which agrees with that estimated from their Antoine equations.

Spectrofluorimetry exhibits the high sensitivity and precision needed for determining the partition coefficients of other aromatic hydrocarbons and even fluorescing pesticides in water. The measurements are performed without removal, handling, or destruction of samples of the solution as is done with gas chromatography (*3*). The application of this method to determination of the partition coefficients of higher polycyclic aromatic hydrocarbons in water is now in progress.

Literature Cited

(1) Bohon, R. L., Claussen, W. F., *J. Am. Chem. Soc.*, **73**, 1571 (1951).
(2) Blumer, M., *Environ. Aff.*, **1**, 1 (1971).
(3) Brown, R. L., Wasik, S. P., *J. Res. Natl. Bur. Stand., Sect. A*, **78**, 453 (1974).
(4) Daglish, C., *J. Am. Chem. Soc.*, **72**, 4859 (1950).
(5) Frankenfeld, J. W., "Proceedings of Joint Conference on Prevention and Control of Oil Spills", Washington, D.C., March 13–15, 1973, p 485.
(6) Hermann, R. B., *J. Phys. Chem.*, **76**, 2754 (1972).
(7) Hertz, H. S., Chesler, S. N., May, W. E., Gump, B. H., Enogonio, D. P., Cram, S. P., "Preliminary Proceedings of the Marine Pollution Monitoring (Petroleum) Symposium and Workshop, NBS", Gaithersburg, Md., May 13–17, 1974, p 104.
(8) Iwai, I., Heraska, T., *Chem. Pharm. Bull.*, **11**, 638 (1963).
(9) Karyakin, N. V., Rabinovich, I. B., Pakhomov, L. G., *Zh. Fix. Khim.*, **42**, 1814 (1968).
(10) Littlewood, A. B., "Gas Chromatography, Principles, Techniques, and Applications", Academic Press, New York, N.Y., 1962, p 73.
(11) McAuliffe, C., *J. Phys. Chem.*, **70**, 1267 (1966).
(12) Ramart-Lucas, P., Hock, J., *Bull. Soc. Chim. Fr.*, **19**, 422 (1952).
(13) Schwarz, F. P., Wasik, S. P., *Anal. Chem.*, **48**, 524 (1976).
(14) Schwarz, F. P., Wasik, S. P., Proceedings of the International Conference on Environmental Sensing and Assessment, Las Vegas, Nev., Sept 1975, in press.
(15) Sutton, C., Calder, J. A., *J. Chem. Eng. Data*, **20**, 320 (1975).
(16) Wauchope, R. D., Getzen, F. W., *J. Chem. Eng. Data*, **17**, 38 (1972).
(17) Zwolinski, B. J., Wilhoit, R. C., Vapor Pressures and Heats of Vaporization of Hydrocarbons and Related Compounds, America Petroleum Institute Research Project 44, Thermodynamics Research Center, Texas A&M University, College Station, Texas, 1971, p 71.

Received for review June 28, 1976. Accepted January 6, 1977. This work has been supported by the Office of Air and Water Measurement at the National Bureau of Standards, Washington, D.C. Certain commercial equipment, instruments, and materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material, instruments, or equipment identified is necessarily the best available for the purpose.

Determination of Temperature Dependence of Solubilities of Polycyclic Aromatic Hydrocarbons in Aqueous Solutions by a Fluorescence Method

Frederick P. Schwarz
Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234

The fluorescence intensities of saturated aqueous polycyclic aromatic hydrocarbon (PAH) solutions equilibrated at temperatures between 281 and 303 K are proportional to the PAH concentration. The fluorescence measurements are put on an absolute solubility scale by UV absorption measurements at 298.2 K. This method was applied to the determination of the solubilities of naphthalene, 1-methylnaphthalene, 1-ethylnaphthalene, phenanthrene, anthracene, pyrene, and benz[*e*]pyrene in water and in 0.5 mol L^{-1} sodium chloride solution. Ethalpies of solution of the PAH were calculated.

Data on the temperature dependence of the aqueous solubilities of the polycyclic aromatic hydrocarbons (PAH) are considerably less than the corresponding data on naphthalene and the benzene derivatives. Bohon and Claussen (*1*) measured the solubilities of naphthalene and several benzene homologues in water from 0 to 43 °C. Decreases in the naphthalene solubility in water due to the presence of various electrolytes ("salting-out" effect) were investigated by Paul (*16*) at 25 and 0.1 °C. A temperature dependence of the "salting-out" effect was observed by Morrison (*14*) for phenol, phenylacetic acid, and benzoic acid in salt solutions. More recently, Wasik and Brown (*3*) determined the solubilities of benzene, ethylbenzene, and toluene in water and in 0.5 mol L^{-1} NaCl solutions from 8 to 40 °C. Wauchope and Getzen (*21*) have extended these data to larger PAH molecules ranging in size from naphthalene to pyrene. They determined the PAH solubilities in water from 25 to 75 °C.

Previous investigations of the solubility dependence on temperature have been based on extraction and analysis by UV spectrophotometry (*1, 16, 21*) or by gas chromatography (*3*). This paper describes a spectrofluorimetric method for the measurement of the temperature dependence of the solubilities of PAH in aqueous solutions. To demonstrate the capability of the method, it was applied to saturated solutions in water and in 0.5 mol L^{-1} NaCl solution of naphthalene, 1-methylnaphthalene, 1-ethylnaphthalene, phenanthrene, anthracene, pyrene, and benz[*e*]pyrene. These PAH range in size from two to five fused aromatic rings.

Experimental Section

Materials. The purities of naphthalene, 1-methylnaphthalene, and 1-ethylnaphthalene were determined by gas chromatography and found to be greater than 99.9%. The purities of the phenanthrene, anthracene, pyrene, and benz[*e*]pyrene crystals were greater than 99 mole %. Measurements of these crystals dissolved in ethanol showed no fluorescing impurities above 0.001 mole %.

The water was distilled over a potassium permaganate–sodium hydroxide solution and passed through a Sephadex column (*9*). The absolute ethanol, cyclohexane, and sodium chloride were reagent grade.

Solubility Measurements by Spectrofluorimetry. Standard 1 × 1 cm quartz fluorescence cells were modified by the addition of a quartz tube to the top of each cell. Each cell could then be sealed by a stainless steel Swagelok cap. The sealed cells contained 5 mL of the aqueous solution and an excess of the PAH. The cells were rotated at 20 rpm for at least 72 h in a water bath at 8.5 ± 0.1 °C. Each cell was removed from the bath, quickly wiped dry, and placed in the fluorimeter. Because the rate of thermalization of the solution was observed to be slow relative to the fluorescence measuring time, it was not necessary to thermostat the cell in the fluorimeter. Upon completion of all the solubility measurements, the water bath temperature was raised several centigrade degrees to the next temperature point

Table I. Absorptivities of the PAH in Ethanol

PAH	Absorption peak (nm)	Absorptivity (L mol^{-1} cm^{-1})	Lit ref
Naphthalene	276	5.75×10^3	8
1-Methylnaphthalene	271	5.1×10^3	9
1-Ethylnaphthalene	271	5.0×10^3	10
Phenanthrene	293	1.26×10^4	11
Anthracene	252	1.70×10^5	12
Pyrene	272	5.01×10^4	13

Table II. Solubility of Naphthalene

In water			In 0.5 mol L^{-1} NaCl solution	
T, °C	Obsd (10^{-4} mol L^{-1})	Lit. (10^{-4} mol L^{-1})	*T*, °C	Obsd (10^{-4} mol L^{-1})
8.4	1.40 ± 0.02	1.39,[a] 1.43[b]	8.6	0.84 ± 0.09
10.0			11.1	0.92 ± 0.03
11.1	1.49 ± 0.03		14.0	1.09 ± 0.03
12.0		1.55[b]	17.1	1.23 ± 0.03
14.0	1.66 ± 0.05	1.64[b]	20.0	1.37 ± 0.03
15.9		1.77[a]	23.0	1.58 ± 0.02
17.5	1.88 ± 0.03		25.0	1.73 ± 0.04
19.3		2.02[a]	31.8	2.22 ± 0.04
20.2	2.07 ± 0.02			
22.2		2.21[c]		
23.2	2.22 ± 0.03			
24.5		2.40		
25.0	2.36 ± 0.02	2.57,[a] 2.31,[b] 2.44[c]		
26.3	2.48 ± 0.02			
29.2	2.68 ± 0.02			
29.9		2.79[a]		
31.8	2.83 ± 0.02			

[a] Extraction and UV absorption method. Reference 1. [b] Partition coefficient measurements and vapor pressure data. Reference 15. [c] Extraction and UV absorption method. Reference 5.

Table III. Solubility of 1-Methylnaphthalene

In water		In 0.5 mol L^{-1} NaCl Solution	
T, °C	Obsd (10^{-4} mol L^{-1})	*T*, °C	Obsd (10^{-4} mol L^{-1})
8.6	1.40 ± 0.03	8.1	1.23 ± 0.01
14.0	1.59 ± 0.03	11.1	1.35 ± 0.01
17.1	1.61 ± 0.03	15.5	1.49 ± 0.01
20.0	1.78 ± 0.02	17.4	1.53 ± 0.02
23.0	1.94 ± 0.02	18.2	1.54 ± 0.01
25.0	2.11 ± 0.07	20.7	1.54 ± 0.01
26.1	2.14 ± 0.02	23.3	1.63 ± 0.01
29.2	2.34 ± 0.05	25.0	1.69 ± 0.06
31.7	2.55 ± 0.04	28.5	1.81 ± 0.02

Table IV. Solubility of 1-Ethylnaphthalene

In water		In 0.5 mol L^{-1} NaCl solution	
T, °C	Obsd (10^{-5} mol L^{-1})	*T*, °C	Obsd (10^{-5} mol L^{-1})
8.6	5.2 ± 0.3	8.1	3.65 ± 0.07
11.1	5.2 ± 0.2	11.1	3.87 ± 0.07
14.0	5.3 ± 0.1	17.4	4.23 ± 0.07
17.1	5.5 ± 0.1	20.3	4.45 ± 0.07
20.0	5.4 ± 0.1	23.3	4.38 ± 0.07
23.0	5.5 ± 0.1	25.0	4.67 ± 0.07
25.0	6.4 ± 0.1	26.2	4.53 ± 0.07
26.1	6.3 ± 0.1	28.5	4.82 ± 0.07
31.7	7.5 ± 0.2		

and the cells were rotated for 24 h. Longer submersion times did not increase the concentration of the PAH solutions. This procedure was repeated up to 31 °C.

The spectrofluorimeter used in this investigation employs ratio-photon counting and is described elsewhere (*18*). At Naperian absorptivities of ≤ 0.05, the PAH concentration, *S*, is linearly related to the fluorescence signal, *F* (*18*),

$$F = AS + B \qquad (1)$$

where *A* is a constant at fixed UV excitation and fluorescence wavelengths but may vary with the temperature and *B* is a background factor due primarily to the thermal noise of the photomultiplier and is invariant over the spectral range 300–425 nm. For each concentration measurement, a value for *B* was measured at a wavelength where the solutions do not fluoresce; i.e., where $A = 0$. The fluorescence and excitation wavelengths chosen were respectively 350 and 315 nm for naphthalene, 350 and 320 nm for the naphthalene homologues, 365 and 300 nm for phenanthrene, 395 and 258 nm for pyrene and anthracene, and 410 and 265 nm for benz[*e*]pyrene.

The dependence of *A* on the temperature was determined by fluorescence measurements on diluted solutions of the PAH in water and in the 0.5 mol L^{-1} NaCl solution. These solutions were sealed in the modified 1 × 1 cm fluorescence cells and were thermally equilibrated simultaneously with the PAH saturated solutions. Since the concentration of the diluted solutions remained constant over the entire temperature range, any temperature variation in the fluorescence signal would reflect a temperature dependence in *A*. For all the PAH, the fluorescence signal variation with temperature was less than the experimental error of 1–3% over the entire temperature range. Therefore, it was convenient to determine values for *A* at 25.0 °C using fluorescence measurements on known saturated PAH solutions.

Solubility Measurements by UV Absorption. Stock solutions of all the PAH except benz[*e*]pyrene in absolute ethanol were prepared at the 10^{-4} mol L^{-1} level. Hundredths of a gram of the PAH weighed within an error of 2% was dissolved in ethanol in 1-L volumetric flasks. Ten-milliliter aliquots of the stock solutions were diluted with water or the 0.5 mol L^{-1} NaCl solution to a total volume of 50 mL for the UV absorption measurements. All the UV absorptivities of the diluted solutions were found to be within 3% of their literature values in pure ethanol. The literature values were used for the concentration determinations of the PAH saturated solutions at 25 °C. These values are presented in Table I.

The saturated PAH solutions were prepared in Pyrex cylinders capped by Pyrex ground glass stoppers. Half way up the side of each cylinder was a Pyrex tube protruding several centimeters from the side of the cylinder which could be sealed by a stainless steel Swagelok cap. Each cylinder was filled with an excess amount of the PAH in either water or the NaCl solution and a Teflon coated magnetic stirring bar. For several days, the cylinders were stirred in an upright position in a water bath at 25.0 °C. Since the excess solute either floated at the top or settled to the bottom after the stirring, aliquots of the pure solution could be removed through the tubular opening. The aliquots were dispensed directly into 50-mL volumetric flasks containing 10 mL of absolute ethanol. Prior to the dispensing, the flasks were rinsed by aliquots of the saturated solutions. Possible losses of the solute from the solution by wall adsorption were minimized by this technique. Absorption spectra of the collected diluted solutions were measured in 10 cm long absorption cells. The

Table V. Solubility of Phenanthrene

In water			In 0.5 mol L^{-1} NaCl solution	
T, °C	Obsd (10^{-6} mol L^{-1})	Lit. (10^{-6} mol L^{-1})	T, °C	Obsd (10^{-6} mol L^{-1})
8.4	2.81 ± 0.07		11.1	2.88 ± 0.06
11.1	3.09 ± 0.07		14.0	3.2 ± 0.2
14.0	3.59 ± 0.06		17.5	4.07 ± 0.09
17.5	4.40 ± 0.04		20.2	4.51 ± 0.08
20.2	4.94 ± 0.09		23.2	5.75 ± 0.09
23.3	6.09 ± 0.07		25.0	5.72 ± 0.02
24.6		6.5[a]	29.3	7.2 ± 0.2
25.0	6.46 ± 0.02	6.6 ± 0.1[a]	31.8	7.9 ± 0.2
29.3	7.7 ± 0.2			
30.3		8.5[a]		
31.8	9.13 ± 0.08			

[a] Extraction and UV absorption method. Reference 5.

Table VI. Solubility of Pyrene

In water			In 0.5 mol L^{-1} NaCl solution	
T, °C	Obsd (10^{-7} mol L^{-1})	Lit. (10^{-7} mol L^{-1})	T, °C	Obsd (10^{-7} mol L^{-1})
12.2	2.70 ± 0.03		8.6	2.00 ± 0.02
15.5	3.39 ± 0.03		12.2	2.50 ± 0.03
17.4	3.91 ± 0.05		15.5	2.85 ± 0.01
20.3	4.57 ± 0.04		18.2	3.22 ± 0.05
22.2		6.44[a]	20.7	3.57 ± 0.01
23.0	5.78 ± 0.06		23.0	3.90 ± 0.04
23.3	5.82 ± 0.03		25.0	4.41 ± 0.04
25.0	6.40 ± 0.05	7.33[a]	28.1	5.19 ± 0.07
26.2	7.13 ± 0.07		31.1	5.96 ± 0.08
26.7	7.18 ± 0.04			
27.0		8.17 ± 0.55[b]		
28.5	8.09 ± 0.08			
31.3	9.3 ± 0.1			

[a] Extraction and UV absorption method. Reference 5. [b] Nephelometric method. Reference 16.

Table VII. Solubility of Anthracene

In water			In 0.5 mol L^{-1} NaCl solution	
T, °C	Obsd (10^{-7} mol L^{-1})	Lit. (10^{-7} mol L^{-1})	T, °C	Obsd (10^{-7} mol L^{-1})
8.6	1.31 ± 0.04		8.2	0.93 ± 0.04
11.1	1.37 ± 0.03		8.6	1.01 ± 0.04
12.2	1.44 ± 0.03		11.7	1.22 ± 0.04
14.0	1.54 ± 0.04		19.2	1.47 ± 0.05
15.5	1.66 ± 0.03		21.5	1.68 ± 0.02
18.2	1.81 ± 0.03		25.0	2.04 ± 0.02
20.3	2.22 ± 0.03		25.3	1.92 ± 0.04
23.0	2.34 ± 0.03		27.1	2.02 ± 0.03
23.3	2.30 ± 0.04	4.21 ± 0.03[a]	30.2	2.46 ± 0.03
25.0	2.30 ± 0.05			
26.2	2.67 ± 0.03			
27.0		4.0 ± 0.3[b]		
28.5	3.25 ± 0.06			
31.3	3.90 ± 0.02			

[a] Extraction and UV absorption method. Reference 15. [b] Nephelometric method. Reference 16.

Table VIII. Solubility of Benz[*e*]pyrene

In water			In 0.5 mol L^{-1} NaCl solution	
T, °C	Obsd (10^{-8} mol L^{-1})	Lit. (10^{-8} mol L^{-1})	T, °C	Obsd (10^{-8} mol L^{-1})
8.6	1.29 ± 0.07		8.9	0.82 ± 0.16
14.0	1.42 ± 0.05		10.8	0.88 ± 0.16
17.0	1.76 ± 0.13		15.6	1.01 ± 0.20
17.5	1.56 ± 0.08		17.0	1.01 ± 0.10
20.0	1.82 ± 0.09		19.2	1.04 ± 0.10
20.2	1.90 ± 0.14		21.7	1.13 ± 0.22
23.2	2.12 ± 0.10		25.3	1.35 ± 0.27
23.0	2.01 ± 0.20		27.1	1.42 ± 0.14
27.0		1.8 ± 0.2[a]		
29.2	2.53, 2.57		30.2	1.66 ± 0.17
31.7	2.70 ± 0.15			

[a] Nephelometric method. Reference 16.

Table IX. Setschenow's Constants and the Liquid Molar Volumes of PAH

PAH	$k^{298.2\mathrm{K}}$ (L mol^{-1})	Liquid molar volume (cm^3 mol^{-1})
Naphthalene	0.62 ± 0.02	124[a]
1-Methylnaphthalene	0.44 ± 0.02	129[b]
1-Ethylnaphthalene	0.62 ± 0.02	141[b]
Phenanthrene	0.24 ± 0.01	159[a]
Anthracene	0.44 ± 0.03	160[a]
Pyrene	0.74 ± 0.01	172[a]
Benz[*e*]pyrene	0.98 ± 0.09	206[a]

[a] Reference 19. [b] Calculated from the densities in ref 20.

concentrations of the PAH were determined from the absorption spectra and the absorptivities in Table I. To ensure that the solutions in the cylinders were saturated, they were stirred again for several days and the measurements repeated until the concentrations remained the same. This usually took a week.

Since the absorbance of benz[*e*]pyrene in the 20% ethanol-water solution was too low to be measured accurately, the saturated aqueous benz[*e*]pyrene solutions were concentrated by extraction with cyclohexane and then determined by absorption measurements. Three hundred millimeters of the saturated benz[*e*]pyrene solution was dispensed directly into a separatory funnel containing 30 mL of cyclohexane. After separation of the two phases, an absorption spectrum of the benz[*e*]pyrene in cyclohexane was taken with a 10 cm long absorption cell. The concentration of the saturated solution was calculated from an absorptivity of 7.41 × 10^4 L mol^{-1} cm^{-1} at 297 nm in cyclohexane (*11*).

Results and Discussion

Solubility Measurements. Experimental values of the solubilities of the PAH in water and in salt water are presented in Tables II through VIII. The underlined values were determined from the UV absorption measurements and were used to calculate A in eq 1. All the other values are the combined fluorescence results of two different temperature runs from 8 to 32 °C for each PAH.

For all the PAH in water with the exception of anthracene, the agreement between the experimental and literature values is excellent. This is particularly true for naphthalene where the literature values are available from both extraction and UV absorption measurements (*1*) and from partition coefficient and vapor pressure data (*19*).

Literature values for anthracene were determined by two

Table X. Enthalpies of Solution of the PAH

	In water			In 0.5 mol L^{-1} NaCl solution	
PAH	ΔH_s (kcal mol^{-1})[c]	Lit. values[a] (kcal mol^{-1})	Standard deviation of least-squares fit[b]	ΔH_s (kcal mol^{-1})	Standard deviation of least-squares fit[b]
Naphthalene	5.29 ± 0.10	6.10 ± 0.28	0.0005	7.20 ± 0.13	0.004
1-Methylnaphthalene	4.57 ± 0.30		0.02	3.02 ± 0.23	0.02
1-Ethylnaphthalene	3.41 ± 0.60		0.03	2.18 ± 0.22	0.02
Phenanthrene	8.68 ± 0.23	7.7 ± 0.9	0.007	8.25 ± 0.44	0.01
Anthracene	8.32 ± 0.38	10.4 ± 0.8	0.01	6.97 ± 0.29	0.02
Pyrene	11.4 ± 0.2	7.3 ± 0.2	0.003	8.02 ± 0.20	0.02
Benz[*e*]pyrene	6.11 ± 0.34		0.01	5.35 ± 0.44	0.02

[a] Determined from the enthalpies of solvation in ref 21 and the enthalpies of vaporization in ref 22. [b] Standard deviation of the least-squares fit = $[\Sigma_{i=1}{}^{n}(\ln S_i' - \ln S_i)^2/(N-2)]^{1/2}$ where S_i' is the solubility at temperature T_i from the least-squares fit and S_i is the experimental value for the solubility at temperature T_i. [c] 1 kcal = 4.184 kJ.

methods. The value from Wauchope and Getzen (*21*) at 23.3 °C is an extrapolated value from solubility measurements above 35 °C. A nephelometric method was used to determine the literature value at 27.0 °C (*7*). Briefly, this method calculates the solubility from reduction of the turbidity of anthracene particles in a dilute acetone-water solution upon the addition of large volumes of water to the solution. The extrapolation in the former method and the presence of acetone in the latter may lead to higher solubility values for anthracene.

The solubilities of the PAH in 0.5 mol L^{-1} NaCl solution are not available in the literature. A comparison of Paul's (*16*) values for the optical density of naphthalene in water to that of naphthalene in 0.440 mol L^{-1} NaCl solution yields a ratio of 1.34 at 25 °C. This is in excellent agreement with the corresponding ratio of 1.36 ± 0.04 calculated from the values in Table II for water and a 0.5 mol L^{-1} NaCl solution.

"Salting Out" Effect. Setschenow (*20*) found an empirical relationship between the magnitude of the salting out effect and the concentration of the salt,

$$\ln (S_0/S) = kC_s$$

where S_0/S is the ratio of the nonelectrolyte solute concentration in water to its concentration in the salt solution, k is the Setschenow constant for the salt solution, and C_s is the salt concentration. The k values determined at 25 °C for all the PAH for NaCl solutions are presented in Table IX.

The theory developed by McDevit and Long (*12*) for the "salting out" effect predicts an increase in k with an increase in the liquid molar volume of the nonelectrolyte solute. The liquid molar volumes of the PAH are also presented in Table IX in order to examine this prediction. This relationship holds for the series of PAH's from phenanthrene to benz[*e*]pyrene but breaks down for the more soluble naphthalene homologues.

Determination of the Enthalpies of Solution. The enthalpy of solution can be calculated from

$$d(\ln S)/d(1/T) = \Delta H_s/R \qquad (2)$$

where T is the absolute temperature and R is the ideal gas constant. From the solubilities in Tables II through VIII, values of ΔH_s at 298 K, $\Delta H_s{}^{298}$, can be determined by least-squares fits to the integrated form of eq 2,

$$\ln S = -\Delta H_s/RT + a$$

where a is a constant. Values of ΔH_s from the least-squares fits are presented in Table X with their standard deviations and the standard deviations of the least-squares fits. Least-squares fits of the data points to a second power dependence on $1/T$ increased the standard deviations of all the fits except those of anthracene and 1-ethylnaphthalene.

The literature values shown in Table X were calculated from the enthalpies of solvation of Wauchope and Haque (*22*) and from the enthalpies of vaporization at 298.15 K of Bradley and Cleasby (*2*). The enthalpies of solvation from Wauchope and Haque were calculated from solubility measurements by Wauchope and Getzen (*21*) from 25 to 75 °C. The enthalpies of solution determined by fluorimetry between 8 and 33 °C are in good agreement with the literature values for naphthalene, phenanthrene, and anthracene.

Except for naphthalene, the presence of NaCl lowers the enthalpy of solution from 5 (phenanthrene) to 36% (1-ethylnaphthalene). Morrison's data (*14*) exhibited an enthalpy decrease for phenol, phenylacetic acid, and benzoic acid in going from water to a 1 mol L^{-1} NaCl solution. The enthalpy decreases for all the PAH except naphthalene are consistent with Morrison's (*14*) observations. For naphthalene, Paul (*16*) found a decrease in k from 25 to 0.1 °C which would cause an increase in the enthalpy of solution in salt water in agreement with Table X.

Conclusion

The fluorescence method was found to be suitable for determining the temperature dependence of the solubilities of PAH in aqueous solutions. The PAH solubilities at different temperatures are in agreement with the available literature values. The enthalpies of solution determined by least-squares fits of the logarithms of the solubilities to the reciprocal of the absolute temperatures are in agreement with the literature values between 25 and 75 °C.

Spectrofluorimetry exhibits the high sensitivity and precision needed for determining the temperature dependence of the low solubilities of PAH in aqueous solutions. The measurements have the advantage of not requiring removal, handling, or destruction of samples.

Literature Cited

(1) Bohon, R. L., Claussen, W. F., *J. Am. Chem. Soc.*, **73**, 1571 (1951).
(2) Bradley, R. S., Cleasby, T. G., *J. Chem. Soc.*, 1690 (1953).
(3) Brown, R. L., Wasik, S. P., *J. Res. Natl. Bur. Stand., Sect. A*, **78**, 453 (1974).
(4) Christol, H., Mousseron, M., Salle, R., *Bull. Soc. Chim. Fr.*, 556 (1958).
(5) Dannenburg, H., Dannenberg-von Dresler, D., *Chem. Ber.*, **89**, 1326 (1959).
(6) Davis, H. G., Goltlieb, S., *Fuel*, **8**, 37 (1962).
(7) Davis, W. W., Krahl, M. E., Clowes, G. H. A., *J. Am. Chem. Soc.*, **64**, 108 (1942).
(8) "Handbook of Chemistry and Physics", 41st ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1960, p 1106.
(9) Hertz, H. S., Chesler, S. N., May, W. E., Gump, B. H., Enogonio, D. P., Cram, S. P., "Preliminary Proceedings of the Marine Pollution Monitoring (Petroleum) Symposium and Workshop, NBS," Gaithersburg, Md., May 13-17, 1974, p 104.
(10) Iwai, J., Heraksa, J., *Chem. Pharm. Bull.*, **11**, 638 (1963).
(11) Lindsay, A. J., *Anal. Chim. Acta*, **18**, 22 (1959).
(12) Long, F. A., McDevit, W. F., *Chem. Rev.*, **51**, 128 (1952).
(13) Long, L., Ed., "Absorption Spectra in the Ultraviolet and Visible Region", Publishing House of the Hungarian Academy of Science, Budapest, 1959.
(14) Morrison, T. J., *Trans Faraday Soc.*, **40**, 25 (1940).
(15) Moyle, M., Ritchie, E., *Aust. J. Chem.*, **11**, 211 (1958).
(16) Paul, M. A., *J. Am. Chem. Soc.*, **74**, 5274 (1952).

(17) Ramart-Lucas, P., Hoch, J., *Bull. Soc. Chim. Fr.*, **5,** 422 (1952).
(18) Schwarz, F. P., Wasik, S. P., Proceedings of the International Conference on Environmental Sensing and Assessment, Las Vegas, Nev., Sept 1975.
(19) Schwarz, F. P., Wasik, S. P., to be submitted for publication.
(20) Setschenow, J., *Z. Phys. Chem.*, **4,** 117 (1889).
(21) Wauchope, R. D., Getzen, F. W., *J. Chem. Eng. Data,* **17,** 38 (1972).
(22) Wauchope, R. D., Haque, R., *Can. J. Chem.*, **50,** 133 (1972).

Received for review December 13, 1976. Accepted February 26, 1977. This work has been supported by the Office of Air and Water Measurement at the National Bureau of Standards, Washington, D.C. Certain commercial equipment, instruments, and materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material, instruments, or equipment identified is necessarily the best available for the purpose.

Solubilities of Gases in Aqueous Solutions of Amine

Eizo Sada,* Hidehiro Kumazawa, and M. A. Butt
Department of Chemical Engineering, Nagoya University, Nagoya, Japan

Solubilities of nitrous oxide and ethylene were measured in aqueous solutions of diethanolamine, triethanolamine, and ethylenediamine at 25 °C and 1 atm. The data are useful to evaluate the solubilities of reacting gases in the amine solutions under consideration from the solubilities of the corresponding nonreacting gases, if the interaction parameters of the reacting gases are quite close to those of the nonreacting gases.

Solutions of amines are widely encountered in gas–liquid contact operations as absorbents of acidic gases. The rational design of the gas–liquid contactor requires a knowledge of the solubility as well as the diffusivity of the gas in these solutions. However, for the time being it is impossible to estimate the solubility of the reacting gas from that of the nonreacting gas in the same solutions except in the case of electrolyte solutions (*4*). Furthermore, for aqueous solutions of weak electrolytes such as amines and organic acids, it should be emphasized that there are few experimental data. In view of these facts, the solubilities of nitrous oxide and ethylene in aqueous monoethanolamine solutions were measured and the possibility of correlation for the prediction of solubility was discussed in a previous paper (*5*). In another paper (*6*), the data on the solubilities of carbon dioxide and nitrous oxide in aqueous solutions of weak acids were reported and correlated in terms of the hyperbolic equation proposed by Markham and Kobe (*3*).

In the present work, the solubilities of nitrous oxide and ethylene in aqueous solutions of diethanolamine, triethanolamine, and ethylenediamine were measured by a volumetric method at 25 °C under atmospheric pressure.

Experimental Section

Aqueous solutions of amines were prepared from distilled water and reagent grade amines of guaranteed purity. The composition of the aqueous solutions of amine was determined by volumetric titration. The solutions were thoroughly degassed before being used in the experiment as described in a previous paper (*4*).

For gases, nitrous oxide and ethylene of high purity were supplied from commercial cylinders with minimum purities of 99.8 and 99.6%, respectively, and confirmed by analyzing by gas chromatograph.

The solubilities were measured with the same apparatus as described in our previous papers (*4–6*). The apparatus and technique employed were discussed in detail in an early paper (*4*). The reliability of the apparatus was checked by measuring the solubilities of nitrous oxide, ethylene, and carbon dioxide in pure water. These measured values (in pure water) were in excellent agreement with those reported in the literature. The accuracy of the experiments was within ±1.0%.

The working temperature was 25 ± 0.01 °C and kept constant by a water bath.

Results and Discussion

The vapor pressure of the amine–water solutions at 25 °C is required for the calculation of the solubility. The vapor pressure for amine–water solutions was calculated by assuming that the vapor phase was an ideal mixture.

The solubility data are shown in Table I for nitrous oxide and in Table II for ethylene. The solubilities are expressed in terms of the Bunsen coefficient. The Bunsen coefficient is defined as the volume of gas, reduced to 0 °C and 760 mm pressure of mercury, which is absorbed by the unit volume of solvent (at the temperature of the measurement) under a gas pressure of 760 mm.

For nitrous oxide–monoethanolamine and ethylene–monoethanolamine systems, Sada and Kito (*5*) presented the results in terms of log (α/α_w) vs. concentration (C), as in electrolyte solutions (*4*). For both systems, reasonable straight lines were found which held good up to a concentration of 3 M, and the contribution parameter for the amine was evaluated by a modified empirical Setschenow equation (*7*),

$$\log(\alpha/\alpha_w) = (x_a + x_g)C \qquad (1)$$

The results for the present systems are also shown in graphical form in Figure 1 in the same manner as in previous papers (*4–6*), to evaluate the contribution parameters for the amines, if possible. In this figure, the dependence of log (α/α_w) (the negative logarithm of the activity coefficient of the gaseous species) on the concentration of amine is given. As can be seen from the figure, these plots cannot be correlated by straight lines as in monoethanolamine systems, even in moderately dilute solutions of the amines. The results for the "salting out" of nitrous oxide by these amines differ markedly from those for the "salting in" of ethylene. It was found that salts of both large ions and large cations usually cause salting in and, in addition, the salting in is increased as the dipole moment of the molecule increases. Anyhow, at present, observed salt effects cannot be interpreted from existing knowledge on salt effects and are not in line with the above predictions. In general, the activity coefficient of any solute in solution is a function of all solute species present. At a given temperature log (α/α_w) can be expressed by a power series in the concentrations of all solute species (*2*). In reality, eq 1 is obtained by retaining only the first term in the power series. The results in Figure 1 may be fitted by the power series function with several terms, but the meanings of the coefficients in the correlation obtained thus are not clear. The