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Thermal Effect of Carbohydrate Dissolution in Aqueous-Organic Media

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This work is devoted to the theoretical substantiation of connection of temperature dependence of the solubility of carbohydrates with thermal effect of their dissolution in the water-containing organic solvents that is of great importance for optimization of the technology of their extraction from plant raw materials and further purification and separation by recrystallization. The dependence of the solubility of fructose, glucose, sucrose, and maltose in aqueous isopropanol and acetone at temperatures of 298 K (25°C) and 275 K (2°C) from water content in a solvent was studied. The constancy of the mechanism of solubility of carbohydrates in these environments in the given temperature interval is experimentally proved. For the first time based on the equation of Vant-Goff the logical connection of temperature dependence of solubility and thermal effect of solubility of carbohydrates is strictly grounded. The values of the thermal effect that are determined by the experimental data allow calculating the solubility of the studied carbohydrates in the aqueous–organic solvent of different concentration in the temperature range from 2°C to 25°C. It has been established that the main contribution to the thermal effect of dissolving carbohydrates is the hydration process. Solvation by molecules of organic solvent practically does not change the value of the specified thermal effect. The significance of determined temperature dependences of the solubility of fructose, glucose and maltose is shown to optimize the technological conditions for the separation of glucose-fructose and glucose-maltose syrups by selective crystallization.

Keywords: solubility, temperature dependence, thermal effect, fructose, glucose, saccharose, maltose, isopropanol, acetone.

Introduction

Experimental data of dependence of the solubility of substances from temperature is accepted to represent either in the form of tables and graphs or through empirically chosen equations by authors of the researches. For example, this kind of dependence for the sucrose system - water in the interval from -12°C to + 81°C with a step of one degree is given in the work (Sapronov, 1998). In the same source, it is noted that in the interval from 0 to 90°C the content of sucrose in saturated aqueous solution *S* (mas.%) With sufficient accuracy is described by the equation in the form of polyoma

$$S = 64{,}397 + 7{,}251\cdot10^{-2}t + 20{,}569\cdot10^{-4}t^2 - 9{,}035\cdot10^{-6}t^3,$$

where *t* is the solution temperature in degrees Celsius.

It is essential to know the dependence of sucrose solubility in the water on the content of various inorganic salts such as KCl, NaCl, MgCl, and CaCl for sugar production. These salts can both increase and reduce the sucrose solubility (Wang, 1993). Dependence from temperature and appropriate theoretical interpretation of the results of sucrose solubility and other carbohydrates in water solutions and the applicability of the UNIFAC model for this purpose are provided in the works (Zhang, 2010; Baghbanbashi, 2014; Peres,1997). This dependence is usually well described by the Vant Goff equation.

Data on the dependence of sucrose solubility in water-ethanol from alcohol content in the full range of concentrations at temperatures of 0°C, 14°C, and 40°C is presented in tabular form in the handbook (Simanova, 2004) are described in detail in a wide range of temperatures in other sources (Peres, 1997; Peres, 1997; Spiliotis, 2000). Such information allows calculating multi-component crystallization and rectification with high accuracy, to design new processes and types of apparatuses in sugar, alcohol and liquor-vodka industry on this basis. Similar data for other three-component carbohydrate systems - water - organic solvent are obtained and described by the authors in the works (Peres, 1997; Peres, 1997; Spiliotis, 2000). In addition to sucrose, the solubility of glucose, maltoses, fructose,

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xylose, mannose, lactulose, lactose, tagatose, galactose, etc. in solvents such as ethanol, methanol, propanol-1, butanol, pentanol, propylene glycol, glycerin were studied (Tinjacá, 2019; Ye, 2017; Gabas,1988). The solvents were used both in their purest form and in various water relations (Ye, 2017; Gabas,1988).

More complex multi-component systems for studying the solubility of carbohydrates in order to extract and separate them from natural and synthetic raw materials are of interest. For instance, the study (Montanes, 2009) explores the possibility of using complex supercritical carbon dioxide with ethanol:water (95:5, vol./vol.) used as a co-solvent at T = (60 and 100) °C, P = (10-30) MPa and co-solvents content from 6 to 21% (weight/weight) for the selective extraction of components from lactulose/lactose and tagatose/galactose binary mixtures.

The study of carbohydrate extraction processes of different chemical nature from lignocellulose biomass by extraction by waterless complex organic salts - ion liquids (ILs) (Teles, 2016; Mohan, 2016) has an essential practical meaning for the production of green fuel and other useful substances. In the same works, the mechanism of dissolving carbohydrates in ILs with the formation of solvate complexes of monosaccharides with ion pairs of complex salts is discussed.

Despite the abundance of work devoted to the study of the carbohydrates dissolution mechanism in complex multi-component systems, the researchers did not conduct a systematic study of the role of water, and the process of dissolution in terms of the fundamental laws of physical chemistry.

The author of this work has developed and implemented a new method of separating carbohydrates from two-component mixtures by selective crystallization of one of them when adding an organic solvent to the water solution of the mixture (Danilchuk, 2012). This method is applicable for the separation of glucose-fructose and glucose-maltose syrups (RU Patent No. 2347818, 2009[7]; Danilchuk, 2016). Widely used solvents - isopropanol, acetone, acetonitrile - can be used to implement the method. The author proposed a physical and chemical model of the process of dissolving carbohydrates in mixed water-organic solvents, showing the decisive role of hydration in the process of carbohydrates dissolving.

Previously for the first time (Danilchuk, 2013) we have demonstrated that the process of dissolving carbohydrates in water-organic environments (water-containing isopropanol, acetone, acetonitrile) from the law of acting masses can be considered as a quasi-chemical reaction of equilibrium between carbohydrate in solid $(\text{Carbohydrate})_{\text{solid}}$ and dissolved states $[(\text{Carbohydrate})b\text{H}_2\text{O}]_{\text{solution}}$.

$$(\text{Carbohydrate})_{\text{solid}} + b\text{H}_2\text{O} = [(\text{Carbohydrate})\ b\text{H}_2\text{O}]_{\text{solution}}.$$

The right side of this equilibrium equation the formation of a hydrated carbohydrate complex that directly passes into the solution is depicted symbolically. In this case, the constant of physicochemical equilibrium K, replacing the volumetric concentrations on the mass fraction, can be recorded as

$$K = P/C^b, \tag{1}$$

where C is the mass fraction of water in the binary solvent; P – solubility expressed in g of carbohydrate dissolved in 1 g of a binary solvent; the indicator b is equal to the stoichiometric coefficient in the chemical equation. In the mathematical expression of the equilibrium constant (1) the concentration of solids $(\text{Carbohydrate})_{\text{solid}}$ as usual, do not include.

This description of the solubility process is the physicochemical substantiation of the established experimental equation of solubility of carbohydrates in water-organic media:

$$P = aC^b \tag{2}$$

or in logarithmic form

$$\lg P = b \lg C + \lg a,$$

a, b – coefficients derived from experimental linear graphs in logarithmic coordinates $x = \lg C$ and $y = \lg P$ by least squares method for each of the carbohydrates in this binary solvent since the linear dependence is performed in these coordinates

$$y = bx + \lg a.$$

The coefficient a, as seen in the comparison of equations (1) and (2), is a non-dimensional constant of equilibrium.

It is known that the amount of carbohydrates solubility and the change of this magnitude from the temperature is determined by the chemical nature of the carbohydrate and the solvent composition. Changing these parameters can affect the solubility of different carbohydrates in different ways and, in particular to achieve selective crystallization of one of the components, which allows us to separate and purify the components of the mixture.

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[7] Danilchuk, V. D. (2009). *RU Patent No. 2347818.*

One of the objectives of this study was to confirm the persistence of the physicochemical mechanism of the dissolution process of fructose, glucose, sucrose, and maltose in aqueous isopropanol and acetone, with a decrease in temperature from T1 = 298 K (25°C) to T2 = =275 K (2°C). For this purpose coefficients of solubility equation *a* and *b* at the temperature of 25°C, which are received in work (Danilchuk, 2013), were refined, and the similar coefficients at temperature of 2°C have been clarified.

The solution of the identified problem will theoretically justify the connection of the temperature dependence of the solubility of the specified carbohydrates with the thermal effect of their dissolution in the water-containing organic solvents of different composition. Establishment of such connection is the primary purpose of the research and is of great practical importance for optimization of technological processes of heat and mass exchange of extraction of carbohydrates from vegetative raw materials and their further purification and separation of the method of selective crystallization (Danilchuk, 2012; RU Patent No. 2347818, 2009; Danilchuk, 2016; RU Patent No. 2604288, 2016[8]) proposed by us. The theoretical value of the sought connection is that this relationship will allow to accurately calculate the solubility of carbohydrates at any temperature for any composition of the water-organic solvent within limits required for carrying out technological processes.

Materials and methods

For the study were used: distilled water, carbohydrates - glucose, fructose, maltose and saccharose chemical purity 99.9 mas. %, organic solvents – chemically pure and non-aqueous isopropanol and acetone.

The solubility of carbohydrates was determined by titration of binary mixtures (aqueous solutions of carbohydrates) of different composition by the third component (organic solvent) to the turbidity of the solution[9]. This method is usually used to build phase diagrams of three-component systems when all three components are liquids. The essence of the titration process is to add the third component to the homogeneous two-component solution to the point of turbidity associated with the formation of the second liquid phase. Thus, the composition of the saturated solution is calculated and one point is obtained on the solubility curve of the phase diagram separating the single-phase area from the two-phase. The method of titration shown was firstly applied and modified to determine the solubility of solids – carbohydrates in two-component solvents. The modification allows in the process of repeated titration using two measuring burettes and during one procedure to obtain a large number of points on the curve of the solubility of carbohydrates in the organic solvent from the content of water in a wide range from 10 to 70 mas. % (C = 0.1-0.7). Processing of the received data of titration by the method of the least squares in logarithmic coordinates $x = \lg C$ and $y = \lg P$ allows defining parameters *a* and *b* in equation (2).

As an example, we will describe the procedure of getting a dependence of sucrose solubility in water–based acetone with the help of the method of repeated titration at the temperature of 25°C. For the experience it is necessary to have: distilled water, sucrose with the content of the principal substance 99.9 mas. %, exceptionally pure waterfree acetone, scales with the accuracy of weighing 0.01 g, conical flask on 250 cm^3, two measuring burettes: for water - on 25 cm^3, for acetone - on 50 cm^3.

In the conical flask the weighed portion of sucrose with a mass of 6.00 g dissolved in 4.00 cm^3 (4.00 g) of water at a given ambient temperature (25°C) to the formation of a transparent solution. We have installed two measuring burettes, filled with water (25 cm^3) and acetone (50 cm^3) on a tripod. After exhausting the first 50 cm^3 of acetone in the process of titration added a second portion of acetone in the same volume. Equipment and reagents must take the ambient temperature of 25°C before titration. The results of multiple titration were made in the first two columns of table 1, where the first column shows the total water volume *V*W added to the system, taking into account the 4 $cm^{3,}$ initially inside the flask before titration, and the second column shows the total volume of acetone *V*A, which went on titration till the moment of clouding at this step.

The process of multiple titration was performed as follows. In the flask to the original solution 6.00 g sucrose (*M*S = 6.00 g) in 4.00 g of water (*V*W = 4.0 cm^3), acetone was gradually poured from the burette at stirring to the point of turbidity, which came after the addition of *V*A = 5,9 cm^3 (see Table 1). Then from another burette in the received mix was poured 0.5 cm^3 of water (*V*W = 4.5 cm^3) at hashing. The general mixture became transparent, i.e., homogeneous. The process of titration by acetone to turbidity was

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[8] Danilchuk, J. (2016). *RU Patent No. 2604288.*

[9] Konyukhov, V. Yu., & Popov, K.I. . (2002). *Physicochemical foundations of food industry.* Publishing complex of the Moscow State University of Food Production.

repeated. In the second stage of titration 1.6 cm^3 of acetone was spent, i.e., from the moment of the beginning of titration, the total spent VA = 5.9 cm^3 of acetone that corresponds to a position of a meniscus in the burette and was entered in the second line of the second column of Table 1. The procedure was repeated many times and finished when the total mixture contained 6.00 grams of sucrose, 24.5 cm^3 (24.50 g) of water and 99.4 cm^3 (78.63 g) acetone.

To fill Table 1 and further processing of results it was necessary to transfer volumes of water and acetone characterizing points of titration in corresponding masses *M*W and *M*A. For this purpose the volumetric density of water and acetone, equal respectively 1.000 and 0.791 g/cm^3 were used. Water content *C* and solubility of sucrose *P* counted on formulas

$$C = M_W/(M_W + M_A),$$

$$P = M_S/(M_W + M_A).$$

In the last two columns Table 1 show the modules of decimal logarithms of parameters *C* and *B*, necessary

Table 1
Solubility of sucrose in water acetone at 25°C

VW, cm^3	**VA, cm^3**	**MA, g**	**MW + MA, g**	**C**	**P**	**-lg C**	**-lg P**
4,0	4,3	3,40	7,40	0,5405	0,8108	0,267	0,091
4,5	5,9	4,67	9,17	0,4907	0,6543	0,309	0,184
5,0	7,1	5,62	10,62	0,4708	0,5650	0,327	0,248
5,5	8,5	6,72	12,22	0,4501	0,4910	0,347	0,309
6,0	9,9	7,83	13,83	0,4338	0,4338	0,363	0,363
6,5	11,4	9,02	15,52	0,4188	0,3866	0,378	0,413
7,0	13,1	10,36	17,36	0,4032	0,3456	0,394	0,461
7,5	14,8	11,71	19,21	0,3904	0,3123	0,408	0,505
8,0	16,9	13,37	21,37	0,3744	0,2808	0,427	0,552
8,5	18,8	14,87	23,37	0,3637	0,2567	0,439	0,591
9,0	20,8	16,45	25,45	0,3536	0,2358	0,451	0,628
9,5	22,8	18,03	27,53	0,3451	0,2179	0,462	0,662
10,0	24,6	19,46	29,46	0,3394	0,2037	0,469	0,691
10,5	26,9	21,28	31,78	0,3304	0,1888	0,481	0,724
11,0	28,9	22,86	33,86	0,3249	0,1772	0,488	0,752
11,5	30,8	24,36	35,86	0,3207	0,1673	0,494	0,776
12,0	32,9	26,02	38,02	0,3156	0,1578	0,501	0,802
12,5	34,9	27,61	40,11	0,3116	0,1496	0,506	0,825
13,0	37,2	29,43	42,43	0,3064	0,1414	0,514	0,850
13,5	39,5	31,24	44,74	0,3017	0,1341	0,520	0,873
14,0	41,4	32,75	46,75	0,2995	0,1283	0,524	0,892
14,5	43,8	34,65	49,15	0,2950	0,1221	0,530	0,913
15,0	46,9	37,10	52,10	0,2879	0,1152	0,541	0,939
15,5	49,3	39,00	54,50	0,2844	0,1101	0,546	0,958
16,0	51,8	40,97	56,97	0,2808	0,1053	0,552	0,977
16,5	53,9	42,63	59,13	0,2790	0,1015	0,554	0,994
17,0	56,8	44,93	61,93	0,2745	0,0969	0,561	1,014
17,5	59,0	46,67	64,17	0,2727	0,0935	0,564	1,029
18,0	61,7	48,80	66,80	0,2695	0,0898	0,570	1,047
18,5	65,3	51,65	70,15	0,2637	0,0855	0,579	1,068
19,0	68,9	54,50	73,50	0,2585	0,0816	0,588	1,088
19,5	71,3	56,40	75,90	0,2569	0,0791	0,590	1,102
20,0	73,8	58,38	78,38	0,2552	0,0766	0,593	1,116
20,5	76,6	60,59	81,09	0,2528	0,0740	0,597	1,131
21,0	79,4	62,81	83,81	0,2506	0,0716	0,601	1,145
21,5	81,9	64,78	86,28	0,2492	0,0695	0,603	1,158
22,0	84,5	66,84	88,84	0,2476	0,0675	0,606	1,170
22,5	87,3	69,05	91,55	0,2458	0,0655	0,609	1,184
23,0	90,4	71,51	94,51	0,2434	0,0635	0,614	1,197
23,5	92,9	73,48	96,98	0,2423	0,0619	0,616	1,209
24,0	96,0	75,94	99,94	0,2401	0,0600	0,620	1,222
24,5	99,4	78,63	103,13	0,2376	0,0582	0,624	1,235

for plotting the graphs in Figures 1*a*, 1*b*, 2*a*, 2*b* and definition of parameters of the equation of solubility *a* and *b* of Table 2. The obtained results described as an example of the experience of determining the solubility of sucrose in aqueous acetone at 25°C are reflected in the corresponding graph (Figure. 2^a). Thus, in the process of repeated titration, 42 points were obtained on the specified chart in the logarithmic coordinates $x = \lg C$ and $y = \lg P$, which gives the possibility after mathematical processing with great accuracy to define parameters *a* and *b* in the solubility equation (2) based on the obtained trend line equation

$y = 3{,}3211x + 0{,}8518$.

Obviously, in this case, $b = 3{,}32$ and $a = 10^{0{,}8518} = = 7{,}11$, that is, the equation of solubility of sucrose in water-based acetone at 25°C has the form

$P = 7{,}11C^{3{,}32}$.

Results and discussion

The results of the study are shown in Figures 1*a*, 1*b*, 2*a*, 2*b* and in Table 2.

As it can be seen from the figures, at both temperatures of the study $T_1 = 298$ K and $T_2 = 275$ the experimental dependences of solubility on the mass fraction of water in aqueous-organic solvents in logarithmic coordinates are well straightened, which confirms feasibility of the equation of solubility (2), thus the coefficient of inclination *b* of corresponding straight lines of a trend within the limits of error of measurements and calculations at transition from one temperature to another does not change.

The invariability of indicator *b* in the solubility equation (see Table 2) at two temperatures confirms the safety of stoichiometric coefficient in the corresponding quasi-chemical equation of equilibrium, i.e. necessary for hydration of one carbohydrate molecule quantity of water molecules is preserved. So, for example, for hydration of glucose molecule in aqueous isopropanol requires two molecules of water, in aqueous acetone - an average of 2.57 molecules of water. In general, for the studied systems carbohydrate -water-organic solvent experimentally defined values *b* vary within 1.85-3.73, i.e., in the process of hydration involved about two to four molecules of water. In the case of water–based acetone, the amount of water molecules required for hydration is significantly higher than in the case of aqueous isopropanol.

Thus, the constancy of the physicochemical mechanism of carbohydrate solubility in this temperature range is confirmed.

The preservation of the dissolution mechanism allows using the ratio of equilibrium constants at different temperatures $n = a_1/a_2$ to determine the thermal effect - the calculation of enthalpy ΔH^0 and heat *Q* of the dissolution process, which corresponds to the stoichiometric equation. For this purpose we use the Van't Hoff' isobar in an integral form

$$\ln\left(\frac{a_1}{a_2}\right) = -\frac{\Delta H^0}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right), \qquad (3)$$

where ΔH^0 – enthalpy (J/mol); R – gas constant, equal to 8.31 J/mol, deg; a_1 and a_2 are equilibrium constants respectively at absolute temperatures T_1 and T_2.

It is important to note that in the implementation of the solubility equation (2) at two temperatures T_1 and T_2 with the preservation of indicator *b*, the ratio of constants $n = a_1/a_2$ at the same time equal to the ratio of the corresponding solubility of carbohydrate P_1/P_2 at the set water content *C* in a binary water-organic solvent. Thus, the Van't Hoff' equation (3) for a given carbohydrate and a given solvent composition

Table 2

Coefficients of the equation of solubility of carbohydrates at temperatures $T_1 = 298$ K (a_1, b_1) u $T_2 = 275$ K (a_2, b_2)

Carbohydrate	**Isopropanol**					**Acetone**				
	a_1	b_1	a_2	b_2	a_1/a_2	a_1	b_1	a_2	b_2	a_1/a_2
Fructose	1,96	1,86	1,70	1,85	1,15	2,34	2,30	2,01	2,29	1,16
Glucose	1,74	2,01	0,49	2,00	3,55	2,22	2,57	0,62	2,57	3,58
Sucrose	2,57	2,11	1,26	2,11	2,04	7,11	3,32	3,56	3,32	2,00
Maltose	2,36	2,74	1,12	2,74	2,11	4,83	3,72	2,29	3,73	2,11

Figure 1a
Solubility of carbohydrates in isopropanol at a temperature of 25°C

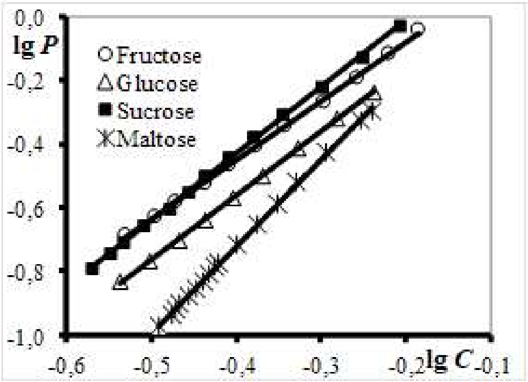


Figure 1b
Solubility of carbohydrates in isopropanol at a temperature of 2°C

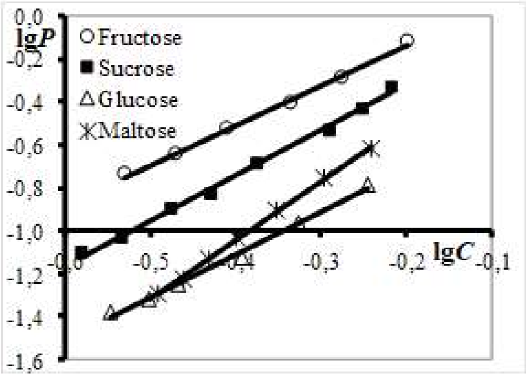


Figure 2a
Solubility of carbohydrates in acetone at a temperature of 25°C

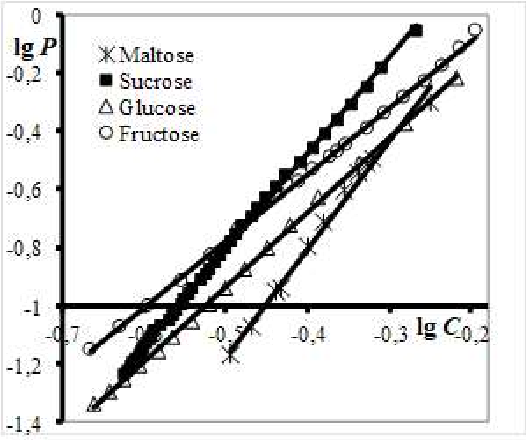
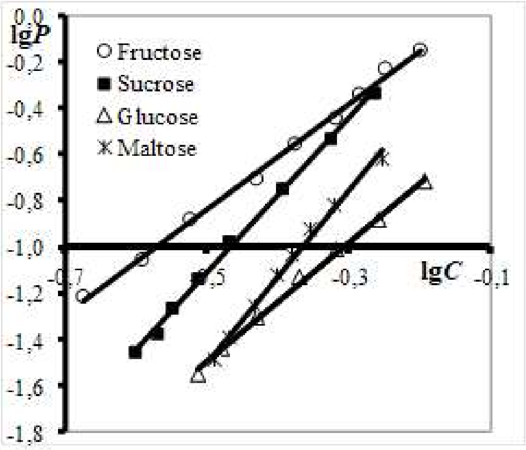


Figure 2b
Solubility of carbohydrates in acetone at a temperature of 2°C



is essentially a carbohydrate solubility dependence on temperature.

The thermal effect of dissolution process *Q* is equal in absolute value to the change of enthalpy and is opposite in the sign $Q = -\Delta H^0$ [21]. Since the relative changes in coefficients *n* in the case of aqueous isopropanol and acetone were equal among themselves within the measurement error, the corresponding calculations for these two binary solvents are summarized in the general table (Table 3), in which the average of the two values of *n* are shown. Proximity of the relationship $n = a_1/a_2$ for different water-organic mediums indicates the main contribution to the thermal effect of carbohydrate dissolution of the hydration process and relatively small contribution of the process of solvation by organic solvent molecules.

Table 3
Enthalpy and the heat of dissolving carbohydrates in aqueous isopropanol and acetone

Carbohydrate	n	ΔH⁰, kJ/mol	Q, kJ/mol
Fructose	1,16	4,4	-4,4
Glucose	3,57	37,7	-37,7
Sucrose	2,02	20,8	-20,8
Maltose	2,11	22,1	-22,1

From Table 3 it can be seen that the heat of dissolution of carbohydrates in aqueous isopropanol and acetone is negative, that is, the process of dissolution of crystals occurs with heat absorption. The greatest amount of heat is absorbed at the dissolution of glucose, and the smallest - at the dissolution of fructose; the thermal effects of the dissolution of sucrose and maltose are almost identical.

Using the values of ΔH^0 from the Table 3 in accordance with the Van't Hoff' equation (3) based on solubility data (Table 2) at a temperature of T_1 = 298 K (25°C), it is possible to calculate the solubility of carbohydrates at any temperature T_2 in the studied range of temperatures from 2°C to 25°C.

As an example, we determine the solubility of sucrose in a water solution containing 50 mas. % isopropanol (C = = 0.5) at a temperature of 14°C (287 K). To do this, we use the Van't Hoff' equation (3), where T_1 = 298 K (25°C) and T_2 = 287 K (14°C). The value a_1 = 2.57 is taken from Table 2, and the value ΔH^0 = 20800 J/mol is taken from Table 3. Thus, in equation (2), all parameters except a_2 which value can be calculated are known. As a result of the calculation from equation (2), we get a_2 = 1.86. Since the value of parameter b = 2.11 remains the same as at the temperature of 298 K (25°C), the equation of solubility of sucrose in aqueous isopropanol has the form

$P = 1{,}86C^{2{,}11}$.

In particular from this equation for C = 0.5 we get

$P = 1{,}86(0{,}5)^{2{,}11} = 0{,}431$.

Thus, the solubility of sucrose in aqueous acetone containing 50 mas. % of water, at 14°C is 43 g in 100 g of mixed solvent (P = 0.43).

Knowledge of the temperature dependence of the solubility of carbohydrates in mixed water-organic solvents allows making practically important recommendations for an increase of efficiency of technological processes of separation and purification of glucose-fructose and glucose-maltose syrups previously developed by the author method of selective crystallization (Danilchuk, 2012; RU Patent No. 2347818, 2009; Danilchuk, 2016; RU Patent No. 2604288, 2016). For example, for any composition of aqueous isopropanol and acetone with a decrease in temperature from 25°C to 2°C according to the Table 3 the solubility of fructose falls in 1.16 times, and solubility of glucose in 3.57 times, that is, the solubility of fructose in relation to glucose in this case increases by 3,57/1,16 = 3.08 times. The increase in the solubility ratio of fructose and glucose in aqueous isopropanol with a decrease in temperature from 25°C to 2°C significantly increases the efficiency of the process of separating of these carbohydrate by selective crystallization of glucose-fructose syrup, as it was established experimentally by us earlier (Danilchuk, 2012; RU Patent No. 2347818). The same decrease in temperature will reduce the separation efficiency of glucose-maltose syrup (Danilchuk, 2016; RU Patent No. 2604288, 2016), since as it decreases the relative difference between the solubility of glucose and maltose by 3,57/2,11 = 1.69 times due to the fact that the solubility of glucose falls faster than less soluble maltose. Therefore, in the latter case, it is recommended to conduct the process at the highest possible temperature. This recommendation applies equally to the separation of glucose-maltose syrup by isopropanol and acetone (Danilchuk, 2016).

It was interesting to conduct the processing of reference data (Simanova, 2004) on the solubility of sucrose in water–based ethanol within the framework of the above concept of the mechanism of solubility of carbohydrates and the connection of solubility with thermal effect. For this purpose tabular data from the reference book for temperature T_1 = 313 K (40°C) and T_2 = 287 K (14°C) in the field of change of ethanol concentration from 40 vol. % (33.30 mass %) up to 90 vol. % (85, 66 mass %) were plotted on the corresponding graphs in the coordinates of lg C – lg P (Fig. 3).

From Fig. 3, it can be seen that the slope coefficients of the trend line for two temperatures b_1 = 2,88 and b_2 = 2,95 have close values, given the measurement error. That means that in this range of temperatures from 14 to 40°C the mechanism of solubility of sucrose in ethyl alcohol is preserved and the corresponding solubility equations have the form

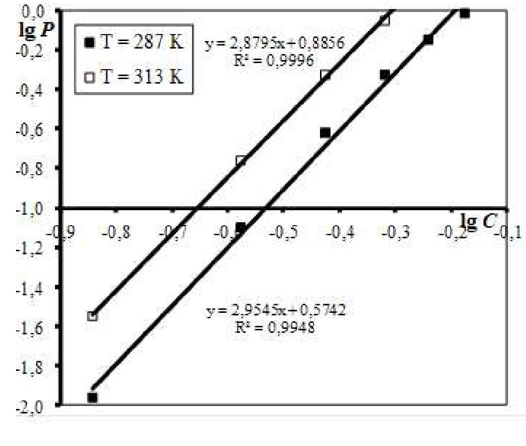
$$P = 7{,}68C^{2{,}88} \text{ for } T_1 = 313 \text{ K (40°C)}, \tag{4}$$

$$P = 3{,}75C^{2{,}95} \text{ for } T_2 = 287 \text{ K (14°C)}. \tag{5}$$

The preservation of the dissolution mechanism allows to use the ratio of coefficients a_1/a_2 = 7,68/3,75 = 2,048 to

Figure 3

Solubility of sucrose in ethanol at temperatures of 287 K (14°C) and 313 K (40°C) according to the handbook [6]



calculate the enthalpy ΔH^0 and heat Q of sucrose solubility in ethanol, substituting this ratio in the left part of the Van't Hoff' equation (3), which gives $\Delta H^0 = 20.6$ kJ/mol and $Q = -20.6$ kJ/mol. This result almost coincided with the data of Table 3 for sucrose. Thus, the important conclusion of this work on weak dependence of the solubility of carbohydrates in water-organic solvents from the chemical nature of organic solvent at middle and high concentrations of the latter is confirmed. The main contribution to the thermal effect of solubility of carbohydrates makes the hydration process.

For comparison with the results of carbohydrate solubility obtained by us in aqueous isopropanol and acetone at 25°C, we define the equation of sucrose solubility in water-based ethanol at the same temperature. As b, we take the average value of this indicator from the equations (4) and (5), which is 2.92. From the Van't Hoff' equation (3), we calculate the coefficient $a = 5.16$. Therefore, the sought for equation has the form

$$P = 5{,}16C^{2{,}92}. \quad (6)$$

With the help of this equation, we define, for example, the solubility of sucrose in ethanol containing 80 vol. % alcohol at a temperature of 25°C. According to the reference data (Simanova, 2004) the mass fraction of ethanol in such a solvent is 73.5%, which corresponds to the water content $C = 0.265$, when substituting it into equation (6) we get $P = 0.107$, that is, in 100 grams of binary solvent dissolves 10.7 g of sucrose.

Conclusions

The dependence of the solubility of fructose, glucose, sucrose, and maltose in aqueous isopropanol and acetone at temperatures of 298 K (25°C) and 275 K (2°C) from water content in a solvent is studied. The constancy of the mechanism of dissolution of carbohydrates in these mediums in the given temperature interval is experimentally proved. The results of this work allowed to theoretically justify the applicability of the Van't Hoff' equation to the description of the temperature dependence of the solubility of carbohydrates in the water-containing organic solvents, which allows linking this dependence with the thermal effect of solubility. The results obtained, in general, are of great importance for optimizing the technology of extracting carbohydrates from plant raw materials, further purification and separation by selective crystallization.

The values of the thermal effect determined from experimental data allow calculating the solubility of the studied carbohydrates in water-organic mediums in a temperature range from 2°C to 25°C. It has been established that the main contribution to the thermal effect of dissolving carbohydrates is made by the hydration process. Solvation by organic solvent molecules practically does not change the value of the specified thermal effect. It was revealed that the increase in the ratio of solubility of fructose and glucose in aqueous isopropanol with a decrease in temperature from 25 to 2°C significantly increases the efficiency of the process of separating glucose and fructose by the method of selective crystallization of glucose-fructose syrup. The same decrease in temperature will reduce the separation effectiveness of glucose-maltose syrup, as it decreases the relative difference between the solubility of glucose and maltose due to the fact that the solubility of glucose falls faster than less soluble maltose. Therefore, in the latter case, it is recommended to carry out the process at the highest possible temperature.

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Тепловой эффект растворения углеводов в водно-органических средах

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Данная работа посвящена теоретическому обоснованию связи температурной зависимости растворимости углеводов с тепловым эффектом их растворения в водосодержащих органических растворителях, что имеет большое значение для оптимизации технологии их извлечения из растительного сырья и дальнейших очистки и разделения путем перекристаллизации. Изучена зависимость растворимости фруктозы, глюкозы, сахарозы и мальтозы в водных изопропаноле и ацетоне при температурах 298 К (25°C) и 275 К (2°C) от содержания воды в растворителе. Экспериментально доказана неизменность механизма растворения углеводов в данных средах в приведенном интервале температур. Впервые на основе уравнения Вант-Гоффа строго обоснована аналитическая связь температурной зависимости растворимости и теплового эффекта растворения углеводов. Определенные по экспериментальным данным величины теплового эффекта позволяют рассчитать растворимость изученных углеводов в водно-органическом растворителе различной концентрации в диапазоне температур от 2°C до 25°C. Установлено, что основной вклад в тепловой эффект растворения углеводов вносит процесс гидратации. Сольватация молекулами органического растворителя практически не меняет величину указанного теплового эффекта. Показано значение полученных температурных зависимостей растворимости фруктозы, глюкозы и мальтозы для оптимизации технологических условий разделения глюкозно-фруктозных и глюкозно-мальтозных сиропов методом селективной кристаллизации.

Ключевые слова: растворимость, температурная зависимость, тепловой эффект, фруктоза, глюкоза, сахароза, мальтоза, изопропанол, ацетон.

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