mixture must be discarded.

With this procedure, the complex **1a–2a** was readily obtained as single crystals with average dimensions 2 × 1 × 0.2 mm (Figure 1); attempts to obtain satisfactory crystals of this complex by other methods of crystallization or sublimation had failed. The method was equally successful with the complex **1b–2b.**

When the chloroquinone **1b** was allowed to diffuse into a gel containing the unchlorinated hydroquinone **2a,** only the unchlorinated quinhydrone **1a–2a** was formed. A redox hydrogen transfer must have occurred in the gel during the diffusion process. An interesting point was that, in this case, there was formed a high proportion of untwinned crystals of **1a–2a,** whereas, when the same complex **1a–2a** was produced from

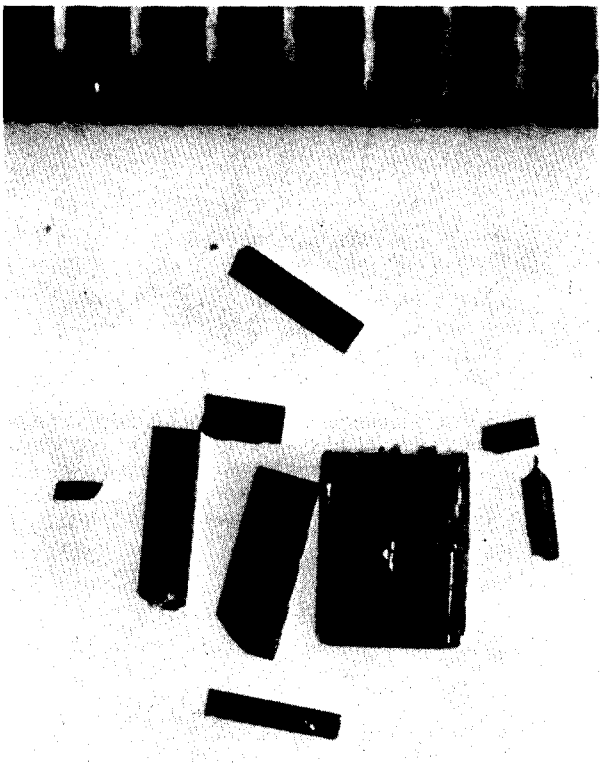


Figure 1. Crystals of the 1:1 complex **1a–2a** of 2-phenyl-1,4-hydroquinone–2-phenyl-1,4-benzoquinone grown by nonaqueous gel diffusion. A millimeter scale is shown at the top of the photograph.

1a and **2a,** many of the crystals of the product were twinned.

The nonaqueous gel diffusion method has also been successful with the naphthalene–picric acid complex[6] and with the phenol–benzoquinone (2:1) complex.[7]

It appears likely that crystallization with nonaqueous gels could have broad application to organic complexes. In addition, it seems probable that it can be adapted to the crystallization of single substances by diffusion of a poorer solvent into a gel prepared from a solution of the substance in a solvent in which it is more soluble.

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References and Notes

(1) Taken from the Ph.D. Thesis of Gautam R. Desiraju, submitted to the University of Illinois, Urbana, Ill.
(2) J. Dennis and H. K. Henisch, *J. Electrochem. Soc.*, **114**, 263 (1967); B. Rubin, *AIChE J.*, **15**, 206 (1969); H. K. Henisch, "Crystal Growth in Gels", Pennsylvania State University Press, University Park, Pa., 1970; H. N. Holmes, *J. Franklin Inst.*, **184**, 743 (1917).
(3) G. R. Desiraju, D. Y. Curtin, and I. C. Paul, unpublished work.
(4) See also H. Matsuda, K. Osaki, and I. Nitta, *Bull. Chem. Soc. Jpn.*, **31**, 611 (1958).
(5) Typically, to 0.65 g of hydroquinone **2a** in 3.8 mL of 3:1 toluene–methanol is added 1.7 g of Sephadex LH-20 (Pharmacia Fine Chemicals). The gel sets immediately. A solution of 0.25 g of quinone **1a** in 4 mL of the same solvent is poured on top of the gel and the container allowed to stand at room temperature. A black precipitate forms at the interface and, as the solutions slowly diffuse together, a deep coloration develops. Small well-formed crystals grow within the body of the gel after ~24 h. The crystals, after they have attained the desired size, are removed from the gel by washing with water.
(6) F. G. Baddar and H. Mikhail, *J. Chem. Soc.*, 2927 (1949).
(7) T. T. Harding and S. C. Wallwork, *Acta Crystallogr.*, **6**, 791 (1952); T. Sakurai, *Acta Crystallogr., Sect. B*, **24**, 403 (1968).

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