



## Abraham model correlations for solute transfer into 2-ethoxyethanol from water and from the gas phase



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### ABSTRACT

Infinite dilution activity coefficients ( $\gamma_{\infty}$ ) were measured at 298 K for 13 different aliphatic hydrocarbons (alkanes, cycloalkanes, alkenes), 12 different aromatic compounds (benzene, alkylbenzenes, halobenzenes, naphthalene), and 2-chloro-2-methylpropane dissolved in 2-ethoxyethanol, along with solubilities for 11 crystalline organic compounds (xanthene, phenothiazine, acenaphthene, diphenyl sulfone, 3,5-dinitro-2-methylbenzoic acid, 3-chlorobenzoic acid, 2-methylbenzoic acid, 4-chloro-3-nitrobenzoic acid, 3,5-dinitrobenzoic acid, benzil, and thioxanthene-9-one) dissolved in 2-ethoxyethanol at 298 K. The experimental values were converted to gas-to-2-ethoxyethanol partition coefficients, water-to-2-ethoxyethanol partition coefficients, and molar solubility ratios using standard thermodynamic relationships. The calculated partition coefficient data and molar solubility ratios, combined with published literature values, were used to derive Abraham model correlations for solute transfer into 2-ethoxyethanol from both water and the gas phase. The derived Abraham model correlations predicted the observed values to within 0.15 log units (or less).

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### 1. Introduction

Hydrogen bonding has received considerable attention over the years due to its role in determining solubilities, molecular shapes and spectral properties of biomolecules dissolved in fluid solution. Hydrogen bonding interactions can be intermolecular or intramolecular in nature, and generally result from the electrostatic attraction between a hydrogen atom bonded to a highly electronegative element (e.g., bonded to a nitrogen, oxygen or fluorine atom) and a lone electron pair residing on a nearby electronegative atom or group. C–H···Y (Y = lone-pair electron donor) interactions have also been classified as hydrogen-bonds, with the strength increasing when the C–H bond is in close proximity of electronegative atoms that are capable of withdrawing electron density from the hydrogen atom. The first ever established C–H···Y hydrogen-bond involved the participation of the acidic C–H group in the chloroform molecule [1].

Differences in hydrogen bonding interactions are important considerations in predicting solute transfer between water and hydrogen bonding solvents such as alcohols and alkoxyalcohols. If the water-solute hydrogen bonds are stronger than the organic solvent-solute hydrogen bonds then solute transfer into the organic solvent is generally not favored. If on the other hand the organic solvent-solute

interactions are the stronger of the hydrogen bonding interactions, then one would predict a greater molar solute concentration in the organic solvent relative to that in the aqueous phase. Over the past two decades we have been demonstrating the applicability of the Abraham solvation parameter model to describe solute transfer into organic solvents of varying polarities and hydrogen bonding character from both water and the gas phase. The Abraham model includes not only the effects from hydrogen bonding interactions, but also contains contributions from the other types of solute-solute, solute-solvent and solvent-solvent interactions as well. Neglect of these contributions can lead to significant errors in predicting solute transfer, particularly in the case of weak H-bonded molecular solute-solvent complexes.

To date we have published correlations for describing the solubility and partitioning behavior of solutes into inert solvents (hexane-hexadecane [2,3], cyclohexane [2], methylcyclohexane [2], and isooctane [4]), into several alkylbenzene [2,5,6] and halobenzene [7] solvents, into several aprotic H-bond acceptor solvents (dibutyl ether [2], diethyl ether [2], diisopropyl ether [8], 1,4-dioxane [9], tetrahydrofuran [9], acetone [10], butanone [10], cyclohexanone [10], methyl acetate [11], ethyl acetate [11], butyl acetate [11], tributyl phosphate [12] and dimethyl sulfoxide [2]), and into several protic alcohol solvents (methanol-decanol [2,13], 2-propanol [2,14], 2-butanol [2,14], 2-methyl-1-propanol [2,14], 2-methyl-2-propanol [2,14], ethylene glycol [2,15] and propylene glycol [16]) that possess both H-bond donor and H-bond acceptor character. In total we have reported correlations for

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more than 80 common organic solvents [2], for more than 35 different ionic liquids [17–37], and for aqueous micellar sodium dodecylsulfate [38] and aqueous micellar cetyltrimethylammonium bromide [39] solvent media. In the present communication we are extending our considerations to include 2-ethoxyethanol, which contains both an ether (R–O–R) and hydroxyl (R–OH) functional group. Infinite dilution activity coefficients ( $\gamma_\infty$ ) were measured at 298 K for 13 different aliphatic hydrocarbons (alkanes, cycloalkanes, alkenes), 12 different aromatic compounds (benzene, alkylbenzenes, halobenzenes, naphthalene), and 2-chloro-2-methylpropane dissolved in 2-ethoxyethanol using a gas chromatographic headspace analysis method, and gas-to-liquid partition coefficients ( $K$ ) were calculated using these results and saturated vapor pressures of solutes taken from literature. As part of this study solubilities were also measured for xanthene, phenothiazine, acenaphthene, diphenyl sulfone, 3,5-dinitro-2-methylbenzoic acid, 3-chlorobenzoic acid, 2-methylbenzoic acid, 4-chloro-3-nitrobenzoic acid, 3,5-dinitrobenzoic acid, benzil, and thioxanthene-9-one dissolved in 2-ethoxyethanol at 298 K. The measured partition coefficients, combined with published infinite dilution activity coefficient data for liquid organic compounds [40–52], gas solubility data for 2-methylpropane [53] and hydrogen gas [54], and solubility data for crystalline nonelectrolyte organic compounds [55–66] dissolved in 2-ethoxyethanol, were used to derive Abraham model correlations for both water-to-2-ethoxyethanol partition coefficients (as  $\log P$ ) and gas-to-2-ethoxyethanol partition coefficients (as  $\log K$ ).

## 2. Experimental methods

### 2.1. Gas chromatographic headspace measurements

Limiting activity coefficients of low polar liquid organic compounds in 2-ethoxyethanol were measured using PerkinElmer Clarus 580 chromatograph with a headspace autosampler. The autosampler takes portions of equilibrium vapor phase from sealed thermostated vials (22 ml glass vials containing 5 ml of liquid). In two sequential experiments with pure liquid solute and its solution in 2-ethoxyethanol, the areas of the chromatographic peaks of the solute are proportional to its saturated vapor pressure  $p_{sat}$  and the vapor pressure  $p$  over solution respectively. The activity coefficient of the solute  $\gamma$  is given by  $\gamma = p / (p_{sat} \cdot x)$ , where  $x$  is the equilibrium molar fraction of a solute in the liquid phase. To obtain the value of  $x$ , we subtracted the quantity of solute evaporated into the equilibrium gas phase from the quantity of solute initially added into a vial [67]. To determine the limiting activity coefficient  $\gamma_\infty$ , we measured activity coefficients at 3–4 different concentrations of a solute in the range of 0.1–1.5 vol.% and repeated 2 times for each concentration. Since the considered solutes form no dimers or other associates, it is likely that at such concentrations the solutions behave like infinitely diluted ones. This was confirmed experimentally by the absence of concentration dependence of the activity coefficients. Gas-to-liquid partition coefficients  $K$  can be calculated using a formula  $\log K = \log \left( \frac{RT}{\gamma_\infty p_{solute}^0 V_{solvent}} \right)$ , where  $p_{solute}^0$  is the saturated vapor pressure over pure dissolved compound (taken from [68,69]) and  $V_{solvent}$  is the molar volume of 2-ethoxyethanol. The Gibbs free energy of solvation is calculated according to the equation  $\Delta_{solv}G = RT \ln(\gamma_\infty p_{sat})$ . Average values of  $\log K$  and  $\Delta_{solv}G$  calculated from all measurements for the same system were taken. Results are presented in Table 1.

Comparison with the VLE data for the mixtures of hexane, heptane, and cyclohexane with 2-ethoxyethanol at 303 and 323 K (Carmona et al. [40]) shows that our limiting activity coefficients are 7–12% lower than the values extrapolated to 298 K using the results of that study. However, the lowest concentrations of hydrocarbons at which authors conducted their measurements were 3 and 6 mol%. This corresponds to 3.3–9 vol.% of a hydrocarbon, and is certainly not at infinite dilution. Extrapolation to zero concentration made by authors [40] is likely to lead to the overestimation of  $\gamma_\infty$ .

**Table 1**

Experimental values of limiting activity coefficients, gas-to-liquid partition coefficients, and the Gibbs free energies solvation in 2-ethoxyethanol at  $T = 298.15 \text{ K}^a$ .

Solute	$\gamma_\infty$	$u(\gamma_\infty)$	$\log K$	$\Delta_{solv}G^b / (\text{kJ} \cdot \text{mol}^{-1})$
n-Hexane	7.65	0.4	2.22	1.1
n-Heptane	9.63	0.3	2.64	–1.3
n-Octane	12.16	0.3	3.05	–3.7
n-Nonane	14.70	0.6	3.47	–6.0
n-Decane	20.80	0.9	3.81	–8.0
n-Undecane	30.40	0.6	4.19	–10.1
Cyclohexane	5.47	0.3	2.56	–0.9
Methylcyclopentane	5.52	0.6	2.40	0.0
Methylcyclohexane	6.93	0.4	2.78	–2.1
Cyclooctane	8.70	0.2	3.60	–6.8
Cyclohexene	3.98	0.2	2.73	–1.9
1,7-Octadiene	5.38	0.5	3.20	–4.5
4-Vinyl-1-cyclohexene	4.53	0.2	3.43	–5.8
Benzene	1.91	0.1	3.03	–3.5
Toluene	2.42	0.15	3.45	–5.9
Fluorobenzene	1.52	0.1	3.21	–4.6
Chlorobenzene	1.69	0.1	3.98	–8.9
Bromobenzene	2.01	0.2	4.36	–11.1
o-Dichlorobenzene	2.00	0.4	4.85	–13.9
o-Xylene	3.18	0.15	3.96	–8.9
m-Xylene	3.36	0.2	3.84	–8.2
p-Xylene	3.38	0.15	3.81	–8.0
Ethylbenzene	3.16	0.1	3.80	–7.9
p-Cymene	5.46	0.3	4.38	–11.3
Naphthalene	9.97	1.4	5.36	–16.8
tert-Butyl chloride	2.30	0.55	2.43	–0.1

<sup>a</sup> Standard uncertainty for temperature  $u(T) = 0.2 \text{ K}$ .

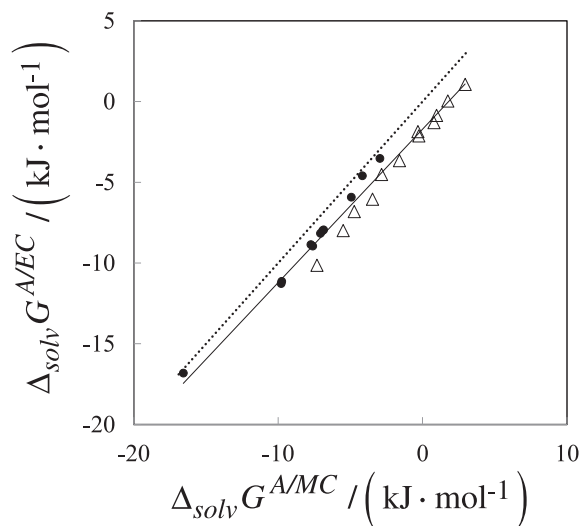
<sup>b</sup> Standard state for the  $\Delta_{solv}G$  is a hypothetical ideal solution at unit mole fraction and a gas at 1 bar fugacity.  $\Delta_{solv}G$  calculated in this fashion are not the same as values calculated as  $\Delta_{solv}G = -RT \ln K$  where  $K$  is the equilibrium constant in the table.

Comparison with the previously reported Gibbs free energies of solvation in 2-methoxyethanol at 298 K ( $\Delta_{solv}G^{A/MC}$ ) [70] shows a good correlation between the data in two solvents:

$$\Delta_{solv}G^{A/EC} = 0.951 \Delta_{solv}G^{A/MC} - 1.712$$

$$n = 25, \sigma = 0.62 \text{ kJ} \cdot \text{mol}^{-1}, R^2 = 0.9780.$$

This correlation is shown in Fig. 1. For all the considered solutes the Gibbs free energy of solvation in 2-ethoxyethanol is lower than in 2-



**Fig. 1.** Comparison of the Gibbs free energies of solvation of low polar solutes in 2-ethoxyethanol (EC) and 2-methoxyethanol (MC) at  $T = 298.15 \text{ K}$ . Triangles are aliphatic, circles are aromatic solutes. Dotted line is  $y = x$ .

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