Measurement of infinite dilution activity coefficients of common solvents in squalane using gas chromatography

Caroline KURZAWA

Introduction

The infinite dilution activity coefficient ($\gamma\infty$) is a unitless quantity that can be use to correct the concentration of a species contained in a mixture. $\gamma\infty$ gives information onto the intermolecular energies between a solvent and a solute. Numerous methods have been proposed by former authors to measure the infinite dilution activity coefficient: dilutor method, static cell measurement, as well as ebulliometry or chromatography (liquid or gas). Here, we consider gas chromatography GC.
Processium wanted to develop the limits of a new activity coefficient calculation method called relative method. In this calculation method, the retention time and the solute vapor pressure are the only factors considered.

Experimental method

The infinite dilution activity coefficient of a selection of 6 common solvents (Acetone, butan-1-ol, benzene, heptane, hexane and toluene) in squalane was measured with GC. This was accomplished using 2 different calculation methods: the absolute, proposed in most chromatography books, and the new method, the relative. The temperature range of measurement was 60 to 100°C. The experimental values were then compared with the predictive values by using UNIFAC (for acetone and benzene) and with values determined from literature for the 4 other solvents. $\gamma\infty$ of solute 1 in solvent 2 was obtained by the following equation (absolute method):

$$\ln(\gamma^{\infty}) = \ln(273{,}15R/V^{0}_{g}M_{1}P^{0}) - (P^{0}B_{22}/RT)$$

P^0 is the vapor pressure of the solute, V^0_g is the specific retention volume and B_{22} is the viriel solute coefficient.

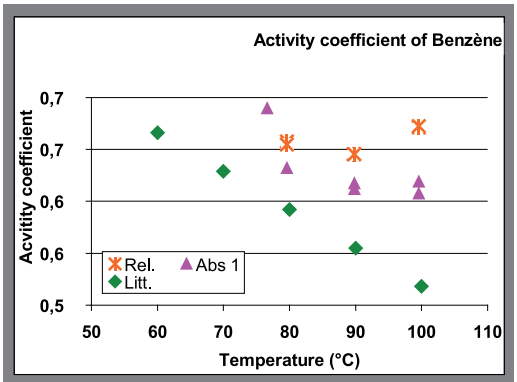
Concerning the relative method, the following equation used was:

$$\gamma^{\infty}A/\gamma^{\infty}B = (P^{0}B/P^{0}A)\alpha BA$$

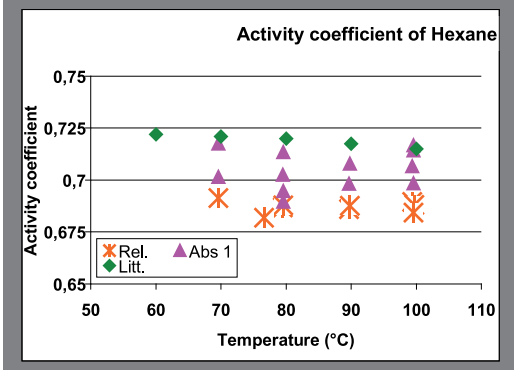
The principle: 2 components are injected simultaneously, and due to their retention times, the γ^{∞} of one solute can be determined if the γ^{∞} of the other one is exactly known. With this method, measurement of the stationnary phase mass and the carrier gas flow rate, which are necessary to obtain V^0_g, are no longer needed.

Results and discussion

The relative and absolute calculation methods of γ^{∞} for the 6 solvents were found to be between 1 and 16%, which is comparable to literature. These results are encouraging because Processium
wanted to be situated in this range of percentages. Graphs 1 and 2 show the infinite dilution activity coefficients of two solvents (benzene and hexane) dependent on temperature. All the experimental points are situated around the theoretical values and the gap between the two methods was not significant. The relative method has never been tested in this laboratory. Its results are similar to those calculated with the absolute method as well as theoretical values.



Graph 1



Graph 2

Graphes 1 and 2: $\gamma\infty$ of benzène and hexane depending on the temperature

Processium
CEI3 – BP 2132
62 Bd. Niels Borh
69603 Villeurbanne cedex
FRANCE

Caroline KURZAWA - caroline.kurzawa@wanadoo.fr