INFINITE DILUTION ACTIVITY COEFFICIENTS OF SOLVENTS IN FATTY OIL DERIVATIVES

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Abstract - Inverse gas-liquid chromatography has been applied to measure infinite dilution activity coefficients ($\gamma^\infty$) of different solutes in low and high molecular weight triacylglycerides (TAGs) and in mixtures of carboxylic acids with TAGs. The $\gamma^\infty$ data obtained were used to determine binary interaction and size related parameters for the GCA-EOS group contribution with association equation of state.

Keywords - Activity coefficients, Infinite dilution, Carboxylic acids, Triglycerides, Parameters determinations, Binary interaction

I. INTRODUCTION

Experimental information on thermodynamic properties of fatty acids and triacylglycerides (TAGs) is required for the design and simulation of separation processes applied in the extraction and fractionation of fatty oil derivatives from vegetable and animal oils.

In previous work (Foco et al., 1996; Bermudez et al., 2000), infinite dilution activity coefficients ($\gamma^\infty$) of a series of organic solutes in palmitic acid, tripalmitin and triacetin, were measured. These data were obtained by inverse gas chromatography, using the non volatile TAG or fatty acid as stationary phase and injecting the volatile solute at infinite dilution in the carrier gas stream. Those data have been used (Bottini et al, 1999) to determine molecular and group interaction parameters for the group contribution with association equation of state GCA-EOS proposed by Gros et al (1996).

The functional groups characteristic of TAGs and fatty acids are, respectively, the triglyceride TG ((CH$_2$COO)$_2$-CHCOO) and acid (COOH) groups. The interaction parameters between the TG and COOH groups are not available in the GCA-EOS parameter table. Also the interaction between TG and the primary (CH$_2$OH) and secondary (CHOH) alcohol groups are missing. The purpose of this work is to measure infinite dilution activity coefficients in order to fit these interaction parameters to the experimental data.

The use of inverse gas chromatography to measure infinite dilution activity coefficients requires the solvent in the stationary phase to be a non-volatile compound, so that the amount of solvent in the stationary phase remains constant during the measurements. On the other hand, the solutes injected into the gas carrier should give sharp and neat chromatograms. Solutes of low volatility and/or highly retained in the stationary phase will give broad chromatographic peaks. In this case the values of the retention times, and consequently the calculated $\gamma^\infty$ would be uncertain.

All TAGs are low volatile compounds and can always be used as solvents in a chromatographic stationary phase. Even the first member of the family, triacetin, has negligible vapor pressures at temperatures up to 353K. Unfortunately, carboxylic acids are highly retained in TAGs stationary phases; this makes inverse gas chromatography an unsuitable technique to measure $\gamma^\infty$ of carboxylic acids in TAGs.

In order to obtain experimental information to fit the GCA-EOS interaction parameters between TG and COOH groups, an alternative procedure was followed in this work. Stationary phases were prepared using mixtures of TAGs with high molecular weight non volatile fatty acids ($\gamma^\infty$ of volatile solutes in these mixtures were measured. With these values and the corresponding $\gamma^\infty$ of the same solutes in each pure solvent (TAG and fatty acid) it was possible to quantify the interaction between TG and COOH. Mixtures of palmitic acid with two different TAGs (triacetin and tripalmitin) were prepared, and the $\gamma^\infty$ of a series of organic solutes in these mixtures were measured.

II. EXPERIMENTAL RESULTS

The infinite dilution activity coefficients were measured by gas-liquid chromatography. The specific retention volume $V^g_o$ at 273.15 K, i.e. the normalized volume of carrier gas necessary to elute solute $i$ out of a column with a mass $W_s$ of solvent, is calculated from the measured retention time ($t_i$) of solute $i$ by:

$$V^g_o = (t_i - t_o)F \frac{273.15 P_i - P^\infty}{T_i} \frac{J^2}{P_o \frac{w_s}{w_i}}$$ (1)