the wide concentration range 0-4.6 *m*. The deviation plot of Figure 14 displays the comparison between the measurements of Korosi and Fabuss (*14*) and the present correlation. The maximum deviation is about 1.8% and the standard deviation is ±1.0% which is within the mutual uncertainty. Figure 14 also displays the corresponding comparison for the measurements of Goncalves and Kestin (*5*). Here the correlation predicts values that are consistently higher than the measurements with a maximum absolute deviation of 2.9% and a standard deviation of about ±1.1%, again within the mutual uncertainty.

Figure 15 shows a comparison between the correlations given in ref 5 and 14 and the present correlation in the temperature and concentration ranges where the correlations apply, i.e., 25-150 °C and 0-3.5 *m* for ref 14 and 25-50 °C and 0-4.6 *m* for ref 5. The lines exhibit the same general behavior as the experimental points shown in Figure 14.

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Literature Cited

(1) Bell, J. T., Helton, D. M., Rogers, T. G., *J. Chem. Eng. Data*, **15**, 44 (1970).
(2) Egorov, V. Ya., Zarembo, V. I., Fedorov, M. K., *Zh. Prikl. Khim.* (*Leningrad*), **49**, 124 (1976).
(3) Ellis, A. J., *J. Chem. Soc. A*, 1579 (1966).
(4) Gibson, R. E., *J. Am. Chem. Soc.*, **57**, 284 (1935).
(5) Goncalves, F. A., Kestin, J., *Ber. Bunsenges. Phys. Chem.*, **81**, 1156 (1977).
(6) Kell, G. S., Whalley, E., *J. Chem. Phys.*, **62**, 3496 (1975).
(7) Kestin, J., Khalifa, H. E., *Appl. Sci. Res.*, **32**, 483 (1976).
(8) Kestin, J., Khalifa, H. E., Abe, Y., Grimes, C. E., Sookiazian, H., Wakeham, W. A., *J. Chem. Eng. Data*, **23**, 328 (1978).
(9) Kestin, J., Khalifa, H. E., Sookiazian, H., Wakeham, W. A., *Ber. Bunsenges. Phys. Chem.*, **82**, 180 (1978).
(10) Kestin, J., Leidenfrost, W., Liu, C. Y., *Z. Angew. Math. Phys.*, **10**, 558 (1959).
(11) Kestin, J., Moszynski, J. R., *Trans. ASME*, **80**, 1009 (1958).
(12) Kestin, J., Sokolov, M., Wakeham, W. A., *J. Phys. Chem. Ref. Data*, **7** (3) (1978).
(13) Kestin, J., Wang, H. E., *J. Appl. Mech.*, **79**, 197 (1957).
(14) Korosi, A., Fabuss, B. M., *J. Chem. Eng. Data*, **13**, 548 (1968).
(15) Mikhailov, I. G., Shutilov, V. A., *Akust. Zh.*, **10**, 450 (1964).
(16) Potter, R. W., II, Babcock, R. S., Brown, D. L., *J. Res. U.S. Geol. Surv.*, **5**, 389 (1977).
(17) Potter, R. W., II, Brown, D. L., *U.S. Geol. Surv.* (open file report), **No. 76-243** (1976).
(18) Potter, R. W., II, Shaw, D. R., Haas, J. L., Jr., *U.S. Geol. Surv., Bull.*, **No. 1417** (1975).
(19) Seidell, A., "Solubilities of Inorganic and Metal Organic Compounds", Vol. 1, Van Nostrand, New York, 1940.
(20) Swindells, J. F., Coe, J. R., Jr., Godfrey, T. B., *J. Res. Natl. Bur. Stand.*, **48**, 1 (1952).
(21) Vaslow, F., *J. Phys. Chem.*, **70**, 2286 (1966).

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Supplementary Material Available: Figures 6-10, which display the viscosity of the five solutions as a function of pressure along various isotherms (5 pages). Ordering information is given on any current masthead page.

Solubility of Metal Sulfides in Sodium Polysulfide Melts

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The solubilities of six transition metal sulfides are reported in Na_2S_x melts over the composition range $Na_2S_{2.7}$ to Na_2S_5, at temperatures of 275-375 °C. The apparatus for these solubility measurements is described.

The use of sodium polysulfide melts in the sodium-sulfur battery, and the solubility behavior of metal sulfides that are potential corrosion products in some designs, led to our making solubility measurements in several such systems. Primarily, we have considered solubility as a function of polysulfide composition, which is of interest over the range Na_2S_2 to Na_2S_5.

Experimental Section

Measurement of solubilities in molten polysulfides is complicated by the volatility of sulfur from the melt with consequent compositional changes. The cell used is illustrated in Figure 1. A product with the approximate composition Na_2S_3 was prepared by the method of Cleaver et al. (*1*). Other compositions were prepared by adding additional sulfur to this. Approximately 5 g of Na_2S_x and the metal sulfide were placed in the side arm through the port B. The cell was evacuated, entrance port B sealed, and the cell placed in the furnace. Any sulfur vapor condensed in the cold part of the capillary tube that extends out of the furnace; in practice only a small amount was evolved. After equilibrium was achieved (7 days were allowed, with occassional shaking) the cell was inverted to let the melt rest on the frit and replaced in the furnace, and the capillary tube opened to vacuum to initiate filtration through the frit. The sulfur vapor lost in this way was negligible in the time required for filtration. After cooling, the cell was broken open and the dissolved metal content in the Na_2S_x determined by atomic absorption spectroscopy after dissolution in acid. Most solubilities were such that dilutions of the order of 1 g of Na_2S_x/L were in the appropriate range, so that generally the dilution steps necessary for the atomic absorption analyses did not introduce excessive error into the measurements. The Na_2S_x composition was determined from the weight of NaCl formed when an aqueous solution of the melt was treated with HCl, filtered, and evaporated to dryness.

Table I. Equilibrium Solubilities of Some Metal Sulfides in Sodium Polysulfide Melts

		solubility					
melt compn	temp, °C	Cr_2S_3, μg/g	MnS, mg/g	FeS, mg/g	NiS, mg/g	CuS, mg/g	Cu_2S, mg/g
$Na_2S_{2.74}$	375	6.0	0.50	3.99	4.64		
$Na_2S_{2.9}$	300			2.0	0.8		
Na_2S_3	275					24.3	10.5
$Na_2S_{3.2}$	375	40.6	1.18	2.72	1.18		
Na_2S_4	375	46.2	2.12	1.28	0.47		
Na_2S_4	325	30.0		0.6			
Na_2S_5	375	71.4	3.42	0.17	0.15		
Na_2S_5	300			0.1	0.1		
Na_2S_5	275					106.5	40.5

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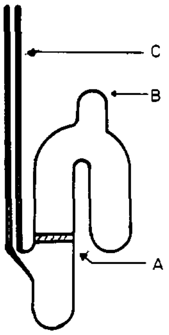

Figure 1. Cell for solubility measurements: (A) 10-mm fritted glass disk; (B) filling port (sealed); (C) capillary side arm sealed by clamped rubber hose or an attached stopcock.

Results

The solubility data are given in Table I. It is notable first that the solubility of Cr_2S_3 is 1 to 2 orders of magnitude smaller than those of the other sulfides. Secondly, the solubilities of FeS and NiS decrease with increasing sulfur content while the rest increase. These solubilities help to explain some of the observations of Bones et al. (*2*) on the corrosion of stainless steel in an Na/S electrochemical cell; an adherent corrosion layer on the steel in the charged state is lost in the discharged state as the greater solubility of the FeS and NiS in S-poor melts allows them to dissolve more readily in the melt of discharged composition.

Literature Cited

(1) B. Cleaver, A. J. Davies, and M. D. Hames, *Electrochim. Acta*, **18**, 719 (1973).
(2) R. J. Bones, R. J. Brook, and T. L. Markin, "Power Sources 5: Research and Development of Nonmechanical Electric Power Sources, Proceedings of the International Symposium", 9th, Brighton, 1974; D. H. Collins, Ed., Academic Press, London, 1975, p 539.

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Solubilities and Partitioning 2. Relationships between Aqueous Solubilities, Partition Coefficients, and Molecular Surface Areas of Rigid Aromatic Hydrocarbons

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The aqueous solubilities of 31 polycyclic aromatic hydrocarbons and indan can be accurately estimated from melting point and either molecular surface area or *f* values. (The latter being an approximation of the octanol–water partition coefficient based upon group contribution values.) In both cases, the coefficient of the melting point term is close to 0.01 and the correlation coefficient exceeds 0.987.

In recent years, several workers (*1–5*) have attempted to correlate the aqueous solubilities or activity coefficients of aromatic hydrocarbons with a variety of molecular properties. In most cases, it has been found necessary to incorporate empirical correction factors for branching, ring formation, and/or proximity effects. In this report, it will be shown that when either molecular surface area [as calculated by Valvani et al. (*6*)] or *f* values [as calculated by Nys and Rekker (*7*)] are used as correlating parameters, it is not necessary to utilize additional correction factors. The use of molecular surface area and *f* values as correlating parameters will be illustrated and compared. (The *f* values are group contributions which are used to estimate octanol–water partition coefficients.)

Methods

Aqueous solubilities, molecular surface areas, calculated log partition coefficients, and melting points for all the compounds listed in Table I were obtained as follows.

Selection of Solubility Data. Aqueous solubilities of 31 polynuclear aromatic hydrocarbons and indan were obtained from Mackay and Shiu (*2*). Triple points for all the compounds reported by them were used as melting points. For liquid solutes, 25 °C was used instead of the melting point.

Calculation of Molecular Surface Areas. Molecular surface areas were calculated according to method C of Valvani et al. (*6*). The following values for interatomic distances between various atoms or groups in a molecule were used: aromatic C–C, 1.40 Å; aromatic C–H, 1.08 Å; aromatic–aliphatic C–C, 1.54 Å; aliphatic C–C, 1.53 Å. The van der Waal radii used were as follows: aromatic, C, 1.70 Å; aromatic H, 1.20 Å; methyl or methylene group, 2.0 Å. Total surface area (TSA) is the sum of individual atoms or group surface area contributions.

Calculation of Log Partition Coefficients. The logarithm of the partition coefficient (for the octanol–water system) for all the solutes was calculated by summation of *f* values for all the groups in a molecule as described by Nys and Rekker (*7*). These values are also included in Table I.

Statistical Analysis of Data. Multiple regression analysis of all the data was performed using standard statistical procedures.

Results and Discussion

For compounds which do not associate in aqueous solution, the infinite dilution activity coefficients can be assumed to be equal to the activity coefficient at saturation. For liquids, this means that the mole fractional solubility is simply the reciprocal of the activity coefficient. For poorly soluble solutes, the mole fractional solubility is proportional to the molar solubility so that the molar solubility of a liquid in water S_w^l is given by

$$\log S_w^l = -\log \gamma + \text{constant} \qquad (1)$$

For crystalline substances it is necessary to account for crystal

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