

THE USE OF BINARY STATIONARY PHASES IN GAS-LIQUID PARTITION CHROMATOGRAPHY*

ANDRZEJ WAKSMUNDZKI AND ZDZISŁAW SUPRYNOWICZ

Department of Physical Chemistry, The University, Lublin (Poland)

(Received September 8th, 1964)

The separation efficiency in gas-liquid chromatography depends upon column performance (in terms of the number of theoretical plates) and upon the selectivity of the liquid phase. For analytical separations a stationary liquid is required to give a complete and selective separation. However, different liquid phases give different separations but in many cases an intermediate separation condition is required. Therefore, in more complicated analysis of mixtures with separation factors on one liquid phase close to unity, combined columns find increasing application. The following types of such columns have been used:

- (1) Columns with various single liquid phases in each arranged in a sequence.
- (2) Single columns composed of sections packed with various liquids.
- (3) Single columns loaded with mixed binary liquid phases.

By changing the proportions of the lengths of the columns (or their sections) in the first and second case, or of the composition of the liquid phase in the third type, it is possible to effect a continuous change of properties between those of the pure liquids and thus to control within certain limits the relative retention times and the total duration of analysis.

Many examples of the use of combined columns have been reported in literature; some are distinguished by their quantitative approach to the problem of choice of optimal proportions of column (or section) lengths, or of the composition of the liquid phases, for practical analytical applications¹⁻⁷.

THEORETICAL CONSIDERATIONS

Determination of optimal composition of the stationary phase

Various methods of determination of the optimal weight or volume proportions of two stationary liquids have been suggested. ROHRSCHEIDER⁶ determined graphically the ratio of two section lengths containing different liquid phases. JUVET, CHIU AND SIMBORG⁷ have derived mathematical relationships which permit the calculation of the weights of the two liquid phases necessary to obtain any intermediate retention time. From the weights of the two liquids, the necessary column length can be calculated.

* This paper was submitted to the Fifth International Symposium on Gas Chromatography held at Brighton, England, on September 8th to 10th, 1964. As it did not quite fit into the scheme for the formal morning sessions it was preprinted separately and distributed as a basis for discussion at the informal afternoon sessions. It was not read or formally presented at the symposium and will not appear in the final reprints.

PRIMAVESI³ has found a linear relationship between the relative retention volume (uncorrected for the pressure drop), or the retention time for a constant flow rate of the carrier gas, and the weight percentage of one of the liquid phases. For a small pressure drop along the column, and assuming an ideal mixing of the two stationary liquids, columns of the three types give similar separations⁴.

If, however, the mixing deviates strongly from ideal behaviour, columns of the type 2 and 3 may give results differing from those obtained with columns of the type 1. In the limiting case of two practically immiscible liquids, columns of type 1 and 2 give very similar results which have been confirmed experimentally by PRIMAVESI³. For columns of the type 1, further mathematical relationships have been derived, permitting the calculation of the retention times for high pressure drops of the carrier gas¹.

In our investigations on the determination of optimal composition of the mixed liquid phase, we have utilized the KEMULA-BUCHOWSKI equation transferred from liquid-liquid partition equilibria to gas-liquid systems⁸⁻¹⁰. There are two forms of this equation, differing in their concentration units:

$$\log k' = u_1 \log k'_1 + u_2 \log k'_2 + \frac{V_{(m)}}{V_z^\circ} \cdot \frac{g^{E*}_{(m)}}{4.575 T} \quad (1)$$

$$\log {}^x k' = x_1 \log {}^x k'_1 + x_2 \log {}^x k'_2 + \frac{g^{E}_{(m)}}{4.575 T} \quad (2)$$

where:

$k' = Kr =$ partition number of the vapour in the system: mixed liquid phase-carrier gas;

$K =$ partition coefficient;

$r =$ ratio of cross-sectional areas of the fixed and mobile phase;

$k'_1, k'_2 =$ partition numbers of the vapour in the system between a single component of the liquid phase and the carrier gas;

$u_1, u_2 =$ volume fractions of the components of the mixed stationary phase;

${}^x k', {}^x k'_1, {}^x k'_2 =$ the respective "rational" partition numbers (concentrations in both phases expressed in mole fractions);

$x_1, x_2 =$ mole fractions of the components of the mixed stationary phase;

$V_z^\circ =$ molar volume of the solute;

$V_{(m)} = \sum x_i V_i^\circ =$ molar volume of the mixed solvent;

$V_i^\circ =$ molar volume of a single pure solvent;

$g^{E}_{(m)} =$ excess free enthalpy of the mixed solvent;

$$g^{E*}_{(m)} = g^{E}_{(m)} - RT \sum_i x_i \ln \frac{l_i}{x_i}$$

where

$$l_i = \frac{V_i^\circ}{V_{(m)}^\circ}$$

$$- R \sum_i x_i \ln \frac{l_i}{x_i} = S^{E}_{(ath)} = \text{excess entropy of athermal solutions.}$$

For ideal solutions of two stationary liquids the relationship between $\log k'$ (log partition number of a vapour) and the molar per cent composition of the mixture is linear. With eqn. (2), however, linear relationships of $\log {}^x k' = f$ (composition)

are rarely obtained in practical investigations of binary liquid mixtures. Therefore, in our work¹¹⁻¹³ we have employed eqn. (1) for the determination of optimal composition of the mixed liquid phase for a given separation. Furthermore, linear relationships are often obtained when using eqn. (1), even for non-regular mixtures, which may be explained by a compensation of the deviations related to the excess free enthalpy of mixing $g^E(m)$ by the excess entropy of mixing of athermal solutions $S^E_{(ath)}$ (cf. the commentary to eqns. (1) and (2)^{9,10,13}). This further increases the possibilities of application of eqn. (2) for analytical purposes. Thus, from the relationship (1), the composition of the liquid phase can be determined at which the optimal separation of a given mixture is obtained.

The experimental determination of these relationships is carried out as follows:

(1) The determination of retention times for columns loaded with the pure stationary liquids.

The following parameters are to be identical in both cases: column length and diameter, volume of stationary phase at column temperature, carrier gas flow rate. The ratio p/p_t should be as similar as possible in both experiments. If the relationship $\log k' = f(\text{composition})$ is to be determined more exactly, a few (2-4) measurements of the retention times must be carried out at intermediate compositions of the mixed liquid phase.

(2) Calculation of $\log k'$ (log partition number) from the retention times, using the formulae:

$$t = t_0 (1 + k') \quad (3a)$$

$$\log k' = \log \left(\frac{t}{t_0} - 1 \right) \quad (3b)$$

where:

t and t_0 = retention times of a given vapour and of an inert gas not retarded on the column, respectively.

(3) The plotting of the calculated values of $\log k'$ on 100 % composition axes (corresponding to pure liquids) and connecting the points with straight lines (Fig. 1).

(4) The determination of the composition of the liquid phase at which the distance between the $\log k' = f(\text{composition})$ lines is the longest, taking into account the time axis t/t_0 . This composition corresponds to optimal conditions of separation of the analysed mixture.

The above theoretical considerations have been discussed more fully and confirmed experimentally in our earlier work¹¹⁻¹³, in which the effect of the nature and composition of liquid mixed phases of various polarities on the separation efficiency has been investigated. It has been demonstrated that, by changing the composition of the mixed stationary phase, the separation efficiency can be controlled within certain limits, as well as the total duration of analysis. The following substances were analysed: cyclic and aromatic hydrocarbons, ethers, halogenated aliphatic hydrocarbons¹¹, aliphatic hydrocarbons C_5-C_7 ¹², methyl esters of *n*-, iso- and unsaturated fatty acids¹³, the isomeric hexanes (petroleum ether)¹⁴.

In Fig. 1 the relationship between $\log k'$ and volume composition of quinoline in diethyl malonate is illustrated for the following vapours: isopentane, pentane, 3-methylpentane, cyclopentane, hexane, furan, cyclohexane, heptane, cyclohexane, benzene and thiophene.

The fundamental differences between the relationship given by PRIMAVESI and eqns. (1) and (2) lie in the range of their application. The relationship between V_G and composition of the liquid phase holds well only for two immiscible, or ideally miscible stationary phases, when the experimental results coincide for all three types of column. Eqns. (1) and (2) do not apply at all to immiscible liquids, but only to two liquids miscible in all proportions, with the excess energy effect as small as possible (ideal systems).

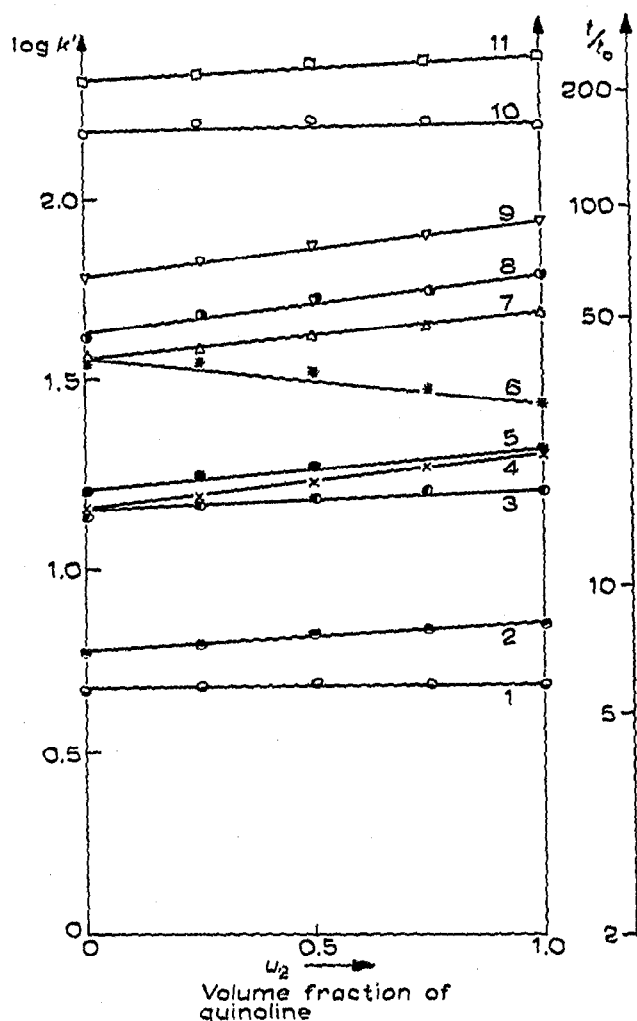


Fig. 1. Log of partition number k' of isopentane (1), *n*-pentane (2), 3-methylpentane (3), cyclopentane (4), *n*-hexane (5), furan (6), cyclohexane (7), *n*-heptane (8), cyclohexene (9), benzene (10) and thiophene (11). v_2 = volume fraction of quinoline in the system diethyl maleate-quinoline-nitrogen. Temperature of measurement: 35°; average inlet pressure 0.8 ± 0.01 atm; outlet pressure: atmospheric; carrier gas: N_2 ; flow rate at 20° (the permeability of capillary uncorrected for reference chamber): 60.1 ml/min; loading of stationary phase: 16.8% v/w; supporting material: Polish diatomite D (0.1–0.315 mm).

The determination of excess free enthalpy of mixing of binary solvents

As the value of K depends upon the nature of the solvent, it is possible to determine in this way the deviations from ideality of mixing of regular or approximately regular solutions employed as stationary phases. The value of K may easily be calculated from the retention times (eqns. (3a) and (3b)), thus, the method

described may be utilized not only for analytical purposes, but also for physico-chemical investigations, particularly for the determination of excess free enthalpy of mixing of binary solutions.

For the calculation of $g^E_{(m)}$, the relationship following from eqn. (2) was used¹⁵; as less simplifying assumptions were made in the derivation of eqn. (2), it reflects even small deviations of simple (regular) mixtures from ideality. In practice it leads to non-linearity of $\log {}^x k'$ as a function of composition of the mixed solvent.

It should be pointed out that the partition coefficient K is related to V_g by the equation:

$$K = \frac{V_g T \rho}{273}$$

where ρ is the density of liquid phase at column temperature. It follows, therefore, that the excess free enthalpy of mixed solvents at column temperature can be found from deviations from linearity of the relationship $V_g = f$ (composition of stationary phase in mole fractions), provided that the flow rate is constant and the ratio p/p_i similar in all experiments. Of course, any variation of the density of the solution with its composition should be taken into account, as well as parallel changes of the ratio of mean molar volume of liquid to the molar volume of the gas (V°_l/V°_g). In the experimental part of this work, a method is given for the calculation of $g^E_{(m)}$ from the deviations of $\log {}^x k' = \log {}^x K r$, as a function of the composition of the mixed liquid phase (at a constant value of r). It is demonstrated that the partition coefficient K of the vapours at column temperatures can be calculated with good accuracy from values of k' ; the variation of $\log K$ with the composition of the stationary phase may also be utilized for the determination of the excess free enthalpy of mixing.

EXPERIMENTAL

The measurements were carried out at 32° and 50° using a Model 116E Perkin-Elmer chromatograph with a thermoconductometric detector. Glass columns 105 cm long and of 5 mm internal diameter were employed. The stationary phases were triacetin, pelargonic acid (BDH, England), *n*-tetradecane (Light, England), quinoline (redistilled, Xenon, Poland); Polish diatomite D¹⁶ was used as the supporting material; it was loaded with 16.8 % of the stationary liquids from their ether solutions. The flow rate of nitrogen was constant in all experiments and equal to 60 ml/min (measured with a bubble flowmeter at the column outlet). The flow rate was not corrected for the permeability of the capillary nor on the reference chamber of the detector. For a given binary system of stationary phases, care was taken to keep identical input pressures in all experiments, by a uniform packing of the columns. The chromatographed substances were: furan (Schuchardt, West Germany), *n*-hexane, cyclopentane (Light, England), cyclohexane, cyclohexene (Azoty Plant, Poland), and benzene (Chemical Reagents, Poland).

CALCULATION OF PARTITION COEFFICIENTS

It follows from the explanation to eqns. (1) and (2) that the partition number $k' = Kr$. Thus, for the calculation of the partition coefficients K , it is sufficient to

find the ratio of the volumes of the stationary (liquid) phase and the mobile (gas) phase and to divide the corresponding values of k' by r . Table I gives a comparison of partition coefficients calculated in this way (K_I) with those calculated from retention data (K_{II}). The volumes of the liquid and gas phase in the column, necessary for the calculation of r at column temperature were determined from retention data, according to the relationship:

$$V_{M(1)} = V_{A(1)} j \frac{T_1}{T_2}$$

$$V_{M(2)} = V_{A(2)} j \frac{T_1}{T_2}$$

$$V_{(L)} = V_{M(1)} - V_{M(2)}$$

$$r = \frac{V_{(L)}}{V_{(g)}} = \frac{V_{(L)}}{V_{M(2)}}$$

where:

$V_{M(1)}$ and $V_{M(2)}$ = the corrected retention volumes of an unadsorbed solute on a column containing the support alone (1) and with the stationary phase on it (2), respectively;

$V_{A(1)}$ and $V_{A(2)}$ = measured (uncorrected) retention volumes of unadsorbed solute on the two columns (as above);

V_L = volume of the stationary phase at column temperature;

T_1/T_2 = ratio of absolute column temperature (1) to temperature of measurement (2);

j = pressure correction factor.

The value of K_{II} calculated from the ratio of net retention volume and volume of liquid phase at temperature of analysis:

$$K = \frac{V_N}{V_L}$$

DETERMINATION OF $g^E(m)$

As mentioned above, excess free enthalpies of mixing of binary solvents were determined graphically from the deviations of the relationship between logarithm of partition number ($\log {}^x k'$) and the composition of the mixed phase, expressed in mole fractions (eqn. 2). From the retention times of analysed substances, the k' values were calculated from eqn. (3b) corresponding to partition numbers expressed in volume scale of concentrations. In order to calculate the value of $\log {}^x k'$ (concentrations in molar fractions) the values of k' were multiplied by the ratio of the molar volumes of the liquid V°_L and V°_g under column conditions⁹.

$${}^x k' = k' \frac{V^{\circ}_L}{V^{\circ}_g}$$

where:

$$V^{\circ}_L = \sum x_i V^{\circ}_i = x_1 V^{\circ}_1 + x_2 V^{\circ}_2$$

$$V^{\circ}_g = 22.4 \frac{T_1}{273} j$$

TABLE I

COMPARISON OF THE PARTITION COEFFICIENTS CALCULATED FROM THE VALUES OF PARTITION NUMBER FOR FURAN, *n*-HEXANE, CYCLOPENTANE, CYCLOHEXANE, CYCLOHEXENE AND BENZENE WITH THOSE CALCULATED FROM RETENTION DATA

Solute	<i>n</i> -Tetradecane 50°		Quinoline 32°		Tetralin 32°		Pelargonic acid 50°		Triacetin 50°	
	K_I^*	K_{II}^{**}	K_I	K_{II}	K_I	K_{II}	K_I	K_{II}	K_I	K_{II}
Furan	57.680	57.134	223.565	225.565	153.111	150.780	94.466	94.192	177.979	178.05
<i>n</i> -Hexane	265.653	263.343	173.404	174.626	365.407	359.947	218.302	218.344	45.815	45.819
Cyclopentane	163.966	162.551	163.356	164.432	269.614	265.558	147.098	147.091	50.714	50.739
Cyclohexane	454.964	451.057	408.901	411.641	784.808	773.220	393.764	393.777	113.441	113.472
Cyclohexene	490.864	486.658	748.802	753.658	1033.397	1018.121	493.670	493.637	211.820	211.877
Benzene	367.760	364.580	1286.600	1294.956	1105.870	1089.551	479.613	479.604	556.244	556.294

* $K_I = k'/r$.** $K_{II} = V_N/V_L$.

The calculated values of ${}^x k'$ were plotted on a diagram with a concentration scale expressed in mole fractions for the binary mixture of stationary phases. In Fig. 2, the relationship $\log {}^x k' = f(\text{composition of stationary phase})$ is presented for furan (I), *n*-hexane (II), cyclohexane (III), cyclohexene (IV), and benzene (V) in the system triacetin-pelargonic acid. The values of deviations between the straight line

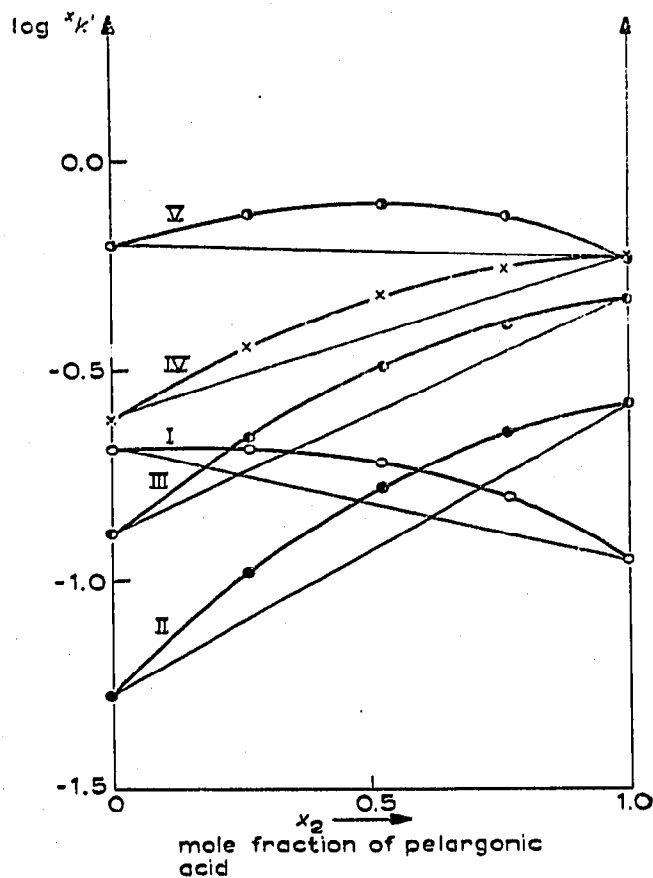


Fig. 2. Log of partition number ${}^x k'$ of *n*-hexane (●), furan (○), cyclohexane (●), cyclohexene (×) and benzene (○), x_2 = mole fraction of pelargonic acid in the system triacetin-pelargonic acid-nitrogen. Temperature of measurements: 50° ; average inlet pressure: 0.97 ± 0.03 atm; the remaining conditions of experiments as in Fig. 1.

and the curve, measured vertically at a given composition of the mixed stationary phase are a quantitative measure of its deviation from ideality and are proportional to the value of $g^E(m)$, as according to eqn. (2):

$$\Delta \log {}^x k'_{(\text{ex})} = \frac{g^E(m)}{4,575 T_1} \quad (4)$$

From these deviations, determined graphically for the five substances given, mean values of $\Delta \log {}^x k'_{(\text{ex})}$ were calculated for a series of compositions of the mixed stationary phase and also the corresponding values of $g^E(m)$ in cal/mol. A plot of $g^E(m)$ as a function of molar fraction of pelargonic acid in triacetin is presented in Fig. 3. The maximal calculated value of $g^E(m)$ in this system is equal to ca. 160 cal/mol and corresponds to the concentration of ca. 0.52 molar fraction of pelargonic acid.

The method of calculation of partition coefficients from partition numbers (k') and the volume of the liquid phase in the column (V_L) is a simplification of calculation methods employing other retention data. It follows from the fact that, by mathematical transformations of the k' value, analogous relationships are obtained between partition coefficient and retention data.

$$k' = \frac{t - t_0}{t_0} = \frac{V_R - V_A}{V_A} = \frac{V'_R}{V_A}$$

As

$$k' = K\gamma = K \frac{V_L}{V_M} \quad \text{and} \quad \frac{V_M}{V_A} = j \frac{T_1}{T_2}$$

it follows that:

$$K = k' \frac{V_M}{V_L} = \frac{V'_R}{V_A} \times \frac{V_M}{V_L} = \frac{V'_R j T_1}{V_L T_2} = \frac{V_N}{V_L}$$

It seems, however, that the use of relative values $(t - t_0)/t_0$ may eliminate partly the error due to the calculation of the correction factor for pressure drop along column, and the inaccurate measurement of actual carrier gas flow rate in some chromatographs. The agreement of partition coefficients calculated from k' values, and those calculated from other retention data, is quite good, as is seen from the comparison in Table I. Relatively large differences in K values observed in the case of tetralin as stationary phase may be explained by inaccurate measurements due to evaporation of the liquid from the column at the temperature employed. We were not able to ascertain which of these K_I or K_{II} values were more accurate.

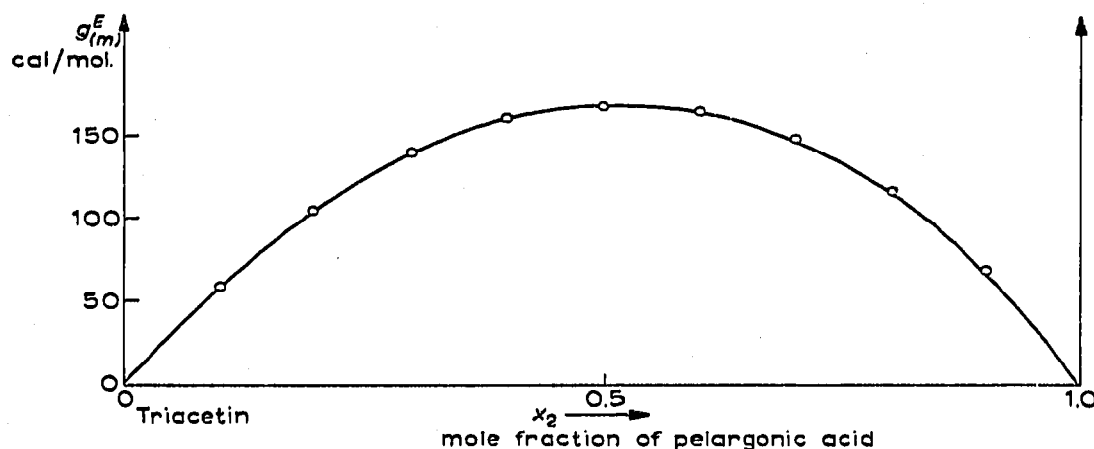


Fig. 3. Excess free enthalpies ($g^E(m)$) of mixtures of triacetin and pelargonic acid, calculated from data of Fig. 2.

Excess free enthalpies of mixed solvents are a measure of deviations from ideality of the system studied and one of the measurable functions determining the thermodynamic state of the system. Therefore, they may be found useful for the estimation of the interaction forces between two solvents and between the solvent mixture and the solute.

The described methods by gas chromatography permit the determination of the function $g^E(m)$ rapidly and quite accurately.

It is evident that the accuracy of determination will be proportional to the magnitude of deviations from linearity of the relationship $\log {}^x k' = f$ (composition in mole fractions). According to eqns. (1) and (2), the value of $g^E(m)$ found in practice decreases with the absolute temperature of measurement. It follows, therefore, that the determinations of $g^E(m)$ by the chromatographic method should be carried out at as low temperatures as possible. It should also be pointed out that eqns. (1) and (2) were derived for single (regular) solutions (conformal system).

Assuming a limiting, very low concentration of the solute, the interactions between the solute and the mixed solvent may then be neglected. If, however, the mixture of solvents cannot be classed as regular (especially when stronger interactions of the hydrogen bond type are brought into play) then the nature of the solute may also influence the magnitude of deviations from linearity of the relationship $\log {}^x k' = f$ (composition). It is evident that in these cases the deviations from linearity are not only a measure of $g^E(m)$ but also reflect the magnitude and character of interactions between the solute and the mixture of solvents. In the system described pelargonic acid and triacetin were employed which belong to groups of compounds¹ capable of hydrogen bonding. It is probable that here lies the cause of slight differences in the magnitude of deviations observed for different solutes at a given composition of the mixed solvent. If that is the case, the deviations should be considered as due to a sum of excess free enthalpy of mixing and of excess thermodynamic potential, the latter related to interactions between the solute and the solvent.

Thus the differences between magnitudes of deviations for various solutes would be a measure of the differences of interactions between these solutes and the mixed solvent of a given composition. In our calculations of $g^E(m)$ for the system pelargonic acid/triacetin/hydrocarbons we had too few experimental data to take these considerations into account, and thus the plot of $g^E(m) = f$ (composition) in Fig. 3 represents arithmetic mean values. The curve representing the variation of mean values of $g^E(m)$ is asymmetrical, and the maximum is shifted in the direction of higher concentrations of pelargonic acid.

Judging from its shape, the system studied is intermediate between regular (simple) and complex solutions.

SUMMARY

The theoretical basis of choice of optimal composition of the binary mixed stationary phase for a given separation problem is described; a number of practical applications is presented. The possibility of the application of binary solvent systems in gas chromatography is considered for the investigation of the energy effect due to deviations from ideality of binary liquid mixtures. In the experimental part a method of calculation of excess free enthalpies of mixing solvents $g^E(m)$ is given, together with an experimental illustration. The values of $g^E(m)$ have been calculated from the deviations from linearity of the relationship $\log {}^x k' = f$ (composition of mixed phase). The values of partition numbers (k') determined from retention times have been used for the calculation of partition coefficients (K) of solutes at column temperature. The results obtained are compared with partition coefficients calculated from other retention data.

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