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The Solubility of the Chloromethanes in Water

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Summary. There are more than 150 papers that report on the solubility of the four chloromethanes in water. Volume 62 of the Solubility Data Series compiles and evaluates the papers concerned with the liquid–liquid solubility of the chloromethanes with water. A similar evaluation has not been carried out for the vapor–liquid solubility at a partial pressure up to the saturation vapor pressure of the four chloromethanes. This paper uses the liquid–liquid evaluated solubility values to calculate vapor–liquid *Henry*'s constants. They are compared with a compilation of *Henry*'s constants with good agreements between the calculated constants and the median of the compiled constants. It is believed that the calculated constants are a reliable set of values to use for the vapor–liquid solubility of the chloromethanes in water.

Keywords. Aqueous solution; Chloromethanes; *Henry*'s constant; Solubility.

Introduction

The chloromethanes: tetrachloromethane, trichloromethane, dichloromethane, and chloromethane are important industrial chemicals and also environmental pollutants. Their solubility in water is important to workers in many fields. A large number of studies of the equilibrium of the liquid–liquid and liquid–vapor systems are in literature. *A. L. Horvath* [1] and *R. Sander* [2] have summarized most of these data.

The liquid–liquid and the liquid–vapor studies should be compatible. The liquid–liquid solubility should be the same, or nearly the same, as the liquid–vapor solubility at the saturation pressure of the chlorocarbon at the same temperature. The chlorocarbon molality in the water phase of the liquid–liquid equilibrium divided by the chlorocarbon vapor pressure in bar should give the value of *Henry*'s constant determined in the liquid vapor study in the units of $\mathrm{mol\,kg^{-1}\,bar^{-1}}$. This paper makes that comparison for the $CCl_4 + H_2O$, $CHCl_3 + H_2O$ and $CH_2Cl_2 + H_2O$ systems. The $CH_3Cl + H_2O$ system is treated differently because no liquid–liquid solubility data are available for the lower boiling CH_3Cl over the desired temperature interval.

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Dedicated to Prof. Dr. *Heinz Gamsjäger* on the occasion of his 70th birthday

Results and Discussion

A. L. Horvath [1] has compiled and evaluated the liquid–liquid solubility data for three of these systems. His evaluated data are given as mass percent chlorocarbon in water as a function of temperature. His values at five-degree intervals are given in his publication. *Horvath* also evaluated data on the solubility of water in the chlorocarbon. This allows a *Raoult*'s law correction of the vapor pressure of the chlorocarbon due to the dissolved water at equilibrium. We find this correction is negligible for the three digit significant figures we use, and so we have not applied it.

Accurate vapor pressure values are needed. The NIST Chemical Webbook [2] gives evaluated *Antoine* Equations for the chlorocarbons and vapor pressure values from these equations were used. These equation constants are given in Table 1 along with the chlorocarbon registry number, molecular mass, and normal boiling point.

R. Sander's compilation of liquid–vapor data is in the NIST Chemical Webbook. He uses *Henry*'s constant, $k_H = m/p$, with molality in mol kg^{-1}, pressure in bar, and k_H in $\text{mol kg}^{-1}\text{bar}^{-1}$. His data have not been evaluated. He gives k_H at 298.15 K and the slope, $\text{dln}k_H/\text{d}(1/T)$. A test of the present calculation is to compare the *Henry*'s constant and slope with *Sander*'s values. The test is not as definitive as we had hoped because *Horvath*'s and *Sander*'s lists are not completely independent. Some references appear on both lists.

In this work we have converted *Horvath*'s evaluated data to *Henry*'s constants by converting the mass per cent values to molalities and then dividing by the chlorocarbon saturation vapor pressure as calculated from the *Antoine* equation derived by NIST from the vapor pressure data of *Stull* [3]. The calculated *Henry*'s constants were fitted to a *van't Hoff* equation and the value at 298.15 K and the slope were compared with the values tabulated by *Sander.*

What we outline above works well for the first three systems, but *Horvath* did not report liquid–liquid data for the low boiling CH_3Cl. For this system we have used the early classical study of the liquid–vapor equilibrium by *Glew* and *Moelwyn-Hughes* [4]. These researchers have the reputation of being very careful,

Table 1. Some properties of chloromethane, dichloromethane, trichloromethane, and tetrachloromethane as listed in the NIST Chemistry Webbook [2]

Substance formula registry no.	Mol mass/g mol^{-1}	Normal bp/K	Vapor pressure: *Antoine* equation constants		
			A	B	C
CH_3Cl [74-87-3]	50.49	247	4.91858	1427.529	45.137
CH_2Cl_2 [75-09-2]	84.93	313 ± 0.1	3.97323	1016.865	-56.623
$CHCl_3$ [67-66-3]	119.38	334.3 ± 0.2	4.20772	1233.129	-40.953
CCl_4 [56-23-5]	153.82	349.8 ± 0.3	4.56992	1486.455	-8.612

Antoine equation: $\log_{10}(p/\text{bar}) = \text{A} - (\text{B}/((T/\text{K}) + \text{C}))$

Table 2. The solubility of tetrachloromethane in water from 273.15 to 308.15 K

T/K	Weight fraction 100 w_2	Molality $m_2/\mathrm{mol\,kg^{-1}}$	Vapor pressure p_2/bar	*Henry*'s constant $k_H/\mathrm{mol\,kg^{-1}\,bar^{-1}}$
273.15	0.0970	0.006312	0.044704	0.1412
278.15	0.0898	0.005843	0.058335	0.1002
283.15	0.0846	0.005505	0.075273	0.0731
288.15	0.0813	0.005290	0.096114	0.0550
293.15	0.0800	0.005205	0.121519	0.0428
298.15	0.0813	0.005290	0.152218	0.0347
303.15	0.0832	0.005413	0.189012	0.0286
308.15	0.0878	0.005713	0.232770	0.0246

and in our judgment their data are among the most reliable available. Thus, we present their data for the $CH_3Cl + H_2O$ liquid–vapor system.

Tetrachloromethane + Water

Horvath [1] found and compiled the data from 41 laboratories. Of these he discarded the data from 16 as unreliable, and used the remaining 26 over the 273 to 308 K temperature interval for his smoothing equation. The curve shows a distinct minimum at 294 K and a solubility of 0.0799 mass percent. We have converted *Horvath*'s mass percent data at five-degree intervals to molality and divided the values by the CCl_4 vapor pressure at each temperature to obtain *Henry*'s constant. The data are in Table 2.

Sander [2] reports unevaluated data on the solubility of CCl_4 vapor in liquid water from 22 papers. The 25 values of *Henry*'s constants at 298.15 K range from 0.028 to 0.051 with a median of 0.034 and an average of 0.036 ± 0.005. He reports 17 slopes, $(\mathrm{d}\ln k_H)/\mathrm{d}(1/T)$, which range from 1100 to 5600 with a median of 4200. The average is 4087 ± 467 with the greatest and least values omitted.

The *Henry* constants calculated in this work were fitted to the equation $\ln k_H = -17.4828 + 4219.21/T$ with $r^2 = 0.9914$. The *Henry*'s constant at 298.15 K is 0.0357 and the slope is 4219; which yields $\Delta H_s = -35.1\,\mathrm{kJ\,mol^{-1}}$. Both values agree well with the medians of *Sander*'s compiled data. We had hoped this comparison would be between independent data sets. Since *Horvath* used 7 of the 22 references used by *Sander* that hope was not met. However, we believe that *Horvath*'s evaluation of the liquid–liquid data is reliable and that converting it to liquid–vapor data valid at tetrachloromethane partial pressures up to the saturation pressure at each temperature is successful.

Trichloromethane + Water

A. L. Horvath [1] found and compiled the data from 54 references to the liquid–liquid equilibrium of the system. Of the 54 references he discarded 14 as unreliable. He combined data from 40 laboratories to obtain an equation for the mass percent of $CHCl_3$ in water as a function of temperature. His values at five-degree intervals from 273.15 to 333.15 K are given in Table 3. His equation shows a

Table 3. The solubility of trichloromethane in water from 273.15 to 333.15 K

T/K	Weight fraction 100 w_2	Molality m_2/mol kg^{-1}	Vapor pressure p_2/bar	*Henry*'s constant k_H/mol kg^{-1} bar^{-1}
273.15	0.988	0.08359	0.07889	1.060
278.15	0.938	0.07932	0.10208	0.777
283.15	0.895	0.07565	0.13070	0.579
288.15	0.857	0.07421	0.16567	0.437
293.15	0.825	0.06968	0.20804	0.335
298.15	0.798	0.06738	0.25895	0.260
303.15	0.778	0.06568	0.31962	0.205
308.15	0.763	0.06441	0.39142	0.165
313.15	0.755	0.06372	0.47579	0.134
318.15	0.752	0.06347	0.57429	0.111
323.15	0.755	0.06372	0.68858	0.0926
328.15	0.763	0.06441	0.82041	0.0785
333.15	0.778	0.06568	0.97163	0.0676

minimum in solubility of 0.752 mass per cent at 318.18 K. He has evaluated both the solubility of trichloromethane in water and the solubility of liquid water in trichloromethane.

R. Sander [2] has compiled 32 values of *Henry*'s constant from 25 papers on the solubility of trichloromethane vapor in liquid water. Some papers report several values by different methods. These data have not been evaluated. Nine of these papers are also in *Horvath*'s compilation. They are available on the NIST Chemistry WebBook site [2]. *Sander*'s values of the *Henry*'s constant at 298.15 K range from 0.15 to 0.90 with a median of 0.25 and an average of 0.29 ± 0.13 for all, or 0.26 ± 0.035 after omitting the three greatest outriders. He reports 20 slopes, $(\mathrm{dln}k_H)/\mathrm{d}(1/T)$, that range from 2800 to 7300 with a median of 4200/4300. The average is 4282 ± 332 with omission of the three least filling values.

The values calculated in this work were fitted to the equation $\ln k_H = -15.3711 + 4195.38/T$ with $r^2 = 0.9974$. The calculated value of *Henry*'s constant at 298.15 K is 0.273 and the slope is 4195 which gives $\Delta H_s = -34.9\,\mathrm{kJ\,mol^{-1}}$. All these values are in satisfactory agreement with the median and average of *Sander*'s collection of data. The comparison is not as definitive as we hoped because 9 of the 25 references used by *Sander* were also used by *Horvath*.

Dichloromethane + Water

Horvath [1] located 32 research groups who reported the solubility of CH_2Cl_2 in water between 273 and 333 K. Of these he rejected 7, which included all data over 308 K. The smoothing curve shows a distinct minimum at 299 K and a solubility of 1.70 mass percent. Again, *Horvath*'s smoothed values at 5-degree intervals from 273 to 308 K were converted to molality and divided by the equilibrium vapor pressure to obtain *Henry*'s constants, which are given in Table 4.

Sander [2] reports 18 values of the *Henry*'s constant at 298.15 K from 14 papers. Five of these papers are also reported by *Horvath* so the data sets are

Table 4. The solubility of dichloromethane in water from 273.15 to 308.15 K

T/K	Weight fraction 100 w_2	Molality $m_2/\mathrm{mol\,kg^{-1}}$	Vapor pressure p_2/bar	*Henry*'s constant $k_H/\mathrm{mol\,kg^{-1}\,bar^{-1}}$
273.15	2.126	0.2558	0.1892	1.357
278.15	1.977	0.2375	0.2415	0.987
283.15	1.860	0.2214	0.3050	0.729
288.15	1.766	0.2117	0.3813	0.559
293.15	1.722	0.2063	0.4722	0.440
298.15	1.701	0.2038	0.5795	0.354
303.15	1.712	0.2051	0.7055	0.294
308.15	1.754	0.2102	0.8521	0.249

not as independent as we had hoped. The values range from 0.31 to 1.2. We dropped the two greatest values of 1.2 and 0.85, the remaining 16 values averaged 0.38 ± 0.05. Eleven of the studies included the temperature dependence. The slope, $(\mathrm{dln}k_H)/(1/T)$, ranged from 3600 to 4500 with a median of 4100 and an average of 4027 ± 283.

The *Henry* constants calculated in this work are in Table 4. They were fitted to the equation $\ln k_H = -14.725 + 4088.77/T$ with $r^2 = 0.9943$. The enthalpy of solution calculated from the slope is $\Delta H_s = -34.0\,\mathrm{kJ\,mol^{-1}}$. The *Henry*'s constant at 298.15 is 0.364 and the slope is 4089 both in good agreement with *Sander*'s compilation.

Chloromethane + Water

Glew and *Moelwyn-Hughes* [4] measured the solubility of CH_3Cl in water as a function of pressure and temperature. The partial pressures ranged from about 0.27 to 1.23 atm and the temperatures ranged from 277 to 353 K. The variation with pressure is reported for only 298.16 K in the paper. The *Henry*'s constants were given as $k_H = p/c$ with pressure in mmHg, concentration in $\mathrm{mol\,L^{-1}}$, and *Henry*'s constant in $\mathrm{mmHg\,L\,mol^{-1}}$. We have converted pressure to bar and concentration to molality, assuming solution and water density were the same, to calculate the *Henry*'s constants in the units used in this paper. The values are given in Table 5. The concentrations and molalities are given for 1 atm partial pressure CH_3Cl.

Sander [2] reports 11 studies of *Henry*'s constant of the $CH_3Cl + H_2O$ system. The 298.15 K *Henry*'s constant values range from 0.029 to 0.13 with a median of 0.11 and an average, with the smallest value omitted, of 0.11 ± 0.01. Of these studies five included temperature dependent values and the slope, $(\mathrm{dln}k_H)/\mathrm{d}(1/T)$, ranges from -630 to 4200 with the median 2900. *Sander* did not include the *Glew* and *Moelwyn-Hughes* data in his compilation.

The values of *Henry*'s constant we calculated are in Table 5. They were fitted to the equation $\ln k_H = -10.708 + 2537.17/T$ with $r^2 = 0.9935$. The enthalpy of solution from the slope is $\Delta H_s = -21.1\,\mathrm{kJ\,mol^{-1}}$. The 298.15 K *Henry*'s constant is 0.111, in excellent agreement with the average of *Sander*'s data. The slope of 2537 is 14% less than the median of 2900. The slopes given by *Sander* show a large

Table 5. The solubility of chloromethane in water at 1 atm partial pressure from 277 to 353 K. Based on data from *Glew* and *Moelwyn-Hughes* [4]

T/K	*Henry*'s constant $10^{-3}\,k/\mathrm{mmHg\,L\,mol^{-1}}$	Solubility $c_l/\mathrm{mol\,L^{-1}}$	Solubility $m_l/\mathrm{mol\,kg^{-1}}$	*Henry*'s constant $k_H/\mathrm{mol\,kg^{-1}\,bar^{-1}}$
277.24	3.28	0.2317	0.2344	0.231
283.32	4.26	0.1784	0.1801	0.178
288.21	5.11	0.1487	0.1500	0.148
293.18	6.12	0.1242	0.1252	0.124
298.16	7.18	0.1059	0.1068	0.105
313.06	11.06	0.0687	0.0695	0.069
322.93	13.94	0.0545	0.0553	0.055
333.14	16.95	0.0448	0.0457	0.045
343.21	20.6	0.0369	0.0378	0.037
353.23	23.8	0.0319	0.0329	0.032

scatter. It is difficult to judge the significance of the difference in the median and our value.

Conclusion

In this paper *Horvath*'s [1] evaluated liquid–liquid data for three chlorocarbon + water systems along with literature vapor pressures of the chlorocarbons have been used to calculate the *Henry*'s constants at the liquid–liquid saturation point. It is assumed that the calculated *Henry*'s constants will be reliable at lower chlorocarbon partial pressures than the saturation pressure at each temperature. The results have been checked against *Sander*'s [2] compilation of *Henry*'s constants and their slopes, $(\mathrm{dln}k_H)/\mathrm{d}(1/T)$, with good success. The weakness of the comparison is that just over one-third of *Sander*'s references were also used by *Horvath* so the lists are not independent. In spite of this the author feels that the paper gives a self-consistent reliable set of values that can be used with good confidence.

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References

[1] Horvath AL (1995) In: Horvath AL, Getzen FW (eds), Solubility Data Series Volume 60, Halogenated Methanes with Water, Oxford University Press; CCl_4 pp 17–21 (evaluation), 22–57 (compiled data); $CHCl_3$ pp 92–96 (evaluation), 97–131 (compiled data); CH_2Cl_2 pp 151–155 (evaluation), 156–176 (compiled data)

[2] Sander R (2001) In: NIST Chemistry Webbook, Standard Reference Database Number 69, July 2001 release, http://www.nist.gov/srd

[3] Stull DR (1947) Ind Eng Chem **39**: 517

[4] Glew DN, Moelwyn-Hughes EA (1953) Disc Faraday Soc **15**: 150