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# Limiting Activity Coefficients of Some Aromatic and Aliphatic Nitro Compounds in Water

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Limiting activity coefficients of nine nitroaromatic compounds and four nitroalkanes in water were determined in the range of environmentally related temperatures by measuring suitable phase equilibria. For liquid and solid nitroaromatics (nitrobenzene, 2-nitrotoluene, 3-nitrotoluene, 4-nitrotoluene, 2-nitrophenol, 3-nitrophenol, 4-nitrophenol, 1-chloro-2-nitrobenzene, and 1-chloro-4-nitrobenzene) the aqueous solubilities were measured by a conventional batch contacting method with UV spectrophotometric analysis, while for nitroalkanes (nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane) the air−water partitioning (Henry's law constant $H_{12}$ or air−water partition coefficient $K_{aw}$) was determined by the inert gas stripping method employing gas chromatography. Whenever possible, our results were compared to literature values. Calculation of $H_{12}$ or $K_{aw}$ for nitroaromatics from the measured solubilities is hindered by the lack of reliable vapor pressure data. On the basis of the temperature dependences of the solubilities measured, the enthalpies of solution at infinite dilution for the nitroaromatics in water were evaluated.

## Introduction

Nitro compounds are important, industrially produced substances with a variety of applications. They are used as synthetic intermediates to manufacture dyes, explosives, and agricultural and rubber chemicals, and they serve as special solvents, corrosion inhibitors, and fuel additives. However, during their manufacture and use they penetrate into the environment through fugitive emissions and spills and in wastewater. The nitroaromatics present an especially great hazard because of their relatively high stability and tendency to leach into groundwater. In general, nitro compounds constitute a class of organic substances of special environmental interest appearing on most priority pollutant lists (Mackay, 1991; Lide, 1994).

For rational treatment of respective ecological problems, knowledge of contaminants' physicochemical properties, such as aqueous solubility and air−water partitioning, is required. At the very low contaminant concentrations encountered under environmental conditions the thermodynamic state of the solute corresponds to that at infinite dilution and the key thermodynamic quantity governing phase equilibria is the limiting activity coefficient of the solute in water, $\gamma_1^\infty$. Its value is a measure of the solution nonideality and the solute hydrophobicity.

With few exceptions, the information on phase equilibria in highly dilute aqueous solutions of nitro compounds is lacking or unreliable. In this work, we have focused on experimental determination of limiting activity coefficients of selected aliphatic and aromatic nitro compounds in water, measuring suitable phase equilibria in the region of environmentally important temperatures. Two experimental techniques, inert gas stripping to measure the air−water partitioning and the batch contacting method to measure the aqueous solubility, have been employed.

The present work is a continuation of similar systematic studies we have recently undertaken on other classes of priority pollutants, viz. phenols (Dohnal and Fenclová, 1995) and halogenated hydrocarbons (Hovorka and Dohnal, 1997).

## Experimental Section

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

***Aqueous Solubilities.*** The conventional batch contacting technique was used to measure the aqueous solubilities of liquid or solid nitroaromatic compounds. Excess amounts of nitroaromatics were added into jacketed 50 cm$^3$ glass equilibrium cells containing twice-distilled water and thermostated to ±0.02 K by a Medingen electronic circulating thermostat U6CP. The mixtures were magnetically stirred for 12 h and allowed to settle at the controlled temperature for at least 48 h. Samples of saturated solutions were withdrawn with 20 cm$^3$ syringes through glass wool plugs. For experimental temperatures higher that the ambient, the syringes were preheated. The first portions of the samples were discarded to avoid possible adsorption effects on glass wool. After appropriate dilution, the samples were assayed spectrophotometrically using a computer-interfaced ECOM (Prague, Czech Republic) UV absorbance detector, Model LCD 2082, through which they were pumped by a chemically inert pump at a low flow rate. The analyses were carried out at the maximum absorbance wavelengths as given in Table 1. The concentrations were established on the basis of previously obtained absorbance values of standard calibration solutions which were observed to obey Lambert−Beer's law precisely. Three independent solubility determinations for each of the solutes were done, the agreement of the replicates being typically within ±1−2%.

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**Table 1. Maximum Absorbance Wavelengths[a] $\lambda$, Melting Temperatures[b] $T_m$, Enthalpies of Fusion[b] $\Delta_{fus}H$, and Heat Capacities in Liquid[c] $C_p^L$ and Solid State[d] $C_p^S$ for Nitroaromatic Compounds**

| compound | $\lambda$/nm | $T_m$/K | $\Delta_{fus}H$/(kJ·mol$^{-1}$) | $C_p^L$/(J·K$^{-1}$·mol$^{-1}$) | $C_p^S$/(J·K$^{-1}$·mol$^{-1}$) |
|---|---|---|---|---|---|
| nitrobenzene | 290 | 278.85 | | | |
| 2-nitrotoluene | 265 | 269.30 | | | |
| 3-nitrotoluene | 273 | 289.25 | | | |
| 4-nitrotoluene | 290 | 324.75 | 16.81 | | |
| 2-nitrophenol | 278 | 317.95 | 17.44 | | |
| 3-nitrophenol | 274 | 369.95 | 19.20 | 247 | 160.9 |
| 4-nitrophenol | 317 | 386.95 | 18.25 | 247 | 162.0 |
| 1-chloro-2-nitrobenzene | 266 | 306.15[e] | 17.58[e] | | |
| 1-chloro-4-nitrobenzene | 282 | 356.15 | 20.77 | 200 | 182.6[b] |

[a] This work. [b] Domalski and Hearing (1990). [c] Estimated from the group contribution method of Růžička and Domalski (1993). [d] Satoh (1942). [e] Yalkowsky and Wells (1979).

***Inert Gas Stripping.*** The method of inert gas stripping (IGS), which we used for nitroalkanes, involves measuring the rate of elution of a solute as an entraining inert gas is passed through a highly dilute solution ($x_1 < 10^{-3}$). The experimental setup and procedure for the IGS method were the same as those we have used recently to measure air–water partitioning of halocarbons (Hovorka and Dohnal, 1997). The apparatus was designed around a Hewlett-Packard gas chromatograph (GC), Model 5890 II. The chromatograph is equipped with a flame ionization detector (FID) and a pneumatic six-port gas sampling valve which is housed in an independently heated zone of the GC and kept at 150 °C. The equilibrium stripping cell, described in detail previously, is an all-glass jacketed device composed of the presaturator and the dilutor holding the solvent and the dilute solution, respectively. About 13 cm$^3$ of the solvent was loaded gravimetrically into the dilutor which has a the total volume of 17 cm$^3$. The solute was added volumetrically with a chromatographic syringe, and then the contents were vigorously mixed with an efficient magnetic stirrer. The cell was thermostated with an electronic water circulating bath (Medingen, U6CP) to ±0.02 K. The temperature of the water bath was measured with a calibrated standard mercury thermometer (Karl Schneider, Wertheim, Germany) to ±0.01 K. The constant flow of stripping gas ($N_2$) was supplied by an auxiliary-gas channel of the GC and introduced into the cell through a very fine porosity glass tip. Before entering the cell, the stripping gas was brought to the temperature of the solution by passing through a thermostating coil immersed in the bath and then, in the presaturator of the cell, it was presaturated by the solvent vapor. The stripping gas flow rate was digitally controlled by the electronic flow controller of the channel and measured, before and after each experiment, with a thermostated soap-bubble flow meter. Typical flow rates used for the measurements of the systems studied in this work were from 15 to 25 mL·min$^{-1}$, which lead to small relative rates of the solute elution (about 0.01 min$^{-1}$). 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 (140 °C) transfer line to the respective port of the gas sampling valve. The volume of the sampling loop used was 250 $\mu$L. 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, chemically inert support was employed. At the carrier gas flow rate 10 mL·min$^{-1}$ and oven temperatures set close to the normal boiling temperatures of the solute, this provided narrow peaks and short times of analyses (2 min). The operation of the gas chromatograph, including all zone temperature and 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. In a typical run, the process of the solute elution was monitored for 2.5 to 3 h, during which 18 samples were taken.

**Table 2. Experimental Solubilities $S$, Mole Fraction Solubilities $x_1$, and Derived Values of Limiting Activity Coefficients $\gamma_1^\infty$ for Aromatic Nitro Compounds in Water**

| solute | equilibrium | $T$/K | $S$/(g·L$^{-1}$) | $10^4 x_1$ | $\gamma_1^\infty$ |
|---|---|---|---|---|---|
| nitrobenzene | LLE | 283.15 | 1.77 | 2.60 | 3850 |
| | LLE | 293.15 | 1.93 | 2.84 | 3520 |
| | LLE | 303.15 | 2.06 | 3.03 | 3300 |
| | LLE | 313.15 | 2.20 | 3.25 | 3100 |
| 2-nitrotoluene | LLE | 283.15 | 0.531 | 0.698 | 14300 |
| | LLE | 293.15 | 0.609 | 0.802 | 12500 |
| | LLE | 303.15 | 0.688 | 0.908 | 11000 |
| | LLE | 313.15 | 0.773 | 1.026 | 9700 |
| 3-nitrotoluene | LLE | 283.15 | 0.450 | 0.591 | 16900 |
| | LLE | 293.15 | 0.491 | 0.646 | 15500 |
| | LLE | 303.15 | 0.534 | 0.705 | 14200 |
| | LLE | 313.15 | 0.565 | 0.750 | 13300 |
| 4-nitrotoluene | SLE | 283.15 | 0.179 | 0.235 | 17000[a] |
| | SLE | 293.15 | 0.242 | 0.319 | 16000[a] |
| | SLE | 303.15 | 0.322 | 0.425 | 15100[a] |
| | SLE | 313.15 | 0.418 | 0.555 | 14300[a] |
| 2-nitrophenol | SLE | 283.15 | 0.895 | 1.16 | 3830[a] |
| | SLE | 293.15 | 1.35 | 1.76 | 3250[a] |
| | SLE | 303.15 | 2.00 | 2.60 | 2790[a] |
| | SLE | 313.15 | 2.84 | 3.72 | 2430[a] |
| 3-nitrophenol | SLE | 283.15 | 7.20 | 9.38 | 238[b] |
| | SLE | 293.15 | 10.8 | 14.1 | 190[b] |
| | SLE | 303.15 | 16.7 | 22.0 | 147[b] |
| | SLE | 308.15 | 19.0 | 25.2 | 140[b] |
| 4-nitrophenol | SLE | 283.15 | 8.05 | 10.5 | 210[b] |
| | SLE | 293.15 | 12.2 | 16.0 | 160[b] |
| | SLE | 303.15 | 17.8 | 23.5 | 126[b] |
| | SLE | 311.15 | 23.9 | 31.8 | 106[b] |
| 1-chloro-2-nitrobenzene | SLE | 283.15 | 0.228 | 0.261 | 21900[a] |
| | SLE | 293.15 | 0.336 | 0.385 | 19100[a] |
| | SLE | 303.15 | 0.504 | 0.579 | 16100[a] |
| | LLE | 313.15 | 0.673 | 0.777 | 12900 |
| 1-chloro-4-nitrobenzene | SLE | 283.15 | 0.153 | 0.175 | 9900 |
| | SLE | 293.15 | 0.209 | 0.239 | 9640 |
| | SLE | 303.15 | 0.274 | 0.315 | 9580 |
| | SLE | 313.15 | 0.370 | 0.427 | 9100 |

[a] Calculated neglecting the heat capacity term in eq 2. [b] Corrected to infinite dilution using the two-suffix Margules equation.

## Results and Discussion

The aqueous solubilities of nine aromatic nitro compounds as measured by the batch contacting method at four environmentally important temperatures, 283.15, 293.15, 303.15, and 313.15 K, are given in Table 2. Listed are the solubilities $S$ (g·L$^{-1}$) as well as the mole fraction solubilities $x_1$, which were calculated from $S$ assuming the densities of the dilute solutions to be equal to those of pure water. For 4-nitrophenol, we set the highest temperature to 311.15 K, because above 312.75 K there are two heterogeneous regions (LLE, SLE) in the 4-nitrophenol + water system (Sidgwick et al., 1915). A similar precaution was taken also for 3-nitrophenol, where at temperatures close to 313.15 K the crystals of 3-nitrophenol in water were observed to melt, forming with water another liquid phase. The measured solubilities are compared to data from the literature

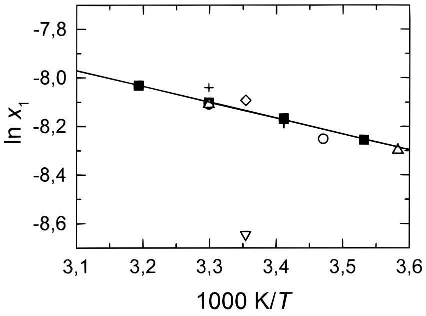

**Figure 1.** Mole fraction solubility $x_1$ of nitrobenzene (1) in water (2) as a function of temperature: (■) this work; (+) Davis (1916); (○) Gross and Saylor (1931); (△) Vermillion et al. (1941); (▽) Booth and Everson (1948); (◇) Banerjee et al. (1980).

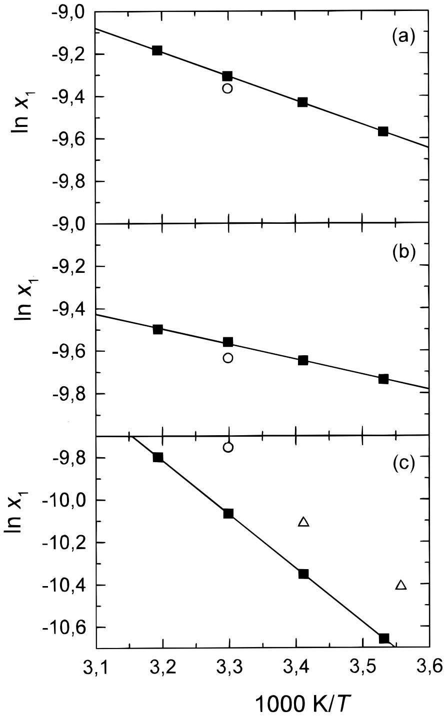

**Figure 2.** Mole fraction solubility $x_1$ of nitrotoluenes (1) [2-nitrotoluene (a), 3-nitrotoluene (b), 4-nitrotoluene (c)] in water (2) as a function of temperature: (■) this work; (○) Gross et al. (1933); (△) Tzscheutschler and Gelbin (1982).

in Figures 1−3, where ln $x_1$ versus the reciprocal absolute temperature is plotted. Here, chloronitrobenzenes are not included, since we have not found any experimental data on their solubility in the literature. For nitrobenzene (Figure 1), our values are seen to be in a very good agreement with those from various other authors, the only discrepancy being the value by Booth and Everson (1948) measured by a volumetric method. Since a volumetric method is not well suited for determination of such low solubilities, their result is not considered reliable. For nitrotoluenes (Figure 2), the literature information available for comparison with our data is very limited. For both 2-nitrotoluene and 3-nitrotoluene, the only literature value, due to Gross et al. (1933), agrees within 5 to 10% with our measurement, while, for 4-nitrotoluene, the value of Gross et al. (1933) as well as the values of Tzscheutschler and Gelbin (1982) are 25 to 30% higher. As seen from Figure 3, nitrophenols have received more attention of experimenters; our values agree well with the values of Britzinger et al. (1937) and, except at the highest temperature, also very well (within 5%) with recent conductometric measurements of Achard et al. (1997) done for 2-nitrophenol and 4-nitrophenol. In contrast to this, the largest deviations encountered for the oldest measurements of Desvergnes (1927) and Duff and Bills (1930) amount to 20 to 50%.

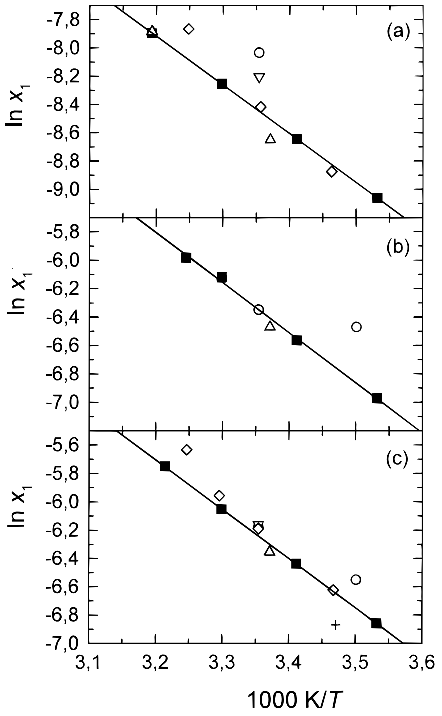

**Figure 3.** Mole fraction solubility $x_1$ of nitrophenols (1) [2-nitrophenol (a), 3-nitrophenol (b), 4-nitrophenol (c)] in water (2) as a function of temperature: (■) this work; (+) Desvergnes (1927); (○) Duff and Bills (1930); (△) Britzinger and Beier (1937); (▽) Buchholz and Pawliszyn (1994); (◇) Achard et al. (1996).

In addition to the measured solubility values, Table 2 gives limiting activity coefficients derived from them. For liquid solutes, $\gamma_1^\infty$'s were calculated as the inverse mole fraction solubilities

$$\gamma_1^\infty = 1/x_1^{\mathrm{LLE}} \tag{1}$$

For solid solutes, $\gamma_1^\infty$'s referring to the hypothetical pure liquid standard state were calculated with the following equation (Tsonopoulos and Prausnitz, 1971)

$$\gamma_1^\infty = \frac{1}{x_1^{\mathrm{SLE}}} \exp\left[\frac{\Delta_{\mathrm{fus}}H}{RT_{\mathrm{m}}}\left(1 - \frac{T_m}{T}\right) - \frac{\Delta_{\mathrm{fus}}C_{\mathrm{p}}}{R}\left(1 - \frac{T_{\mathrm{m}}}{T} + \ln\frac{T_{\mathrm{m}}}{T}\right)\right] \tag{2}$$

where the expression in parentheses accounts for the fugacity difference between the solid and the hypothetical liquid states. The values of the solute melting temperature $T_{\mathrm{m}}$, the enthalpy of fusion $\Delta_{\mathrm{fus}}H$, and the heat capacity change upon fusion $\Delta_{\mathrm{fus}}C_{\mathrm{p}} \equiv C_{\mathrm{p}}^{\mathrm{L}} - C_{\mathrm{p}}^{\mathrm{S}}$, necessary for this calculation, are from Table 1. Note that for temperatures close to $T_{\mathrm{m}}$ the effect of the heat capacity term is small and hence this term can be neglected. The uncertainty of the limiting activity coefficients obtained from eq 1 corresponds to that of the solubility measurements, amounting to 1 to 2%. The $\gamma_1^\infty$ values calculated from eq 2 are, however, less accurate due to the error propagation from rather uncertain caloric data, the estimated uncertainty levels of $\gamma_1^\infty$ being 5% for 4-nitrotoluene, 2-nitrophenol, and 1-chloro-2-nitrobenzene and 10% for 3-nitrophenol, 4-nitrophenol, and 1-chloro-4-nitrobenzene.

As seen from Table 2, the values of $\gamma_1^\infty$ of the studied nitroaromatics span over 2 orders of magnitude; the highest

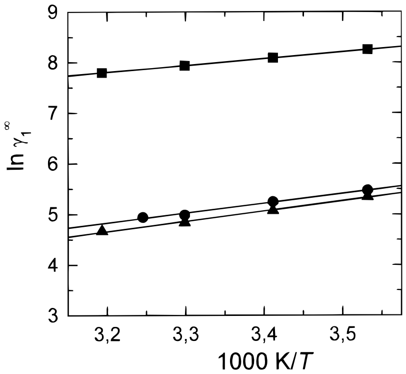

**Figure 4.** Limiting activity coefficients $\gamma_1^\infty$ of nitrophenols (1) in water (2) as a function of temperature: (■) 2-nitrophenol; (●) 3-nitrophenol; (▲) 4-nitrophenol.

**Table 3. Enthalpies of Solution at Infinite Dilution in Water[a] for Nitroaromatic Compounds in Their Prevailing Physical State at Environmental Temperatures and in the State of Hypothetical Liquid**

| substance | physical state | $\Delta_{\mathrm{sol}}H_1^\infty$/(kJ·mol$^{-1}$) | $\Delta_{\mathrm{sol}}H_1^{\infty(\mathrm{hyp})}$/(kJ·mol$^{-1}$) |
|---|---|---|---|
| nitrobenzene | liquid | 5.4 ± 0.2 | |
| 2-nitrotoluene | liquid | 9.4 ± 0.1 | |
| 3-nitrotoluene | liquid | 5.9 ± 0.2 | |
| 4-nitrotoluene | solid | 21.1 ± 0.1 | 4.3 ± 0.1 |
| 2-nitrophenol | solid | 28.7 ± 0.1 | 11.2 ± 0.1 |
| 3-nitrophenol | solid | 29.3 ± 1.1 | 16.1 ± 1.1 |
| 4-nitrophenol | solid | 28.9 ± 0.1 | 16.9 ± 0.8 |
| 1-chloro-2-nitrobenzene | solid | 28.4 ± 1.0 | 12.9 ± 1.3 |
| 1-chloro-4-nitrobenzene | solid | 21.7 ± 0.5 | 1.9 ± 0.5 |

[a] The uncertainties given are the standard deviations obtained through fitting ln $x_1$ or ln $\gamma_1^\infty$ versus $1/T$.

values of the order $10^4$ were observed for 1-chloro-2-nitrobenzene, while the lowest ones of the order $10^2$ were observed for 3-nitrophenol and 4-nitrophenol. The differences between isomeric substances are quite distinct, and for nitrophenols they become even spectacular (see Figure 4); the $\gamma_1^\infty$ values for 2-nitrophenol are greater by an order of magnitude than those for the other two nitrophenol isomers. The enhanced values of $\gamma_1^\infty$ for 2-nitrophenol can be explained by its capability of forming intramolecular hydrogen bonds between adjacent hydroxyl and nitro groups, which greatly limits its possibilities of forming hydrogen bonds with water. Thus, 2-nitrophenol is considerably more hydrophobic than the two other isomers for which the formation of the intramolecular hydrogen bond is not possible for steric reasons.

The temperature dependences of both the measured solubilities and the derived limiting activity coefficients, plotted in van't Hoff-like coordinates, are linear within the temperature range investigated. From the temperature dependence of the solubilities, the enthalpies of solution at infinite dilution in water, $\Delta_{\mathrm{sol}}H_1^\infty$, were then easily calculated according to the following relation

$$[\partial \ln x_1/\partial(1/T)] = -\Delta_{\mathrm{sol}}H_1^\infty/R \qquad (3)$$

In addition, for solid solutes (SLE), the enthalpies of solution at infinite dilution for the respective hypothetical liquids $\Delta_{\mathrm{sol}}H_1^{\infty(\mathrm{hyp})}$ were evaluated from

$$[\partial \ln \gamma_1^\infty/\partial(1/T)] = \Delta_{\mathrm{sol}}H_1^{\infty(\mathrm{hyp})}/R \qquad (4)$$

The calculated values of $\Delta_{\mathrm{sol}}H_1^\infty$ and $\Delta_{\mathrm{sol}}H_1^{\infty(\mathrm{hyp})}$ are listed in Table 3. For all nitroaromatic compounds studied their transfer from the solid state as well as from the liquid state into their infinitely dilute aqueous solutions is endothermic.

**Table 4. Limiting Activity Coefficients $\gamma_1^\infty$, Henry's Law Constants $H_{12}$, and Air−Water Partition Coefficients $K_{\mathrm{aw}}$ for Nitroalkane Solutes in Water Measured by the Inert Gas Stripping Method[a]**

| solute | $T$/K | $\gamma_1^\infty$ | $H_{12}$[a]/kPa | $10^3K_{\mathrm{aw}}$[a] |
|---|---|---|---|---|
| nitromethane | 293.15 | 34.8 | 126 | 0.94 |
| | 303.15 | 33.4 | 203 | 1.48 |
| | 313.15 | 30.8 | 303 | 2.15 |
| | 323.15 | 29.1 | 447 | 3.09 |
| nitroethane | 293.15 | 93.4 | 196 | 1.47 |
| | 303.15 | 90.7 | 329 | 2.40 |
| | 313.15 | 87.4 | 526 | 3.73 |
| | 323.15 | 82.1 | 788 | 5.45 |
| 1-nitropropane | 293.15 | 314 | 317 | 2.39 |
| | 303.15 | 309 | 559 | 4.09 |
| | 313.15 | 294 | 909 | 6.46 |
| | 323.15 | 274 | 1395 | 9.67 |
| 2-nitropropane | 293.15 | 291 | 500 | 3.77 |
| | 303.15 | 287 | 859 | 6.27 |
| | 313.15 | 276 | 1370 | 9.75 |
| | 323.15 | 261 | 2070 | 14.3 |

[a] Henry's law constant and the air−water partition coefficient are related to $\gamma_1^\infty$ through $H_{12} = \gamma_1^\infty P_1^{\mathrm{s}}$ and $K_{\mathrm{aw}} = (\gamma_1^\infty P_1^{\mathrm{s}} v_{\mathrm{w}}^{\mathrm{L}})/(RT)$, where $v_{\mathrm{w}}^{\mathrm{L}}$ is the liquid molar volume of pure water.

To calculate the quantities characterizing the air−water partitioning, the Henry's law constant $H_{12}$ or the air−water partition coefficient $K_{\mathrm{aw}}$, knowledge of pure solute vapor pressures is necessary. Unfortunately, in the region of environmental temperatures, the situation in the literature with these data for nitroaromatic compounds is very unfavorable. The data are completely lacking for 2-nitrotoluene and 3-nitrotoluene, and for 4-nitrotoluene the results published by various authors (Lenchitz and Velicky, 1970; Ambrose and Gundry, 1980; Tzscheutschler and Gelbin, 1982) disagree mutually by more than an order of magnitude. Except for nitrobenzene, for which the vapor pressure data of Lynch and Wilke (1960) are estimated to be accurate to 10%, the published vapor pressures are scarce and subject to unacceptably high uncertainties. Their values at ambient temperatures are very low (ranging from a few Pa down to $10^{-2}$ Pa) and were typically determined by the effusion method, which is rather unreliable. Under this situation, the derived $H_{12}$ or $K_{\mathrm{aw}}$ values have a semiquantitative character and will not be presented here. For nitroaromatics exhibiting sufficiently high volatilities from their dilute aqueous solutions (nitrobenzene, 2-nitrophenol, chloronitrobenzenes), a direct measurement of air−water partitioning by a suitable technique would be preferable to determine $H_{12}$ or $K_{\mathrm{aw}}$.

The limiting activity coefficients of four nitroalkanes (nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane) were determined from the IGS measurements using the following formula (Hovorka and Dohnal, 1997)

$$\gamma_1^\infty = \frac{n_2^\circ RT}{P_1^{\mathrm{s}}D}\left(-\frac{\mathrm{d}\ln A_1}{\mathrm{d}t}\right)(1 - P_2^{\mathrm{s}}/P)\xi \qquad (5)$$

where $n_2^\circ$ is the amount of solvent loaded into the stripping cell, $D$ is the flow rate of pure stripping gas at temperature $T$ and pressure $P$ of the cell, $P_i^{\mathrm{s}}$ are the pure component vapor pressures, and ($-$d ln $A_1$/d$t$) is the slope of the semilogarithmic plot of solute peak area $A_1$ versus time $t$. The last term in eq 5, $\xi$, is a dimensionless correction factor accounting for some minor effects, viz. the change of the stripping gas flow rate due to the saturation in the

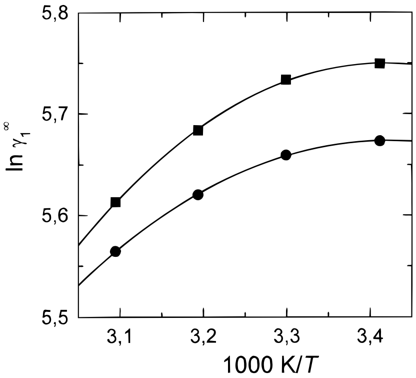

**Figure 5.** Limiting activity coefficients $\gamma_1^\infty$ of nitropropanes (1) in water (2) as a function of temperature: (■) 1-nitropropane; (●) 2-nitropropane.

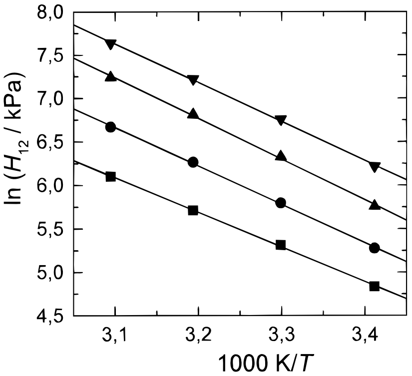

**Figure 6.** Henry's law constants $H_{12}$ of nitroalkanes (1) in water (2) as a function of temperature: (■) nitromethane; (●) nitroethane; (▲) 1-nitropropane; (▼) 2-nitropropane.

cell, the amount of the solute in the vapor space, and the vapor-phase nonideality. For systems studied in this work, these corrections were small, in total not exceeding 1%, and hence they could be neglected. The limiting activity coefficients were determined at four temperatures in the range from 293.15 K to 323.15 K, and they are given, together with the related air−water partitioning characteristics $H_{12}$ and $K_{aw}$, in Table 4. As estimated from the error propagation law, the uncertainty of each of these quantities is about 1%, since the vapor pressures of the nitroalkanes are known to a good accuracy (Toops, 1956). To our knowledge, with the exception of two $\gamma_1^\infty$ values at 298 K for nitromethane (Rohrschneider, 1973; Park et al., 1987), which were measured by a less accurate headspace gas chromatographic technique (the offset from the course of our data is 23% and 7%, respectively), there are no direct experimental data in the literature on activity coefficients or gas−liquid partitioning of nitroalkanes in highly dilute aqueous solutions.

The limiting activity coefficients of lower nitroalkanes in water are much smaller than those of most nitroaromatics; only 3-nitrophenol and 4-nitrophenol exhibit limiting activity coefficients that are of similar magnitude due to their hydroxyls' capability of participating in hydrogen bonding with water. It can be seen from Table 4 that each methylene increment in the nitroalkane molecule causes the limiting activity coefficient to increase by approximately a factor of 3. Compared to this, the difference in $\gamma_1^\infty$ of the isomeric nitropropanes is rather small but easily recognizable, as shown in Figure 5. For all nitroalkanes studied, the nonideality of their aqueous solutions decreases with increasing temperatures, thus implying endothermic mixing. The dependences of ln $\gamma_1^\infty$ versus $1/T$ exhibit, however, a distinct curvature, and it appears that for nitroethane and both nitropropanes a maximum occurs close to 293 K. This finding is supported by very low values of enthalpies of solution at infinite dilution which were determined calorimetrically for nitroethane and 1-nitropropane at 298 K by Trampe and Eckert (1991). Plots of ln $H_{12}$ (or ln $K_{aw}$) versus $1/T$, on the other hand, show quite good linearity, as illustrated in Figure 6.

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