

Refined non-steady-state gas–liquid chromatography for accurate determination of limiting activity coefficients of volatile organic compounds in water

Application to C₁–C₅ alkanols

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Abstract

This work presents a new refined method of non-steady-state gas–liquid chromatography (NSGLC) suitable for determination of limiting activity coefficients of VOCs in water. The modifications done to the original NSGLC theory address its elements (as the solvent elution rate from the column) as well as other new aspects. The experimental procedure is modified accordingly, taking advantage of current technical innovations. The refined method is used systematically to determine limiting activity coefficients (Henry's law constants, limiting relative volatilities) of isomeric C₁–C₅ alkanols in water at 328.15 K. Applied to retention data measured in this work the refined NSGLC theory gives values 15–20% higher than those from the original approach. The values obtained by the refined NSGLC method agree very well (typically within 3%) with the most reliable literature data determined by other experimental techniques, this result verifying thus the correct performance of the refined method and demonstrating an improved accuracy of the new results.

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1. Introduction

Limiting activity coefficient (γ^∞) is a fundamental thermodynamic quantity characterizing the behavior of an organic solute in highly dilute solutions and governing its phase distribution in such systems. Reliable data on this quantity are required for numerous practical and theoretical applications in a variety of chemical disciplines ranging from process engineering, through environmental chemistry and theory of solutions, to biochemistry. Today, a number of experimental methods is available to measure the limiting activity coefficients. Yet, further development in this direction is needed to improve the measurement accuracy and extend the method applicability.

One of the traditional routes for the experimental determination of the limiting activity coefficients is the GLC retention measurement. In its classical version, the GLC method can be

applied well only to volatile solutes in effectively non-volatile solvents; a volatile stationary phase is continuously stripped from the column by the carrier gas flow, which causes a continuous change of the retention of injected solute samples. To achieve the desired extension of the classical GLC technique to volatile solvents (e.g. water), one has three different possibilities: (i) to presaturate the carrier gas by the solvent vapor [1,2], (ii) to measure the retention relatively to a reference solute which is injected simultaneously with the studied solute in a mixed sample [3,4], (iii) to measure the retention as a function of the sample injection time [5,6]. The first procedure solves the problem of the volatile stationary phase only partially: though the elution of the volatile stationary phase decelerates, it does not completely cease due to the pressure drop across the column, and the knowledge of the exact amount of the solvent in the column continues to be required for the calculation of γ^∞ . A distinct merit of the second procedure is that the knowledge of the stationary phase amount is not at all needed, but the determination is relative, fully relying on the knowledge of the value γ^∞ for a reference solute. The third procedure, proposed and applied by Belfer and coworkers

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[5–8] and denoted as non-steady-state gas–liquid chromatography (NSGLC) requires neither of these entries. However, despite this strength and other advantages (simplicity, speed, robustness), the NSGLC technique appears to be considered less accurate than other methods and has been only rarely used. Moreover, preliminary measurements by Belfer’s NSGLC method carried out formerly in our laboratory on aqueous oxygenates showed excessive scatter and a definite bias towards lower γ_1^∞ values.

Being motivated by the facts given above and focusing on water as a solvent, we have explored Belfer’s method and found some potential for its improvement. As an outcome, we present in this paper a new refined NSGLC theory, together with the experimental procedure and retention data treatment modified accordingly. The refined method is then applied systematically to determine limiting activity coefficients of C₁–C₅ alkanols in water. Careful comparison of the results with the most reliable γ_1^∞ values obtained by other experimental methods allows us to verify the correct performance of the refined NSGLC method and to demonstrate an improved accuracy of the new results.

2. Theory

2.1. Classical GLC

In the classical GLC working with an effectively non-volatile stationary phase (solvent), the limiting activity coefficient of solute (1) can be calculated from the retention measurements using the following well-known formula [9]

$$\gamma_1^\infty = \frac{RTn_2}{p_1^s V_N} \quad (1)$$

Here, p_1^s stands for the solute vapor pressure at the column temperature T , n_2 for the molar amount of the solvent (2) in the column, and V_N for the solute net retention volume. Representing the difference of the corrected retention volume V_R^0 and the corrected mobile phase holdup of the column (column “dead” volume) V_M^0 , the net retention volume is related through

$$V_N = (t_R - t_M)jF \quad (2)$$

to the measured solute retention time t_R , the retention time of a non-sorbed solute t_M , the carrier gas flow rate F at temperature T and pressure p_0 at the column outlet, and the compressibility correction j for the column pressure drop

$$j = \frac{3(p_i/p_0)^2 - 1}{2(p_i/p_0)^3 - 1}, \quad (3)$$

p_i being the column inlet pressure. Eq. (1) assumes the ideal behavior of gas phase and the validity of Henry’s law.

2.2. Original non-steady-state GLC

In the non-steady-state GLC, working with a volatile stationary phase (solvent), the amount of solvent in the column decreases as the solvent continuously evaporates into the carrier gas. As a consequence, the retention of gradually injected solute samples decreases as well. According to Eq. (1), the decrease in

the net retention volume is directly proportional to the decrease in the amount of solvent

$$dV_N = -\frac{RT}{p_1^s \gamma_1^\infty} dn_2 \quad (4)$$

If the carrier gas flow rate F is kept constant and one assumes that neither the compressibility correction j , nor the column “dead” volume V_M vary with time, the differentiation of Eq. (2) gives

$$dV_N = jF dt_R \quad (5)$$

At constant jF and T , Belfer et al. [6] consider that the loss of solvent from the column due its evaporation is given by the following relation

$$dn_2 = -\frac{p_2^s jF}{RT} dt \quad (6)$$

Combining Eqs. (4)–(6), one gets

$$\gamma_1^\infty = -\frac{p_2^s/p_1^s}{dt_R/dt} \quad (7)$$

Thus, according to Belfer et al. the dependence of the retention time of a solute on the time of its injection into the column is linear and the limiting activity coefficient can be determined from the slope of this dependence using Eq. (7).

2.3. Refined non-steady-state GLC

The refined theory of NSGLC modifies Belfer’s original approach in the following five aspects.

1. Assuming that the carrier gas is saturated with the solvent vapor at the column outlet, the solvent elution rate from the column is at a constant T determined solely by the outlet carrier gas flow rate and does not depend on the pressure gradient across the column. Thus, Eq. (6) employed by Belfer et al. is considered to be incorrect and is replaced by

$$dn_2 = -\frac{p_2^s F}{RT} dt \quad (8)$$

2. Since our monitoring of the pressure gradient across the column has shown that this gradient changes consistently and significantly with the amount of solvent water in the column (and hence with time), the compressibility correction is, contrary to the original Belfer’s theory, no longer considered to be time-independent. As a result, Eq. (5) is replaced by

$$dV_N = F d(jt_R) = F dt_R^0 \quad (9)$$

where $t_R^0 = jt_R$ is the corrected retention time. By joining Eqs. (8) and (9) with Eq. (4), the relation for limiting activity coefficient is

$$\gamma_1^\infty = -\frac{p_2^s/p_1^s}{dt_R^0/dt} \quad (10)$$

Although Eqs. (10) and (7) look very similar, the replacement of the retention time by the corrected retention time, as inferred

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