

WSTĘPNE BADANIA PRODUKTÓW TERMOLIZY CHITYNY I CHITOZANU Z α -HYDROKSYKWASAMI

Marek Sikora^a, Piotr Tomasił^a, Koji Araki^b

^aKatedra Technologi Węglowodanów, Katedra Chemii, Akademia Rolnicza, Kraków, Instytut Nauk Przemysłowych, Uniwersytet Tokijski, Tokio, Japonia

Chitynę i chitozan poddano termolizie w temperaturach 200, 230 i 250°C, z dodatkiem kwasów mlekowego, cytrynowego i winowego. Stwierdzono, że dodane kwasy przyspieszają termiczny rozkład obu sacharydów. W wyniku termolizy chityny z hydroksykwasami, otrzymano stałe, kruche substancje, o ciemnym zabarwieniu i o zapachu grzybów (tab. 3), których 10 g/kg wodne suszenie charakteryzowały się kwasnym odczynem (pH 5,42–5,67) (tab. 1). Rozpuszczalność w wodzie produktów termolizy chityny i hydroksykwasów rosła wraz ze wzrostem ilości dodanego kwasu, nie przekraczając 110 g/kg. Zdolność wiązania wody natomiast malała wraz ze wzrostem ilości dodanego kwasu oraz ze wzrostem temperatury reakcji (tab. 1).

Chitozan poddany termolizie z kwasem mlekowym dawał w wyniku stałe, kruche substancje, o ciemnym zabarwieniu i zapachu hydrolizatu białkowego, podczas gdy ogrzany w obecności kwasu cytrynowego wytwarzał substancje o zapachu podobnym do leoniady, natomiast poddany termolizie w obecności kwasu winowego generował aromat karmelowy (tab. 4). Rozpuszczalność w wodzie i zdolność wiązania wody otrzymanych substancji kształtowała się podobnie, jak w przypadku produktów termolizy chityny. Wodne suszenie termolizatów chitozanu były minimalnie zasadowe (pH 7,19–7,60) (tab. 2).

VISCOSITY OF AQUEOUS SOLUTIONS OF SACCHARIDES

Józef Mazurkiewicz, Maria Nowolny-Różańska

Department of Physics, University of Agriculture, Cracow

Key words: disaccharide aqueous solutions, intrinsic viscosity, monosaccharide aqueous solutions, reduced viscosity

Concentration and temperature effects upon the viscosity of aqueous solutions of various mono- (D-glucose, D-fructose, D-fucose, L-rhamnose) and di-saccharides (sucrose, maltose, lactose) as well as some of their two-component blends were recognized. Intrinsic viscosities determined for these solutions provided an insight into such details of the structure of solutions as structure of mers and bulk of the sugar hydrates. Parameters of linear equations $[\eta] = a + b/c + d$ where $[\eta]$ and c are reduced viscosity and concentration, respectively, were determined. Irrespective of temperature (20, 40 and 60°C) and composition, the viscosity of aqueous solutions of disaccharide blended with monosaccharide significantly increased with concentration. However, the resulting viscosities were always lower than those for corresponding aqueous disaccharide solutions and higher than those for aqueous monosaccharide solutions. Viscosity of aqueous solutions of disaccharide blends were practically concentration independent.

INTRODUCTION

Aqueous saccharide solutions are known for their relatively high viscosity. Solutions of sucrose are perhaps best recognized because of their important role as the sweetener of foodstuffs and large manufacture scale. Attempts of understanding the sweetness mechanism as well as links between sweetness and structure also pushed such studies forward [Mathlouthi, 1984].

In a sucrose molecule there are only single interatomic bonds and rings are free of constraints which would affect natural bond angles. Simultaneously, among

Author's address for correspondence: Józef Mazurkiewicz, Zespół Fizyki, Wydział Rolniczy, Akademia Rolnicza, Al. Mickiewicza 21, 31-120 Kraków, tel. (48 12) 321620 ext. 321; fax (48 12) 336245

eight hydroxylic groups five do not participate in any intramolecular hydrogen bonds. The latter exhibit a considerable affinity to water being responsible for good aqueous solubility of this disaccharide.

Approach to the analysis of aqueous sucrose solutions depends on the concentration. At low concentration the ratio of water molecules to sucrose molecules is well above one and the structure of such solutions is controlled by the extended, tridimensional structure of water. According to Pauling [1940] in the interval of 0 to 40°C only half of the total number of intermolecular hydrogen bonds between the water molecules are active. Strong association builds up cages of 20 to 200 water molecules [Drost-Hanson, 1965]. As the sucrose concentration in solution increases sucrose hydrates are formed. They interact with one another *via* the hydrogen bonds. Some suggestions have been also made that sucrose hydrates interact with bigger water aggregates with an involvement of the hydrogen bonds of various energy [Velikobnyi & Chernogorienko, 1964]. As the sucrose concentration in solution increases, there are gradually less water molecules surrounding sucrose hydrates and in a certain moment number of water molecules becomes insufficient for exhaustive sucrose hydration. Under such circumstances the direct contact between sucrose molecules results in their association. The 30% concentration is limiting [Schliephake *et al.*, 1968]. Because one sucrose molecule has eight hydroxylic groups capable for inter- and intra-molecular hydrogen bond interactions and at 40% concentration there is approximately 26 water molecules per one sucrose molecule the model of associates may be fairly complex. The solution viscosity rapidly increases with association. As the concentration of solution increases gradually, less water molecules are left between sucrose molecules. At the point of oversaturation sucrose diffuses through the solution to the crystal surface [Ramaiah & Gupta, 1983].

Studies of aqueous solutions of sucrose in the interval of 30 to 40°C have recognized some new solid phases [Mauch, 1971]. However, information on hypothetical disucrose penta- and hepta-hydrates are scarce. The composition of saturated aqueous sucrose solutions as the function of temperature was interpreted in terms of degree of hydration of sucrose in solution [Genie, 1974]. This approach left some facts unexplained. It is not clear why at 40°C in saturated solution one sucrose molecule traps eight water molecules whereas at 100°C one sucrose molecule is satisfied with four water molecules. Perhaps, already in unsaturated solutions some viscosity anomalies appear due to sucrose aggregation which then induces crystallization [Genie, 1976b]. Solubility of sucrose in water can be explained in terms of high dielectric constant, ϵ , of water, but in spite of decrease of ϵ with the temperature increase the solubility of sucrose increases. Up to date any universal theory of quantitative composition of saturated solutions is lacking although several hypotheses were presented [Genie, 1976a].

Solubility of sucrose is affected by several additives [Genie, 1983]. Solvents miscible with water decrease the sucrose solubility because their ϵ are lower than that for water. Many chemical compounds, among them also monosaccharides, added in low concentrations decrease sucrose solubility at room temperature. This effect results from the competition for hydrating water molecules. Effect of metal salt addition is nonuniform. If metal cations are poorly hydrated (for instance Na⁺

and K⁺) sucrose solubility increases, otherwise (for instance Mg²⁺ and Ca²⁺) the solubility of sucrose is suppressed. The anion accompanying metal cation can be essential. Hydroxides, carbonates, sulphides, and carboxylates favour the solubility.

Majority of rheological studies of aqueous saccharide solutions provided merely a recognition of the macrostructure of such solutions. In this paper unknown intrinsic viscosities of solutions of several saccharides were determined following formerly developed approach [Mazurkiewicz *et al.*, 1994; Mazurkiewicz & Tomasił, 1982]. Specially modified viscometer [Zimm & Crothers, 1962] provided an insight into structure of solution mers of low-molecular saccharides.

MATERIALS AND METHODS

MATERIALS: Aqueous solutions of the following monosaccharides: D-(+)-fructose, D-(+)-glucose, D-(+)-fructose and L-rhamnose, and disaccharides: lactose, maltose and sucrose were studied. The saccharides of analytical grade were products of Sigma. Water was redistilled.

METHOD: Viscosity of aqueous solutions of saccharides of the concentrations given in Table 1 was measured at 25, 40 and 60°C with the precision of $\pm 0.1^\circ\text{C}$ in every case. Modified Zimm rotary viscometer [Zimm & Crothers, 1962] was used. It provided the measurement precision of ± 0.01 cP. Reduced viscosity, $[\eta]$, was first determined by measurements of the viscosity, η , of aqueous solutions of a given saccharide of gradually increasing concentration, c . These viscosities were related to the viscosity of pure solvent, η_0 in the manner given in equation 1.

$$\frac{[\eta]}{\eta_0} = \frac{\eta - \eta_0}{\eta_0 c} \quad (1)$$

Then using the least square method the linear regression was calculated. Its intercept with ordinate at $c = 0$ corresponded to intrinsic viscosity, $[\eta]$, for a given solute.

RESULTS AND DISCUSSION

Reduced viscosities for aqueous solutions of saccharides measured at 25, 40 and 60°C are given in Table 1.

Figures 1, 2 and 3 visualize the effect of concentration and temperature on intrinsic viscosities of sugar solutions. The concentration increments for particular sugars vary from 0.1 to 2.5 mol/dm³. Linear regressions at lower concentrations turned into curvilinear as the concentration increased, although increasing temperature flattened this curvilinearity.

Table 2 collects parameters of equation 2 for all sugars

$$[\eta] = a + b[\eta]_0 \quad (2)$$

TABLE 1. Reduced viscosities η_{sp}/c of aqueous solutions of mono- and di-saccharides of varying concentrations and at varying temperature.

Concentration c , [mol/dm ³]	η_{sp}/c 25°C	η_{sp}/c 40°C	η_{sp}/c 60°C	Concentration c , [mol/dm ³]	η_{sp}/c 25°C	η_{sp}/c 40°C	η_{sp}/c 60°C
D-Fructose							
0.18	0.0258	0.0244	0.0220	0.47	0.0316	0.0285	0.0238
0.22	0.0263	0.0249	0.0223	0.51	0.0320	0.0283	0.0239
0.26	0.0265	0.0257	0.0224	0.55	0.0321	0.0287	0.0242
0.28	0.0261	0.0256	0.0224	0.61	0.0328	0.0293	0.0246
0.30	0.0265	0.0258	0.0232	Sucrose			
0.34	0.0270	0.0261	0.0230	0.10	0.0273	0.0255	0.0230
0.37	0.0271	0.0262	0.0230	0.12	0.0274	0.0258	0.0232
0.40	0.0274	0.0268	0.0232	0.13	0.0277	0.0266	0.0237
0.43	0.0276	0.0268	0.0232	0.15	0.0285	0.0265	0.0237
0.46	0.0276	0.0267	0.0231	0.16	0.0288	0.0277	0.0242
0.50	0.0278	0.0270	0.0231	0.18	0.0293	0.0277	0.0249
0.56	0.0285	0.0273	0.0234	0.19	0.0297	0.0274	0.0250
D-Glucose							
0.18	0.0263	0.0250	0.0230	0.21	0.0299	0.0280	0.0250
0.22	0.0270	0.0253	0.0235	0.22	0.0303	0.0289	0.0251
0.26	0.0278	0.0269	0.0238	0.24	0.0307	0.0288	0.0255
0.28	0.0279	0.0269	0.0238	0.27	0.0309	0.0290	0.0258
0.30	0.0281	0.0267	0.0241	0.29	0.0313	0.0295	0.0261
0.34	0.0287	0.0271	0.0240	Maltose			
0.37	0.0291	0.0276	0.0244	0.12	0.0299	0.0274	0.0252
0.40	0.0293	0.0273	0.0245	0.13	0.0304	0.0278	0.0247
0.43	0.0295	0.0276	0.0246	0.14	0.0308	0.0278	0.0252
0.46	0.0297	0.0279	0.0250	0.15	0.0312	0.0281	0.0251
0.50	0.0302	0.0280	0.0252	0.16	0.0314	0.0286	0.0259
0.56	0.0304	0.0280	0.0257	0.17	0.0314	0.0286	0.0264
Fucose							
0.20	0.0301	0.0270	0.0240	0.18	0.0317	0.0290	0.0262
0.24	0.0302	0.0265	0.0245	0.20	0.0320	0.0293	0.0264
0.28	0.0304	0.0267	0.0247	0.21	0.0319	0.0292	0.0267
0.30	0.0309	0.0279	0.0249	0.23	0.0322	0.0293	0.0267
0.33	0.0312	0.0284	0.0256	0.25	0.0326	0.0302	0.0271
0.37	0.0315	0.0287	0.0254	0.28	0.0334	0.0305	0.0277
0.41	0.0317	0.0287	0.0252	Lactose			
0.44	0.0323	0.0288	0.0255	0.08	0.0311	0.0250	0.0262
0.47	0.0325	0.0289	0.0255	0.09	0.0305	0.0255	0.0261
0.51	0.0328	0.0296	0.0256	0.10	0.0308	0.0250	0.0263
0.55	0.0330	0.0301	0.0259	0.11	0.0306	0.0253	0.0263
0.61	0.0337	0.0310	0.0263	0.12	0.0306	0.0263	0.0264
Rhamnose							
0.20	0.0292	0.0265	0.0248	0.13	0.0309	0.0269	0.0266
0.24	0.0296	0.0270	0.0249	0.14	0.0318	0.0269	0.0268
0.28	0.0297	0.0270	0.0250	0.15	0.0320	0.0267	0.0270
0.30	0.0297	0.0274	0.0250	0.16	0.0320	0.0270	0.0278
0.33	0.0297	0.0281	0.0253	0.17	0.0323	0.0271	0.0278
0.37	0.0311	0.0281	0.0251	0.18	0.0328	0.0276	0.0279
0.41	0.0316	0.0279	0.0252	0.20	0.0339	0.0279	0.0278
0.44	0.0315	0.0282	0.0253	0.21	0.0343	0.0280	0.0285

Continue TABLE 1.

Concentration c , [mol/dm ³]	η_{sp}/c 25°C	η_{sp}/c 40°C	η_{sp}/c 60°C	Concentration c , [mol/dm ³]	η_{sp}/c 25°C	η_{sp}/c 40°C	η_{sp}/c 60°C
D-Fructose							
0.63	0.0209	0.0281	0.0245	0.63	0.0350	0.0304	0.0279
0.74	0.0306	0.0292	0.0251	0.73	0.0356	0.0307	0.0285
0.89	0.0329	0.0307	0.0268	0.88	0.0372	0.0324	0.0306
1.11	0.0369	0.0337	0.0298	1.10	0.0414	0.0362	0.0334
1.29	0.0398	0.0359	0.0310	1.28	0.0443	0.0374	0.0352
1.41	0.0417	0.0375	0.0318	1.40	0.0464	0.0388	0.0361
1.55	0.0447	0.0393	0.0335	1.54	0.0492	0.0407	0.0377
1.71	0.0478	0.0406	0.0349	1.69	0.0520	0.0454	0.0402
1.85	0.0512	0.0432	0.0372	1.83	0.0547	0.0475	0.0418
2.02	0.0555	0.0466	0.0396	2.00	0.0585	0.0505	0.0439
2.22	0.0617	0.0513	0.0425	2.20	0.0660	0.0566	0.0476
D-Glucose							
0.63	0.0318	0.0305	0.0271	0.63	0.0343	0.0312	0.0270
0.74	0.0330	0.0327	0.0279	0.39	0.0352	0.0328	0.0282
0.89	0.0336	0.0336	0.0304	0.47	0.0372	0.0345	0.0299
1.11	0.0381	0.0371	0.0341	0.58	0.0404	0.0389	0.0357
1.29	0.0400	0.0388	0.0354	0.68	0.0446	0.0422	0.0385
1.41	0.0419	0.0413	0.0365	0.74	0.0468	0.0441	0.0374
1.55	0.0455	0.0433	0.0381	0.82	0.0500	0.0465	0.0399
1.71	0.0495	0.0450	0.0404	0.90	0.0538	0.0479	0.0433
1.85	0.0555	0.0479	0.0428	0.97	0.0594	0.0521	0.0459
2.02	0.0605	0.0516	0.0448	1.06	0.0661	0.0566	0.0493
2.22	0.0675	0.0576	0.0489	1.17	0.0762	0.0630	0.0555
Fucose							
0.70	0.0353	0.0304	0.0273	0.37	0.0372	0.0332	0.0309
0.81	0.0370	0.0307	0.0282	0.44	0.0401	0.0350	0.0325
0.97	0.0403	0.0324	0.0296	0.56	0.0452	0.0389	0.0361
1.22	0.0442	0.0352	0.0329	0.65	0.0491	0.0415	0.0385
1.42	0.0480	0.0374	0.0348	0.71	0.0525	0.0432	0.0398
1.55	0.0509	0.0388	0.0363	0.78	0.0555	0.0461	0.0421
1.71	0.0540	0.0407	0.0390	0.85	0.0600	0.0502	0.0449
1.87	0.0586	0.0454	0.0425	0.93	0.0654	0.0530	0.0476
2.03	0.0625	0.0475	0.0440	1.01	0.0727	0.0576	0.0512
2.21	0.0710	0.0505	0.0467	1.11	0.0814	0.0639	0.0548
2.44	0.0808	0.0556	0.0505	Maltose			

where a is the regression slope, b is the intercept and c is concentration (g/dm^3). Intrinsic viscosities are also given therein.

Relatively small variation in reduced viscosity of D-fructose solutions with concentration could result from the equilibrium shift between isomers-conformers of that saccharide [Mazurkiewicz, 1997] and, in the case of sucrose, structural variation of the D-fructosyl moiety could be charged for it. Assumptions that the viscosity changes might be linked to mutarotation, i.e. to the specific rotation changes was not experimentally confirmed. Viscosity was stable against time whereas specific rotation varied. Therefore, one might accept that the solvent viscosity was

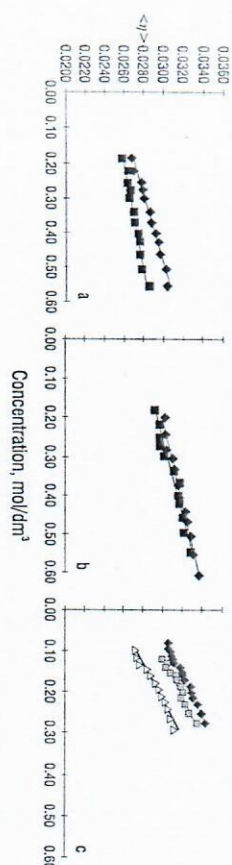


FIGURE 1. Reduced viscosity, $\langle \eta \rangle$, vs. concentration of: (a) aqueous solutions of D-glucose (thombes) and D-fructose (squares); (b) aqueous solutions of fucose (thombes) and rhamnose (squares); (c) aqueous solutions of sucrose (triangles), lactose (thombes) and maltose (squares) at 25°C.

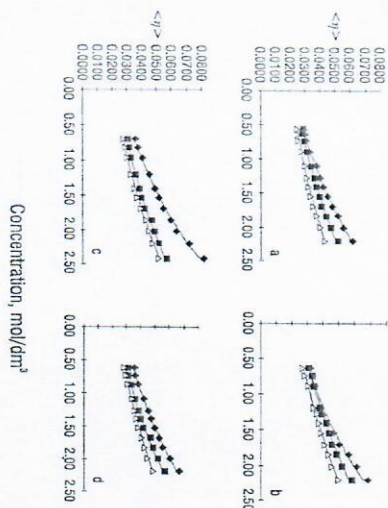


FIGURE 2. Reduced viscosity, $\langle \eta \rangle$, vs. concentration of: (a) aqueous D-glucose solutions; (b) aqueous D-glucose solutions; (c) aqueous D-glucose solutions; and (d) aqueous D-fucose solutions at 25°C (thombes), 40°C (squares), and 60°C (triangles).

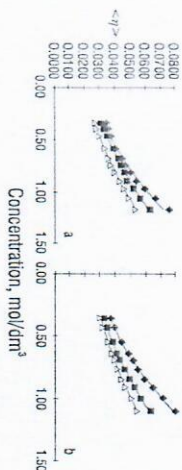


FIGURE 3. Reduced viscosity, $\langle \eta \rangle$, vs. concentration of: (a) aqueous sucrose solutions and (b) aqueous maltose solutions at 25°C (thombes), 40°C (squares) and 60°C (triangles).

independent of the hydrate geometry, but dependent on its molecular weight. Experiments led to the conclusion that intermolecular interactions in solution were weak. Slopes of correlations in Table 2 support this point of view.

The response of viscosity of saccharide solutions to the temperature changes is essential for the application of such solutions as adhesives and thickeners. Small changes would be beneficial. Reduced, as well as intrinsic viscosities decreased as temperature increased. The temperature effect in the interval of 25–40°C is less pronounced than in the more interval of 40–60°C (Table 2). Inspection of Table 2 revealed that aqueous solutions of all investigated saccharides similarly react to the temperature changes. Such result corresponds to results of Noguchi *et al.* [1986] who have found that all of sugars are hydrated by the same number of the water mole-

cules. On the other hand intrinsic viscosities of aqueous solutions of disaccharides are significantly different, suggesting that their hydration spheres are different. In contrast to other disaccharide solutions studied, reduced viscosity of maltose solution strongly increased with its concentration irrespective of temperature.

Determined intrinsic viscosities of saccharides under study confirmed different distribution of the hydroxyl groups capable of interaction with the water molecules. Intrinsic viscosity depends on the volume of hydrated solute species. This calculated decrease of intrinsic viscosities with the temperature increase can result from the thermal destruction of the hydration sphere around the sugar molecules.

Equation 3 presents the intrinsic viscosity as a function of the volume, V_h , occupied by a solute.

$$[\eta] = V_h N/M$$

where N is the Avogadro number and M is molecular weight. Such approach provides a comparison of the volumes occupied by solute molecules, *i.e.* comparison of the hydration degrees.

Thus, one might see that the volume occupied by two glucose molecules (8.8 relative units) is higher than that occupied by one maltose molecule (8.5 relative units) and almost the same as that occupied by one sucrose molecule (8.5 relative units).

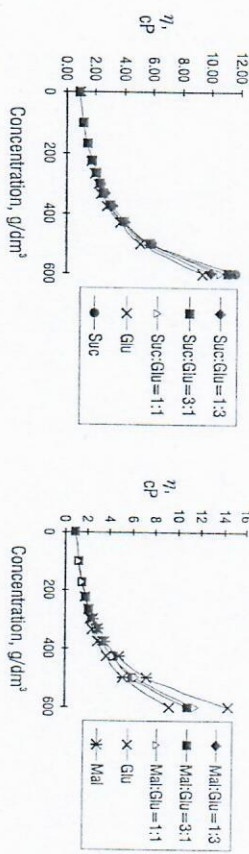


FIGURE 4. Viscosity, η , vs. concentration and composition of aqueous sucrose-glucose blends at 25°C.

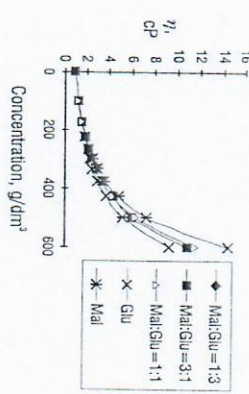


FIGURE 5. Viscosity, η , vs. concentration and composition of aqueous maltose-glucose blends at 25°C.

TABLE 2. Parameters of equation 2 and intrinsic viscosities append saccharide solution.

Saccharide in solution	Temp.	a ^a	b ^b	r ^c	$[\eta]$ dm ³ /g
Fructose	20°C	0.00004	0.0247	0.97	0.0247
	40°C	0.00004	0.0235	0.92	0.0235
	60°C	0.00002	0.0216	0.74	0.0216
Glucose	20°C	0.00006	0.0250	0.98	0.0250
	40°C	0.00004	0.0243	0.79	0.0243
	60°C	0.00004	0.0217	0.96	0.0217
Fucose	20°C	0.00006	0.0280	0.99	0.0280
	40°C	0.00006	0.0245	0.92	0.0245
	60°C	0.00003	0.0234	0.83	0.0234
Rhamnose	20°C	0.00006	0.0273	0.95	0.0273
	40°C	0.00004	0.0255	0.90	0.0255
	60°C	0.00003	0.0238	0.89	0.0238
Sucrose	20°C	0.00007	0.0251	0.97	0.0251
	40°C	0.00006	0.0237	0.93	0.0237
	60°C	0.00005	0.0215	0.96	0.0215
Maltose	20°C	0.00006	0.0278	0.96	0.0278
	40°C	0.00005	0.0254	0.96	0.0254
	60°C	0.00005	0.0229	0.90	0.0229
Lactose	20°C	0.00006	0.0287	0.99	0.0287
	40°C	0.00005	0.0241	0.83	0.0241
	60°C	0.00004	0.0248	0.94	0.0248

TABLE 3. Viscosities, η , of aqueous two-component blends of varying concentrations and ratio at 25°C.

Suc: Glu=1:3 g/dm ³	Visco- sity cP	Suc: Glu=8:1 g/dm ³	Visco- sity cP	Suc: Glu=1:1 g/dm ³	Visco- sity cP
0.0	0.89	0.0	0.89	0.0	0.89
100.0	1.17	100.0	1.16	100.0	1.16
171.4	1.45	171.4	1.46	171.4	1.45
225.0	1.74	225.0	1.75	225.0	1.75
266.7	2.02	266.7	2.04	266.7	2.05
300.0	2.27	300.0	2.27	300.0	2.30
333.3	2.47	333.3	2.51	333.3	2.69
375.0	2.90	375.0	3.01	375.0	3.18
428.6	3.83	428.6	3.91	428.6	4.05
500.0	5.51	500.0	5.74	500.0	5.81
600.0	9.98	600.0	11.05	600.0	10.62

Mal- Glu=1:3 g/dm ³	Visco- sity cP	Mal- Glu=1:1 g/dm ³	Visco- sity cP	Mal- Glu=8:1 g/dm ³	Visco- sity cP
0.0	0.89	0.0	0.89	0.0	0.89
100.0	1.17	100.0	1.18	100.0	1.18
171.4	1.47	171.4	1.49	171.4	1.50
225.0	1.78	225.0	1.82	225.0	1.84
266.7	2.07	266.7	2.12	266.7	2.17
300.0	2.39	300.0	2.41	300.0	2.43
333.3	2.68	333.3	2.71	333.3	2.73
375.0	3.25	375.0	3.27	375.0	3.30
428.6	4.28	428.6	4.30	428.6	4.36
500.0	6.03	500.0	6.05	500.0	6.28
600.0	10.75	600.0	10.89	600.0	11.55

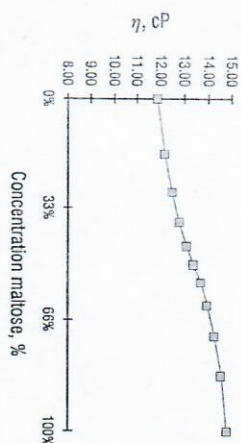


FIGURE 6. Viscosity, η , of aqueous sucrose-maltose blends at 25°C. The overall solution concentration is always 600 g/dm³ at varying sucrose-to-maltose ratio.

It means that the hydration of glucose proceeds in such manner in order to achieve more dense packing in solution. In contrast to maltose also sucrose may take such beneficial conformation.

Studies carried out on solutions containing only one saccharide showed that there was no linearity between intrinsic viscosity and solution concentration. It could be interpreted in terms of either increasing number of intermolecular interactions or variation of their nature. It was an argument for studies of the viscosity of solutions containing combinations of maltose with glucose, sucrose with glucose, and sucrose with maltose. Table 3 and Figure 4 and 5 present relevant data. One might note an essential increase of the solution viscosity with concentration. Irrespective of the disaccharide-to-monosaccharide ratio viscosities of such solutions were in the region below viscosity of solutions of pure disaccharide and above the viscosity of solutions of pure monosaccharide.

Stability of the viscosity of aqueous two-component solutions containing increased concentration disaccharides was striking (Figure 6). This property can be employed for a decrease of the viscosity of aqueous solutions of maltose, sucrose and, possibly, other disaccharides by blending them with other disaccharides.

CONCLUSIONS

Viscosity changes of sugar solutions in the concentration range 0.2 to 0.6 mol/dm³ are linear against concentration. Reduced and intrinsic viscosity decrease with the temperature increase. Corresponding increments are higher between 25 and 40°C than between 40 and 60°C. Blending of the aqueous sugar solutions did not result in any significant viscosity increase what means that intermolecular sugar-sugar interactions are almost independent on the molecular structure of saccharide.

ACKNOWLEDGEMENT

The authors are much indebted to the State Committee for Scientific Research for supporting the grant CPBP 0509.

REFERENCES

1. Drost-Hanson W. 1965. Chemistry and Physics of Interfaces. *Ann. Chem. Soc. Washington*, D. C., pp. 22-27.
2. Genie G.V., 1974. Evaluation of the efficiency of beet diffusers by transfer units. *Zeitschrift für die Zuckerindustrie*, 1974, 24, (9), 473-477.
3. Genie G.V., Influence of slice thickness on evaluation of the efficiency of beet diffusers. *Ibid.*, 1976a, 26, (5), 317-322.
4. Genie G.V., Sugar extraction by diffusion under non-steady conditions. *Ibid.*, 1976b, 29, (1), 9-14.
5. Genie G.V., A new diffuser for beet sugar extraction. *Int. Sugar J.*, 1983, 9, 119.
6. Mathlouthi M., Relationship between the structure and the properties of carbohydrates in aqueous solutions: Part II. Solute-solvent interactions and the sweetness of D-fructose, D-glucose and sucrose in solution. *Food Chem.* 1984, 13, 1-16.
7. March W., Chemical properties of sucrose. *Sugar Technol. Rev.*, 1971, 1, 239-90.
8. Mazurkiewicz J., Structure of aqueous D-fructose solutions, *Pol. J. Food Nutr. Sci.*, 1997, 6/47, 1, 99-106.
9. Mazurkiewicz J., Tomasiak P., Viscosimetric evaluation of solvent effects. *Monatsh. Chem.*, 1982, 113, 1253-1262.
10. Mazurkiewicz J., Tomasiak P., Zaleska H., Zaplotny J., 1994. Modyfikacja węglowodanów i funkcjonalne właściwości produktów. Projekt badawczy No 5 0738 91 01 - sprawozdanie. Komitet Badań Naukowych, Warszawa (in Polish).
11. Noguchi S., Nakazawa F., Takada M., Takahashi J., Bound water of six kinds of sugar by pulse NMR and sorption isotherm. *Kaseigaku Zasshi*, 1986, 37, 347-50.
12. Pauling L., 1940. The Nature of the Chemical Bond. Cornell University Press. Ithaca, New York, U.S.A.
13. Ramnath N.A., Gupta R.C., A new diffuser for beet sugar extraction. *Int. Sugar J.*, 1983, 992, 231-234.
14. Schliephake D., Zeichner E., Orłowski F.A., Schneider F., The influence of nonsugars on the kinetics of crystallization [of sucrose]. *Ibid.*, 1968, 70, 131-4.
15. Velikoboyi E.L., Chernogoriantko B.V., Determination of structural stability of aqueous solutions of sucrose by measurement of evaporation limits. *Sukharu. Prom.*, 1964, 38, (12), 9-10.
16. Zimm B., Crothers D., Simplified rotating cylinder viscometer for deoxyribonucleic acid. *Proc. Natl. Acad. Sci. U.S.A.*, 1962, 48, 905-10.

Received May 1997. Revision received September 1997 and accepted October 1997.

LEPKOŚĆ WODNYCH ROZTWORÓW CUKRÓW

Józef Mazurkiewicz, Maria Nowotny-Różańska

Zespół Fizyki, Wydział Rolnictwa, Akademia Rolnicza, Kraków

Zbadano wpływ stężenia i temperatury na lepkość wodnych roztworów różnych monosacharydów (D-glukozy, D-fruktozy, D-fuktozy i L-ramnozy) oraz disacharydów (sacharozy, maltozy i laktlozy). Zbadano również wpływ tych czynników na lepkość wodnych roztworów mieszanin niektórych z powyższych sacharydów. Wyznaczenie lepkości granicznych (Tab. 1 i Rys. 1, 2, 3) pozwoliło ująć w sposób ogólny budowę tych roztworów jak budowa meru i objętość hydratów sacharydów. Wyznaczono czułość lepkości wodnych roztworów poszczególnych sacharydów na wzrost stężenia wyznaczając parametry równania liniowego $<\eta> = a + b \cdot c$, w którym $<\eta>$ jest lepkością zredukowaną, a c stężeniem. Tabela 2 oprócz tych danych opisuje też wpływ temperatury na lepkość wodnych roztworów sacharydów.

Bez względu na temperaturę (20, 40 i 60°C) i skład, lepkość wodnych roztworów disacharydów w mieszaninie z monosacharydami wyraźnie wzrastała ze stężeniem, zawsze, jednak była mniejsza od lepkości wodnych roztworów czystych dwucukrów i wyższa od lepkości wodnych roztworów monosacharydów (Tab. 3, Rys. 4 i 5). Lepkość wodnych roztworów mieszaniny dwóch sacharydów była praktycznie niezależna od ich składu (Rys. 6).

AROMA CHARACTERISTICS OF DILL SEEDS VARIETIES GROWN IN POLAND

Renata Zawirska-Wojtasiak, Erwin Wasowicz, Henryk Jeleń, Magdalena Rudzińska, Edward Kamiński, Piotr Błażczak

Institute of Food Technology of Plant Origin, Agricultural University, Poznań

Key words: aroma, dill seeds, gas chromatography, genetical variation, sensory analysis

Aroma of dill seeds was analysed by gas chromatography-mass spectrometry and sensory methods. Seven different varieties of dill grown in Poland in three experimental stations and from three harvest years were investigated to observe genetic variation and differences between place and years of crop. Several compounds were identified in the essential oils obtained by distillation/extraction method: α -pinene, α -phellandrene, p-cymene, limonene, terpinen-4-ol, dihydrocarvone, carvone, eugenol and vanillin. Two main aroma compounds: carvone and limonene amounted to 90-96% of total volatiles content. The significant influence of the variety on the content of carvone and limonene as well as total volatiles was stated. The sensory analysis revealed rather great differentiation in the sensory odour profile between the varieties.

INTRODUCTION

Dill seeds because of their essential oil, which possesses a very characteristic caraway like aroma, are broadly used for food flavouring. The volatile constituents of dill seeds as well as dill herb are known in the literature [Blank & Grosch, 1991; Huopalahti, 1986]. It was stated that carvone and limonene are the two main components of dill seeds oil due to their high concentration and high odour activity value, which is the highest one for carvone. Both enantiomers of limonene and carvone were detected in seeds of dill, but the predominant forms are (+)-limonene and (+)-carvone [Bouwmeester *et al.*, 1995].

Author's address for correspondence: Renata Zawirska-Wojtasiak, Instytut Technologii Żywności Podłożenia Roślinnego, Akademia Rolnicza w Poznaniu, 60-624 Poznań, ul. Wojska Polskiego 31, tel. (48 61) 8487275, fax (48 61) 8487314, e-mail: erwinwasowicz@ow.ia.uz.poznan.pl