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USE OF OLEFIN- $\text{Ag}^+$  COMPLEXES FOR CHROMATOGRAPHIC SEPARATIONS OF HIGHER OLEFINS IN LIQUID-SOLID SYSTEMS\*

J. JANÁK, Z. JAGARIĆ\*\* AND M. DRESSLER

*Institute of Instrumental Analytical Chemistry, Czechoslovak Academy of Sciences, Brno (Czechoslovakia)*

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## SUMMARY

The selectivity effect caused by the formation of olefin-silver ion complexes in systems of propanol-water- $\text{AgNO}_3$ /porous polymers (like Porapak Q) were studied under static and dynamic conditions.

Liquid as well as thin-layer chromatographic separations of higher olefins from mixtures with other hydrocarbons are possible with a selectivity equivalent to seven carbon atoms when comparing the chromatographic retention of *n*-paraffin and *n*-olefin (heptane, tetradecene) under conditions used.

## INTRODUCTION

Olefins form unstable  $\pi$ -complexes with  $\text{Ag}^+$ . The bond between the olefinic ligand and the metal ion is formed<sup>1</sup> by donation of electrons from the double bond to the vacant s-orbital of  $\text{Ag}^+$  and then donation of d-electrons from the metal ion to the antibonding orbitals of the olefin. Because the symmetry is not correct for interaction, the two bonds are distinct. Stability of  $\pi$ -complexes is therefore, low, formation depending a great deal on the steric hindrance of a double bond. This fact has been utilized in gas chromatography (GC) by BRADFORD *et al.*<sup>2</sup> for selective separation of isomeric butenes; they used glycol saturated with  $\text{AgNO}_3$  as a stationary phase at 0°. GIL-AV *et al.*<sup>3</sup> gave a survey of positive results on the separation of cyclic olefins having a four- to seven-membered ring by GC on columns containing  $\text{AgNO}_3$  solutions at temperatures up to 50°. However, the optimum working conditions of this type of chromatographic system are within the temperature range 0-30°. The complex stability at temperatures exceeding 50-60° drops to a value that is no longer significant for the separation. Further, the stability of  $\text{AgNO}_3$  solutions in the organic solvents used is poor even at room temperature and chromatographic columns only retain their original properties for a few minutes. Therefore, only very volatile olefins can be separated in this way. In addition, on account of reasons mentioned above, this

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\*\* Present address: Organsko Kemijska Industrija, Zagreb, Yugoslavia.

method is suitable only for research work and fails in common analytical practice. However, the very separation of higher olefins from paraffinic, cyclic, and aromatic hydrocarbons is important from an analytical point of view.

To solve this problem we utilized the high sorption affinity of porous polyhydrocarbons (styrene-ethylvinylbenzene copolymers, type Porapak) to hydrocarbons; this has lately led to successful separations in liquid-solid systems<sup>4,5</sup>. Using a complex forming solution as mobile phase, a change in partition coefficients of paraffin (aromatic compound)-olefin pairs can be expected also with higher olefins. Since olefins should be eluted before the corresponding paraffins, the separation should be more rapid unlike the experiments of BRADFORD *et al.*<sup>2</sup> and GIL-AV *et al.*<sup>3</sup> in which olefins were retained more than paraffins. The method may not be limited due to the low stability of  $\text{AgNO}_3$  solutions because  $\text{Ag}^+$  solutions remain only a short time in the column. We carried out static and dynamic measurements of the partition stage of model hydrocarbons (paraffin-olefin-aromatic compounds) using the system Porapak Q- $\text{AgNO}_3$  in propanol containing various quantities of water. Our results are promising.

## EXPERIMENTAL AND RESULTS

### Static measurements

The established equilibria of some hydrocarbons were measured in the system Porapak Q/ $\text{AgNO}_3$ -propanol-water, expressed by adsorbed\* hydrocarbons on Porapak Q. *n*-Nonane, *n*-decene and benzene (pure products of BDH, London) were used as a model mixture. Porapak Q (100-120 mesh, batch. No. 558, Waters Associates Inc., Framingham, Mass., U.S.A.) and a mixture of *n*-propanol (Lachema N.E., Brno, Czechoslovakia), water and  $\text{AgNO}_3$  were used as sorbent and solvent, respectively. The concentration of  $\text{AgNO}_3$  and the propanol-water ratio were changed when necessary.

The mixture of hydrocarbons was dissolved in a known amount of the solvent; then a known amount of sorbent was added and the decrease in concentration of the solution was determined. The quantity of adsorbed hydrocarbons was determined by GC from the ratios of the chromatographic peak heights of hydrocarbons obtained before adding Porapak and after establishing equilibrium. The complex of an olefinic hydrocarbon with silver is unstable and a temperature above 100° in the injection chamber allows complete complex breakdown.

### Dynamic measurements

A dark glass column (43 cm long and 0.3 cm I.D.) was used for liquid chromatography and Teflon tubing was used for all connections to prevent the reduction of  $\text{AgNO}_3$ . The concentration of  $\text{AgNO}_3$  was 0.08 g/ml of mobile liquid in all cases. Porapak Q (150-200 mesh, batch No. 413) served as the column packing. Since the paraffins and olefins used give no adequate signals when using conventional liquid chromatographic detectors<sup>6</sup>, the column effluent composition was followed by GC (data in chromatograms mean GC peak heights according to ref. 7).

Fig. 1 illustrates the effect of the concentration of  $\text{AgNO}_3$  on the adsorption of *n*-nonane, *n*-decene, and benzene. The propanol-water ratio was kept constant (2:1).

\* The term adsorption is used in this paper but it is unclear whether the process is ad- or absorption, or both.

The quantity of adsorbed hydrocarbon does not change within the concentration range of  $\text{AgNO}_3$  examined (0–0.10 g/ml) in the case of nonane as well as of benzene. However, in the case of olefin the fraction of adsorbed decene changes with the concentration of silver salt in the solvent. With the increasing  $\text{AgNO}_3$  concentration the quantity of olefin adsorbed on Porapak Q decreases. The fraction of adsorbed decene is less than that of nonane but still higher than that of benzene in the concentration range 0.015–0.045 g/ml. The quantity of decene adsorbed at still higher concentrations of silver salt is the least of all model mixture compounds; the quantity within a concentration range of about 0.060 up to 0.100 g/ml remains constant.

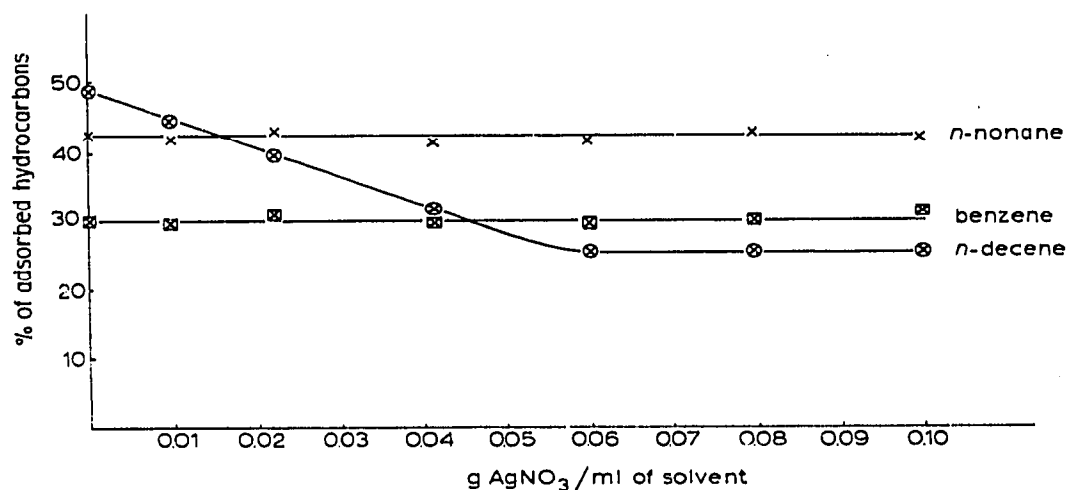


Fig. 1. Effect of the  $\text{AgNO}_3$  concentration in the solvent on hydrocarbon adsorption on Porapak Q. 0.2 g of Porapak Q, 5 ml of propanol–water (2:1), 0.1% hydrocarbon solution in a given mixture.

The effect of the propanol–water ratio on adsorption equilibria of hydrocarbons is given in Table I. The concentration of  $\text{AgNO}_3$  was 0.10 g/ml; the quantity of adsorbed hydrocarbons was always measured before and after adding  $\text{AgNO}_3$  for each mixture again. The quantity of adsorbed hydrocarbons on Porapak Q increases with increasing water content for all three compounds investigated as expected. With nonane and benzene there are no concentration changes after adding silver salt to the solvent mixture. With decene the quantity of adsorbed hydrocarbon decreases regularly

TABLE I

INFLUENCE OF RATIO OF PROPANOL–WATER ON THE ADSORPTION OF MODEL HYDROCARBONS

Propanol– water ratio	$\text{AgNO}_3$ (g/ml)	Fraction of adsorbed hydrocarbons on Porapak			$C_{11}/C_{10}$
		$C_{11}$	Benzene	$C_{10}$	
1:2	0.0	95.3	71.5	97.5	0.98
1:2	0.1	95.5	71.4	89.3	1.07
1:1	0.0	68.2	49.5	72.0	0.94
1:1	0.1	68.0	49.7	40.4	1.68
2:1	0.0	42.4	31.2	48.9	0.87
2:1	0.1	42.2	31.0	25.6	1.65

again. The adsorption selectivity which is represented by the ratio  $C_9/C_{10}$  increases with increasing water content up to a propanol–water ratio of 1:1;  $C_9/C_{10}$  ratio tends to be constant for the mixtures 1:1 and 2:1.

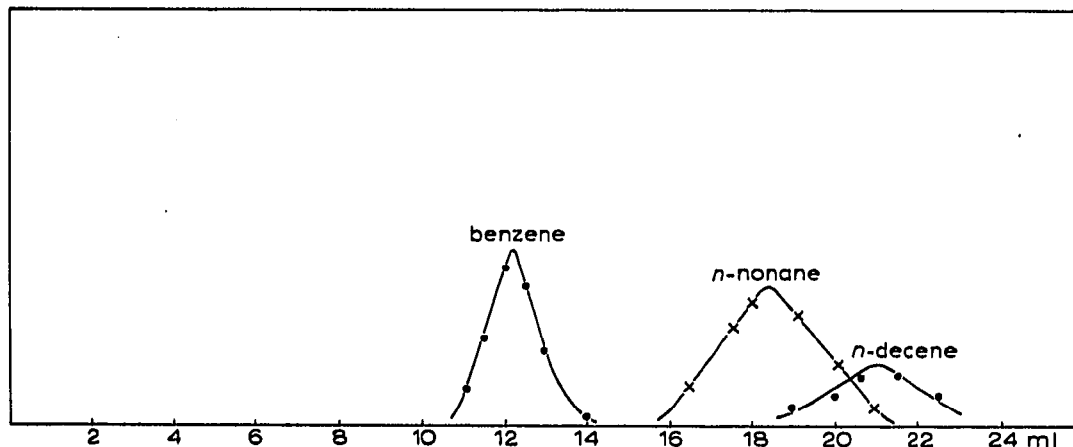


Fig. 2. Liquid chromatogram of a model mixture. Solvent: mixture of *n*-propanol–water (2:1); flow rate: 0.3 ml/min.

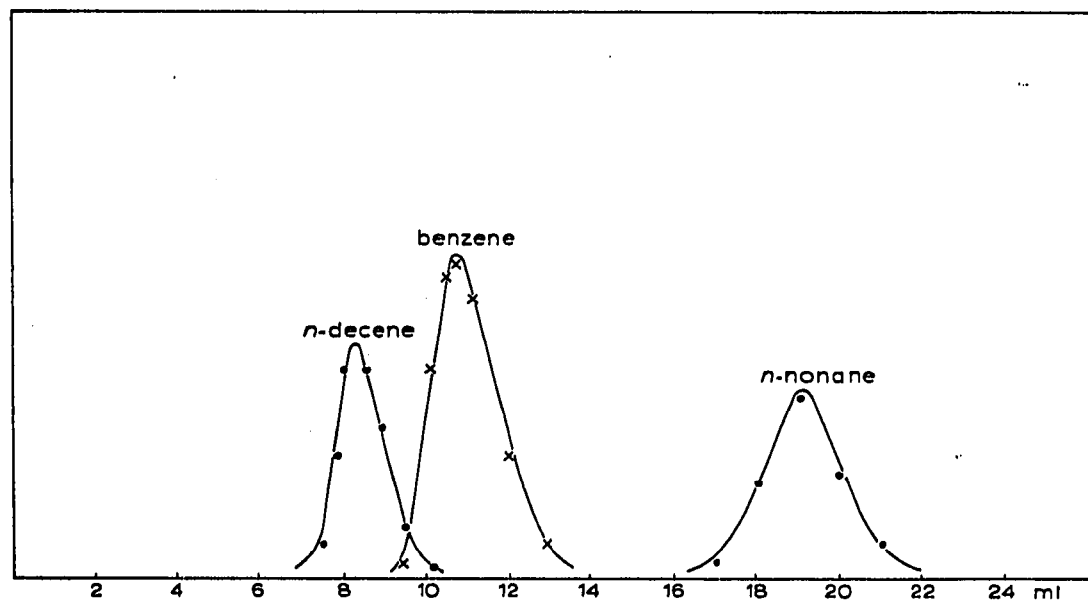


Fig. 3. Liquid chromatogram of a model mixture — the effect of  $\text{AgNO}_3$ . Solvent: mixture of *n*-propanol–water (2:1), and  $\text{AgNO}_3$  (0.08 g/ml); flow rate: 0.24 ml/min.

The chromatogram of a model mixture containing *n*-nonane, *n*-decene, and benzene eluted with propanol–water (2:1) is shown in Fig. 2. The retention sequence is the following: benzene, *n*-nonane, *n*-decene. The effect of complex formation on the retention behavior of hydrocarbons mentioned is evident from Fig. 3. The retention sequence is principally changed; decene forming a silver complex has the lowest retention volume. Thus the results confirm the data obtained by static equilibrium measurements.

Fig. 4 shows the chromatogram of the hydrocarbon mixture which consists of

*n*-heptane, *n*-nonane, *n*-dodecene, and *n*-tetradecene separated under the same conditions as given in Fig. 3. It is evident that the effect of the complex formed is so high that the tetradecene peak overleaps the peak of heptane so that the selectivity effect achieves 7 carbon atoms.

The effect of the ratio of propanol-water on the retention of model compounds is evident from Fig. 5. Higher relative propanol content shifts the adsorption equilibrium of all hydrocarbons in favor of the mobile phase which is manifested by more rapid elution.

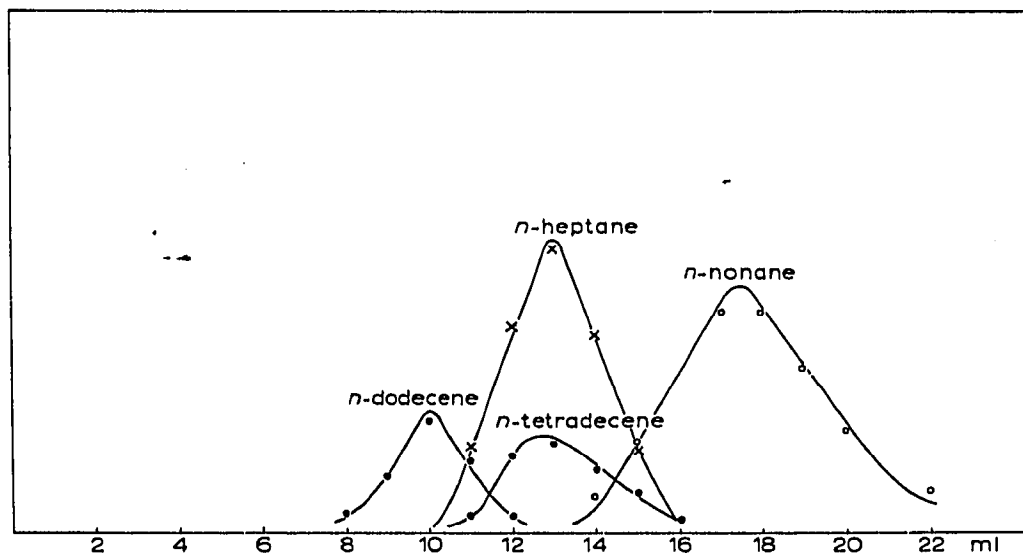


Fig. 4. Liquid chromatogram of a more complex mixture. Solvent: mixture of *n*-propanol-water (2:1), and  $\text{AgNO}_3$  (0.08 g/ml); flow rate: 0.25 ml/min.

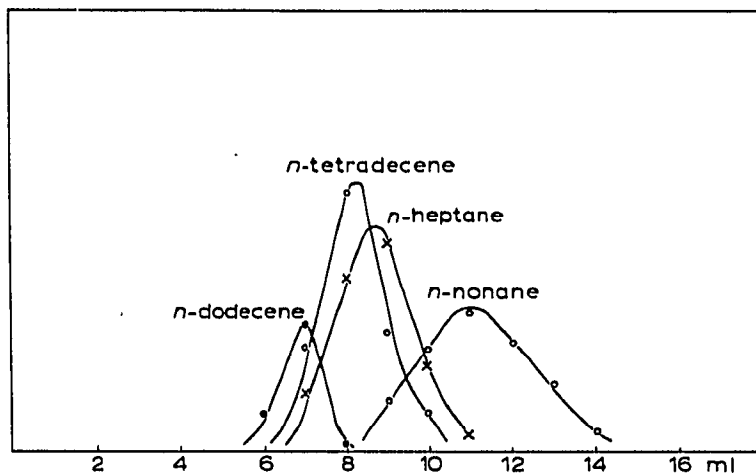


Fig. 5. Effect of an increased water content on retention of model compounds. Solvent: mixture of *n*-propanol-water (3:1), and  $\text{AgNO}_3$  (0.08 g/ml); flow rate: 0.27 ml/min.

## CONCLUSIONS

The  $\pi$ -complex formation of olefinic hydrocarbons and silver ions in liquid mobile phase produces a change of their retention volumes. This allows the separation

of olefins from the mixture containing other hydrocarbons by liquid chromatography and/or thin-layer chromatography. The olefin elution is more rapid in the system mentioned, as compared with systems in which the mobile liquid does not contain Ag<sup>+</sup> while the retention of aromatic and paraffinic hydrocarbons does not change. The selective effect is considerable; a shift equivalent to the effect of 7 carbon atoms has been found.

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