Determination of Air−Water Partitioning of Volatile Halogenated Hydrocarbons by the Inert Gas Stripping Method

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Air−water partitioning for 21 volatile chlorinated or brominated alkanes, alkenes, and aromatics was measured at 20 °C by the inert gas stripping method. Results of the measurements are presented in the form of Henry's law constants (H_{12}), air−water partition coefficients (K_{aw}), and limiting activity coefficients (γ_1^∞), accurate γ_1^∞ values being obtained only if accurate pure solute vapor pressure data are available. The halocarbons studied in this work are hydrophobic and exhibit enhanced volatilities from their dilute aqueous solutions representing approximately ranges of γ_1^∞ from 230 to 70 000 and H_{12} from 2 to 70 MPa. Correct performance of the stripping method for such systems requires special precautions. As confirmed by test measurements on benzene, chlorobenzene, 1,1,1-trichloroethane, and 1,1,2-trichloroethane, the complete equilibration in the stripping cell can be achieved under vigorous mixing of the cell, low stripping gas flow rates (approximately 10 $\text{cm}^3\cdot\text{min}^{-1}$), and low relative elution rates (0.01 min^{-1}). Choosing for each system a cell of a suitable volume made it possible to comply with the latter requirement. The results compare well with recent literature values obtained by various methods for some of the halocarbons. For two selected halocarbons (bromobenzene and 1,1-dichloroethane), detailed measurements of the temperature dependence of air−water partitioning were carried out in the range of (10−50) °C. These measurements corresponding to the range of H_{12} from 5 to 72 MPa provide additional support for the validity of the method.

Introduction

Volatile halogenated hydrocarbons are produced on a large scale and are widely used in many manufacturing industries as solvents, extractants, dry cleaning agents, metal degreasers, aerosol propellants, and chemical intermediates. Through evaporation and spills and in waste water effluents, these toxic compounds, having carcinogenic and/or mutagenic potential, are discharged into the environment. The population may be exposed to these substances in urban air and, in particular, from drinking water from contaminated water supplies (Howard, 1990, 1991, 1993, 1995).

Thus, volatile halogenated hydrocarbons constitute a class of organic compounds of extreme environmental interest appearing on most priority pollutants lists (Mackay, 1991; Howard, 1995). For environmental transport and fate studies and for design of water remediation processes, a knowledge of air−water partitioning and aqueous solubility of these pollutants is indispensable.

At very low contaminant concentrations encountered under environmental conditions, the air−water partitioning is usually characterized either by the Henry's law constant

$$H_{12} = \lim_{x_1 \to 0} \frac{f_1^{\text{L}}}{x_1} \tag{1}$$

where f_1^{L} is the solute fugacity and x_1 is the solute mole fraction in the liquid solution, or by the air−water partition coefficient

$$K_{\text{aw}} = \lim_{c_1^{\text{w}} \to 0} \frac{c_1^{\text{a}}}{c_1^{\text{w}}} \tag{2}$$

where c_1^{a} and c_1^{w} are the solute concentrations in air and water, respectively. The fundamental thermodynamic quantity to characterize air−water partitioning is the limiting activity coefficient of the solute in water, γ_1^∞. Its value is a measure of the solution nonideality or the solute hydrophobicity. H_{12} and K_{aw} are closely related to γ_1^∞, and under the assumption that the vapor phase behaves as an ideal gas they are given by

$$H_{12} = \gamma_1^\infty P_1^{\text{s}} \tag{3}$$

$$K_{\text{aw}} = (\gamma_1^\infty P_1^{\text{s}} v_{\text{w}}^{\text{L}})/(RT) \tag{4}$$

where P_1^{s} and v_{w}^{L} denote the saturated vapor pressure of the pure liquid solute and the liquid molar volume of pure water, respectively, and T is the absolute temperature. In addition, since the mutual solubilities of the components in most halocarbon−water systems are very small, the reciprocal value of γ_1^∞ approximates the aqueous mole fraction solubility of the halocarbon

$$x_1^{\text{sol}} = 1/\gamma_1^\infty \tag{5}$$

Accurate experimental determination of air−water partitioning or aqueous solubility of volatile halocarbons is not a trivial task. Most data published until quite recently are unreliable or in error as can be illustrated e.g. for trichloromethane for which the following values of γ_1^∞ at room temperature have been reported: 310 (296.55 K; Hardy, 1959), 540 (297.25 K; Hardy, 1959), 571 (293.15 K; Pecsar and Martin, 1966), 640 (285.65 K; Chatterjee *et al.*, 1972), 781 (298.15 K; Mash and Pemberton, 1980), 938 (298.15 K; Bao *et al.*, 1993), 1000 (293.15 K; Thomas *et al.*, 1982). For comparison, solubility data (Horvath, 1982; Stephenson, 1992) and some recent γ_1^∞ measurements (Barr and Newsham, 1987; Wright *et al.*, 1992) indicate a value of about 820 (293.15 K), which is also supported by results of the present study. Large discrepancies are also encountered in the solubility data. The most dramatic is perhaps

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the case of 1,1,1-trichloroethane for which there is an order of magnitude difference between the maximum and minimum value reported, the other measured values being roughly uniformly spread in this interval (Horvath, 1982). Major experimental difficulties originate from the hydrophobicity of the halocarbon solutes, which enhances the solute adsorption on phase boundaries and increases the solute relative volatility, thus leading to solute losses and slow equilibration. It appears, however, that appropriate experimental precautions can be exercised to considerably reduce these problems. Recent careful measurements of limiting activity coefficients for some halocarbons in water (Barr and Newsham, 1987; Cooling *et al.*, 1992; Tse *et al.*, 1992; Wright *et al.*, 1992; Li *et al.*, 1993) have yielded results of rather higher reliability. Nevertheless, further reliable measurements are still desired to verify or improve the accuracy of recent results and fill existing data gaps.

The purpose of this work is to report new measurements of air−water partitioning carried out for 21 selected chlorinated and brominated hydrocarbons using the inert gas stripping method and compare the results with available literature data. The method of inert gas stripping (IGS) to measure gas−liquid partitioning was first described and applied by Burnett (1963). The method consists of measuring the rate of elution of a solute as an entraining inert gas is passed through a highly dilute solution. The most frequently cited work on the IGS technique is the paper of Leroi *et al.* (1977) who substantially improved the experimental design and clearly demonstrated a good performance and convenience of this technique. Since then, the IGS technique has been applied to a great variety of systems, the experimental setup and procedure being further developed and modified to extend its applicability (Mackay *et al.*, 1979; Richon *et al.*, 1980; Richon and Renon, 1980; Endler *et al.*, 1985; Richon *et al.*, 1985; Elsner *et al.*, 1986; Wobst and Hradetzky, 1988; Li *et al.*, 1993). In recent years, extensive experience with the IGS technique has been acquired also in our laboratory (Vrbka and Dohnal, 1997; Vrbka *et al.*, 1997; Dohnal *et al.*, 1997). Major advantages favoring the IGS technique over some other methods are its applicability to a broad range of solute volatilities ($10\ \text{kPa} < H_{12} < 10^5\ \text{kPa}$), its precision (1−2%), no need for the calibration of the GC detector, and no or rather marginal importance of knowing exactly the initial solute concentration.

In this work, we have first verified the performance of the IGS method for the systems in question. Our measurements were done generally at 293.15 K; for two solutes, bromobenzene and 1,1-dichloroethane, they were, however, extended to the range (283.15−323.15) K to demonstrate the applicability of the IGS method to obtain the temperature dependence of air−water partitioning. The results are presented in the form of Henry's law constants, air−water partition coefficients, and limiting activity coefficients.

Principles and Theory of the IGS Method

Consider a highly dilute ($x_1 < 10^{-3}$) binary solute (1) + solvent (2) system kept well-mixed and under isothermal conditions in an equilibrium stripping cell. The inert gas to strip volatile components from the liquid solution is introduced into the cell and dispersed in small bubbles, at a constant flow rate. The outlet gas, assumed to be in equilibrium with the liquid solution in the cell, is periodically analyzed for the solute content by gas chromatography to determine the rate of the solute removal. The temperature T, the total pressure P, the flow rate of the pure inert gas entering the cell D, the total amount of solvent in the cell n_2, and the detector response (peak area) to the solute A_1 as a function of time t are measured. As shown by Leroi *et al.* (1977), when the partial pressure of the solute is small compared to the total pressure and vapor-phase nonideality corrections and the effect of the vapor space of the cell are neglected, the rate of the solute elution from a nonvolatile solvent follows a simple exponential first-order kinetics pattern; provided the detector is linear, the limiting activity coefficient can be determined from the measurements outlined above as follows

$$\gamma_1^\infty = \frac{n_2RT}{P_1^{\rm s}D}\left(-\frac{{\rm d}\ln A_1}{{\rm d}t}\right) \tag{6}$$

a plot of ln A_1 against t giving a straight line.

For solvents of appreciable volatility, the amount of the solvent in the cell decreases during the experiment, which requires the use of another, more complicated relation to calculate γ_1^∞ (Leroi *et al.*, 1977) and imposes some experimental restrictions. Thus, a simpler and preferred practice applicable to volatile solvents is to keep n_2 constant by presaturating the stripping gas with the solvent vapor. Upon presaturation, the flow rate of the stripping gas entering the cell changes by a factor $1/(1 - P_2^{\rm s}/P)$, where $P_2^{\rm s}$ is the pure solvent vapor pressure. Consequently, the formula to calculate γ_1^∞ from the IGS experiment in the presaturation mode becomes

$$\gamma_1^\infty = \frac{n_2RT}{P_1^{\rm s}D}\left(-\frac{{\rm d}\ln A_1}{{\rm d}t}\right)(1 - P_2^{\rm s}/P) \tag{7}$$

The *first-order approximation* provided by eq 6 or 7 is often sufficiently accurate. However, when a better accuracy is needed or the simplifying assumptions underlying eqs 6 and 7 are violated appreciably, e.g. for solutes of high volatility ($H_{12} > 10^3$ kPa), these simplifications should be eliminated. This, however, leads to involved and rather complex relations (Burnett, 1963; Duhem and Vidal, 1978). Alternatively, using the perturbation approach, Vrbka and Dohnal (1997) derived separate corrections to each of the simplifying assumptions in the form of correcting factors $k_{\rm i}$ and calculated the *second-order approximation* $\gamma_1^{\infty,\rm II}$ of the limiting activity coefficient value as

$$\gamma_1^{\infty,\rm II} = \gamma_1^{\infty,\rm I}\prod_i^4 k_i \tag{8}$$

where $\gamma_1^{\infty,\rm I}$ is given by eq 6 or 7. If the individual corrections are not too high, then their interference is negligible and the perturbation formula (eq 8) yields almost exact results. The resulting correction factors, as derived by Vrbka and Dohnal (1997), are listed below.

(1) Change of the stripping gas flow rate due to the saturation in the cell. For the IGS mode without the presaturation of the stripping gas by the solvent vapor ($\gamma_1^{\infty,\rm I}$ calculated from eq 6) the respective correction factor is given by

$$k_1 = 1 - (\bar{n}_1/n_2)\gamma_1^{\infty,\rm I}\, P_1^{\rm s}/P - P_2^{\rm s}/P \tag{9}$$

while for the presaturation mode ($\gamma_1^{\infty,\rm I}$ calculated from eq 7) it is

$$k_1 = (1 - (\bar{n}_1/n_2)\gamma_1^{\infty,\rm I}\, P_1^{\rm s}/P - P_2^{\rm s}/P)/(1 - P_2^{\rm s}/P) \tag{10}$$

Here, $\bar{n}_1$ is the mean amount of the solute in the cell during the measurement obtained from

$$\bar{n}_1 = n_1^0(A_1^f/A_1^0 - 1)/\ln(A_1^f/A_1^0) \qquad (11)$$

where n_1^0 is the initial solute amount in the cell and A_1^f and A_1^0 are the GC responses to the solute at the end and at the beginning of the IGS experiment, respectively. The correction factor k_1 is always less than unity, its importance becoming greater with increasing volatility of the solute (H_{12}) and the solvent (P_2^s).

(2) Removal of the solvent due to its volatility. The respective correction factor for the IGS without the presaturation of the stripping gas is

$$k_2 = 1 - (P_2^s Dt)/(2n_2^0 RT) \qquad (12)$$

where n_2^0 is the initial amount of the solvent in the cell and t is the total stripping time. The correction factor k_2 is less than unity, and its importance rises with increasing solvent volatility (P_2^s) and decreasing cell volume. Obviously, when presaturating the stripping gas, $k_2 = 1$.

(3) Amount of the solute in the vapor space of the cell. Assuming complete mixing in the vapor space of the cell, the appropriate correction factor can be written as

$$k_3 = [1 - (-\mathrm{d}\ln A_1/\mathrm{d}t)(V/D)]^{-1} \cong [1 - (\gamma_1^{\infty,\mathrm{I}} P_1^s V)/(n_2 RT)]^{-1} \qquad (13)$$

where V denotes the vapor space volume. As seen from relation 13, $k_3 > 1$ and rises with the solute volatility (H_{12}) and with the increasing ratio of the vapor space volume to the amount of the solvent in the cell.

(4) Vapor-phase nonideality. Using the virial equation of state, the vapor-phase nonideality correction factor is

$$k_4 = [1 + B_{33}P/(RT)]\exp\{[P(2B_{13} - B_{33} - v_1^L) - P_1^s(B_{11} - v_1^L)]/(RT)\} \qquad (14)$$

where v_1^L is the pure solute liquid molar volume and B_{ij} are the second virial coefficients, the components 1, 2, 3 being the solute, the solvent, and the stripping gas, respectively. The vapor-phase nonideality correction can be either greater or smaller than unity depending on the system and conditions.

The perturbation approach was also used for accurate calculation of the Henry's law constant and air−water partition coefficient. The first-order approximations of H_{12} and K_{aw} were determined from $\gamma_1^{\infty,\mathrm{I}}$ using eqs 3 and 4, respectively. The second-order approximations were calculated in an analogous manner to that for γ_1^∞. The correction factors k_1, k_2, k_3 take the same form as for γ_1^∞. The correction factor k_4 for the case of H_{12} is determined by the relationship

$$k_4 = [1 + B_{33}P/(RT)]\exp\{[P(2B_{13} - B_{33} - v_1^L) + P_2^s v_1^L]/(RT)\} \qquad (15)$$

For K_{aw}, on the assumption that stripping gas (nitrogen) has the same properties as air, the correction factor $k_4 = 1$, because the nonideality of vapor phase is included by definition (eq 2). We verified that nitrogen gave the same results as air at the conditions of our experiment. Differences in results for air and for nitrogen were found to be smaller than 0.01%.

Validity of the Method. Correct performance of the inert gas stripping method, especially for hydrophobic solutes exhibiting enhanced volatilities from their dilute aqueous solutions, requires special precautions. According to a commonly adopted two-film theory, the flux of a hydrophobic solute (large H_{12}) from the liquid phase into a bubble of the stripping gas is limited by liquid film resistance (Betterton, 1992). As shown by Richon *et al.* (1980), the approach to equilibrium τ for such systems is given by

$$\tau = 1 - \exp\left(-k_L \frac{3}{r_B} \frac{RT}{H_{12} v_w^L} t_R\right) \qquad (16)$$

where k_L is the liquid mass transfer coefficient, r_B is the bubble radius, and t_R is the residence time of the bubble in the solution. As the system approaches to equilibrium, τ approaches unity; the approach becomes closer as r_B gets smaller and t_R gets longer. If the liquid in the dilution cell is only mildly stirred, t_R for a given system under given conditions is determined by the height of the liquid above the point where the stripping gas is introduced into the cell. Adopting Richon's analysis, Li *et al.* (1993) calculated for benzene in water at 298.15 K ($H_{12} = 32$ MPa) that for a 1 mm diameter bubble the height for 99% approach to equilibrium should be 6 cm. Since the fritted glass tips used to disperse the stripping gas in our cells produce bubbles of an even smaller diameter than 1 mm and the height of the liquid in our large-volume cell for measuring solutes with large Henry's law constants ($H_{12} > 10$ MPa) is 14 cm, we should safely approach a 99% equilibrium value.

The real situation in the cell is much more complex than that described by eq 16, in particular, due to hydrodynamic effects. As will be stressed below, our cells were very intensively stirred. The vigorous stirring not only provides the necessary composition uniformity of the liquid but also changes dramatically hydrodynamic conditions in the cell; a vortex is formed, and, by virtue of its suction, bubbles are held in the liquid for a considerably longer time. This effect contributes substantially to appropriate equilibration. The equilibration in a vigorously mixed system is further supported also by the enlargement of the vapor−liquid interface and its constant renewal resulting from the vortex formation.

Equation 16 assumes independent behavior of all bubbles in the solution. In real systems, however, mutual influencing of bubbles and their coalescence occur, which affects unfavorably the equilibration. The problem can be avoided only at low flow rates of the stripping gas when the number of bubbles in the solution is small. The suitable working range of the flow rates can be identified by examining the effect of the inert gas stripping flow rate on the measured value of limiting activity coefficient.

A well-known general condition for the appropriate equilibration in all dynamic phase-equilibrium separation processes is to maintain a sufficiently low rate in the separation. For the IGS technique, our experience with a large number of systems studied over the years indicates that this condition is met at relative elution rates 0.01 min^{-1} or lower. With respect to this last requirement, one should have the possibility of choosing for each system the equilibrium cell of a suitable volume.

Experimental Section

Materials. Analytical or pure grade chemicals obtained from various suppliers were of 99 mol % or higher stated purity with the exception of 1,1,2,2-tetrachloroethane (98 mol %) and *trans*-1,2-dichloroethylene (>97 mol %). The samples for the IGS measurements were taken directly from fresh bottles without further purification. Water was doubly distilled in all-glass still.

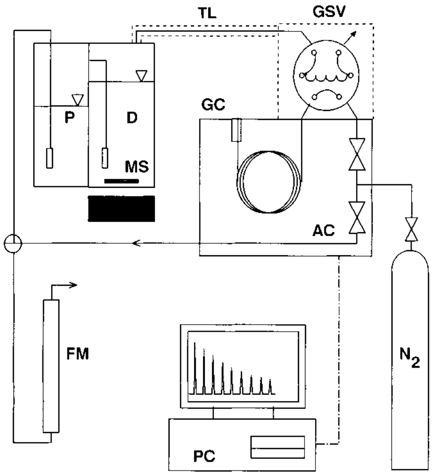

Figure 1. Schematic diagram of the IGS experimental setup: GC, gas chromatograph; GSV, thermostated pneumatic six-port gas sampling valve; PC, personal computer; P, presaturator of IGS cell; D, dilution cell of IGS cell; MS, magnetic stirrer; N_2, stripping gas source; AC, auxiliary gas GC channel; FM, thermostated soap-bubble flow meter; TL, heated transfer line.

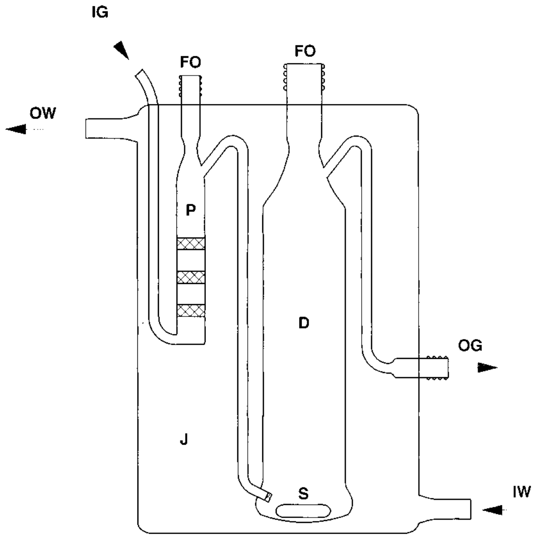

Figure 2. Equilibrium stripping cell (214 mL): P, presaturator with fritted glass disks; D, dilution cell; S, stirrer; J, thermostated jacket; IW, input of thermostating water; OW, output of thermostating water; IG, input of stripping gas; OG, outlet of saturated stripping gas; FO, filling openings.

Apparatus and Procedure. A schematic diagram of our experimental setup is shown in Figure 1. The IGS apparatus was designed around a computer-interfaced Hewlett-Packard gas chromatograph (GC), Model 5890 II, with a flame ionization detector. The chromatograph is equipped with a pneumatic six-port gas sampling valve (GSV) that is housed in an independently heated zone of the GC and kept at 160 °C.

The equilibrium stripping cell is an all-glass jacketed device composed of the presaturator (P) and the dilution cell (D), which are destined to hold the solvent and the dilute solution, respectively. The constant flow of the stripping gas (N_2) introduced into the cell was supplied from an auxiliary-gas channel (AC) of the HP 5890 II gas chromatograph. The stripping gas flow rate was digitally controlled by the electronic pressure controller of the channel and measured, before and after each stripping experiment, with a thermostated soap-bubble flow meter (FM). Typical flow rates used for the measurements of the systems studied in this work were from 7 to 13 cm^3/min; the flow rates showed a very good stability and could be determined to ±0.3 %.

The cell outlet is connected via Teflon glass-to-metal joints and a heated (150 °C) transfer line (TL) made of $^1/_8$ in. stainless steel tubing to the respective port of the gas sampling valve. The volume of the sampling loop used ($^1/_{16}$ in. stainless steel tubing) was 250 μL. Since the flame ionization detector does not respond to water, no separation of the components was necessary. Hence, a short (0.5 m) stainless steel packed GC column filled with a bare highly inert support (Inerton Super, 0.125−0.160 mm) was employed. At the carrier gas flow rates of 10 cm^3/min and oven temperatures set close to the normal boiling temperature of the solute, this provided narrow peaks and short times of the analyses (2 min). The operation of the gas chromatograph, including all zone temperature controls, the carrier gas and the stripping gas flow controls, the timing of the gas sampling valve, and the signal acquisition and integration was achieved by the interfaced personal computer using the HP ChemStation software.

To accommodate with the wide range of solute volatilities (Henry's law constants), three equilibrium cells of similar design but of different capacities were used in this work. The total volumes and the solution load volumes (the latter given in parentheses) of the three dilution cells are 17 cm^3 (13 cm^3), 47 cm^3 (35 cm^3), and 214 cm^3 (190 cm^3). A detailed view of the largest cell used is shown in Figure 2. The stripping gas enters first the presaturator (P). Its compartment is divided by fritted glass disks into several plates to achieve efficient presaturation with the solvent vapor yet keeping a small pressure drop across the presaturator. The presaturated gas passes then into the dilute solution in the dilution cell (D) through a fine porosity fritted glass tip where it is dispersed into small-diameter bubbles. The solution is vigorously mixed with an efficient magnetic stirrer (S), which extends considerably the path and the residence time of the bubbles in the solution. The vapor space of the cell and a special design of the gas outlet prevent liquid droplet entrainment. The cell was thermostated by an electronic water-circulating bath (Medingen U6CP) to better than ±0.02 °C. The temperature of the water was measured with a calibrated standard mercury thermometer (Karl Schneider, Wertheim, Germany) to ±0.01 °C.

The measurement procedure starts with flushing thoroughly a clean equilibrium cell and all of the manifold with dry nitrogen. The dilution cell is then gravimetrically loaded with the solvent water. For measurements in the low volume cell and/or at temperatures higher than 25 °C, additional water was loaded also into the presaturator. In other cases presaturation was unnecessary, and hence the presaturator was left empty. The solute was added volumetrically with a gas-tight syringe, the added amount being always small enough to correspond safely to a homogenous solution and the Henry's law region. The dissolution of the studied hydrophobic solutes is slow; under vigorous mixing it required 2−5 h. Then, after the stripping gas flow rate was set and measured, the equilibrium cell was connected to the manifold and the stripping gas introduced into the cell. At this moment, an automatic data acquisition process controlled by the computer is started. A typical run, during which 18 samples are taken, lasts 2−3 h.

Results and Discussion

As exemplified in Figure 3 for trichloroethylene (1) + water (2), the observed dependencies of ln A_1 on time were linear, thus providing an evidence of the detector linearity

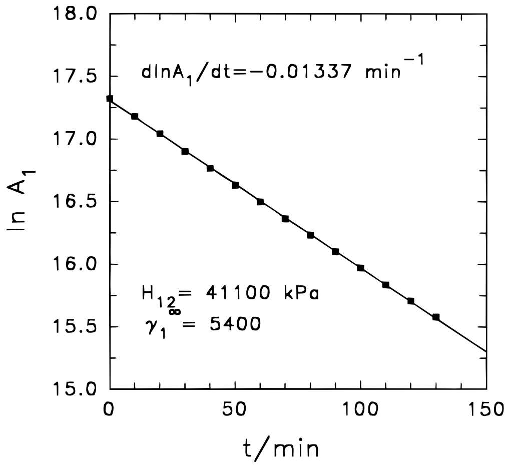

Figure 3. Typical plot of ln A_1 vs t: trichloroethylene (1) + water (2), 293.15 K.

Table 1. Test Measurements by the IGS Method for Four Selected Solutes in Water. Effect of the Stripping Gas Flow Rate *D* on the Measured Values of γ_1^∞ and H_{12}

D/cm^3·min^{-1}	γ_1^∞	H_{12}/MPa	D/cm^3·min^{-1}	γ_1^∞	H_{12}/MPa
		Benzene (T = 298.15 K)[a]			
4.80	2550	32.10	18.6	2518	31.70
8.52	2552	32.13	25.4	2496	31.42
10.8	2560	32.22	34.8	2452	30.87
13.0	2554	32.16	38.5	2433	30.63
		Chlorobenzene (T = 293.15 K)[a]			
8.08	13060	15.69	13.04	13060	15.69
10.56	13080	15.71	17.20	12910	15.51
		1,1,1-Trichloroethane (T = 293.15 K)[a]			
7.99	5185	67.54	11.02	5205	67.80
8.43	5449	70.97	13.47	5647	73.55
		1,1,2-Trichloroethane (T = 293.15 K)[b]			
8.09	1667	3.672	13.24	1665	3.667
10.37	1651	3.641			

[a] 214 cm^3 stripping cell. [b] 47 cm^3 stripping cell.

Table 2. Henry's Law Constant H_{12} and Air−Water Partition Coefficients K_{aw} for 21 Halocarbons at 293.15 K in Water Measured by the IGS Method[a]

Solute	H_{12}/MPa	$K_{aw} \times 10^3$
dichloromethane	10.8	80.7
trichloromethane	17.1	128
1,1-dichloroethane	25.6	191
1,2-dichloroethane	5.24	39.3
1,1,1-trichloroethane	70.0[b]	525[b]
1,1,2-trichloroethane	3.67	27.4
1,1,2,2-tetrachloroethane	1.87[c]	14.1[c]
1,2-dichloropropane	12.1	90.9
cis-1,2-dichloroethylene	17.5	131
trans-1,2-dichloroethylene	42.3	317
trichloroethylene	41.1	308
tetrachloroethylene	65.5	492
chlorobenzene	15.7	118
1,2-dichlorobenzene	7.65	57.8
1,3-dichlorobenzene	11.7	88.6
1,4-dichlorobenzene	10.3	77.0
benzyl chloride	1.96	14.8
dibromomethane	3.65	27.4
tribromomethane	2.38	17.9
1,2-dibromoethane	2.87	21.6
bromobenzene	9.12	68.7

[a] Relative standard errors, $\sigma_{rel}(H_{12})$, $\sigma_{rel}(K_{aw})$, as estimated by the error propagation law, are approximately 1%. [b] $\sigma_{rel}(H_{12}) = \sigma_{rel}(K_{aw})$ = 5% was estimated on the basis of replicated measurements. [c] $\sigma_{rel}(H_{12}) = \sigma_{rel}(K_{aw})$ = 2%.

and the Henry's law behavior. To obtain the slope (−d ln A_1/dt), data were fitted to a straight line by the least-squares method. For all measurements, the determination of the slope could be done quite precisely, its uncertainty, except for 1,1,2,2-tetrachloroethane, never exceeding 1%. The values of limiting activity coefficients, Henry's law constants, and air−water partition coefficients were calculated using the second-order approximation approach. Virial coefficients to account for vapor-phase nonideality were obtained from Hayden and O'Connell's correlation (Hayden and O'Connell, 1975) with parameters from Prausnitz *et al.* (1980) and *CDATA* (1991). Densities of pure liquids were taken from *CDATA* (1991) and Riddick *et al.* (1986). The total correction for the second-order approximation effects amounted typically from 1 to 3%, and just in extreme cases (1,1-dichloroethane and 1,2-dichloroethylenes) extended to 5%. The values of the individual correction factors were in the following ranges: $0.92 \le k_1 \le 1$, $0.9995 \le k_2 \le 1$, $1 \le k_3 \le 1.07$, $0.985 \le k_4 \le 1.005$. Uncertainties (standard errors) in the reported properties (γ_1^∞, H_{12}, K_{aw}) were estimated by means of the error propagation law. Since the errors in the correction factors were found negligible, the uncertainty estimates were based on the first-order approximation calculations.

In order to test our experimental technique, we carried out some measurements for selected test solutes at different flow rates of the stripping gas. These measurements, listed in Table 1, enabled us to identify a suitable working range of the flow rates and, through comparison of the results with reliable literature data, to verify the correct performance of the whole procedure. The first test solute that we chose was benzene; the value of its γ_1^∞ in water at 298.15 K is known with a good accuracy and its H_{12} (32 MPa) is higher than for most halocarbons studied in this work. As seen from Table 1, for stripping gas flow rates lower than 13 cm^3/min the measured values of γ_1^∞ and H_{12} are constant to 0.5%. Our result γ_1^∞ = 2550 agrees to 3% with the literature values γ_1^∞ = 2475 obtained by Tucker *et al.* (1981) from their precise static vapor pressure measurements and γ_1^∞ = 2610 obtained recently by Bao *et al.* (1993) using the IGS method. A similar experiment using chlorobenzene, a solute with much lower H_{12} but much higher γ_1^∞ compared to benzene, showed again excellent agreement of the results measured for $D < 13$ cm^3/min. The average value for the three measurements of γ_1^∞ = 13 060 compares favorably well with data published in literature, *viz.* γ_1^∞ = 12 960 obtained by Cooling *et al.* (1992) using GLC or γ_1^∞ = 13 400 derived from the recommended value of aqueous solubility (Horvath *et al.*, 1985). Additional literature data can be found in Table 4.

The independence of measured values for $D < 13$ cm^3/min was further verified for two trichloroethane isomers, 1,1,1-trichloroethane and 1,1,2-trichloroethane, which represent, respectively, the higher (H_{12} = 70 MPa) and the lower (H_{12} = 3.7 MPa) volatility limits for the systems studied. As seen from Table 1, at flow rates below 13 cm^3/min, the results for 1,1,1-trichloroethane do not indicate any systematic trend, but they are scattered considerably more than those for the two previous solutes. Clearly, this scatter is a reflection of experimental difficulties encountered for systems with such high volatilities. For comparison, recently published γ_1^∞ values for 1,1,1-trichloroethane in water range from 5245 to 5900 (see Table 4), and γ_1^∞ values derived from solubilities are dispersed even more. The measurements for 1,1,2-trichloroethane, which were carried out in the smaller stripping cell, show for $D < 13$ cm^3/min again excellent reproducibility. The obtained value of γ_1^∞ = 1660 agrees well with those derived from literature solubility data (see Table 4). Comparison with recently published γ_1^∞ values measured by ad hoc VLE

Table 3. Vapor Pressures of Halocarbon Solutes at 293.15 K

solute	P_1^s/kPa	$\sigma_{rel}(P_1^s)$/%	ref
dichloromethane	47.283	0.1	*CDATA*, 1991
trichloromethane	21.086	0.1	*CDATA*, 1991
1,1-dichloroethane	24.491	0.5	*CDATA*, 1991
1,2-dichloroethane	8.214	1.	Boublík *et al.*, 1984
1,1,1-trichloroethane	13.15	0.5	*CDATA*, 1991
1,1,2-trichloroethane	2.206	6.	*TRC*, 1994
1,1,2,2-tetrachloroethane	0.517	15.	*TRC*, 1994
1,2-dichloropropane	5.144	0.6	Dykyj and Repáš, 1979
cis-1,2-dichloroethylene	21.759	0.5	Dykyj and Repáš, 1979
trans-1,2-dichloroethylene	35.82	0.1	*CDATA*, 1991
trichloroethylene	7.669[a]	5.	Dohnal and Fenclová, 1985
tetrachloroethylene	1.845	2.	*CDATA*, 1991
chlorobenzene	1.211[b]	3.	Roháč, 1996
1,2-dichlorobenzene	0.135[b]	10.	Roháč, 1996
1,3-dichlorobenzene	0.186[b]	10.	Roháč, 1996
1,4-dichlorobenzene	0.177[b,c]	20.	Roháč, 1996
benzyl chloride	0.114	7.	*CDATA*, 1991
dibromomethane	4.658	5.	Dykyj and Repáš, 1979
tribromomethane	0.535[d]	10.	Dykyj and Repáš, 1979
1,2-dibromoethane	1.150	6.	Dykyj and Repáš, 1979
bromobenzene	0.402[e]	10.	*CDATA*, 1991

[a] Extrapolated from data in the range 312−357 K (Antoine equation). [b] Extrapolated from high-temperature data by means of simultaneous correlation of vapor pressure data and thermal properties (Cox equation). [c] Value for hypothetical liquid (melting temperature 326 K). [d] Extrapolated from data in the range 320−413 K (Antoine equation). [e] Extrapolated from data in the range 329−427 K (Antoine equation).

methods requires, however, a closer inspection of differing vapor pressure data for pure 1,1,2-trichloroethane (see below).

Having sufficiently proved good precision and accuracy of our IGS method, we measured the air−water partitioning for 21 chlorinated and brominated alkanes, alkenes, and aromatics at 20 °C. Results are given in the form of Henry's law constants and air−water partition coefficients in Table 2, and limiting activity coefficients in Table 4, along with their relative standard errors σ_{rel} estimated by the error propagation law. The measurement of the air−water partitioning alone has been done with a very good accuracy; the error propagation estimates $\sigma_{rel}(H_{12})$ and $\sigma_{rel}(K_{aw})$ amount in general to about 1% and, except for 1,1,1-trichloroethane which was discussed above, agree reasonably well with the reproducibility of the measurements. For 1,1,1-trichloroethane exhibiting extremely high volatility from its dilute aqueous solution, σ_{rel} was estimated on the basis of replicate measurements to account for the observed excessive scatter of the data.

As seen from eq 6, accurate limiting activity coefficients can be obtained from the stripping measurements only if accurate pure solute vapor pressure data are available. For this reason, we critically reviewed vapor pressure data for halocarbon solutes from various sources and selected the most reliable values of P_1^s(293.15 K). They are listed together with our estimates of probable uncertainty in Table 3. Depending on data available, the uncertainty estimate was based on correlation deviations, differences in data from different authors, and possible risks of extrapolation (error propagation and model adequacy). While for compounds having P_1^s(293.15 K) of the order of 10 kPa directly measured values known to better than 1% are typically available, for compounds whose P_1^s(293.15 K) are about 1 kPa or lower, the values had to be obtained by extrapolation, and thus they are much more inaccurate. Uncertainties as high as 10−20 % are to be expected for 1,1,2,2-tetrachloroethane, all three dichlorobenzenes, tribromomethane, and bromobenzene. For 1,1,2-trichloroethane, data encountered essentially split into two values, 2.2 kPa and 2.4 kPa; preference was given here to the lower value, matching well results of our previous ebulliometric measurements at higher temperatures (Dohnal and Fenclová, 1985).

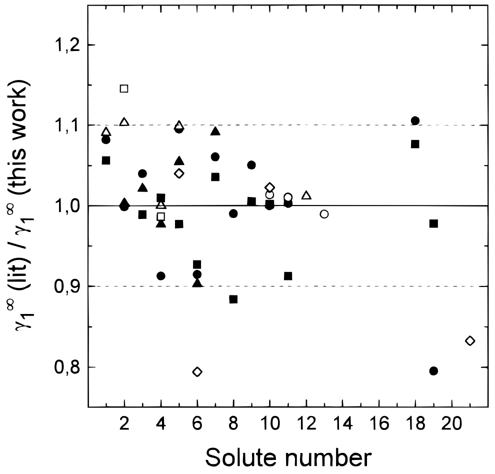

Figure 4. Comparison of limiting activity coefficients measured in this work with literature values determined by ad hoc VLE methods. ■, Tse *et al.* (1992); ●, Wright *et al.* (1992); ▲, Barr and Newsham (1987); □, Bao *et al.* (1993); ○, Cooling *et al.* (1992); △, Li *et al.* (1993); ◇, Hansen *et al.* (1993). The solutes are numbered as in Table 4.

Table 4 gives our experimental values of limiting activity coefficients along with their relative standard errors, which were estimated by the error propagation law taking into account the above mentioned uncertainties in the solute vapor pressure data. For comparison, Table 4 lists also recently published γ_1^∞ data from literature determined by ad hoc VLE methods and some γ_1^∞ values we obtained from solubility measurements reported in the original works of McNally and Grob (1983, 1984) and Stephenson (1992) and in the compilations by Horvath (1982) and Horvath *et al.* (1985). The agreement of our measurements with those from literature obtained by ad hoc VLE methods is generally very good, the only large discrepancy is encountered in the result of Li *et al.* (1993) for trichloroethylene, which is about 60% higher than that of ours. As clearly seen in Figure 4, the accord of our measurements with a great majority of recent literature data is within

Table 4. Comparison of Experimental γ_1^∞ of Halocarbons in Water (T = 293.15 K) with Literature Data

		this work		literature			
no.	solute (1)	γ_1^∞	$\sigma_{rel}(\gamma_1^\infty)$/%	γ_1^∞	T/K	method[a]	ref
1	dichloromethane	232	1	251	293.15	TENS	Wright *et al.*, 1992
				245	293.15	GLC	Tse *et al.*, 1992
				253	298.15	IGS	Li *et al.*, 1993
				243[b]	293.15	SOL	Horvath, 1982[c]
				270[b]	290.45	SOL	Stephenson, 1992
2	trichloromethane	819	1	818	293.15	TENS	Wright *et al.*, 1992
				821	293.15	GLC	Barr and Newsham, 1987
				903	298.15	IGS	Li *et al.*, 1993
				938	298.15	IGS	Bao *et al.*, 1993
				2600	303.15	SOL	McNally and Grob, 1984
				821[b]	293.15	SOL	Horvath, 1982[c]
				836[b]	293.15	SOL	Horvath, 1982[c]
				816[b]	292.75	SOL	Stephenson, 1992
3	1,1-dichloroethane	1058	1	1100	293.15	TENS	Wright *et al.*, 1992
				1046	293.15	GLC	Tse *et al.*, 1992
				1080	293.15	GLC	Barr and Newsham, 1987
				1126	303.15	SOL	McNally and Grob, 1983
				1190	303.15	SOL	McNally and Grob, 1984
				1087	293.15	SOL	Horvath, 1982[c]
				1133	293.15	SOL	Horvath, 1982[c]
4	1,2-dichloroethane	641	1	585	293.15	TENS	Wright *et al.*, 1992
				647	293.15	GLC	Tse *et al.*, 1992
				626	293.15	GLC	Barr and Newsham, 1987
				632	298.15	IGS	Bao *et al.*, 1993
				641	298.15	IGS	Li *et al.*, 1993
				1550	303.15	SOL	McNally and Grob, 1984
				643[b]	293.15	SOL	Horvath, 1982[c]
				656[b]	293.15	SOL	Horvath, 1982[c]
				687[b]	293.15	SOL	Horvath, 1982[c]
				772[b]	292.85	SOL	Stephenson, 1992
5	1,1,1-trichloroethane	5370	5	5880	293.15	TENS	Wright *et al.*, 1992
				5245	293.15	GLC	Tse *et al.*, 1992
				5660	293.15	GLC	Barr and Newsham, 1987
				5900	298.15	IGS	Li *et al.*, 1993
				15300	303.15	SOL	McNally and Grob, 1984
				5610	293.15	SOL	Horvath, 1982[c]
				4770	293.15	SOL	Horvath, 1982[c]
				10580	293.35	SOL	Stephenson, 1992
				5586[e]	299.45	HSA	Hansen, 1993
6	1,1,2-trichloroethane	1662	6	1520	293.15	TENS	Wright *et al.*, 1992
				1540	293.15	GLC	Tse *et al.*, 1992
				1500	293.15	GLC	Barr and Newsham, 1987
				1690	303.15	SOL	McNally and Grob, 1984
				1670	293.15	SOL	Horvath, 1982[c]
				1610	304.45	SOL	Stephenson, 1992
				1320[e]	299.35	HSA	Hansen, 1993
7	1,1,2,2-tetrachloroethane	3630	15	3850	293.15	TENS	Wright *et al.*, 1992
				3758	293.15	GLC	Tse *et al.*, 1992
				3960	293.15	GLC	Barr and Newsham, 1987
				3190	303.15	SOL	McNally and Grob, 1984
				3230	293.15	SOL	Horvath, 1982[c]
				3087	293.15	SOL	Horvath, 1982[c]
8	1,2-dichloropropane	2360	1	2340	293.15	TENS	Wright *et al.*, 1992
				2089	293.15	GLC	Tse *et al.*, 1992
				2590	303.15	SOL	McNally and Grob, 1983
				3020	303.15	SOL	McNally and Grob, 1984
				2320	293.15	SOL	Horvath, 1982[c]
9	*cis*-1,2-dichloroethylene	815	1	856	293.15	TENS	Wright *et al.*, 1992
				819	293.15	GLC	Tse *et al.*, 1992
				1535	293.15	SOL	Horvath, 1982[c]
10	*trans*-1,2-dichloroethylene	1200	1	1200	293.15	TENS	Wright *et al.*, 1992
				1202	293.15	GLC	Tse *et al.*, 1992
				1216	293.15	GLC	Cooling *et al.*, 1992
				863[b]	293.15	SOL	Horvath, 1982[c]
				1227[e]	299.35	HSA	Hansen, 1993
11	trichloroethylene	5400	5	5410	293.15	TENS	Wright *et al.*, 1992
				4922	293.15	GLC	Tse *et al.*, 1992
				5450	293.15	GLC	Cooling *et al.*, 1992
				8750	298.15	IGS	Li *et al.*, 1993
				9770	303.15	SOL	McNally and Grob, 1984
				5670	293.15	SOL	Horvath, 1982[c]
				6685	293.15	SOL	Horvath, 1982[c]

Table 4. (Continued)

		this work		literature			
no.	solute (1)	γ_1^∞	$\sigma_{rel}(\gamma_1^\infty)$/%	γ_1^∞	T/K	method[a]	ref
12	tetrachloroethylene	35600	2	36000	298.15	IGS	Li *et al.*, 1993
				44500	293.15	SOL	Horvath, 1982[c]
				46000	293.15	SOL	Horvath, 1982[c]
				61400	293.15	SOL	Horvath, 1982[c]
				76700	293.15	SOL	Horvath, 1982[c]
				105300	293.15	SOL	Horvath, 1982[c]
				32200	292.65	SOL	Stephenson, 1992
13	chlorobenzene	13100	6	12960	293.15	GLC	Cooling *et al.*, 1992
				13060	303.15	SOL	McNally and Grob, 1984
				13400	293.15	SOL	Horvath, 1985[d]
				12750	293.15	SOL	Horvath, 1982[c]
				13900	293.15	SOL	Horvath, 1982[c]
14	1,2-dichlorobenzene	56700	10	54600	303.15	SOL	McNally and Grob, 1983
				57100	303.15	SOL	McNally and Grob, 1984
				58820	293.15	SOL	Horvath, 1985[d]
				60900	293.15	SOL	Horvath, 1982[c]
				64800	293.15	SOL	Horvath, 1982[c]
				263200	292.65	SOL	Stephenson, 1992
15	1,3-dichlorobenzene	63000	10	64500	303.15	SOL	McNally and Grob, 1983
				80650	293.15	SOL	Horvath, 1985[d]
				83000	292.75	SOL	Horvath, 1982[c]
				73500	293.15	SOL	Horvath, 1982[c]
16	1,4-dichlorobenzene	57900	20	53100	303.15	SOL	McNally and Grob, 1983
				51700	303.15	SOL	McNally and Grob, 1984
				53900	293.15	SOL	Horvath, 1985[d]
				55600	293.15	SOL	Horvath, 1982[c]
				52200	295.35	SOL	Horvath, 1982[c]
17	benzyl chloride	17200	7	14200	293.15	SOL	Howard, 1990
18	dibromomethane	786	5	869	293.15	TENS	Wright *et al.*, 1992
				846	293.15	GLC	Tse *et al.*, 1992
				855[b]	293.15	SOL	Horvath, 1982[c]
				759[b]	292.45	SOL	Stephenson, 1992
19	tribromomethane	4440	10	3530	293.15	TENS	Wright *et al.*, 1992
				4340	293.15	GLC	Tse *et al.*, 1992
				3570	303.15	SOL	McNally and Grob, 1984
				4510	298.15	SOL	Horvath, 1982[c]
				4660	288.15	SOL	Horvath, 1982[c]
20	1,2-dibromoethane	2490	6	2580	293.15	SOL	Horvath, 1982[c]
				3090	293.15	SOL	Horvath, 1982[c]
				2522	292.65	SOL	Stephenson, 1992
21	bromobenzene	22700	10	26200	303.15	SOL	McNally and Grob, 1984
				20500	293.15	SOL	Horvath, 1985[d]
				21200	292.75	SOL	Horvath, 1982[c]
				18900[e]	303.15	HSA	Hansen, 1993

[a] TENS, tensimetry; GLC, retention time gas−liquid chromatography; IGS, inert gas stripping; SOL, measurement of solubility; HSA, head-space analysis. [b] Two-suffix Margules's equation used for extrapolation to infinite dilution [c] Secondary reference. [d] Recommended data. [e] Calculated from given H_{12}.

10%; in many cases this accord is even excellent, within 1−2%. On the other hand, the agreement with values derived from solubility measurements is often not so good. In a number of cases the limiting activity coefficients derived from solubilities are too high (solubilities too low), these discrepancies ranging from several tens to several hundreds of percents. From the comparison in Table 4 it appears that especially solubility data for trichloromethane, 1,2-dichloroethane, 1,1,1-trichloroethane, and trichloroethylene of McNally and Grob (1984) and for 1,2-dichlorobenzene and 1,1,1-trichloroethane of Stephenson (1992) are greatly in error. Also for tetrachloroethylene there is a considerable scatter in solubility measurements; our IGS value of γ_1^∞, however, appears to be supported by a recent IGS measurement of Li *et al.* (1993) and by an older Rayleigh distillation measurement (γ_1^∞ = 39 600, T = 298.15 K) of Prosyanov *et al.* (1973). In addition, a closer inspection of VLE and solubility-based values for cis- and trans-isomers of 1,2-dichloroethylene in Table 4 obviously suggests that in Horvath (1982) compilation solubility values for these isomers were by mistake mutually interchanged. For several solutes (dichlorobenzenes, benzyl chloride, 1,2-dibromoethane), there are no ad hoc VLE

Table 5. Experimental Henry's Law Constants H_{12},[a] Air−Water Partition Coefficients K_{aw},[a] and Limiting Activity Coefficients γ_1^∞ of Bromobenzene and 1,1-Dichloroethane in Water as a Function of Temperature

T/K	H_{12}/MPa	$K_{aw} \times 10^3$	γ_1^∞	$\sigma_{rel}(\gamma_1^\infty)$/%
		Bromobenzene[b]		
283.15	5.01	39.1	24600	10
293.15	9.12	68.7	22700	10
303.15	15.3	111	20400	8
313.15	23.2	165	17480	5
323.15	32.8	227	14570	2
		1,1-Dichloroethane[c]		
283.15	15.0	116	977	1
293.15	25.6	191	1058	1
303.15	38.5	279	1050	1
308.15	46.5	332	1044	1
313.15	54.8	388	1019	1
318.15	63.5	443	986	1
323.15	72.3	498	943	1

[a] $\sigma_{rel}(H_{12}) = \sigma_{rel}(K_{aw})$ = 1%. [b] $\log P_1^s/\text{kPa} = 5.99238 - 1443.265/(T/K - 67.21)$, ref *CDATA* (1991). [c] $\log P_1^s/\text{kPa} = 6.11022 - 1171.420/(T/K - 45.03)$, ref *CDATA* (1991).

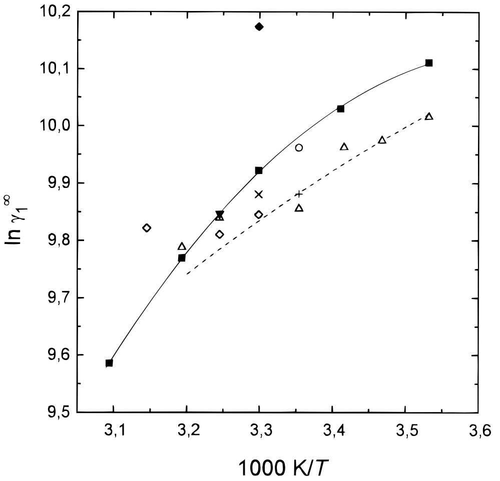

Figure 5. Limiting activity coefficient γ_1^∞ of bromobenzene (1) in water (2) as a function of temperature: ■, this work, IGS; ×, Gross and Saylor (1931), SOL; ○, Andrews and Keefer (1950), SOL; ▼, Hine *et al.* (1963), SOL; △, Vesala, (1973), SOL; +, Vesala (1974), SOL; ◆, McNally and Grob (1984), SOL; - - -, Horvath *et al.* (1985), SOL—IUPAC recommended fit; ◇, Hansen *et al.* (1993), HSA. For the abbreviation of experimental techniques, see the footnote of Table 4. All solubility data were extracted from IUPAC compilation by Horvath *et al.* (1985).

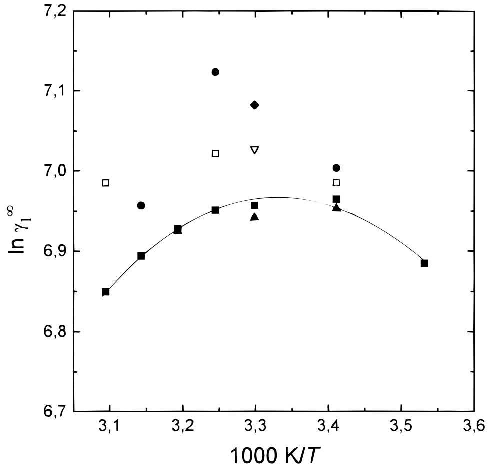

Figure 6. Limiting activity coefficient γ_1^∞ of 1,1-dichloroethane (1) in water (2) as a function of temperature: ■, this work, IGS; ▽, McNally and Grob (1983), SOL; ◆, McNally and Grob (1984), SOL; □, Barr and Newsham (1987), GLC; ●, Wright *et al.* (1992), TENS; ▲, Tse *et al.* (1992), GLC. For the abbreviation of experimental techniques, see the footnote of Table 4.

measurements of γ_1^∞ in literature, and only solubility derived γ_1^∞ values are available for comparison with our IGS results. Considering the difficulties inherent in determining fluid-phase equilibria in these systems (extremely high γ_1^∞ values for dichlorobenzenes, uncertainty in pure component vapor pressures, and lower chemical stability of benzyl chloride and 1,2-dibromoethane), the degree of agreement is satisfactory. Let us stress, however, that we believe that our direct measurements of H_{12}, K_{aw} are of quite high accuracy, and therefore they should be preferred to values of H_{12}, K_{aw} derived from solubility measurements in cases when the uncertainty in pure component vapor pressure is appreciable.

The validity of our experimental results and the good performance of the IGS technique demonstrated for 20 °C by the comparison in Table 4 and Figure 4 is further documented by detailed measurements of the temperature dependence of air—water partitioning, which we have carried out for two selected solvents, bromobenzene and 1,1-dichloroethane, in the range of (10—50) °C. Results of these measurements, corresponding to the range of H_{12} from 5 to 72 MPa, are summarized in Table 5 and graphically depicted and compared to available literature data in Figures 5 and 6. For both solutes the measured data follow a very smooth ln γ_1^∞ vs $1/T$ curve exhibiting in the case of bromobenzene a marked concave pattern and in the case of 1,1-dichloroethane a distinct maximum around the ambient temperature. This otherwise special behavior of temperature dependence of γ_1^∞ is relatively often encountered in dilute aqueous solutions. Agreement of our results with rather fragmentary and more scattered literature data is in most cases better than 10%.

In summary, the inert gas stripping method has been shown to be a precise, reliable, and efficient experimental technique to measure air—water partitioning of halocarbons. The results presented in this work improve our knowledge about air—water partitioning of these environmentally important substances. It is believed that our data will be of value for estimations of the environmental transport of halocarbons and for feasibility assessment of their separation from contaminated water effluents and supplies.

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