for silver sulfate and silver acetate (Table VI) is positive and passes through a maximum at $X_{Me_2SO} = 0.45$ with $\Delta_{max} = 5.8$ and 5.1, respectively. Thus an increase of 3.0 and 3.7 moles of AN occurs in the case of dioxane + AN mixtures for silver sulfate and silver acetate and an increase of 5.8 and 5.1 moles of Me_2SO occurs in the case of dioxane + Me_2SO for silver sulfate and silver acetate, respectively, per faraday, relative to the mean molar velocity of the solvent mixtures as reference (*23*) in the cathode compartment when the solutions of these salts are electrolyzed at the given composition of the solvent mixtures. The enrichment of AN or Me_2SO in the cathode compartment arises largely through their transport by the silver ion while the anion transports dioxane in the opposite direction, i.e., toward the anode. These two effects add together and thus a heteroselective solvation results in large Δ values. These results support the conclusions based on the transfer energy variation of the ions observed earlier.

Registry No. AN, 75-05-8; Ag_2SO_4, 10294-26-5; CH_3COOAg, 563-63-3; Me_2SO, 67-68-5; SO_4^{2-}, 14808-79-8; CH_3COO^-, 71-50-1; Ag, 7440-22-4; dioxane, 123-91-1.

Literature Cited

(1) Parker, A. J. *Chem. Rev.* **1969**, *69*, 1.
(2) Benter, G.; Schneider, H. *Ber. Bunsenges. Phys. Chem.* **1973**, *2*, 997.
(3) Schneider, H. *Electrochim. Acta* **1976**, *21*, 711.
(4) Parker, A. J.; Diggle, J. W.; Avraamide, J. *Aust. J. Chem.* **1974**, *27*, 721.
(5) Parker, A. J. *Electrochim. Acta* **1976**, *21*, 671.
(6) Janardhanan, S.; Kalidas, C. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2363.
(7) Janardhanan, S.; Kalidas, C., *Proc. Indian Acad. Sci.* **1981**, *90*, 89.
(8) Subramanian, S.; Rao, S. C. A. V. S. S.; Kalidas, C. *Indian J. Chem., Sect. A* **1981**, *20*, 723.
(9) Vogel, A. I. "Practical Organic Chemistry", 3rd ed.; Longmans: London, 1975; p 177.
(10) Subramanian, S.; Kalidas, C. *Electrochim. Acta* **1984**, *29*, 753.
(11) Maricle, D. L.; Hodgson, W. G. *Anal. Chem.* **1965**, *37*, 1562.
(12) Hill, D. *J. Am. Chem. Soc.* **1921**, *43*, 254.
(13) Rodehüser, L.; Schneider, H. *Z. Phys. Chem.* (*N.F.*) **1976**, *100*, 119.
(14) Rodehüser, L.; Schneider, H. *J. Solution Chem.* **1980**, *9*, 683.
(15) Carmody, W. *J. Am. Chem. Soc.* **1928**, *51*, 2901.
(16) Kalidas, C.; Schneider, H. *Z. Phys. Chem.* **1961**, *10*, 847.
(17) Alexander, R.; Parker, A. J.; Sharp, J. H.; Waghorne, W. E. *J. Am. Chem. Soc.* **1972**, *94*, 1148.
(18) Wagner, C. In "Advances in Electrochemistry and Electrochemical Engineering"; Delahay, P., Tobias, C. W., Eds.; Wiley-Interscience: New York, 1966; Vol. 4, pp 1-46.
(19) Kielland, J. *J. Am. Chem. Soc.* **1937**, *59*, 1675.
(20) Cram, D. J. "Fundamentals of Carbanion Chemistry"; Academic: New York, 1965; Vol. 4, p 28, 32.
(21) Davolio, F.; Pedrosa, G. C.; Miguel Katz, *J. Chem. Eng. Data* **1981**, *26*, 26.
(22) Von Quitzch, K.; Ulbrecht, H.; Geiseler, G. *Z. Phys. Chem.* **1966**, *234*, 33.
(23) Schneider, H. In "Solute-Solvent Interactions"; Coetzee, J. F.; Ritchie, C. D., Eds.; Marcel Dekker: New York, 1976; pp 155-216.

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Henry's Constants for Phenol over Its Diluted Aqueous Solution

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Henry's constants for phenol over its aqueous solution were measured in the temperature range from −2 to 27 °C. An equation was proposed to correlate these data and those estimated from the literature data at 44–90 °C.

In connection with our study if stripping of phenol from a diluted aqueous phenol solution into air at ambient temperatures, we noticed that little information is available on Henry's constant for phenol at temperatures below about 40 °C. Therefore, we carried out measurements of Henry's constants for phenol in the phenol–water–air system at ambient temperatures.

Judging from the data reported in ref *1–3*, the equilibrium relation is represented by Henry's law when liquid-phase phenol concentrations are less than about 0.1 mol % (about 5200 ppm). At atmospheric pressure, phenol forms an azeotrope with water when the phenol concentration is 1.9 mol % (*1*). This explains the success of Henry's law in this very low concentration range.

Experimental Section

A simple apparatus consisting of four bubbling flasks connected in series was found good enough to produce an equilibrium gas. Each 300-mL flask had about 250 mL of phenol solution in it, and a glass tube with a nozzle at the lower end extended through the solution to the bottom of the flask. Nitrogen gas of a stated purity of 99.999% was introduced at a rate of about 0.3 mL/s onto the bottom of the first flask through the glass tube. Fine nitrogen gas bubbles rose from the nozzle in the solution and the effluent gas went to the bottom of the second flask and so on. Stripping of phenol took place while the bubbles rose in the solutions. The apparatus consisting of the bubbling flasks was placed in a constant temperature chamber.

The aqueous phenol solutions were prepared by dissolving the proper amount of reagent grade phenol (Kanto Chemicals Co., Tokyo) with a stated purity of 99+% in a known amount of deionized water. Phenol concentrations were measured in a Model GC-7A (Shimdadzu Co., Kyoto) gas chromatograph equipped with an FID detector and a 2-m-long column packed with Unisole F-200 50/60 mesh (Nihon Gaschro Co., Tokyo). Liquid analysis was done by withdrawing 5 μL liquid sample by a 10-μL PS (Precision Sampling Corp., LA) syringe and then injecting it into the gas chromatograph. For gas analysis a 5-mL PS syringe was employed to withdraw 2 mL of gas leaving from the fourth flask. The samples were withdrawn slowly and carefully at a rate less than that of nitrogen gas introduced into the first flask. This was done by putting a glass tube for exit gas from the fourth flask into a beaker of water and watching bubble formation at the tube end. The gas was then immediately injected into the gas chromatograph. The operating conditions of the chromatograph were as follows: injection and

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Table I. Henry's Constants for Phenol

	equilib phenol concn				
temp, °C	aq soln, mol fractn	gas, mol/m^3	Henry's const *H*, kPa	error,[b] %	source
90.0			132.0[a]	2.0	Schreinemakers (*3*)
75.0			68.5[a]	8.6	
56.3			24.3[a]	5.0	
44.4			10.7[a]	−7.6	Weller et al. (*4*)
27.0	1.980×10^{-4}	3.162×10^{-4}	3.99	5.6	this work
18.3	1.854×10^{-4}	1.580×10^{-4}	2.07	0.95	
4.0	1.980×10^{-4}	0.6047×10^{-4}	0.704	1.4	
−2.0	2.088×10^{-4}	0.3704×10^{-4}	0.400	−6.5	

[a] Gmehling et al. (*5, 6*) give the Antoine vapor pressure equations for phenol and activity coefficients of phenol at infinite dilution, γ^∞, based on the experimental data (*3, 4*). With γ^∞ and the saturation vapor pressure, *P*, found from the Antoine equations the Henry's constants are evaluated from the relation $H = \gamma^\infty P$. [b] Error defined by [1 − (Henry's constant of eq 2/Henry's constant measured)] × 100.

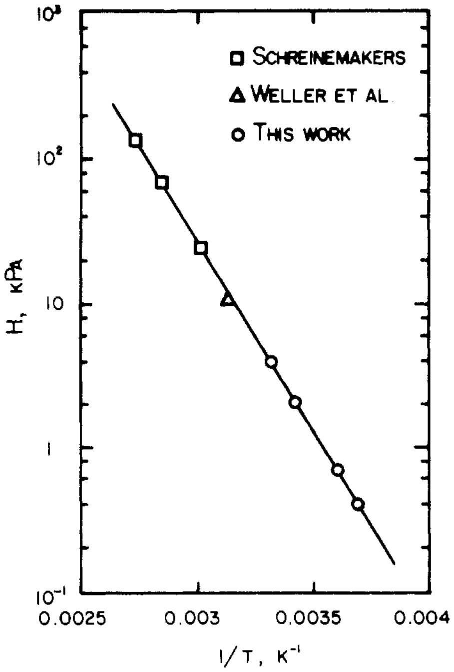

Figure 1. Henry's constant for phenol vs. temperature.

column temperatures, 135 °C; carrier gas, helium with a stated purity of 99.995% and flow rate 0.6 mL/s. The chromatograph was calibrated for aqueous phenol solutions of different concentrations. Also, note that the temperature of the system was measured by a thermometer put in the beaker where bubble formation was observed.

Results

Table I lists the Henry's constants evaluated from the measured phenol concentrations based on the definition

$$H = P/X \tag{1}$$

where *P* is a partial pressure of phenol and *X* is the mole fraction of phenol in the solution.

The Henry's constants estimated from the literature data (*3*, *4*), selected by Gmehling et al. (*5*, *6*), are also included in Table I. The data of Schreinemakers (*3*) and Weller et al. (*4*) are those obtained from the distillation measurements in phenol–water system at low pressures, whereas our data are from the measurements of phenol concentration in a phenol–water–air system at atmospheric pressure. The experimental methods are different from each other, but they are supposed to give identical Henry's constant values. In fact, the Henry's constants plotted in terms of *H* vs. 1/*T* in Figure 1 show that all of the data are well represented by the equation

$$H = 2.69 \times 10^9 \exp[-(6120/T)] \tag{2}$$

where Henry's constant *H* is in kilopascals and *T* is temperature in kelvin. As also listed in Table I, the errors between the Henry's constants measured and those estimated from eq 2 are within 8.6%.

The data and equation presented in this article will supply the information necessary for the desorption of phenol into air from water slightly contaminated with this material.

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Registry No. Phenol, 108-95-2.

Literature Cited

(1) Bogart, M. J. P.; Brunjes, A. S. *Chem. Eng. Prog.* **1948**, *44*(2), 95–104.
(2) Rhodes, F. H.; Wells, J. H.; Murray, G. W. *Ind. Eng. Chem.* **1925**, *17*, 1199–1201.
(3) Schreinemakers, F. A. H. *Z. Phys. Chem.* **1900**, *35*, 459–479.
(4) Weller, R.; Schuberth, H.; Leibnitz, E. *J. Prakt. Chem.* **1963**, *21*(5–6), 234–249.
(5) Gmehling, J.; Onken, U. "Vapor-Liquid Equilibrium Data Collection"; DECHEMA: Frankfurt, 1971; Vol. 1, Part 1.
(6) Gmehling, J.; Onken, U.; Arlt, W. "Vapor-Liquid Equilibrium Data Collection"; DECHEMA: Frankfurt, 1981; Part 1a.

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