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APPLICATION OF HANSEN SOLUBILITY PARAMETERS TO EXTRACTION PROCESS OF PHENOLIC COMPOUNDS FROM CHAMOMILE INFLORESCENCES

ZASTOSOWANIE PARAMETRÓW ROZPUSZCZALNOŚCI HANSENA DO PROCESU EKSTRAKCJI ZWIĄZKÓW FENOLOWYCH Z KWIATÓW RUMIANKU

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Abstract: The aim of this work was to determine a practical usefulness of literature Hansen solubility parameters to determine the composition of solvents for efficient extraction of active compounds present in chamomile inflorescences. The Hoy's method was used to compute the components of the Hansen solubility parameters for mixtures of solvents and for some model phenolic compounds present in this plant material. The numerical values of the parameters obtained in such a way for mixtures of two components systems: water – ethanol, were presented using Bagley's plot. It was assumed that the condition for a correct selection of the extrahent mixture is the distance on the Bagley's plot below 5 $MPa^{(1/2)}$ between the mixture of solvents and the extracted component. On this basis the optimum composition of the used solvents was found. This result was verified for the extraction process of polyphenolic compounds present in chamomile inflorescences. It was shown experimentally that in case of chamomile inflorescences the extrahent composition determined in such a way leads to obtainment of extracts with a high content of polyphenolic compounds.

Keywords: antioxidants, chamomile inflorescences, extraction, solubility parameters.

Streszczenie: Celem badań podjętych w niniejszej pracy było określenie praktycznej przydatności tablicowych wartości składowych parametrów rozpuszczalności Hansena do określania składu rozpuszczalników, zapewniających wydajną ekstrakcję składników aktywnych zawartych w kwiatach rumianku. Stosując metodę Hoya, obliczono wartości składowych parametrów rozpuszczalności mieszanin rozpuszczalników oraz modelowych związków fenolowych obecnych w tym surowcu roślinnym. Tak otrzymane wartości oraz odpowiednie wartości dla mieszanin dwuskładnikowych układów: woda – etanol przedstawiono na wykresie Bagleya. W pracy założono, że warunkiem poprawnego doboru składu mieszaniny ekstrakcyjnej jest odległość tej mieszaniny od ekstrahowanego składnika na wykresie Bagleya poniżej 5 $MPa^{(1/2)}$. Na tej podstawie wyznaczono optymalny skład mieszaniny ekstrakcyjnej. Wynik zweryfikowano dla procesu ekstrakcji związków polifenolowych z kwiatów rumianku.

Doświadczalnie wykazano, że w przypadku kwiatów rumianku tak wyznaczony skład ekstrahentu prowadzi do uzyskania ekstraktów o wysokiej zawartości związków polifenolowych.

Słowa kluczowe: przeciwutleniacze, kwiat rumianku, ekstrakcja, parametr rozpuszczalności.

1. INTRODUCTION

At a given temperature the solubility of a solute is defined as the property of solid, liquid, or gaseous chemical substance called solute to dissolve in a given single or mixed solvent to form a homogeneous solution of the solute in the solvent. One has to note, however, that this definition of solubility refers only to a non-reactive interaction. The concept of the solubility parameter, δ, proposed by Hildebrand [Hildebrand 1935; Hildebrand and Scott 1970] is an important idea that can be used for the rational selection of solvents. The value of δ was defined as the total cohesion energy, E_{coh}, divided by the molar volume, V, by the following relationship:

$$\delta = \sqrt{\frac{E_{coh}}{V}}$$

In literature the numerical values of solubility parameters are usually given in $MPa^{(1/2)}$ ($1\ cal^{1/2}cm^{-3/2} = 2.0455\ MPa^{(1/2)}$). They are used in a huge number of scientific works and practical fields for estimating interaction capacities and solubilities of various organic liquids, polymers, and even some solids [Karger 1978; Duclairoir et al. 1998; Ramos et al. 2013; Sarode et al. 2013]. In literature [Hansen 1967; Barton 1983; Just et al. 2013] one can find numerous further examples of their application. It should be noted, however, that simple Hildebrand solubility parameter concept does not adequately describe solute solubility behavior when polar and hydrogen bonding interaction occur in the system. To overcome this problem it was proposed [Hansen 1967; Hansen 2007] to divide the total cohesion energy density, δ^2, into three components and represent the value of δ^2 as a sum of the cohesion energy densities required to overcome atomic London dispersion forces, δ_d^2, forces to overcome polar interactions, δ_p^2, and forces needed to break hydrogen bonds between molecules, δ_h^2:

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$

Some computational methods for determination numerical values of δ_d, δ_p and δ_h based on summation of group contributions attributed to chemical structure of solvents and solutes are published in literature [Hansen 1967; Hoy 1970; van Krevelen 1976; Hoy 1989; Hansen 2007; Stefanis and Panayiotou 2008; Just et al. 2013]. According to the group-contribution method proposed by Hoy [Hoy 1970; Hoy 1989] in order to estimate the solubility parameters we have to use the system of equations containing four additive molar functions (auxiliary equations) and

the final expressions for the components of δ. In the case of low-molar mass solvents and solutes the additive molar functions used in Hoy's method are as follows:

$$F = \sum_i N_i \cdot F_{ti} \qquad F_p = \sum_i N_i \cdot F_{pi} \qquad V = \sum N_i \cdot V_i \qquad \Delta_T = \sum_i N_i \cdot \Delta_{Ti}$$

where F is the molar attraction function, F_p is its polar component, V is the molar volume (in cm^3/mol) and Δ_T is the Lydersen's correction for non-ideality which is used in the auxiliary equations. The auxiliary equations are as follows:

$$\log \alpha = 3.39 \cdot (T_b / T_c) - 0.1585 - \log V$$

$$T_b / T_c = 0.567 + \Delta_T - (\Delta_T)^2$$

where α is the molecular aggregation number which describes the association of molecules, T_b is the boiling point, and T_c is the critical temperature.

The numerical values of the total solubility parameter, δ, and its components in the Hoy's method are computed using the following equations:

$$\delta = \frac{F_t + B}{V} \qquad \delta_p = \delta \cdot \left(\frac{1}{\alpha} \cdot \frac{F_p}{F_t + B} \right)^{1/2} \qquad \delta_h = \delta \cdot \left(\frac{\alpha - 1}{\alpha} \right)^{1/2}$$

$$\delta_d = \left(\delta^2 - \delta_p^2 - \delta_h^2 \right)^{1/2}$$

where B is the base value (B = 277).

In this work there is applied solubility parameters concept in evaluation of solvent composition for extraction of active compounds present in plant material. It is well known that antiradical activity of phenolic compounds and flavonoids is a very important property utilized not only in food but also in cosmetic and farmaceutical products. Chamomile inflorescences tea is used as a liquid feed and mild plant tonic. An essential oil from the whole chamomile plant is used as a flavoring and in making perfume. The dried chamomile inflorescences are used as an effective insect repellent. In some cases the inflorescences are added to cosmetics as an anti-allergenic agent or made into a salve for use on hemorrhoids and wounds. An infusion of chamomile inflorescences is used as an active component of hair shampoo, especially for fair hair. It is reasonable to suppose that antiradical activity of chamomile inflorescences extracts should strongly depend on the solvent composition used in the extraction process.

Chamomile inflorescences (*Chamomilla Recutita*) contain few biologically active compounds such as a volatile oil (0,3–1,2%) of a dark blue color (becoming yellow during storage), a little anthemic acid (having a bitter taste), tannic acid, sesquiterpenes (up to 50%) i.e. (-)-alfa-bisabolol [Cavalieri et al. 2011], poliacethylenes: mainly enin dicycloether, sesquiterpene lactones: deacetylomatricarine,

matricarine, matricine, flavonoids (up to 8%): apigenin, quercetin, luteolin, patuletin, 7-glucosides of apigenin, luteolin, quercetin, and 7-monoglucosides of apigenin and luteolin. In chamomile inflorescences we can also find some mucous substances (0,5–17%), hydroxylcumarines (herniarine and umbeliferon), phenolic acids and choline.

In the previous work [Wagemann and Zieliński 2011] there was studied the effect of extraction time of chamomile inflorescences using various of ethanol – water mixtures in order to obtain the information on the antiradical activity the extracts of a potential use in cosmetics. In this work there were described results of experimental work on extraction of active compounds present in chamomile inflorescences using the same solvent systems. The authors compared the experimentally found optimum composition of the used solvents based on few experimental methods to the results obtained from the Hoy's method [Hoy 1970; Hoy 1989].

2. EXPERIMENTAL

2.1. Materials

Chamomile inflorescences (*chamomilla recutita*) were a product of herba lux company. A special grade of ethyl alcohol sample containing 99.9% of etoh (poch, poland) was used as supplied. In all experiments redistilled water was used which was additionally purified by means of a further boiling with alkaline $kmno_4$ solution and finally fractionally distilled.

2.2. Methods

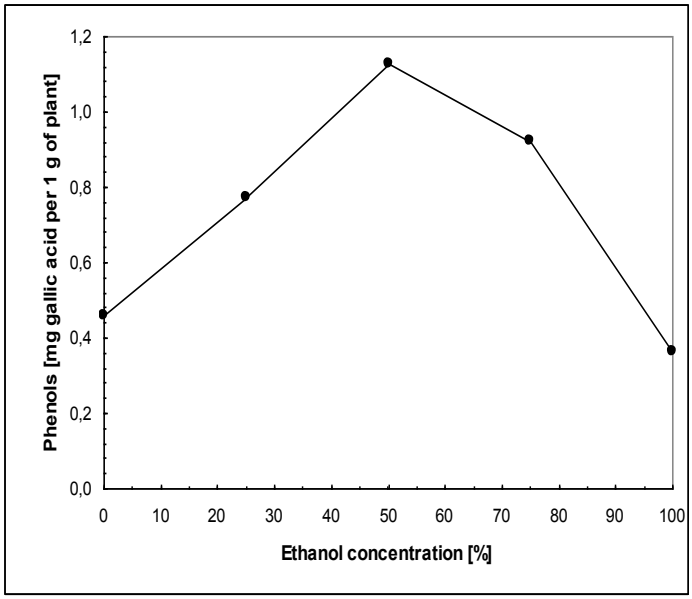
In the extraction research as solvents were used several ethanol – water mixtures containing 0, 25, 50, 75 and 100% (v/v) of ethanol. In each experiment the 3 g of chamomile inflorescences were placed in dark bottles and stirred at room temperature for 5 minutes with 200 cm^3 of the designed solvent. After that the samples were kept without stirring in a dark compartment for 24 hours at room temperature and then filtered under a slightly reduced pressure. The filtrates obtained in such a way were analyzed for antiradical properties using standard methods described in details in the previous work [Wagemann and Zieliński 2011].

3. RESULTS AND DISCUSSION

Figure 1 shows the effect of ethanol concentration on total content of phenolic compounds found in extracts. As can be seen the highest amount of phenolics is extracted from chamomile inflorescences using 50% ethanol solution in water.

In order to show the solubility parameters data in 2-D plane the author draw the data using a plot proposed by Bagley [Bagley and Chen 1969] in the $\delta_v - \delta_a$ coordinates system defined by:

$$\delta_v = \left(\delta_d^2 + \delta_p^2\right)^{1/2} \qquad \delta_a = \left(\delta_p^2 + \delta_h^2\right)^{1/2}$$



Source: own results.

Fig. 1. Effect of ethanol concentration in aqueous solution on phenolics content (in mg of gallic acid) in the extracts obtained after 24 h extraction of 1 g of chamomile inflorescences

Rys. 1. Wpływ stężenia etanolu w roztworach wodnych na całkowitą zawartość związków fenolowych (w mg kwasu galusowego) w ekstraktach otrzymanych po 24-godzinnej ekstrakcji 1 g kwiatów rumianku

The results of the computations of Hansen solubility parameters for some active components present in extracts of chamomile inflorescences are shown in Fig. 3. Following Bagley's work, it was assumed that the condition for a correct selection of the extrahent mixture is the distance on the plot below 5 $MPa^{(1/2)}$ between

the mixture of solvents and the extracted component. On this basis the optimum composition of the used solvents was found. The corresponding regions for two mixtures are given in Fig. 3 for extrahents containing 50% ethanol (dotted circle) and 100% ethanol (solid circle).

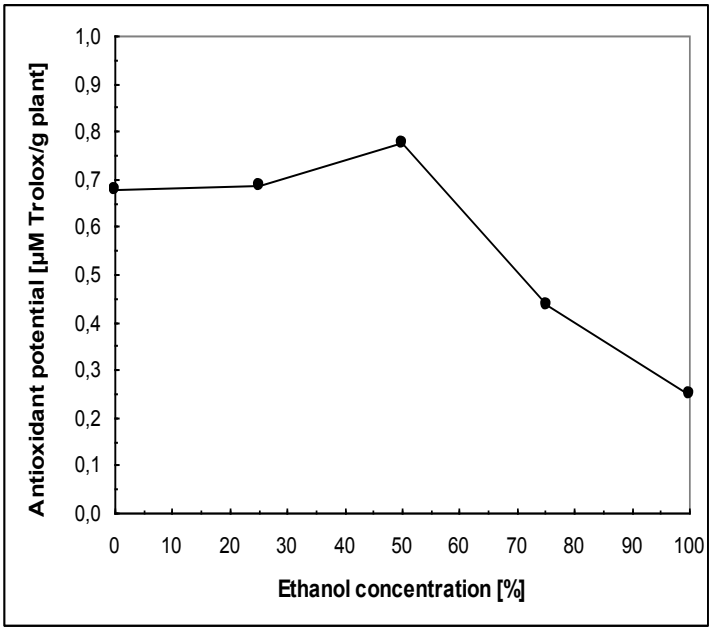


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Fig. 2. Effect of ethanol concentration in aqueous solutions on the antioxidant potential of extracts after 24 h extraction of 1 g of chamomile inflorescences by means of TEAC assay

Rys. 2. Wpływ stężenia etanolu w roztworach wodnych na potencjał przeciwutleniający ekstraktów po 24-godzinnej ekstrakcji 1 g kwiatów rumianku wyznaczoną metodą TEAC

As can be seen, the maximum phenols concentration (Fig. 1) and antioxidant potential of the extracts (Fig. 2) corresponds to *ca.* 50% concentration of ethanol in extrahent mixture. In general, a location of the solute in the Bagley's plot inside the circle of radius of 5 $MPa^{(1/2)}$ is attributed to good solubility of the solute by a tested solvent composition. It is generally accepted that the location of the solute far from the center of the solvent mixture in the Bagley's plot suggests a poor affinity of the solute to the solvent, thus such a solvent usually does not work efficiently as the extrahent of a given component.

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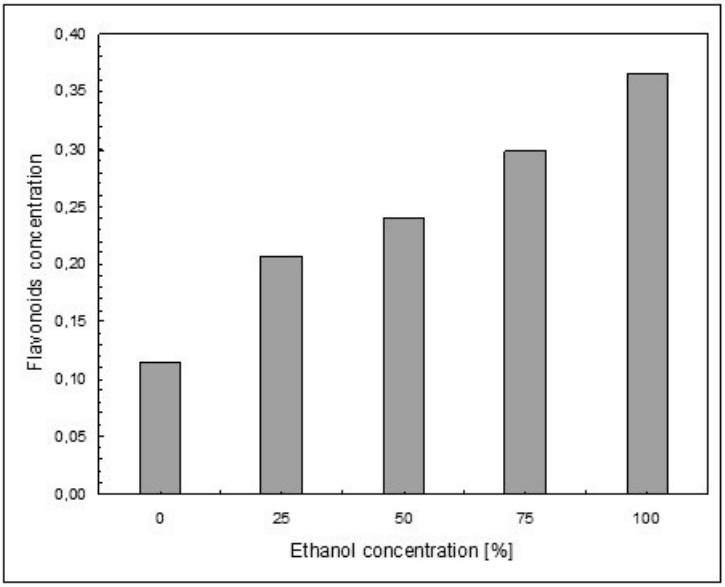

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Fig. 3. Effect of ethanol concentration in aqueous solutions on the total flavonoids content (in mg of (–)epicatechin) in extracts after 24 h extraction of 1 g of chamomile inflorescences

Rys. 3. Wpływ stężenia etanolu w roztworach wodnych na całkowitą zawartość flawonoidów (w mg (-)epicatechiny) w ekstraktach po 24-godzinnej ekstrakcji 1 g kwiatów rumianku

Figure 3 shows that the total content of flavonoids in the extracts increases with the increase of ethanol concentration in the solvent used for extraction of chamomile inflorescences reaching the maximum value for the solvent without water. The maximum concentration of flavonoids in this solvent is more than three times higher than that found in water. This result indicates the importance of the dispersive contribution to the extraction process of flavonoids from plants.

According to the data given in Fig. 4 a high antiradical activity of extracts obtained for aqueous solutions containing 50% ethanol can be attributed mainly to the presence of quercetin, luteolin and apigenin (located in this order from top to the bottom of the dotted circle in the Bagley's plot) of the extracts. Slightly lower activity of the ethanolic extracts can be related mainly to the effect of the presence of apigenin, caffeic acid and salicylic acid in the extracts.

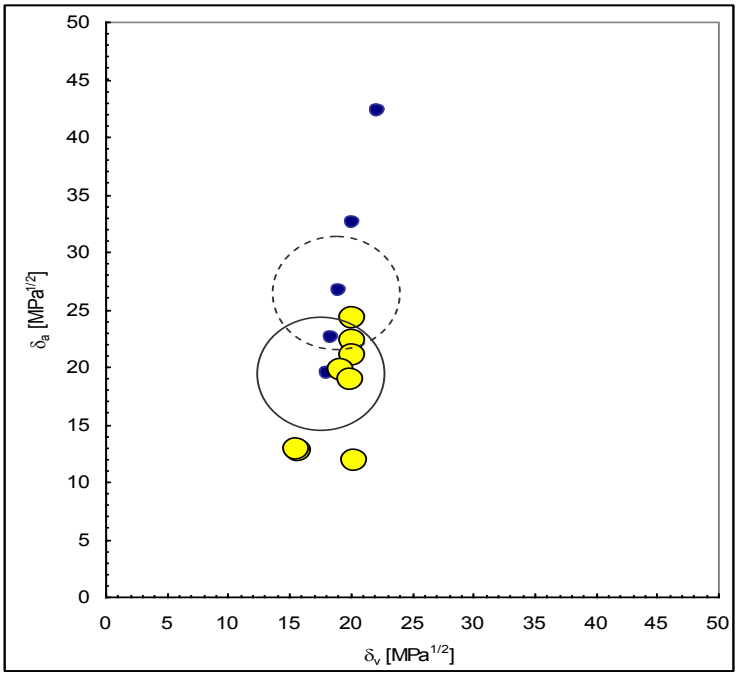

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Fig. 4. Bagley's plot for ethanol-water extracts of chamomile inflorescences

Rys. 4. Wykres Bagleya dla etanolowo-wodnych ekstraktów kwiatów rumianku

It was found that three compounds having δ_a values of *ca.* 12–13 MPa$^{(1/2)}$ correspond to alpha-bisabolol, beta-bisabolol and azulene. As can be seen in Fig. 4 they are located far outside of the Bagley's circle even for pure ethanol. Therefore, one can suppose that these compounds do not contribute significantly to the antioxidant properties of the chamomile extracts.

4. CONCLUSIONS

In this work the author examined a practical usefulness of literature Hansen solubility parameters to determine the composition of solvents for efficient extraction of active compounds present in the chamomile inflorescences. Using the Hoy's group contributions to the values of Hansen solubility parameters for mixtures of solvents and selected model phenolic compounds present in the tested plant material the author plotted the data using Bagley's plot. The author experimentally found that the optimum composition of ethanol-water mixtures allows for effective extraction of polyphenolic compounds present in chamomile inflorescences.

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