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GAS CHROMATOGRAPHIC STUDY OF CHEMICAL INTERACTIONS IN SOLUTIONS

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SUMMARY

A thermodynamic analysis of the dependence of retention values on the composition of binary stationary phases in gas–liquid chromatography is presented. The existence of extrema (maxima or minima) in the solute retention–binary stationary phase composition plots is shown experimentally.

It has been established that the appearance of extrema is due to an interaction between the components of the binary stationary phase. The positions of the extrema relate to the compositions of the molecular compounds being formed.

INTRODUCTION

The vast possibilities of gas chromatography in physicochemical studies are revealed, in particular, in the study of chemical interactions in solutions. In this respect, the work carried out with multicomponent stationary phases is of interest. The existence of interactions between the components of such a phase can be seen from the shape of the solute retention–stationary phase composition curve.

In early work (*e.g.*, ref. 1) a linear relationship between the logarithm of the solute retention volume and the composition of the stationary phase was suggested for completely miscible components of a binary stationary phase. In more recent works[2–5], mention has been made of a curvilinear, and particularly a parabolic, relationship between the logarithm of the retention volume and the composition of the binary stationary phase, provided that the stationary phase is a non-ideal solutior.

THEORETICAL

To elucidate the general nature of the dependence of retention values on the composition of the binary stationary phase we have used the Wool equation for ternary liquid systems. It should be noted, however, that this equation is an approximate one similar to an expansion of a series. However, in agreement with the Gibbs-Duhem theorem, it correctly presents the dependence of the thermodynamic properties of a binary solution on concentration.

The Wool equation of the third order for ternary systems has the following form[6]:

$$\log \gamma_{1(2,3)} = x_2^2[A_{12} + 2x_1(A_{21} - A_{12})] + x_3^2[A_{13} + 2x_1(A_{31} - A_{13})] + x_2x_3[A_{21} + A_{13} + 2x_1(A_{31} - A_{13}) + 2x_3(A_{32} - A_{23})] - C(1 - 2x_1) \quad (1)$$

where γ is the activity coefficient; x is the molar fraction of a particular component; A_{ij} is a constant characterizing the paired interactions of molecules and is equal to the limiting value of the logarithm of the activity coefficient of component i in solvent j when the concentration of the component i is infinitely small; C characterizes the ternary interaction of molecules and is approximately equal to $^1/_2\,(A_{21} - A_{12} + A_{31} - A_{13} + A_{32} - A_{23})$, the subscripts 1, 2 and 3 referring to the sorbate, the first and the second component of the binary stationary phase, respectively.

In the case of gas chromatography, when the concentration of the sorbate tends to be infinitely small, eqn. 1 acquires the form:

$$\log \gamma_{1(2,3)} = x_2^2A_{12} + x_3^2A_{13} + x_2x_3[A_{21} - A_{13} - A_{32} + 2x_3(A_{32} - A_{23}) - C] \quad (2)$$

The partition coefficient (K) of the sorbate is equal to the ratio of its concentration, in molar fractions, in the liquid phase to its concentration in the gas phase:

$$K_1 = \frac{x_1}{p} = \frac{x_1}{\gamma_1 x_1 p_{01}} = \frac{1}{\gamma_1 p_{01}} \quad (3)$$

where p is the sorbate vapour pressure above the solution, and p_{01} is the vapour tension of the pure sorbate (1).

From eqns. 2 and 3, it follows that

$$\log K_1 = -x_2^2A_{12} - x_3^2[A_{13} - 2x_2(A_{32} - A_{23})] - x_2x_3(A_{21} + A_{13} + A_{32} - C) - \log p_{01} \quad (4)$$

Taking into consideration that $x_2 + x_3 = 1$, the dependence of the retention value on the composition of the binary stationary phase is obtained in a general form:

$$\log K_{1(2,3)} = ax_2^3 + bx_2^2 + cx_2^2 + d \quad (5)$$

The contribution of the cubic term in eqns. 4 and 5 will be the greater the larger is the magnitude of the difference $A_{32} - A_{23}$, which shows the magnitude of the interaction of molecules (3) situated in the medium of molecules (2) compared with the interaction of molecules (2) with the molecules (3) that surround them (energy of mutual interchange).

If the components of the binary stationary phase form with each other an ideal solution, that is, $A_{32} = A_{23}$, then eqn. 4 assumes the form:

$$\log K_{1(2,3)} = (A_{21} + 2A_{13} - A_{12} - C)x_2^2 + (A_{13} - A_{21} - C)x_2 + (-A_{13} - \log p_{01}) \quad (6)$$

The parabolic dependence of retention values on the composition of the binary stationary liquid phase is therefore justified only in the case when an ideal solution is formed between the components of the stationary liquid phase.

The equations of Van Laar and Margules, previously proposed[7,8] to describe the chromatographic behaviour of solutes on binary stationary phases, represent particular cases of the Wool equation and are valid only in certain cases (for closely similar molecular volumes of the components that constitute the solution).

It follows from eqns. 1 and 5 that the appearance of extrema on the graph of log K *versus* composition of the binary solvent may be expected.

PURNELL *et al.*[9] have studied retention on the binary stationary phase *n*-octadecanol + magnesium stearate in the temperature range 40°–91°. The appearance of extrema on the curves of retention *versus* composition of the binary stationary phase has been explained[9] by the formation of complexes between the components of the binary stationary phase. As the individual components (*n*-octadecanol and magnesium stearate) melt at 59° and 88.5°, respectively, the conclusion concerning complex formation between components cannot be regarded as quite definite. The extrema were more probably observed as a result of phase transitions.

The formation of two layers within the binary liquid phase also results in breaks on the curves of sorbate retention *versus* composition of the binary stationary phase.

To ascertain the applicability of the gas chromatographic method in revealing molecular compounds in solutions and in studying the type of relationships that occur between the sorbate retention and the composition of the binary stationary phase we investigated a number of binary stationary phases. The conclusion about the formation of molecular compounds and their compositions in these binary stationary phases was made also as a result of a study of a number of physicochemical properties of binary systems.

EXPERIMENTAL

The retention values were measured on a chromatograph equipped with a katharometer. The katharometer, chromatographic column and saturator were immersed in a liquid thermostat controlled to within ± 0.05°. The saturator was a metallic tube, 0.5 m long and 3–4 mm I.D., packed with 40 % (w/w) of the stationary phase. If the volatility of the stationary phase could be neglected at the operating temperature the saturator was shut off.

The metallic chromatographic columns were 0.5–1 m long and 4 mm I.D. Celite 545 was used as the solid support. It was shown experimentally that the adsorptive properties of Celite 545 did not affect the retention value when the degree of stationary phase coating was 25 % (w/w). Stationary phases with a high volatility were coated directly without any solvent, while those with a low volatility were coated from a solution in diethyl ether. Helium was used as the carrier gas. The retention time was measured with an accuracy of 0.2 sec. The standard deviation of an individual measurement of the partition coefficient did not exceed 1–2 % relative.

The density, d, was measured with a picnometer with an error of $5 \cdot 10^{-4}$ g/ml. The viscosity, η, was measured with an Ostwald viscometer with an error of 0.05 cP. The index of refraction, n_D, was measured with an IRF-23 refractometer to within

TABLE I

RESULTS OF GAS CHROMATOGRAPHIC AND PHYSICOCHEMICAL ANALYSIS OF BINARY STATIONARY PHASES

+, Results confirming the formation of molecular compounds have been obtained; —, no results confirming the formation of molecular compounds have been obtained; O, the property has not been measured.

System	*Binary system*		*Physicochemical measurements*					*Gas chromatographic measurements*	
	Component 1	*Component 2*	*Property*				*Composition of molecular compounds (molar ratio)*	*Sorbate retention*	*Composition of molecular compounds (molar ratio)*
			d	n_D	η	ε			
1	Tributyl phosphate	Nonyl alcohol	+	+	+	+	1:1	+	1:1
2	Tributyl phosphate	*o*-Nitroanisole	+	+	+	+	1:1	+	1:1
3	Tributyl phosphate	Glutaronitrile	+	—	+	O	1:1	+	1:1
4	Tributyl phosphate	α-Methylnaphthalene	+	+	O	O	1:1	+	1:1
5	Acetophenone	Adiponitrile	+	+	+	+	1:1	+	1:1
6	Dibutyl phthalate	Nonyl alcohol	+	—	O	+	1:2	+	1:2
7	Dibutyl phthalate	*o*-Nitroanisole	+	O	O	O	1:2	+	1:2
8	Dimethylformamide	Mesitylene	—	—	O	O	—	+	1:1

$1 \cdot 10^{-4}$ units. The dielectric constant, ε, at 500 kHz was measured to within ±2% relative.

Acetylenic hydrocarbons, allene, *n*-paraffins, cycloparaffins, ketones, chorinated hydrocarbons, ethers and esters were used as sorbates.

The substances used as components of the binary stationary phases were purified by distillation. The physicochemical properties of the stationary phases almost coincided with those found in the literature. All these substances were liquids at the temperatures of measurement and were completely miscible with one another.

RESULTS AND DISCUSSION

The binary systems which were used as sorbents are listed in Table I, together with the results of their physicochemical analysis. The physicochemical analysis of systems 5 and 8 was discussed by us earlier[10].

In all the systems except systems 6 and 8 the existence of molecular compounds was confirmed unambiguously. In systems 6 and 8, no distinct evidence of the formation of molecular compounds could be obtained, although the presence of electron donor and electron acceptor groups suggests an interaction between the components of these systems.

It would seem that in some cases gas chromatography can furnish more reliable evidence of the formation of molecular compounds in a solution than the common physicochemical methods, provided that solutes are selected that are particularly sensitive to the interaction of the components of a binary solvent.

Fig. 1 shows the relationships between the composition of the binary stationary phase and the logarithm of the partition coefficient of acetone on binary stationary phases 1 to 4 (Table I), one of the components of which was tributyl phosphate. The existence of breaks in all the curves can be distinctly seen, their positions corresponding to a 0.5 molar fraction of tributyl phosphate in the binary stationary phases. A similar situation was also observed with other polar sorbates.

For systems 6 and 7 (Fig. 2), one component of which is dibutyl phthalate, the position of the extrema on the curve of the logarithm of the partition coefficient of acetone *versus* the composition of the binary stationary phase corresponds to about a 0.35 molar fraction of dibutyl phthalate.

It can also be seen in Table I that in systems 1–4, methods of physicochemical analysis show the formation of molecular compounds with a molar ratio of 1:1, while in systems 6,7 this ratio is 1:2.

It can therefore be seen that the formation of molecular compounds between the components of binary stationary phases is the reason for the appearance of extrema on the curve showing the relationship between retention and the composition of the binary stationary phase. The positions of the extrema indicate the composition of the molecular compounds formed. This opens up new possibilities in the use of gas–liquid chromatography (GLC) as a method for the physicochemical analysis of binary liquid systems.

The great advantages of GLC are displayed in the study of systems that show weak interactions. Thus, in systems 6 and 8, methods of physicochemical analysis do not distinctly reveal the composition of the compounds formed, while a chromatographic study of these systems may provide the necessary information (Table I).

Of particular interest as sorbates are substances that may be both donors and acceptors of electrons and are thus able to interact between the two components of a binary stationary phase. Such substances include acetylenic hydrocarbons and allenes.

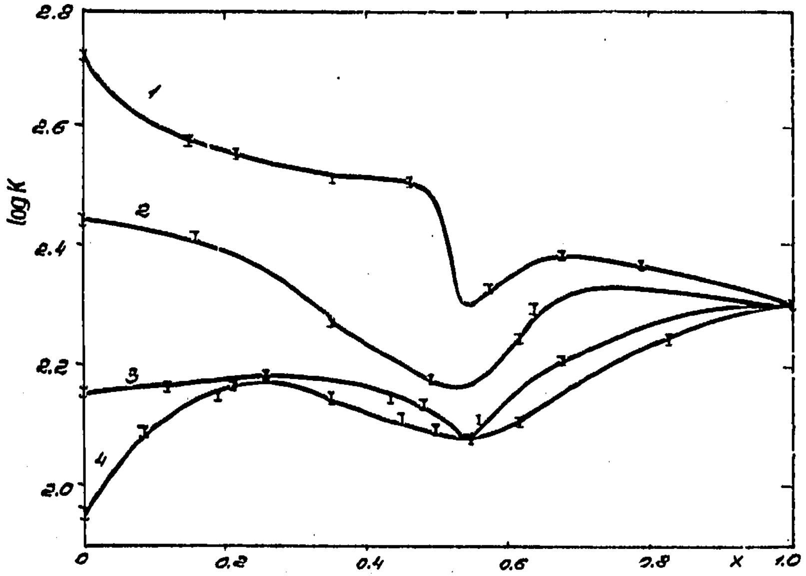

Fig. 1. Logarithm of partition coefficient of acetone *versus* molar fraction (x) of tributyl phosphate in binary stationary liquid phases at 40°. 1 = Tributyl phosphate–glutaronitrile; 2 = tributyl phosphate–*o*-nitroanisole; 3 = tributyl phosphate–α-methyl naphthalene; 4 = tributyl phosphate–nonyl alcohol. The sign I corresponds to a triple error of the technique used (also in Figs. 2 and 4).

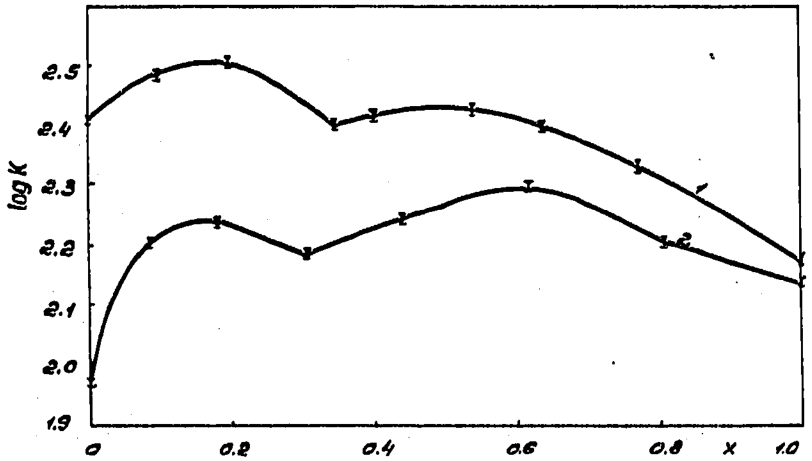

Fig. 2. Logarithm of partition coefficient of acetone *versus* molar fraction (x) of dibutyl phthalate in binary stationary liquid phases at 40°. 1 = Dibutyl phthalate–*o*-nitroanisole; 2 = dibutyl phthalate–nonyl alcohol.

As can be seen in Fig. 3, the relationships between retention and the composition of the binary stationary phase show breaks (singularity points) that correspond to the equimolecular composition of a binary stationary phase. Similar relationships for hexane are monotonous, and this is typical of other non-polar compounds. As the temperature is raised, the stability of molecular compounds decreases, and the relationship between the retention of the polar sorbate and the composition of the binary stationary phase becomes monotonous.

The breaks can be seen more clearly in plots of the heats of solution of the sorbates *versus* the composition of binary stationary phases, as shown in Fig. 4 for diacetylene, vinylacetylene and methylacetylene on binary stationary phase 1. A study of the

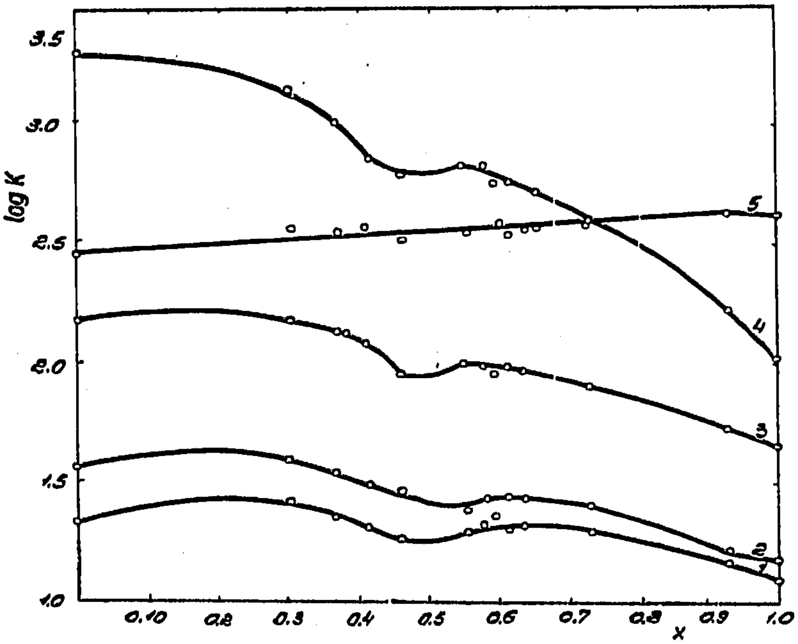

Fig. 3. Logarithm of partition coefficient of acetylenic hydrocarbons, allene and *n*-hexane *versus* molar fraction of tributyl phosphate in a binary stationary liquid phase (tributyl phosphate-nonyl alcohol, 20°). 1 = Allene; 2 = methylacetylene; 3 = vinylacetylene; 4 = diacetylene; 5 = *n*-hexane.

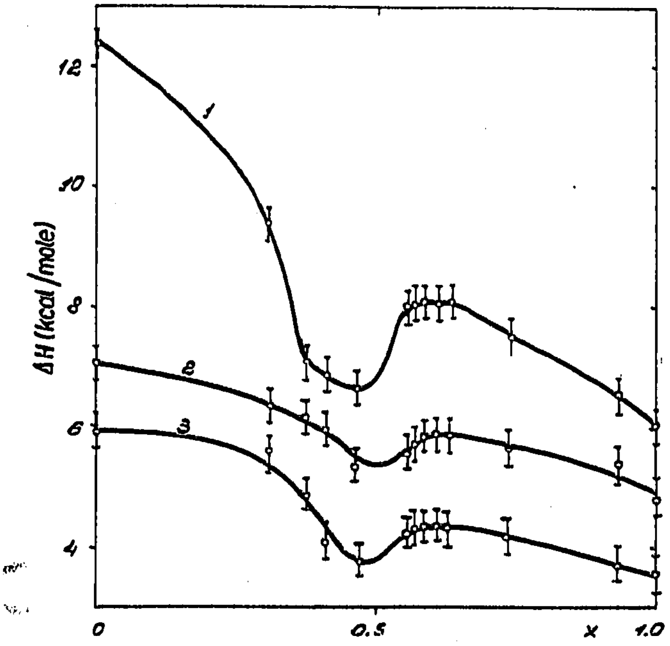

Fig. 4. Heats of solution (ΔH) of some substances *versus* molar fraction of tributyl phosphate in a binary stationary liquid phase (tributyl phosphate–nonyl alcohol). 1 = Diacetylene; 2 = vinylacetylene; 3 = methylacetylene.

temperature dependence of retention values on binary stationary phases will probably provide some interesting results for the determination of the constants of complexes in solutions.

Finally, it should be noted that in order to establish the formation of molecular compounds in binary stationary liquid phases, use can be made also of the dependence of the kinetic characteristics of the chromatographic process (number of theoretical plates, mass transfer coefficients) on the composition of the binary stationary phase.

CONCLUSION

A thermodynamic study has shown that the dependence of retention parameters on the composition of binary stationary phases can be described by a curve with extrema. For the case when an ideal solution is formed between the binary stationary phase components, this relationship is parabolic.

GLC has been proved to be a convenient method for indicating the existence of molecular compounds in solutions. The compositions of molecular compounds formed between the components of some binary stationary phases can also be determined by GLC.

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