Optimization of Separation on the Basis of Unifac Parameters and Evaluation of the Composition of the Stationary Phase in Gas-Liquid Chromatography

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Summary
An algorithm for the optimization of separation in gas-liquid chromatography based on varying the composition of the stationary phase and the column temperature is presented using the critical parameter $R_s > 0.75$ ($2R_s \approx \max$). The stationary phase composition, on the basis of retention parameters expressed in terms of vapour pressure and activity coefficient, has been derived. Determination of the composition of the stationary liquid was carried out by defining the nature of solute-solvent interactions using group additive value contributions to the activity coefficients. Predicting values on experimentally determined parameters reduced calculation errors by a factor 2 to 3.

The results of the analysis of liquid products from the synthesis of vinyl chloride and chloroprene from acetylene and HCl are presented. The results reveal the mechanism of the reaction and allow optimum conditions to be obtained.

Introduction

Various methods of optimising GLC separation have been proposed based on retention parameters, factorial analysis and other methods [1]. However, such methods require preliminary experiments, which limits their application. For a description of the solute-solvent interactions involved in GLC, the theories of dilute solutions of non-electrolytes have been applied, particularly those involving group additive interactions such as UNIFAC (unified field activity coefficient) derived from van der Waals volumes. From such predictions, the optimum composition of the stationary phase can be derived.

Theory

The degree of resolution ($R_s$) between two adjacent components is given by [1]:

$$R_s = \frac{[(\alpha - 1)/\alpha + 1][(k\sqrt{N/(2(1 + k))}]^{1/2}}$$

where $\alpha = \text{the selectivity between the two compounds}$, i.e. $\text{Retention}_{1}/\text{Retention}_{2}$

$k = \text{the average retention factor for the two compounds}$

$N = \text{the column efficiency (average number of theoretical plates for the two compounds)}$

The retention in terms of vapour pressure and activity coefficient at infinite dilution ($\gamma_i$) is given by Eq. (2):

$$V_R = V_G + V_L K = V_G + V_L P_R \gamma_i \gamma_i^0,$$

where $V_R = \text{retention volume of the substance}$

$V_G = \text{the free gas volume of the column}$

$V_L = \text{the volume of the stationary liquid in the column}$

$\gamma_i = \text{the activity coefficient of the substance at infinite dilution}$

$p^* = \text{the vapour pressure of analyzed substance at the column temperature}$

The activity coefficient can be calculated from Eq. (3) [2]

$$\ln \gamma_i = \ln \gamma_i^G + \ln \gamma_i^R + \ln \gamma_i^{FV}$$

where $\gamma_i^G = \text{the summed activity of the groups in the compound}$

$\gamma_i^R = \text{the remaining contribution to the activity of the compound}$

$\gamma_i^{FV} = \text{a component of the activity related to the free volume of the compound}$

Optimising the stationary phase composition for the separation of specific mixtures is carried out with the help of the energetic parameters of the structural groups involved ($\alpha_{mm}$ and $\alpha_{mn}$) [3] and by varying the column temperature.

We have constructed an algorithm for the calculation shown in Figure 1.
The criterion for optimisation for the separation of two peaks is \( R_s \geq 0.75 \) and for the whole mixture \( \Sigma R_s \Rightarrow \text{max} \).

All calculations were carried out on a PC with the algorithm written in BASIC.

To express the retention in terms of Retention Index, vapour pressure and activity coefficient we have Eq. (4)

\[
I = 100\left[\log \frac{y_p}{y_r} - \log \gamma + \log \frac{\gamma}{1 + \gamma} \right] + 100m = 100\left[\log \frac{\gamma}{y_r} + \log \frac{\gamma}{1 + \gamma} \right] + 100m.
\]

From Eq. (3) it follows that \( \gamma \) for a substance can be calculated if \( I \) and \( P \) for the substance are known.

\[
\gamma = \exp\left[\frac{\log (y_p) - (I/100 - n)}{(\gamma + 1)/P + (1/\gamma)}\right].
\]

At a spelling of the formula (5) it is taken into account features of the balance of sorbate-sorbent, i.e. a mol fraction of sorbate much more time is less than a mol fraction of sorbent. Therefore, it is accepted, that a mol fraction of sorbate \( X_1 \) comes nearer to zero, and a mol fraction of sorbent \( X_2 \) to unit.

Conversely, if \( \gamma \) and the UNIFAC solvating equation are known it is possible to calculate the contribution of the groups within the stationary liquid to the overall activity. Nelder-Mid's simplex method was used to determine the contributions of various groups in some cyanosiloxane stationary phases (see below).

**Apparatus and Materials**

All experiments were carried out on a Tswett 100 Model 165 GC with FID and a 2 m \( \times \) 4 mm glass column packed with 0.250–0.315 mm Chromaton N-AW coated with 15% Lestosile, which has the formula shown below. Column temperature was programmed from 80 °C to 250 °C at 20 °C min \(^{-1}\). The injector temperature was 280 °C. Sample size was 0.5–1 µL (see below).

**Results and Discussion**

Various mixtures such as obtained in the synthesis of nitriles, gas extracts of shale oils and fatty acid esters have been examined. The calculated values on retention parameters varied from the experimental values by \( \pm 7\% \).

The retention values for compounds at various temperatures have been used to calculate the UNIFAC parameters.

The liquid products of the catalytic hydrochlorination of acetylene at various temperatures were analysed. A fully factored set of experiments involving the parameters temperature, catalyst composition and acetylene flowrate were used to assess the output of vinyl chloride and...