

# Henry's law constants and infinite dilution activity coefficients of *cis*-2-butene, dimethylether, chloroethane, and 1,1-difluoroethane in methanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, isobutanol, *tert*-butanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 3-methyl-1-butanol, and 2-methyl-2-butanol

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## Abstract

Henry's law constants and infinite dilution activity coefficients of *cis*-2-butene, dimethylether, chloroethane, and 1,1-difluoroethane in methanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, isobutanol, *tert*-butanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 3-methyl-1-butanol, and 2-methyl-2-butanol in the temperature range of 250 K to 330 K were measured by a gas stripping method and partial molar excess enthalpies were calculated from the activity coefficients. A rigorous formula for evaluating the Henry's law constants from the gas stripping measurements was used for the data reduction of these highly volatile mixtures. The uncertainty is about 2% for the Henry's law constants and 3% for the estimated infinite dilution activity coefficients. In the evaluation of the infinite dilution activity coefficients, the nonideality of the solute such as the fugacity coefficient and Poynting correction factor cannot be neglected, especially at higher temperatures. The estimated uncertainty of the infinite dilution activity coefficients includes 1% for nonideality.

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## 1. Introduction

A systematic study of gas solubilities including the Henry's law constant is useful in providing data for the design of absorption processes as well as indirectly in aiding the analysis of molecular interactions in solutions. Although a large number of (alkane + alcohol)

and (alkene + alcohol) solubility results have been published, few are available for C<sub>4</sub>-gases like butane, 1-butene, and their isomers. Solubility data will be useful for the development of predictive methods. Especially for group contribution methods, it may be necessary to take into account the differences between isomers.

To estimate the gas solubility from a molecular theory or molecular simulation, on the other hand, an accurate intermolecular potential is necessary. The Henry's law constant is directly related to the residual chemical potential of the solute at infinite dilution, which is evaluated

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from the intermolecular potential between a solute molecule and a solvent molecule. Therefore, the Henry's law constant is a suitable macroscopic property for correlating the intermolecular potential between different kinds of molecules.

Oxygenates such as ethers and alcohols have been used widely as fuel additives to increase the octane number, improve the combustion process, and reduce emissions. Dimethylether is being considered as a new alternative diesel fuel. In the design of these production facilities, solubility data of gases in alcohols are needed.

The gas stripping method, proposed by Leroi *et al.* [1], has been used to measure the activity coefficients at infinite dilution of liquid solutes in nonvolatile solvents. In previous work [2–8], the Henry's law constants for propane, propene, butane, isobutane, 1-butene, isobutene, *trans*-2-butene, and 1,3-butadiene in alcohols, were measured with this method.

In this work, the Henry's law constants for *cis*-2-butene, dimethylether, chloroethane, and 1,1-difluoroethane in methanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, isobutanol, *tert*-butanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 3-methyl-1-butanol, and 2-methyl-2-butanol are measured by the gas stripping method, and the infinite dilution activity coefficients of solutes and the partial molar excess enthalpies are evaluated.

In the literature, we have found the following experimental data of the mixtures studied in this work. (Vapour + liquid) equilibrium (VLE) for {*cis*-2-butene + methanol, + 2-propanol, + 2-butanol, and + 2-methyl-2-propanol (*tert*-butanol)} at  $T = 337$  K were previously measured with a static pressure apparatus [9]. The VLE for (*cis*-2-butene + 1-propanol) was also measured with the same method at  $T = 332$  K [10]. The VLE for (dimethylether + methanol) was measured from  $T = (273.15 \text{ to } 453.15)$  K [11] and from  $T = (254 \text{ to } 352)$  K [12]. Henry's law constants of 1,1-difluoroethane in methanol and 2-propanol were measured by means of a flow method [13]. Henry's law constants of 1,1-difluoroethane in methanol were also measured but using head-space gas chromatography [14] at  $T = (318 \text{ and } 323)$  K.

## 2. Theory

The gas stripping method, originally proposed by Leroi *et al.* [1], is based on the variation of the vapour-phase composition when the highly diluted solute in a liquid mixture in an equilibrium cell is stripped from the solution by the flow of inert gas (helium). The composition of the gas leaving the cell was periodically sampled and analyzed by means of gas chromatography (g.c.). The g.c. signal area,  $S$ , of the solute decreases exponentially with the volume of inert gas flowing out of the cell by the following rigorous relation [2]:

$$\ln \frac{S}{S_0} = \left( \frac{(H_g/\varphi_g^V)}{(1 + \alpha)P_s^{\text{sat}} - \alpha(H_g/\varphi_g^V)} - 1 \right) \times \ln \left( 1 - \frac{(1 + \alpha)P_s^{\text{sat}} - \alpha(H_g/\varphi_g^V)}{ZRTn_{s,0}^L + V_{\text{GP},0}(H_g/\varphi_g^V)} V \right), \quad (1)$$

where  $H_g$  is the Henry's law constant defined as

$$H_g = \lim_{x_g \rightarrow 0} \frac{f_g^V}{x_g}. \quad (2)$$

The  $f_g^V$  is the fugacity of the solute in the vapour phase,  $x_g$  is the mole fraction of the solute in the liquid phase, the subscript g indicates the solute. The  $S_0$  is the signal area of the solute at time  $t = 0$ ,  $P_s^{\text{sat}}$  is the saturated vapour pressure of the pure solvent (s),  $Z$  is the compressibility factor of the saturated vapour in the cell, and  $\varphi_g^V$  represents the fugacity coefficient of the solute in the vapour phase. Superscripts V and L denote vapour and liquid phases, respectively. The  $n_{s,0}^L$  is the number of moles of solvent in the liquid phase in the cell at  $t = 0$ . The  $V_{\text{GP},0}$  is the initial volume of the vapour phase in the cell, and  $V$  is the volume of the saturated gas flowing out of the cell. The volume of the vapour phase in the cell at time  $t$ ,  $V_{\text{GP}}$ , slightly depends on the gas volume withdrawn from the cell, and it is expressed as

$$V_{\text{GP}} = V_{\text{GP},0} + \alpha V, \quad \alpha = \frac{P_s^{\text{sat}} v_s^{\text{L,sat}}}{ZRT}, \quad (3)$$

where  $v_s^{\text{L,sat}}$  is the liquid molar volume of the solvent at saturation,  $R$  is the gas constant, and  $T$  is the absolute temperature.

Equation (1) requires the assumption that a linear relation exists between the signal area,  $S$ , and the concentration. As the concentration of the solute in the vapour phase was so diluted, all solutes satisfied this assumption, and the proportionality constants between the signal area and the partial pressure could be experimentally determined for each solute.

From equation (1), the Henry's law constant of the solute can be obtained as the slope of the line in a log–log plot as follows. The initial value of the Henry's law constant was set equal to zero, and the logarithm on the right-hand side in equation (1) was calculated. Then the new value of the Henry's law constant was obtained. By a process of successive iterations, the value of the Henry's law constant was determined.

The infinite dilution activity coefficient of the solute,  $\gamma^\infty$ , can be obtained from the following relationship:

$$H_g = f_g^{\text{L},\circ} \gamma^\infty = f_g^{\text{sat}} \lambda_\gamma^\infty = \varphi_g^{\text{sat}} P_g^{\text{sat}} \lambda_\gamma^\infty, \quad (4)$$

$$\gamma^\infty = \frac{H_g}{\varphi_g^{\text{sat}} P_g^{\text{sat}} \lambda_\gamma^\infty}, \quad (5)$$

where  $f_g^{\text{L},\circ}$  is the fugacity of the pure solute at the reference state (pure liquid at the system temperature and

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