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Blended liquid crystalline stationary phases in capillary gas chromatography

FRANK HAHNE, GÜNTER KRAUS* and HORST ZASCHKE

Department of Chemistry, Martin-Luther-University Halle-Wittenberg, 4010 Halle/Saale (G.D.R.)

ABSTRACT

Neat and blended liquid crystalline and silicone phases were investigated as stationary phases in glass capillary columns and by use of light and scanning electron microscopes. The columns with blended liquid crystals showed better efficiency and permit better film homogeneity.

INTRODUCTION

Laub and co-workers [1,2] used liquid crystals blended with silicone gum phases and reported increased column efficiencies in capillaries. The application of admixed phases in packed columns was used for the separation of pesticides [3]. The high resolution of the mixture is attributed to the high efficiency of silicone gum and the better selectivity of the mesogenic phase, dispersed in the silicone gum phase [4]. Plots of retention data of admixed non-mesogenic phases against volume fraction of solvent give linear graphs [5].

We have investigated neat and blended liquid crystalline and silicone oil phases in glass capillary columns using isomeric benzene derivatives as solutes.

EXPERIMENTAL

Measurements were carried out with a Varian Model 3600 gas chromatograph equipped with a flame ionization detector and nitrogen as the carrier gas. Glass capillary columns (20 m × 0.3 mm I.D.) were etched with gaseous hydrogen chloride, deactivated with Carbowax 20M and statically coated with neat and blended liquids of 4-propoxy-4'-ethoxyazobenzene (PEAB), Cr 101 N 147 Is (crystalline 101°C, nematic 147°C, isotropic), and polymethylhydrogensiloxane (PMHS), film thickness, $d_f = 0.3 \mu\text{m}$.

Microscopic investigations of the phases were done with a light microscope and a JOEL scanning electron microscope.

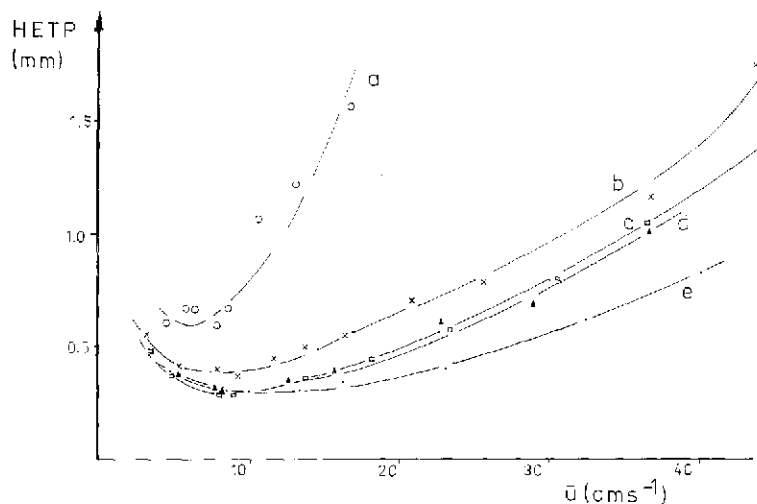


Fig. 1. Plots of the height equivalent to a theoretical plate (HETP) against average linear velocity \bar{u} for glass capillary columns at 110°C with neat and admixed stationary phases for C_{12} – C_{14} *n*-alkane solutes at 100°C : (a) PEAB, C_{14} , capacity factor, $k' = 3.3$; (b) PEAB-PMHS (83:17), C_{13} , $k' = 2.8$; (c) PEAB-PMHS (50:50), C_{13} , $k' = 4.0$; (d) PEAB-PMHS (25:75), C_{12} , $k' = 2.4$; (e) PMHS, C_{12} , $k' = 3.8$.

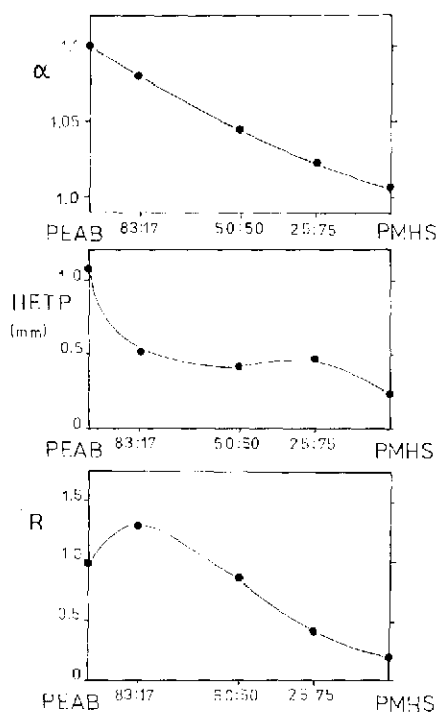


Fig. 2. Plots of separation factor (α), HETP and resolution, R , for the solute pair *m*- and *p*-xylene at 100°C in the supercooled state as a function of stationary phase composition.

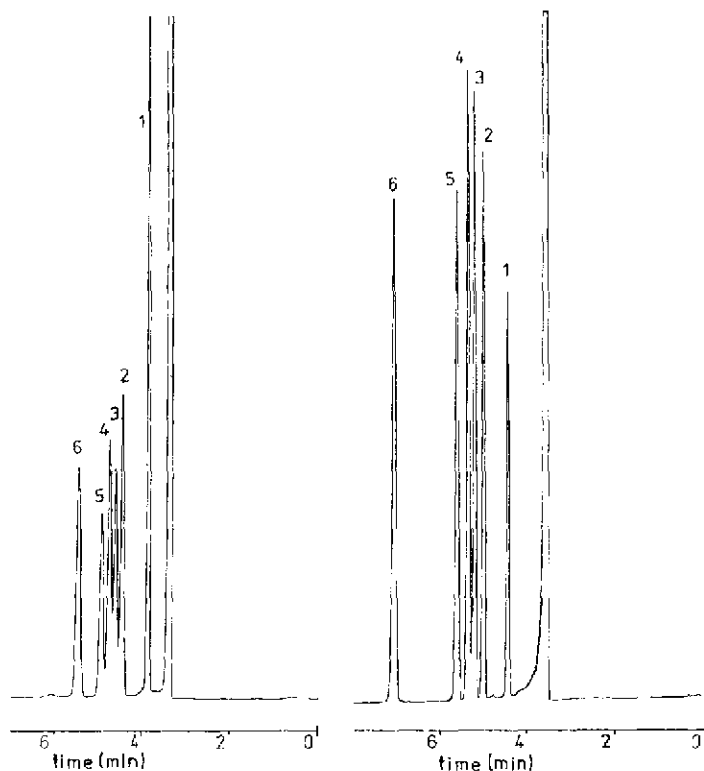


Fig. 3. Separation of ethylbenzene and *m*-, *p*- and *o*-xylene at 100°C in the supercooled state with PEAB and PEAB-PMHS (83:17) stationary phases. Peaks: 1 = nonane; 2 = ethylbenzene; 3 = *m*-xylene; 4 = *p*-xylene; 5 = *o*-xylene; 6 = undecane.

RESULTS AND DISCUSSION

Fig. 1. illustrates the Van Deemter plots as a function of the the proportion of PMHS in the blend. It shows that the mixture and the neat PMHS have a lower resistance to mass transfer in the stationary phase. In the liquid crystalline phase the diffusion may be too slow so that the efficiency is very low.

The influence of the composition of the stationary phase on the selectivity, efficiency and resolution [6] for the solute pair *p*- and *m*-xylene as substrate is shown in Fig. 2. The selectivity shows a nearly linear dependence on the composition of the liquid phase. With regard to the efficiency, only a small amount of silicone oil phase is necessary in order to obtain many more theoretical plates. This results in a maximum resolution with the use of the mixture PEAB-PMHS (83:17) (Figs. 2 and 3).

A light microscopic photograph of the pure mixture with the highest resolution [PEAB-PMHS (83:17)] is shown in Fig. 4a (nematic state) and Fig. 4b (isotropic state). In both instances drops of PMHS silicone oil are visible. Fig. 4a shows the typical texture of a nematic mesophase, demonstrating that the mixture is not homo-

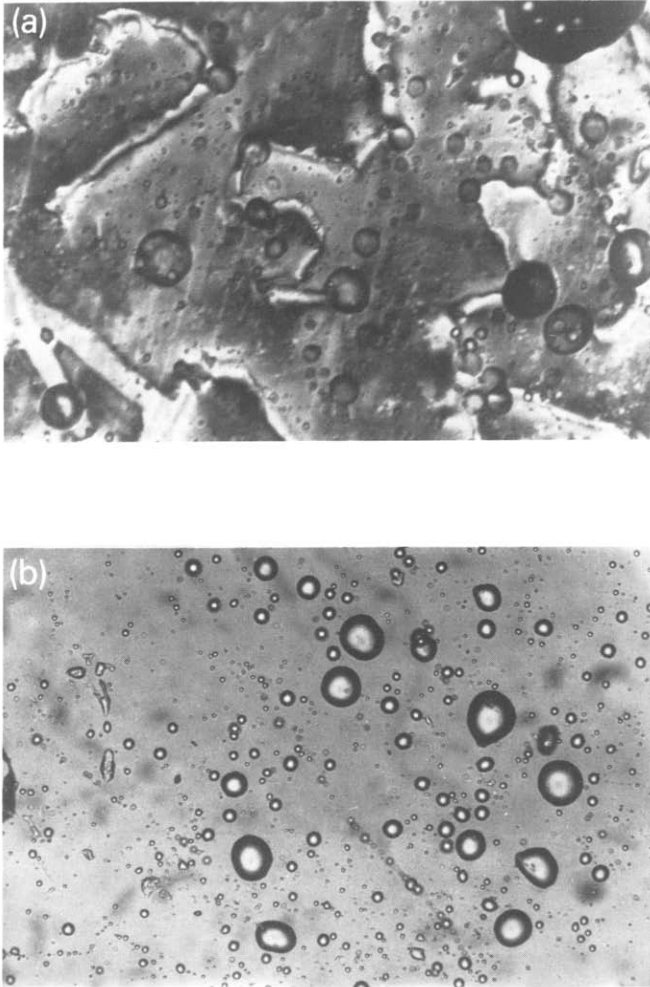


Fig. 4. Polarizing microscope observation of the PEAB-PMHS (83:17) mixture (a) in the nematic state and (b) in the isotropic state with crossed polarizers.

ogeneous, one of the components being dispersed in the other. Additional investigations using mixtures of PEAB with SE-54 provided similar results.

Scanning electron microscopic (SEM) photographs of the inner surface of the glass capillary columns were taken (Fig. 5). In comparison with the pure mesogenic phase (Fig. 5a), the PEAB-PMHS (83:17) mixture leads to an improved formation of the stationary phase film. With pure PMHS the film of the stationary phase has been deposited homogeneously.

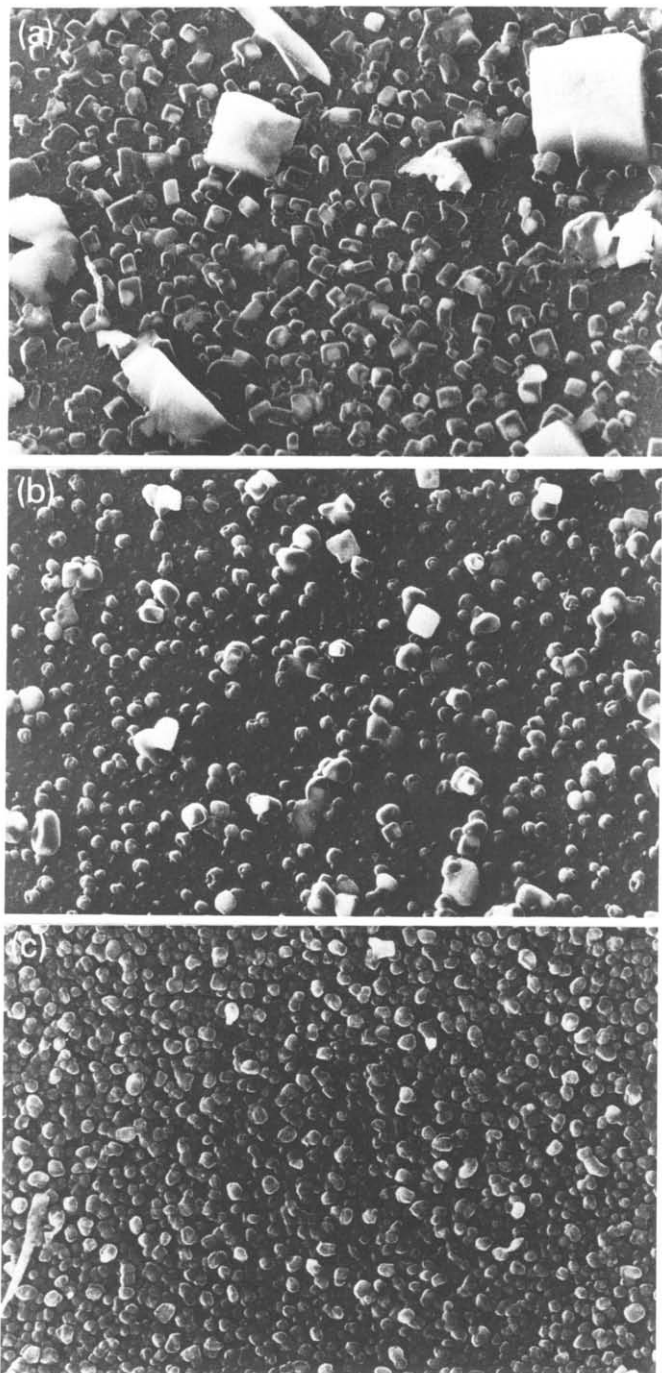


Fig. 5. SEM photographs ($\times 5000$) of the inner surface of glass capillaries coated with (a) PEAB, (b) PEAB-PMHS (83:17) and (c) PMIIS.

CONCLUSIONS

The better resolution obtained with mixture of mesogenic phase with a non-mesogenic silicone phase is due to the improved efficiency. It has been shown that only a small amount of non-mesogenic phase is necessary. The two phases show no mutual solubility. The mixture permits a better film homogeneity.

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