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Inverse gas chromatographic determination of solubility parameter and binary parameters of α,ω -diamino oligoethers

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Abstract

The solubility parameter and its components corresponding to dispersive, polar and hydrogen bonding interactions, determined by inverse gas chromatography, were used for physico-chemical characterization of nineteen α,ω -diamino oligoethers. The influence of the structure of examined compounds on the solubility parameters was examined. Relationships between solubility and polarity parameters are presented.

1. Introduction

Inverse gas chromatography appeared to be a rapid, sensitive and accurate method for characterizing polymers, their blends, composites, fibres and surfactants [1,2]. The properties of the substance, which were liquids under the experimental conditions, were often quantified by the solubility parameter introduced by Hildebrand and Scott [3]. The procedure of DiPaola-Baranyi and Guillet [4,5] was most often applied to polymers and their blends [1,6–8]. Voelkel and Janas [9,10] proposed a modification that allowed the solubility parameter to be separated into components corresponding to different solute–solvent intermolecular interactions. Recently, Voelkel *et al.* [11] presented a procedure for the determination of binary interaction param-

eters I_{12p} and I_{12h} , which are a measure of deviations from regular solution.

Alkyl derivatives of α,ω -diamino oligoethers have been tested as drugs [12,13] and pesticides and as crown ether analogues for the extraction of mercury(II) chloride and metals [14].

The aim of this work was to determine the solubility parameter and its increments for the group of extractants, to study the relationships between the structure and physico-chemical parameters of the compounds examined and to establish the relationships between polarity and solubility parameters.

2. Experimental

2.1. Materials

Nineteen pure, model compounds with the structures shown were used as liquid stationary

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phases. Methods for their preparation and some physico-chemical data were presented in a previous paper [15].

2.2. Chromatographic measurements

Chromatographic measurements were carried out using a Chrom 5 gas chromatograph (Kovo, Czech Republic) equipped with a flame ionization detector. The conditions were as follows: column, 1 m × 3 mm I.D.; column temperature, 90°C; column packing, 25% (w/w) of the compound on Porolith (mesh size 0.2–0.5 mm); carrier gas (helium) flow-rate, 40 ml/min; solutes, C₅–C₁₀ *n*-alkanes, benzene, toluene, C₁–

C₄ alkanols, 2-butanone, 2-pentanone, nitropropane and pyridine; time for column stabilization, 10 h.

The solubility parameter δ_2 was calculated from the equation proposed by DiPaola-Baranyi and Guillet [4,5]:

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

where δ_1 and δ_2 are the solubility parameters of the test solute and stationary phase, respectively, χ^∞ and χ_s^∞ are the Hildebrand–Schatchard interaction parameter and its entropic component, respectively, V_1^0 is the molar volume of the test solute, R is the gas constant and T is absolute temperature.

Components of the solubility parameter corresponding to dispersive (δ_d), polar (δ_p) and hydrogen bonding (δ_h) interactions and the corrected solubility parameter were determined and calculated according to the procedure proposed previously [9,10]. Eq. 1 was used separately for three groups of solutes; (i) *n*-alkanes; (ii) polar non-hydrogen-bonding test solutes (aromatic hydrocarbons, ketones and nitropropane); and (iii) alcohols and pyridine. It was assumed that the slope of Eq. 1 for *n*-alkanes is proportional to the dispersive component of the solubility parameter:

$$\delta_d = \frac{\text{slope}_{n\text{-alkanes}} \cdot RT}{2} \quad (2)$$

The polar increment of the solubility parameter, δ_p , was calculated from the difference in the slopes for polar solutes and *n*-alkanes:

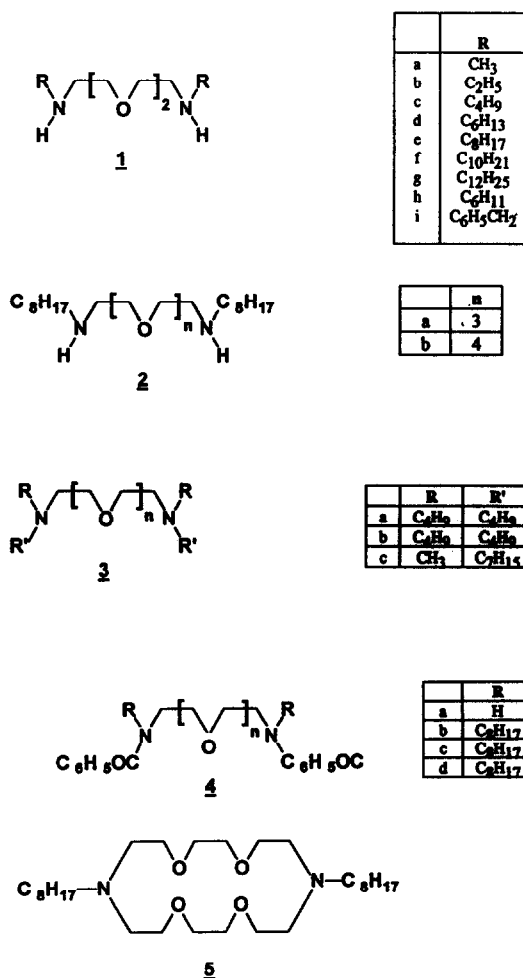
$$\delta_p = \frac{(\text{slope}_{\text{polar}} - \text{slope}_{n\text{-alkanes}})RT}{2} \quad (3)$$

and the hydrogen bonding component, δ_h , from the corresponding relationship for *n*-alkanols, pyridine and *n*-alkanes:

$$\delta_h = \frac{(\text{slope}_{\text{alcohols}} - \text{slope}_{n\text{-alkanes}})RT}{2} \quad (4)$$

The corrected value of the solubility parameter was calculated from the equation

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



The procedure for the determination of binary interactions parameters of hydrogen bonding (I_{12h}) and polar (I_{12p}) interactions was presented elsewhere [9].

3. Results and discussion

The compounds examined are of relatively low molecular mass. The first question was the applicability of DiPaola-Baranyi and Guillet's procedure for the calculation of the solubility parameter δ_2 . As previously [9,10], we observed some small deviations from the linear relationship in Eq. 1, an upward curvature being found for all the stationary phases examined. The values of the solubility parameter and its components are presented in Table 1. The confidence intervals for all the parameters examined lie in the range ± 0.1 to ± 0.2 units.

The values of the solubility parameter δ_2 of $\text{RHCH}_2(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{NHR}$ depend significantly on the structure, and decrease with increasing of the length of the alkyl group (compounds **1a–g**). The corrected solubility param-

eter δ_T decreases sharply for the first three or four members of this group whereas later the relationship becomes almost linear (Fig. 1). Similar relationships are observed for the components δ_p and δ_h of the solubility parameter. The dispersive component, δ_d , increases almost linearly with increase in the length of the alkyl group. An increase in the length of oligooxyethylene chain from 2 to 4 oxyethylene units causes an increase in δ_2 (compounds **1e**, **2a** and **2b**) from $16.7 \cdot 10^3$ to $17.1 \cdot 10^3$ (J/m^3)^{1/2}.

A decrease in δ_2 (by 1.9 units) is connected with a significant decrease in the polar (δ_p) (by 1.4 units) and hydrogen bonding (δ_h) (by 3.2 units) components, whereas the dispersive component (δ_d) increases by 1.4 units. The corrected solubility parameter is always lower than δ_2 by 1.8–2.4 units. Similar differences between δ_2 and δ_T were observed previously for polyoxyethylene derivatives of fatty alcohols [9] and non-ionic surfactants containing a fluorocarbon hydrophobe [10].

The increase of decrease in the corrected solubility parameter δ_T is caused, of course, by the changes in its components (Fig. 2). However, only the δ_T vs. δ_h relationship may be described as exponential or almost linear. An increase in δ_d causes a significant decrease in δ_T , whereas an increase in δ_p or δ_h leads to an increase in δ_T .

The binary parameters of polar (I_{12p}) and hydrogen bonding (I_{12h}) interactions are measures of deviations from regular solution. For all compounds examined I_{12p} and I_{12h} are negative (Table 2). With an increase in the length of the alkyl chain the binary parameters increase towards zero, reflecting the decreasing differences between actual and regular solutions. The increases in I_{12p} and I_{12h} correspond to decreases in the polar δ_p and hydrogen bonding δ_h components of the solubility parameter.

The distribution of carbon atoms in the groups linked with nitrogen atoms significantly influences all the parameters. The solubility parameter δ_2 and the corrected solubility parameter δ_T for compound **3a** are higher than those for compound **1e** by 1.0 and 0.6 units, respectively.

It was observed that the influence of the

Table 1
Solubility parameters for α,ω -diamino oligoethers at 90°C
[10^3 (J/m^3)^{1/2}]

Compound	δ_2	δ_d	δ_p	δ_h	δ_T
1a	18.1	11.1	5.1	10.2	15.9
1b	17.6	11.2	4.5	9.5	15.4
1c	17.2	11.4	4.0	9.1	15.1
1d	16.9	11.6	3.7	8.5	14.9
1e	16.7	11.8	3.6	8.2	14.8
1f	16.6	12.1	3.5	7.6	14.7
1g	16.2	12.5	3.0	7.0	14.6
1h	17.0	11.5	3.8	8.8	15.0
1i	16.8	11.8	3.7	8.1	14.8
2a	16.9	11.7	3.9	8.4	14.9
2b	17.1	11.7	4.1	8.8	15.2
3a	17.7	11.0	4.6	9.7	15.4
3b	18.2	10.5	5.3	10.1	15.8
3c	17.6	11.1	4.8	9.6	15.5
4a	18.3	10.9	6.0	10.0	16.0
4b	17.0	11.2	4.6	8.7	14.9
4c	17.3	11.1	5.1	8.9	15.1
4d	17.5	11.0	5.3	9.2	15.3
5	17.1	11.7	4.2	8.6	15.1

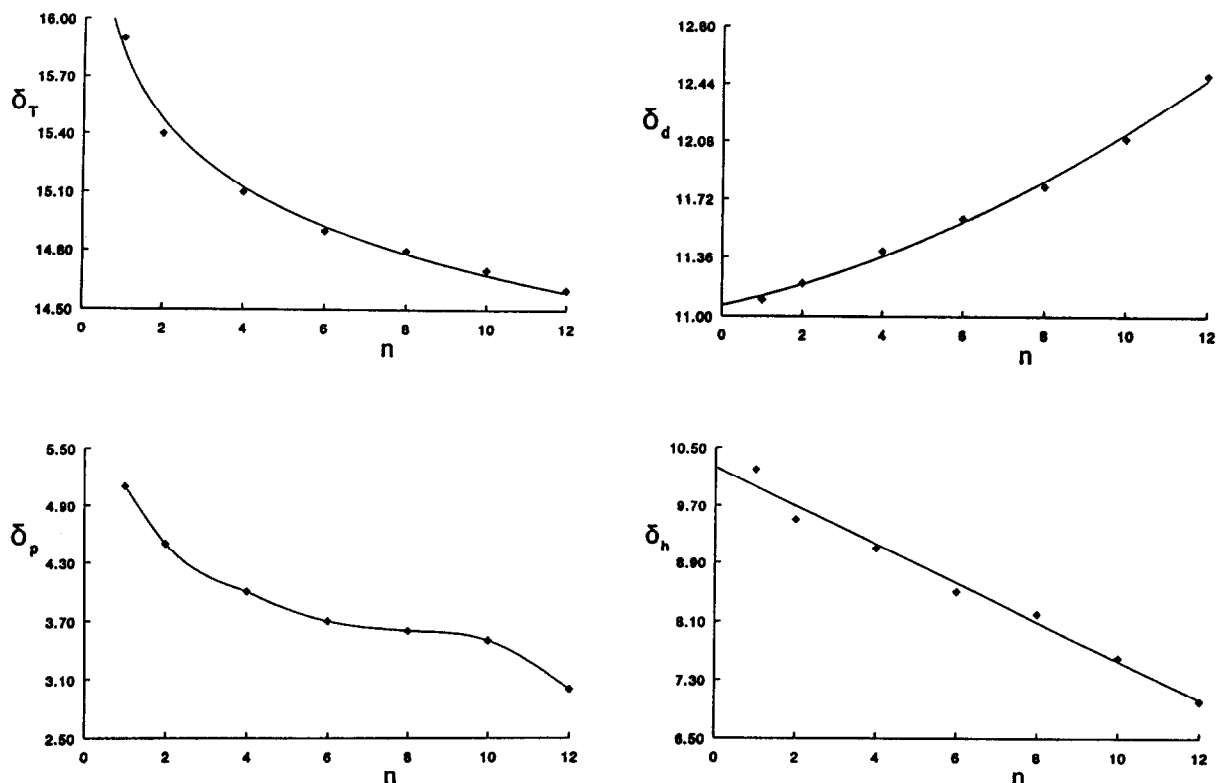


Fig. 1. Influence of the number of carbon atoms in the alkyl chain (group 1) on corrected solubility parameter and increments of solubility parameter.

oligooxyethylene chain length on the polarity of the compounds is much stronger for compounds having two short alkyl chains linked with each nitrogen atom than for compounds with one large alkyl group. For example, the differences in polarity index values for compounds **3a** and **3b** were much higher than those for **1e** and **2b**. However, the difference between the discussed solubility parameters is similar for both pairs of compounds. Here, $\delta_2(\mathbf{3b}) - \delta_2(\mathbf{3a}) \approx \delta_2(\mathbf{2b}) - \delta_2(\mathbf{1e})$. Similar relationships are observed when the corrected solubility parameter δ_T or the components δ_p and δ_h are considered.

The replacement of a hydrogen atom with a methyl group and a further change from a methyl to a butyl group cause significant increases in δ_2 , δ_T and the components of the solubility parameter corresponding to specific interactions. For example, δ_h increases from $8.8 \cdot 10^3$ to $9.6 \cdot 10^3$ and $10.1 \cdot 10^3$ (J/m^3)^{1/2} for com-

pounds **2b**, **3c** and **3b**, respectively. These changes in the structure cause a decrease in δ_d by 1.2 units. For this group of extractants the lowest values of the binary parameter are observed for the compound having four butyl groups linked with two nitrogen atoms.

The linear, "open-chain" compound **2b** exhibits almost the same "activity" as the cyclic crown ether **5** when this "activity" is measured by the solubility parameter or its components. The values of the solubility parameter δ_2 and the dispersive component δ_d are the same for both compounds [$17.1 \cdot 10^3$ and $11.7 \cdot 10^3$ (J/m^3)^{1/2}, respectively]. The other solubility parameters are only slightly different. A similar situation was observed when the polarity parameters of these compounds were discussed previously [15]. We assumed that the relatively low polarity of **2b** is caused by the presence of intramolecular hydrogen bonding. In fact, the hydrogen bonding

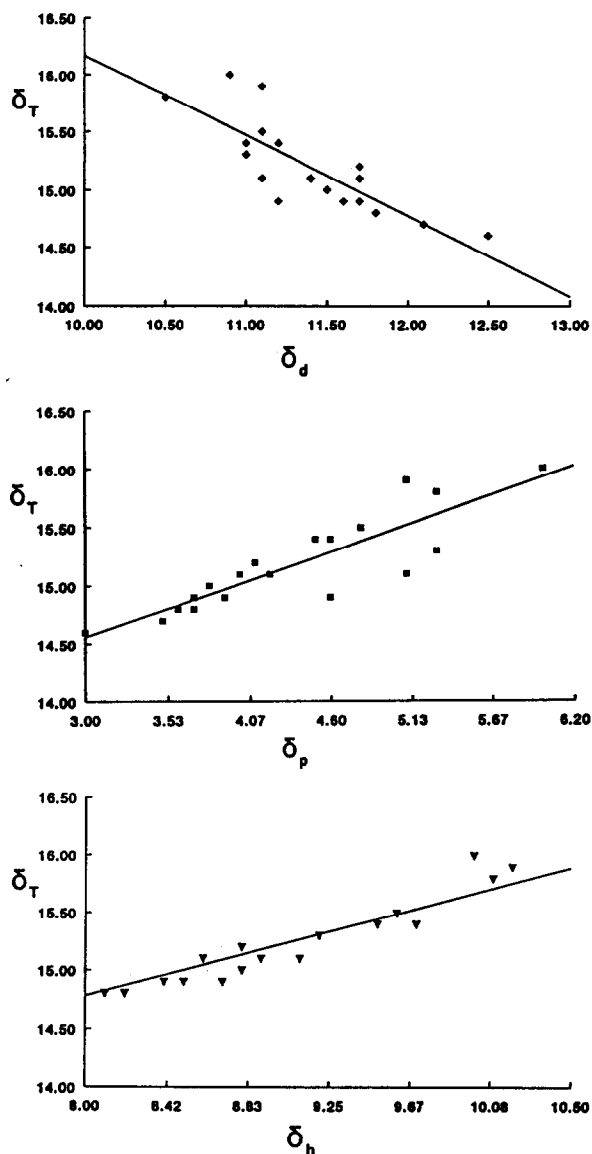


Fig. 2. Relationships between corrected solubility parameter and its components.

increment of the solubility parameter δ_d is slightly higher for the "open-chain" analogue.

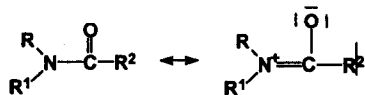
Compounds **1d** and **h** contain linear and cyclic alkyl groups with the same number of carbon atoms. Values of the solubility parameter δ_2 and the corrected solubility parameter δ_T are almost the same for both compounds, the difference being 0.1 unit. However, the specific interaction

Table 2
Binary parameters for α,ω -diaminooligoethers at 90°C

Compound	I_{12h}	I_{12p}
1a	-0.609	-0.453
1b	-0.587	-0.375
1c	-0.526	-0.342
1d	-0.468	-0.305
1e	-0.388	-0.215
1f	-0.382	-0.211
1g	-0.374	-0.183
1h	-0.472	-0.315
1i	-0.430	-0.292
2a	-0.444	-0.287
2b	-0.492	-0.317
3a	-0.537	-0.382
3b	-0.592	-0.433
3c	-0.555	-0.376
4a	-0.624	-0.448
4b	-0.472	-0.303
4c	-0.511	-0.320
4d	-0.547	-0.350
5	-0.500	-0.308

increments δ_p and δ_h are slightly higher for **1h** by 0.1 and 0.3 units, respectively. Values of both binary parameters I_{12p} and I_{12h} are slightly lower for the homologue containing a cyclic alkyl group. The replacement of the octyl group in **1e** with a benzyl group in **1i** results in a small increase in δ_2 while the corrected solubility parameter δ_T remains the same [$14.8 \cdot 10^3$ (J/m³)^{1/2}]. The differences between the values of the components of the solubility parameter for these compounds do not exceed 0.1 unit. When the octyl group is replaced with a benzoyl group a rapid increase in δ_2 , δ_T , δ_p and δ_h is observed, accompanied by a significant decrease in δ_d . The values of δ_2 for these compounds may be arranged in the order: **1e** < **1i** << **4a**. The presence of a benzoyl group in compounds **4** is so significant that compounds **4b**, **c** and **d** exhibit much higher values of all solubility parameters (with exception of δ_d) than the analogous compounds **1e**, **2a** and **2b**, respectively. However, values of δ_2 , δ_T and δ_h for the benzoyl derivatives **4b** and **d** are still lower than those obtained for **3a** and **b** in which each nitrogen atom is connected with two short alkyl groups. The relatively high polarity of compounds **4** was attributed previously [15] to

the presence of slightly acidic nitrogen atoms and the formation of two mesomeric structures:



The activity of compounds 1, 2, 3 and 5 is connected with the strong basicity of nitrogen atoms due to the free electron pairs.

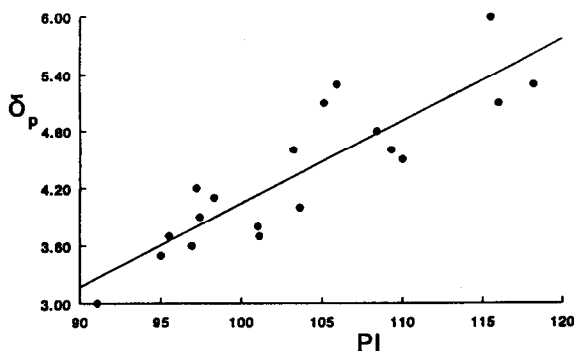
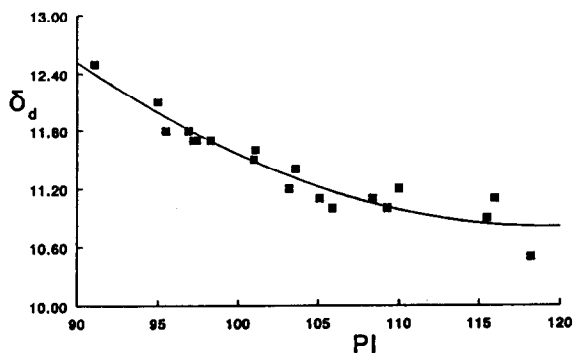
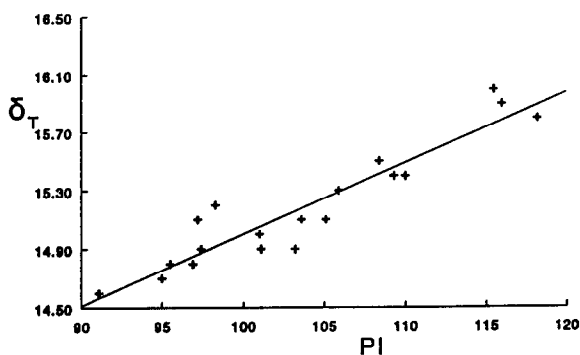


Fig. 3. Relationships between solubility parameters and polarity index for compounds 1–5.

The high values of the corrected solubility parameter δ_T for compounds 4 results from the high values of the polar component of the solubility parameter δ_p as $\delta_p(4) > \delta_p(3)$. The hydrogen bonding interaction component of the solubility parameter δ_h is significantly lower for compounds 4 than for compounds 3.

All compounds in groups 3 and 4 are characterized by low values of the binary parameters I_{12p} and I_{12h} . Hence, for these compounds the deviations from the regular solution state are most significant. I_{12p} and I_{12h} decreases with increase in oligooxyethylene chain length.

The compounds examined were previously characterized by polarity parameters [15]. The corrected solubility parameter δ_T and components corresponding to polar and hydrogen bonding interactions increase whereas the dispersive component decreases with increasing polarity index (PI) (Fig. 3). All the relationships are characterized by acceptable correlation coefficients:

$$\delta_T = 0.048PI + 10.2; \quad R = 0.932 \quad (6)$$

$$\delta_d = -0.057PI + 17.2; \quad R = 0.922 \quad (7)$$

$$\delta_p = 0.087PI - 4.6; \quad R = 0.870 \quad (8)$$

$$\delta_h = 0.104PI - 1.9; \quad R = 0.951 \quad (9)$$

It is worth noting that for δ_h vs. PI relationship a much better correlation coefficient was obtained than for the δ_p vs. PI relationship. This means that PI describes intermolecular interactions corresponding to hydrogen bonding rather than those called generally polar. This is probably a result of the use of alcohols as test solutes in the determination of the polarity index.

4. Conclusions

The solubility parameter δ_2 or, better, the corrected solubility parameter and its components corresponding to dispersive, polar and hydrogen bonding interactions can be used for the physico-chemical characterisation of metal extractants. These parameters reflect small changes in the structure of the compounds examined. Generally, the solubility parameter δ_2 and the corrected solubility parameter δ_T and

also specific components of the solubility parameter increase with decrease in the length of alkyl groups and increase in oligooxyethylene chain length. Higher values of the solubility parameters were found for compounds having shorter alkyl groups linked with nitrogen atoms in comparison than for compounds with one longer alkyl chain. Probably this is connected with the higher basicity of the nitrogen atom in compounds **3**. Statistically significant relationships were found between the corrected solubility parameter δ_T , the components of the solubility parameter δ_p , δ_h and δ_d and the polarity index PI used previously for the characterization of the compounds examined.

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