J. Chem. Eng. Data **2002,** *47,* 183−190

Henry's Law Constants of Chlorinated Ethylenes in Aqueous Alcohol Solutions: Measurement, Estimation, and Thermodynamic Analysis

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Henry's law constants of tetrachloroethylene, trichloroethylene, *cis*-dichloroethylene, and *trans*-dichloroethylene in air−aqueous alcohol systems were measured. Ethanol, 1-propanol, and 2-propanol were employed as cosolvents. Alcohol concentrations ranged from 0 to 20 vol %. Measurements were taken at temperatures from 0.2 to 70.0 °C. Using the experimental results, equations for the estimation of Henry's law constant as a function of both temperature and alcohol concentration were constructed. In addition, the Gibbs free energy ($\Delta_{\text{dis}}G$), enthalpy ($\Delta_{\text{dis}}H$), entropy ($\Delta_{\text{dis}}S$), and heat capacity change ($\Delta_{\text{dis}}C_{\text{p}}$) associated with dissolution (solution to gas transfer) were derived by employing a linear regression analysis of the temperature dependence of the Henry's law constant.

Introduction

Chlorinated ethylenes such as tetrachloroethylene and trichloroethylene are prevalent subsurface contaminants.[1] These compounds are frequently used as degreasing solvents and for dry-cleaning, but careless disposal or spillage poses a serious environmental problem. Because of their low aqueous solubility and high density, chlorinated ethylenes tend to form dense nonaqueous phase liquid pools at confining layers which become persistent sources of underground contamination.[2−4]

One technique for remediating chlorinated ethylene-contaminated sites is a pump-and-treat system.[5−7] Because the aqueous solubilities of chlorinated ethylenes are low (100 to 7000) mg·L^{-1},[1,8,9] the removal of these compounds by water flushing is inefficient. To mobilize pools of nonaqueous phase liquids and enhance the solubility of chlorinated ethylenes in the aqueous phase, alcohols[10−13] or surfactants[14−17] may be added to the flushing water.

When a flushing technique is applied to vadose zones, not only solubility but also gas−solution partitioning must be considered.[18,19] The Henry's law constant, therefore, is an important parameter. Addition of cosolvent into the flushing solution will alter the Henry's law constants,[19] and thus, the magnitude of the effect of the cosolvent must be studied for alcohol flushing-based remediation in vadose zones.

Moreover, the flushing effluent containing chlorinated ethylenes still requires treatment. Air stripping,[20] vacuum stripping,[21] or pervaporation[22] can be used to remove the contaminants from the aqueous solution. To design these treatment systems which involve gas−solution partitioning, information regarding Henry's law constants is necessary to evaluate treatment options. It is important, therefore, to know or to be able to accurately estimate the Henry's law constants of chlorinated solvents in air−aqueous alcohol systems.

The effect of increasing temperature on Henry's law constants is also important. The flushing solution, ground water, or sediment may be heated to enhance the removal of contaminants.[23−25] In the treatment systems for the flushing effluent, increasing temperature will increase the rate of transfer of the contaminant from the solution phase into air. Consequently, increasing temperature will likely improve the efficiency of these systems at the expense of heating cost. To evaluate the effectiveness of the heating, Henry's law constants over a wide range of temperatures are necessary.

Unfortunately, most of the previous studies on Henry's law constants of chlorinated ethylenes are limited to the air−water system and a relatively narrow temperature range.[26−33] Recent works have focused on the effect of cosolvent addition[34,35] or an extended temperature range,[36] but more information is still needed.

This work presents experimentally determined values of Henry's law constants for tetrachloroethylene, trichloroethylene, *cis*-dichloroethylene, and *trans*-dichloroethylene in (0 to 20) vol % aqueous ethanol, 1-propanol, and 2-propanol solutions over the temperature range (0.2 to 70.0) °C. On the basis of the results, equations for Henry's law constants as a continuous function of alcohol concentration and temperature were constructed. In addition, thermodynamic functions associated with the dissolution process (solution to gas transfer) were derived from the experimentally determined Henry's law constants in order to analyze the driving force underlying the gas−solution partitioning.

Experimental Method

Determination of Henry's Law Constants. All chemicals were used without further purification. An 80 mM spiking solution containing tetrachloroethylene (Specro grade, Kodak), trichloroethylene (ACS grade, Fisher), *cis*-dichloroethylene (97%, Aldrich), and *trans*-dichloroethylene (98%, Aldrich) was prepared in methanol (HPLC grade, Pharmco). Aqueous solutions of ethanol (95%, Alpha Tec), 1-propanol (ACS grade, Aldrich), and 2-propanol (ACS grade, Aldrich) were prepared with Milli-Q (Millipore) water at five different concentrations for each alcohol, that is, 0, 5, 10, 15, and 20 vol %.

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10.1021/je010132n CCC: $22.00

The Henry's law constant may be defined in a dimensionless form H,

$$H = \frac{C_{\mathrm{gas}}}{C_{\mathrm{aq}}} \qquad (1)$$

where C_{gas} and C_{aq} are the solute concentrations in the gas and solution phases, respectively.

A dimensioned form of the Henry's law constants is

$$k_{\mathrm{H}} = \frac{P}{x_{\mathrm{aq}}} \qquad (2)$$

where P is the partial pressure of the solute and x_{aq} is the mole fraction of the solute in the solution phase. Measurement of both gas phase and aqueous phase concentrations is not required to obtain Henry's law constants. The equilibrium partitioning in closed systems method allows the determination of Henry's law constants via measurements of the gas-phase concentration in vials with different gas/solution ratios.[28,29,36]

Headspace autosampler vials (20 mL; Chromacol) were used in conducting the equilibrium partitioning in closed systems experiments. For each solution and temperature condition, five vials were prepared. Each vial contained a different volume (2 to 10) mL of the desired solution. The vials were spiked with 5 μL of the chlorinated ethylene/methanol stock. Methanol concentrations in the vials were <0.3 vol % and should not affect partitioning.[29] Each vial was rapidly sealed with a Teflon-faced butyl rubber septum and an aluminum crimp cap (Chrom Tech). The mass of the spike solution injected was determined from the mass of the syringe before and after the injection. Concentrations of the chlorinated ethylenes ranged from (40 to 200) μM depending on the solution volume. Previous works[29] and preliminary experiments in this work demonstrated that Henry's law constants are not altered in multicomponent systems within the concentration range of these experiments.

Vials were equilibrated for 30 min at the desired temperature. For measurement at room temperature (20.6 to 24.0) °C, vials were left at ambient temperature while shaking intermittently. For measurement at lower temperatures (0.2 to 3.9) °C, vials were placed in a water bath in a refrigerator. At (40.0 to 70.0) °C, vials were automatically incubated and shaken with a programmed headspace autosampler (HS2000, ThermoQuest). Recent work by Vane and Giroux[35] has demonstrated that times as short as 15 min are necessary to achieve equilibrium in air−aqueous surfactant or air−aqueous cosolvent systems when vials are shaken. In preliminary experiments, vials equilibrated for 30, 120, and 240 min did not result in statistically different values of the Henry's law constant, and thus 30 min was chosen as an appropriate equilibration interval.

Headspace samples (200 μL) from each vial were analyzed using a gas chromatograph (Trace GC, ThermoQuest) equipped with a GS-GasPro column (J&W Scientific), an FID detector, and a split/splitless injector. Samples incubated in the headspace autosampler were automatically injected at the end of the incubation period. The autosampler syringe was heated to the same temperature at which the vials were equilibrated to prevent condensation of the vapor in the syringe. For samples at refrigerated and room temperatures, samples were injected manually.

Equations for Estimation of Henry's Law Constants. The purpose of this section is to formulate equations for Henry's law constants in air−aqueous cosolvent systems as a function of cosolvent concentration and temperature. As a starting point, the following equation for solubility as a function of cosolvent concentration was used:[37−39]

$$\log S = \log S_{\mathrm{w}} + \sigma f \qquad (3)$$

where S and S_{w} are the solubilities of a solute in an aqueous cosolvent solution and in water, respectively. The symbol σ is a constant, and f is the volume fraction of the cosolvent in the solution. To relate solubility to the Henry's law constant, the following equation was used:

$$H \cong \frac{P_{\mathrm{sat}} M_{\mathrm{w}}}{SRT} \qquad (4)$$

where P_{sat} is the saturated vapor pressure of a pure solute, M_{w} is its molecular weight, R is the universal gas constant, and T is temperature in Kelvin. This equation has been used for the air−water system, but it can be applied to air−aqueous cosolvent systems under an assumption that mutual solubility between the solute and the solvent is low.

Substituting eq 4 for S and S_{w} in eq 3 results in the following equation:

$$\log H = \log H_{\mathrm{w}} - \sigma f \qquad (5)$$

where H_{w} is the Henry's law constant of a solute in water. The above expression is valid at constant temperature because different σ values must be used for different temperatures. H_{w} and σ are independent of cosolvent concentration but are functions of temperature, while f is a function of cosolvent concentration but independent of temperature. To advance this equation so that H can be expressed as a function of cosolvent concentration and temperature at the same time, mathematical expressions for the temperature dependence of H_{w} and σ are necessary.

The following equation was used for the temperature dependence of the Henry's law constants in water:

$$\log H_{\mathrm{w}} = A + \frac{B}{T} + C \ln T \qquad (6)$$

where A, B, and C are constants. This equation was obtained by integrating the van't Hoff equation.[36] These constants were determined by multiple linear regression of $\log H_{\mathrm{w}}$ with $1/T$ and $\ln T$ as variables. The variance (s^2) of $\log H_{\mathrm{w}}$ was used as a weighting factor.

To formulate the temperature dependence of σ, it needs to be associated with physicochemical constants. Rubino and Yalkowsky[37] reported that the best estimate of σ was obtained by the following equation involving interfacial tension:

$$\sigma = \frac{\kappa(\gamma_{13} - \gamma_{23})\Omega_3}{2.303RT} \qquad (7)$$

where γ represents interfacial tension, Ω is a molar surface area, and κ is a constant. The subscripts represent water (1), cosolvent (2), and the hydrophobic portion of a solute (3). Interfacial tension is assumed to be a linear function of temperature:[40]

$$\gamma = \alpha + \beta T \qquad (8)$$

where α and β are constants. Substituting eq 8 for γ in eq 7 and combining terms yields a simple expression for σ as a function of temperature:

Table 1. Henry's Law Constants of Trichloroethylene in Aqueous Alcohol Solutions

t/°C	n	H	$10^{-8}k_H$/Pa	t/°C	n	H	$10^{-8}k_H$/Pa
		water				5 vol % ethanol	
1.8	10[a]	0.14 ± 0.03[b]	0.18 ± 0.03[b]	1.3	10	0.14 ± 0.02	0.17 ± 0.03
21.6	10	0.35 ± 0.05	0.48 ± 0.06	21.9	10	0.31 ± 0.05	0.41 ± 0.06
40.0	10	0.74 ± 0.05	1.06 ± 0.08	40.0	10	0.64 ± 0.04	0.89 ± 0.06
50.0	10	1.00 ± 0.08	1.49 ± 0.12	50.0	10	0.90 ± 0.02	1.30 ± 0.03
60.0	10	1.31 ± 0.24	2.02 ± 0.36	60.0	6	1.24 ± 0.18	1.84 ± 0.26
70.0	12	2.01 ± 0.34	3.18 ± 0.53	70.0	10	1.33 ± 0.17	2.04 ± 0.26
		10 vol % ethanol				15 vol % ethanol	
2.7	6	0.12 ± 0.04	0.14 ± 0.04	3.2	10	0.10 ± 0.02	0.11 ± 0.03
22	10	0.27 ± 0.01	0.34 ± 0.01	20.6	6	0.24 ± 0.07	0.29 ± 0.09
40.0	10	0.53 ± 0.03	0.71 ± 0.04	40.0	10	0.47 ± 0.02	0.62 ± 0.03
50.0	6	0.65 ± 0.12	0.91 ± 0.17	50.0	10	0.58 ± 0.05	0.78 ± 0.07
60.0	6	0.84 ± 0.07	1.21 ± 0.10	60.0	10	0.71 ± 0.02	0.99 ± 0.03
70.0	3	1.03 ± 0.16	1.52 ± 0.23	70.0	3	0.83 ± 0.04	1.20 ± 0.06
		20 vol % ethanol				5 vol % 1-propanol	
3.0	10	0.14 ± 0.05	0.15 ± 0.05	0.2	10	0.08 ± 0.02	0.10 ± 0.03
22.6	6	0.22 ± 0.02	0.26 ± 0.02	22.0	6	0.31 ± 0.07	0.41 ± 0.09
40.0	10	0.37 ± 0.11	0.47 ± 0.14	40.0	10	0.63 ± 0.06	0.88 ± 0.09
50.0	10	0.46 ± 0.00	0.60 ± 0.00	50.0	10	0.80 ± 0.01	1.14 ± 0.01
60.0	10	0.55 ± 0.11	0.74 ± 0.14	60.0	10	1.05 ± 0.10	1.55 ± 0.15
70.0	6	0.59 ± 0.19	0.81 ± 0.25	70.0	6	1.42 ± 0.23	2.17 ± 0.42
		10 vol % 1-propanol				15 vol % 1-propanol	
3.9	6	0.16 ± 0.02	0.18 ± 0.02	3.0	10	0.12 ± 0.01	0.13 ± 0.02
22.0	6	0.30 ± 0.05	0.38 ± 0.06	21.5	10	0.27 ± 0.05	0.33 ± 0.06
40.0	10	0.48 ± 0.01	0.65 ± 0.01	40.0	10	0.39 ± 0.02	0.50 ± 0.03
50.0	6	0.69 ± 0.13	0.95 ± 0.18	50.0	10	0.45 ± 0.05	0.60 ± 0.07
60.0	10	0.77 ± 0.08	1.09 ± 0.12	60.0	6	0.45 ± 0.13	0.62 ± 0.19
70.0	9	0.81 ± 0.12	1.19 ± 0.18	70.0	3	0.60 ± 0.18	0.84 ± 0.18
		20 vol % 1-propanol				5 vol % 2-propanol	
2.3	10	0.13 ± 0.02	0.14 ± 0.02	3.0	6	0.14 ± 0.04	0.17 ± 0.05
21.5	10	0.16 ± 0.02	0.18 ± 0.02	24.0	10	0.33 ± 0.05	0.44 ± 0.06
40.0	6	0.21 ± 0.01	0.26 ± 0.01	40.0	10	0.64 ± 0.05	0.88 ± 0.07
50.0	10	0.27 ± 0.03	0.34 ± 0.04	50.0	10	0.90 ± 0.05	1.29 ± 0.06
60.0	6	0.29 ± 0.05	0.38 ± 0.11	60.0	10	1.09 ± 0.14	1.61 ± 0.20
70.0	12	0.32 ± 0.11	0.44 ± 0.15	70.0	6	1.29 ± 0.10	1.98 ± 0.16
		10 vol % 2-propanol				15 vol % 2-propanol	
2.0	10	0.14 ± 0.01	0.17 ± 0.01	1.8	10	0.13 ± 0.02	0.15 ± 0.02
22.0	10	0.30 ± 0.04	0.38 ± 0.05	22.1	6	0.31 ± 0.02	0.38 ± 0.02
40.0	10	0.54 ± 0.04	0.72 ± 0.05	40.0	6	0.45 ± 0.02	0.58 ± 0.02
50.0	10	0.73 ± 0.09	1.00 ± 0.12	50.0	10	0.54 ± 0.03	0.72 ± 0.05
60.0	10	0.85 ± 0.11	1.21 ± 0.15	60.0	6	0.73 ± 0.21	1.00 ± 0.28
70.0	6	0.86 ± 0.26	1.27 ± 0.38	70.0	9	0.73 ± 0.09	1.02 ± 0.13
		20 vol % 2-propanol					
2.5	6	0.15 ± 0.02	0.16 ± 0.02				
23.5	10	0.23 ± 0.03	0.26 ± 0.03				
40.0	10	0.33 ± 0.02	0.42 ± 0.02				
50.0	10	0.37 ± 0.03	0.47 ± 0.03				
60.0	10	0.40 ± 0.07	0.53 ± 0.09				
70.0	6	0.47 ± 0.18	0.64 ± 0.24				

[a] n is the number of combinations of vials, each of which produces one value of the Henry's law constant. n is not necessarily 10, which corresponds to 5 vials, but vials were added or dropped depending on the precision of the data. [b] Uncertainties for Henry's law constants represent 95% confidence limits calculated from the standard deviation and student's t values.

$$\sigma = \frac{\kappa\{(\alpha_{13}+\beta_{13}T)-(\alpha_{23}+\beta_{23}T)\}\Omega_3}{2.303RT} = \frac{\kappa\Omega_3(\beta_{13}-\beta_{23})T+\kappa\Omega_3(\alpha_{13}-\alpha_{23})}{2.303RT} = a+\frac{b}{T} \quad (9)$$

where a and b are constants. These constants were determined by two-step regression. First, values of σ were determined at each temperature for a given chlorinated ethylene−alcohol combination by linear regression of eq 5 with f as a variable. The slope of the resulting line is σ. In this regression, the intercept ($\log H_w$) was fixed at the value regressed from eq 6. In the experiments at refrigerated and room temperatures, temperatures were not exactly the same for different alcohol concentrations. In these cases, the temperatures 2.0 °C and 22.0 °C, respectively, were used for convenience. In the second step, values of σ were plotted versus $1/T$. A linear regression was performed, and the constants a and b were obtained from the intercept and slope of the resulting straight line, respectively.

Finally, combining eqs 5, 6, and 9, Henry's law constants are expressed as a continuous function with respect to both f and T:

$$\log H = A + \frac{B}{T} + C\ln T - \left(a+\frac{b}{T}\right)f \quad (10)$$

The five coefficients A, B, C, a, and b are independent of f and T and characteristic of chlorinated ethylene−alcohol combinations. Note that the interfacial tension introduced in the derivation of eq 10 is only a mathematical expression to allow the temperature dependence of σ to be expressed. No measurements of interfacial tension were conducted, and this study did not involve prediction of σ from interfacial tension as was performed by Rubino and Yalkowsky.[37]

Thermodynamic Analysis. Analysis of Henry's law constants from a thermodynamic viewpoint provides a deeper understanding of the dissolution process and its

Table 2. Comparison of Experimentally Determined Henry's Law Constants

			H				
solute	solvent	t/°C	this work	ref 29	ref 36	ref 35	ref 34
tetrachloroethylene	water	21.6	0.64 ± 0.09				
		24.8		0.723 ± 0.035[a]			
		40.0	1.33 ± 0.13			1.303 ± 0.023[c]	
		50.0	1.77 ± 0.26			1.773 ± 0.094	
		60.0	2.52 ± 0.62			2.491 ± 0.046	
	15 vol % ethanol	20.6	0.40 ± 0.13				
		25.0					0.484
	20 vol % ethanol	22.6	0.34 ± 0.01				
		25.0					0.299
	5 vol % 2-propanol	40.0	1.15 ± 0.16			1.061 ± 0.027[d,e]	
	10 vol % 2-propanol	40.0	0.87 ± 0.09			0.862 ± 0.027[f]	
	15 vol % 2-propanol	22.1	0.49 ± 0.05				
		25.0					0.416
	20 vol % 2-propanol	23.5	0.33 ± 0.05				
		25.0					0.315
trichloroethylene	water	21.6	0.35 ± 0.05				
		24.8		0.392 ± 0.015			
		40.0	0.74 ± 0.05			0.693 ± 0.009	
		50.0	1.00 ± 0.08			0.922 ± 0.048	
		50.4			0.99 ± 0.08[b]		
		57.1			1.20 ± 0.08		
		60.0	1.31 ± 0.24			1.273 ± 0.02	
		70.0	2.01 ± 0.34				
		71.8			1.60 ± 0.51		
	5 vol % 2-propanol	40.0	0.64 ± 0.05			0.595 ± 0.012	
	10 vol % 2-propanol	40.0	0.54 ± 0.04			0.508 ± 0.015	
cis-dichloroethylene	water	21.6	0.14 ± 0.02				
		24.8		0.167 ± 0.011			
		34.6		0.216 ± 0.011			
		40.0	0.29 ± 0.01				
trans-dichloroethylene	water	21.6	0.34 ± 0.05				
		24.8		0.384 ± 0.008			
		34.6		0.545 ± 0.010			
		40.0	0.69 ± 0.05				

[a] Uncertainties for Henry's law constants represent standard deviations.[29] [b] Mean values and standard deviations were read from a figure in ref 36. [c] Uncertainties for Henry's law constants in water represent standard deviations.[35] [d] Uncertainties for Henry's law constants in aqueous 2-propanol represent 68% confidence limits.[35] [e] 40 $g \cdot L^{-1}$ 2-propanol ≅ 5 vol %.[35] [f] 80 $g \cdot L^{-1}$ 2-propanol ≅ 10 vol %.[35]

driving force. A linear regression analysis method described in the literature[41−43] was applied to the experimentally determined Henry's law constants in order to derive thermodynamic functions of dissolution ($\Delta_{\text{dis}}G$, $\Delta_{\text{dis}}H$, $\Delta_{\text{dis}}S$, and $\Delta_{\text{dis}}C_p$) and the associated standard errors. In short, this method is based on a Taylor series expansion of $R \ln k_H$ around a reference temperature. The details of the method are provided in the Supporting Information.

Results and Discussion

Measured Henry's Law Constants. The experimentally determined Henry's law constants of trichloroethylene in ethanol, 1-propanol, and 2-propanol solutions are shown in Table 1. Because of the large amount of data, trichloroethylene was selected as a representative compound, and corresponding tables for tetrachloroethylene, *cis*-dichloroethylene, and *trans*-dichloroethylene are included in the Supporting Information. Henry's law constants generally increase with increasing temperature and decrease with increasing alcohol concentration for all four compounds. Relative errors are largest at the refrigerated temperature and 70.0 °C, and this is consistent with observations by other investigators employing the equilibrium partitioning in closed systems method.[29,36] In Table 2, Henry's law constants from this study are compared with previously reported values by four research groups including the original measurements with the equilibrium partitioning in closed systems method[29] and those in which cosolvent addition[34,35] and/or an extended temperature range[36] were studied. For all systems shown here, there is good agreement between the reported values. It follows that the experimentally determined Henry's law constants in this study can be regarded as accurate.

Figure 1 shows Henry's law constants of trichloroethylene in (a) ethanol, (b) 1-propanol, and (c) 2-propanol solutions. At 5 vol % alcohol, Henry's law constants are not significantly different from those for water. At higher concentrations, the deviation from water becomes clear for all but the values at the refrigerated temperature. At the lowest temperature, a relationship between alcohol concentration and Henry's law constants is not apparent because of scatter in the data. At 20 vol % 1-propanol and 2-propanol, Henry's law constants do not increase with statistical significance with increasing temperature. This is likely because the effects of increasing solubility (which decreases *H*) and increasing vapor pressure (which increases *H*) with the elevation of temperature cancel under these conditions. 1-Propanol and 2-propanol have a greater effect on the Henry's law constants than does ethanol. These results are consistent with the increased hydrophobicity of these alcohols and, thus, their larger capability to solubilize the chlorinated ethylenes.

Figure 2 depicts a comparison of the Henry's law constants for tetrachloroethylene, trichloroethylene, *cis*-dichloroethylene, and *trans*-dichloroethylene in ethanol solutions. At low concentrations of ethanol, Henry's law constants follow the order tetrachloroethylene > trichloroethylene > *trans*-dichloroethylene > *cis*-dichloroethylene. At 20 vol % ethanol, the order becomes tetrachloroethylene > *trans*-dichloroethylene > trichloroethylene > *cis*-dichlo-

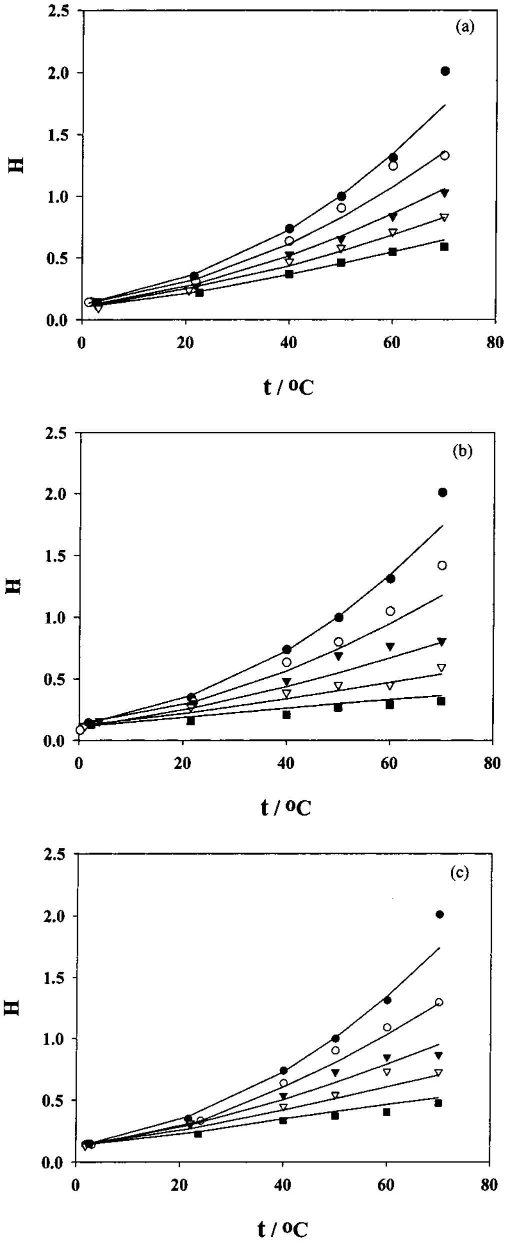

Figure 1. Henry's law constants of trichloroethylene in aqueous solutions of (a) ethanol, (b) 1-propanol, and (c) 2-propanol. The symbols represent averages of experimental values (error bars omitted for clarity). The symbols correspond to different alcohol concentrations: (●) 0 vol %; (○) 5 vol %; (▼) 10 vol %; (▽) 15 vol %; (■) 20 vol %. The lines represent estimated values using eq 10.

roethylene. This reversal of trichloroethylene and *trans*-dichloroethylene was also observed for 1-propanol and 2-propanol, and at 20 vol % 1-propanol, the Henry's law constants of *trans*-dichloroethylene are larger than even those of tetrachloroethylene. This suggests that the more hydrophobic tetrachloroethylene and trichloroethylene are more susceptible to the solubilization effect of alcohol than the less hydrophobic dichloroethylenes. For instance, the Henry's law constants of tetrachloroethylene and trichloroethylene at 70.0 °C decrease by 90% and 84%, respectively, as the 1-propanol concentration is increased from 0 to 20 vol %. Under the same conditions, the Henry's law constants of *cis*-dichloroethylene and *trans*-dichloroethylene decrease by 63% and 71%, respectively.

Equations for the Estimation of Henry's Law Constants. The solid lines in Figures 1 and 2 represent estimated Henry's law constants using eq 10. Overall the lines fit the experimental data points well. A comparison of experimental and estimated values for trichloroethylene is given in Figure 3. Corresponding figures for tetrachloroethylene, *cis*-dichloroethylene, and *trans*-dichloroethylene are included in the Supporting Information. Except for a few of the higher Henry's law constant values, differences between the experimental and estimated values are minimal. Parameters used in eq 10 for all chlorinated ethylene–alcohol combinations are provided in Table 3 together with R^2 values for each equation.

It is necessary to discuss the limitations of eq 10. Deviations between the estimated and experimental values are observed at 70.0 °C and at 5 vol % alcohol. The deviation at the highest temperature arises from the larger errors associated with these values which lessen the "weight" of the data points in the regression. This deviation is inherent because measurement of Henry's law constants is inevitably less precise at high temperature. At the 5 vol % alcohol concentration, Henry's law constants are slightly underestimated by eq 10. Banerjee and Yalkowsky[44] reported that a significant cosolvent effect is not induced at this low concentration, and thus, use of eq 3 may not be appropriate. Additionally, eq 10 should not be extended to a higher cosolvent concentration range than employed here without further investigation. The use of eq 4 to replace S with H is based on an assumption that the mutual solubility between the solute and the solvent is low, and this assumption is valid only at low cosolvent concentrations.[10,11,45,46] At higher alcohol concentrations, empirical relationships of similar form to eq 5 may provide an alternative.[34]

Thermodynamic Analysis. Derived thermodynamic functions of dissolution ($\Delta_{\mathrm{dis}}G$, $\Delta_{\mathrm{dis}}H$, $\Delta_{\mathrm{dis}}S$, and $\Delta_{\mathrm{dis}}C_{\mathrm{p}}$) are provided in the Supporting Information together with values previously reported by other investigators. The influence of temperature on the enthalpy and entropy of dissolution was determined using the following relationships:

$$\Delta_{\mathrm{dis}}H_T = \Delta_{\mathrm{dis}}H_{298.15} + \Delta_{\mathrm{dis}}C_{\mathrm{p}298.15}(T - 298.15) \quad (11)$$

$$\Delta_{\mathrm{dis}}S_T = \Delta_{\mathrm{dis}}S_{298.15} + \Delta_{\mathrm{dis}}C_{\mathrm{p}298.15} \ln \frac{T}{298.15} \quad (12)$$

Overall, increasing temperature results in higher Henry's law constants, lower $\Delta_{\mathrm{dis}}H$ values (consistent with the changes in H), and lower $\Delta_{\mathrm{dis}}S$ values (inconsistent with the changes in H). Similar trends in $\Delta_{\mathrm{dis}}H$ were observed by Heron et al.[32] On the other hand, from the viewpoint of alcohol concentration, increasing ethanol concentration leads to lower Henry's law constants, lower $\Delta_{\mathrm{dis}}H$ values (inconsistent with the changes in H), and lower $\Delta_{\mathrm{dis}}S$ values (consistent with the changes in H). From these trends, it can be concluded that the temperature dependence of the Henry's law constants is enthalpy driven, while entropy controls the alcohol concentration dependence.

Conclusion

Henry's law constants of four chlorinated ethylenes (tetrachloroethylene, trichloroethylene, *cis*-dichloroethylene, and *trans*-dichloroethylene) in aqueous alcohol solutions (ethanol, 1-propanol, and 2-propanol) were experimentally determined using the equilibrium partitioning in closed systems method. The Henry's law constants increased with increasing temperature and decreased with increasing alcohol concentration in most cases. The relative errors associated with the Henry's law constants were

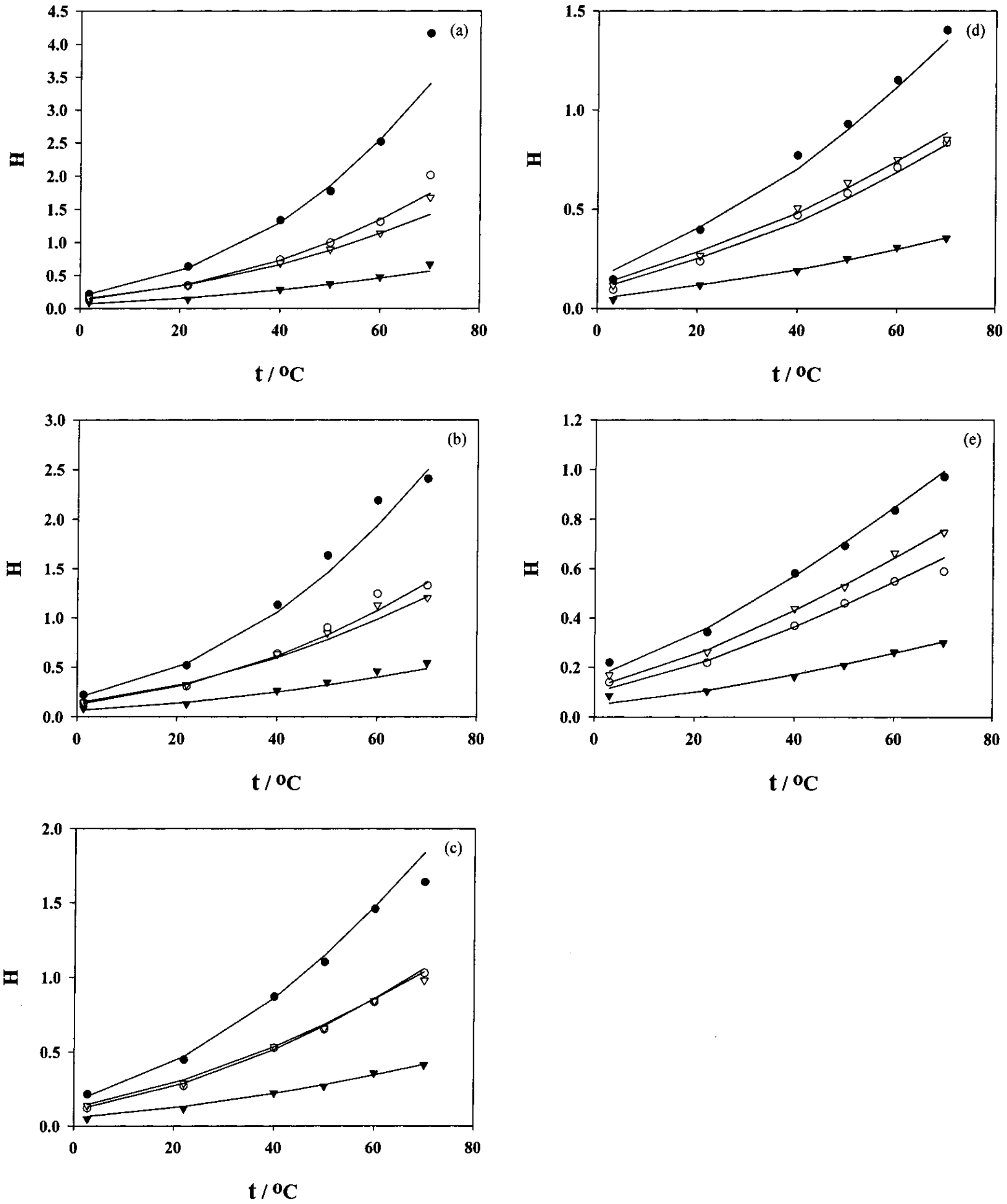

Figure 2. Henry's law constants of tetrachloroethylene, trichloroethylene, *cis*-dichloroethylene, and *trans*-dichloroethylene in aqueous ethanol solutions with ethanol concentrations of (a) 0 vol %, (b) 5 vol %, (c) 10 vol %, (d) 15 vol %, and (e) 20 vol %. The symbols represent averages of experimental values (error bars omitted for clarity) and correspond to different compounds: (●) tetrachloroethylene; (○) trichloroethylene; (▼) *cis*-dichloroethylene; (▽) *trans*-dichloroethylene. The lines represent estimated values using eq 10.

Table 3. Parameters for the Estimation of Henry's Law Constants

cosolvent	solute	*A*	*B*	*C*	*a*	*b*	R^2 value
ethanol	tetrachloroethylene	55.754	−3950	−7.487	11.985	−3195	0.967
	trichloroethylene	53.724	−3746	−7.291	9.027	−2358	0.979
	cis-dichloroethylene	46.085	−3173	−6.352	4.217	−985	0.967
	trans-dichloroethylene	53.180	−3580	−7.296	6.007	−1590	0.975
1-propanol	tetrachloroethylene	55.754	−3950	−7.487	20.626	−5539	0.928
	trichloroethylene	53.724	−3746	−7.291	15.752	−4239	0.964
	cis-dichloroethylene	46.085	−3173	−6.352	9.475	−2519	0.960
	trans-dichloroethylene	53.180	−3580	−7.296	10.714	−2937	0.967
2-propanol	tetrachloroethylene	55.754	−3950	−7.487	18.351	−5089	0.961
	trichloroethylene	53.724	−3746	−7.291	13.451	−3712	0.974
	cis-dichloroethylene	46.085	−3173	−6.352	8.102	−2214	0.921
	trans-dichloroethylene	53.180	−3580	−7.296	10.166	−2880	0.969

largest at the refrigerated temperature and 70.0 °C. A comparison between the four chlorinated ethylenes revealed that the more hydrophobic compounds are more susceptible to the diminishing effect of the alcohol addition on Henry's law constants. An equation was derived to express the Henry's law constants as a continuous function of temperature and alcohol concentration for the purpose of estimation. A linear regression equation was adopted to derive thermodynamic functions of dissolution from the experimental Henry's law constants. Analysis of the ther-

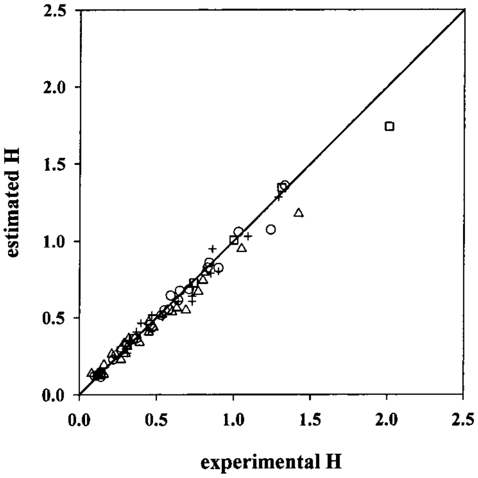

Figure 3. Comparison of estimated (via eq 10) and measured Henry's law constants for trichloroethylene. The symbols represent average values. The symbols correspond to the different cosolvents added: (□) water; (○) ethanol; (△) 1-propanol; (+) 2-propanol. The data for all temperatures and alcohol concentrations are included.

modynamic functions revealed that the temperature dependence of Henry's law constants is driven by enthalpy, while entropy controls the alcohol concentration dependence.

Acknowledgment

We thank Megan Kari for conducting preliminary experiments. The comments provided by the reviewers of this manuscript made this submission a much more substantial contribution.

Supporting Information Available:

Tables containing experimentally determined Henry's law constants for tetrachloroethylene, *cis*-dichloroethylene, and *trans*-dichloroethylene, plots of estimated versus experimental Henry's law constants for tetrachloroethylene, *cis*-dichloroethylene, and *trans*-dichloroethylene, and derived thermodynamic functions of dissolution ($\Delta_{dis}G$, $\Delta_{dis}H$, $\Delta_{dis}S$, and $\Delta_{dis}C_p$). This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review April 23, 2001. Accepted November 12, 2001. This research was enabled by the Rose and Joseph Ling Environmental Engineering Fellowship for T.S.

JE010132N