

CHROMATOGRAPHY OF ORGANIC ELECTROLYTES ON PAPER IMPREGNATED WITH LIQUID ION EXCHANGERS

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In recent years the increasing use of certain water-immiscible solvents which are called "liquid ion exchangers", in view of their mechanism of extraction of ions from aqueous solutions, has been observed. As an example of liquid anionites, some high molecular weight amines are cited¹, while for the liquid cationites di-(2-ethylhexyl) orthophosphoric acid (HDEHP) is given as an example. Liquid ion exchangers combine the advantages of solid ion exchangers with the feasibility of equilibration with aqueous solutions, inherent to liquid solvents. Therefore, they are employed both in batch extraction and in chromatographic systems; reviews on the application of liquid ion exchangers have been recently published by CERRAI^{2,3} and COLEMAN *et al.*⁴.

It seems that papers impregnated with liquid ion exchangers can play a role similar to ion-exchange celluloses, whose wide application, especially in the analysis of proteins and peptides, has been recently reviewed by DAVIDOVA AND RACHINSKI⁵. It is also likely that impregnation of the paper with a liquid ion exchanger may be a simpler and more reproducible procedure than the preparation of papers which incorporate particles of solid ion exchangers.

Some recent papers which describe the use of HDEHP in bulk partition and chromatography of inorganic substances (paper, column, as well as TLC) are refs. 6-12. Extensive data on the chromatography of heterocyclic bases (also on cationite celluloses) have been reported by LULY AND SAKODYNSKY¹³.

In the present communication, the chromatographic behaviour of some alkaloïds and heterocyclic bases on paper impregnated with the liquid cationite, HDEHP, and developed with aqueous solutions of citric acid of varying acidity is reported.

EXPERIMENTAL

Whatman No. 1 paper strips, 6.5 × 23.5 cm, were impregnated by immersion in a 0.1 *M* benzene solution of HDEHP and blotting between two sheets of filter paper. The impregnation was repeated once more; after evaporation of benzene, the paper contained *ca.* 20-30 mg of HDEHP per g of dry paper. The distance of development (by the descending method, in tanks 5 × 8 × 22 cm) was 16 cm. The spots were detected with Dragendorff's reagent.

RESULTS

The experimental results are presented in Figs. 1-3 as R_F - pH relationships

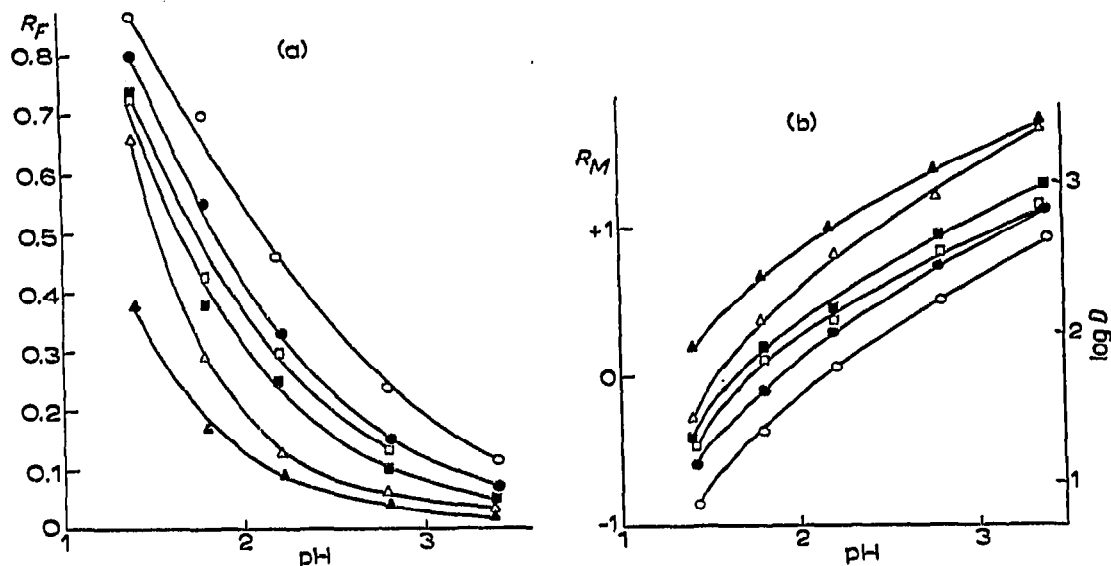


Fig. 1. R_F vs. pH plots (a) and corresponding R_M vs. pH relationships (b) of some heterocyclic bases. Parallel to R_M axis, calculated values of $\log D$ are given. The solutes are: (o) quinoline and isoquinoline; (●) 8-hydroxyquinoline; (□) 6-methylquinoline; (■) 2,6-dimethylquinoline; (△) 5-hydroxyquinoline; (▲) acridine.

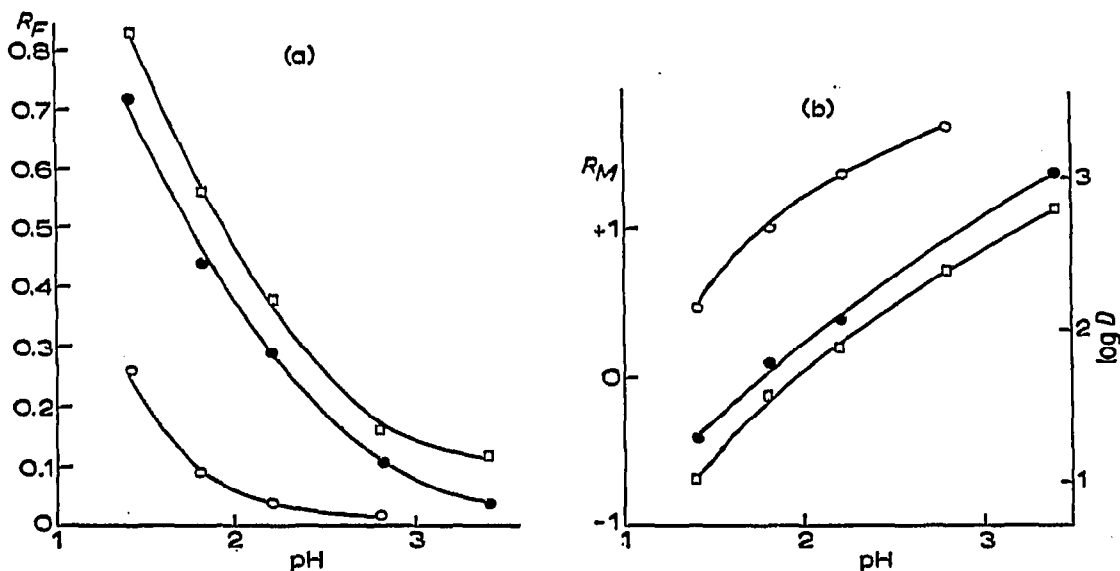


Fig. 2. R_F vs. pH plots (a) and R_M vs. pH plots (b) of some alkaloids: (O) yohimbine; (●) strychnine; (□) brucine.

and corresponding R_M - pH plots, since the R_F coefficient gives direct information about the movement of zones on the paper and on the separations achieved, while the R_M value usually gives simpler relationships with respect to the molecular structure of the solute, temperature¹⁴, phase composition and pH (e.g. ref. 15) etc. Since the R_M values were calculated according to Bate-Smith and Westall's definition ($R_M = \log (1/R_F - 1)$) they theoretically differ from the logarithm of the distribution coefficient

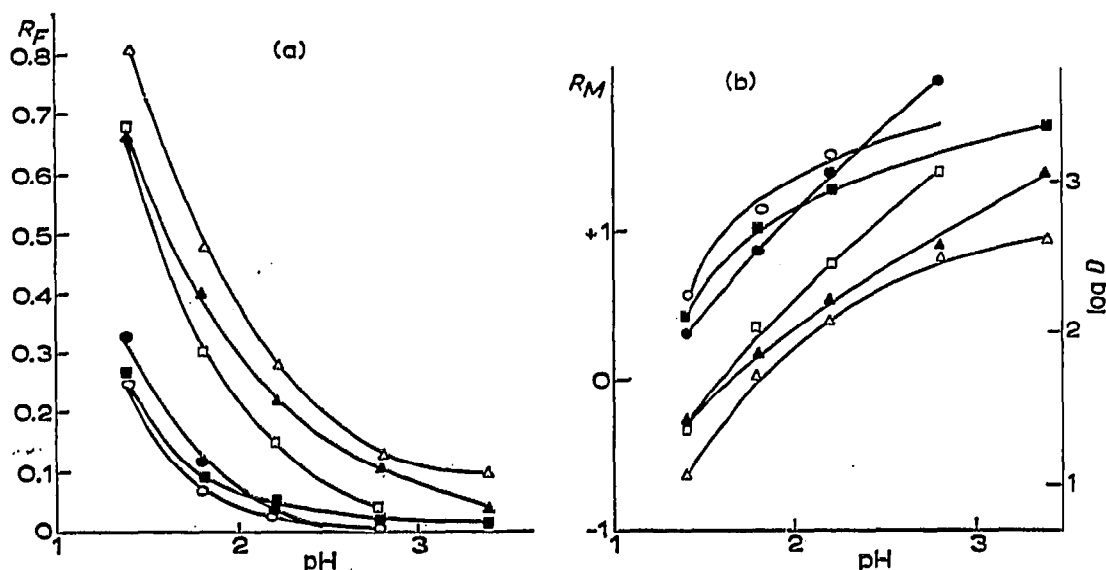


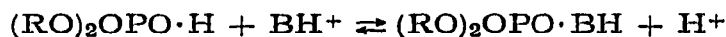
Fig. 3. R_F vs. pH plots (a) and R_M vs. pH plots (b) of some alkaloids: (●) berberine, (○) dicentrine; (■) corydaline; (□) protopine; (▲) narcotine; (△) narceine.

D of the solute in the chromatographic system by a constant equal to the logarithm of the ratio of cross-sectional areas (or volumes) of the two phases:

$$\log \frac{c_{\text{HDEHP}}}{c_w} = \log D = R_M + \log \frac{v_w}{v_{\text{HDEHP}}} \quad (1)$$

By weighing the dry, impregnated and developed paper strips it was found that the volume ratio v_w/v_{HDEHP} was approximately equal to 50. Therefore, parallel axes of $\log D$ have been drawn, assuming the validity of eqn. (1), on the $R_M - \text{pH}$ plots, that is, assuming an idealized partition model of the chromatographic process. The values of $\log D$ obtained in this way are, however, very approximate in view of the low accuracy of determination of the volume ratio and superimposition of sorption effects by the cellulose itself (see below).

It can be seen from the plots that the R_M vs. pH relationships (and thus the $\log D$ vs. pH also) are almost linear, the partition being shifted in favour of the aqueous phase by increased acidity; the slope of the line is close to unity. This is probably due to ion exchange equilibria of the type:



so that the equilibrium constant is approximately given by the equation (substituting activities by concentrations):

$$K = \frac{[(\text{RO})_2\text{OPO}\cdot\text{BH}] [\text{H}^+]}{[(\text{RO})_2\text{OPO}\cdot\text{H}] [\text{BH}^+]} \quad (2)$$

Therefore:

$$D_i = \frac{[(\text{RO})_2\text{OPO}\cdot\text{BH}]}{[\text{BH}^+]} = K \frac{[(\text{RO})_2\text{OPO}\cdot\text{H}]}{[\text{H}^+]} \quad (3)$$

$$\log D_i = \log K + \log [(\text{RO})_2\text{OPO}\cdot\text{H}] + \text{pH} \quad (4)$$

The calculation of the amount of solute in relation to the amount of ion ex-

TABLE II

Substance	pH	HDEHP chromatograms			Reference chromatograms			Corrected partition parameters	
		R_F	$\alpha = \frac{1 - R_F}{R_F}$	$R_M = \log \alpha$	R_F°	$\alpha_a = \frac{1 - R_F^\circ}{R_F^\circ}$	$R_M^\circ = \log \alpha_a$	$\alpha_i = \alpha - \alpha_a$	$R_{Mi} = \log \alpha_i$
Brucine	1.4	0.83	0.205	-0.688	0.90	0.111	-0.955	0.094	-1.028
	1.8	0.56	0.785	-0.105	0.75	0.333	-0.477	0.452	-0.345
	2.8	0.16	5.25	0.720	0.64	0.562	-0.250	4.69	0.671
	3.4	0.07	13.28	1.123	0.50	1.00	0.000	12.3	1.090
Acridine	1.4	0.38	1.63	0.212	0.90	0.111	-0.955	1.52	0.182
	1.8	0.17	4.88	0.688	0.85	0.176	-0.755	4.40	0.644
	2.2	0.09	10.1	1.004	0.70	0.428	-0.369	9.68	0.986
	3.4	0.03	32.3	1.509	0.47	1.127	0.052	31.2	1.494
Quinoline	1.4	0.87	0.149	-0.826	0.92	0.087	-1.061	0.062	-1.207
	1.8	0.70	0.428	-0.368	0.90	0.111	-0.954	0.317	-0.499
	2.2	0.46	1.17	0.070	0.84	0.190	-0.720	0.98	-0.009
	3.4	0.11	8.0	0.908	0.60	0.666	-0.176	7.33	0.865
8-Hydroxy-quinoline	1.4	0.80	0.25	-0.602	0.92	0.087	-1.061	0.177	-0.752
	1.8	0.55	0.818	-0.087	0.88	0.136	-0.865	0.682	-0.166
	2.2	0.33	2.33	0.308	0.75	0.333	-0.477	2.00	0.299
	3.4	0.07	13.3	1.123	0.46	1.17	0.070	12.1	1.083

electrolytes, *cf.* also refs. 2 and 3). Like solid sorbents, liquid ion exchangers can be regenerated by stripping with an acid solution.

As a means of removal of ballast substances, extraction with a liquid ion exchanger and stripping with an acid solution is sometimes found to be more effective than the use of, *e.g.*, chloroform as an extractant of alkaloids, antibiotics etc., since in the latter system some useful hydrophilic electrolytes, less extractable by chloroform, may be lost.

However, in determinations of bulk distribution coefficients from paper chromatographic data, the sorption of solutes by cellulose may introduce a significant error. In order to estimate this contribution, reference runs were carried out under analogous conditions, using paper strips not impregnated with HDEHP. The contributions of the two partition mechanisms could then be estimated by the following reasoning (*cf.* model, Fig. 4).

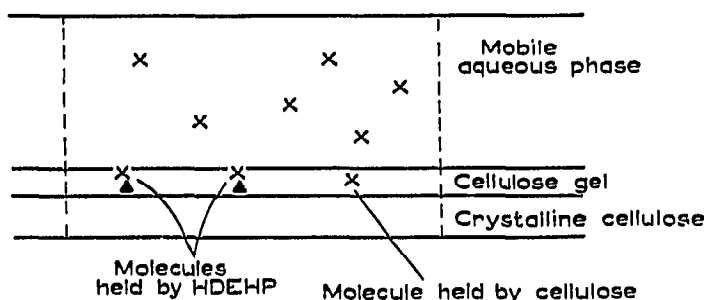


Fig. 4. Idealized model of mixed partition mechanism (ion exchange + sorption by cellulose). In the illustration, $\alpha_i = 2/6$; $\alpha_a = 1/6$; $\alpha = \alpha_i + \alpha_a = 3/6$.

Let α_i and α_a be the distribution ratios due to ion exchange and sorption by cellulose; α = the total distribution ratio, determining the zone migration rate ($\alpha = \alpha_i + \alpha_a$). Thus:

$$R_F = \frac{1}{1 + \alpha}; R_M = \log \frac{1 - R_F}{R_F} = \log \alpha$$

and for reference chromatograms (paper without HDEHP, indices "o"):

$$R_F^0 = \frac{1}{1 + \alpha_a}; R_M^0 = \log \frac{1 - R_F^0}{R_F^0} = \log \alpha_a$$

Therefore, the R_{M_i} value for pure ion exchange mechanism:

$$R_{M_i} = \log \alpha_i = \log (\alpha - \alpha_a) = \log \left(\frac{1 - R_F}{R_F} - \frac{1 - R_F^0}{R_F^0} \right)$$

It is assumed here that the sorption isotherm is linear, *i.e.*, that α_a is independent of concentration; otherwise, the conditions in the two series of experiments would not be comparable, as in the experiments with HDEHP impregnated paper the concentration of molecules available for sorption by cellulose is lower. The assumption does not seem to be unreasonable since the spots showed only a slight tailing tendency even in the case of reference chromatograms. It is also assumed that the sorption by the cellulose is the same in both series of experiments.

Some experimental data are presented in Table II. In Fig. 5 the observed and corrected values of R_M are plotted for the four solutes; it is seen that the sorption effect of cellulose, which tends to increase the R_M values (decrease the R_F coefficients) is noticeable only at low pH values, and for acridine is negligible.

The direct testing of the mechanism of the chromatographic process in liquid ion exchange systems, by comparison of batch distribution coefficients with those calculated from paper chromatographic data, will be the subject of a later investigation, employing another liquid cationite.

It is probable that liquid ion exchangers, employed so far mainly in the separation and isolation of inorganic substances, will also find an increasing application in the extraction of various important organic electrolytes, such as amino acids, alkaloids, antibiotics, etc.

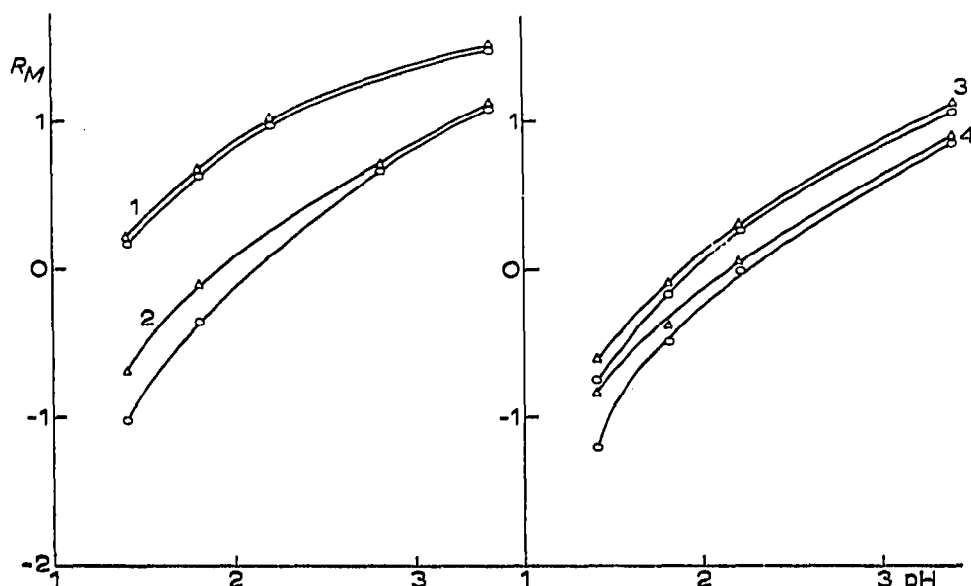


Fig. 5. Observed (Δ — Δ) and calculated (\circ — \circ) R_M values of (1) acridine, (2) brucine, (3) 8-hydroxyquinoline and (4) quinoline.

SUMMARY

R_F - pH relationships of some alkaloids and heterocyclic bases were determined using paper strips impregnated with a liquid ion exchanger. The R_M values and log distribution coefficients were, in most cases, almost linearly dependent on the pH of the mobile aqueous phase, the slope of the line being close to unity. The advantages of liquid ion exchange systems over the conventional liquid two-phase systems are discussed, the main advantage being the extension of the solutes that can be chromatographed.

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