Registry No. N_2, 7727-37-9; *n*-heptane, 142-82-5; *n*-octane, 111-65-9; *n*-nonane, 111-84-2; *n*-decane, 124-18-5; *n*-dodecane, 112-40-3; benzene, 71-43-2; toluene, 108-88-3; methane, 74-82-8; *n*-butane, 106-97-8.

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Solubilities of D-Xylose and D-Mannose in Water–Ethanol Mixtures at 25 °C

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Solubilities of D-xylose and D-mannose were measured in water–ethanol mixtures at 25 °C, in the concentration range of 0–100 wt % ethanol. Sugar solutions were analyzed by two methods: direct refractometry and high-pressure liquid chromatography.

Introduction

D-Xylose ($C_5H_{10}O_5$), commonly called wood sugar, and D-mannose ($C_6H_{12}O_6$) are monosaccharides. D-Xylose is mainly used as a nonnutritive sweetener. It provides a source of energy for diabetics because it can be metabolized without insulin in humans (*1*). It is widely distributed in plant materials, but its commercial production turns out to be difficult. Its selective separation from aqueous extracts of plants, containing in particular D-mannose, represents one of the main problems.

A French patent (*2*) deals with a method of isolating crystalline D-xylose from an aqueous plant extract by precipitating it with methanol. Due to the toxicity of methanol, salting out from ethanol could be preferably envisaged but the feasibility of this process cannot be quite appreciated from the available literature data.

Here are reported some new experimental data concerning D-xylose–water–ethanol and D-mannose–water–ethanol phase equilibria. The solubility of each carbohydrate has been investigated at 25 °C for water–ethanol mixtures of several compositions.

Experimental Method

A common experimental method for the solubility determinations was used. It consists in maintaining at a fixed temperature a stirred solution containing some excess of solid solute until equilibrium is reached, after which the concentration of the solution is measured. In this work two methods were used to analyze the solutions: direct refractometry, and a combined chromatography and refractometry techniques.

The carbohydrates were supplied by Sigma Chemical Co. (purity >99%). They were dried over P_2O_5 at room temperature. Ethanol used for preparation of the mixed solvents was 99.85 vol % pure. The water was deionized grade. The experimental apparatus was a water bath equipped with a vibrating device holding 12 100-cm^3 Erlenmeyer flasks. The temperature of the water bath could be controlled with an accuracy of 0.02 °C.

Liquid and solid phases were assumed to be in equilibrium when the difference between the refractive indexes of liquid samples withdrawn at about 24-h intervals was smaller than 0.000 07. Several days of intimate contact were required depending on the viscosity of the solution which was affected by the ethanol concentration.

The sampling procedure was as follows. The equilibrium mixture was allowed to stand still for 1 h or more at a constant temperature to enable any finely dispersed solids to settle down. Three samples of the clear supernatant liquid were carefully withdrawn by means of Pasteur pipets slightly hotter than the solution in order to avoid any precipitation.

Concerning the first method of analysis (direct refractometry), a linear relationship was established, for all experimental water–ethanol weight ratios, between sugar concentration of a solution close to saturation and its refractive index. A Zeiss refractometer fitted with thermoprisms was used. The temperature of the measurements was fixed at 30 ± 0.03 °C by means of a thermostatic circulating bath. This method proved to be very accurate but very tedious and time consuming.

The second one brings into play a high-pressure liquid chromatograph (HPLC) equipped with a separator column of HPX 87 P and bidistilled water as a solvent (*3*). The components emerging from the column are detected by a differential refractometer. The output signal is recorded on a strip chart and processed by an integrating device. The preparation procedure of the sample solution was as follows. The solution was transferred to 0.2-cm^3 flasks and weighed to ±0.1 mg. Moreover, high concentrations of sugar require appreciable dilution of the samples which might increase experimental errors. Injection volumes of 0.02 cm^3 were employed. Quan-

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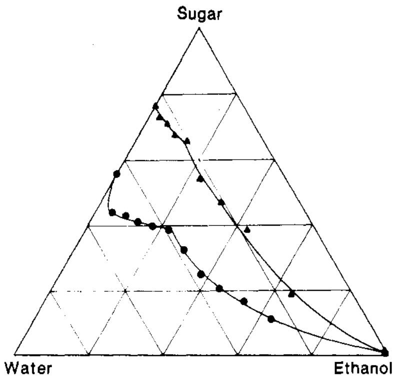

Figure 1. Solubility diagram at 25 °C for the systems D-mannose-water-ethanol (▲) and D-xylose-water-ethanol (●).

Table I. Solubility of D-Xylose in Water-Ethanol Mixtures at 25 °C

wt % ethanol (g of ethanol/ 100 g of solvent)	solubility (g of D-xylose/100 g of soln) *a*	std dev	*b*	std dev	g of water/ 100 g of soln
0.00	55.11	0.03	55.04	0.10	44.96
7.94			43.51	0.08	52.01
14.31			42.85	0.16	48.97
21.47			40.72	0.08	46.55
28.55			39.57	0.11	43.18
35.85			38.35	0.15	39.55
42.92			32.03	0.10	38.80
50.22			24.87	0.20	37.40
56.31			20.28	0.10	34.83
64.00			16.66	0.11	30.00
71.31			11.13	0.09	25.50
100.00	1.08	0.01	1.10	0.04	0.00

[a] First method (direct refractometry). [b] Second method (HPLC).

tification was accomplished by comparing the response factors of the sample components with those of similar retention times stored in the integrator memory after eluting a standard solution.

Results and Discussion

The experimental results are shown in Tables I and II. Figures 1 and 2 represent the solubility data on triangular and rectangular diagrams. D-Mannose being much more soluble than D-xylose, the greater part of the measurements of solubility were carried out according to the first method for D-mannose and according to the second method for D-xylose. The standard deviations are less than 0.04 and 0.20 respectively for direct refractometry and for HPLC. the difference between the solubility data obtained by means of the two methods is smaller than 1 g of sugar per 100 g of solution.

The solubility of the two sugars decreases with the amount of ethanol cosolvent in the mixture. It is noteworthy that the solubilities of D-mannose are always higher than those of D-xylose in any composition of the solvent system. The curves present similar trends for both solutes: an abrupt change in slope occurs at ca. 35-40 wt % ethanol. However, only the solubility of D-xylose widely falls for small amounts of ethanol. Such peculiarities can be attributed to binary interactions between the components.

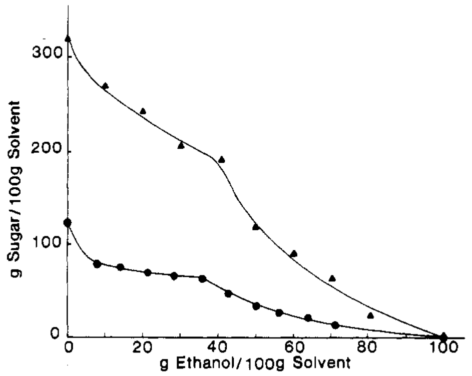

Figure 2. Solubility of D-mannose (▲) and D-xylose (●) at 25 °C in water-ethanol mixtures vs wt % ethanol.

The structure of the solvent is different for each weight percent of ethanol. This appears clearly, for example, from viscosity data (*4*) of the water-ethanol mixture which show a very high peak at ca. 45 wt % ethanol. Structuring of the respective solvent can also be observed from the enthalpy data of mixing ΔH^M vs wt % ethanol at 25 °C (*4*). ΔH^M is always negative (exothermic mixing) and a minimum occurs at ca. 40 wt % ethanol. If the enthalpy of mixing is assumed to be the sum of the two thermal effects (*4*), the endothermic destruction of water-water hydrogen bonds and the exothermic formation of rather strong and well-organized ethanol-water hydrogen bonds, it may be inferred that intercomponent attractions are dominant factors in the formation of the mixture. Moreover, when ethanol and water are mixed there is a contraction in volume which might seem to reflect the strength of intercomponent attraction. Similar trends were observed in a recent study (*5*) of the heat capacity of the same system.

Hydrogen bonding plays also an important role in the solute-solvent interaction. Hydration of saccharide is mainly ascribed to the effect of hydrophilic -OH group in the molecule. It corresponds to the existence of the compressed water molecules attached to the solute. The hydration number of D-xylose and D-mannose in water are respectively 2.6 and 3.3 (*6*). The fact that it does not vary proportionally with the number of -OH groups contained in saccharide molecule has been interpreted in terms of intramolecular hydration bonding and steric hindrance effect. With an increase in the ethanol concentration, hydration decreases and becomes constant at ca. 20 wt % (*7*). Bound water of sugars is transferred from solute molecules to solvent by ethanol. In a saccharide molecule, many functional groups are arranged in close proximity of each other on the cyclic skeleton of the molecule. In contrast to D-xylose, D-mannose contains, bound to the cyclic structure,

Table II. Solubility of D-Mannose in Water-Ethanol Mixtures at 25 °C

wt % ethanol (g of ethanol/100 g of solvent)	solubility (g of D-mannose/100 g of soln) *a*	std dev	*b*	std dev	g of water/ 100 g of soln	n_D[c]
0.00	76.13	0.03			23.87	1.4755
10.22	72.90	0.03	72.47	0.15	24.39	1.4679
20.10	70.83	0.02			23.35	1.4654
30.03	67.26	0.03			22.96	1.4597
40.08	65.49	0.02			20.75	1.4566
49.99	53.97	0.04			23.06	1.4309
60.04	46.51	0.03			21.31	1.4229
70.05	38.13	0.01	37.13	0.10	18.53	1.4027
80.05	18.14	0.02			16.71	1.3810
100.00	1.36	0.01			0.00	1.3583

[a] First method (direct refractometry). [b] Second method (HPLC). [c] Refractive index.

one -CH(OH)- in addition. This -OH is very accessible and establishes stable linking. That could be the reason why the solubility of D-mannose does not fall steeply when a small amount of ethanol is added.

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Viscosities of Trichloroethylene with Ketones and 1,4-Dioxane at 298.15, 308.15, and 318.15 K

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Viscosity data for the binary liquid mixtures of trichloroethylene with methyl ethyl ketone, diethyl ketone, methyl isobutyl ketone, cyclohexanone, and 1,4-dioxane have been determined at 298.15, 308.15, and 318.15 K. The deviation in viscosity has been calculated by using the relation $\Delta \ln \eta = \ln \eta_{mix} - (x_1 \ln \eta_1 + x_2 \ln \eta_2)$ and studied as a function of composition and temperature. In the systems trichloroethylene with methyl ethyl ketone, diethyl ketone, and methyl isobutyl ketone the deviation in viscosity is positive, and the quantity is negative in the remaining systems at the three temperatures. The results have been analyzed in the light of the viscosity relations proposed by Hildebrand and Kosanovich.

Introduction

The evaluation and prediction of viscosities of binary liquid mixtures as a function of composition and temperature are of theoretical and practical importance, but very little data are available. Here, we have reported the viscosities for the binary systems of trichloroethylene with methyl ethyl ketone, diethyl ketone, methyl isobutyl ketone, cyclohexanone, and 1,4-dioxane measured at 298.15, 308.15, and 318.15 K. These systems have been selected with a view to study the effect of molecular structure on the transport property. The viscosity relation proposed by Hildebrand (*1*) and Hildebrand and Lamoreaux (*2*) for pure components and the viscosity relation proposed by Cullilan and Kosanovich (*3*) for binary mixtures have been used to analyze the experimental data.

Experimental Section

The viscosities of pure liquids and liquid mixtures were measured with an Ostwald viscometer and the values were accurate to 0.5%. Densities for the pure components were measured with a bicapillary pycnometer, and densities for mixtures were obtained from excess volume, V^E, data (*4*) by using the relation

$$\rho = \frac{x_1 M_1 + x_2 M_2}{x_1 v_1 + x_2 v_2 + V^E} \qquad (1)$$

Density values in both the cases were accurate to $\pm 5 \times 10^{-5}$ g·cm^{-3}.

Trichloroethylene (BDH) and cyclohexanone (BDH) were dried over anhydrous sodium sulfate for 2 days and fractionally distilled. 1,4-Dioxane was dried with anhydrous magnesium sulfate and refluxed with sodium; then the sample was fractionally distilled. Methyl ethyl ketone (BDH), diethyl ketone (Fluka), and methyl isobutyl ketone (BDH) were purified by the methods described earlier (*5-7*). The purity of the chemicals was ascertained by comparing the density and boiling point data with literature values (*8*, *9*). The measured values of density and boiling point are presented in Table I along with the literature values.

Table I. Boiling Points and Densities of the Pure Components at 298.15 K

	boiling point, K		density, g·cm^{-3}	
compound	present work	lit. (*8*, *9*)	present work	lit. (*8*, *9*)
trichloroethylene	360.00	360.34	1.454 70	1.451 40[a]
methyl ethyl ketone	352.60	352.79	0.799 50	0.799 70
diethyl ketone	375.00	375.14	0.809 60	0.809 45
methyl isobutyl ketone	389.40	389.65	0.796 53	0.796 10
cyclohexanone	428.70	428.80	0.942 01	0.942 07
1,4-dioxane	374.00	374.47	1.027 70	1.027 97

[a] At 303.15 K.

Results

Density and viscosity results determined at the three temperatures are given in Table II. The deviations in viscosities are calculated by using the relation

$$\Delta \ln \eta = \ln \eta_{mix} - (x_1 \ln \eta_1 + x_2 \ln \eta_2) \qquad (2)$$

where x_1 and x_2 are mole fractions and η_1 and η_2 are viscosities of pure components 1 and 2. The values of $\Delta \ln \eta$ are accurate to ± 0.005. $\Delta \ln \eta$ as a function of mole fraction are represented graphically in Figures 1-5 and the data also included in Table II.

The deviations in viscosities are fitted to an empirical equation of the form

$$\Delta \ln \eta = x_1 x_2 [A_0 + A_1(x_1 - x_2) + A_2(x_1 - x_2)^2] \qquad (3)$$

The values of the constants A_0, A_1, and A_2 are obtained by the method of least squares and are given in Table III along with the standard deviation $\sigma(\Delta \ln \eta)$.

According to Hildebrand (*1*), the fluidity, ϕ, of a liquid depends on the ratio of free volume ($V - V_0$) to intrinsic volume,

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