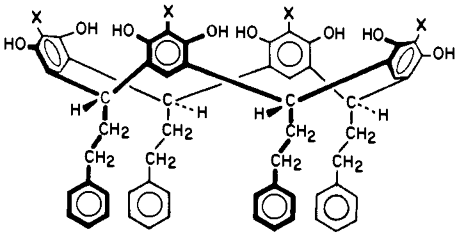
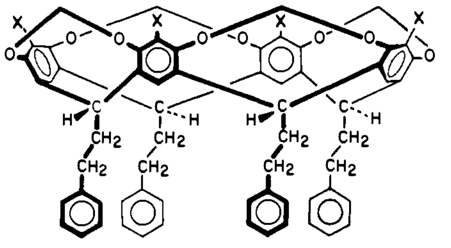
tetrabromide **3**[5,6] (58%). Treatment of **3** with CH_2ClBr–K_2CO_3–DMA gave cavitand **4**[5,6] (52%), whose crystal structure was normal.[7] Metalation of **4** in THF with $(CH_3)_3CLi$ at −78 °C and quenching the organometallic formed with $(CH_3O)_3B$ gave the arylboron intermediate, which was oxidized with H_2O_2–NaOH (−78 °C) to produce tetrol **5**[6] (53% overall). Shell closures of **5** to give **1**·G were conducted under high dilution conditions in purified dry $(CH_3)_2SO$, $(CH_3)_2NCOCH_3$, or $(CH_3)_2NCHO$ solutions at 60–100 °C with Cs_2CO_3 as base and CH_2ClBr (large excesses) being added by syringe pump (3 days). Products **1**·$(CH_3)_2SO$, **1**·$(CH_3)_2NCOCH_3$, and **1**·$(CH_3)_2NCHO$ were purified by chromatography on silica gel–$CHCl_3$/hexane and crystallization ($CHCl_3/CH_3CN$) to give carceplexes in 61%, 54%, and 49% yields, respectively. Analysis of each for C, H, O, and N or S was within 0.20% of theory. Summed analyses were 99.73–99.90% of theory. Each carceplex's mass spectrum gave substantial peaks at masses corresponding to **1**·G.[8,9] Attempts to shell close **5** failed in $(CH_2)_5NCHO$, a solvent too large for incarceration (CPK molecular model examination). A reaction run in 99.5$(CH_2)_5NCHO$–0.5$(CH_3)_2NCOCH_3$ (mol %) gave a 10% yield of **1**·$(CH_3)_2NCOCH_3$. A run in equimolar $(CH_3)_2NCOCH_3$–$(CH_3)_2NCHO$ gave 10% of **1**·$(CH_3)_2NCOCH_3$/**1**·$(CH_3)_2NCHO$ = 5.3. These two complexes were separated chromatographically, showing that the guests "communicate" with their host's environment. Models of **1**·$(CH_3)_2NCOCH_3$ can barely be assembled, whereas the guest in **1**·$(CH_3)_2NCHO$ is liberally housed. Apparently, appropriately sized guests template the shell closures, the product composition being determined in the transition state for completing the second or third interhemispheric bridge.



2; X = H, **3**; X = Br



4; X = Br, **5**; X = OH

The 360 MHz ^{1}H NMR spectra of **1**·G were taken, and all protons were assigned making use of comparisons with the spectra of **4** and appropriate heteronuclear-decoupling experiments involving ^{13}C NMR spectra taken in $CDCl_3$. The guests' protons in $CDCl_3$ all shifted upfield by 1–4 ppm from their normal positions, consistent with their enforced proximity to the arene-shielding zone.[10] Careful proton signal integrations[11] established the **1**·G samples to be >95–98% one-to-one complexes. When heated to reflux for 12 h, a solution of **1**·$(CH_3)_2SO$ in $(CH_3)_2NCHO$ failed to undergo guest exchange. Apparently, guests can enter or depart the carceplexes only by covalent bond making or breaking processes.

Molecular model (CPK) examination of **1**·G indicates that the host's cavity has a long C_4 axis and four, much shorter, C_2 axes as well as four σ_v and one σ_h planes. Models also suggest that $(CH_3)_2NCHO$ and $(CH_3)_2SO$ are loosely held in the cavity, whereas $(CH_3)_2NCOCH_3$ is incorporated only when its long axis matches that of its host. Experimentally, the ^{1}H and ^{13}C NMR spectra of the three carceplexes provide the following conclusions: (1) Incarcerated $(CH_3)_2NCHO$ rotates about the host's short and long axes rapidly on the ^{1}H NMR time scale, even at −38 °C ($CDCl_3$). (2) Incarcerated $(CH_3)_2NCOCH_3$ rotation about the host's long axis is fast, and those about the short axes are slow on the ^{1}H NMR time scale, even at 175 °C ($C_6D_5NO_2$). (3) Incarcerated $(CH_3)_2SO$ rotations about all axes are fast above 2 °C but slow about the short axes below 2 °C on the ^{1}H NMR time scale ($CDCl_3$). (4) The orders of rates of rotation about the C–N bond of amide guests vary with phase changes as follows ($C_6D_5NO_2$ solvent when present): for $(CH_3)_2NCHO$, vacuum > *interior phase* > solution; for $(CH_3)_2NCOCH_3$, vacuum > solution > *interior phase.*

These carceplexes represent a new state of matter whose interiors are new phases (guest plus vacuum in varying proportions). Their guest mobility with respect to host and their physical properties are subject to molecular level manipulation. Several potential applications of carceplexes to material science problems are envisioned and are being examined.

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(5) Modeled after reported procedure: Tucker, J. A.; Knobler, C. B.; Cram, D. J. *J. Am. Chem. Soc.* **1989**, *111*, 3688–3699.

(6) All new compounds gave C and H analyses within 0.30% of theory, the expected ^{1}H NMR spectra, and the FAB MS, M + 1 ions.

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Fluid Electrolyte Solutions for Electrochemistry at Near Liquid Nitrogen Temperatures

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This paper reports the discovery of three remarkable solvent mixtures that extend the useable range of electrochemical voltammetry in fluid electrolyte solutions to temperatures that approach the boiling point of liquid nitrogen. There have been no improvements in low-temperature fluid electrolyte solutions[1] since the classical work of Van Duyne and Reilley[2] in 1972 in which they utilized propionitrile/butyronitrile mixtures containing tetraalkylammonium salts to obtain a low-temperature voltammetric limit of 155 K. As part of an ongoing effort[3] to develop the

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(1) (a) Voltammetry in solid electrolytes and frozen solutions has been reported,[1b,c] and such media may be useful for electrochemical work with superconducting electrodes below T_c. (b) Stimming, U.; Schmickler, W. *J. Electroanal. Chem.* **1983**, *150*, 125. (c) Bond, A. M.; Fleischmann, M.; Robinson, J. *Ibid.* **1984**, *180*, 257.

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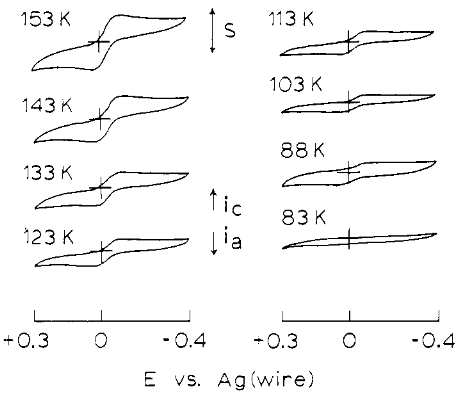

Figure 1. Temperature dependence of the cyclic voltammetry of ca. 1 mM TCNQ in 1:1 butyronitrile/chloroethane with 0.2 M Bu_4NClO_4. Temperatures were maintained in a double wall jacketed cell with cooled N_2 and were monitored with a copper/constantan thermocouple positioned close to the working electrodes and calibrated to ±2 K with several standards. Voltammetry was obtained in the usual three electrode mode (without resistance compensation), with a Au microband, Ag wire, and Pt wire as working, quasi-reference, and auxiliary electrodes, respectively. S = 500 nA for 103 K < T < 153 K; 200 nA for T = 88 K; 100 nA for T = 83 K. Scan rate = 50 mV/s.

methodology to fabricate electrodes from copper oxide ceramic superconductors[4] and study their responses below their superconducting critical temperature, T_c, we found it necessary to extend the limits of low-temperature electrochemistry. Gold microband electrodes are employed in the present report to explore the voltammetric limits of the new low-temperature solvents.

In addition to exhibiting a low freezing point, a solvent medium suitable for low-temperature faradaic electrochemical experiments must promote solubility and ionic dissociation and support reasonably high ionic mobility of an electrochemically inert electrolyte. We have found that low melting liquids with these characteristics can be formed from butyronitrile and halogenated hydrocarbons as the major components of eutectic mixtures. For example, butyronitrile and bromoethane taken separately freeze at 161 and 154 K, respectively, but a 1:1 mixture (by volume at room temperature) has a freezing point[5a] of 130 K. Addition of 0.2 M Bu_4NClO_4 electrolyte lowers the freezing point further to 125 K and provides an ionic fluid in which redox couples like tetracyanoquinodimethane (TCNQ) and bis(pentamethylcyclopentadienyl)iron (Cp^*_2Fe) dissolve and can be studied voltammetrically down to 128 K. A 1:1:2:2 mixture of isopentane (mp 112 K), methylcyclopentane (mp 131 K), butyronitrile, and bromoethane extends the useful voltammetric limit to 115 K, and a 1:1 mixture of butyronitrile and chloroethane (mp 137 K, bp 285 K) extends further to 88 K where the lowest temperature voltammetry to date has been obtained.

The voltammetric response for the $TCNQ^{0/-}$ couple in the butyronitrile/chloroethane mixture is remarkably well-defined over the temperature range[5b] of 153–88 K (Figure 1). Below 88 K, the TCNQ wave was too small to resolve from the background double layer charging currents. Double layer charging could be observed without obvious loss of electrochemical potential control down to ca. 77–83 K. The complications posed by the substantial low-temperature solvent resistance were overcome by using an ca. 20-nm wide, 0.5-cm long Au microband[6] as the working electrode. The benefits of using microelectrodes for electrochemical studies in resistive solvents are well-documented.[6d,7] The voltammetric waves in Figure 1 exhibit quasi-steady-state limiting currents as qualitatively anticipated for small microbands.[6] The limiting currents reflect the rate of TCNQ charge transport through the solution and decrease with decreasing temperature as expected (linear log(i) vs $1/T$ plot) for an activated diffusion process.

Table I. A Comparison of Low-Temperature Electrochemical Solvent Systems and High-Temperature Superconductors

solvent system[a]	low-temperature electrochemistry limit (K)
BN[b]	168
69 wt % BN/31 wt % PN[b]	155
BN/EtBr (1:1)[c]	128
BN/EtBr/isopentane/methylcyclopentane (2:2:1:1)[c]	115
BN/EtCl (1:1)[c]	88
superconductor[d]	T_c (K)
$Tl_2Ca_2Ba_2Cu_3O_{10}$[d]	125
$Bi_2Sr_2Ca_2Cu_3O_{10}$[d]	110
$YBa_2Cu_3O_7$	95

[a] Bu_4NClO_4 electrolyte. Relative volume portions of each component given in parentheses. [b] Using macroelectrodes, see ref 2. [c] Using microelectrodes, this work. [d] Other phases with lower T_c are known, but are not listed. See ref 4.

The low-temperature electrochemical limits for these and previous solvents, and for the purpose of comparison, the zero-resistance superconducting transition temperatures for some of the better defined copper oxide ceramics, are listed in Table I. The new low-temperature solvents, in principle, make electrochemical experiments possible at temperatures at which several of the copper ceramics are below their transition temperature. Further modest solvent improvements should encompass other ceramics as well. We have actively pursued[3] techniques for the necessary fabrication of microelectrodes from the copper ceramic materials and hope to report the results of electrochemical measurements with electrodes in their superconducting states in the near future. In addition, these new low-temperature solvents extend the existing capacity to electrochemically generate and thermally stabilize reactive chemical species[2] and may also find application in low-temperature optical spectroscopy, NMR, ESR, and solvent dynamics studies.

Acknowledgment. This research was supported by grants from the National Science Foundation and the Office of Naval Research. This work is part of a collaborative effort with J. P. Collman, W. A. Little, and G. T. Yee of Stanford University to develop the methodologies needed for conducting electrochemical measurements at superconducting electrodes, and we thank our collaborators for useful suggestions.

Registry No. TCNQ, 1518-16-7; Cp_2Fe, 12126-50-0; Bu_4NClO_4, 1923-70-2; Au, 7440-57-5; isopentane, 78-78-4; methylcyclopentane, 96-37-7; bromoethane, 74-96-4; butyronitrile, 109-74-0; chloroethane, 75-00-3.

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(5) (a) Freezing points of the solvent mixtures represent the temperatures at which the bulk of the liquid solidifies as determined by optical inspection of the mixture. No glasses appear to be formed. Until more careful calorimetric measurements are completed, the freezing points should be treated as approximate values. Our electrochemical data suggest lower melting phases may exist below the cited temperatures. (b) The solvent freezes a few degrees below the useful voltammetric limit. The solution was prepared with approximately 1:1 by volume quantities of butyronitrile (measured at room temperature) and ethyl chloride (measured at −78 °C). The electrolyte was dissolved in the butyronitrile at room temperature.

(6) (a) Analogous to previous work,[6b,c] the microband was a metal film edge. In our case, an ca. 20-nm Au film was evaporated onto a Si/SiO_2 wafer, overcoating with silicon nitride. Fracturing the wafer exposes a Au microband which typically is of larger area than the nominal evaporated film thickness. We do not attempt comparison of currents in Figure 1 to microband electrode theory[6d] because of this present uncertainty. (b) Morris, R. B.; Franta, D. J.; White, H. S. *J. Phys. Chem.* **1987**, *91*, 3559. (c) Wehmeyer, K. R.; Deakin, M. R.; Wightman, R. M. *Anal. Chem.* **1985**, *57*, 1913. (d) Wightman, R. M. *Science* **1988**, *240*, 415.

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