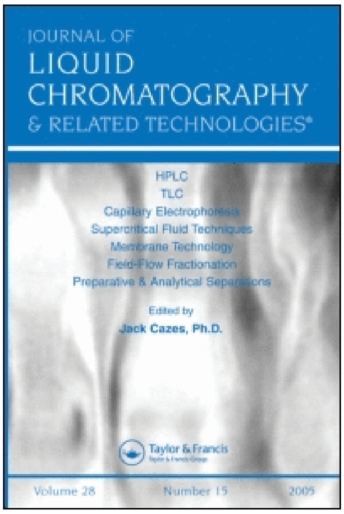

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ANALYSIS OF CHROMATOGRAPHIC PARAMETERS IN THE SYSTEMS WITH TERNARY MOBILE PHASES

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ABSTRACT

A new method is proposed for analysis of chromatographic parameters obtained for ternary mobile phases. The experimental data are presented in Gibbs triangle in the form of isolines i.e. lines connecting the points corresponding to the same chromatographic parameters values. The measurements were made by adsorption thin layer chromatography technique on silica gel at temperature 293 K. After the analysis of the isolines obtained in this way a new method for optimal choosing of the mobile phase composition for test mixture separation has been proposed.

INTRODUCTION

Optimal conditions of mixtures separation by adsorption liquid chromatography require most frequently mixed (multicomponent) mobile phases application. Chromatographic process complexity when mobile phase containing greater number of components is used causes difficulties in aspect of physico - chemical interpretation of experimental data obtained in such systems.

Theoretical considerations related to adsorption liquid chromatography have permitted to obtain the relationship between chromatographic parameters (k', R_F or R_M) and mobile phase composition (1-5). Most experimental investigations verified derived equations were carried out for binary mobile phases (6-9). Little number of published data related to ternary mobile phases exists (10,11). During investigations of such systems exist not only experimental difficulties but also the problem of clear and most rational graphical presentation of experimental data. The question is whether namely of such presentation of results for will can examine possibly comprehensive interpretation either in aspect of physicochemical basis of process or in practical and analytical aspects. In this paper efforts of new graphical presentation of results for ternary mobile phases are described. For such systems method of experimental data interpretation proposed here may be helpful for explanation of complicated mechanism of process.

MATERIALS AND METHODS

Chromatographic measurements were carried out by thin layer chromatography technique in Stahl chambers at temperature 293 K. Silica gel 60 H Merck Darmstad FRG was used as adsorbent. The chromatograms were developed on distance 16 cm and then detected in iodine vapours. Investigations were carried out for 6 model substances namely naphthalene, o-nitrotoluene, o-bromonitrobenzene, o-nitroaniline, o-nitrophenol and fluorenone. Following mobile phases were used : pure solvents : carbon tetrachloride, benzene, trichloroethylene, acetone, n-propanol and their binary and ternary mixtures. Binary mixtures have following concentrations : 0.1, 0.3, 0.5, 0.7 and 0.9 molar fraction of more polar component. A main component of ternary mobile phases was binary mixture of carbon tetrachloride + benzene and changes in chromatographic parameters were observed with changes of elution power of third component. Ternary mobile phases were prepared for three various concentrations of basic binary mixtures i.e. for carbon tetrachloride + benzene molar fraction ratios 1:3, 1:1 and 3:1. To initial solutions prepared in this manner trichloroethylene, acetone and n-propanol were added succesively so that their molar fraction values were 0.1, 0.3, 0.5, 0.7 and 0.9 (basis solution was treated as less polar solvent). The measurements carried out for such mobile phase systems have permitted to presentation of experimental data in the form of Gibbs triangle. Vertexes of this triangle correspond to chromatographic parameters (R_F, R_M or k′) of model substance in pure solvent. Sides of triangle to the same parameters in binary mobile phases and interior of triangle in ternary mobile phases.

RESULTS AND DISCUSSION

Chromatographic parameters values (R_F) of given substance obtained for mobile phases of various composition were marked on Gibbs triangle - circus with marked R_F values. By simple interpolation the lines connecting the points corresponding to the same chromatographic parameters values for given substance were plotted. In this way ilustration of experimental data was obtained which permits as it seems to their comprehensive interpretation - retention characteristic of the systems.Among other the following relationships can be analyzed:

- changes in chromatographic parameters values with changes of one mobile phase component concentration at given and constant concentration ratio of two remaining components,
- changes in chromatographic parameters of substance at constant concentration of one mobile phase component with changes in concentration ratio for two remaining components,
- changes in mobile phase components concentration not causing of changes in chromatographic parameters of the substance - mobile phase concentration values corresponding to isolines in Gibbs triangle,
- dependence of chromatographic parameters isolines course on change of mobile phase components,
- effect of chromatographic substance structure on changes in chromatographic parameters isolines course for ternary mobile phase.

Analysis of chromatographic data presented for many substances in the form of isolines on Gibbs triangle permits to choosing the optimal conditions of chromatographic process. Figures 1-6 present for example the illustration of experimental data R_F for o-nitrotoluene and o-nitroaniline. For four remaining substances analogical graphs were obtained. It appears that isolines course for these data

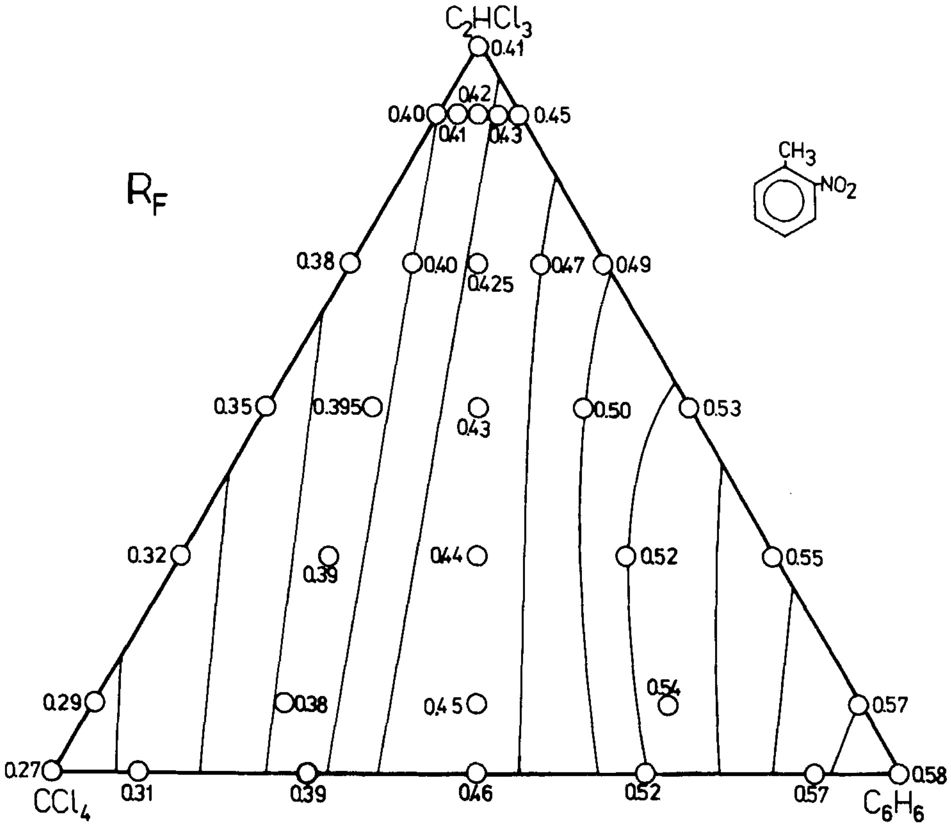

Fig.1 Isolines of R_F values for o-nitrotoluene in carbon tetrachloride + benzene + trichloroethylene system.

changes very significantly with changes in properties of third mobile phase component. It refers especially to change of third component from A to B according to Pimentell and McClellan (12) . In this case a change in direction of R_F isolines course is observed

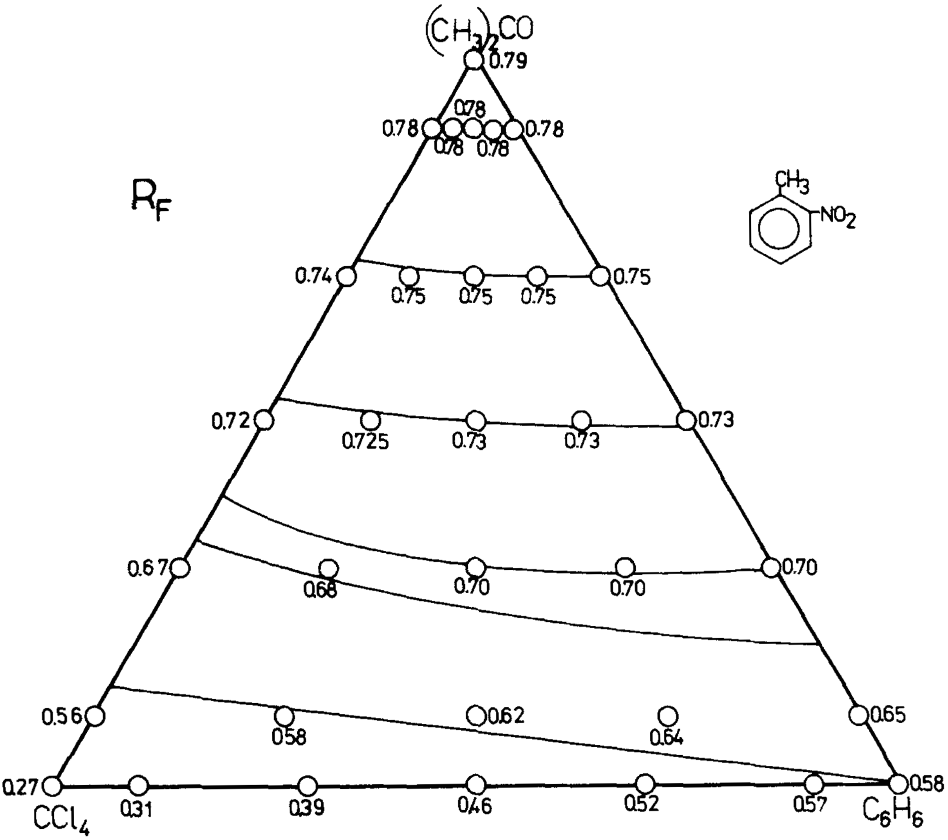

Fig.2 Isolines of R_F values for o-nitrotoluene in carbon tetrachloride + benzene + acetone system.

(Figs 1-6). If third component of mobile phase belongs to AB class then shape of chromatographic data isolines became more complicated (Figs 3,6). "Circular" shape of isolines is caused by existence of R_F values maxima of model substance for n-propanol molar fraction between 0.7 - 0.9.

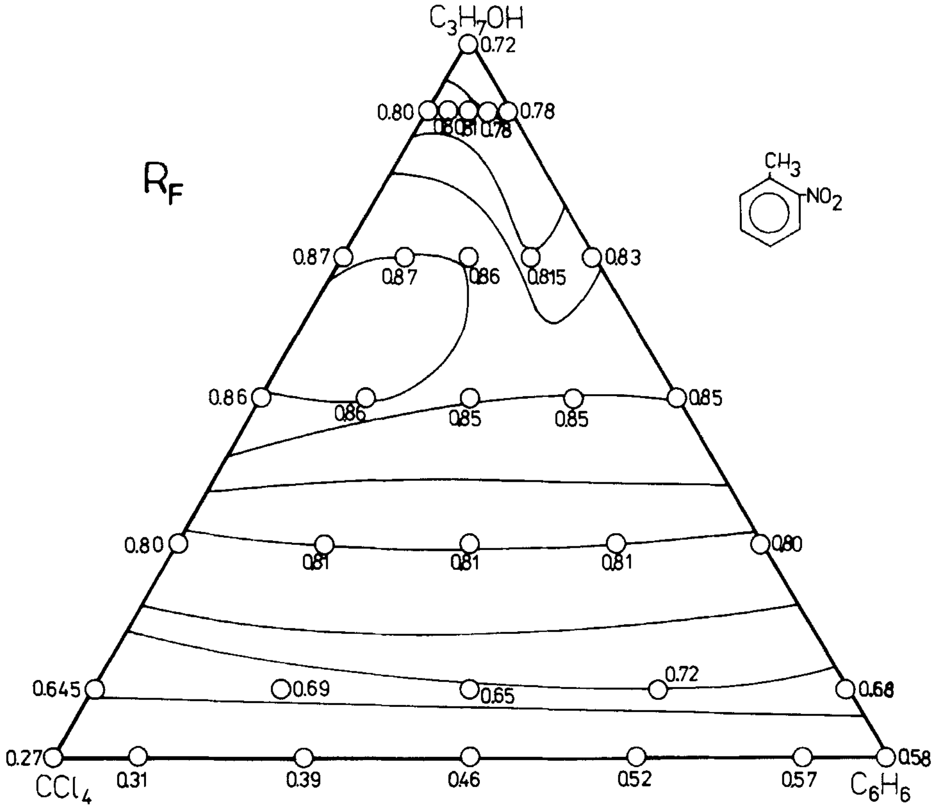

Fig.3 Isolines of R_F values for o-nitrotoluene in carbon tetrachloride + benzene + n-propanol system.

Analysis of isolines shape for the systems containing acetone and n-propanol it can conclude that these isolines are practically parallel and equally distant from triangle vertex corresponding to pure more polar component of mobile phase. In this connection it can

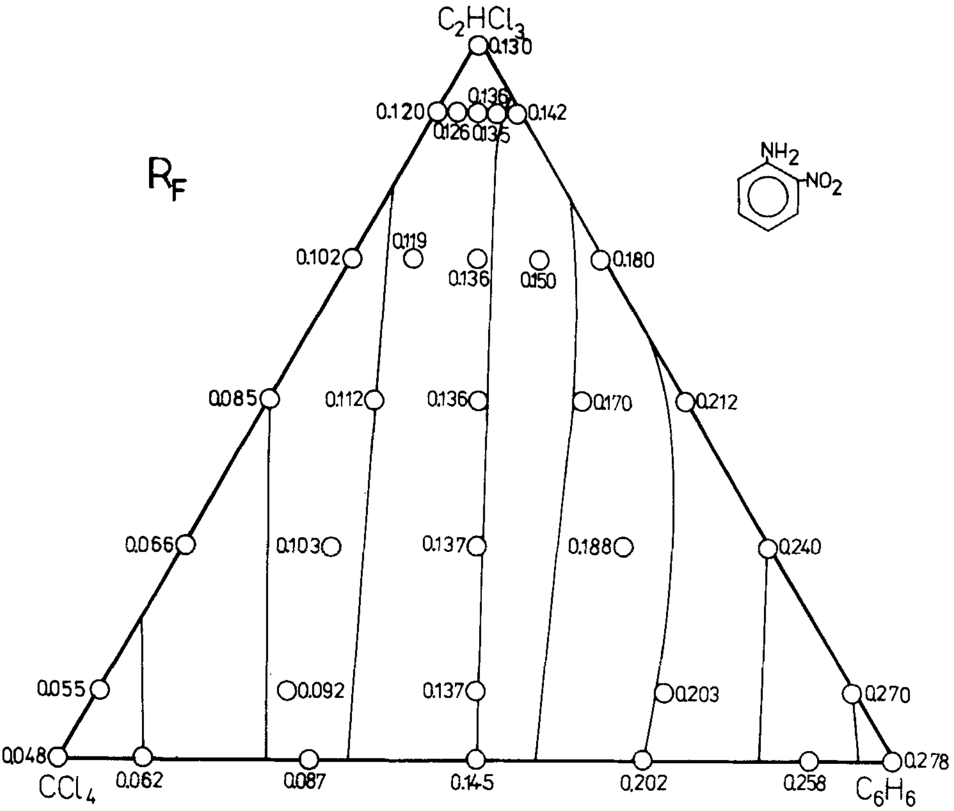

Fig.4 Isolines of R_F values for o-nitroaniline in carbon tetrachloride + benzene + trichloro - ethylene system.

be seen that for these systems a separation process is determined by component of greatest elution power and composition of binary basic mixture (i.e. carbon tetrachloride + benzene) play not a significant role (Figs 2,3,5,6). In this case of ternary mobile

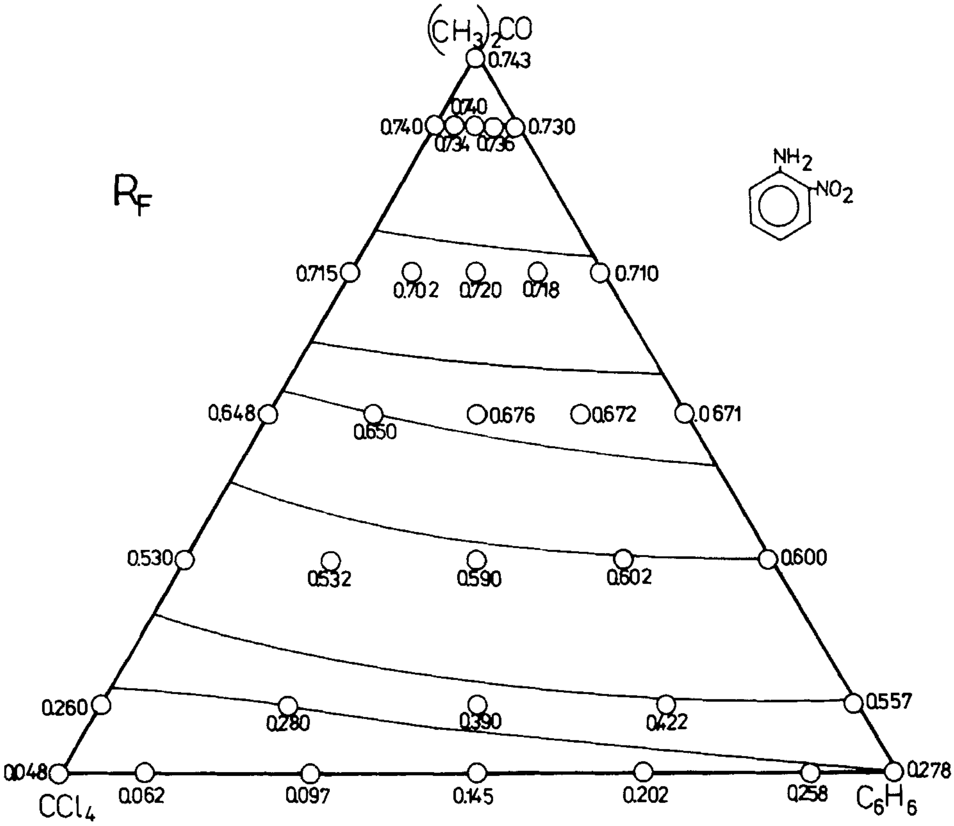

Fig.5 Isolines of R_F values for o-nitroaniline in carbon tetrachloride + benzene + acetone system.

phase containing solvent from A class an isoline position is not symmetrical in relation to triangle vertex corresponding to this solvent. Chromatographic process carried out in such system is determined mainly by composition of basic mobile phase. The experimental data presented in this manner give

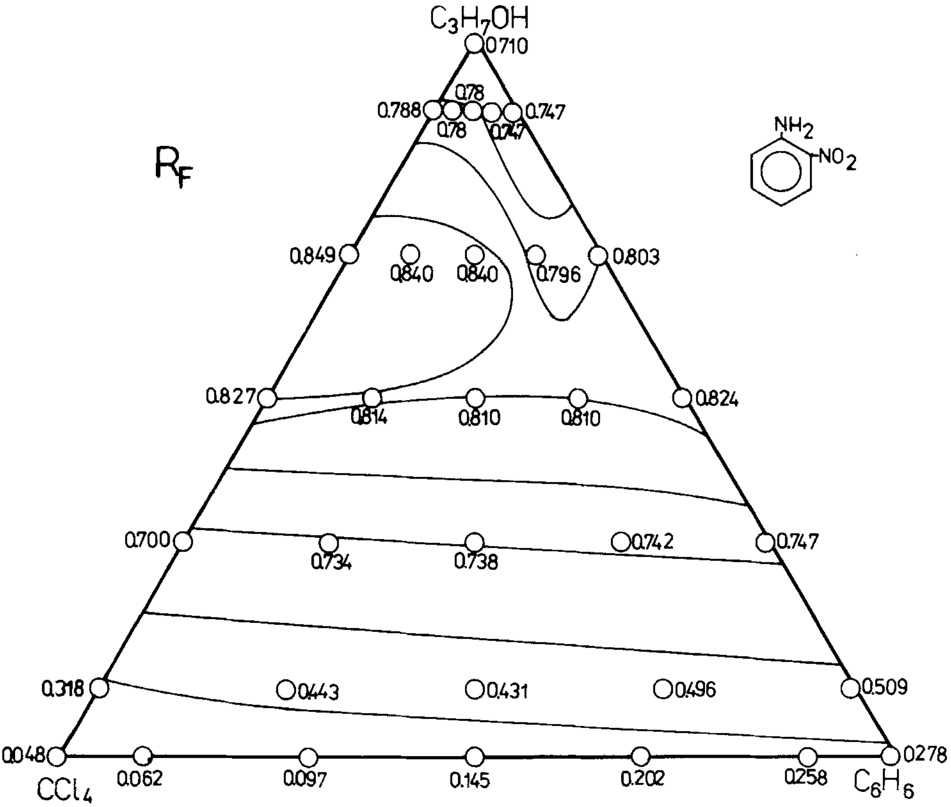

Fig.6 Isolines of R_F values for o-nitroaniline in carbon tetrachloride + benzene + n-propanol system.

a general retention characteristic of the system. Such characteristic permits on physicochemical description of chromatographic process. More detailled conclusions relating to separation conditions may by drawn after analysis of figures 7-9 presenting the relationship

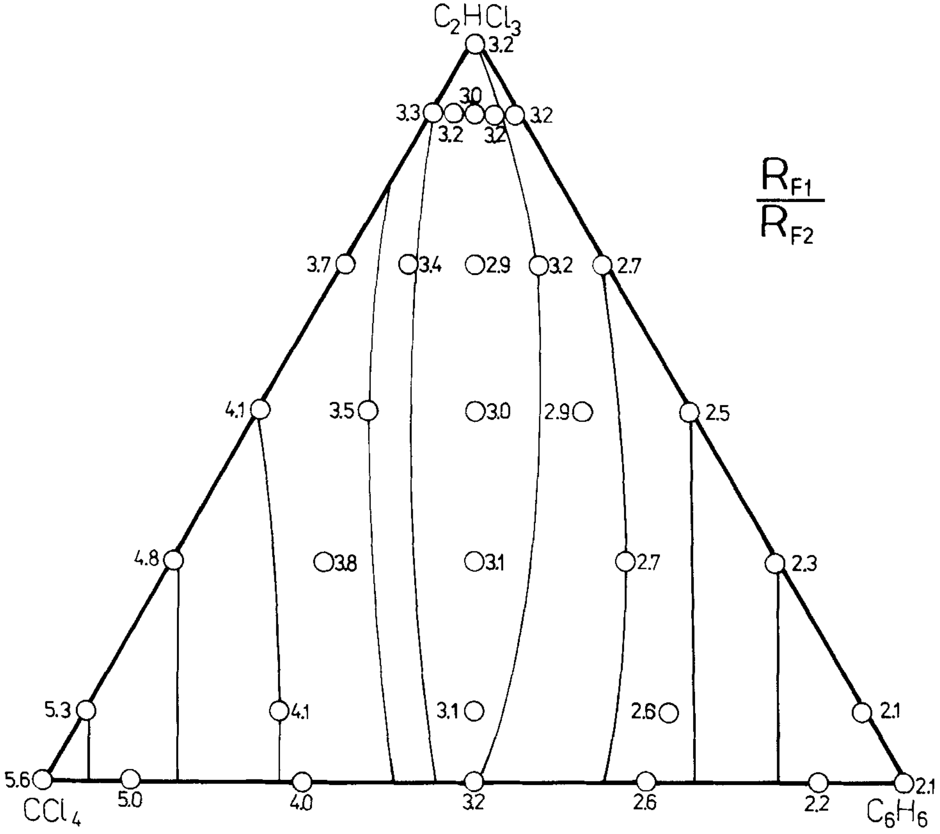

Fig.7 Isolines of R_{F1}/R_{F2} values in carbon tetra - chloride + benzene + trichloroethylene system.

between o-nitrotoluene and o-nitroaniline R_F ratio (R_{F1}/R_{F2}) and mobile phase composition. Similarly as previously the results obtained were marked on Gibbs triangle and the points corresponding to the same R_{F1}/R_{F2} values were connected (isolines of

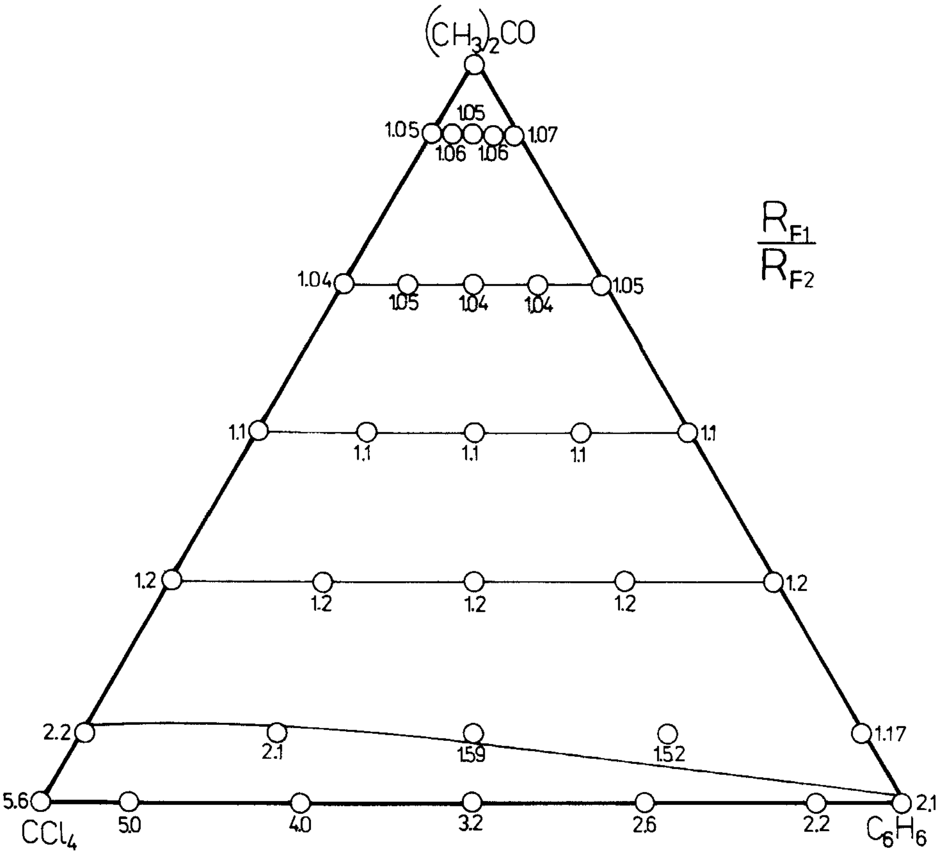

Fig.8 Isolines of R_{F1}/R_{F2} values in carbon tetra - chloride + benzene + acetone system.

R_{F1}/R_{F2} values). In this way a set of mobile phase compositions was obtained for which it can obtain the same separation of two model substances. Isolines of R_{F1}/R_{F2} ratio on presented Gibbs triangles are positioned analogicaly as isolines obtained for single

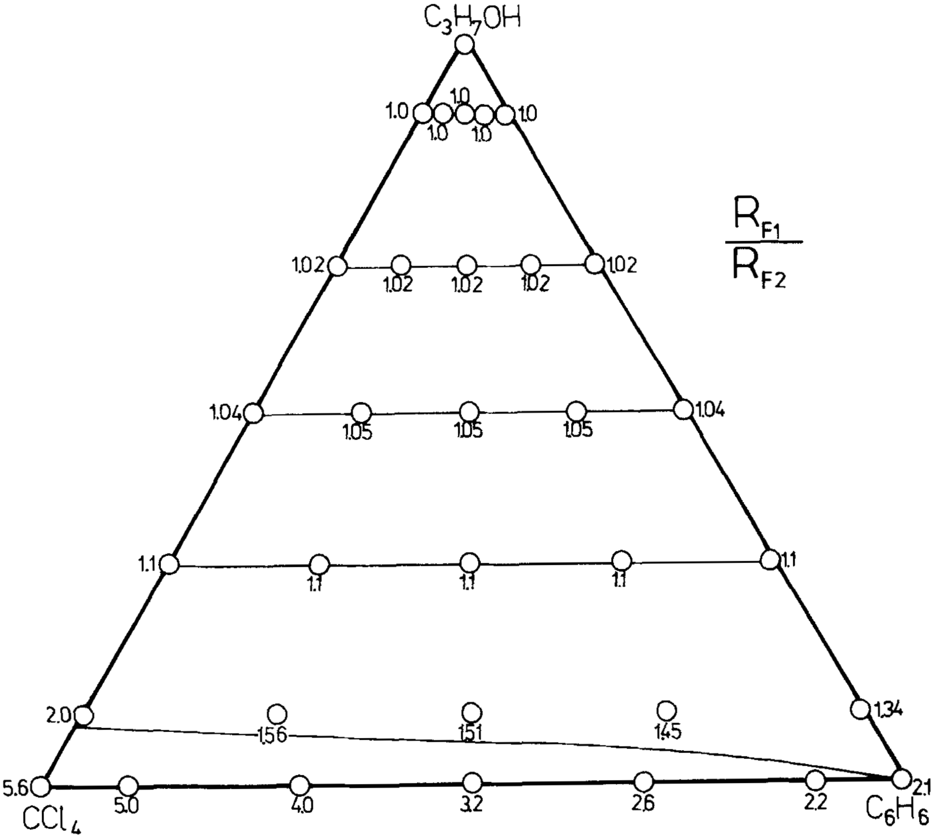

Fig.9 Isolines of R_{F1}/R_{F2} values in carbon tetra - chloride + benzene + n-propanol system.

substance in appropiate mobile phases. In the case of carbon tetrachloride + benzene + acetone it can be seen that for concentration of 0.3, 0.5, 0.7, 0.9 molar fraction of acetone they are idealy parallel and equally distant from the vertex corresponding to acetone. R_{F1}/R_{F2} values corresponding to these concentrations fluctuate around unity. Thus these mobile phases not assure a desired separation of these substances. Separation conditions improve for 0.1 molar fraction of acetone $(R_{F1}/R_{F2}=1.52-2.15)$. They are not fully satisfied however (Fig. 8). Analogous separation conditions have obtained for ternary system containing n-propanol (Fig.9) . The best conditions for separation of model mixture were obtained in the case of pure carbon tetrachloride because in this case R_{F1}/R_{F2} value attains a maximum. Good separation secure also binary mobile phases carbon tetrachloride + benzene of concentration of 0.1, 0.3 and 0.5 molar fraction of benzene $(R_{F1}/R_{F2}$ values are 5.0, 4.02 and 3,15 respectively) . For the system carbon tetrachloride + benzene + trichloroethylene the situation is slightly another. In this case R_{F1}/R_{F2} values for all concentrations of the mobile phases change in the range from 5.63 for carbon tetrachloride to 2.09 for benzene (Fig.7). In this connection such system is more suitable for model mixture separation than the system mentioned above. Optimal separation may be obtained also for greater number of mobile phases, for example carbon tetrachloride + trichloroethylene in whole concentration range $(R_{F1}/R_{F2} = 5.63 - 3.15)$, carbon tetrachloride + benzene for benzene molar fractions 0.1 - 0.5

$(R_{F1}/R_{F2} = 5.63 - 3.15)$ and ternary mobile phase carbon tetrachloride + benzene (3:1) + trichloroethylene for trichloroethylene molar fractions 0.1 - - 0.5 $(R_{F1}/R_{F2} = 4.25 - 3.54)$. So wide concentration range of mobile phases securing optimal separation produces a possibility of greater elasticity on aspect of choosing of optimal chromatographic conditions for greater number of substances. It exists a possibility of such choosing of test mixture that it will contain the substances from all clesses according to Pimentell and McClellan classification. Data marked on Gibbs triangles can then give an answer what among solvent system considered and of that concentration is most suitable for conduct of chromatographic process. This is possible all the more because it has stated that isolines distribution depends on nature of solvents forming mobile phase and not on nature of chromatographed substances. In the solvent system investigated course of isolines of R_F values is analogous for all substances in individula systems and only differences in R_F values exist (Figs 1-3). In this case analysis of R_{F1}/R_{F2} values is more suitable. Analytical aspect of separation process can be considered also basing oneself on the difference of chromatographic parameters

$\Delta R_{F1,2} = R_{F1} - R_{F2}$ indeed their ratio. Course of isolines $\Delta R_{F1,2}$ obtained in this way will make possible a choosing of optimal mobile phase composition for conduct of analysis.

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