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[17] Values are for complex 1 from data set 1FDX deposited with the Brookhaven Protein Data Bank (Berstein, F. C.; Koetzle, T. F.; Williams, G. J. B.; Meyer, E. F., Jr.; Brice, M. D.; Rodgers, J. R.; Kennard, O.; Shimanouchi, T.; Tasumi, M. *J. Mol. Biol.* **1977**, *112*, 535-542).

An Ionic System with Critical Point at 44 °C

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Most ionic compounds have high melting points and exist as liquids only in solution in water or another solvent with high dielectric constant. Organic salts melting near 100 °C have been known, and their properties in solution have been investigated for many years.[1] Recently, Ford and his associates[2,3] prepared tetraalkylammonium tetraalkylborides that are liquid at room temperature and show high electrical conductance and other saltlike properties. We are interested in finding a model ionic system with phase separation and a critical point near room temperature. Our results may be of interest, however, in connection with other applications of liquid salts. The solubility properties of triethyl-*n*-hexylammonium triethyl-*n*-hexylboride ($N_{2226}B_{2226}$) were measured for several solvents, and an equation is presented which correlates the results. The system with diphenyl ether showed a critical point near 44 °C. Measurements of the coexistence curve are reported.

The salt $N_{2226}B_{2226}$ was synthesized by the procedure described by Ford and co-workers.[2] Atmospheric oxygen was carefully excluded. Although the product can be purified by liquid chromatographic separation on a silica gel column with 5% CH_3OH in CH_2Cl_2 as the solvent, it is preferable to carry out careful synthesis with purified reagents. The salt prepared by us had a pale yellow color indicating either an impurity or a low-lying absorption band. Previously, this compound has been reported to form only a glass on cooling, but we were able to crystallize it and observed a melting-point range of −22.5 to −21.7 °C. This indicates reasonably good purity, and it was not possible to separate the color from the salt by partial crystallization or liquid chromatography. This salt has been reported to be colorless;[1] hence, our sample may have had an impurity, but we believe the amount must have been very small.

The solubility of the salt in various solvents is expected to be influenced by two factors. The first relates to the ionic forces and is given by the principle of corresponding states as applied to ionic systems.[4] This implies increase of solubility with increase in dielectric constant ϵ. Also significant is the difference of Hildebrand's solubility parameters δ (the square root of the cohesive energy density): the larger the difference, the smaller the solubility. Thus, where the dielectric constant (or relative permittivity) of the solvent is greater than that given by the following expression for ϵ_m, we found large solubility and usually complete miscibility at room temperature:

$$\epsilon_m = [0.289 - 0.00316(\delta - 22.9)^2]^{-1} \qquad (1)$$

Here δ is in $MPa^{1/2}$. Correspondingly, where ϵ for the solvent is less than ϵ_m, the solubility of salt in solvent was usually small and smaller where this difference was larger. For benzene, diphenyl ether, 1-bromooctane, and ethylene glycol, we observed substantial but limited solubility at room temperature. On moderate increase in temperature, diphenyl ether became miscible, whereas the solubility remained limited for the others. The full list of solvents tested is given below, and the one apparent exception is explained.

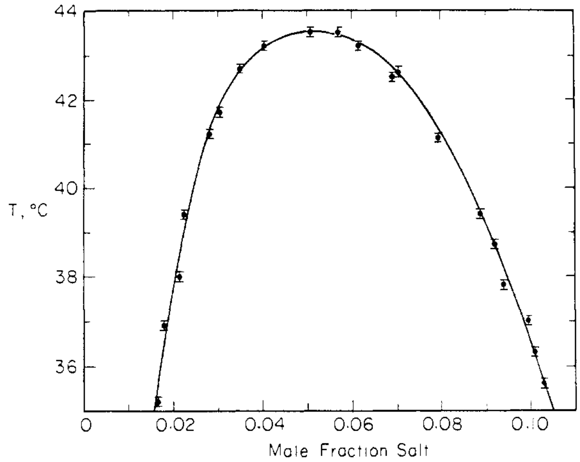

Figure 1. The phase boundary and critical point for the ionic system ($N_{2226}B_{2226}$ + diphenyl ether).

The coexistence curve was obtained with purified salt, and diphenyl ether was obtained as gold label grade from Aldrich Chemical. The desired amounts of each substance were added to glass ampoules, degassed, and then sealed. The phase separation was visually observed with the ampoules placed in a water bath controllable to ±0.01 °C. Strong critical opalescence was noticed in the near critical samples. The equilibrium was checked from both higher and lower temperatures. The sluggishness of the approach to equilibrium in the critical region of this viscous system precluded a match better than 0.08 °C betwen the two sets of temperatures in most of the cases. Thus, accuracy of the measurements is taken as ±0.1 °C.

The phase separation curve is shown in Figure 1. The critical parameters found for this system are T_c = 316.7 K (43.6 °C), V_c = 3330 cm^3 mol^{-1} of boride, and $x_c = 0.052 \pm 0.003$ mole fraction boride. The critical temperature, T_c, is very sensitive to impurities with $\Delta T_c \simeq +40$ °C for salt saturated with water (1.2 wt.% H_2O) and $\Delta T_c \simeq -20$ °C for salt containing 1% methylene chloride. However, measurements of phase separation curves with contaminated salt showed that the other critical parameters including the shape of the curve are not noticeably affected, even at these large impurity levels.

The following equation represents the entire coexistence curve within the experimental uncertainty

$$x = 0.052 + 0.0010(T_c - T) \pm 0.0155(T_c - T)^{1/2} \qquad (2)$$

where x is the mole fraction, and the plus and minus signs give the concentrated and dilute branches, respectively.

One interesting feature is the extreme asymmetry of the curve with $x_c = 0.052$ or volume fraction $\phi_c = 0.135$. This is consistent with the corresponding states pattern for ionic systems.[4] It implies much greater solubility of solvents in the salt than the salt solubility in the solvent, and this was observed for various solvents. In this respect, the ionic system is similar to a high polymer.

Another interesting aspect of eq 2 is the final exponent 1/2 which is the critical exponent β. This exponent is found to be near 1/3 for nonionic systems, both liquid–liquid and vapor–liquid, over a wide range of temperature but has been found[5] to be 1/2 for an ionic system somewhat like the present case but with T_c = 414.4 K. Thus, it appears that the shape of the coexistence curve is systematically different for ionic and nonionic systems. The theoretical implications will be explored after the experiments have been extended by other techniques closer to the critical point.

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0002-7863/88/1510-8723$01.50/0

Finally, we list the solvents tested. In the "soluble" category were acetonitrile, methanol, 1,4-butanediol, acetone, *n*-butyl alcohol, *n*-hexyl alcohol, benzyl alcohol, methylene chloride, 1-bromohexane, 1-chloroheptane, phenyl methyl ether, and chloroform. Propionic acid was found to be soluble, even though its $(\epsilon - \epsilon_m)$ is negative; we attribute this to the dimer structure of zero dipole moment which contributes nothing to ϵ but can readily dissociate to a strongly polar monomer. In the "insoluble" category with low δ and low ϵ were *n*-hexane, 1,4-dioxane, *n*-butyl ether, *n*-propyl ether, isopropyl ether, ethyl ether, and 1-bromodecane. The cohesive energy density of water is so high that it also falls in the "insoluble" category.

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XPS Data for Linear Three-Center, Four-Electron Bonding in Sulfur Species

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The addition of a nucleophile ($X:^-$) to a main group element compound with approximately eight valence shell electrons about the central atom (e.g., the 8-S-3 sulfonium ion: SR_2X^+) often provides a stable adduct (e.g., the 10-S-4 sulfurane: SR_2X_2) in which the nucleophile is bound to the main group element.[2] Bonding occurs by delocalization of the lone pair of electrons of the nucleophile into an unoccupied orbital of the eight-electron species—either a d-orbital or a σ^* antibonding orbital (e.g., the S–X σ^* orbital). The early "perfect pair model" of Pauling[3] suggested that d-orbital occupancy must be invoked to explain the bonding of the nucleophile to the central atom.[4] After the discovery of xenon difluoride, theoretical calculations provided support for the alternative bonding idea—transfer of the nucleophile's electron pair into a σ^* orbital to form a trigonal bipyramidal (TBP), or pseudo-TBP (ψ-TBP), species with linear three-center, four-electron (3c-4e) bonding.[5] Although d-orbital participation is expected, most chemists now agree that d-orbital occupancy is rather small in most of these compounds, making the 3c-4e bond (partly covalent and partly ionic) an important feature in the TBP or ψ-TBP species.[6] Ab initio calculations on sulfane (SH_2), sulfurane (SH_4), and octahedral (Oc) persulfurane (SH_6) showed[7] very small d-orbital occupancy,[8] with total electron populations of sulfur orbitals for SH_2, SH_4, and SH_6 to be 15.95, 15.27, and 14.82, respectively.[7] The decrease in sulfur atomic population on going from SH_2 to SH_4 was 1.51 times the corresponding change between SH_4 and SH_6. X-ray photoelectron spectroscopy (XPS) provides an accurate measure of the electron density (electronic character) at a specific element within a molecule.[9,10] The partial ionic character of the 3c-4e bonds should

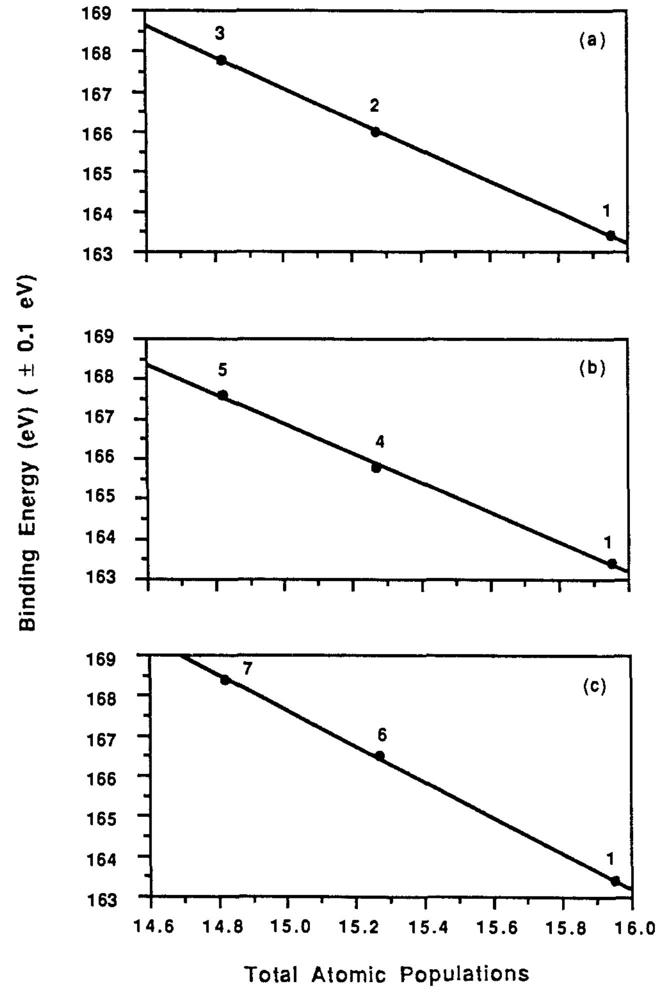

Figure 1. Plot of total atomic populations of a series of sulfur derivatives (SH_2, SH_4, and SH_6)[7] vs XPS binding energies for $S(2p_{3/2})$ for a range of variously oxidized sulfur species. The compounds' numbers correspond to those in Table I.

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[1] General Electric Company Fellow, 1985–1986. American Chemical Society Division of Organic Chemistry Fellow, sponsored by the Rohm and Haas Company, 1986–1987.

[2] (a) In the *N*-X-*L* system *N* is the number of electrons formally associated with the bonding surrounding the central atom X, with *L* ligands associated with atom X: Perkins, C. W.; Martin, J. C.; Arduengo, A. J. III; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753. (b) For examples of stable adducts to 8-S-3 species, see: Hayes, R. A.; Martin, J. C. In *Organic Sulphur Chemistry: Theoretical and Experimental Advances*; Csizmadia, E. G., Mangini, A., Bernardi, F., Eds.; Elsevier Scientific Publishing Company: Amsterdam, 1985; Chapter 8, pp 408–483.

[3] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960. Kwart, H.; King, K. *D-Orbitals and the Chemistry of Silicon, Phosphorus, and Sulfur*; Springer-Verlag: New York, 1977.

[4] Substantial involvement of d-orbital participation in sulfuranes was suggested by the following: Angyan, J. G.; Poirer, R. A.; Kucsman, A.; Csizmadia, I. G. *J. Am. Chem. Soc.* **1987**, *109*, 2237. Purcell, K. F.; Kotz, J. C. *Inorg. Chem.* W. B. Saunders Co.: Philadelphia, PA, 1972; p 65. See, also: Baird, N. C.; Taylor, K. F. *J. Comput. Chem.* **1981**, *2*, 225. Pietro, W. J.; Frach, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039.

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[6] (a) The term "hypervalent" to describe these species was proposed by Musher, J. I. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 54. Musher, J. I. *J. Am. Chem. Soc.* **1972**, *94*, 1370. (b) The d-orbital occupancy was suggested to be small in these hypervalent species by Koutecky and Musher (Koutecky, V. B.; Musher, J. I. *Theor. Chim. Acta* **1974**, *33*, 227), and this suggestion was supported by the authors of ref 7.

[7] Schwenzer, G. M.; Schaefer, H. F. III *J. Am. Chem. Soc.* **1975**, *97*, 1393.

[8] Similar findings were reported for SF_2, SF_4, and SF_6: Kiang, T.; Zare, R. N. *J. Am. Chem. Soc.* **1980**, *102*, 4024. See, also: Angyan, J. G.; Bonnelle, C.; Daudel, R.; Kucsman, A.; Csizmadia, I. G. *J. Mol. Structure* (*THEOCHEM*) **1988**, *165*, 273.

[9] For an introduction to XPS, see: *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*; Briggs, D., Seah, M. D., Eds.; John Wiley and Sons: New York, 1983.

[10] For recent examples from our laboratory, see: Gassman, P. G.; Callstrom, M. R. *J. Am. Chem. Soc.* **1987**, *109*, 7875. Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 4224. Gassman, P. G.; Macomber, D. W.; Willging, S. M. *J. Am. Chem. Soc.* **1985**, *107*, 2380. Gassman, P. G.; Macomber, D. W.; Hershberger, J. W. *Organometallics* **1983**, *2*, 1470.

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