J. Chem. Eng. Data **1998,** *43,* 653−657

Transport Properties of the Binary System Glucose−Water at 25 °C. A Velocity Correlation Study

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Accurate mutual and intradiffusion coefficients have been measured for the binary system glucose (2)−water (1) at 25 °C. The collected diffusion coefficients have been combined with activity coefficients present in the literature to calculate the velocity correlation coefficients (VCC). The results have been interpreted in terms of molecular interactions.

Introduction

This research is part of a program devoted to the study of equilibrium and transport properties of the ternary system ethanol−glucose−water at various compositions. In the preliminary phase of this study, we decided to collect a set of data on the corresponding binary systems. In particular, we remeasured densities and diffusion coefficients of the aqueous glucose solutions in the composition range approaching saturation. The results are in very good agreement with previous literature data. Furthermore, intradiffusion measurements have been performed in the same composition range and the results have been discussed in terms of velocity correlation coefficients (VCC).

Experimental Section

Materials. Glucose purchased from Sigma Chemical Co. (>99.5% purity) was used without further purification. A DSC test was taken on anhydrous glucose and glucose recrystallized from water (see Figure 1). Anhydrous glucose melts at 150 °C (Perry (1984) gives a melting temperature of 146 °C) and decomposes around 170−180 °C. Recrystallized glucose melts around 60 °C and decomposes around 150 °C; a thermogravimetric analysis shows that hydrated glucose loses weight over 60 °C corresponding to one water molecule per glucose molecule.

All solutions were made up by mass using double-distilled water. In all calculations the molecular weight of glucose was assumed to be 180.16 g mol^{-1}.

Density Measurements. A set of density measurements were taken in the molality range of 0−11 mol kg^{-1} with an Anton Paar 602 densimeter. The temperature of the densimeter was regulated at (25.00 ± 0.01) °C.

For the densimeter calibration, air (at measured pressure and humidity) and distilled water (assumed density 0.997 044 kg dm^{-3}) were chosen. The data, collected in Table 1 (see also Figure 2), are in very good agreement with previous literature data (Pulvemacher, 1920; Timmermans, 1960; Taylor and Rowlison, 1955).

The following equation was fitted to the densities given in Table 1

$$\rho(m)/\mathrm{kg\ dm}^{-3} = 0.997\,044 + 0.067\,21(\pm 2.3 \times 10^{-4})m - 0.007\,096(\pm 1.2 \times 10^{-4})m^2 + 0.000\,489\,4(\pm 2.0 \times 10^{-5})m^3 - 0.000\,014\,7(\pm 9.3 \times 10^{-7})m^4 \pm 4.5 \times 10^{-4} \quad (1)$$

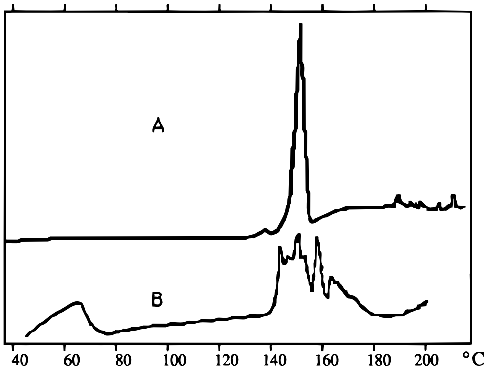

Figure 1. (A) Thermal analysis of anidrous glucose; (B) thermal analysis of glucose recrystallized from water.

Table 1. Densities of Aqueous Glucose Solutions at 25 °C

m/mol kg^{-1}	ρ/kg dm^{-3}	m/mol kg^{-1}	ρ/kg dm^{-3}	m/mol kg^{-1}	ρ/kg dm^{-3}
0.0000	0.997 044	0.5299	1.030 672	3.0321	1.147 364
0.0201	0.998 415	0.7192	1.042 369	3.1257	1.151 752
0.0227	0.998 443	0.7790	1.045 596	3.4986	1.164 100
0.0512	1.000 455	0.9603	1.054 991	5.4821	1.220 479
0.0800	1.002 103	0.9684	1.055 456	5.9860	1.231 119
0.2000	1.010 430	1.0029	1.057 875	7.0029	1.252 123
0.2700	1.014 853	1.0297	1.058 725	7.9728	1.269 965
0.3000	1.016 768	1.9704	1.105 716	8.0650	1.271 802
0.3300	1.018 683	1.9994	1.107 727	8.9957	1.287 889
0.4000	1.023 205	2.0299	1.108 008	11.228	1.315 511
0.4700	1.027 180	2.9657	1.144 554	11.528	1.318 969

where m/mol kg^{-1} of H_2O is the glucose molality. From eq 1 the limiting partial molar volume of glucose was computed by interpolating the total volume of solutions with an eighth power polynomial: $V_2^\infty = (113.089 \pm 0.006)$ cm^3 mol^{-1}.

Mutual Diffusion Coefficients. Mutual diffusion coefficients were measured with a Gouy diffusiometer (Gosting, 1950; Tyrrell and Harris, 1984) using a single channel cell in which the initial boundary was formed with the siphoning technique. The light source was a Unifas PHASE 0.8-nW neon−helium laser operating at $\lambda = 632.8$ nm. Mutual diffusion coefficients were calculated using a series of programs well-described in the literature (Albright and Miller 1988; Miller et al., 1992).

The mutual diffusion coefficients were measured in the range of molality 0−8 mol kg^{-1}; significant data are collected in Table 2. The following equation fits the diffusion experimental data:

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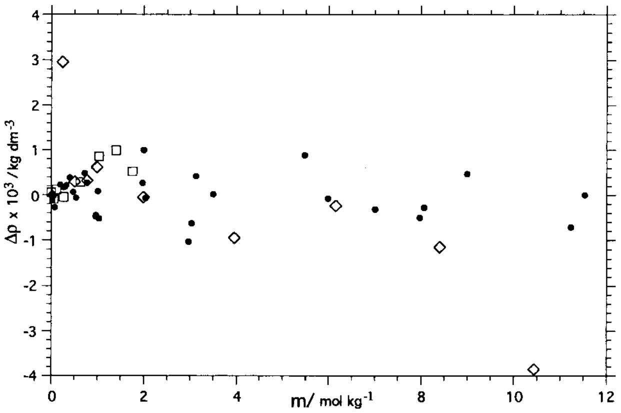

Figure 2. Comparison of glucose aqueous solutions densities from different sources with eq 1: ● our data; ◇, (Pulvemacher, 1920); □, (Taylor and Rowlison, 1955).

Table 2. Diffusion Data on the System Glucose−Water at 25 °C

m/mol kg^{-1}	Δm/mol kg^{-1}	J_m	$D_{12} \times 10^5$/cm^2 s^{-1}	$B(x)$	$D_T \times 10^5$/cm^2 s^{-1}
0.0000			*0.6730*	*1.000*	*0.673*
0.0256	0.0512	51.20	0.6644	1.001	0.664
0.0500	0.0601	59.91	0.6670	1.002	0.666
0.3000	0.0600	55.91	0.6213	1.011	0.614
0.4999	0.0599	52.45	0.5929	1.019	0.582
0.7491	0.0595	49.60	0.5554	1.030	0.539
0.9816	0.0664	52.91	0.5196	1.043	0.498
2.0001	0.0613	34.36	0.4214	1.130	0.373
2.9989	0.0606	25.50	0.3497	1.234	0.283
4.0004	0.1288	33.50	0.2844	1.317	0.216
5.4176	0.0922	55.27	0.2197	1.386	0.158
5.4242	0.0781	53.54	0.2197	1.387	0.158
8.0189	0.1653	23.10	0.1393	1.514	0.092

[a] m, average molality of each diffusion run. Δm, molality difference between bottom and top solutions. J_m, total number of Gouy fringes, in terms of refractive index difference, Δn, between bottom and top solutions at the He−Ne laser red light ($\lambda = 632.8$ nm). $J_m = 3.951 \times 10^6 \Delta n$. D_{12}, diffusion coefficients. D_T, thermodynamic diffusion coefficient (Laity, 1959).

$$D_{12} \times 10^5/\text{cm}^2\,\text{s}^{-1} = 0.673(\pm 0.002) - 9.76(\pm 0.3)x_2 + 94.4(\pm 12)x_2^{\,2} - 641(\pm 151)x_2^{\,3} + 1904(\pm 614)x_2^{\,4} \pm 0.002 \tag{2}$$

where x_2 is the glucose mole fraction.

Intradiffusion Measurement. The intradiffusion coefficients were measured by the pulsed gradient spin−echo (PGSE) NMR method (Stilbs, 1987; Callaghan, 1991). By using a pulse sequence where the echo delay is fixed and only the gradient pulse lengths are varied, the effects of relaxation are constant and need not be taken into consideration. Individual signal amplitudes are described by the equation

$$I = I_0 \exp\left[-\frac{2\tau}{T_2} - \gamma^2 g^2 D_i^* \delta^2\left(\Delta - \frac{\delta}{3}\right)\right] \tag{3}$$

where γ is the gyromagnetic ratio of nucleus, D_i^* is the intradiffusion coefficient of molecules, g is the gradient strength, δ and Δ are the length and spacing of the gradient pulses, τ the time lag between pulses at 90° and 180°, and T_2 is the spin−spin relaxation time, respectively. Measurements were carried on a Varian FT 80 NMR spectrometer using a pulsed magnetic field gradient unit to generate the gradient pulses.

Our intradiffusion measurements raise the problem of short T_2 values due to the strong interactions among molecules in solution. The measurements require a short τ value and consequently a small Δ value. Our magnetic field gradient unit has four pre-emphasis circuits to obtain a step-shaped gradient, which allows us to use δ values of the same order of magnitude as the Δ value.

The glucose intradiffusion measurements were performed in heavy water to enhance the CH_2 NMR signals. The measured D_2^* values have been corrected for the 1.23 factor (Goldammer and Hertz, 1970) to have the values in light water.

The D_{OH}^* values were determined in a different set of measurements performed in light water. However, owing to the very short value of T_2, the measurements in concentrated glucose solutions could not be made. Since the proton exchange between glucose OH's and water is much faster than the single spin−echo sequence, the D_{OH}^* value is a mean value that can be split between glucose and water contributions according to the expression

$$D_{OH}^* = \frac{5x_2}{5x_2 + 2x_1} D_2^* + \frac{2x_1}{5x_2 + 2x_1} D_1^* \tag{4}$$

where x_1 and x_2 are the mole fractions of water and glucose, respectively.

The measured values of D_{OH}^*, D_2^*, and D_1^* are collected in Table 3. A cubic equation was first fitted to the experimental D_2^* data by the method of least squares, which gave an intercept at zero mole fraction $D_2^*(0) \times 10^5$/cm^2 s^{-1} = 0.695 ± 0.013. Since this extrapolation should correspond to that of the mutual diffusion coefficients (Tyrrell and Harris, 1984), which is more accurate, the limiting value given by eq 2 was imposed and the following expression was obtained for the intradiffusion coefficient of glucose:

$$D_2^* \times 10^5/\text{cm}^2\,\text{s}^{-1} = 0.673 - 15.0(\pm 0.4)x_2 + 124(\pm 9)x_2^{\,2} - 334(\pm 49)x_2^{\,3} \pm 0.009 \tag{5}$$

Experimental Results

Mutual diffusion coefficients of the glucose−water system are present in the literature; they are in very good agreement with our data (Gladden and Dole, 1953), while earlier data (Friedman and Carpenter, 1939) are in slight disagreement.

In binary systems, the diffusion coefficients D_{12} defined by the Fick's law

$$J_2 = -D_{12}\,\text{grad}\,C_2 \tag{6}$$

are given by the contribution of two terms: a mobility term, M, describing the actual tendency of molecules to diffuse, and a thermodynamic term, B, accounting for the fact that the diffusion driving force is not the concentration gradient but the chemical potential gradient of the diffusing species

$$J_2 = -M_2\,\text{grad}\,\mu_2 \tag{7}$$

Accordingly

$$D_{12} = M_2 B_2 \tag{8}$$

There is some ambiguity in defining the B term. A correct definition of mobility should be given in terms of molar concentration

$$D_{12} = M_2 B(C_2) \tag{9}$$

where

Table 3. Intradiffusion Data on the System Glucose−Water at 25 °C

m/mol kg^{-1}	x_2	$D_2^* \times 10^5$/cm^2 s^{-1}	m/mol kg^{-1}	x_2	$D_{OH}^* \times 10^5$/cm^2 s^{-1}	$D_1^* \times 10^5$/cm^2 s^{-1}
0.0000	0.0000	(0.673)	0.0000	0.0000	2.299	2.299
0.6269	0.0112	0.533	0.6250	0.0111	1.749	1.784
1.3914	0.0245	0.371	1.4120	0.0248	1.514	1.587
2.3511	0.0406	0.245	2.3270	0.0402	1.102	1.192
3.6977	0.0625	0.141	3.5703	0.0604	0.537	0.599
5.5610	0.0911	0.080				
6.8080	0.1093	0.091				
8.2660	0.1296	0.087				

$$B(C_2) = RT\left(1 + \frac{\mathrm{d}\ln y_2}{\mathrm{d}\ln C_2}\right) \qquad (10)$$

y_2 being the activity coefficient expressed as a function of molar concentration.

Some authors used $B(m)$ expressing the thermodynamic term as a function of molality

$$B(m) = RT\left(1 + \frac{\mathrm{d}\ln \gamma_2}{\mathrm{d}\ln m}\right) \qquad (11)$$

γ_2 being the activity coefficient expressed as a function of molality; this coefficient is directly obtained from the treatment of osmotic coefficients (Lewis and Randal, 1961, p 263).

In this paper we prefer to use the Laity (1959) notation that defines a unique mobility term $M_2 = M_1 = D_T$, called thermodynamic diffusion coefficient, once the thermodynamic term is defined as

$$B(x_2) = \left(1 + \frac{\mathrm{d}\ln f_2}{\mathrm{d}\ln x_2}\right) = \left(1 + \frac{\mathrm{d}\ln f_1}{\mathrm{d}\ln x_1}\right) = B(x_1) \qquad (12)$$

where x_i and f_i are the mole fraction and rational activity coefficient of component i, respectively (note that $f_2 = \gamma_2/x_1$).

The advantage of Laity's notation is due to the fact that writing the flow equations as

$$\mathrm{grad}\,\mu_i = \sum_k r_{ik}x_k(v_i - v_k) \qquad (13)$$

where v_i is the diffusion velocity of component i (Laity, 1959; Klemm, 1953), the terms r_{ik} are *interchange frictional coefficients* relating the friction of component i moving through component k. Among these coefficients the Onsager reciprocal relations hold, $r_{ik} = r_{ki}$. In particular, only one frictional coefficient, as defined by eq 13, exists in binary systems, which is related to the thermodynamic diffusion coefficient by the expression

$$r_{ik} = RT/D_T \qquad (14)$$

The thermodynamic factor $B(x_2)$ was calculated from literature osmotic coefficients (Bonner and Breazeale, 1965). Activity coefficients were computed by interpolating the osmotic data with a seventh power polynomial; the uncertainties could be estimated to be ∼±0.01. Mutual diffusion coefficients and thermodynamic diffusion coefficients are shown in Figure 3, while Figure 4 shows a comparison of D_{12}, D_1^*, and D_2^* drawn as a function of the solute mole fraction.

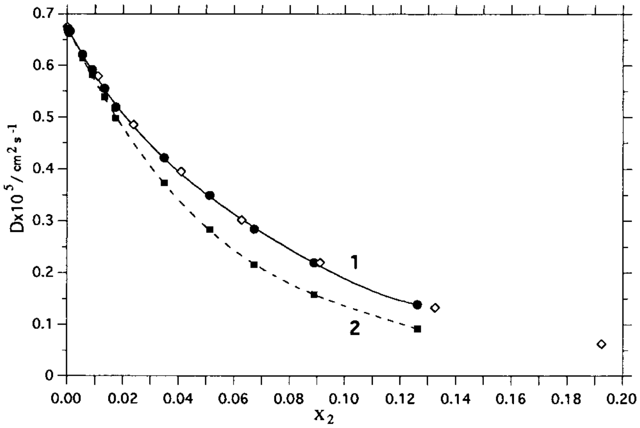

Figure 3. Diffusion coefficients (1) and thermodynamic diffusion coefficients (2) of glucose aqueous solutions at 25 °C: (1) ●, our data; ◇, Gladden and Dole, 1953.

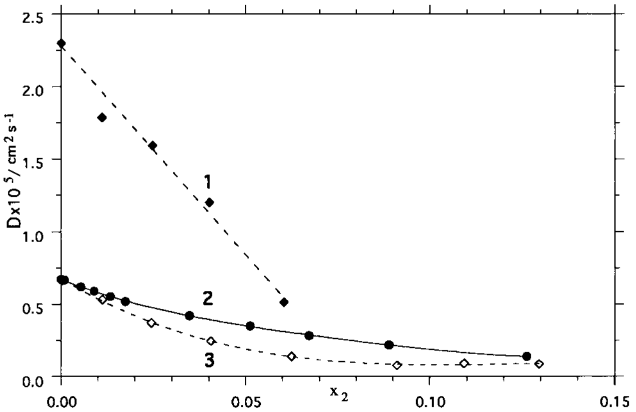

Figure 4. Comparison of mutual diffusion and intra-diffusion coefficients of aqueous glucose solutions at 25 °C: (1) D_1^* intradiffusion coefficients of water; (2) D_{12} mutual diffusion coefficients; (3) D_2^* intradiffusion coefficients of glucose.

Discussion

As shown in Figure 3 both mutual diffusion coefficients and thermodynamic diffusion coefficients decrease with the mole fraction of solute, while the thermodynamic factors increase with x_2 (Table 2). This gives evidence that the mobility contribution prevails on ruling the behavior of diffusion coefficients. An opposite effect can be found in some systems, such as surfactant solutions, where both thermodynamic and diffusion coefficients decrease with solute concentration, while mobilities increase (Leaist, 1986; Paduano et al., 1997).

The behavior of intradiffusion coefficients D_2^* shown in Figure 4 reflects this situation. Moreover, inspection of Figure 4 shows that the intradiffusion coefficients of water decrease quite sharply with the glucose concentration; their trend seems to extrapolate to the glucose intradiffusion curve so that at $x_2 \cong 0.09-010$ both components should have same intradiffusion coefficients.

The minimum number of water molecules in the hydration cosphere is estimated to be 5−6, which corresponds to $x_2 = 0.14$ (Franks et al., 1972). Hence at $x_2 > 0.09$ all the water molecules should be involved in the formation of the hydration cosphere around the glucose molecule. This

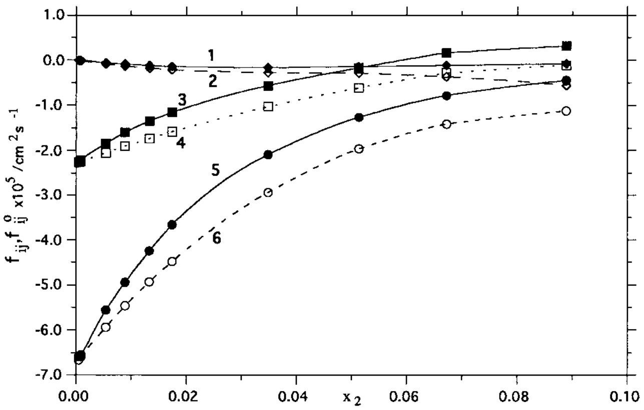

Figure 5. Velocity cross-correlation factors for the system glucose−water at 25 °C: (1) f_{22}; (2) f°_{22}; (3) f_{11}; (4) f°_{11}; (5) f_{12}; (6) f°_{12}.

fact is also responsible for a large obstruction effect on the free motion of water molecules. For these reasons water molecules are largely hindered on their motion and forced to diffuse mainly at the same brownian velocity as that of glucose molecules.

A better description of the system behavior from the microscopic point of view can be given computing the velocity cross-correlation coefficients, VCC's, more sensitive to specific interactions than the experimental diffusion coefficients (Weingartner, 1990; Ambrosone et al., 1995).

The intradiffusion coefficient D_i^* of component i is defined in terms of the velocity autocorrelation function as (Steele, 1969)

$$D_i^* = \frac{1}{3}\int_0^\infty \langle v_\alpha^i(0) - v_\alpha^i(t)\rangle \mathrm{d}t \qquad (15)$$

where the v_α^i is the velocity of a particle numbered α of component i at time 0 and t, respectively. The pointed brackets indicate the ensemble average.

The correlation in the motion of different particles α and β can be expressed through the definition of the velocity correlation coefficients

$$f_{ij} = \frac{N}{3} x_j \int_0^\infty \langle v_\alpha^i(0) - v_\beta^j(t)\rangle \mathrm{d}t \qquad (16)$$

where N is the total number of particles in the system. Equation 16 characterizes the correlation motion between different particles of the same or of different components.

The VCC's can be related to the experimental quantities D_1^*, D_2^*, and D_{12} (McCall and Douglass, 1967)

$$f_{12} = -D_{12}\frac{M_1 M_2}{(x_1 M_1 + x_2 M_2)^2 B(x_1)} x_2 \qquad (17)$$

$$f_{ii} = D_{12}\frac{M_j^2 x_j}{(x_1 M_1 + x_2 M_2)^2 B(x_1)} x_j - D_i^* \qquad (18)$$

where M_i is the molecular weight of the component i and $B(x_1)$ is the thermodynamic factor in the mole fraction scale, as defined by eq 12.

The coefficients defined by eqs 17 and 18 will not play the role of an indicator for the molecular association effect if not compared with their corresponding standard. As discussed in detail elsewhere (Mills and Hertz, 1980; Weingartner, 1990), molecular association should lead to correlated motions in extension to those expected for an "ideal" system. The general association criterion is

$$f_{ij} > f^\circ_{ij} \qquad (19)$$

where f°_{ij} is the VCC in a reference system. We follow the approach of Hertz (1982) who used the law of effective moment conservation together with a simple mixing rule to obtain the following standard coefficients

$$f^\circ_{12} = \frac{M_1 x_2}{(x_1 M_1 + x_2 M_2)} D_1^*(1 + x_1 P_{12}) \qquad (20)$$

$$f^\circ_{ii} = \frac{M_i x_i}{(x_1 M_1 + x_2 M_2)} x_i D_i^*(1 - x_j P_{12}) \qquad (21)$$

where

$$P_{12} = \frac{M_1 D_1^*}{M_2 D_2^*} - 1 \qquad (22)$$

The VCC's and the corresponding standard correlation coefficients are reported in Figure 5.

Inspection of Figure 5 shows that $f_{22} \cong f^\circ_{22}$, which implies, according to eq 19, that there is no self-association between glucose molecules, in agreement with previous results (Franks et al., 1972; Tait et al., 1972).

On the contrary the dominant effect in the binary system glucose−water appears to be water−water and glucose−water association. In fact f_{11} is larger than the corresponding f°_{11} and tends to be positive as the concentration rises; this is interpreted as a water−water aggregation.

Furthermore, considering the behavior of f_{12}, which reflects the interaction between glucose and water, Figure 5 shows that this coefficient is much larger than the corresponding standard coefficients f°_{12} in the whole range of explored concentration, stressing the presence of strong cross-associations between glucose and water.

Acknowledgment

This research was carried on with the financial support of Italian MURST and of Italian CNR.

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Received for review February 23, 1998. Accepted April 17, 1998.

JE980054C