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Partition of Organic Bases in Systems of the Type Organic Solvent — Aqueous Solutions of Orthophosphoric Acid

Распределение органических оснований в системах типа органический растворитель — водные растворы ортофосфорной кислоты

Podział zasad organicznych w układach typu rozpuszczalnik organiczny — wodne roztwory kwasu ortofosforowego

Orthophosphoric acid belongs to moderately weak acids; its pK Avalues are correspondingly 1.89, 6.27 and 10.85 (for solutions of constant ionic strength, 3M $NaClO_4$) (1). However, the acidity of its concentrated aqueous solutions can be as high as $H_0 = -3.5$ (for 80% w/w solutions of H_3PO_4) (2); therefore, it is suitable for controlling the ionization equilibria and optimization of liquid-liquid partition of weak organic bases. It has been reported that the tendency to extract ion pairs, characteristic for strongly acidic partition systems containing HCl, HBr and especially $HClO_4$ (3, 4) is much less strongly pronounced for solutions of orthophosphoric acid (3) which has been utilized for reextraction of ion pairs of organic bases from organic solvents (e. g., ref. (5). In the present paper, the extraction of several organic bases from solutions of orthophosphoric acid is studied, the parameters investigated being the concentration of phosphoric acid in the aqueous phase, type of organic solvent and the molecular structure of the organic base. The partition coefficients were determined from paper chromatographic data, using the „moist paper" technique in which the partition mechanism is the predominating one (6).

EXPERIMENTAL

Whatman No 4 paper strips (5 × 23.5 cm) were impregnated with aqueous solutions of phosphoric acid of known initial concentration (c_0), blotted between two sheets of filter paper to remove excess liquid and weighed. The solutes were spotted as 0.5% w/v solutions in chloroform and the strips dried until the amount of liquid decreased to 0.5 g per 1 gram of dry paper. The final concentration of phosphoric acid was calculated from the weight of the liquid stationary phase just after impregnation and blotting and the weight of the liquid phase after drying to 50% moisture content (6.7); it was assumed that phosphoric acid in view of its low volatility did not evaporate during the partial drying of the strip. The final concentration of phosphoric acid was ca. three times higher than the initial concentration c_0. After reaching the suitable moisture content the strips were immediately transferred to glass tanks 5 × 9 × 24 cm for descending development. The spots were revealed with Dragendorff's reagent. The R_F coefficients are mean values from 3 runs. All experiments were carried out at room temperature (20 ±1°C).

The following developing solvents were used: cyclohexane (class N after Pimentel and McClellan (8), chloroform, trichloroethylene (class A), benzene (class II-B), n-pentanol-1 (class AB). Chloroform and pentanol were saturated with solutions of phosphoric acid of suitable concentration, final equilibration being reached on the 5 cm distance between solvent level and starting line.

RESULTS AND DISCUSSION

It could be expected that solutions of phosphoric acid should have certain common features with solutions of citric acid (9) although in other respects marked differences should also be revealed. The analogies should be expected first of all in these concentration ranges of the two acids where their effect on partition is mainly due to control of ionization equilibria of the solutes, i.e., where the pH of the aqueous phase is the governing parameter (lower concentrations). On the other hand, the differences should be more pronounced for more concentrated solutions where the individual properties of the acids should be revealed (hydration, H-bonding with solute molecules, differences in the structure of the aqueous phase etc.),

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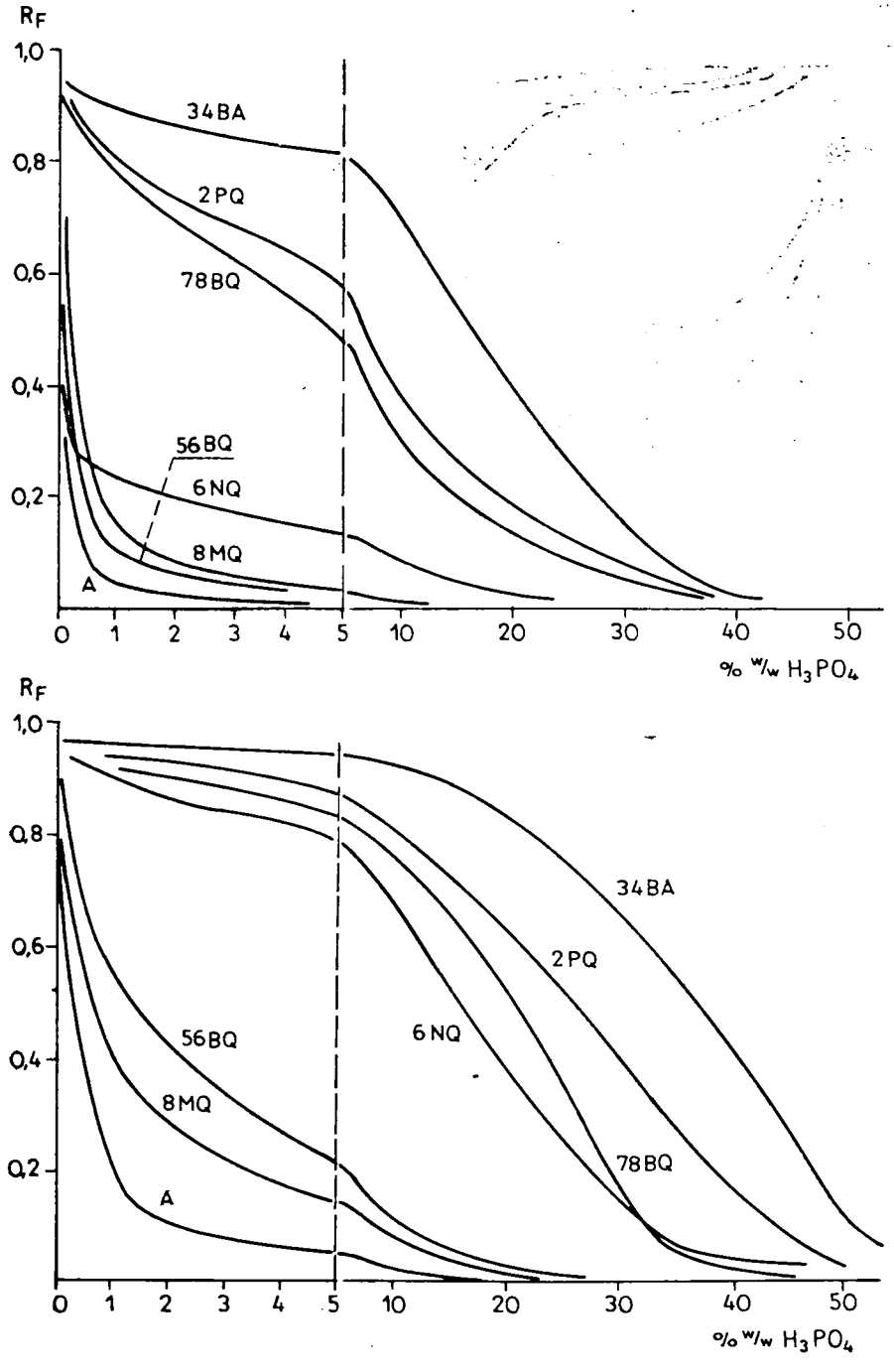
Rys. 1. Wartości R_F zasad organicznych wykreślone jako funkcja procentowego stężenia (w/w) kwasu fosforowego w fazie stacjonarnej. Faza ruchoma: cykloheksan. Substancje oznaczono następująco: A — akrydyna; 8MQ — 8-metylochinolina; 56BQ — 5,6-benzochinolina; 6NQ — 6-nitrochinolina; 2PQ — 2-fenylochinolina; 34BA — 3,4 benzakrydyna

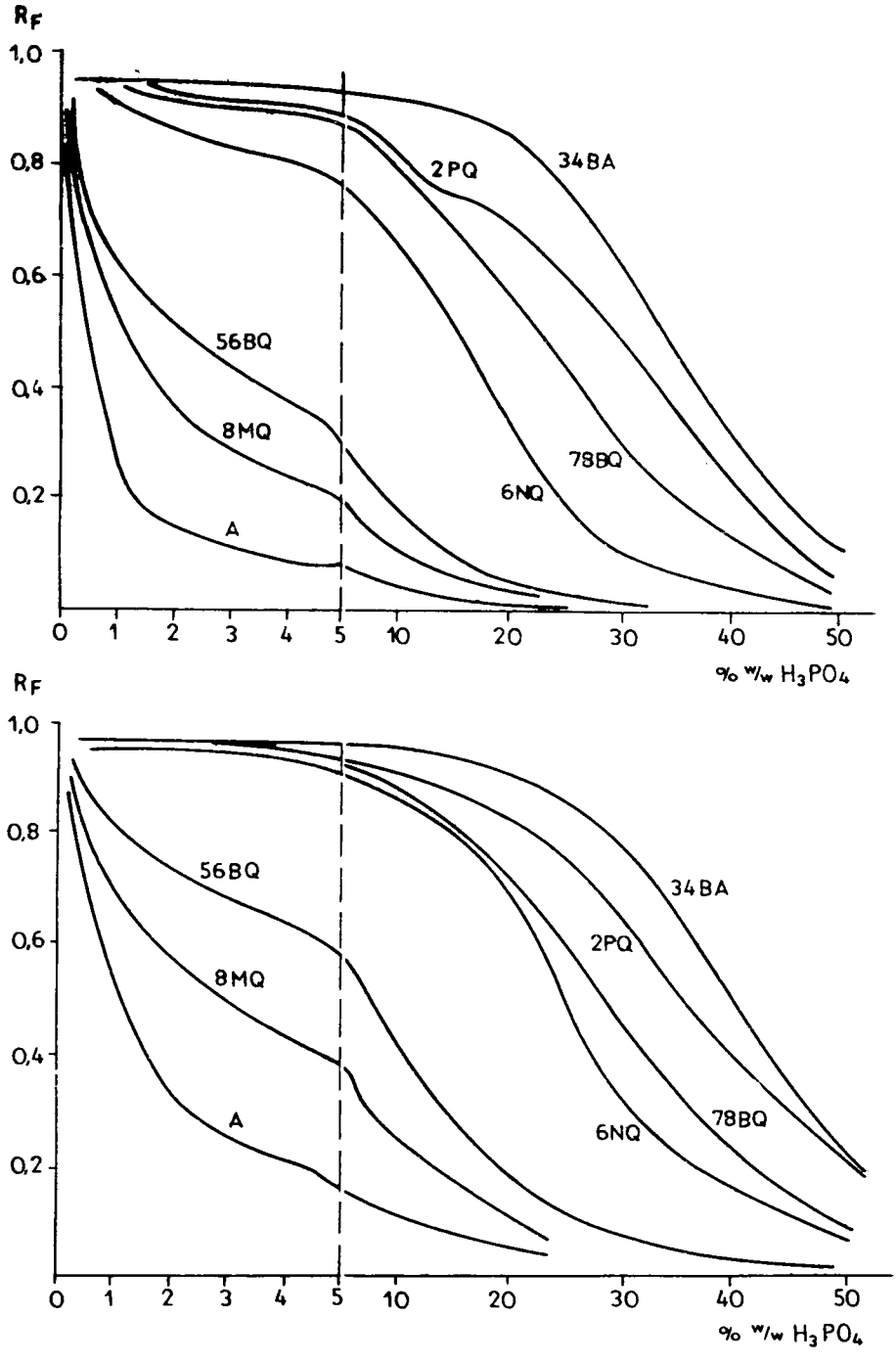
R_F values of organic bases plotted against percent concentration (ww.) of phosphoric acid in the stationary phase. Mobile phase: cyclohexane. The solutes are denoted as follows: A, acridine; 8MQ, 8-methylquinoline; 56BQ, 5,6-benzoquinoline; 78BQ, 7,8-benzoquinoline; 6NQ, 6-nitroquinoline; 2PQ, 2-phenylquinoline; 34BA, 3,4-benzacridine

Rys. 2. Jak na ryc. 1; rozpuszczalnik rozwijający: benzen

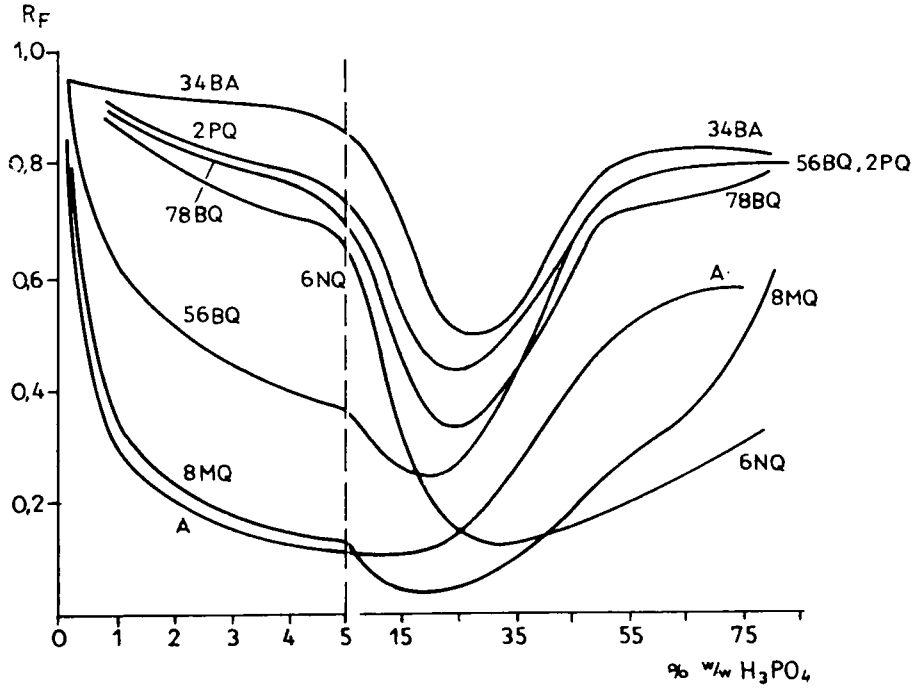
As in Fig. 1. Developing solvent: benzene


RF
1,0
0,8
0,6
0,4
0,2
34BA
2PQ
78BQ
56BQ
6NQ
8MQ
A
0 1 2 3 4 5 10 20 30 40 50
% w/w H3PO4
RF
1,0
0,8
0,6
0,4
0,2
34BA
2PQ
6NQ
56BQ
8MQ
78BQ
A
0 1 2 3 4 5 10 20 30 40 50
% w/w H3PO4

Ryc. 1, 2


R_F
1,0
0,8
0,6
0,4
0,2
2PQ
34BA
56BQ
8MQ
78BQ
6NQ
A
0 1 2 3 4 5 10 20 30 40 50
% w/w H_3PO_4
R_F
1,0
0,8
0,6
0,4
0,2
56BQ
34BA
2PQ
8MQ
78BQ
6NQ
A
0 1 2 3 4 5 10 20 30 40 50
% w/w H_3PO_4

Ryc. 3, 4



Rys. 5. Jak na ryc. 1; rozpuszczalnik rozwijający: n-pentanol
As in Fig. 1. Developing solvent: n-pentanol

especially when there is a marked contribution of partition by the ion pair mechanism.

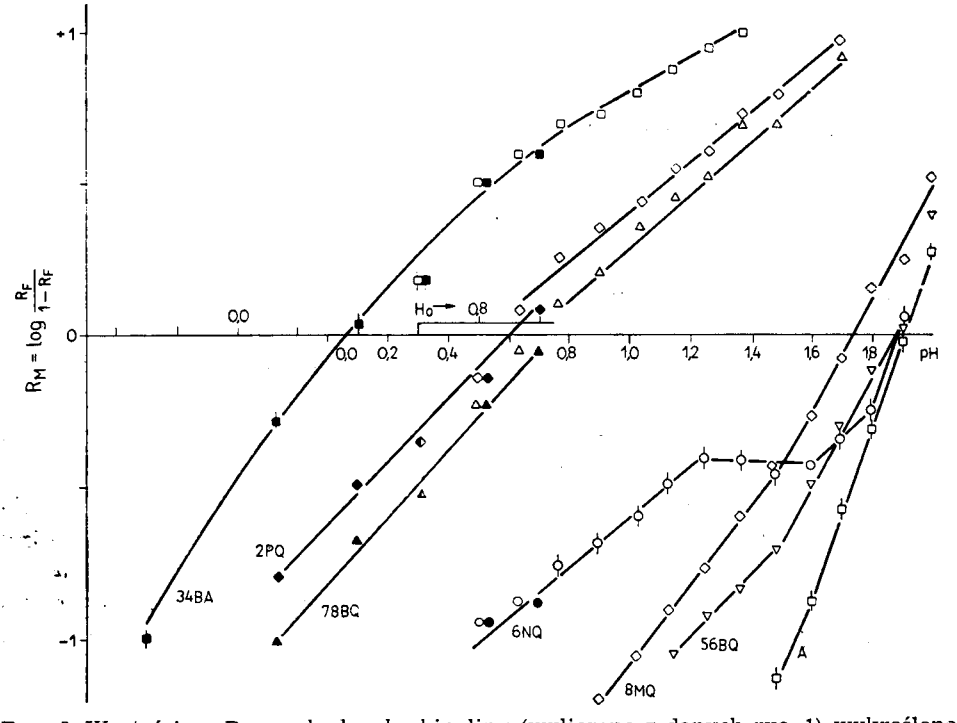
In the first series of diagrams (Figs. 1—5) the experimental data are presented as $R_F = f$ (concentration) plots, the concentration of phosphoric acid being expresed as % w/w in view of the more practical aspect of the plots (optimization of paper chromatographic systems). It can be seen that the solutes are strongly extracted from pure water ($R_F = 1$) and by varying the concentration of phosphoric acid it is possible to secure suitable distribution of the spots along the chromatogram; the optimal concentration of H_3PO_4 is different for various solvents depending on their extraction strength. For sufficiently high concentrations the R_F values of all solutes decrease to zero which indicates that none of the solutes investigated is extracted by the ion pair mechanism, with the

Rys. 3. Jak na ryc. 1; rozpuszczalnik rozwijający: trójchloroetylen
Rys. 4. Jak na ryc. 1; rozpuszczalnik rozwijający: chloroform
As in Fig. 1. Developing solvent: trichloroethylene
As in Fig. 1. Developing solvent: chloroform

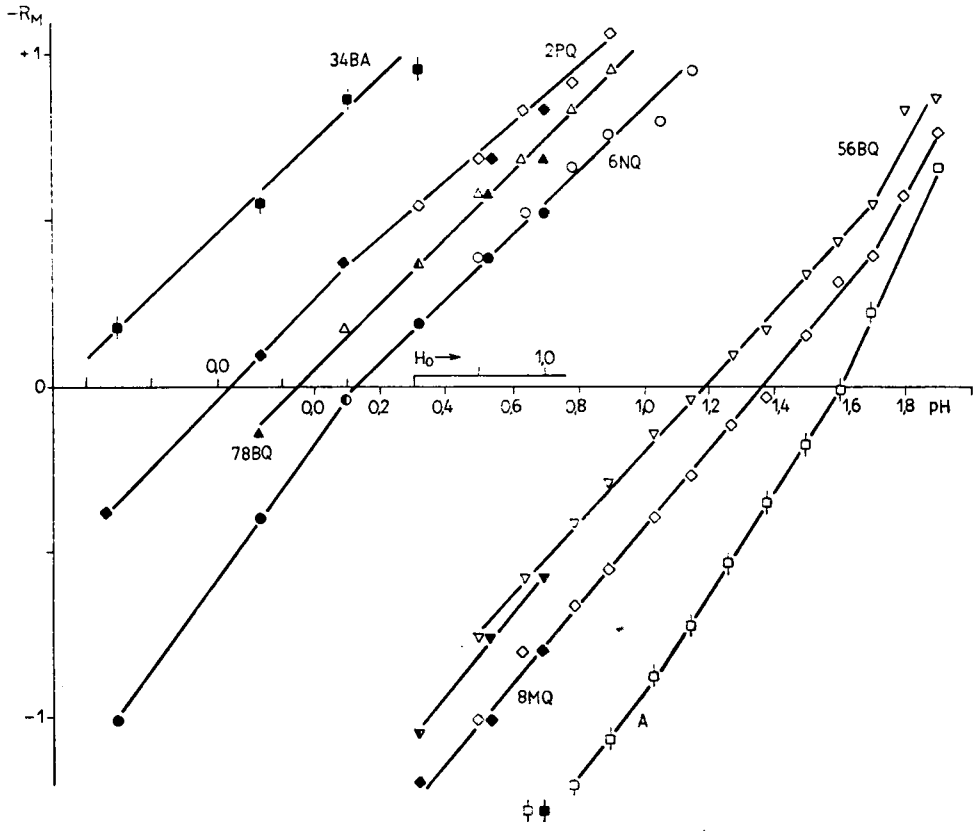
exception of the pentanol systems, where none of the solutes remains on the start line, and even an increase of R_F values is observed for most solutes at higher concentrations by phosphoric acid, indicating extraction of ion pairs.

The sequence of extraction strength of the solvents investigated is in accordance with that observed for quinoline bases chromatographed in buffered systems (10): cyclohexane < pentanol < benzene ≈ trichloroethylene < chloroform. However, at higher concentrations of phosphoric acid, pentanol is the best extractant due to its ability to extract ion pairs.

The effect of the molecular structure of the bases is also typical: it can be considered in terms of the molecular volume and the pK_A value, which influence the partition coefficient of unionized base and the tendency to ionization respectively. The strongest bases: acridine (pK_A = 5.6) and 5.6 benzoquinoline (5.15) have lowest R_F values. Also 8-methylquinoline (4.60) is strongly retarded because of its lower molecular volume. The remaining solutes are more lipophilic in view of their lower pK_A



Ryc. 6. Wartości — R_M pochodnych chinoliny (wyliczone z danych ryc. 1) wykreślone jako funkcja kwasowości fazy wodnej. Rozpuszczalnik rozwijający — cykloheksan
—R_M values of quinoline derivatives plotted against acidity of the aqueous stationary phase from data of Fig. 1. Mobile phase: cyclohexane



Rys. 7. Jak na ryc. 6; rozpuszczalnik rozwijający: benzen (rys. 2)
As in Fig. 6. Mobile phase: benzene (Fig. 2)

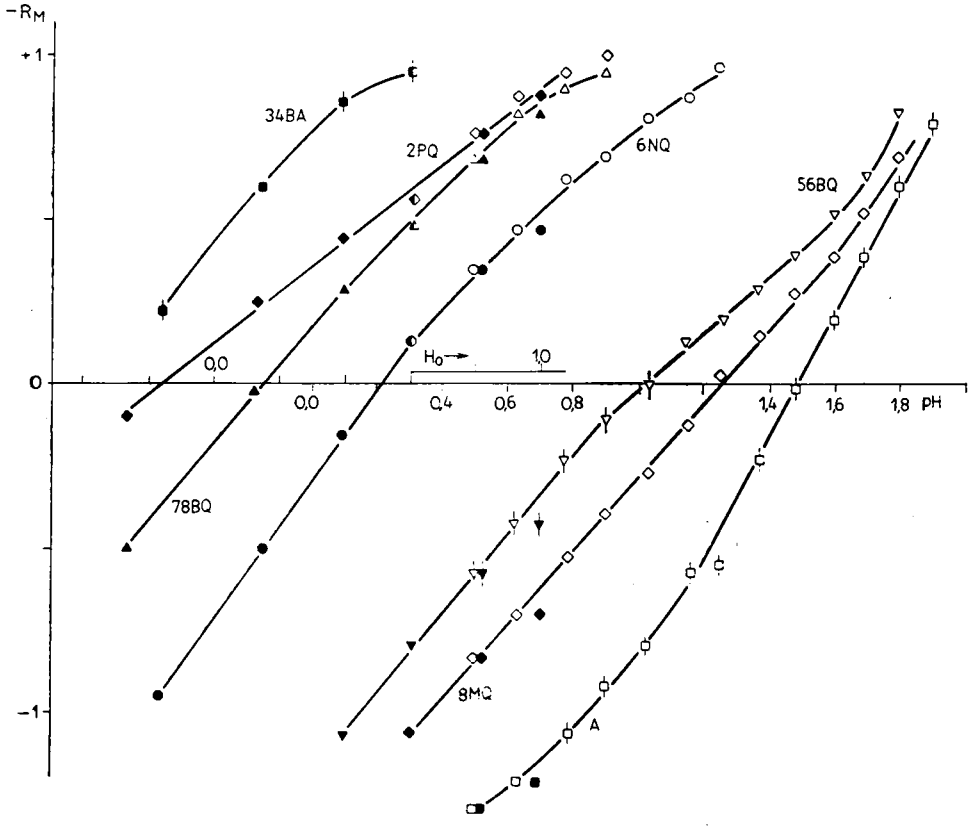
values and/or larger molecules (cf. the isomer of acridine — 7.8 benzoquinoline (4.21) with sterically hindered nitrogen atom, and its homologue — 3.4 benzacridine (4.30). Changed sequence of compounds is observed only for the cyclohexane system, presumably due to stronger adsorption on the liquid-liquid interface.

In most systems acridine formed elongated spots; the spots of the remaining solutes were mostly well defined except for the systems n-pentanol — concentrated solutions of H_3PO_4. Tailing tendency is represented in the plots by vertical lines.

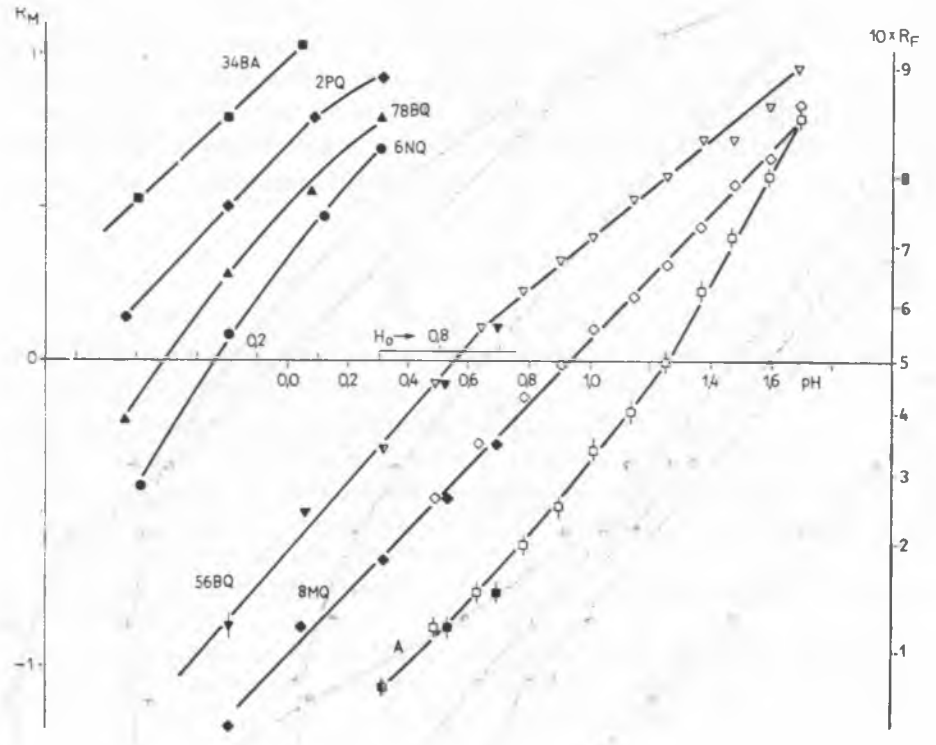
To elucidate the partition mechanism involved, the chromatographic data have also been plotted (Figs. 6—10) in R_M — acidity plots. For dilute solutions of phosphoric acid, the acidity is expressed by the pH scale, the pH values being determined from the actual concentration using a concentration — pH calibration line; the pH values of a series of so-

lutions of H_3PO_4 was determined using a glass electrode and a Ridan pH-meter. For more concentrated solutions of H_3PO_4, Hammett's acidity scale was used, the H_0 values being determined from a H_0 — % H_3PO_4 calibration line (2). The two scales, pH and H_0, partially overlap for moderately concentrated solutions; the transistion point on the plots corresponds to 12.5% H_3PO_4 (pH = 0.3 and H_0 = 0.6). Since the two scales in the common region are not strictly parallel, the R_M values plotted against pH are marked by hollow points, and those plotted against H_0 — by filled points; for each solvent in the transition region there are two double sets of R_M values: for pH = 0.5 (H_0 = 0.84) and pH = 0.63 (H_0 = = 1.0).

It can be seen that the transition from R_M vs. pH to R_M vs. H_0 relationships is quite smooth in the plots, especially if the H_0 values above 0.6 are neglected. The lines are straight or slightly curved — especially at higher $R_M$values where gradient effects are more likely to occur; in



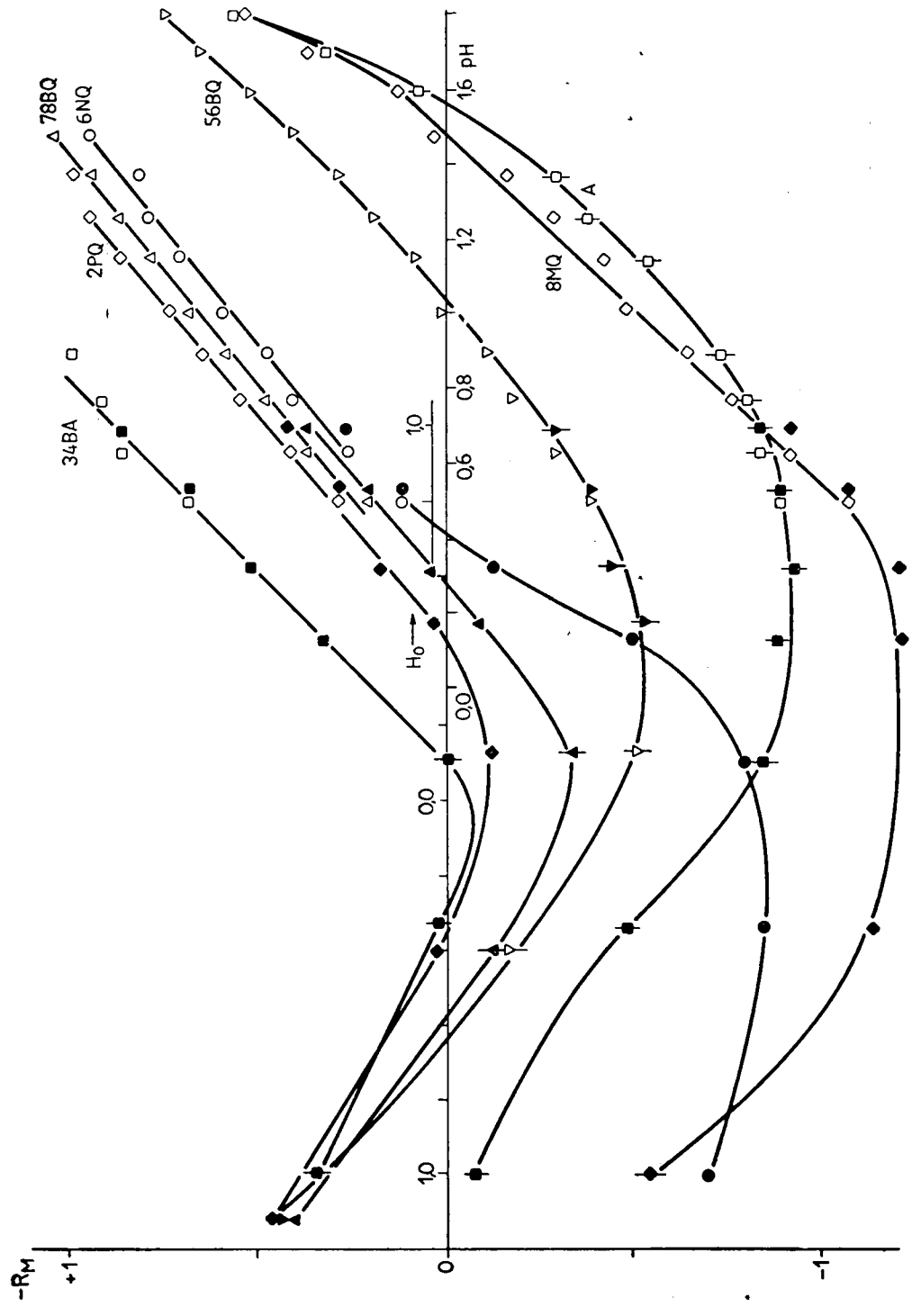
Rys. 8. Jak na ryc. 6; rozpuszczalnik rozwijający: trójchloroetylen (ryc. 3)
As in Fig. 6. Mobile phase: trichloroethylene (Fig. 3)



Ryc. 9. Jak na ryc. 6; rozpuszczalnik rozwijający: chloroform (ryc. 4)
As in Fig. 6. Mobile phase: chloroform (Fig. 4)

accordance with theoretical considerations assuming simple effect of ionization equilibria (see ref. (11) and literature cited therein), the slopes of most lines are close to unity, except for acridine whose R_M values are less accurate in view of tailing tendency. Similar behaviour is observed also for dilute solutions of H_3PO_4 in the pentanol systems, indicating that phosphoric acid controls the partition of organic bases mostly by its effect on the ionization equilibria in wide concentration ranges. However, for pentanol systems, increasing concentration of ion pair partition is already observed at moderately concentrated solutions of H_3PO_4; this is manifested by the appearence of minimums on the $R_M = f(H_0)$ plot (Fig. 10). The minimums occur as a rule in the range $0.0 < H_0 < 1.0$, but their position depends on the molecular structure of the solute. The minimum is less strongly pronounced for 6-nitroquinoline presumably due to its low pK_A value (cf. ref. (4).

The experimental results indicate that solutions of orthophosphoric acid can be used to control the partition of organic bases in liquid-liquid systems. For less polar solvents, the behaviour of phosphoric acid is re-


78BQ
6NQ
56BQ
2PQ
34BA
8MQ
A
pH
1,6
1,2
0,8
0,6
1,0
0,0
0,0
1,0
H_0
$-R_M$
+1
0
-1

gular in wide acidity ranges covering both the conventional pH range and its extension — Hammett's acidity scale. In view of the limited accuracy of paper chromatographic data, the exact partition mechanism and some divergencies from the theoretical relationships could be elucidated by static partition experiments choosing the suitable solvent systems on the basis of the chromatographic results.

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РЕЗЮМЕ

Определены зависимости хроматографических параметров R_F и R_W от концентрации фосфорной кислоты в стационарной водной фазе, применяя циклогексан, бензол, трихлорэтилен, хлороформ и н-пентанол-1 в качестве проявляющего растворителя. Было найдено, что экстракция ($-R_M = \log D + \text{const.}$) линеарно уменьшается с ростом кислотности водной фазы, выраженной шкалой pH для разбавленных растворов H_3PO_4 и функцией Гамметта H_0 для более концентрированных растворов H_3PO_4. Это указывает на то, что роль фосфорной кислоты в распределении сводится прежде всего к регуляции степени ионизации исследованных оснований — производных хинолина. Только для н-пентанола был обнаружен вторичный рост экстракции для высших концентраций H_3PO_4, что указывает на растущее участие распределения ионных пар.

Rys. 10. Jak na ryc. 6; rozpuszczalnik rozwijający: n-pentanol (ryc. 5)
As in Fig. 6. Mobile phase: n-pentanol (Fig. 5)

STRESZCZENIE

Wyznaczono zależności parametrów chromatograficznych, R_F i R_M od stężenia kwasu fosforowego w stacjonarnej fazie wodnej, stosując cykloheksan, benzen, trójchloroetylen, chloroform i n-pentanol-1 jako fazę ruchomą. Stwierdzono liniowy spadek ekstrakcji ($-R_M = \log D + \text{const.}$) ze wzrostem kwasowości fazy wodnej wyrażonej jako pH dla niższych stężeń i funkcją Hammetta dla bardziej stężonych roztworów H_3PO_4. Wskazuje to na wpływ kwasu fosforowego na podział głównie przez regulację jonizacji badanych zasad — pochodnych chinoliny. Jedynie dla n-pentanolu stwierdzono ponowny wzrost ekstrakcji przy wyższych stężeniach H_3PO_4, wskazujący na rosnący udział podziału par jonowych.