Physical Chemistry

O. V. ALT' SHULER, O. M. VINOGRADOVA,

1963

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

Physical Chemistry

O. V. ALT’ SHULER, O. M. VINOGRADOVA,
Corresponding Member of the Academy of Sciences of the USSR S. Z. ROGINSKII, Yu. N. CHIRKOV

ON THE POSSIBILITY OF CHROMATOGRAPHIC SEPARATION ON GAS-LIQUID COLUMNS WITHOUT THE USE OF AN INERT CARRIER GAS

For the isolation of small amounts of compounds of a high degree of purity, at present the most widespread method is the developing variant of preparative chromatography. Alongside it, especially when the task is to obtain low-boiling compounds, for example light hydrocarbons, in a very pure state, it is advisable to use the so-called thermal-displacement separation ([1,2]). In this process the action of an inert carrier gas is replaced by the action of a moving thermal field. However, the use of thermal displacement proves impossible when one passes to high-boiling and reactive compounds, owing to the irreversibility of adsorption and the catalytic action of sorbents with respect to the substances being separated at elevated temperatures.

Fig. 1. a –separation of C_3H_6 and C_4H_8 on a column with dibutyl phthalate with feed of C_4H_6; b –separation of CH_4 and C_2H_6 on silica gel with feed of CO_2

In a number of cases, as our investigations have shown, separation can be carried out by the displacement method, a distinctive feature of which is the use of the displacing agent in concentrated form. The absence of an inert developer ensures that all components of the mixture are also isolated in an undiluted state. As the displacer there must be used a compound that is sorbed sufficiently well, but is nonreactive, and whose subsequent desorption by heating the sorbent does not lead to any side reactions. An even more radical solution, eliminating all complications associated both with side reactions and with irreversibility of adsorption, would be a transition from sorption columns to gas–liquid ones. This would expand the range of compounds isolated in pure form also through a freer choice of liquid phases as compared with the choice of sorbents.

Fig. 2. Solubility isotherms of propane and butane in Vaseline oil. Dots—dilution with air; crosses—dilution with butane (propane)

Figure 2: Fig. 2. Solubility isotherms of propane and butane in Vaseline oil. Dots—dilution with air; crosses—dilution with butane (propane)

In the present work we attempted to use gas-liquid separation columns for preparative purposes, carrying out the process of pseudo-displacement separation without the participation of an inert carrier gas. The agent ensuring the movement of the components of the mixture along the column was a compound more readily soluble than any component of the mixture. Such a method

separation should have had certain features in common with the method of frontal analysis of undiluted mixtures on gas-liquid columns, the theory of which is considered by G. Shaem in his monograph (^{3}). Part of the column was saturated with the mixture to be separated; then a compound, readily soluble in the given stationary liquid, was fed uniformly into it in the undiluted state; the entire process was carried out without an inert carrier gas.

In Fig. 1 the displacement separation of CH_4 and C_2H_6 on a column with silica gel (displacer CO_2) is compared with the separation of C_3H_6 and C_4H_8 under the action of divinyl fed into a column of Inza brick impregnated with tributyl phosphate. As can be seen, in both cases the components of the mixture emerge from the columns in the undiluted state, forming zones adjacent to one another in the order inverse to their retained volume.

Fig. 2. Solubility isotherms of propane and butane in Vaseline oil. Dots—dilution with air; crosses—dilution with butane (propane)

A similar pattern, characteristic of displacement separation, was also observed in the separation of a number of other mixtures of saturated and unsaturated compounds on polar and nonpolar stationary liquids. It could be assumed that, in the actual systems investigated, deviations from Henry's law occur, according to which the solubility of a gas is a function of its partial pressure and does not depend on the presence of other gases.

However, the solubility isotherms that we obtained for the individual compounds studied and for the same compounds in the presence of another soluble component practically coincided. An example is provided by the solubility isotherms of propane and butane in Vaseline oil on an inert support, shown in Fig. 2 (dots —dilution with air, crosses—dilution with the soluble component of the mixture). This rules out the possibility of displacement by any mechanism whatever. To be finally convinced that the separation mechanism on stationary liquids, leading to concentration of all components, is not connected with displacement, an experiment was performed in which one of the components of the mixture was a substance practically insoluble in the stationary liquid (air). And in this case as well, where interaction of the components in the stationary phase was known to be excluded, concentration of the "light" component, air, and its emergence

Fig. 3. Elution of propylene from a column with tricresyl phosphate by substances of different solubility. 1—air, 2—propane, 3—divinyl

Figure 3: Fig. 3. Elution of propylene from a column with tricresyl phosphate by substances of different solubility. 1—air, 2—propane, 3—divinyl

Fig. 4

Figure 4: Fig. 4

in a pure state before the appearance at the outlet of the soluble component (butane) took place.

Fig. 3. Elution of propylene from a column with tricresyl phosphate by substances of different solubility. 1—air, 2—propane, 3—divinyl

From the results of these experiments it may be concluded that a separation accompanied, in contrast to elution separation, by concentration of all components on gas-liquid columns is not associated with displace-

flow, but simply to differences in the rates of movement of the components traveling along the column under the action of the well-soluble pseudo-displacer. True displacement, which occurs on sorbents, is manifested in a more sharply expressed concentration.

The relationship between the degree of concentration of the component saturating the liquid phase and the solubility of the pseudo-displacer fed into the column is illustrated in Fig. 3.

A certain amount of propylene diluted with air (concentration $C_3H_6 = 20\%$) was introduced into a column with tricresyl phosphate. Curve 1 refers to the subsequent blowing out of propylene with air ($V_{R\,\mathrm{air}} < V_{R\,C_3H_6}$), curve 2 to blowing out with propane ($V_{R\,C_3H_8} \simeq V_{R\,C_3H_6}$), curve 3 to blowing out with divinyl ($V_{R\,C_6H_4} > V_{R\,C_3H_6}$).

In the first case the concentration of propylene at the peak maximum is close to the initial concentration; in the second, the concentration at the outlet exceeds the initial concentration but does not reach 100%; and, finally, when displaced by divinyl, the greater part of the propylene is released in undiluted form.

Fig. 4. Dependence of the yield of pure divinyl on the loading (a) and on the column length (b). 1 –yield in cubic centimeters, 2 –yield in percent

In order to determine the optimal purification conditions by the method described, the influence on the separation of such factors as the magnitude of the column loading, the column length, and the concentration of impurities in the initial mixture was studied. The separation criterion adopted was the yield of the isolated product at a specified degree of purification. The yield was calculated as the ratio of the amount of product isolated in pure form to the amount contained in the mixture introduced for separation.

Experiments showed that, when the column loading with the initial mixture is increased up to saturation, the percentage yield decreases, while the absolute yield at first increases and then remains unchanged (Fig. 4).

When the ratio between the saturated and free portions of the bed is kept constant, the percentage yield does not depend on the column length. The optimal column loading for the mixtures studied was 50–60% of the column capacity. At a greater degree of loading, the part of the mixture exceeding this value was discharged unchanged.

The concentration of the main product in the initial mixture has no substantial effect on the percentage yield; the absolute yield, naturally, is higher the richer the initial mixture is.

The time spent carrying out the cycle is much shorter than the time required to carry out separation on sorbents. This is due to the fact that, in the case of impregnated columns, extraction of the displacer does not require heating the column and can be accomplished by simple freezing. Thus the longest operation (heating and subsequent cooling), unavoidable when working with sorbents, is eliminated. The reduction in cycle time to some extent compensates for the lower capacity of impregnated columns compared with sorption columns.

As a result of the work carried out, a variant of gas–liquid chromatography without the use of an inert carrier gas has been proposed, imitating displacement separation on sorbents.

In the case of gas–liquid columns, concentration of components with the formation of adjoining zones occurs without interaction of the components in the stationary phase (displacement). In the absence of gas-

for this purpose, differences in the rates of motion of the components of the mixture moving along the column under the action of a readily soluble compound (a pseudodisplacer) are sufficient. In the case of adsorption columns, the effect of concentrating the components of the mixture is intensified because substances with lower adsorption coefficients are displaced by substances that are relatively more strongly adsorbed.

Pseudodisplacement chromatographic separation may be recommended for solving preparative problems. The use of this method is especially expedient when it is necessary to purify high-boiling or reactive compounds, when displacement separation on sorbents proves impossible. Introduction of the pseudodisplacer in undiluted form ensures the isolation of all products also without dilution, which, naturally, cannot be provided by the usual developing variant.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
12 VII 1963

REFERENCES

1. M. I. Yanovskii, S. P. Ozirainer, Lu Pei-chzhan, *ZhPKh*, **32**, 1084 (1960).
   O. V. Altshuler, O. M. Vinogradova et al., *DAN*, **140**, No. 6 (1961).
   G. Schag, *Theoretische Grundlagen Goschromatographie*, Berlin, 1960.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.