

Note

Modified sorbents in binary stationary phase systems in gas chromatography

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The properties of liquid stationary phases used in gas chromatography (GC) are changed stepwise. Studies carried out by Kemula and Buchowski¹ on the distribution of microcomponents between two immiscible liquids established a theoretical basis for the application of binary stationary phases in GC. The equations that they proposed for the distribution of a microcomponent in a liquid-liquid system were used by Waksmundski *et al.*² for its distribution between a gas and a mixture of two liquid phases. They suggested a relationship between the partition coefficient in a mixture of two phases and their values in the pure components. They also stated that the excess free energy of mixing characterizes only the interaction between components in the binary liquid phase.

Vigdergauz and Pomasanov³ showed that the excess free energy is composed of two components, one of which characterizes the interaction between the components in the system and the other the specific interaction of the sorbate used with a binary system.

The following equation was suggested³:

$$\ln V_{mm} = X_1 \ln V_{mm,1} + X_2 \ln V_{mm,2} + \frac{\Delta f'}{RT} + \frac{\Delta f''}{RT} \quad (1)$$

where

- V_{mm} = molar retention of sorbate at the binary phase;
- $V_{mm,1}$, $V_{mm,2}$ = molar retention of sorbate in the first and second pure components of the binary phase, respectively;
- X_1 , X_2 = molar fraction of the binary phase components;
- $\Delta f'$ = excess free energy of mixing for the binary phase components;
- $\Delta f''$ = value characterizing the specific interaction of sorbate with a binary phase.

However, eqn. 1 is in fact unsuitable for mixtures of liquid stationary phases and for high-molecular-weight and polymeric compounds and also for modified sorbents, where the notion of molecular weight is inapplicable. Therefore, in this work it is proposed to use eqn. 1 in a different form and also to replace the molar fraction by the weight fraction, and the molar retention by the specific retention volume;

$$\log V_g = w_1 \log V_{g,1} + w_2 \log V_{g,2} + \frac{g_1^{IE}}{2.3 RT} + \frac{g_2^{IE}}{2.3 RT} \quad (2)$$

where

$V_g, V_{g,1}, V_{g,2}$ = specific retention volumes for the binary system and the first and second components, respectively;

w_1, w_2 = weight fractions for the components of the binary system;

g_1^{IE} = a value proportional to the excess free energy of mixing of the binary phase components;

g_2^{IE} = a value characterizing the specific interaction of the sorbate with the binary phase.

In the theory of the non-electrolyte solutions, the value of the excess free energy of mixing is expressed through the activity coefficients of the components of the binary solution with the Dewgem–Margules equation:

$$\frac{g^E}{2.3 RT} = X_1 \log \gamma_1 + X_2 \log \gamma_2 \quad (3)$$

where

γ_1, γ_2 = activity coefficients of the binary solution components;

X_1, X_2 = molar fractions of the binary solution components.

Various expressions have been given in the literature⁴ for the g^E value dependence in eqn. 3. One such dependence, suggested by Redlich and Kister⁵, has the following form:

$$\phi = \frac{g^E}{2.3 RT} = X_1(1 - X_1)[B + C(2 X_1 - 1) + D(2 X_1 - 1)^2 + \dots] \quad (4)$$

where B, C and D are constants and X_1 is the molar fraction of one of the components.

In this work it is suggested that the ratio from the theory of non-electrolyte solutions is used to describe the retention dependence on the composition of any binary system with eqn. 2, but g_1^{IE} and g_2^{IE} values with eqn. 4:

$$\phi_1 = \frac{g_1^{IE}}{2.3 RT} = w_1(1 - w_1)[B_w + C_w(2 w_1 - 1) + D_w(2 w_1 - 1)^2 + \dots] \quad (5)$$

$$\phi_2 = \frac{g_2^{IE}}{2.3 RT} = w_1(1 - w_2)[B_s + C_s(2 w_1 - 1) + D_s(2 w_1 - 1)^2 + \dots] \quad (6)$$

where B_w, C_w, D_w are constants characterizing deviations in the behavior of the binary system from ideality and B_s, C_s, D_s are constants characterizing the specific interaction of the sorbate with the binary system.

To find B_w, C_w and D_w , the dependence of $\log V_g$ for n -decane on the composition of binary system was used with the assumption that the retention of n -decane is not characterized by a specific interaction, that is, $\phi_s = 0$. To determine B_s ,

C_s, D_s , we used the dependence of the relative retained volume of sorbates (by decane) on the composition of the binary system:

$$\log r = w_1 \log r_1 + (1 - w_1) \log r_2 + w_1(1 - w_1)[B_s + C_s(2w_1 - 1) + D_s(2w_1 - 1)^2] \quad (7)$$

where r_1 and r_2 are the relative retention volumes of the sorbate by n -decane. To limit the number of constants in equations such as eqns. 2 and 5-7 to two (linear dependence) and for the possible use of relative concentrations, the following empirical equation for Z_1 , which is a reduced variable, is suggested:

$$Z_1 = [b(w_{1,i} - w_{1,0})]^a \quad (8)$$

where

a = the empirical constant which was found experimentally to be equal to 0.25-4.00;

b = reciprocal of the concentration range used;

$w_{1,i}, w_{1,0}$ = variable values at the beginning of the range used and the current value of the same variable, respectively.

The value of Z_1 is varied from 0 to 1, and it should be noted that the value of Z_2 is calculated as the difference $1 - Z_1$.

The influence of the constant a in eqn. 8 on the dependence of $\log V_g$ on the composition of binary systems is illustrated by the example of the retention of diphenyl on the hydroxylated Silochrom-polyethylene glycol adipate (PEGA) system (Fig. 1). In this instance the number of constants in eqn. 1 is limited to only two. According to the experimental data (Fig. 1, curve 2) a linear dependence of the $f(Z_1)$ function (Fig. 2) was found, and the least-squares method gave $B = -1.323$ and $C = -0.483$.

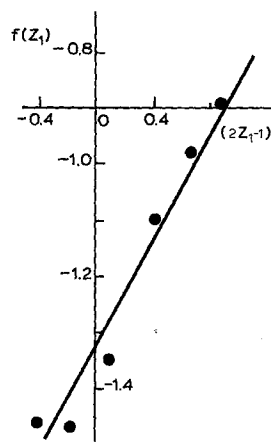
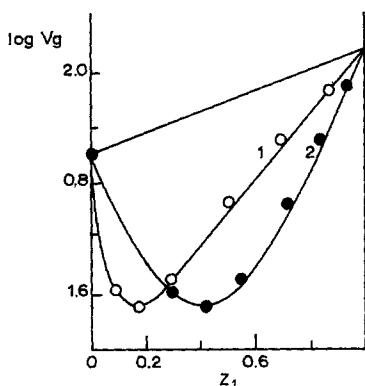


Fig. 1. Logarithmic dependence of the specific retention volume of diphenyl in the binary system hydroxylated Silochrom C-80-PEGA at 200°C on the relative mass fraction of stationary phase (1) and on the relative mass fraction raised to the power 0.5 (2).

Fig. 2. The $f(Z_1)$ function for diphenyl in the binary system Silochrom C-80-PEGA.

The log V_g dependence for diphenyl was obtained by the equation

$$\log V_g = Z_1 \cdot 2.0495 + (1 - Z_1) \cdot 1.8555 + Z_1(1 - Z_2)[-1.323 + 0.483(2Z_1 - 1)] \quad (9)$$

where $Z = [3C/(100 + C)]^{0.5}$ and C is the PEGA mass fraction from Silochrom weight percent, %; 2.0495 and 1.8555 are the log V_g values at the point $C(50\%)$ and for the initial hydroxylated Silochrom, respectively.

We now consider the binary system: *p-n*-dioctyloxybenzene-liquid crystal. As the initial part of the log V_g dependence has a complicated form, we took 3% as the starting point and 20% as the final point. All the points within this range were considered in the relative weight percent.

According to the data in Table I, the dependence of V_g for *n*-decane on the composition of the binary system can be described by

$$\log V_g = Z_1 \cdot 2.0224 + (1 - Z_1) \cdot 2.2188 + Z_1(1 - Z_1)[-0.2822 + 0.0740(2Z_1 - 1) + 0.1435(2Z_1 - 1)^2] \quad (10)$$

where $B_w = -0.2822$, $C_w = 0.0740$ and $D_w = 0.1435$; 2.0224 and 2.2188 are the log V_g values at the points 20 and 3 wt.-%, respectively; $Z_1 = [(C - 3)/17]^{0.81}$; C is the mass fraction of the liquid crystal from the Silochrom weight percent.

For specifically retained sorbates such as benzene, ethanol, methyl ethyl ketone and nitromethane, eqns. 6-9 were obtained, together with those describing the dependence of V_g on the composition of the binary system by the $f_w(Z_1)$ function for *n*-decane and also by the constants B_s , C_s and D_s . The equations have the following forms:

for benzene,

$$\log V_g = 1.1072 Z_1 + 1.4579(1 - Z_1) + Z_1(1 - Z_1)f_w(Z_1) + Z_1(1 - Z_1)[-0.5701 + 0.4992(2Z_1 - 1) - 0.1435(2Z_1 - 1)^2] \quad (11)$$

TABLE I

RELATIVE (TO *n*-NONANE) RETENTION VOLUMES FOR SORBATES AT 100°C ON HYDROXYLATED SILOCHROM C-80 (80 m²/g) MODIFIED WITH 0-20% *p-n*-DIOCTYLOXYBENZENE

Sorbate	<i>p-n</i> -Octyloxybenzene content (%)							
	0	1	3	6	9	12	15	20
Benzene	0.541	0.528	0.353	0.229	0.205	0.212	0.225	0.242
Ethanol	10.40	8.18	4.66	2.23	1.66	1.55	1.47	1.42
Methyl ethyl ketone	22.60	22.60	21.00	10.70	4.00	2.39	2.09	1.89
Nitromethane	2.28	2.32	1.45	0.870	0.758	0.733	0.672	0.713
<i>n</i> -Hexane	0.136	0.133	0.125	0.118	0.114	0.116	0.122	0.124
<i>n</i> -Decane	1.94	1.97	2.04	2.05	1.97	1.98	1.98	1.98
<i>n</i> -Nonane ^a	77.80	57.80	81.30	63.80	59.10	55.10	54.50	53.00

^a The specific retention volume is given in ml/g.

for ethanol,

$$\log V_g = 1.1874 Z_1 + 2.5786 (1 - Z_1) + Z_1(1 - Z_1) f_w(Z_1) + Z_1(1 - Z_1)[-0.8040 + 0.4855 (2 Z_1 - 1) - 0.1435 (2 Z_1 - 1)^2] \quad (12)$$

for methyl ethyl ketone,

$$\log V_g = 2.000 Z_1 + 2.9395 (1 - Z_1) + Z_1(1 - Z_1) f_w(Z_1) + Z_1(1 - Z_1)[-1.1960 + 0.4839 (2 Z_1 - 1) + 0.3546 (2 Z_1 - 1)^2] \quad (13)$$

and for nitromethane,

$$\log V_g = 1.5775 Z_1 + 2.0719 (1 - Z_1) + Z_1(1 - Z_1) f_w(Z_1) + Z_1(1 - Z_1)[-0.4979 + 0.3015 (2 Z_1 - 1) - 0.6939 (2 Z_1 - 1)^2] \quad (14)$$

where

$$f_w(Z_1) = -0.2822 + 0.0740 (2 Z_1 - 1) + 0.1435 (2 Z_1 - 1)^2.$$

Eqns. 6-9 allow the contribution of the specific interaction of the sorbate with a binary system to be quantified and its influence on the separation coefficient (relative retention) to be estimated. A comparison of the data calculated using eqns. 6-9 with the experimental results shows that the deviation does not exceed 5-6%.

The calculation of V_g for *n*-nonane and *n*-hexane was effected using eqn. 10 with substitution of the values 2.0224 and 2.2188 by the relevant data for *n*-nonane and *n*-hexane at the points of 20 and 3% (w/w). The calculated and experimental data are given in Table II.

Similar calculations for binary systems of Silochrom C-80 with cholesterol pelargonate (liquid crystal), phthalocyanine dilithium and vinyl acetate-ethylene copolymer were also made.

Hence the possibility of using thermodynamic principles from the theory of non-electrolyte solutions to express the retention from the composition of a binary system through the activity coefficients of the constituents and also through the activity coefficients that characterize the specific interaction of a sorbate with a binary system has been demonstrated.

TABLE II

DATA CALCULATED USING EQNS. 6-9 AND THE CORRESPONDING EXPERIMENTAL VALUES

V_g values for various sorbates on dehydroxylated Silochrom C-80 modified with *p*-*n*-dioctyloxazoxybenzene at 100°C are given.

C (%, w/w)	Z_1	Benzene		Ethanol		Methyl ethyl ketone		Nitromethane		n-Hexane		n-Nonane	
		$V_g^{calc.}$	$V_g^{exp.}$	$V_g^{calc.}$	$V_g^{exp.}$	$V_g^{calc.}$	$V_g^{exp.}$	$V_g^{calc.}$	$V_g^{exp.}$	$V_g^{calc.}$	$V_g^{exp.}$	$V_g^{calc.}$	$V_g^{exp.}$
6	0.245	14.0	14.6	143.0	142.0	255	255	55.8	55.5	8.12	7.50	64.9	63.8
9	0.430	12.4	12.1	98.9	98.2	143	141	45.3	44.8	7.18	6.72	57.4	59.1
12	0.597	11.9	11.7	84.2	85.2	113	115	40.0	40.4	6.80	6.40	54.4	55.1
15	0.754	12.5	12.3	82.2	80.0	108	108	36.3	36.6	6.72	6.67	53.9	54.5

EXPERIMENTAL

The gas chromatographic measurements were made with the Tsvet-152 chromatograph under isothermal conditions. Glass columns (200 × 0.3 cm I.D.) and a flame ionization detector were used. The oven temperature was maintained constant within $\pm 0.1^\circ\text{C}$. The relative error of the retention volume ($P = 0.95$) was 2.5–3.5%.

Binary systems of Silochrom C-80 with cholesterol pelargonate⁶, *p*-*n*-dioctyloxyazoxybenzene, phthalocyanine dilithium⁷, polyethylene glycol adipate and ethylene–vinyl acetate copolymer⁸ were studied.

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