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Molecular Self-Assembly in the Solid State. The Combined Use of Solid-State NMR and Differential Scanning Calorimetry for the Determination of Phase Constitution

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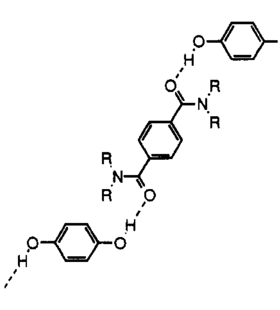
The construction and use of phase diagrams for the study of self-assembled systems are extremely useful. While well-known in various fields of metallurgy, phase diagrams have not been widely applied to multicomponent organic systems of contemporary interest. The blending of hydroquinone (**1**) with bis(*N*,*N*-diethyl)terephthalamide (**2**) or bis(*N*,*N*-dimethyl)terephthalamide (**3**) in the solid state has been demonstrated to generate stable binary phases as determined by both solid-state NMR and differential scanning calorimetry. Compounds **1** and **2** form a single phase of a 1:1 composition, while compounds **1** and **3** form two stable phases, one of a 1:1 composition and the other of a hydroquinone/terephthalamide composition of 2:1. Phase diagrams of these systems are constructed and structural features discussed.

Introduction

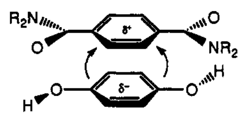
Hydroquinones have found widespread use as developers in photographic systems.[1] At sufficiently elevated pH hydroquinones are fully deprotonated, forming anionic species which are both soluble and mobile in aqueous media, including thin-film photographic systems. At neutral pH, on the other hand, hydroquinones are nonionic, and therefore in such systems insoluble and immobile. Quinones, the oxidation products of hydroquinones, cannot undergo deprotonation in alkaline solution. Therefore, in aqueous environments at both high and neutral pH, quinones are insoluble and immobile. These phenomena are exploited in diffusion-controlled, silver halide photographic imaging systems such as Polaroid instant photography. In such systems a multilayer, thin-film negative (which is coated from water at neutral pH) is treated after exposure with a highly alkaline reagent to solubilize the hydroquinones and allow them to effect silver halide developement.

While a simple description of the diffusivities of hydroquinones and their reaction products is adequate to explain the general principle of diffusion-controlled imaging, in practice the situation is unfortunately not so straightforward. Some photographically useful hydroquinones have sufficient aqueous solubility in their protonated state to present a particular problem. In these cases, the marginal solubility may lead to migration of reagents in the multilayer film structure prior to pH elevation. This compromises the performance of the imaging system and must be anticipated and compensated for in some way. Our research efforts have been directed toward more effectively controlling hydroquinone immobilization at neutral pH while not interfering with the solubility, and therefore reactivity, of the deprotonated species.

The formation and properties of quinhydrones have been thoroughly investigated.[2] A quinhydrone may be thought of as a bulk 1:1 stoichiometric complex of a hydroquinone with a quinone, held together by a network of hydrogen bonds and π-stacking. These complexes are often insoluble in aqueous environments at neutral pH. At high pH, the hydroquinone component of the quinhydrone is deprotonated, disrupting the hydrogen bonding. The absence of the hydrogen bonding network allows for the dissociation of the solid complex, thereby allowing the deprotonated hydroquinone to dissolve. Such a solubility modification of hydroquinones could accomplish our task of immobilization. Unfortunately however, quinones, being oxidizing reagents which are reactive in photographic systems, cannot be used to form the complex. Some other molecule would be needed to mimic the behavior of the quinone in forming complexes with hydroquinones. We expected that the complexes of hydroquinones with bis(*N*,*N*-dialkyl)terephthalamides would resemble quinhydrones as π-stacked extended hydrogen bonded networks.



Hydrogen Bonding



π Stacking

Results and Discussion

The two complex systems investigated were those of hydroquinone **1** with bis(*N*,*N*-diethyl)terephthalamide (**2**, system 1), and hydroquinone (**1**) with bis(*N*,*N*-dimethyl)-

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(1) Lee, W. E.; Brown, E. R. In *The Theory of the Photographic Process,* 4th ed.; James, T. H., Ed.; Macmillan: New York, 1977; Chapter 11.

(2) Patil, A. O.; Pennington, W. T.; Desiraju, G. R.; Curtin, D. Y.; Paul, I. C. *Mol. Cryst. Liq. Cryst.* **1986,** *134,* 279.

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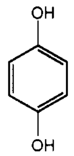
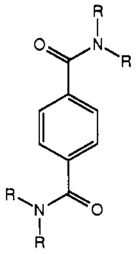
terephthalamide (**3**, system 2). To characterize the phase behavior of these systems, mixtures of the components at various molar ratios were prepared. Following examples of Etter[3] and Lehn,[4] we prepared mixtures of the components by solid-state grinding.[5]



1



2: R = Et
3: R = Me

Examination of the ^{13}C CP/MAS spectra (Figure 1) of pure hydroquinone (**1**), pure bis(*N*,*N*-diethyl)terephthalamide (**2**), and the five mixtures of **1** and **2** of molar ratios 3:1, 2:1, 1:1, 1:2, and 1:3 (**2a–e**, respectively, system 1) shows the presence of a unique spectrum which is derived from the 1:1 mixture, **2c**. The nonequivalent mixtures give spectra that are the simple sums of the excess constituent component **1** or **2**, and the 1:1 mixture, **2c**. In pure **1**, the 1 and 4 phenolic carbons display a triplet resonance at 148.1 ppm. In the 1:1 mixture, **2c**, this resonance is simplified to a singlet at 149.2 ppm. The 3:1 and 2:1 mixtures, **2a** and **2b**, display combinations of these peaks that are proportional to the excess hydroquinone, **1**, and the 1:1 mixture, **2c**. In the 1:2 and 1:3 mixtures, **2d** and **2e**, where there is no excess hydroquinone **1**, but there is excess bis(*N*,*N*-diethyl)terephthalamide **2**, no triplet resonances at 148.1 ppm appear at all.

The chemical shifts of the two, three, five, and six carbons of bis(*N*,*N*-diethyl)terephthalamide (**2**) serve as diagnostic resonances for the mixtures which have this compound in excess. In pure **2**, these atoms display a doublet at 124.0 ppm. The 1:1 mixture, **2c**, displays a doublet at 126.0 ppm. The 1:2 and 1:3 mixtures, **2d** and **2e**, show the 124.0 and 126.0 doublets in proportion to the excess of **2** with respect to **2c**. In the 3:1 and 2:1 mixtures, **2a** and **2b**, where no free **2** exists, only the doublet at 126.0 ppm is observed. Each of the other carbon resonances show analogous behavior.

These dramatic variations in spectra are quite remarkable in light of the fact that these mixtures were prepared by simple solid grinding at room temperature.[5] To obtain a thermodynamic measure of the complexation, differential scanning calorimetry was performed on the mixtures of **1** and **2**. The phase diagram so derived exhibits the thermal behavior that can be expected from a binary mixture that forms a stable 1:1 complex (Figure 2). Pure hydroquinone (**1**) has a melting endothermic transition at 173 °C and pure bis(*N*,*N*-diethyl)terephthalamide (**2**) displays a melting endothermic transition at 129 °C. The 1:1 mixture, **2c**, exhibits a sharp endotherm at 147 °C. The 3:1 and 2:1 mixtures, **2a** and **2b**, indicate the presence of a eutectic with an endothermic transition at 122 °C, while the 1:2 and 1:3 mixtures, **2d** and **2e**, indicate the presence of a different eutectic with an endotherm at 118 °C. This thermal behavior is typical of a mixture where the components form a stable complex;[6] for instance, phenol and aniline display this property.[7]

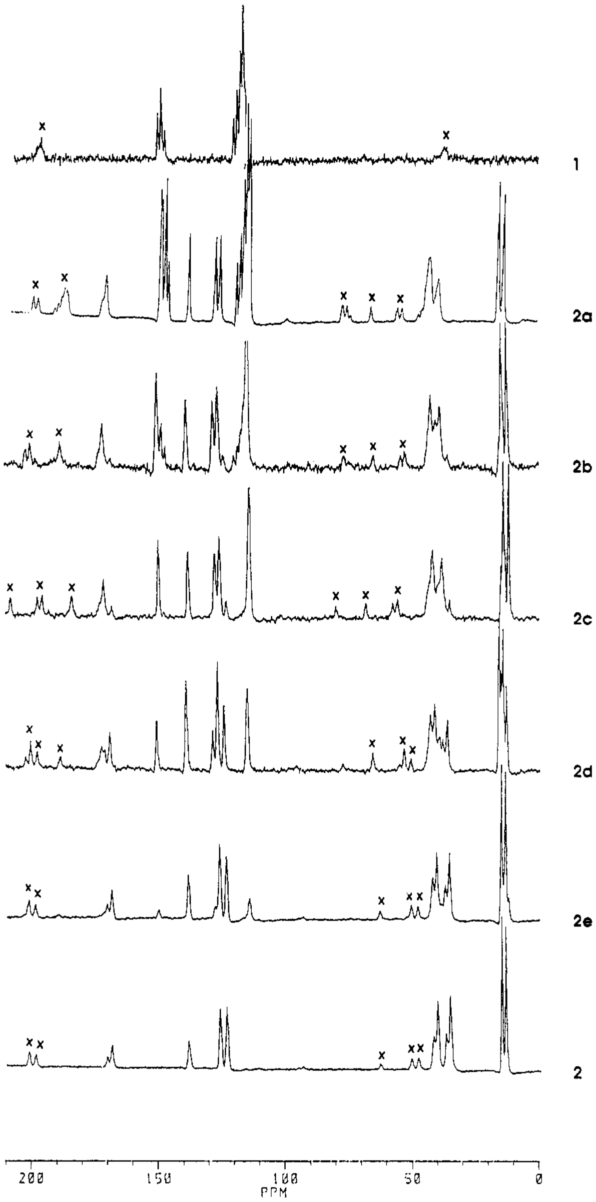


Figure 1. ^{13}C CP/MAS spectra for the hydroquinone–bis(*N*,*N*-diethyl)terephthalamide system (system 1). Lines marked by an × indicate spinning sidebands.

When bis(*N*,*N*-dimethyl)terephthalamide (**3**) was used in place of bis(*N*,*N*-diethyl)terephthalamide (**2**) to form similar mixtures **3a–e** (system 2), we were surprised to find significantly different phase behavior. In addition to the formation of the new stable phase of 1:1 composition, **3c**, the 2:1 mixture, **3b**, also formed a stable binary phase.

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(3) (a) Etter, M. C.; Hoye, R. C.; Vojta, G. M. *Cryst. Rev.* **1988**, *1*, 281. (b) Etter, M. C.; Frankenbach, G. M.; Bernstein, J. *Tetrahedron Lett.* **1989**, *30*, 3617. (c) Etter, M. C. *J. Phys. Chem.* **1991**, *95*, 4601. (d) Etter, M. C. *J. Am. Chem. Soc.* **1991**, *113*, 2586. (e) Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120. (f) Etter, M. C.; Reutzel, S. M.; Choo, C. G. *J. Am. Chem. Soc.* **1993**, *115*, 4411.

(4) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304.

(5) The ability to use solid grinding techniques to form new molecular phases has been elegantly demonstrated by Etter with hydrogen-bonded cocrystals. This work represents an application of this methodology to explore phase constitution in hydroquinone/terephthalamide mixtures. The kinetics and efficiency of this technique is being explored for these and similar binary systems.

(6) Gutt, W.; Majumdar, A. J. In *Differential Thermal Analysis*; Mackenzie, R. C.; Ed.; Academic: London, 1972; Chapter 29.

(7) Moore, W. J. *Physical Chemistry*; Prentice-Hall: Englewood Cliffs, NJ, 1972; Chapter 7.

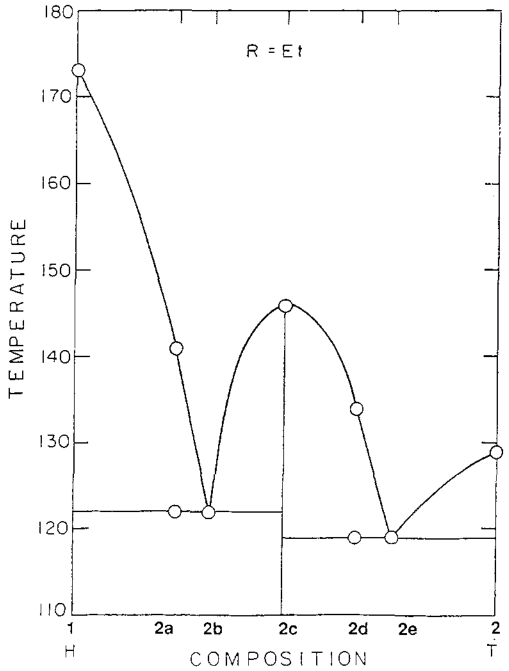

Figure 2. Phase diagram for the hydroquinone–bis(*N*,*N*-diethyl)terephthalamide system (system 1). The eutectic compositions were estimated (not experimentally determined).

The formation of a nonequivalent molar complex of a hydroquinone has to our knowledge been described only once,[8] in a case where the complexing molecules reported contain just one amide functionality.

The ^{13}C CP/MAS spectra of these mixtures (Figure 3) with **3** are somewhat more complicated than those of the mixtures with **2**. Consideration of the one and four phenolic carbons of hydroquinone reveals the triplet resonance at 148.1 of pure **1** to emerge as a very tight doublet at 148.5 ppm for the 2:1 mixture, **3b**. In the 1:1 mixture this resonance appears as a singlet at 151.0 ppm. The 3:1 mixture, **3a**, appears to be a mixture of **1** and **3b**, while **3d** and **3e** are proportional mixtures of **3** and **3c**.

This same additivity is observed for the two, three, five, and six carbons of **3**. Pure bis(*N*,*N*-dimethyl)terephthalamide (**3**) exhibits a singlet resonance at 126.7 ppm. The 1:1 mixture, **3c**, displays an asymmetric pair of peaks at 129.0 and 124.9 ppm, and the 2:1 mixture, **3b**, shows a tight doublet at 125.4 ppm.

The phase diagram derived from differential scanning calorimetry of the binary mixtures was difficult to interpret. It was necessary to prepare and examine several additional ratios of hydroquinone (**1**), and bis(*N*,*N*-dimethyl)terephthalamide (**3**). Having these additional data, we were able to construct a phase diagram consistent with the NMR data (Figure 4). Pure bis(*N*,*N*-dimethyl)terephthalamide (**3**) displays a melting endotherm at 203 °C. The 2:1 mixture **3b** exhibits a sharp endothermic transition at 198 °C, and the 1:1 mixture **3c** has its endotherm at 169 °C. A eutectic appears between the 1:1 mixture **3c** and pure **3** at 163 °C. Another eutectic is apparent between the 2:1 mixture **3b** and pure **1** at 161 °C. The eutectic between the 2:1 mixture **3b** and the 1:1 mixture **3c** appears to be exhibited at 167 °C.

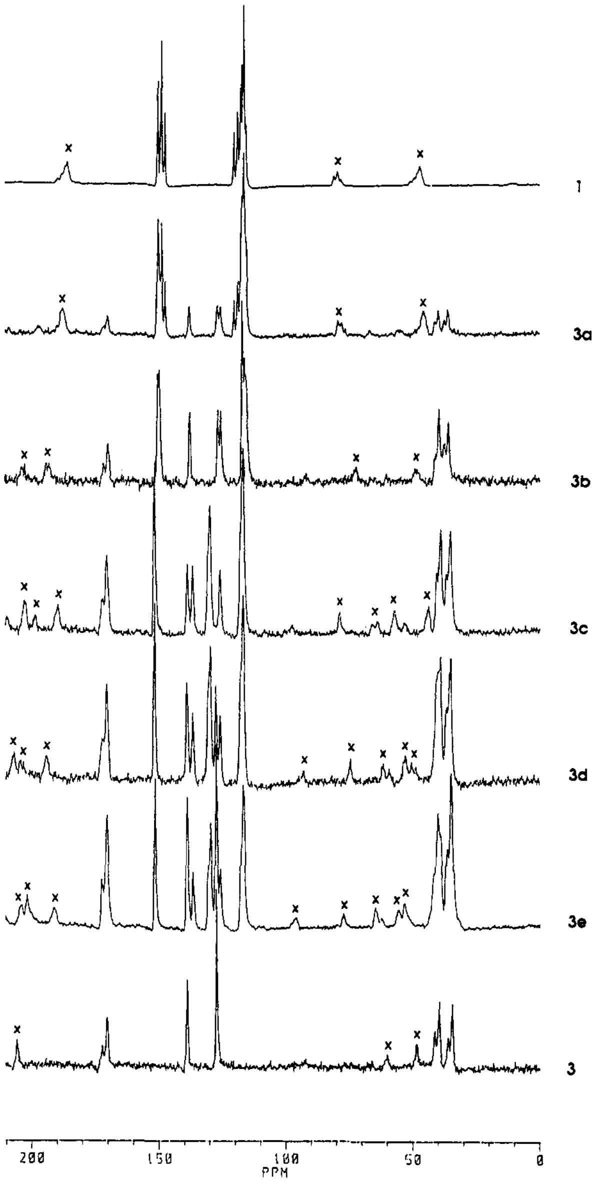

Figure 3. ^{13}C CP/MAS spectra for the hydroquinone–bis(*N*,*N*-dimethyl)terephthalamide system (system 2). Lines marked by an × *indicate spinning sidebands.*

Pure samples of the complexes could be prepared by cocrystallization of hydroquinone with the terephthalamides from solvent. These samples showed the same spectral and thermodynamic properties as those obtained by grinding, and most importantly allowed the determination of structure by X-ray crystallography.[9]

An examination of the preliminary X-ray crystal structures of **2c**, **3b**, and **3c** have provided some structural insights. Upon examination of the structure of **2c**, the 1:1 complex of system 1, the extended hydrogen bonding network is evident. We were surprised to find that the hydroquinone and terephthalamides were not π-stacked in a *face-to-face* manner but were actually packed *edge-to-face*. Examples of this type of aryl interaction have been well documented.[10] The X-ray crystal structure of **3b**, the 2:1 complex of system 2, shows similar hydrogen bonding features to that of **2c**. The absence of the methylene carbons in the dimethyl amides of **3b** allows room to accommodate the extra hydroquinone molecule.

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[8] Barry, J. E.; Cipollini, N. E.; Finkelstein, M.; Ross, S. D. *Tetrahedron* **1981**, *37*, 1669.

[9] Foxman, B.; Guarrera, D.; Taylor, L. D.; Van Engen, D.; Warner, J. C., unpublished observations.

[10] Muehldorf, A. V.; Van Engen, D.; Warner, J. C.; Hamilton, A. D. *J. Am. Chem. Soc.* **1988**, *110*, 6561.

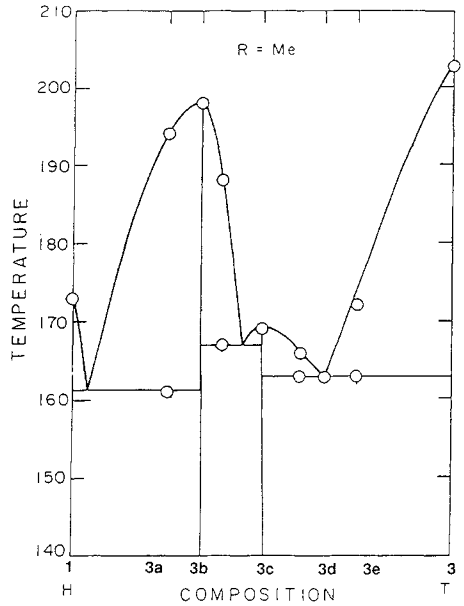

Figure 4. Phase diagram for the hydroquinone–bis(*N*,*N*-dimethyl)terephthalamide system (system 2). The eutectic compositions were estimated (not experimentally determined).

In the case of **3c**, the 1:1 complex of system 2, extended networks of hydrogen bonds are not observed. The X-ray crystal structure of **3c** shows the presence of isolated rings consisting of two hydroquinones and two terephthalamides connected by hydrogen bonds.

Conclusions

These results demonstrate the valuable information that can be obtained by the combination of solid-state NMR and differential scanning calorimetry, allowing the construction and use of phase diagrams for the study of self-assembled systems. While well-known in various fields of metallurgy, phase diagrams have not been applied to multicomponent organic systems of contemporary interest. The differences in behavior between the mixtures of hydroquinone (**1**) with bis(*N*,*N*-diethyl)terephthalamide (**2**, system 1), and bis(*N*,*N*-dimethyl)terephthalamide (**3**, system 2) probably arise from the steric interactions produced by the alkyl substituents. When the alkyl substituents are ethyl groups, only a 1:1 ratio can be accommodated in the molecular assembly. When the less sterically imposing methyl substituents are present, the additional "fitting" of a second hydroquinone is possible and thus two stable binary phases can be observed. Interestingly, our initial expectation that complexes of hydroquinone with terephthalamides would be structurally similar to quinhydrones was only partially fulfilled. As anticipated, a hydrogen-bonding network was evident; but *face-to-face* π stacking was not. Fortunately, however, the complexes have indeed proven useful as solubility inhibitors in photographic systems, as intended.[11]

Experimental Section

Hydroquinone (**1**) was purchased from Aldrich Chemical and used without further purification. Bis(*N*,*N*-diethyl)terephthalamide (**2**) and bis(*N*,*N*-dimethyl)terephthalamide (**3**) were prepared from the condensation of terephthaloyl chloride and the appropriate amine. The products were purified by recrystallization from ethanol and confirmed by comparison to literature properties.[12]

Solid-state grinding was performed with either a Bel-Art Products Micro-Millmill for combined weights exceeding 2.0 g for 4 h or by shaking less than 2.0 g of combined weight in a Nalgene container with a Teflon-coated stirring bar on a Vortex stirrer for 4 h. Pure samples of each complex were prepared by dissolving the appropriate molar amounts of hydroquinone with the terephthalamides in a mutually miscible solvent (typically ethanol or acetonitrile) and allowing the complexes to crystallize slowly at room temperature.

^{13}C CP/MAS spectra were obtained on a Bruker 200-MHz FT NMR spectrometer equipped with a Doty solid-state probe. Differential scanning calorimetry (DSC) scans were obtained on a DuPont 9900 DSC and a Perkin-Elmer DSC4. The samples were weighed into aluminum sample pans, where the sample size ranged from 1 to 3 mg. The samples were then heated at a rate of 10 °C/min under a nitrogen atmosphere. Nitrogen gas purged the DSC at a rate of 30 mL/min.

Acknowledgment. We are grateful to many members of the Polaroid Chemical Research division for helpful discussions. NMR spectra and some of the DSC data were obtained at the Polymer Central Facility, Center for Materials Science and Engineering, at MIT by C. V. Berney. We wish to thank Joy Rogers, Polaroid Student Intern, Southern University, for obtaining some of the DSC scans. X-ray crystallography was performed by Donna van Engen at Princeton University and Bruce Foxman at Brandeis University.

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(11) Taylor, L. D.; Warner, J. C. US Patent 5,177,262, Jan 5, 1993.
(12) Beilstein E IV 9 p 3321. Syst.-Nr. 978/H 845; E III 4253.