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Comparison of Partition Chromatographic Parameters of Lipophilic Organic Electrolytes for Solvents of Various Donor–Acceptor Properties. III. Quinoline Bases in Systems of the Type Organic Solvent/Buffer Solution*

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Summary

Chromatographic parameters of several quinoline bases are compared for 20 water-immiscible solvents, using a method elaborated by Rohrschneider and Littlewood for gas-liquid partition chromatography. As reference solvents, *n*-heptane and chloroform were chosen so that characteristics of the remaining solvents with respect to their solvent power were obtained. The spectra of the quinolines, with 2-methylquinoline as standard solute, are approximately parallel, except for 8-hydroxyquinoline, which behaved in a more individual manner. This means that the partition coefficients of quinoline bases are generally in a constant proportion, and the selectivities are similar for all solvents studied, although some disturbances are also observed.

The experimental results are discussed from the viewpoint of the molecular structure of solutes and solvents and the molecular interactions involved.

In the systematization of chromatographic data and prediction of partition chromatographic behavior the additivity principle applied to liquid-liquid partition has been proved to be very useful. Bate-Smith and Westall (*1*) simplified greatly the application of the additivity principle by introducing the R_M coefficient, which is linearly

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* For Parts I and II, cf. Ref. (*10*).

dependent on the energy of transfer of the solute across the phase boundary and thus should be additive with respect to the constituent groups of the molecule [assuming certain simplification of the chromatographic process and excluding constitutive effects; cf. Marcinkiewicz et al. (2)].

Reviews on the subject have been recently published by Bush (*3*), Green and McHale (*4*), and Prochazka (*5*). A similar approach is often applied in gas-liquid partition chromatography, using the log of retention volume (corrected for the dead volume of the column) as a value analogous to R_M.

The purpose of the present work was to investigate a less frequently considered aspect of this approach—the comparison of partition coefficients in various solvent systems. In this respect the theoretical considerations in the field of GLC are much more advanced than those in liquid-liquid partition. Recently, the publications concerning the classification of stationary liquids have been reviewed by Rohrschneider (*6*), including a very interesting paper by Littlewood (*7*) on the comparison of chromatographic parameters for a number of stationary phases. Numerous examples of correlations of gas-chromatographic parameters in pairs of solvent systems are also known, in the form of $\log v_R - \log v_R$ plots; on the other hand, few attempts have been made to find such correlations for liquid-liquid partition data (*8,9*).

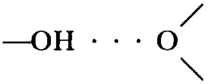
The solutes investigated in the present work belong to the class of "lipophilic" substances, i.e., those giving high partition coefficients in aqueous solvent systems, difficult to determine experimentally. In the first publications from this series (*10*), it was shown that partition parameters can be compared for solutes of this type when they are electrolytes, by determining their R_M–pH relationships and extrapolation to a chosen pH value. Although the absolute values of partition coefficients cannot usually be determined in this way (unless the ionization constants of the electrolytes are known accurately), the relative values are determinable, in relation to a chosen reference solvent. In terms of R_M values (*11*),

$$\Delta R_{Ms} = R_{M1w} - R_{M2w} = R_{M12} \tag{1}$$

where the indices *w*, 1, and 2 denote water and two organic solvents immiscible with water, respectively. The sense of this equation is that the difference of R_M values of a solute in two solvent systems, $1/w$ and $2/w$, is equal to the R_M value of the solute in a hypothetical nonaqueous system 1/2 (e.g., ether/chloroform); the latter R_M value is in turn simply related to the energy of transfer of the solute from solvent 1 to solvent 2 (under standard conditions), which is determined by the molecular structure of the solute and the solvents.

The last equation follows immediately from the analogous equation

$$k_{1w}:k_{2w} = c_1/c_w:c_2/c_w = c_1/c_2 = k_{1,2} \tag{2}$$

assuming that the ratio of volumes of the organic and aqueous phase is identical in the two chromatographic systems compared. For batch partition, a number of hypothetical partition coefficients for the system ethyl ether/chloroform have been calculated by Sandell (*12*), who has found that for solutes possesing hydroxyl groups (carboxylic acids, oximes, phenols, alcohols) the ratio $k_{\mathrm{eth}/w}:k_{\mathrm{chlf}/w}$ is above 10, owing to strong interactions with ether molecules,  $—\mathrm{OH}\cdots\mathrm{O}\langle$ and for remaining solutes—in the range 0.15 to 0.50. Thus comparisons of this type permit us, on the one hand, to systematize the experimental data and to predict partition parameters in new systems; on the other hand, they provide information concerning the molecular interactions and the molecular structure of solutes. Needless to say, these possibilities multiply when the partition parameters are compared for more than two solvent systems.

EXPERIMENTAL

To secure a constant ratio of volumes in the chromatographic system and a partition mechanism, the "moist buffered paper" technique was employed, the amount of the stationary buffer solution being controlled by weighing (0.5 ml/1 g of dry paper). The buffer solutions were prepared after McIlvaine (0.1 *M* citric acid + 0.2 *M* Na_2HPO_4); Whatman No. 4 paper strips (7 × 23.5 cm, cut at right angles to the machine direction) were used; the distance of development was 16 cm. The glass chromatographic tanks for descending development, 6 × 14 × 21 cm, were saturated with the vapors of the two phases. The quinoline bases were detected with Dragendorff's reagent. The experiments were carried out at room temperature (20 ± 1.0°C).

pH_i values below 2.2 were estimated by extrapolation of the R_F-pH plot, using a standard $R_F = f$/pH/templet (*13*), and thus are less accurate.

RESULTS AND DISCUSSION

In all cases regular sigmoid R_F vs. pH curves were obtained, in accordance with theoretical anticipation (*13–15*). Typical results obtained for cyclohexane are presented in Fig. 1. Almost all curves, even for nonpolar solvents, are high so that their pH_i values (pH corresponding to the inflexion point at $R_F = 0.5$) are given with sufficient accuracy by the simpler form of equation (*15*):

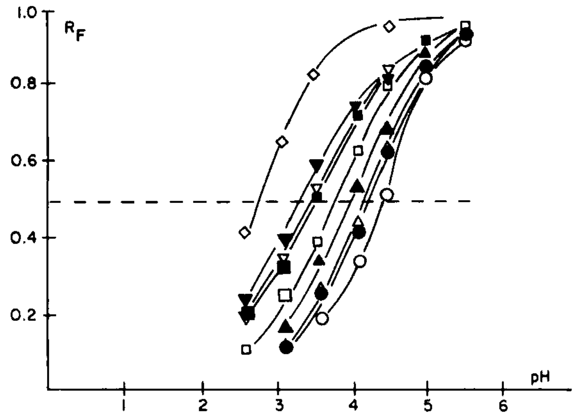


FIG. 1. R_F–pH curves of quinoline bases. Mobile phase, cyclohexane. The solutes are: ○, isoquinoline; ●, 2-methylquinoline; △, 3-methylisoquinoline; ▲, 2,6-dimethylquinoline; □, quinoline; ■, 6-methylquinoline; ▽, 8-hydroxyquinoline; ▼, acridine; ◇, 8-methylquinoline.

$$pH_i = pK_A - \log(kr + 1) \doteq pK_A - \log kr = pK_A + R_M^0 \qquad (3)$$

where K_A is the acidic ionization constant of the base, k its partition coefficient at suppressed ionization, and r the ratio of volumes of the phases ($r = v_{org}/v_w$). Since pK_A may be assumed constant for a given solute, the pH_i vs. solvent plot of solute is equivalent to its R_M^0 vs. solvent diagram, with the origin of the ordinate axis shifted by pK_A of the solute (this is not essential, since the primary purpose is to determine the relative values of partition parameters). R_M^0, i.e., the R_M value at suppressed ionization, is defined here after

Bate-Smith and Westall (*1*): ($R_M = \log (1 - R_F)/R_F = -\log Dr$; $R_M^0 = -\log kr$.

The experimentally determined pH_i values are given in Table 1; in Table 2 the values of $-R_M^0 = \log kr$ are given, calculated from Eq. (3) and pK_A values reported by Albert (*16*). Since in the experimental technique used the volume ratio r is equal to 2.0 to 2.5 (*14*),

TABLE 1

pH_i Values Determined from R_F–pH Relationships

	Quinoline (4.95)[a]	Isoquinoline (5.40)	2-Methylquinoline (5.40[b])	6-Methylquinoline (4.90[b])	8-Methylquinoline (4.60[b])	2,6-Dimethylquinoline (5.45[b])	3-Methylisoquinoline	8-Hydroxyquinoline (5.15)	Acridine (5.60)
Heptane	3.9	4.6	4.4	3.7	2.9	4.05	4.35	3.65	3.55
Cyclohexane	3.85	4.45	4.3	3.65	2.8	4.05	4.3	3.6	3.4
Carbon tetrachloride	3.15	3.7	3.65	2.85	2.25	3.4	3.6	2.9	2.5
Decalin	3.6	4.3	4.15	3.4	2.65	3.9	4.1	3.35	3.05
Benzene	2.9	3.55	3.5	2.65	2.1	3.25	3.45	2.75	2.25
Xylene	3.05	3.65	3.6	2.85	2.2	3.35	3.55	2.9	2.55
Toluene	2.9	3.5	3.45	2.65	2.1	3.25	3.4	2.7	2.35
Ethylbenzene	2.75	3.25	3.2	2.5	2.0	2.95	3.15	2.8	2.05
Tetralin	2.9	3.5	3.4	2.7	2.1	3.1	3.35	2.85	2.25
Chlorobenzene	2.85	3.4	3.35	2.6	2.0	3.05	3.3	2.5	2.15
Trichloroethylene	2.7	3.3	3.25	2.45	2.0	2.95	3.2	2.65	2.1
Chloroform	2.15	2.6	2.6	1.9	1.65	2.35	2.55	2.25	1.7
1,2,3-Trichloropropane	2.5	3.1	3.15	2.3	2.0	2.9	3.1	2.5	2.0
Diisoamyl ether	3.45	4.25	4.1	3.1	2.55	3.6	4.1	3.35	2.9
Diethyl ether	3.05	3.8	3.7	2.9	2.3	3.5	3.75	2.75	2.6
Methyl isobutyl ketone	2.9	3.45	3.5	2.75	2.15	3.3	3.45	2.55	2.25
Benzyl methyl ketone	2.6	3.15	3.2	2.45	2.1	3.05	3.2	2.35	2.1
Hexanol	2.6	3.05	3.15	2.4	2.2	2.9	3.0	2.9	2.15
Octanol	2.75	3.2	3.25	2.5	2.25	3.0	3.15	2.9	2.2
Benzyl alcohol	1.95	2.3	2.35	1.8	1:75	2.0	2.1	2.3	1.6

[a] pK_A in parentheses refer to 20°C.

[b] Values to 25°C.

log *k* values can also be estimated from Table 2 by subtraction of ca. 0.3 to 0.4 from the values given.

The reliability of the data presented in Table 2 depends also on the accuracy of pK_A values, which, as Albert points out, is not very high; with this exception, the following conclusions can be made.

1. The partition coefficients of un-ionized bases depend to a marked extent on their molecular size; the log *kr* values increase in most cases in the following sequence:

quinoline, isoquinoline, 2-methylquinoline < 6-methylquinoline, 2,6-dimethylquinoline < 8-hydroxyquinoline < 8-methylquinoline < acridine

TABLE 2

Log $kr = -R_M^0$ Values Calculated from Eq. (3) and Data of Table 1

	Quinoline	Isoquinoline	2-Methylquinoline	6-Methylquinoline	8-Methylquinoline	2,6-Dimethylquinoline	8-Hydroxyquinoline	Acridine
Heptane	1.0	0.7	0.95	1.15	1.7	1.4	1.5	2.05
Cyclohexane	1.05	0.9	1.05	1.25	1.8	1.4	1.55	2.2
Carbon tetrachloride	1.8	1.7	1.75	2.05	2.35	2.05	2.25	3.1
Decalin	1.35	1.05	1.25	1.50	1.95	1.55	1.8	2.55
Benzene	2.05	1.85	1.9	2.25	2.5	2.2	2.4	3.35
Xylene	1.9	1.75	1.8	2.05	2.4	2.1	2.25	3.05
Toluene	2.05	1.9	1.95	2.25	2.5	2.2	2.45	3.25
Ethylbenzene	2.2	2.15	2.2	2.40	2.6	2.5	2.35	3.55
Tetralin	2.05	1.9	2.0	2.20	2.5	2.35	2.3	3.35
Chlorobenzene	2.10	2.0	2.05	2.30	2.6	2.4	2.65	3.45
Trichloroethylene	2.25	2.1	2.15	2.45	2.6	2.5	2.5	3.5
Chloroform	2.8	2.8	2.8	3.0	2.95	3.1	2.9	3.9
1,2,3-Trichloropropane	2.45	2.3	2.25	2.6	2.6	2.55	2.65	3.6
Diisoamyl ether	1.5	1.15	1.3	1.8	2.05	1.85	1.8	2.7
Diethyl ether	1.9	1.6	1.7	2.0	2.30	1.95	2.4	3.0
Methyl isobutyl ketone	2.05	1.95	1.9	2.15	2.45	2.15	2.6	3.35
Benzyl methyl ketone	2.35	2.25	2.2	2.45	2.5	2.4	2.8	3.5
Hexanol	2.35	2.35	2.25	2.50	2.40	2.55	2.25	3.45
Octanol	2.20	2.2	2.15	2.40	2.35	2.45	2.25	3.40
Benzyl alcohol	3.0	3.10	3.05	3.10	2.85	3.45	2.85	4.0

It is striking that substitution of a methyl group in position 2 does not seem to increase the partition coefficient. On the other hand, a methyl group in position 8 causes a significant increase of log k, probably due to steric effects, i.e., screening of the nitrogen atom and thus reducing hydrogen bonding with water molecules (*17*).

2. Although 8-hydroxyquinoline possesses an additional H-bonding center (the hydroxyl group), its partition coefficients are higher than those of unsubstituted quinolines. This is probably due to the formation of an intramolecular hydrogen bond so that the molecule becomes less hydrophilic. The relatively high partition coefficients of 8-hydroxyquinoline are consistent with the low solubility of this compound in water, as compared to the solubilities of quinoline and isoquinoline. The position of 8-hydroxyquinoline in the sequence is changed in the case of B-class solvents, for which the partition coefficient of 8-hydroxyquinoline is even higher than that of 8-methylquinoline. This is probably due to the breaking of the intramolecular OH · · · N bond in the solvent phase with resulting higher solvent power.

To test the validity of Eq. (3), which assumes that the migration rate of solute is determined by its static (batch) partition coefficient k, the chromatographic data obtained for cyclohexane were compared with those reported by Golumbic and Orchin (*17*) for batch partition, although the two series of experiments are not strictly comparable in view of the difference in the temperature of the experiments (20.0 and 25.0°C, respectively). It was found that the sequence and relative values of pH_i and log D are in a very good agreement (D extraction coefficient, or observed partition coefficient, i.e., ratio of total concentrations of the electrolyte at a given pH of the aqueous phase). This is illustrated in Fig. 2, where a parallel axis is added with log D values of quinolines for $\mathrm{pH} = 3.72$.

Therefore, chromatographic data in the system studied seem to give quite reliable information concerning batch partition coefficients. On the other hand, it seems more reliable to calculate partition coefficients from $\mathrm{p}K_A$ values which are determinable with greater accuracy, especially when partition coefficients are high [in the case of quinolines, $k = 13 \div 164$ (*17*)]; that is why we have used in Table 2 $\mathrm{p}K_A$ values reported in the literature rather than those calculated by Golumbic and Orchin. Needless to say, the use of numerical values of $\mathrm{p}K_A$ given by these authors would result in log k values very similar to those reported in their work, with somewhat changed sequence and interpretation of results.

The data of Table 1 are also presented in the form of pH$_i$–solvent "spectra" (Figs. 2 to 5), grouping the solvents after their donor-acceptor properties [N, A, B, AB; cf. Pimentel and McClellan, (*18*)] and arranging them within the groups on the abscissa axes so that a linear spectrum is obtained for a reference solute for which 2-methylquinoline was chosen. As the extreme points of the "scale of interactions" between the quinoline bases and organic phases, two solvents were chosen: heptane = 0 (no interactions, lowest solvent power) and chloroform = 100 (strong interactions —H · · · N). In this way four pH$_i$ (R_M)–solvent spectra are obtained, analogous to retention spectra reported by Rohrschneider (*19*) and Littlewood (*7*) for gas chromatography. The position of the solvent on the scale thus characterizes the solvent power of the organic phase relative to the reference solute; however, since the spectra of most quinoline bases are approximately parallel, it is seen that, owing to analogy of molecular structure, the characterization refers in practice

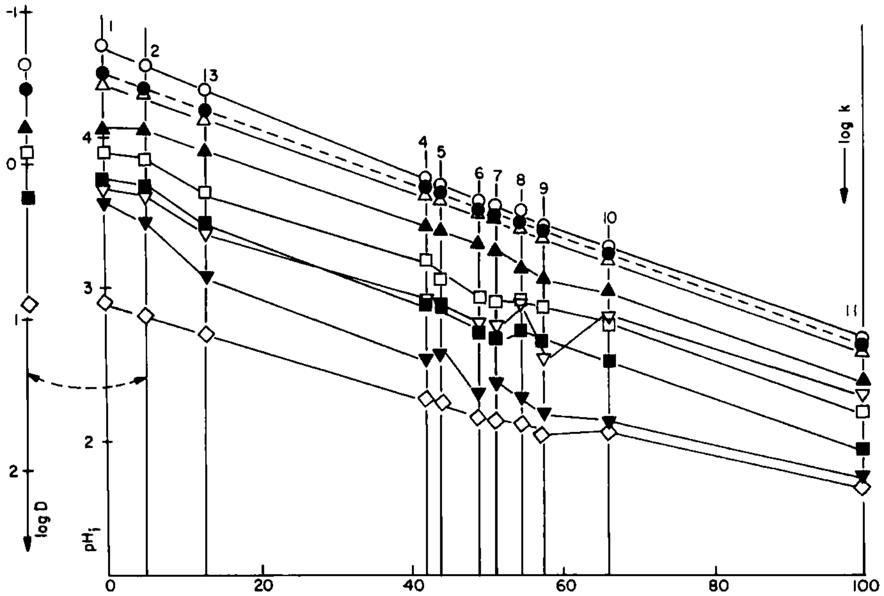


FIG. 2. pH$_i$–solvent spectra of quinoline bases. Solvents of class N: 1, heptane; 2, cyclohexane; 3, decalin; 4, carbon tetrachloride; 5, *m*-xylene; 6, benzene; 7, toluene; 8, tetralin, 9, chlorobenzene; 10, ethylbenzene. Parallel left-side ordinate: log *D* values (batch partition) reported by Golumbic and Orchin (*17*) for the system cyclohexane/buffer solution.

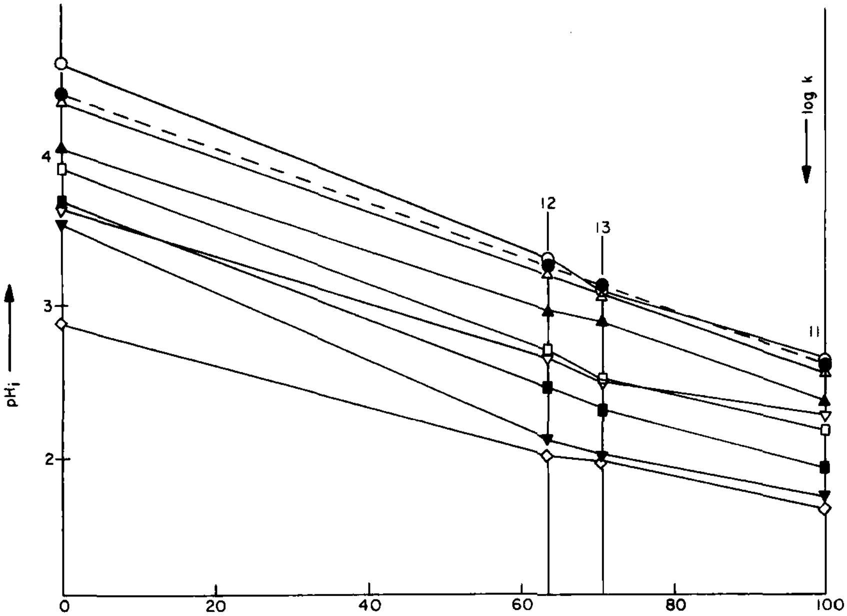


FIG. 3. Solvents of class A: 11, chloroform; 12, trichloroethylene; 13, 1,2,3-trichloropropane.

not only to quinoline, but also to all solutes studied (except 8-hydroxyquinoline for some solvents). Minor disturbances observed in the spectra may have been caused by experimental errors, chromatographic effects, or specific interactions. If R_F spectra were used, the parallelity could not have been observed *(10)*, since R_F is related to the energy of transfer in a more complex way.

The following general conclusions can be made from inspection of the experimental data.

Solvents of class N possess the lowest solvent power, in view of the absence of H-bonding in the organic phase. However, aromatic hydrocarbons are somewhat better extractants [owing to the presence of π bonds, aromatic hydrocarbons behave to some extent as electron donors, class B *(18)*]. Also typical B-class solvents (ethers, ketones, etc.) are mostly weak extractants in spite of their marked polarity, in view of the absence of H-bond formation in the organic phase (B + B mixture). For solvents of classes B and N, the main reason for the relatively high partition coefficients of quinolines in favor of the organic phase is the "squeezing" of the solute molecules from the aqueous phase due to the three-dimensional association of water. The squeezing effect is only partly compensated by hydration of the heterocyclic nitrogen, in view of the relatively large molecular size of quinoline bases.

On the other hand, the highest solvent power is exhibited by solvents of classes A and AB, since in these cases the extraction of solute is facilitated by hydrogen-bond formation in the organic phase (A + B, AB + B), so that a kind of "push-pull effect" results. It is striking that in some cases benzyl alcohol is an even stronger extractant than chloroform.

In view of the decisive role of H-bonding, the position of the solvent in the heptane-chloroform scale characterizes to some extent the force of solute-solvent interaction (for solvents of AB class, association of solvent is to be taken into account), with the following formal objection. The partition coefficients in Eqs. (1) to (3) are expressed in terms of mole/volume concentration, so that the number of solute molecules is related to a certain volume of the solvent; the number of solvent molecules in that volume (and thus also the

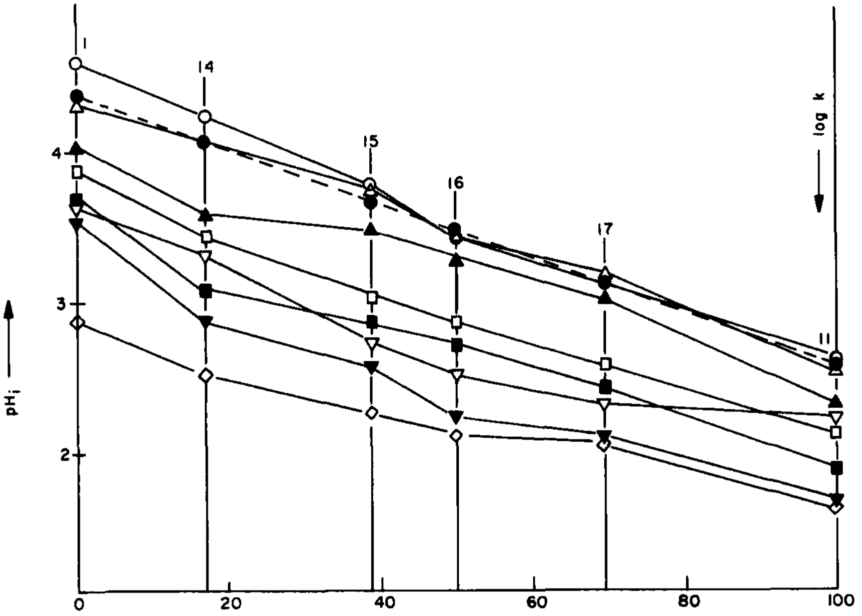


FIG. 4. Solvents of class B: 14, diisoamyl ether; 15, diethyl ether; 16, methylisobutyl ketone; 17, benzyl methyl ketone.

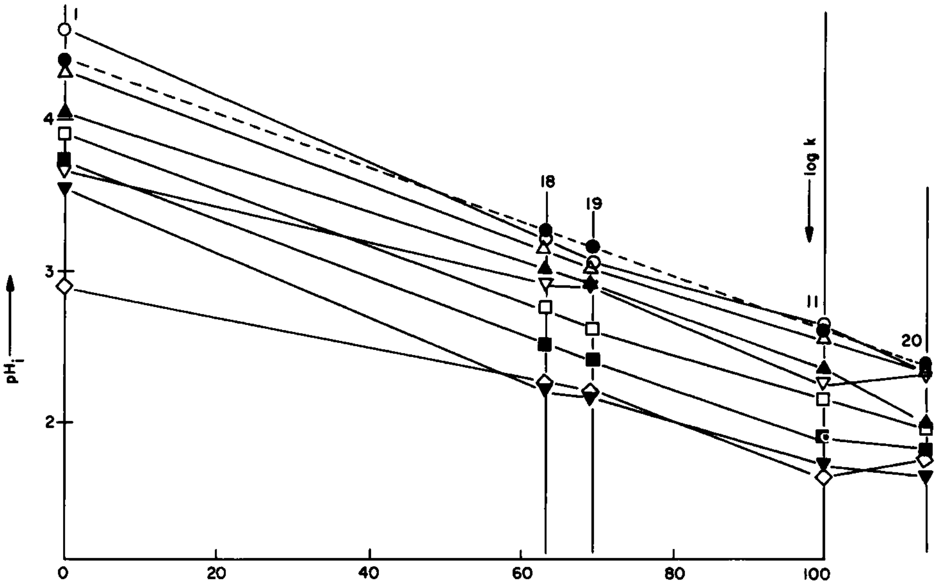


FIG. 5. Solvents of class AB: 18, *n*-octanol; 19, *n*-hexanol; 20, benzyl alcohol.

number of active H-bonding centers) depends on the molar volume of the solvent. Therefore, ordinary partition parameters are not strictly comparable, because, for instance, benzene and xylene, or pentanol and heptanol, contain various "concentrations" of benzene rings or hydroxyls, respectively, owing to "dilution" of higher homologs by methylene groups. Therefore, in strict comparison of solvent effects on the molecular level, "rational" partition coefficients should be employed in which the concentrations are expressed in mole fractions (*20*); this would cause some shifts in the spectra. In the present work this subtlety is neglected for practical reasons (to characterize the solvent power on the bulk level) and in view of the similar molar volumes of the solvents studied.

The experimental results may also be looked upon from another viewpoint. The ordinate is equivalent to the log Dr axis directed downward, r being practically constant (cf. Fig. 2). Therefore, the vertical distance of two points is equal to the selectivity of the solvent with respect to the given pair of solutes ($\log D''r - \log D'r = \log D''/D' = \log \beta$, where β is the separation factor); since the spectra are generally parallel, it means that most solvents have similar selectivities, with some slight variations. A more individual behavior is observed in the case of 8-hydroxyquinoline, owing to the presence of an additional H-bonding center—the hydroxyl group. It may be concluded, therefore, in accordance with previous reports, that the selectivity of separation can be improved by change of solvent primarily in cases when the solutes differ in molecular structure (i.e., in the number and type of H-bonding groups).

Furthermore, the difference of levels of two points of the same solute (two different organic solvents) is, in accordance with Eqs. (1) and (2) ($r = \text{const.}$) equal to the log partition coefficient of the solute in the hypothetical nonaqueous system composed of the two solvents. The parallelity of the spectra means from this viewpoint that these hypothetical partition coefficients of quinolines are approximately the same for a given pair of solvents (in some cases, however, 8-hydroxyquinoline behaves differently than quinoline bases and their methyl substitutes). The regularity is more striking, at least in some cases, because the solutes are probably extracted in hydrated form, in view of mutual saturation of the phases.

This observation may be explained by assuming that the force of interaction of the quinolines (except for 8-hydroxyquinoline) with the organic solvents is very similar, so that the hypothetical nonaqueous systems have negligible selectivity. This conclusion is in accord with the common rule that the selectivity of two-phase solvent systems is greatest for phases differing much in their properties—or to say it more exactly, when the solubility parameters of the two solvents differ maximally. In the case of organic electrolytes, the main cause of selectivity is usually the difference of ionization constants, since $\beta = k'K'_A/k''K''_A$ (bases); it follows, however, from Table 2, that in aqueous systems the quinoline bases differ also in their partition coefficients in un-ionized form. Since it may be assumed by analogy that the force of interaction of quinolines is also similar for water-solute interactions, the logical conclusion seems to be that the relatively high selectivity of aqueous partition systems is caused, beside differences in pK_A values, by steric factors, and mostly by the differentiated "squeezing" effect of the water phase due to various molecular shapes and sizes of the quinoline bases. For 2- and 8-substituted methylquinolines, some screening of the nitrogen atom could also contribute to the observed selectivity. The effect of molecular size is substantiated by the fact that for the un-ionized state the partition coefficients generally decrease in the order acridine–dimethyl substitutes–monomethyl substitutes–simple bases.

Further experiments on lipophilic electrolytes of more complex molecular structures are now in progress in this laboratory. The experimental results are another example of application of paper chromatography in physicochemical investigations. Lower accuracy of the chromatographic technique is more than balanced by its great simplicity (only a qualitative method of detection is necessary) and economy in time and chemicals; it is also possible to use solutes of low purity, since they are separated out on the chromatogram.

REFERENCES

1. E. C. Bate-Smith and R. G. Westall, *Biochim. Biophys. Acta,* **4**, 427 (1950).
2. S. Marcinkiewicz, J. Green, and D. McHale, *J. Chromatog.*, **10**, 42 (1963).
3. I. E. Bush, *Methods Biochem. Analy.*, **13**, 357 (1965).
4. J. Green and D. McHale, *Advan. Chromatog.*, **2**, 99 (1966).
5. Z. Prochazka, *Chem. Listy,* **58**, 911 (1964).
6. L. Rohrschneider, *J. Chromatog.*, **22**, 6 (1966).
7. I. Littlewood, *J. Gas Chromatog.*, **1**(11), 16 (1963).
8. R. Collander, *Acta Chem. Scand.*, **5**, 774 (1951).
9. E. Soczewiński, *Anal. Chem.*, **37**, 1439 (1965).
10. E. Soczewiński, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.*, **13**, 209, 213 (1965).
11. I. E. Bush, *The Chromatography of Steroids,* Pergamon Press, London, 1961.
12. K. B. Sandell, *Monatsh.*, **89**, 36 (1958).
13. A. Waksmundzki and E. Soczewiński, *J. Chromatog.*, **3**, 252 (1960).
14. A. Waksmundzki and E. Soczewiński, *Roczniki Chem.*, **32**, 863 (1958); **33**, 1423 (1959).
15. E. Soczewiński, *Roczniki Chem.*, **37**, 467 (1963).
16. A. Albert, in: *Physical Methods in Heterocyclic Chemistry,* Vol. I (A. R. Katritzky, ed.), Academic Press, New York, 1963, Chap. 1.
17. C. Golumbic and M. Orchin, *J. Am. Chem. Soc.*, **72**, 4145 (1950).
18. G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond,* Freeman, San Francisco, 1960.
19. L. Rohrschneider, *Z. Anal. Chem.*, **170**, 256 (1959).
20. W. Kemula, H. Buchowski, and J. Teperek, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.*, **9**, 595, 601 (1961).

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