Experimental Investigation and Modelling of Inulin and Glycyrrhizin Extraction

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Inulin and glycyrrhizin extraction from crushed roots of chicory and licorice (Glycyrrhiza glabra) in batch contacting, with various liquid media, was studied in order to identify specific parameters characterizing process dynamics and equilibrium. In the case of non reactive extraction the process equilibrium was expressed by means of species distribution law between solid and liquid phases. Due to the structure of particle of chicory and licorice roots the extraction dynamics is controlled by species diffusion in its inside. In the case of chicory roots the rapid swelling of solid enhances the extraction process, whereas for the licorice roots this phenomenon can be neglected. The determined values of diffusion coefficients, which are near to those characterizing gel or liquid diffusion, can be explained as a swelling consequence. The obtained data can be used to scale-up a specific process for inulin and glycyrrhizin extraction.

Keywords: inulin, glycyrrhizin, solid-liquid extraction, effective diffusion coefficient, distribution coefficient

Inulin is a polysaccharide belonging to a class of fibres known as fructans. It is a linear polymer of D-fructose units joined by β-(2-1) glycoside bonds and terminated with a D-glucose molecule. Inulin can be found in some plants such as chicory, artichoke, dahlia, dandelion, agave, burdock, leek, onion, garlic etc. Plants inulin generally contains a number of fructose residues (degree of polymerization) between 2 to 65, with an average of about 10 [1]. Inulin is produced on an industrial scale from chicory roots [1-3]. Jerusalem artichoke tubers with 14-19 % inulin can be a valuable source of inulin, too [4,5]. From various extraction methods used to separate the active principles from plants tissues, e.g. solvent extraction, steam extraction, supercritical fluid extraction, pressurized liquid extraction, ultrasound-assisted extraction, microwave-assisted extraction etc [4,6-8], conventional extraction with hot solvent under stirring and ultrasound-assisted extraction are the most common techniques to obtain inulin. Extraction yield and quality of inulin depend on extraction technique, temperature and pH of extraction medium, operating time and solid/solvent ratio [4]. There are a lot of applications of inulin in food and pharmaceutical industries, due to its special properties such as very low caloric value, sweetening power, prebiotic activity and solubility in water with obtaining of viscous solutions [9]. Inulin is a soluble fibre which acts as a prebiotic, stimulating the growth and activity of bifid bacteria in colon, which implies a regulation of intestinal flora and thus an improvement of host health [9-11]. It can increase the calcium absorption in humans [1,12,13] and reduce the glucose and cholesterol absorption in rats [3,14].

Glycyrrhizin (also known as glycyrrhizic acid) is a triterpenoid saponin glycoside which is found up to 25 % in licorice (*Glycyrrhiza glabra*) roots together with other substances including other triterpenoids, polyphenols, polysaccharides, essential oils, pectins, flavonoids, amino acids, mineral salts, microelements etc [15]. It is an extremely sweet glycoside, from fifty to two hundred times sweeter than sugar. Glycyrrhizin has a lot of applications as a sweetener or flavouring agent in food industry, pharmaceuticals and tobacco products. It was established that it presents various types of pharmacological activity (antiviral, antiinflammatory, antiallergic, hepatoprotective, mineralocorticoid and expectorant) therefore it is used for numerous medical purposes, such as treatment of disorders in lungs, liver, respiratory tract, stomach, kidneys, hormones equilibrium etc [16-18].

This paper focuses on the qualitative and quantitative characterization of inulin and glycyrrhizin from particles of chicory and licorice roots by means of solvent batch extraction. The study aims at obtaining primary data which can be used to scale-up the extraction process in the industrial plants where these roots are processed.

Experimental part

Dried and crushed roots of chicory and licorice were used as starting vegetal material. The polydisperse granular structure of root particles was characterized by means of a volume equivalent diameter. Accordingly, the chicory crushed roots can be assumed as spheres with a volume equivalent diameter of 2.1 mm, whereas an equivalent diameter of 2.4 mm characterizes the licorice crushed roots. Distilled water and ethylic alcohol aqueous solutions with concentrations between 0.1 v/v and 0.9 v/v were tested as solvents for inulin extraction. Distilled water, ammonia aqueous solutions and ethylic alcohol aqueous solutions were used as initial liquid phases for glycyrrhizin extraction.

Experiments of batch extraction were performed at a constant temperature ($t = 70^0$C or $t = 20^0$C) under continuous stirring. The value of solvent/solid mass ratio was $r_w = 10$ and those of extraction medium volume was 0.5 L in each experiment. Extraction was made in two stages, the presented results referring to the first stage. Samples of inulin and glycyrrhizin solutions obtained during extraction, specially filtered to remove the colour, were used for species concentration measuring using an UV-VIS spectrophotometer CINTRA 6 GBS-Scientific. The crushed granular material was also characterized with respect to its swelling by measuring of volume increase when the material was immersed into the extraction medium.

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Table 1
SWELLING DYNAMICS OF CRUSHED ROOTS OF CHICORY AND LICORICE

No.	Time	Swelling coefficient $k_{SW} = \frac{V}{V_0} - 1$	
	min	m^3_l/m^3_s	
		chicory	licorice
1	5	0.09	0.04
2	10	0.17	0.08
3	15	0.23	0.10
4	20	0.26	0.11
5	25	0.28	0.12
6	30	0.29	0.12
7	35	0.29	0.12

Results and discussion

Dynamics of particles swelling

Data concerning swelling dynamics of crushed roots of chicory and licorice in distilled water at 70^{0}C are presented in table 1.

It was established that the change of liquid phase with other extraction liquids does not strongly affect the swelling coefficient, k_{SW}. The reported data emphasize that the swelling process lasts about 30 min and the chicory root particles present an accentuated swelling ($k_{SW,in}$=0.29 m^3_l/m^3_s) unlike those of licorice ($k_{SW,gh}$=0.12 m^3_l/m^3_s). Time evolution of the swelling for the both materials shows that this process is more rapid in comparison with the species diffusion from solid and, consequently, these processes can be decoupled.

Dynamics of inulin batch extraction

The curves from figure 1 and figure 2 show the dynamics of inulin concentration in liquid and solid phases at 70^{0}C. The both figures emphasize that inulin concentration in each phase is practically constant for contacting time greater than 5 h, when the system can be considered in equilibrium. It is obvious that distilled water is the most efficient solvent, the equilibrium extraction degree achieving a maximum value of 68.3 % (fig. 2). Data of extraction dynamics show that the particles are rapidly saturated with extraction medium and thus they swell, which determines an increase of mobility of inulin in swollen particles.

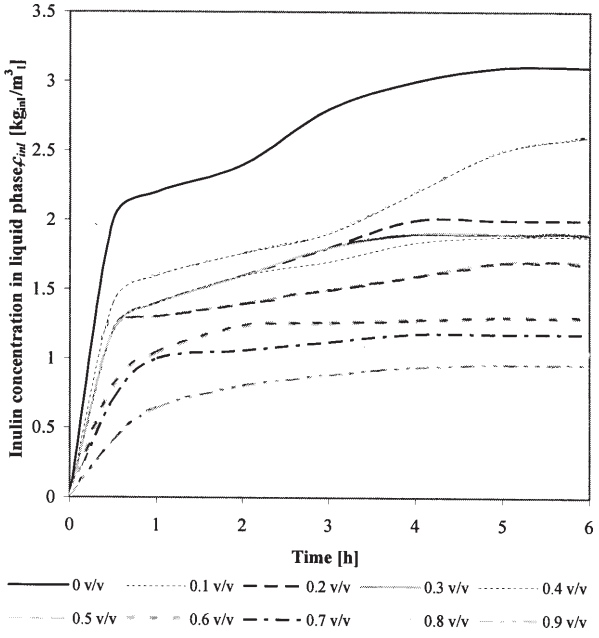

Fig. 1. Dynamics of inulin concentration in liquid phase for batch extraction with various ethylic alcohol solutions (r_m = 10, t = 70 ^{0}C)

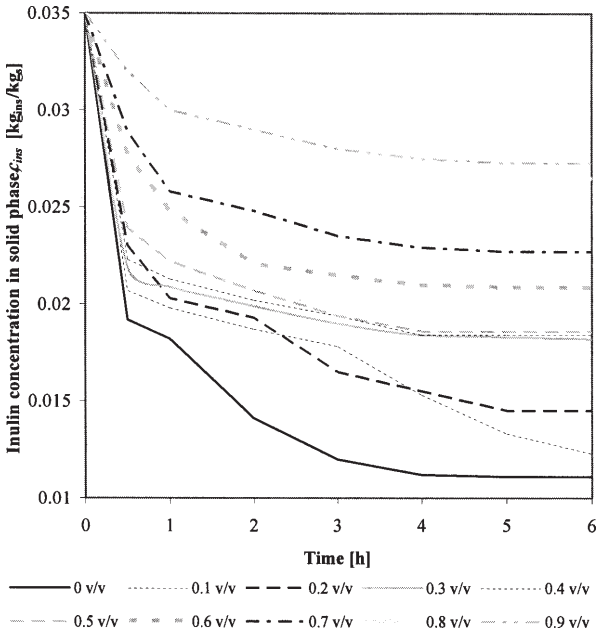

Fig. 2. Dynamics of inulin concentration in solid phase for batch extraction with various ethylic alcohol solutions (r_m = 10, t = 70 ^{0}C)

The equilibrium state is characterized by an inulin distribution coefficient, $K_{d,in}$, calculated with relationship (1), wherein $c_{ins\infty}$ and $c_{inl\infty}$ represent equilibrium inulin concentration in solid and liquid phase, respectively:

$$K_{d,\text{in}} = \left(c_{ins\infty} / c_{inl\infty}\right)_{t=const} \quad (1)$$

Figure 3, which illustrates inulin distribution coefficient, $K_{d,in}$, versus alcohol concentration in extraction medium, c_{alc}, emphasizes the linear dependency (2):

$$K_{d,\text{in}}(70\,^0C) = 0.027 c_{alc} + 1.25 \cdot 10^{-3} \quad (2)$$

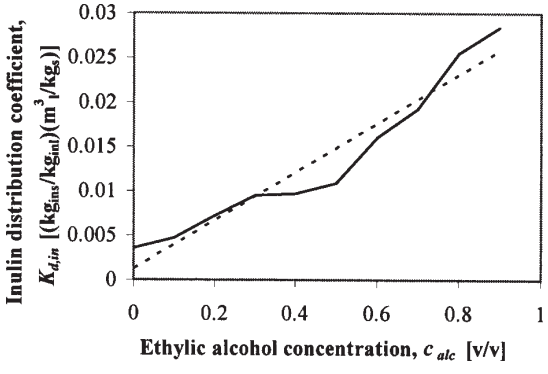

Fig. 3. Inulin distribution coefficient versus ethylic alcohol concentration: — eq. (1), - - - eq. (2)

Dynamics of glycyrrhizin batch extraction

In the case of glycyrrhizin extraction data given in figure 4 and figure 5 characterize the process dynamics for 5 initial extraction liquids (distilled water at 70°C, ammonia-water solution 0.0013 g_{NH3}/g_{sol} at 20°C, ammonia-water solution 0.0013 g_{NH3}/g_{sol} at 70°C and ethylic alcohol-water solution 0.3 v/v and 0.5 v/v at 70°C). We can retain as important by means of values of process efficiency the cases of extraction in cold ammonia-water solution and in ethylic alcohol-water solution 0.5 v/v. When the glycyrrhizin extraction occurs in ammonia-water solution, a chemical reaction of glycyrrhizin turning into an ammonia salt takes place at the particle surface. Consequently, the glycyrrhizin concentration at the particle surface becomes very small and this fact accelerates its transport from particle inside to surface. An esterification reaction between ethylic alcohol and glycyrrhizin can explain the results obtained when an ethylic alcohol aqueous solution is used as liquid phase in extraction process.

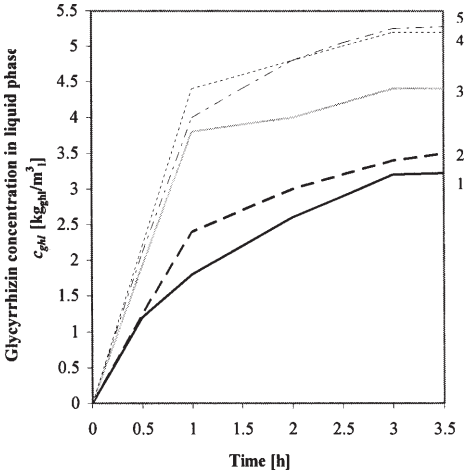

Fig. 4. Dynamics of glycyrrhizin concentration in liquid phase for batch extraction .
(r_m = 10, 1: distilled water at 70°C, 2: ammonia-water 0.0013 g_{NH3}/g_{sol} at 70°C, 3: ethanol-water 0.3 v/v at 70°C, 4: ethanol-water 0.5 v/v at 70°C, 5: ammonia-water 0.0013 g_{NH3}/g_{sol} at 20°C)

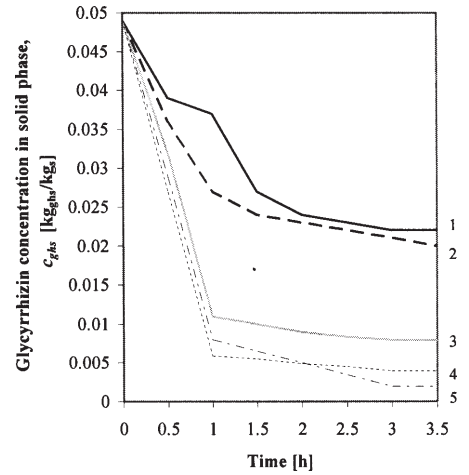

Fig. 5. Dynamics of glycyrrhizin concentration in solid phase for batch extraction
(r_m = 10, 1: distilled water at 70°C, 2: ammonia-water 0.0013 g_{NH3}/g_{sol} at 70°C, 3: ethanol-water 0.3 v/v at 70°C, 4: ethanol-water 0.5 v/v at 70°C, 5: ammonia-water 0.0013 g_{NH3}/g_{sol} at 20°C)

The curves from figure 4 and figure 5 emphasize the following conclusions:

-due to the ammonia removal from working solution in case of glycyrrhizin extraction with ammonia-water solution at 70°C (curve 2), dynamics of this process is almost the same as in case of extraction with distilled water at 70°C (curve 1); accordingly, the extraction with ammonia-water solution at 70°C can be considered a non-reactive process;

-curves 4 and 5, illustrating dynamics of extraction with aqueous solutions of ethanol (0.5 v/v at 70°C) and ammonia (0.0013 g/g at 20°C), denote reactive extraction processes with sufficient quantity of reactant;

-curve 3 is characteristic of a reactive extraction with an insufficient quantity of ethanol (0.3 v/v) in reaction medium.

The values of the distribution coefficient of glycyrrhizin, $K_{d,gh}$, are presented in table 2. It is observed that these values are high for non-extractive process and low for reactive extractions.

Process modelling

The mathematical model characterizing *j* species (inulin or glycyrrhizin) transfer from solid to liquid without chemical reaction is represented by relations (3)-(6). It was considered a batch contacting with perfect mixing and finite volume of liquid phase, swollen porous particles with spherical shape and identical diameter, uniform initial distribution of species in solid phase and species flux at particle interface corresponding to an intensive mixing of liquid phase.

$$\frac{\partial c_{js}}{\partial \tau} = D_{ef,j}\left(\frac{\partial^2 c_{js}}{\partial r^2} + \frac{2}{r}\frac{\partial c_{js}}{\partial r}\right) \tag{3}$$

$$\tau = 0 \qquad 0 \prec r \prec R \qquad c_{js} = c_{js0} \tag{4}$$

$$\tau \succ 0 \qquad r = 0 \qquad \frac{dc_{js}}{dr} = 0 \tag{5}$$

$$\tau \succ 0 \qquad r = R \qquad \frac{3}{R}\frac{\rho_l D_{ef,j}}{r_m}\frac{dc_{js}}{dr} = \frac{dc_{jl}}{d\tau} \tag{6}$$

The usual analytical solution of this system of equations and restrictions is given [19,20] by relation (7), wherein c_{jsmn} is mean species concentration in solid phase and α_n are solutions of transcendent equation (8). The separation factor, ν_j, is expressed by relationship (9), depending on liquid density, ρ_l, solvent/solid mass ratio, r_m, and *j* species distribution coefficient, K_{dj}.

$$\frac{c_{js0} - c_{jsmn}}{c_{js0} - c_{js\infty}} = 1 - \sum_{n=1}^{\infty}\frac{6\nu_j(1+\nu_j)}{(9 + 9\nu_j + \alpha_n^2\nu_j^2)}e^{-\alpha^2 n D_{ef,j}\tau / R^2} \tag{7}$$

$$tg\alpha_n = \frac{3\alpha_n}{3 + \nu_j\alpha_n^2} \tag{8}$$

$$\nu_j = \frac{r_m}{\rho_l K_{d,j}} \tag{9}$$

Table 2
VALUES OF DISTRIBUTION COEFFICIENT OF GLYCYRRHIZIN

Curve from Fig.5	1	2	3	4	5
$10^3 K_{d,gh}$ (kg_{ghs}/kg_{ghl})(m^3_l/kg_s)	6.71	5.51	1.82	0.77	0.39

Table 3
IDENTIFIED VALUES OF $D_{ef,in}$ AND v_{in} DEPENDING ON ALCOHOL CONCENTRATION AT INULIN EXTRACTION

Exp.	Alcohol concentration	Effective diffusion coefficient	Separation factor	Distribution coefficient
	c_{alc}	$D_{ef,in}$	v_{in}	$10^3 K_{d,in}$
	v/v	m^2/s	-	$(kg_{ins}/kg_{inl})(m^3_l/kg_s)$
1	0	$7 \cdot 10^{-10}$	8	1.25
2	0.1		2.532	3.95
3	0.2		1.504	6.65
4	0.3		1.070	9.35
5	0.4		0.830	12.05
6	0.5		0.678	14.75
7	0.6		0.573	17.45
8	0.7		0.496	20.16
9	0.8		0.438	22.83
10	0.9		0.391	25.58

For each extraction case illustrated in figure 2, the function $\Phi(D_{ef}, j, v_j)$defined by relationship (10) was minimized and the values of effective diffusion coefficient of j species in the swollen particle, $D_{ef,j}$, and of separation factor, v_j, were identified.

$$\Phi(D_{ef,j}, v_j) = \sum_{i=1}^{N}\left[\left(\frac{c_{js0} - c_{jsmn}}{c_{js0} - c_{js\infty}}\right)_{i,\exp} - \right.$$

$$\left. - \left(1 - \sum_{n=1}^{\infty}\frac{6v_j(1+v_j)}{(9+9v_j+\alpha_n^2 v_j^{\,2})} e^{-\alpha^2 n D_{ef,j}\tau_i / R^2}\right)_i\right]^2 \qquad (10)$$

In case of inulin extraction, the minimizing results given in table 3 emphasize that inulin effective diffusion coefficient inside of porous particle does not depend on the alcohol concentration. The obtained value of effective diffusion coefficient agrees with the values reported for other similar materials and denotes that the swollen particle of chicory root has a structure corresponding to an unconsolidated porous material which is strongly saturated with liquid. It can be observed that the values of distribution coefficient increase with alcohol concentration and they are in good agreement with those given by the relationship (2).

The above presented model can correlate the data of glycyrrhizin extraction in the case wherein at the particle surface does not take place a chemical interaction. In the case of extraction with cold water-ammonia solution we can turn the limit condition (6) into the form (11), which shows that the glycyrrhizin concentration at particle surface converges to zero due to chemical reaction.

$$\tau \succ 0 \qquad r = R \qquad c_{ghs} = 0 \qquad (11)$$

Accordingly, the correlation (12) was obtained as a solution of extraction process dynamics [20,21]:

$$E_{gh} = \frac{c_{ghs0} - c_{ghsmn}}{c_{ghs0} - c_{ghs\infty}} = \frac{c_{ghl} - c_{ghl0}}{c_{ghl\infty} - c_{ghl0}} =$$

$$= 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2} e^{-n^2\pi^2 D_{ef,gh}\tau / R^2} \qquad (12)$$

Minimizing the functional which shows the mean quadratic deviation between experimental and computed values of glycyrrhizin extraction efficiency, E_{gh}, values of $D_{ef,gh}$ between $4.4 \cdot 10^{-11}$ m^2/s and $6.4 \cdot 10^{-11}$ m^2/s were obtained. Figure 6 illustrates a comparison between experimental and computed values of process efficiency.

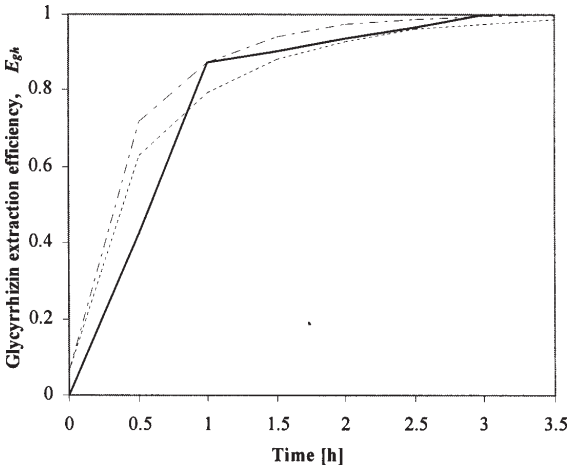

Fig. 6. Comparison between experimental and theoretical dynamics of efficiency of glycyrrhizin extraction with ammonia-water solution at 20 °C (— exp, - - - eq. (13) with $D_{ef,gh}=4.4 \cdot 10^{-11}$ m^2/s, – · – eq. (13) with $D_{ef,gh}=6.4 \cdot 10^{-11}$ m^2/s)

The obtained values of effective diffusion coefficient for glycyrrhizin transport in swollen particle of licorice root prove a structured porous material with pores having the radius over 10μm [22]. This consideration concerning solid material structure is sustained also by the swelling data from table 1.

The established data characterizing the extraction equilibrium of inulin and glycyrrhizin from chicory and licorice roots with various liquid phases allow the computation and the equilibrium design for all extraction procedures (simple extraction with a single contact, simple extraction with multiple contact, co-current and counter-current stages extraction etc).

The results concerning the diffusion of inulin and glycyrrhizin inside of solid particle can be used, together with the equilibrium data, for simulation of all contacting procedures which are considered for extraction scale-up. We recommend for large laboratory pilots to use the percolation procedure with fixed bed solid, when the extraction is coupled with the deep bed filtration of the percolating medium.

Conclusions

For a qualitative and quantitative characterization of inulin and glycyrrhizin extraction from particles of chicory and licorice (*Glycyrrhiza glabra*) crushed roots, the following were achieved:

-batch contacting under continuous stirring, using as extraction media distilled water and ethylic alcohol-water solutions for chicory roots and distilled water, ethylic

alcohol-water and ammonia-water solutions for licorice roots, was performed;

-for inulin extraction a linear increase of inulin distribution coefficient with alcohol concentration in extraction medium was established;

-the low values of distribution coefficient for some cases of glycyrrhizin extraction prove a reactive extraction;

-a mathematical model was proposed to simulate the inulin and glycyrrhizin transport inside of solid particles of chicory and licorice roots, respectively;

-for inulin extraction experimental data were used to identify the model parameters, namely inulin effective diffusion coefficient inside of porous particle, $D_{ef,in}$, and inulin distribution coefficient, $K_{d,in}$; it was emphasized that identified values of $D_{ef,in}$ do not depend on the alcohol concentration and the values of $K_{d,in}$ increase with alcohol concentration;

-for glycyrrhizin extraction with cold ammonia-water solution the chemical reaction, which occurs at the particle surface, reduces the considered model to a form where only the effective diffusion coefficient is responsible for process dynamics;

-the identified values of effective diffusion coefficient give, by coupling with the swelling data, information concerning the structure of the porous solid.

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Nomenclature

c_{alc} - concentration of ethylic alcohol aqueous solution, m^3_{alc}/m^3_{sol}
c_{ajl} - concentration of *j* species in liquid phase, kg_{jl}/m^3_l
c_{js} - concentration of *j* species in solid phase, kg_{js}/kg_s
$D_{ef,j}$ - effective diffusion coefficient of species in swollen particle, m^2/s
E - efficiency of extraction process
k_{SWj} - swelling coefficient of *j* species, m^3_l/m^3_s
$K_{d,j}$ - distribution coefficient of *j* species, $(kg_{js}/kg_{jl})(m^3_l/kg_s)$
r - radial coordinate, m
r_m - solvent/solid mass ratio, kg_l/kg_s
R - radius of swollen particle, m
t - operating temperature, ^0C
V - volume of swollen particle, m^3_s
V_o - volume of dried particle, m^3_s
ρ_l - extraction liquid density, kg_l/m^3_l
τ - time, s
τ_j - separation factor of *j* species

Subscripts

alc - ethylic alcohol
exp - experimental
gh - glycyrrhizin
in - inulin
j - molecular species (*j*=gh, in)
l - liquid phase
mm - mean
s - solid phase
sol - solution
0 - initial
∞ - equilibrium

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