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On the Solubility of Glycerides and Fatty Acids in Compressed Gases in the Presence of an Entrainer

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ABSTRACT

The solubility of fatty acids and their glycerides in dense supercritical gases increases with increasing pressure at constant temperature. The temperature influences the solution equilibria in a more complicated way than the pressure. Addition of an entrainer increases the solubility in the gas phase. Furthermore, the temperature dependence of the solvent power is increased so much that the regeneration of the circulating gas in a separation process becomes possible by a change of temperature only. By a suitable entrainer the separation factor can also be improved.

INTRODUCTION

Extraction with supercritical gases is considered a new tool for separating substances, especially those having a low volatility. Since the thirties of this century supercritical gases have been considered as solvents in technology and one tries to use them for many old and new problems in chemical engineering (1).

We have done that also and, in course of our work, we came to the conclusion that, in designing a large-scale separation process which can be operated continuously and economically at constant pressure, one cannot restrict oneself by using a supercritical gas alone as the solvent but should consider adding a substance which we call an entrainer and which has a volatility between the substances to be separated and the supercritical gas. Often such an entrainer is part of the system anyway (2).

In the first part of this paper, we want to explain how a separation process using supercritical gases and entrainers could work. In the second part of this paper, we shall discuss the properties of a mixture of a supercritical gas and an entrainer in combination with high boiling mixtures.

THE SEPARATION PROCESS

In Fig. 1 a schematic of the separation unit is shown. It consists of at least two separation columns. In the first the separation of the high boiling substances from the mixture takes place and in the second the high boiling materials dissolved in the gas-phase are separated from the gas--which is thus regenerated and can be recycled to the first separation column.

In the first column the mixture to be separated is introduced, for example, in the middle of the column. The supercritical gas entering the column at the bottom dissolves the high boiling materials. The substances which are more soluble in the gas will preferentially be carried to the top of the column where they leave it.

The column operates at a temperature which is higher than the critical temperature of the supercritical gas, for example, in the reduced temperature range of 1.1 to 1.5, and at a pressure above the critical pressure of the gas, say in the reduced pressure range of 2 to 3.

The thermodynamic conditions which have to be realized in the column are schematically shown in the right hand part of Fig. 1. There the phase equilibria are shown of the quasiternary

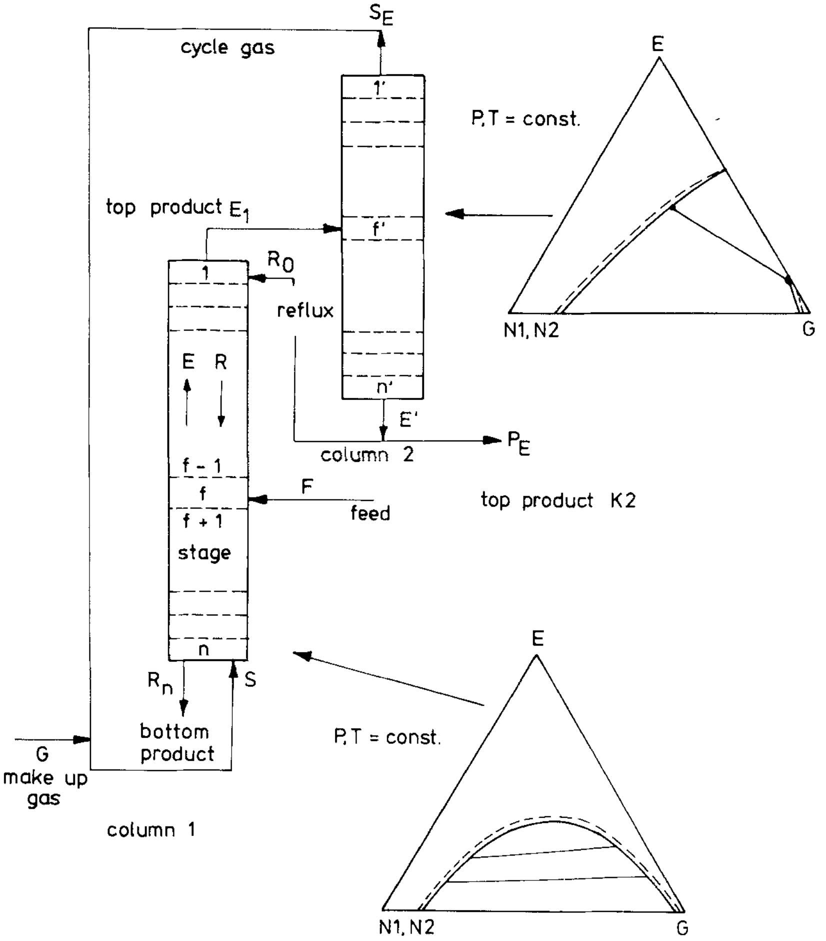

FIGURE 1. Flow diagram of gas extraction with an entrainer and related phase equilibria. E - entrainer, G - gas, N1, N2 nonvolatile substance 1 and 2.
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system consisting of the gas, entrainer, and the mixture to be separated. If the conditions are such that the binary system of entrainer and gas is supercritical, a type I phase equilibrium with a miscibility gap in one binary system only is maintained in the first column, resulting in a relatively high solubility of the high boiling substances in the gas phase.

The second column is operated at the same pressure as the first column but at a somewhat higher temperature. The temperature has to be raised to such an extent that a type II phase equilibrium exists with an additional miscibility gap in the entrainer - gas system. The solubility of the high boiling material in the gas phase is reduced dramatically by this procedure. The entrainer is condensed partially also, since the slope of the tie lines has changed.

The condensing substances flow downward in the column, washing out the heavy components from the uprising gas-stream. The regenerated gas leaves the second column at the top and is recycled to the first column.

The stream withdrawn from the bottom of the second column is split into the top product and the reflux for the first column. The liquid reflux flows down countercurrently to the gas stream and changes its composition due to repeated mass transfer operations along the column, until at the bottom a product stream can be withdrawn, more or less enriched with the compounds less soluble in the gas.

A mixture of glycerides resulting from the production of stearic monoglycerides by esterification of stearic acid and glycerin has been treated in the above described way. The various fractions were analyzed by gas chromatography using the following conditions: 1% OV-17 on Supelcoport; length of column, 30 cm; temperature, 150 to 350°C at a rate of 4°C/min; FID; gas chromatograph, HP 5830; silylation of the samples with MSHFBA.

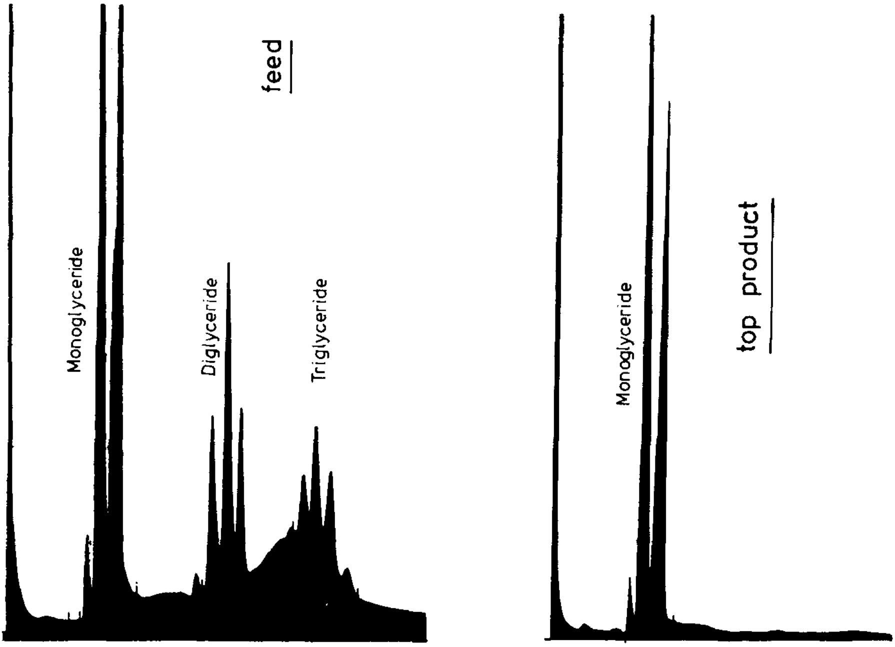

FIGURE 2. Gas chromatograms of feed and top product from separating glycerides of stearic acid. Conditions of gas chromatographic analysis are 1% OV-17 on Supelcoport; length of column, 30 cm; temperature, 150 to 350°C at a rate of 4°C/min; FID; gas chromatograph, HP 5830; silylation of the samples with MSHFBA.

The sort of separation which can be achieved with this process is demonstrated in Fig. 2 where the results of a separation of glycerides is shown (2). In this figure, the gas chromatograms of feed and top product are shown. While in the feed there are about 40% by weight diglycerides, in the top product there are practically no diglycerides (about 0.5%). The experiments were carried out using bench-scale equipment with columns of 65 mm inner diameter at 130 bar and 70°C. It was operated continuously and produced 0.5 kg/h monoglycerides as a top product.

SOLUBILITY CONSIDERATIONS

Pure Supercritical Gases as Solvents

After this introduction to the process, the solubility of the heavy components in the gas phase will be considered. In Fig. 3 the solubility of palm oil in different gases is plotted against pressure at a temperature of 70°C (75°C for carbon dioxide). The solid lines are smoothed curves of the experimental data and the points are calculated solubilities at certain pressures.

For the calculation we have used an equation of state of the Van der Waals type, namely, a modification of the Redlich-Kwong equation of state (3). In this modified form the equation has three parameters which are independent of temperature. For mixtures a temperature dependent interaction parameter has to be added. Sets of parameters can be calculated by fitting the equation of state to properties of the pure substances like liquid density, vapour pressure and enthalpy of vaporization. For the glycerides this is not possible since they occur in a relatively complex mixture and the properties of the pure glycerides are are unknown in most cases. Therefore, a correlation of the parameters of the equation of state has been developed which uses only the molar volumes. It is based on the parameters of nearly 400 pure substances and can be used to evaluate parameters for high boiling materials and complex mixtures (4). The solubility of solid organic substances in compressed gases can also be calculated by means of an equation of state (5).

From Fig. 3 one can see that the solubility in a certain gas increases exponentially with pressure at constant temperature. If a logarithmic scale is used for the solubility, one obtains straight lines over a fairly wide pressure region. Up to pressures of about 150 bar, the solubility of palm oil in the compressed gases lies markedly below 0.5 wt%. A concentration of 2 wt% in the gas phase is obtained with ethylene at 250 bar and with carbon

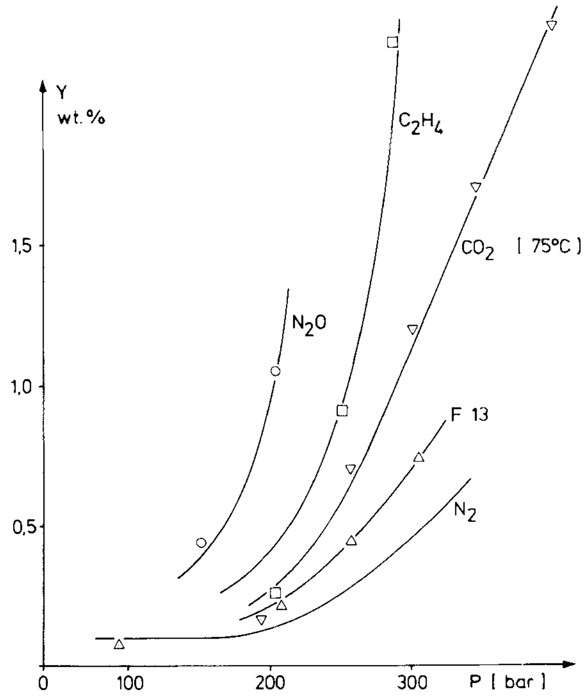

FIGURE 3. Solubility of palm oil (85% triglycerides) in various gases. Solid lines: smoothed values of experimental results. Individual points: calculated solubilities assuming a molar volume of 865.4 cm^3 for the palm oil mixture.

dioxide at about 300 bar. This includes all components. However the solubility of the substances with a lower volatility is more increased than the solubility of the more volatile substances. At the same temperature the solubility of the glycerides in the different gases is different. It is generally claimed that at given conditions of pressure and temperature the solubility of a certain substance in different gases increases with the critical temperature of the gas. We have plotted this for the glycerides in Fig. 4 for a temperature of 70°C and a pressure of 200 bar. In this figure the solubility of palm oil in different gases is plotted against their critical temperature. As about 85% by weight of the palm oil consists of triglycerides, this means that the solubility of the triglycerides is mainly considered. One can see that the general trend can be confirmed as far as compressed gases with very different critical temperatures and pressures are concerned. However, in gases with nearly equal critical temperatures the solubilities are significantly different, as can be seen from the group of gases having critical temperatures of about 30°C. Of these gases, CO_2 and CF_3Cl are poor solvents and ethane and nitrous oxide are good solvents for glycerides. Ethylene with a somewhat lower critical temperature of 9.5°C lies in between. The difference in solubility can be explained neither by density (the density of ethane is much lower--about 0.37 g/cm^3--than the density of carbon dioxide--0.645 g/cm^3--at 70°C and 200 bar) nor by polarity (ethane is a nonpolar molecule while N_2O has a dipole moment of about 0.2 D and CF_3Cl, one of 0.5 D).

Some qualitative hints to the solubility in the gas phase can be obtained if some data on the solubility of the gases in the liquid phase are known. In general, one can see from Fig. 5, where the solubilities of some gases in palm oil have been plotted against pressure, the gases which dissolve more readily in the liquid phase are also able to dissolve more of the material of low volatility. Although in this case CO_2 is an exception, this trend has been confirmed with several similar systems. Other examples are systems with oleic acid, stearic acid, sunflower oil, squalane, mineral oil (2,6). Further, the temperature dependence of the solubility changes with pressure as can be seen in Fig. 6. At low pressures the enthalpy of solution is negative; at high pressures the enthalpy of solution is positive.

If we want to use the compressed supercritical gas as a solvent that is to be recycled, the regeneration of the gas stream is most important. Since a regeneration caused by a pressure drop is likely not to be a good solution from an economic point of view

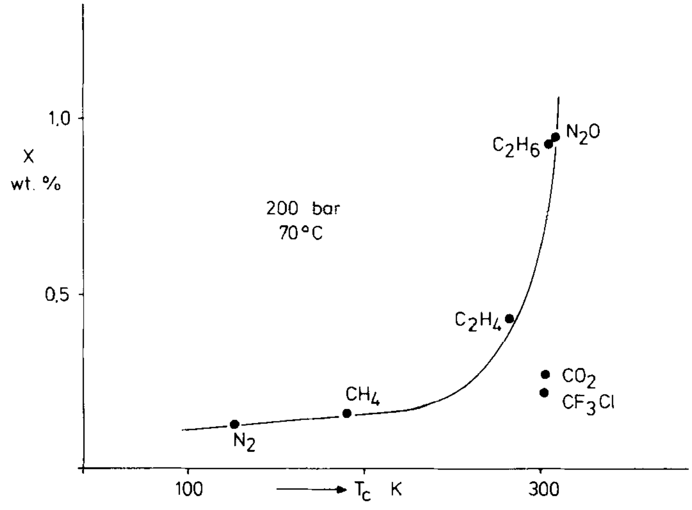

FIGURE 4. Solubility of palm oil in different gases as a function of their critical temperatures.

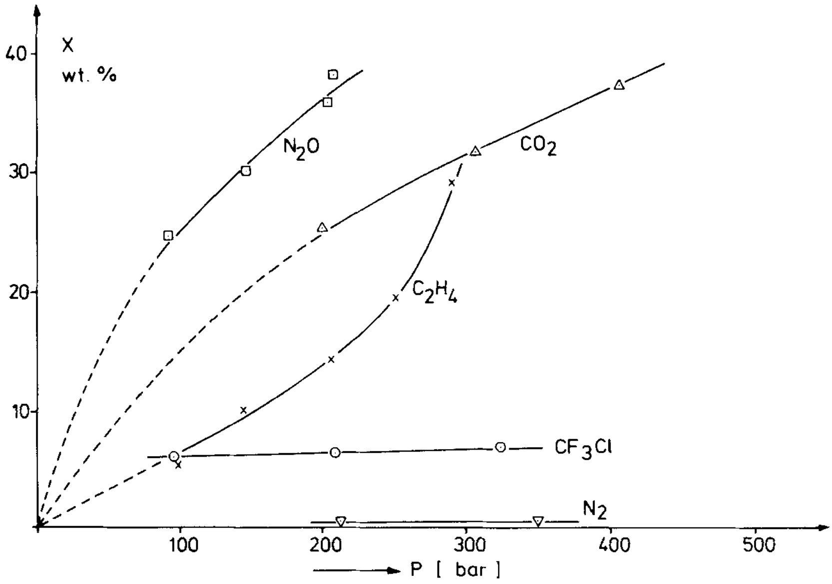

FIGURE 5. Solubility of different gases in palm oil.

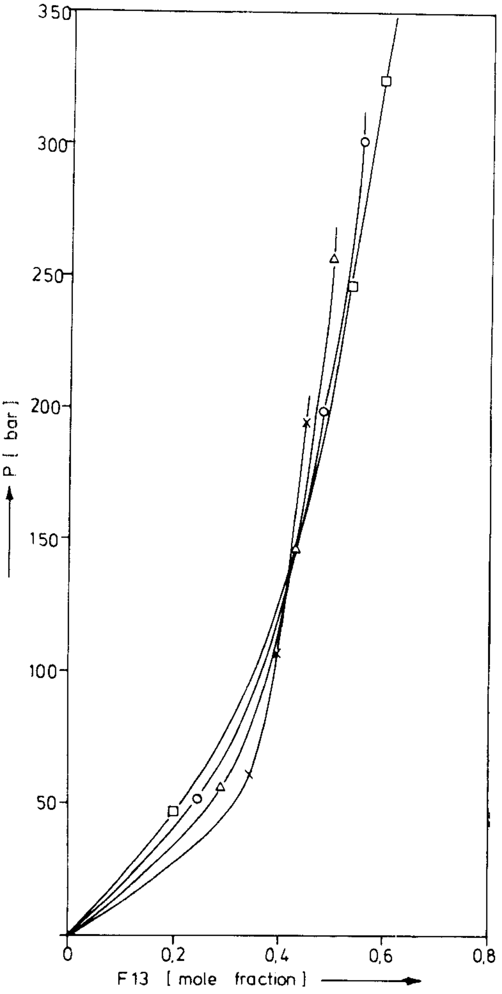

FIGURE 6. Solubility of monochlorotrifluoromethane in oleic acid as a function of pressure at different temperatures.
□ - 125°C; o - 100°C; Δ - 75°C; × - 50°C

because of the energy consumption, a regeneration by changing the temperature alone should be feasible. Therefore, a temperature dependence of the solubility of the high boiling materials in the gas is essential. In Fig. 7 there is plotted the solubility of oleic acid in ethylene as a function of density. The solid lines are isotherms and the broken ones, isobars. At a pressure of 200 bar, a temperature change from 55°C to 127°C results in a decrease of the concentration of oleic acid from 2.5 to 1 wt% only. Similar results have been obtained with even heavier molecules, e.g., squalane (6). Obviously, when using a supercritical gas as a solvent, the regeneration of the gas by changing the temperature can be done only partially.

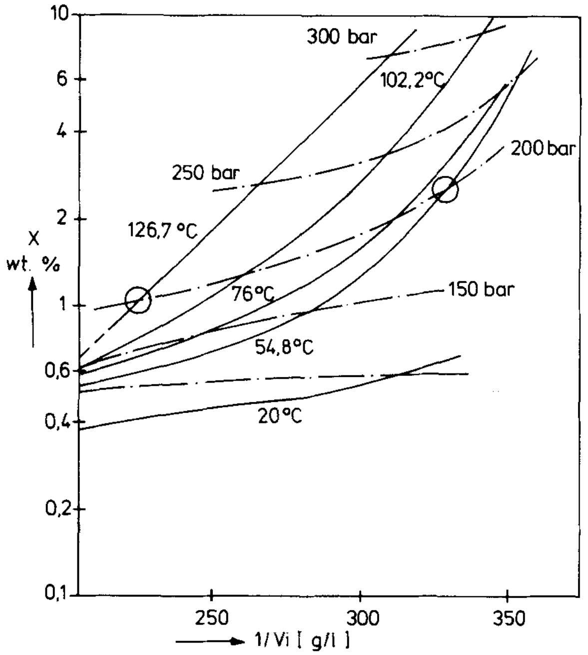

FIGURE 7. Solubility of oleic acid in ethylene as a function of the density of the gas phase.

Supercritical Gases Plus Entrainer as Solvents

How do things behave if we add an entrainer? Adding a substance complicates the system and will probably make separation equipment more expensive. So these disadvantages must at least be met by the advantageous properties of an entrainer. The advantages of an entrainer may be outlined as follows:

(1) The solubility is enhanced. Under equal conditions the concentration of materials of low volatility in the compressed gas is markedly higher using an entrainer than with the supercritical gas alone. This means that one can operate at a lower pressure.

(2) By using an entrainer the regeneration of the gas can be achieved by changing the temperature alone.

(3) By using a suitable entrainer the separation factor can be enhanced.

In Fig. 8 the solubility of palm oil in carbon dioxide with ethanol as an entrainer has been plotted against pressure at different temperatures. The diagram refers to a constant content of entrainer in the gas phase of about 10 wt%. At 200 bar and 70°C, more than 5 wt% of glycerides dissolve in the gas phase. At the same conditions CO_2 alone dissolves only 0.25 wt%. If special interaction forces are absent, the lower the vapour pressure of the substance the more the solubility is enhanced.

If the temperature dependence of the solubility is considered, e.g., at 130 bar--the pressure for our separation experiments, one can see from Fig. 8 that the solubility decreases from about 2 wt% at 70°C to a negligible amount at 110°C so that a complete regeneration of the gas phase is possible by a temperature change only and the gas can be recycled without any marked pressure change. The thermodynamic reason for this will be explained using Fig. 9.

In this diagram the phase equilibria of the quasiternary system comprised of the heavy compounds to be separated, the entrainer,

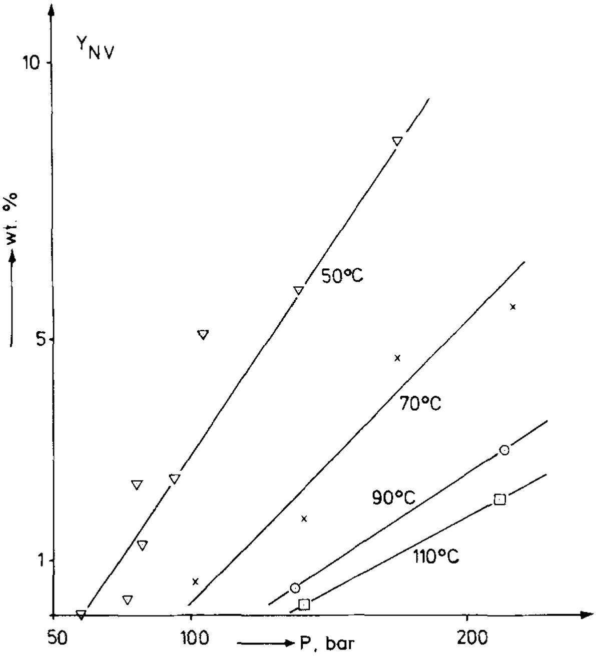

FIGURE 8. Solubility of palm oil in carbon dioxide with ethanol as entrainer. Concentration of ethanol in the gas phase about 10 wt%.

and the gas are plotted in a triangular diagram at an operating pressure suitable for a supercritical gas extraction. The temperature dependence of these equilibria is shown by horizontal cuts of the vertical temperature axis. The miscibility gaps of the binary systems are shown on the surfaces of the triangular prism: in the foreground, the miscibility gap between the low volatile materials and the gas; and on the right surface in the background, the miscibility gap between the gas and the entrainer. In the temperature range, for which the phase equilibria of the ternary system are shown in the diagram, the binary T,x-diagram of gas and entrainer shows a closed loop for the two phase region. At relatively low temperatures there exists a type I system with high

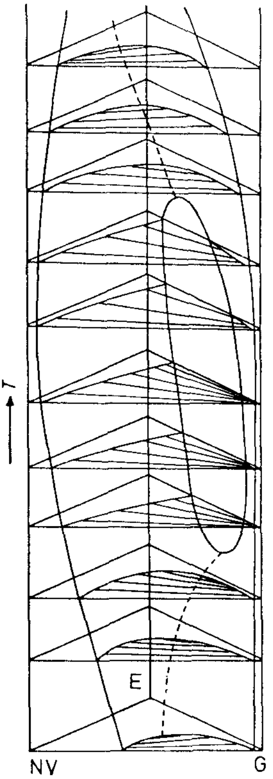

FIGURE 9. Temperature dependence of phase equilibria of a quasi-ternary system consisting of substances of low volatility (NV), an entrainer (E) and a supercritical component (G).

concentrations of low volatile material in the gas phase. At higher temperatures, where there is a miscibility gap between entrainer and gas, a type II system exists with a very low solubility of heavy material in the gas phase. The same effect can be achieved starting from a high temperature by lowering the temperature.

The improvement of the separation factor by a suitable entrainer is illustrated in Fig. 10 where the distribution factors for the free fatty acids in a glyceride mixture have been plotted

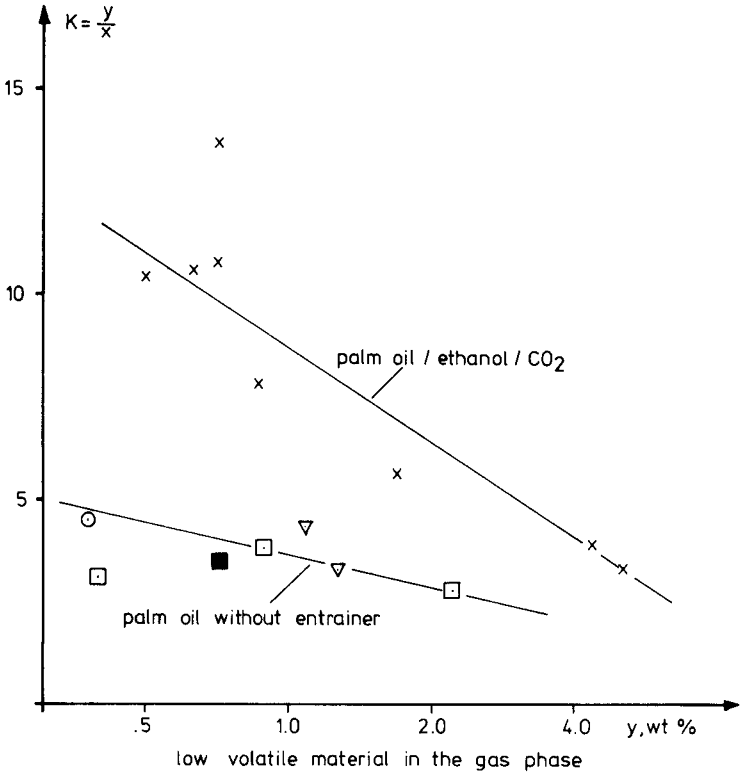

FIGURE 10. K-factors of the free fatty acids of palm oil at 71°C and 137 bar.

system with entrainer (palm oil/ethanol/CO_2): ×
systems without entrainer: ○ F13; □ C_2H_4; ▽ N_2O; ■ CO_2

as a function of the amount of heavy materials dissolved in the gas phase. The distribution factor in this case is the concentration in the gas phase divided by the concentration in the liquid phase on a mass basis. The higher this factor, the more fatty acids will be in the gas phase. The lower curve shows the results for several gases like CO_2, CF_3Cl, N_2O and ethylene without entrainer. The distribution factor has a value of about 5 at low pressures or low concentrations in the gas phase and decreases with increasing concentration of heavy material in the gas phase. The upper line represents measurements of the distribution factor using CO_2 as a compressed gas and ethanol as entrainer. The distribution factor is enhanced by a factor of 2 in this case.

CLOSING COMMENTS

We have tried other entrainers (acetone (2), benzene, hexane, formaldehyde - dimethylacetal, methylene chloride, chloroform) and, in general, one can say so far that most substances do not enhance the distribution factor in a certain system. This situation is similar to the problem of finding an entrainer for an extractive distillation. One has to look for a suitable entrainer, that is, one with specific interactions with the substances to be separated. On the other hand, the primary two effects-- enhanced solubility and enhanced temperature dependence of the solubility-- hold for all substances one can use as an entrainer as long as the thermodynamic conditions explained in Fig. 9 can be realized.

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