THE EFFECT OF THE COMPOSITION OF THE MIXED PHASE UPON R_M COEFFICIENTS IN SOLVENT SYSTEMS OF THE TYPE: NONPOLAR SOLVENT + n-PENTANOL/AQUEOUS BUFFER SOLUTION

EDWARD SOCZEWIŃSKI* AND WIESŁAWA MACIEJEWICZ

Department of Inorganic Chemistry, Medical Academy, Lublin (Poland)

(Received June 15th, 1964)

The effect of the composition of the phases upon the partition of solutes is not only of practical importance in the choice of optimal conditions for separations, but it can also provide information concerning the partition mechanism and molecular interactions. Thus, the slope of the log K = f(log x) line (K = the partition coefficient; x = the molar fraction of the complexing solvent in the mixed phase) often permits the determination of the formula of the complex formed by the metal ion with the solvent[1]. For solvent systems in which only weaker interaction forces of the dispersion type are involved (simple solutions), KEMULA, BUCHOWSKI AND TEPEREK[2] and BUCHOWSKI[3] have derived equations relating the partition coefficients to the composition of the mixed phase. In another paper[4] these authors determined the excess free enthalpy of mixtures of carbon disulphide and hexadecane, on the basis of the experimental relationship between the partition coefficients and the composition of the mixed phase.

Assuming certain simplifications the R_M value is related to the partition coefficient of the chromatographed solute, and its dependence on the composition of the solvent is then analogous to that of partition coefficient[5]. In a series of studies[5-10] (*cf.* also ref. 11) several R_M vs. composition relationships were determined. They were found to be practically linear; however, in most cases investigated the solvent systems did not deviate far from ideal solutions. These investigations suggested that paper chromatographic data may also provide information concerning the deviations from ideality of mixed solvents and the partition mechanism[12]. Chromatographic data are less accurate on comparison with bulk partition methods and are confined to a narrower range of values (R_M can be determined with a sufficient accuracy only in the range —1.0 to +1.0); nevertheless, these disadvantages are compensated by the simplicity of the chromatographic technique, economy in solvents and solute and by the feasibility of serial experiments with several solutes simultaneously.

For moderate departures from ideality (g^E of the order of several tens of calories per mole for an equimolar mixture) the deviation of the R_M vs. composition relationship from linearity will lie within the experimental error of the chromatographic method (deviations from linearity are the differences between an experimental curve and a straight line joining the R_M values between 0 and 100 % pentanol). According to one of the papers cited[2] the deviation for an equimolar mixture a-

* Address: Staszica 6, Lublin, Poland.

mounted to, e.g., 50/4.575 $T = 0.04\ R_M$, which corresponds to less than 0.03 R_F units. Deviations of that order have been obtained for the system cyclohexane + benzene/ aqueous buffer solution[9]. Also WALDI's data[13] on the systematic analysis of alkaloids in the system cyclohexane + chloroform/formamide and presented as R_M vs. composition relationships, are approximately linear in view of the moderate deviations from ideality of the mixed phase.

In the present work the R_M vs. composition relationships were determined for several solvent systems in which the mixed (organic) phase was composed of pentanol and a non-polar solvent (decalin, xylene, chlorobenzene, tetralin, or iso-amyl ether). Systems of this type have proved very useful in the separation of alkaloids (see ref. 14).

The investigation had a double purpose:

(1) To find out if the R_M coefficients deviate from linearity for solvent systems in which stronger interactions between the component solvents of the mixed phase occur (in the systems investigated the dilution of pentanol caused its dissociation).

(2) To investigate whether paper chromatographic data may be used for the evaluation of deviations from ideality in mixed solvent systems.

The chromatographed substances were isoquinoline, quinoline and acridine. The pH values of the buffered aqueous phase were chosen so that the R_M values were in the optimal range of —1.0 to + 1.0.

EXPERIMENTAL

The manufacturer and the degree of purity of the solvents used are listed below:

n-Pentanol—British Drug Houses, Great Britain, laboratory reagent.

m-Xylene—Merck Darmstadt, Germany, redistilled.

Tetralin—Xenon Łódź, Poland, analytical reagent.

Decalin—VEB Laborchemie, Germany, laboratory reagent.

Chlorobenzene—Chem. Plants Oświęcim, Poland, laboratory reagent.

Iso-amyl ether—Reagent Distribution Bureau Gliwice, Poland, laboratory reagent.

The paper strips (Whatman No. 4, 5 × 23.5 cm, cut at right angles to the machine direction) contained 0.5 ml of buffer solution per 1 g of dry paper, which was controlled by weighing (the "moist paper method", cf. ref. 15). The strips were impregnated with McIlvaine's buffer solutions: 0.2 M Na_2HPO_4 + 0.1 M citric acid; the pH was controlled with a Radiometer Copenhagen type PHM 22e valve pH-meter. The glass chromatographic tanks, 6 × 14 × 21 cm, were saturated with the vapours of both phases. The bases were spotted as solutions in benzene (0.5 μl, 0.5 % w/v) and detected with Dragendorff's reagent. The experiments were carried out at room temperature (18.0° ± 1.0°).

RESULTS

The results are presented in Figs. 1–6 as R_M vs. molar composition plots. R_M is defined here, as in previous papers, according to REICHL: $R_M = \log[R_F/(1 — R_F)]$.

It can be shown that in the systems studied the R_M coefficient can be expressed on a mol/volume concentration scale (as is usual) instead of in molar fractions (^xR_M derived from ^xk, cf. ref. 3). Owing to the comparable molar volumes of the organic
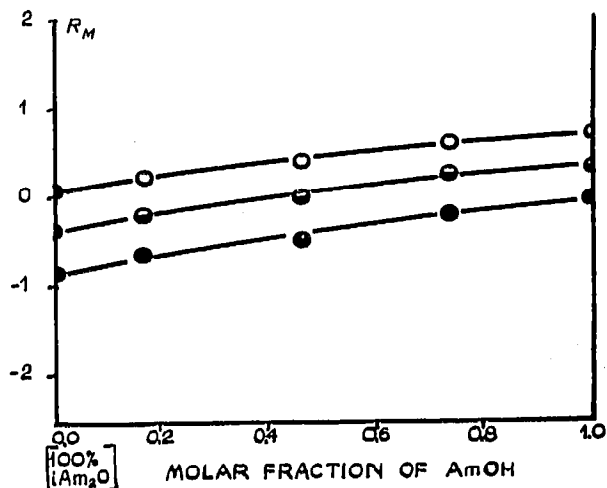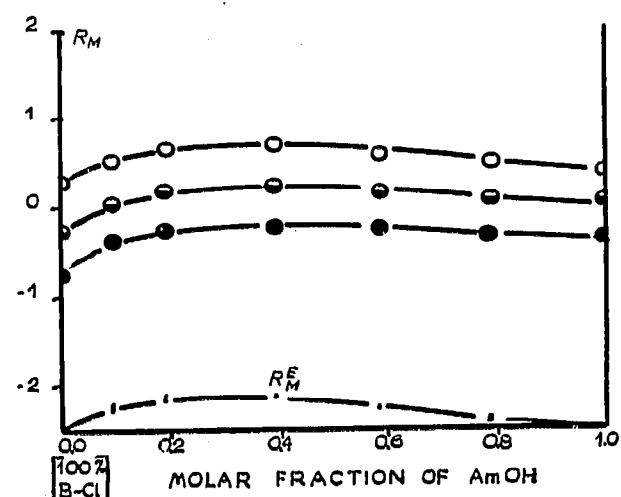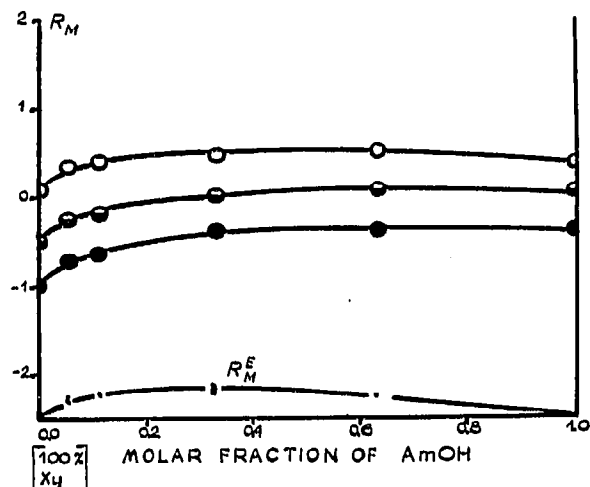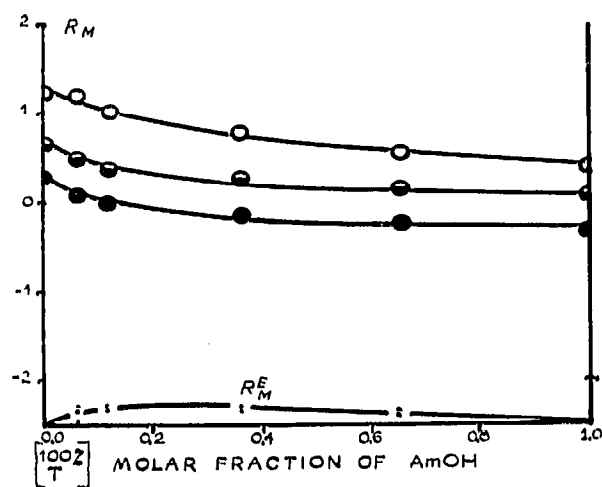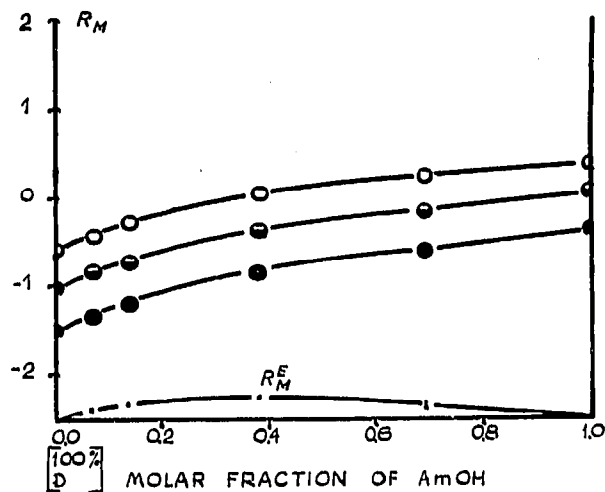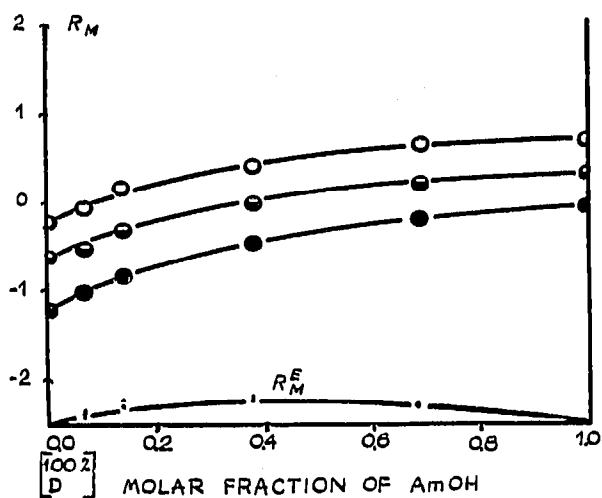
Figs. 1–6. The effect of dilution of pentanol with non-polar solvents on the R_M value. O—O = acridine; ⊖—⊖ = quinoline; ●—● isoquinoline. Diluting solvents: 1 and 2= decalin; 3 = tetralin; 4 = m-xylene; 5 = chlorobenzene; 6 = iso-amyl ether; $R_M{}^E$ at the bottom denotes deviations of R_M from linearity.

solvents investigated, only the slope of the R_M vs. composition curve will be changed; the shape of the curve and its deviations from linearity will remain practically unchanged. For chlorobenzene and xylene, which have molar volumes very similar to that of pentanol, the molar composition scale on the abscissa could be replaced by volume composition.

Except for the tetralin + pentanol/buffer solution (Fig. 3), in all the systems marked positive deviations from linearity of the R_M vs. composition relationships are observed. This was to be expected, as mixtures of alcohols with non-polar solvents usually exhibit strong positive deviations from ideality (mixture of solvents of classes II and V, according to the classification proposed by EWELL, HARRISON AND BERG[16]). The deviations of R_M coefficients from ideal values (linearity) amounted to 0.3 R_M units for solvents of class V (up to ca. 0.15 R_F units), the maximum deviations occurring at the left hand side of the diagrams, at ca. 30 mol % of pentanol. Smaller deviations were observed for mixtures of pentanol with iso-amyl ether (class III according to EWELL et al.[16]). The dissociation effect of pentanol was in this case compensated by the formation of hydrogen bonds between the ether and alcohol molecules.

The interpretation of the R_M vs. composition relationship for the tetralin + pentanol system is difficult. In this case negative deviations from linearity are observed (Fig. 3), although it is a mixture of the "II + V" type and should exhibit positive deviations, as was the case for the remaining systems. It is perhaps worth noting that the R_M and R_F values of the solutes are higher for tetralin than for pentanol while the reverse is observed for the remaining non-polar solvents. Furthermore, all the systems studied are characterized by strong interactions of the hydrogen bond type between the molecules of the heterocyclic bases and pentanol, and this interaction may influence the magnitude of deviations from linearity.

The deviations from linearity were in a given system identical (within experimental error) for all three heterocyclic bases, which is probably due to the similarity of their molecular structure. The comparison of Figs. 1 and 2 indicates that the pH of the buffer solutions, which controls the R_M values of the organic bases studied, does not influence the magnitude of the deviations. The curves in Fig. 2 are shifted towards a lower range of R_F values; since their shape remains unaltered, this suggests that any gradient effects are negligible in the technique employed, provided that R_F values are in the optimal range 0.1–0.8.

SUMMARY

The relationships between R_M values and composition of the mixed phase were determined for a number of solvent systems of the type: non-polar solvent + n-pentanol/buffer solution. The following solvents were mixed with pentanol: decalin, tetralin, m-xylene, chlorobenzene and iso-amyl ether. Except for tetralin (negative deviations), marked positive deviations from linearity of the R_M vs. molar composition relationship were observed. The deviations did not exceed 0.3 R_M units and the maxima were in the range of lower concentrations of pentanol. The deviations were practically equal for all three chromatographed substances and were caused by dissociation of pentanol due to dilution with the non-polar solvents. The experimental results indicate that chromatographic data may provide information concerning the non-ideality of solvent mixtures.

REFERENCES

1 A. M. Rozen, *Extraktsiya*, Vol. 1, Gosatomizdat, Moscow, 1962.
2 W. Kemula, H. Buchowski and J. Teperek, *Bull. Acad. Polon. Sci., Ser. Chim.*, 9 (1961) 595.
3 H. Buchowski, *Bull. Acad. Polon. Sci., Ser Chim.*, 10 (1962) 195.
4 W. Kemula, H. Buchowski and J. Teperek, *Rev. Chim., Acad. Rep. Populaire Roumaine*, 7 (1962) 285.
5 E. Soczewiński, *Nature*, 191 (1961) 68.
6 E. Soczewiński and C. A. Wachtmeister, *J. Chromatog.*, 7 (1962) 311.
7 E. Soczewiński, *J. Chromatog.*, 8 (1962) 119; *Chem. Anal. (Warsaw)*, 8 (1963) 337.
8 E. Soczewiński, *Bull. Acad. Polon. Sci., Ser. Chim.*, 10 (1962) 635.
9 E. Soczewiński, *Bull. Acad. Polon. Sci., Ser. Chim.*, 11 (1963) 29.
10 E. Soczewiński, *J. Chromatog.*, 11 (1963) 275.
11 A. Waksmundzki, E. Soczewiński and Z. Suprynowicz, *Collection Czech. Chem. Commun.*, 27 (1962) 2001.
12 E. Soczewiński, *Thesis*, Lublin, Poland, 1963.
13 D. Waldi, in *Some General Problems of Paper Chromatography, Symposium, Prague, 1961*, p. 139.
14 J. Büchi and H. Schumacher, *Pharm. Acta Helv.*, 32 (1957) 462.
15 A. Waksmundzki and E. Soczewiński, *Roczniki Chem.*, 35 (1961) 1363.
16 R. H. Ewell, J. M. Harrison and L. Berg, *Ind. Eng. Chem.*, 36 (1944) 871.