Distribution Coefficients of Chlorinated Hydrocarbons in Dilute Air–Water Systems for Groundwater Contamination Applications

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Distribution coefficients are reported for 21 chlorinated hydrocarbons plus benzene and toluene in dilute air–water systems over the temperature range 0–30 °C. It is anticipated that these data might prove especially useful for groundwater contamination applications. The measurements were performed with a simple experimental apparatus consisting of an equilibrium cell followed by gas-chromatographic analysis. This technique is shown to achieve a random error of less than ±1% and a systematic error, primarily attributable to gas-chromatograph peak separation and integration error, of less than 5% for most of the compounds considered which exhibit room-temperature distribution coefficients between 100 and 1000. The experimental distribution coefficients agreed reasonably well with those estimated from UNIFAC infinite dilution activity coefficients.

Introduction

The contamination of groundwater with solvents and other toxic wastes is an important current national problem, which is only expected to intensify in the near future (*1*, *2*). In order to provide a rational basis for regulatory legislation in situ cleanup strategies, evaluation of possible aboveground separations processes, groundwater reservoir modeling, and related activities, it is absolutely imperative to have a quantitative measure of how chemical compounds distribute themselves in the environment between air, water, and soil, as a function of ambient conditions. For the most part, however, these data are nonexistent.

In particular, when the compounds are relatively volatile and exhibit low solubility in water, air stripping may be a viable aboveground treatment technique. Some compounds which exhibit these characteristics are certain chlorinated hydrocarbons, commonly used as solvents, which also tend to be responsible for some pervasive groundwater contamination problems (e.g., see ref *3*). However, accurate and extensive air–water distribution coefficient measurements for these species are rare. The most comprehensive compilation of distribution coefficients for these compounds found in the literature (*4*) cites only two sources of such experimental data, both at room temperature only (*5*, *6*). Of these two, one (*6*) presents calculated distribution coefficients with no citations for cases which differ from the authors' results, and the other is a private communication (*5*).

Brown's (*5*) experiments were primarily directed at determining purge efficiencies, but some direct measurements of distribution coefficients at infinite dilution were also performed. The technique involves first preparing a dilute, known quantity of the liquid solution. Then, a 25-cm^3 aliquot of this solution is withdrawn into a 50-cm^3 syringe followed by 25 cm^3 of pure dry nitrogen. The syringe is then shaken for 2–5 min in order to attain equilibrium between the liquid and the nitrogen. The gas phase is then introduced into a calibrated volume sample injection loop for analysis in a gas chromatograph. Although this technique is obviously quick and simple, several drawbacks are apparent. First, the standard solutions are very difficult to prepare and preserve when low solubility, high vapor pressure compounds are involved. In order to generate reproducible standards with these compounds, it is necessary first to dissolve them in a suitable solvent, such as methanol. The presence of relatively large amounts of the solvent serves as a potential source of error. Second, the syringe technique is not very suitable for accurate temperature control, or indeed, temperature studies in general. Finally, it is very difficult to correct for errors arising from the dead volume in the tip of the syringe which, if a low-gauge (i.e., large-bore) needle is used, could become quite significant.

In the present paper, we report experimental measurements for 21 chlorinated hydrocarbons plus benzene and toluene in the dilute air–water system, obtained with a simple experimental apparatus consisting of an equilibration cell followed by gas-chromatographic analysis. Although the apparatus works especially well for compounds which exhibit large distribution coefficients, with suitable modifications a similar apparatus could be used for other systems of interest as well.

Apparatus and Experimental Procedure

Air–water distribution coefficients were measured by comparing the response of a gas chromatograph for a known quantity of air to that for a known quantity of water. The experimental procedure is described below with reference to Figure 1.

A liquid solution is prepared for analysis by filling the 2.3-L equilibration cell (B) with distilled water, injecting the compound(s) of interest (typically 5 μL), and shaking vigorously for ~5 min. The headspace intentionally left in the cell to enhance mixing is reduced to less than 10 cm^3 with distilled water before the experimental run. Homogeneity of the liquid sample is maintained during the course of an experiment by mechanical agitation with the magnetic stirrer (D) and by the action of the air bubbles. Concentration measurements from various regions of the cell verified that the liquid solution remained homogeneous during the relatively short duration of an experiment. The temperature of the water sample was maintained with a constant-temperature bath. The thermal capacitance of the bath was sufficient to maintain the temperature to within ±0.25 °C over the duration of an experiment. Subambient temperatures were achieved by adding ice. The temperature of the liquid sample was measured with an ordinary laboratory thermometer calibrated at 0 and 100 °C.

In order to equilibrate a known quantity of air with the liquid sample, compressed air is filtered through the activated charcoal trap (A) and then admitted to the equilibration cell via a glass frit (C). After passing through an equilibration height of ~40 cm, the effluent gases from the cell pass through the concentrator trap (G) (part of a Tekmar LSC-1 liquid-sample concentrator) and then through a soap film flowmeter (F). The latter provides a very accurate measurement of the total gas flow through the trap. Total amounts of gas corresponding to 3–4 mL/min for 5 min were typically used. The absolute pressure required to determine the molar volume of air was assumed to be the same as that recorded on a barometer at a nearby airport.

The chlorinated hydrocarbons extracted from the air by the trap are subsequently desorbed at 100 °C into the gas-chro-

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Table I. Distribution Coefficient Data as a Function of Temperature

temp,[a] °C	1,1,1-$C_2H_3Cl_3$	C_2HCl_3	C_2Cl_4
1.0	297.0	131.6	206.9
1.0	297.9	139.5	226.7
1.2	307.0	138.8	236.1
2.5	327.8	168.4	260.4
7.0	418.5	200.9	314.1
10.0	504.0	232.7	370.2
12.0	556.8	254.8	401.0
12.0	569.6	265.8	437.3
12.9	586.2	287.0	452.9
14.0	652.7	309.9	501.5
18.0	766.7	375.0	615.1
18.0	793.4	379.6	627.2
18.0	802.9	375.0	627.5
19.0	828.3	393.5	644.9
19.2	836.7	417.3	633.9
19.5	788.1	396.5	647.9
24.3	1027.6	537.1	868.1
25.2	1094.3	539.9	889.8
25.3	1110.7	545.7	905.4
26.0	1090.2	551.1	896.8
26.0	1131.4	563.8	938.8
26.1	1073.8	558.1	920.7
error,[b] %	±2.5	±2.1	±2.3

[a] Temperature measurement error, ±0.5 °C. [b] Represents overall estimated experimental error as discussed in the text.

matograph nitrogen carrier stream. The compounds were separated and detected in an HP 5700A dual flame ionization detector gas chromatograph, equipped with an 8-ft Supelco $^1/_8$-in. column packed with Carbowax 1500 on 80/100 Carbopack C support, and an HP 3380A recorder/integrator.

Relative concentrations in the liquid sample were determined by withdrawing a 5-mL aliquot and stripping the dissolved volatiles into the concentrator trap (G). Ten minutes of purging was found sufficient to quantitatively strip out most of the compounds in the present study. Those compounds with relatively low distribution coefficients (e.g., 1,2,3-trichloropropane) which could not be totally stripped out in this time were treated with an appropriate correction factor when their distribution coefficients were calculated. The contents of the concentrator trap are subsequently desorbed into the gas chromatograph for analysis.

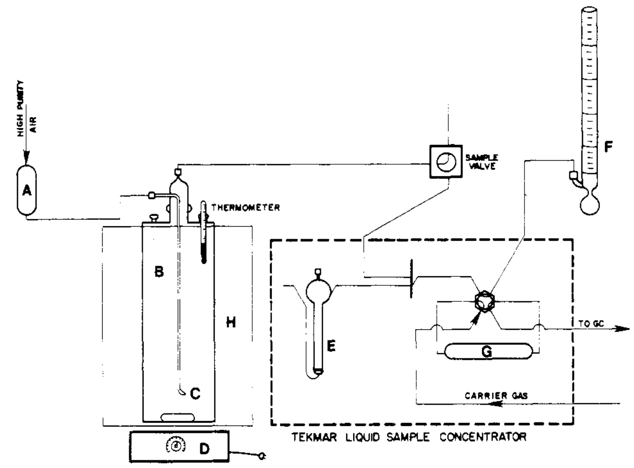

Figure 1. Schematic drawing of the experimental apparatus.

Results

Distribution coefficients were calculated from

$$K_i = y_i/x_i = (A_{air}\tilde{V}_{air}/V_{air})Q/(A_{water}\tilde{V}_{water}/V_{water}) \quad (1)$$

where A_{air} = integrated peak area of the air fraction, A_{water} = integrated peak area of the water fraction, V_{air} = volume of air analyzed, V_{water} = volume of water analyzed, $\tilde{V}_{air}$ = specific molal volume of air, and $\tilde{V}_{water}$ = specific molal volume of water. Q is a correction factor applied for incomplete purging which may be determined from successive purge data from

$$Q = 1 - \{1 - [1 - 4R(1 - R)]^{1/2}\}/2R \quad (2)$$

where $R = A_1/(A_1 + A_2)$, A_1 = integrated peak area for the first 10-min purge, and A_2 = integrated peak area for the second 10-min purge.

Distribution coefficients for 21 chlorinated hydrocarbons plus benzene and toluene, determined in the preceding manner, are presented in Tables I–V. The total error estimate reported represents the combination of separation error, due to GC resolution of asymmetric peaks, and experimentally determined random error contributions, as discussed below. In addition, all of these data were fit to the empirical expression

$$\ln(K_i) = A_i - B_i/T \quad (3)$$

The two parameters in eq 3, determined by a least-squares

Table II. Distribution Coefficient Data as a Function of Temperature

temp,[a] °C	CH_2Cl_2	$CHCl_3$	2-C_4H_9Cl	1,2-$C_3H_6Cl_2$	1,3-$C_3H_6Cl_2$	1,2,3-$C_3H_5Cl_3$	1,4-$C_4H_8Cl_2$
1.9	61.4	68.9	358.2	45.8	17.71	11.66	
13.5	111.5	128.7	773.6	90.2	31.70	11.46	15.27
15.7	121.5	146.7	847.2	101.6	36.21	13.55	20.05
17.1	141.6	155.0	891.0	108.6	37.14	14.18	21.35
22.0	157.1	194.5	1109.3	131.4	44.97	15.12	24.76
24.9	161.9	204.8	1243.3	153.5	53.57	19.81	26.61
error,[b] %	±4.8	±10.1	±3.3	±5.0	±5.0	±6.1	±6.1

[a,b] See corresponding footnotes of Table I.

Table III. Distribution Coefficient Data as a Function of Temperature

temp,[a] °C	1-C_4H_9Cl	C_6H_5–CH_3	C_6H_5Cl	1-$C_6H_{13}Cl$	1,5-$C_5H_{10}Cl_2$	o-$C_6H_4(CH_3)Cl$
1.0	325.5	121.8	68.0	399.5	16.36	87.4
3.0	375.3	129.2	68.8	365.5	23.10	66.9
12.4	536.9	204.6	104.1	668.3	21.41	97.85
12.5	569.2	198.1	112.8	728.4	28.87	118.5
17.9	693.4	251.5	133.2	873.2	26.96	133.5
19.1	738.2	278.7	153.3	969.7	36.69	175.3
22.7	833.9	309.8	148.7	1161.4	79.33	176.7
23.0	839.0	342.7	175.9	1267.7		202.7
error,[b] %	±2.1	±3.0	±15.0	±5.8	±12.9	±5.8

[a,b] See corresponding footnotes of Table I.

Table IV. Distribution Coefficient Data as a Function of Temperature

temp,[a] °C	1,2-$C_2H_4Cl_2$	CCl_4	C_6H_6	*s*-$C_2H_2Cl_4$
1.0	30.62	412.1	97.5	
1.3	30.89	412.4	95.2	
11.0	46.56	719.5	153.7	10.94
13.0		859.5	181.0	12.52
21.0	68.89	1280.3	257.7	17.03
22.0	76.59	1319.4	264.3	19.40
27.2	95.46	1571.4	327.6	20.94
error,[b] %	±5.0	±3.4	±2.3	±5.6

[a, b] See corresponding footnotes of Table I.

Table V. Distribution Coefficient Data as a Function of Temperature

temp,[a] °C	1,1-$C_2H_2Cl_2$	1,1,2-$C_2H_3Cl_3$	1-$C_5H_{11}Cl$
2.5	533.5	16.67	362.4
7.0	780.1	20.96	464.2
12.9	1161.8	26.91	683.0
18.0	1336.4	34.14	906.6
19.5	1752.0	33.64	955.2
24.3	1714.5	44.61	1302.6
26.1	2146.8	48.47	1318.2
error,[b] %	±14.0	±10.0	±3.3

[a, b] See corresponding footnotes of Table I.

Table VI. Coefficients for the Expression $\ln K = A - B/T$, Determined by Least-Squares from the Experimental Data

compd	*A*	*B*, K
1,1,1-trichloroethane (1,1,1-$C_2H_3Cl_3$)	21.68	4375
1,1-dichloroethylene (1,1-$C_2H_2Cl_2$)	23.12	4618
trichloroethylene (C_2HCl_3)	21.89	4647
tetrachloroethylene (C_2Cl_4)	22.68	4735
methylene chloride (CH_2Cl_2)	17.42	3645
chloroform ($CHCl_3$)	18.97	4046
carbon tetrachloride (CCl_4)	22.22	4438
ethylene dichloride (1,2-$C_2H_4Cl_2$)	16.05	3539
1,1,2-trichloroethane (1,1,2-$C_2H_3Cl_3$)	16.20	3690
s-tetrachloroethane (*s*-$C_2H_2Cl_4$)	14.91	3547
1,2-dichloropropane (1,2-$C_3H_6Cl_2$)	19.60	4333
1,3-dichloropropane (1,3-$C_3H_6Cl_2$)	17.13	3917
1,2,3-trichloropropane (1,2,3-$C_3H_5Cl_3$)	14.61	3477
1-chlorobutane (1-C_4H_9Cl)	18.51	3482
2-chlorobutane (2-C_4H_9Cl)	22.29	4499
1,4-dichlorobutane (1,4-$C_4H_8Cl_2$)	13.79	3128
1-chloropentane (1-$C_5H_{11}Cl$)	23.04	4727
1,5-dichloropentane (1,5-$C_5H_{10}Cl_2$)	8.79	1597
1-chlorohexane (1-$C_6H_{13}Cl$)	22.16	4459
benzene (C_6H_6)	19.02	3964
chlorobenzene (C_6H_5Cl)	16.83	3466
toluene ($C_6H_5CH_3$)	18.46	3751
o-chlorotoluene (*o*-$C_6H_4(CH_3)Cl$)	17.18	3545

analysis, for all 23 compounds are presented in Table VI.

Analysis and Discussion of Results

Error Analysis. Random experimental errors can arise from temperature and liquid volume measurements, chromatogram integration error, concentration inhomogeneities in the equilibration cell, and incomplete purging of liquid sample fractions. Air volume measurement errors are insignificant in comparison to other sources using the procedure described here (<0.5%). An assumed temperature measurement error of ±0.5 °C yields ~±2.4% uncertainty in the distribution coefficients. Liquid-fraction GC measurements for 1,1,2-trichloroethane indicated that random GC integration and liquid volume measurement errors and incomplete mixing combined contribute ~±1.4% to the uncertainty.

Table VII. Comparison of Present Results with Those of Brown (*5*), as Reported by Dilling (*4*)

compd	*K*(25 °C)[a]	*K*(25 °C)[b]	*T*(match), °C
CH_2Cl_2	161.9	149.5	20.8
$CHCl_3$	204.8	176.7	20.8
CCl_4	1533.6	1182.6	20.1
CCl_2CCl_2	889.8	679.6	20.0
CH_2ClCH_2Cl	65.4	54.37	15.5

[a] This work. [b] Brown, as reported by Dilling (*4*).

For the typical compound in the present study (i.e., no significant integration error; $Q = 1$) the total random error contributed a maximum uncertainty of ~±2.8%. In the relatively narrow temperature range used here, all of the compounds exhibited a linear relationship between the logarithm of the distribution coefficient and $1/T$ (i.e., eq 3). A least-squares fit of the data yielded a typical error of ±1.1%. A significantly greater number of data points were collected for the three primary compounds of interest in the present study (i.e., 1,1,1-trichloroethane, trichloroethylene, and tetrachloroethylene). Thus a least-squares fit yielded a smaller typical error of ~ ±0.6%.

Potentially, the greatest errors with the present technique are those arising from systematic sources. The primary causes identified are incorrect integrator zeroing, incomplete GC peak resolution, and inadequate residence time in the equilibration cell. Improper zeroing of the GC integrator generally increased the areas of both the liquid- and air-fraction peaks but was significant only for peaks with small areas; e.g., air-fraction peaks of compounds with low distribution coefficients. The net effect of this error is to underestimate the temperature dependence. For example, the low measured temperature dependence of the distribution coefficients of 1,5-dichloropentane is most probably due to this source. The magnitude of this error is difficult to quantify accurately but, with the exception of 1,5-dichloropentane, probably does not exceed 5%, and it should be totally negligible for $K > 100$. Also, zeroing errors can be almost completely eliminated if compounds are analyzed for separately, and the liquid- and air-fraction volumes are adjusted such that their integrated areas are approximately equal.

Peak resolution was generally good for the liquid fractions, but for the air fractions the asymmetry introduced by the concentrator trap caused significant integration error due to inadequate peak separation. Under the conditions of the present work, errors from this source were large only for ethylene chloride, and, to a lesser extent, chlorobenzene. Distribution coefficients determined for ethylene chloride were corrected by using Brown's data (*5*). No such comparable data are available for chlorobenzene. However, an examination of the GC traces indicates that the estimated distribution coefficients for chlorobenzene are probably no more than 15% too high. For most of the other compounds studied, this source contributed less than 5% to the total error. Of the major industrial solvents studied, only chloroform had a high separation error (~10%). Contributions to the error from this course can be virtually eliminated by performing separate analyses for single compounds.

The most serious source of error for compounds with large distribution coefficients is nonattainment of equilibrium in the equilibration cell. A detailed analysis of this possibility, including bubble size and mass transfer effects, indicates that the error should be insignificant for $K < 1500$. For distribution coefficients greater than this upper limit, the primary manifestation in the results will be a reduced temperature dependence at higher temperatures.

Comparison with Other Results and Predictions. A comparison between Brown's data (*5*), as reported by Dilling (*4*), and our own results reveals that the former are consistently

Table VIII. Comparison of Present Results with Those of McConnell et al. (*6*) and Brown (*5*), as Reported by Dilling (*4*), at 21 °C

compd	K^a	K^b	K^c
CH_2Cl_2	152.7	149.5	167.4
$CHCl_3$	184.1	176.7	157.7
CCl_4	1280.3	1182.6	1233
CH_2ClCH_2Cl	55.6	54.37	51.4
CH_3CCl_3	904.3	-	1910
CH_2CCl_2	1670.8	-	8474
C_2HCl_3	442.5	-	494.8
CCl_2CCl_2	722.9	679.6	1111

[a] This work. [b] Brown, as reported by Dilling (*4*), assuming T = 21 °C. [c] McConnell et al. (*6*).

lower than the latter, as shown in Table VII. However, the temperature at which Brown's reported distribution coefficient exactly matches our own (i.e., T(match) in Table VII, determined from eq 3) is surprisingly quite constant at or near 20–21 °C for two of the five compounds which can be compared. Since Brown's technique made no provision for temperature control, and in view of the fact that considerable care was taken in the present work to control and accurately measure temperature, it is quite likely that Brown's reported temperature of 25 °C was actually closer to room temperature, or 20–21 °C. The primary source of discrepancy with respect to the remaining compound (ethylene chloride) was most probably incomplete separation of the ethylene chloride and carbon tetrachloride peaks by the GC in the air-fraction analysis in our work. Thus Brown's ratio for these two species was used to correct our results for ethylene chloride, taking the assumed temperature discrepancy into account.

A comparison of our results with those reported by McConnell et al. (*6*) is presented in Table VIII. As can be seen, there is reasonable agreement among the three sets of data for methylene chloride, chloroform, carbon tetrachloride, ethylene chloride, and trichloroethylene. However, there is considerable disagreement between our data and those of McConnell et al. for 1,1,1-trichloroethane, 1,1-dichloroethylene, and tetrachloroethylene. It is noted that Brown's value for tetrachloroethylene agrees with our own. On the basis of a comparative consistency analysis, including mass transfer effects in our equilibration cell, we conclude that the data of McConnell et al. (*6*) for 1,1,1-trichloroethane, 1,1-dichloroethylene, and tetrachloroethylene are in error.

The distribution coefficients for all 23 compounds were compared to predictions determined from UNIFAC infinite dilution activity coefficients. The appropriate UNIFAC parameters for all of the compounds, except 1,1-dichloroethylene, trichloroethylene, and tetrachloroethylene, which were not available, were obtained from Fredenslund et al. (*7*) and Skjold-Jørgensen et al. (*8*). The parameters for the three chlorinated olefins were estimated as follows. Group van der Waals volume and surface area parameters have been published for double-bonded carbon atoms and alkane chlorine atoms (*9*). For estimation purposes, the alkene chlorine atoms were assumed to exhibit the same group volume and surface area as those bonded to alkanes. The group energy interaction parameters were estimated from mutual solubility data for the three chlorinated hydrocarbon–water systems (*10*). All of the parameters estimated in this fashion are presented in Table IX.

Table IX. UNIFAC Parameters for the Three Chlorinated Olefins Estimated as Outlined in the Text

compd	R_k	Q_k	$a_{H_2O,i}$	a_{i,H_2O}
$C_2H_2Cl_2$	2.731	2.44	759.7	477.5
C_2HCl_3	3.309	2.86	477.1	965.7
C_2Cl_4	3.888	3.40	553.4	1237.0

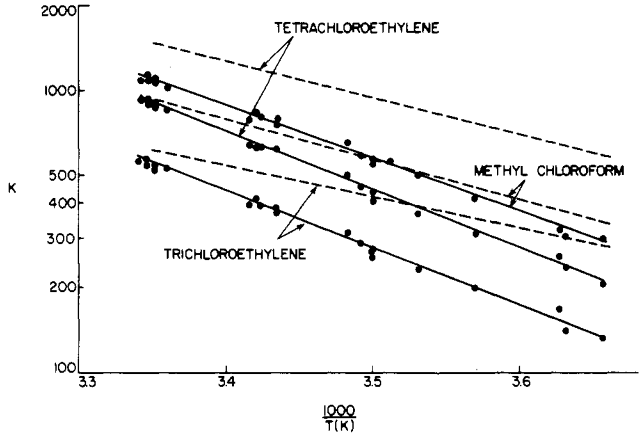

Figure 2. Comparison of the experimental data (solid lines) with UNIFAC predictions (dashed lines) for 1,1,1-trichloroethane (methyl chloroform), trichloroethylene, and tetrachloroethylene.

In general, agreement between experimental and predicted distribution coefficients was reasonable, especially for the chlorinated methanes and the less chlorinated of the higher carbon number compounds. Rather than present the result graphically for all 23 compounds, for the sake of brevity Figure 2 is intended to typify the results. This figure presents the experimental and predicted distribution coefficients for 1,1,1-trichloroethane, trichloroethylene, and tetrachloroethylene, the three compounds for which the most data were collected (see Table I). As shown, the agreement between experimental and predicted values is best for 1,1,1-trichloroethane and worsens as the compounds become more chlorinated. This trend is also evident for the other species studied. However, the most obvious single feature in all of the predictions is that UNIFAC consistently overestimated the temperature dependence of the activity coefficient. Experimentally, the activity coefficient was found to be nearly independent of temperature for all 23 compounds over the temperature range considered. This result is quite similar to that found for benzene and toluene by Tsonopoulos and Prausnitz (*11*).

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