CHROM. 25 385

Inverse gas chromatography in characterization of surfactants

Determination of binary parameter

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ABSTRACT

Binary parameters corresponding to hydrogen bonding ($I_{12\,h}$) and polar ($I_{12\,p}$) interactions were determined by inverse gas chromatography. The influence of the structures of broad-range and narrow-range distributed oxyethylene derivatives of 1-hexadecanol on the binary parameters was studied. The relationship between the binary parameters ($I_{12\,h}$ and $I_{12\,p}$) and the polarity of the compounds used as stationary phases is presented and discussed, in addition to the effect of the solubility parameter and its increments on the values of the two binary parameters.

INTRODUCTION

Inverse gas chromatography (IGC) is widely used in the characterization of the physico-chemical properties of a variety of liquid and solid materials. The term "inverse" indicates that the material of interest is placed in a chromatographic column (as the stationary phase) and that the retention data for the test solutes are measured. Physico-chemical parameters calculated from retention data described intermolecular solute–examined material interactions, which are influenced by the properties of

the liquid or solid used as the stationary phase [1] in the chromatographic system.

The properties of polymers and their blends can be determined relatively easily and accurately by IGC parameters. The Flory–Huggins solute–polymer interaction parameter is given as

$$\chi_{1,2}^{\infty} = \ln\left(\frac{273.15R}{p_1^0 V_g^0 M_1}\right) - \frac{p_1^0}{RT}(B_{11} - V_1^0)$$
$$+ \ln\left(\frac{\rho_1}{\rho_2}r\right) - \left(1 - \frac{V_1^0}{V_2^0}\right) \quad (1)$$

where M_1, p_1^0, B_{11}, V_1^0, ρ_1 and V_g^0 are the molecular mass, saturated vapour pressure, second virial coefficient, molar volume and specific retention volume of the solute, respectively; ρ_2

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and V_2^0 are the density and molar volume of the polymer, respectively, T is the column temperature and R is the gas constant. In the evaluation of eqn. 1, the value of V_1^0/V_2^0 is normally taken as zero. The parameter χ^∞ exhibits high values for poor solvents [2-6] whereas low values indicate good solubility.

The cohesive energy, E_{coh}, of a substance in a condensed state is defined as the increase in internal energy, U, per mole of substance if all intermolecular forces are eliminated. The square root of the cohesive energy density is called the solubility parameter, δ, and is defined as $\delta_1 = (E_{coh}/V)^{1/2}$ $(J/m^3)^{1/2}$. The units of solubility parameter are $(cal/cm^3)^{1/2}$, $(J/m^3)^{1/2}$ or $(MPa)^{1/2}$.

The solubility parameter of a volatile compound can be calculated from the basic equation

$$\delta = \left(\frac{\Delta H_v - RT}{V_1^0} \right)^{1/2} \qquad (2)$$

where ΔH_v is the enthalpy of vaporization, R in the gas constant, T is the absolute temperature and V_1^0 is the molar volume of the compound.

For low-volatile or non-volatile species, the use of eqn. 2 is not possible. Guillet and DiPaola-Baranyi [7,8] presented a procedure for the evaluation of the solubility parameter for polymeric substances with the use of the solute-solvent interaction parameter χ^∞. They applied the Hildebrand-Scatchard expression of χ^∞ in the form

$$\chi^\infty = \frac{V_1^0(\delta_1 - \delta_2)^2}{RT} + \chi_s^\infty \qquad (3)$$

where V_1^0 is the solute molar volume, δ_1 and δ_2 are solubility parameters of the solute and solvent, respectively, and χ_s^∞ is the entropic factor of the interaction parameter. This led to the equation

$$\frac{\delta_1^2}{RT} - \frac{\chi^\infty}{V_1^0} = \frac{2\delta_2}{RT} \cdot \delta_1 - \left(\frac{\delta_2^2}{RT} + \frac{\chi_s^\infty}{V_1^0} \right) \qquad (4)$$

which allowed the calculation of the solubility parameter, δ_2, of the substance used as the stationary phase in the chromatographic system.

The application this procedure has been reported in several papers [7,9-19]. Most often,

excellent linearity is obtained when using eqn. 4 [1]. However, Price [13] reported the significant deviations from linearity for compounds (stationary phases) having relatively low molecular mass. Price determined the contributions to the solubility parameter attributed to dispersive (δ_d) and polar (δ_p) solute-solvent interactions. Recently, Voelkel and Janas [20,21] followed up this idea. They examined oligooxyethylene derivatives of 1-hexadecanol and oligooxyethylene surfactants having perfluoroalkane groups in their hydrophobic parts. They separated three contributions corresponding to the dispersive, polar and hydrogen bonding interactions. This allowed the determination of the total, corrected solubility parameter from the equation earlier proposed by Hansen [22,23] for cohesive energy contributions:

$$\delta_T^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \qquad (5)$$

However, the Hildebrand-Scatchard theory [24,25] and eqn. 3 are valid under the assumptions that the volume change of mixing is zero and the segment interactions are binary, and these assumptions are valid only for non-polar systems, where the only molecular forces are London or dispersive forces. It is possible that deviations observed by Price et al. [13], Becerra et al. [14] and Voelkel and Janas [20,21] are caused by Debye, Keesom or hydrogen bonding interactions negligible for high-molecular-mass polymer-solute systems.

As was shown by Mikos and Peppas [26], the enthalpic component of the solute-solvent interaction parameter should be modified as follows:

$$\chi_h^\infty = \frac{V_1^0}{RT} [(\delta_1 - \delta_2)^2 + 2I_{12}\delta_1\delta_2] \qquad (6)$$

where I_{12} is a binary parameter. Binary parameters depend on the molecular size and the chemical nature of the interacting species, and may be positive or negative depending on molecular interactions [24,25]. For the applicability of the Hildebrand-Scatchard theory, $I_{12} = 0$.

Rearranging eqn. 6, we obtain

$$\frac{\delta_1^2}{RT} - \frac{\chi^\infty}{V_1^0} = \frac{2\delta_2(1 - I_{12})}{RT} \cdot \delta_1 - \left(\frac{\delta_2^2}{RT} + \frac{\chi_s^\infty}{V_1^0} \right) \qquad (7)$$

where the slope of hypothetical straight line depends on the value of I_{12}.

Plotting the left-hand side of eqn. 7 *versus* δ_1, it is possible to obtain straight lines of different slopes [20,21] if only solutes of one of the following three groups are used, each group representing different types of intermolecular interactions, *i.e.*, dispersive, polar and hydrogen bonding interactions:

(a) The first group is *n*-alkanes. Here the slope of the straight line would be the same as that obtained with eqn. 4, as it may be assumed that no specific intermolecular interactions exist between the examined material and this type of test probe (*i.e.*, $I_{12} = 0$).

(b) A second group of probes represent polar interactions, for which the slope of the line obtained on application of eqn. 7 would be

$$\text{slope}_{\text{polar}} = \frac{2\delta_2}{RT}\,(1 - I_{12p}) \qquad (8)$$

where I_{12p} denotes a binary parameter for polar interactions.

(c) The third group of probes represent hydrogen bonding properties. Here,

$$\text{slope}_{\text{H-bond}} = \frac{2\delta_2}{RT}\,(1 - I_{12h}) \qquad (9)$$

where I_{12h} represents a binary parameter for hydrogen bonding interactions.

The aim of this work was to evaluate binary parameters for the set of oligooxyethylene derivatives of 1-hexadecanol, evaluate and discuss the relationships between polarity parameters, solubility parameters and derived binary parameters, discuss the effect of the structures of the compounds examined on the binary parameters and examine the temperature dependence of both binary parameters.

EXPERIMENTAL

Materials

1-Hexadecanol of 94.5% purity was used to obtain conventional products with a broad-range distribution (BRD) of homologues and narrow-range distributed ethoxylates (NRD) having an average ethoxylation number from 3 to 11. NRD products are characterized by a lower content of

homologues with a number of oxyethylene units significantly different from the average. Moreover, comparison of the homologue distribution in NRD products indicates a slight shift of the maximum towards a higher content of oxyethylene groups. Conventional products were obtained using sodium hydroxide as a catalyst, whereas a proprietary catalyst was utilized to produce NRD ethoxylates. All products were synthesized at the Institute of Heavy Organic Synthesis "Blachownia". Kędzięrzyn-Koźle, Poland. Other data on these products were presented in previous papers [20,27].

IGC experiments

The examined oxyethylate was placed in a GC column as liquid stationary phase coated on an inert support of Celite (80–120 mesh) (25%, w/w). The use of such a high content of liquid phase is suggested to eliminate adsorption effects. Other conditions for the GC experiments were as follows: chromatograph CHROM 5 (Kovo, Prague, Czech Republic) equipped with a flame ionization detector; column, 1 m × 3 mm I.D.; column temperatures (isothermal), 70, 90 and 110°C; injector temperature, 150°C; detector temperature, 200°C; and carrier gas (helium) flow-rate, 40 ml/min. The testing probes were *n*-alkanes from *n*-pentane to *n*-decane, benzene, toluene, xylene, ethylbenzene, *n*-alkanols from methanol to 1-butanol, 2-butanone, 2-pentanone, nitropropane and pyridine. Their adjusted retention times were determined as described [28–30].

RESULTS AND DISCUSSION

We assumed that the values of I_{12} are similar within each of the three selected groups of test solutes, *i.e.*, alkanes, hydrogen-bonding probes and polar probes. This assumption is justified by the occurrence of straight lines for each group. If the I_{12} values within a group were significantly different for each solute–solvent pair, application of eqn. 7 would not produce a straight line. Moreover, we also assumed that the value of I_{12} for an alkane–stationary phase pair is zero, although Preston and Prausnitz [31] reported I_{12} values for carbon dioxide–alkanes mixtures dif-

ferent from but very close to zero. In other words, one should treat our values of binary parameters $I_{12\,p}$ and $I_{12\,h}$ as a measure of the deviation from the stationary phase–alkane system.

The values of the binary parameters are presented in Tables I and II. We should discuss the dependence of I_{12} on the type of stationary phase–BRD and NRD series of oxyethylates examined, the length of the oxyethylene chain, the series of test solutes and the temperature of the chromatographic column. Almost all reported values are negative and lie, with a few exceptions, in the range 0 to −0.5. The values of $I_{12\,h}$ for donor–acceptor series of solutes decrease with increase in oxyethylation ratio for both the BRD and NRD series of oxyethylates. The lowest values are observed for "homologues" containing 7 (BRD) or 6–8 (NRD) oxyethylene units. For products having more than 8–9 oxyethylene units $I_{12\,h}$ increases. For NRD products one may observe a wide minimum for both $I_{12\,h}$ and $I_{12\,p}$ (Fig. 1). $I_{12\,p}$ is

TABLE I

BINARY PARAMETER $I_{12\,h}$ FOR HYDROGEN BONDING INTERACTIONS IN PROBE–STATIONARY PHASE SYSTEMS

Type	Average number of EO units	$I_{12\,h}$		
		70°C	90°C	110°C
BRD	3	−0.063	0.087	−0.082
	4	−0.237	−0.252	−0.174
	5	−0.375	−0.385	−0.349
	6	−0.410	−0.458	−0.446
	7	−0.636	−0.650	−0.672
	8	−0.547	−0.596	−0.579
	9	−0.435	−0.385	−0.475
	10	−0.283	−0.337	−0.405
	11	−0.292	−0.286	−0.233
NRD	3	−0.315	−0.300	−0.321
	4	−0.322	−0.330	−0.347
	5	−0.440	−0.430	−0.461
	6	−0.489	−0.477	−0.542
	7	−0.480	−0.420	−0.461
	8	−0.485	−0.424	−0.428
	9	−0.358	−0.380	−0.417
	10	−0.273	−0.335	−0.344
	11	−0.282	−0.323	−0.335

TABLE II

BINARY PARAMETER $I_{12\,p}$ FOR POLAR INTERACTIONS IN PROBE–STATIONARY PHASE SYSTEMS

Type	Average number of EO units	$I_{12\,p}$		
		70°C	90°C	110°C
BRD	3	0.026	0.001	−0.010
	4	−0.110	−0.125	−0.062
	5	−0.126	−0.170	−0.255
	6	−0.159	−0.166	−0.173
	7	−0.404	−0.418	−0.428
	8	−0.342	−0.368	−0.388
	9	−0.272	−0.275	−0.282
	10	−0.253	−0.292	−0.356
	11	−0.312	−0.307	−0.365
NRD	3	−0.089	−0.079	−0.108
	4	−0.146	−0.183	−0.206
	5	−0.276	−0.258	−0.278
	6	−0.310	−0.290	−0.335
	7	−0.321	−0.264	−0.268
	8	−0.382	−0.351	−0.406
	9	−0.203	−0.230	−0.261
	10	−0.140	−0.208	−0.224
	11	−0.112	−0.107	−0.165

always higher and for $C_{16}E_3$ (BRD) it is even positive. The influence of the oxyethylation ratio on $I_{12\,p}$ is similar to that on $I_{12\,h}$. The difference between $I_{12\,h}$ and $I_{12\,p}$ for BRD oxyethylates decreases with increasing oxyethlation ratio whereas for NRD products this difference is approximately constant and equal to 0.2 (Fig. 2). The type of distribution of oxyethylene products significantly influences the range of changes in the $I_{12\,h}$ and $I_{12\,p}$ binary parameters. The difference between their highest and lowest values is much larger for BRD products, e.g., at 70°C the maximum $\Delta I_{12\,h}$ (BRD) = 0.573 whereas the maximum $\Delta I_{12\,h}$ (NRD) = 0.212.

The effect of temperature on the values of $I_{12\,h}$ and $I_{12\,p}$ can be given various interpretations. Both $I_{12\,h}$ and $I_{12\,p}$ increase or decrease in value depending on the particular stationary phase used. In several extreme cases deviations were observed at 90°C. No general rule can be formulated for the temperature dependence of the binary parameters determined by an IGC method.
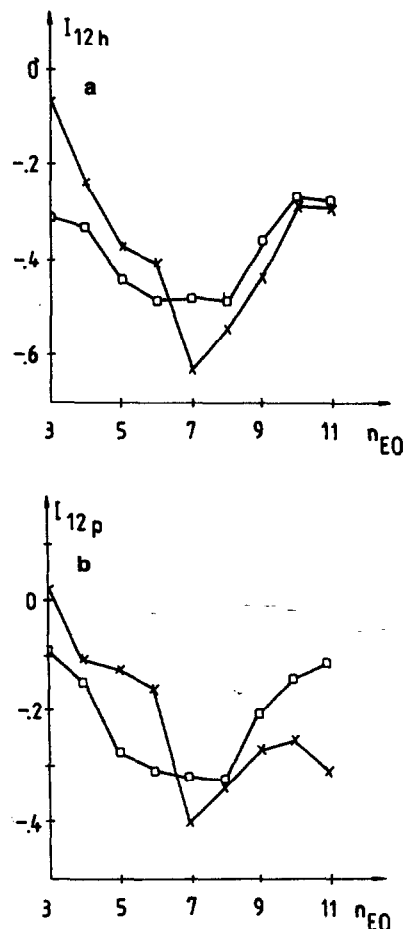
Fig. 1. Influence of the number of oxyethylene units and the type of their distribution on binary parameters at 70°C. × = BRD oxyethylates; □ = NRD oxyethylates.

Fig. 2. Comparison of binary parameters for (a) BRD oxyethylates and (b) NRD oxyethylates at 70°C. × = $I_{12\,h}$; □ = $I_{12\,p}$.

Oligooxyethylene derivatives of 1-hexadecanol were previously characterized by polarity parameters [27] and also by the solubility parameter δ_2 and its increments corresponding to dispersive, polar and hydrogen bonding interactions. $I_{12\,h}$ and $I_{12\,p}$ decrease with increasing polarity of the stationary phase as measured by the sum of the first five McReynolds constants [32] $\Sigma_{i=1}^{5}\,\Delta I_i$ and/or the polarity index PI (Fig. 3). A narrow minimum is observed for an $\Sigma_{i=1}^{5}\,\Delta I_i$ value of ca. 1100 i.u. for BRD products, whereas for NRD analogues minimum I_{12} values are observed over a fairly wide range of $\Sigma_{i=1}^{5}\,\Delta I_i$ values (1000–1200).
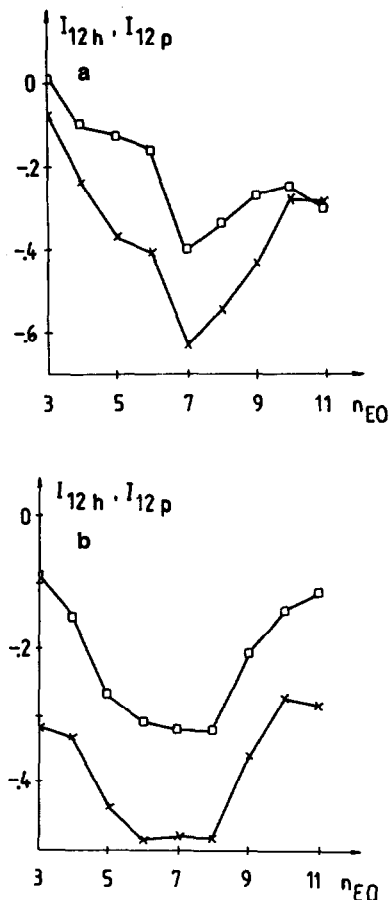
A strong relationship exists between the bina-

ry parameters discussed here and the increments of the solubility parameters corresponding to interactions of the hydrogen bonding (δ_h) and polar (δ_p) types determined earlier by Voelkel and Janas [20]. The respective linear relationships are as follows:

$$I_{12\,h} = -9.944\delta_h + 1.604 \quad R = 0.960 \tag{10}$$

$$I_{12\,p} = -11.563\delta_p + 0.702 \quad R = 0.976 \tag{11}$$

Both $I_{12\,h}$ and $I_{12\,p}$ decrease with increase in the corresponding component of the solubility parameter (Fig. 4). The deviations from a regular solution (as measured by I_{12}) increase with increasing contribution of hydrogen bonding and
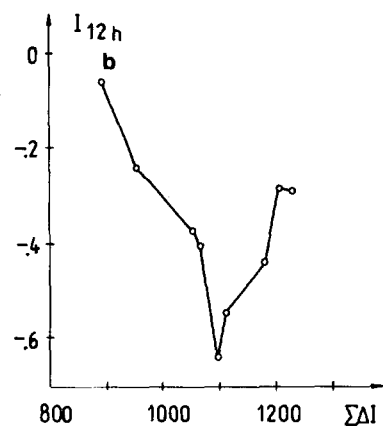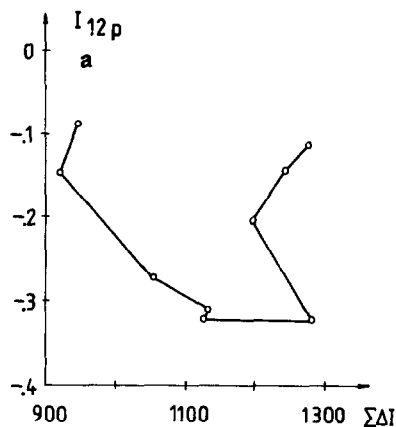
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Fig. 3. Influence of the polarity of the stationary phase on its binary parameters at 70°C: (a) $I_{12\,h}$ *vs.* $\Sigma_{i=1}^{5}\Delta I_i$ for BRD oxyethylates; (b) $I_{12\,p}$ *vs.* $\Sigma_{i=1}^{5}\Delta I_i$ for NRD oxyethylates.

polar binary parameters to the total solute–solvent interactions.

CONCLUSIONS

It has been shown that the binary parameters $I_{12\,h}$ and $I_{12\,p}$ can be calculated from GC data. The values of the binary parameters were determined not for single species but for two groups of test solutes representing hydrogen bonding and polar solute–solvent interactions. This means that a given value of a binary parameter (*e.g.*, $I_{12\,h}$) is characteristic of solutes that can interact with the solvent (stationary phase) by hydrogen bonding interactions. As the sets of test solutes were the same for each oxyethylate examined, the changes in the hydro-
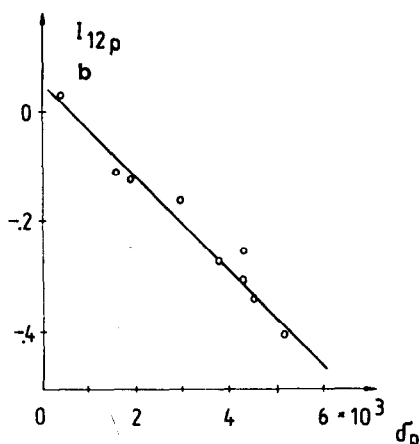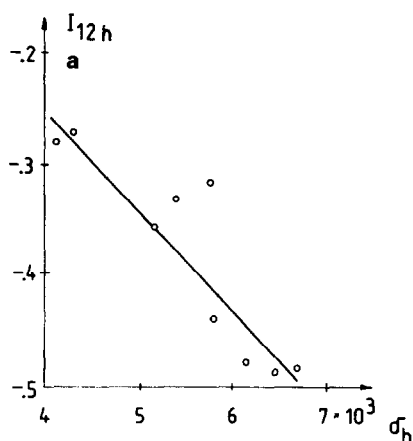

Fig. 4. Relationship between binary parameters and increments of solubility parameter at 70°C: (a) $I_{12\,h}$ *vs.* δ_h for NRD oxyethylates; (b) $I_{12\,p}$ *vs.* δ_p for BRD oxyethylates.

gen bonding $I_{12\,h}$ and polar $I_{12\,p}$ binary parameters may be attributed to changes in the structure of the stationary phase and to the temperature of the chromatographic column. $I_{12\,h}$ and $I_{12\,p}$ are a measure of the deviations from a regular solution for a given solute–solvent system. No general relationship was found between $I_{12\,h}$ and $I_{12\,p}$ and the temperature of the chromatographic column.

The relationships between the binary parameters and polarity parameters exhibit minima of different character depending on the type of oxyethylate (BRD or NRD). The significant relationship between $I_{12\,h}$ and $I_{12\,p}$ and the corresponding increments of the solubility parameter indicates that an increasing contribution

of hydrogen bonding and polar interactions increases the deviations from a regular solution.

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