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Note

The problem of solute retention in mixed stationary phases in gas-liquid chromatography

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Purnell and co-workers¹⁻⁴ have shown that the gas chromatographic behaviour of mixed stationary phases can be generally described by the simple equation

$$K_{(mix)} = \varphi_A K_A^\circ + \varphi_B K_B^\circ \quad (1)$$

where K_A° and K_B° are the partition coefficients for the pure liquids A and B, respectively, and φ represents the corresponding volume fraction. All published data relating to infinite dilution partition coefficients (K) were found to fit the above equation. If the stationary phase is composed of more than two solvents, the retention of any solute can then be calculated from the following general equation:

$$K_{(mix)} = \sum \varphi_i K_i^\circ \quad (2)$$

In fact, the solvent properties of liquid mixtures seem to be simply related to those of the pure components. To explain this unexpected behaviour of physically mixed solvents of different natures, a "local immiscibility model" was postulated¹, so that there "is no random mixing in A + B mixtures, but rather a high degree of aggregation such that the local concentration of A is always that corresponding to pure A".

It is interesting to consider whether copolymers can be treated in a similar manner to physical mixtures if they are used as stationary phases in gas-liquid chromatography (GLC). Assuming a given overall composition and comparing a homopolymer blend with a copolymer, the microscopic "degree of mixing" is determined mainly by covalent bonding and is definitely different if incompatible polymers are considered.

In this work, polystyrene-polybutadiene copolymers with different structures and polymeric blends of the two homopolymers on Chromosorb W (AW/DMCS) were considered. Benzene and some *n*-alkanes were injected as solutes at a column temperature of 170°. To establish the GLC conditions, the column temperature obviously has to be well above the glass transition temperature of both polymers.

At first, the validity of eqn. 1 was tested by using a series of polystyrene-polybutadiene blends as stationary phases. From the measured specific retention

volumes of the pure polymers (V_g°), the absolute and relative retention data of the polymeric blends can be calculated from the following equation if density changes are considered to have only a negligible influence (Fig. 1):

$$V_{g(\text{mix})} = w_A V_{gA}^\circ + w_B V_{gB}^\circ \quad (3)$$

The data obtained in this way agreed well with the measured retention indices⁵ (Table I and Fig. 2), thus confirming the validity of eqn. 2. It should be noted that the same results were obtained with different degrees of mixing, whether a column in which the polystyrene and polybutadiene had been mixed prior to coating the support or whether a column made by physically mixing a polystyrene stationary phase and a polybutadiene stationary phase was used.

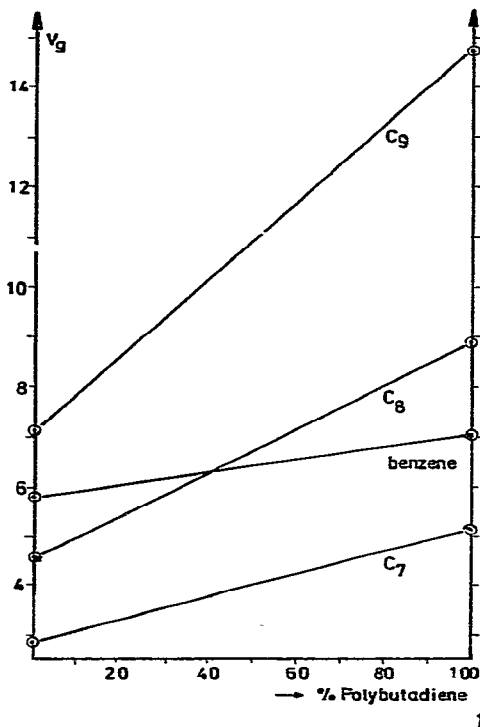


Fig. 1. Interpolation between experimentally determined V_g° values for homopolymers A and B assuming the validity of eqn. 1.

The retention data of some commercial styrene-butadiene copolymers with different sequence structures were studied, and their overall chemical compositions were evaluated gas chromatographically by using Fig. 2 as a calibration graph. Table II shows the excellent agreement between the specification of the polymers given by the manufacturer and the composition data obtained with the GLC method. It should be emphasized that this is especially true for copolymers with different sequence length distributions. Hence no information on sequence structure can be derived from GLC partition experiments.

TABLE I

DEPENDENCE OF RETENTION INDICES ON THE DEGREE OF MIXING (POLY-STYRENE:POLYBUTADIENE = 1:1)

<i>Degree of mixing</i>	<i>Measured retention index</i>
Mixture of separated support beads	789
Deposition of both homopolymers from one solution	790
Partial block polymer	788
Graft polymer	788

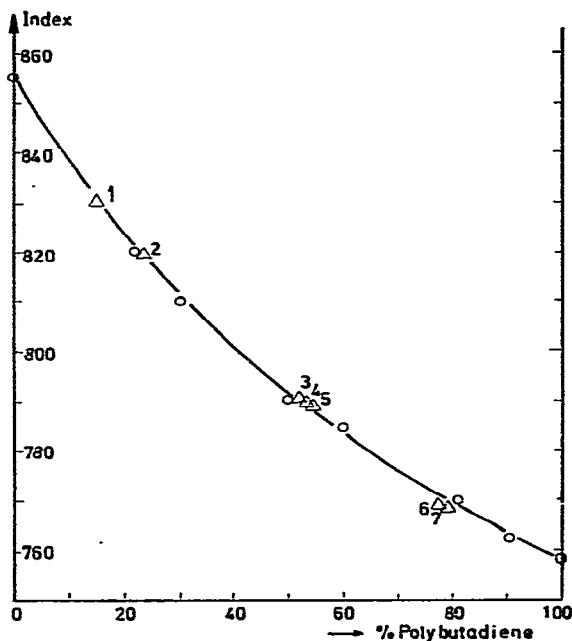


Fig. 2. Comparison of retention index values: solid line, calculated from Fig. 1; O, experimental values for polymer blends; Δ , experimental values for copolymers (numbers according to Table II).

TABLE II

VALIDITY OF EQN. 1 FOR COPOLYMERS WITH DIFFERENT SEQUENCE STRUCTURES

No. (Fig. 2)	Copolymer	Producer	Sequence structure	Polybutadiene(%)	
				From Fig. 2	Producer specification
1	Duravit 15S	Hüls	Statistical	15	15
2	C118	Höchst	Graft + homopolymer	25	22
3	C26II		Graft	52	51
4	Solprene 303	Phillips	II block	53	52
5	Solprene 410		32 block	55	52
6	Solprene 1205		18 block	78	75
7	Solprene 1204		Statistical	80	75

In conclusion, the validity of eqn. 1 has been demonstrated for copolymeric systems. In general, more attention should be paid to polymeric blends and copolymers as non-volatile mixed stationary phases in analytical gas chromatography if all of the possible variations in co-monomer composition are considered.

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