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Experimental Determination of the Thermophysical Properties of Water–Xylitol Mixtures

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■ In the last few years many new refrigerant–absorbent pairs have been proposed for use in heat transformers. Water–Xylitol mixtures are examined in the present paper. The experimental work on water–xylitol mixtures consists of measuring pressure–temperature–concentration data at saturation conditions to trace the whole P–T–X chart. In addition, the specific heat and kinematic viscosity are measured at various concentrations and temperatures.

Measurements of specific heat are effected by means of a heat flux calorimeter in the range of temperatures between 313 and 373 K and in the range of concentrations between pure water and saturated solutions. Measurements of viscosity are obtained by means of an Ubbelohde viscosimeter, in the range of temperatures between 273 and 353 K and in the range of concentrations between pure water and saturation.

The results from the P–T–X chart verify that the maximum attainable temperature difference between external fluids connected with the engine would be within the range of 5–10 K. Thus, it is concluded that water–xylitol solutions are not suitable for applications in the field of heat transformers and absorption machines.

Keywords: *water–xylitol mixtures, thermophysical properties, pressure–temperature–concentration data, specific heat, kinematic viscosity*

INTRODUCTION

The successful operation of a heat transformer is related to the selection of appropriate refrigerant–absorbent pairs [1]. In the present paper the water–xylitol pair, a completely nontoxic and low-cost substance, is considered as a possible candidate for use in heat transformers. By measuring the specific heat, kinematic viscosity (both at constant pressure), and vapor pressure data of the water–xylitol mixture, we attempt to verify whether this pair could actually be used in heat transformers.

All samples of the solution were prepared from a single batch of xylitol (lot No. H1250899, purity 99.8%, manufactured by Suomen Xyrofin) and pure distilled water.

EXPERIMENTAL OPERATION AND DATA

Vapor pressure

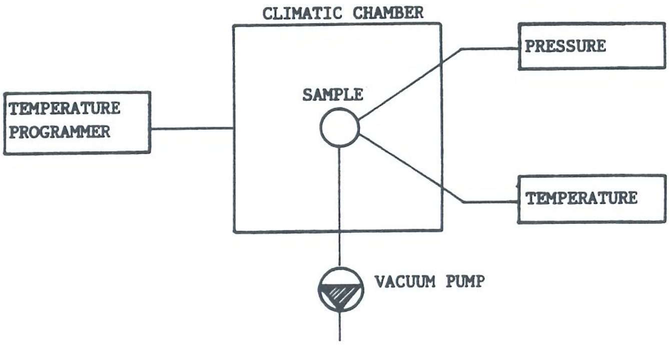

Figure 1. P–T–X measurement: Block diagram of experimental set up.

Apparatus The experimental apparatus was described in a previous work [2]. A simplified sketch is given in Fig. 1. The temperature is measured by a resistance thermometer PT 100 and a digital transmitter according to DIN 43760. The pressure is measured by a digital manometer with a Druck pressure transducer (Model PDCR 350) in the range 0–500 kPa and by a mechanical manometer in the range 0–100 kPa.

Sample Preparation The samples are prepared by weighing solute and solvent in the desired quantities: 30,

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50, 60, 70, and 90% by weight of solvent (the 90% only for C_p measurements). All samples are prepared at room temperature. A preheating to 313 K is needed only for the 30% sample, to get complete solubility. For each P–T–X measurement a 20 cm^3 sample of solution is used. The ratio $V_{\text{liquid}}/V_{\text{sample container}}$ is equal to 0.923.

Operating Procedure The P–T–X lines are determined by measuring temperature and pressure at constant concentrations. The solution sample is placed within a thermally controlled chamber, and the vacuum system is activated to avoid the presence of air in the sample container. Afterwards, the desired environment temperature is achieved and equilibrium conditions are reached. At least five experimental points were determined for each sample. Figure 2 presents the P–T–X lines obtained by interpolation of the experimental data; the numeric values of P–T–X lines are also reported in Table 1.

A more detailed description of the operating procedure is reported in Ref. 2, where corrections for the concentration variations (due to water evaporation in the free volume over the solution) have been considered.

Specific Heat at Constant Pressure

Apparatus and Instruments The specific heat is measured by means of a differential thermal flux calorimeter of the Calvet type (Setaram, Model C80). The calorimeter allows measurements of differential and absolute thermal fluxes according to the block diagram in Fig. 3. The calorimeter essentially consists of a cylinder containing two identical cells surrounded by a number of serially connected thermocouples, stainless steel cells, and a calibration unit and other standard components, including a temperature programmer, amplifier, digital voltmeters, and a data acquisition system. A more detailed description of the apparatus is reported in Ref. 3.

Operating Procedure The initial calibration of the apparatus is carried out by fixing a temperature T_i for the calorimetric unit and sending an electric impulse of known energy, which generates a quantity of heat Q_t within a special calibration cell (see Fig. 3). The thermocouples generate an emf that, after being amplified, produces a signal function $f(t)$ given by

$$f(t) = S(T_i)\frac{dQ}{dt} \tag{1}$$

where dQ/dt is thermal flux and $S(T_i)$ is the sensitivity of the apparatus at temperature T_i.

Integration of Eq. (1) yields

$$S(T_i) = \frac{1}{Q_t}\int_0^{\infty} f(t)\,dt \tag{2}$$

The value of $S(T_i)$ can be calculated by numerical integration of the curve $f(t)$ presented in Fig. 4. Using other temperature values, the calibration curve shown in Fig. 5 can be obtained.

The measurement is performed by the following procedure. A 5×10^{-3} kg sample of the substance is introduced within the cell. As soon as equilibrium is reached, the supply of energy is started to get a linear increase of temperature; a signal function $F(t)$ is generated and is given by the same equation as (1). Therefore, during the heating process, we can write

$$\frac{dQ}{dt} = C_p(T)m\frac{dT}{dt} \tag{3}$$

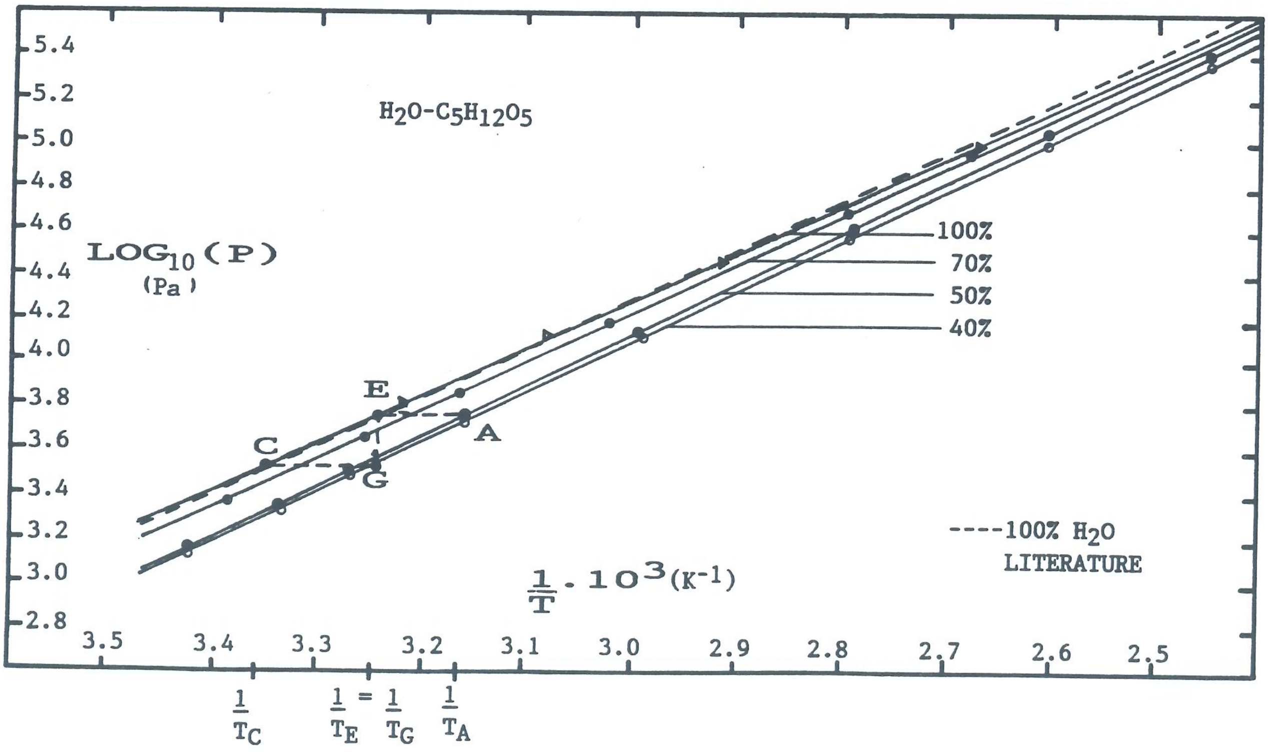

Figure 2. P–T–X experimental data of the water–xylitol solutions. Example of the heat transformer cycle.

Table 1. P–T–X Data for Water–Xylitol Solutions*

	Pressure (kPa)				
T(K)	*100% H_2O (Lit)*	*100% H_2O (Exptl)*	*70% H_2O (Exptl)*	*50% H_2O (Exptl)*	*40% H_2O (Exptl)*
288	1.706	1.756	1.584	1.113	1.078
293	2.339	2.385	2.146	1.534	1.481
298	3.169	3.210	2.878	2.092	2.015
303	4.245	4.280	3.822	2.824	2.712
308	5.627	5.640	5.030	3.775	3.616
313	7.381	7.390	6.562	4.999	4.777
318	9.600	9.607	8.488	6.562	6.255
323	12.344	12.330	10.893	8.541	8.123
328	15.752	15.680	13.874	11.029	10.466
333	19.932	19.691	17.542	14.132	13.381
338	25.022	24.562	22.026	17.976	16.985
343	31.176	30.442	27.474	22.705	21.409
348	38.563	37.497	34.053	28.487	26.808
353	47.373	45.916	41.951	35.513	33.354
358	57.815	55.907	51.380	43.999	41.247
363	70.117	67.705	62.579	54.193	50.710
368	84.529	81.566	75.810	66.371	61.995
373	101.32	97.776	91.369	80.845	75.384
378	120.79	116.65	109.58	97.964	91.191
383	143.24	138.52	130.79	118.11	109.77
388	169.02	163.77	155.41	141.72	131.50
393	198.48	192.79	183.84	169.26	156.81
398	232.01	226.03	216.57	201.26	186.16
403	270.02	263.96	254.08	238.27	220.07
408	312.93	307.09	296.93	280.93	259.09
413	361.19	355.95	345.69	329.91	303.83
418	415.29	411.13	401.00	385.94	354.94

* Lit = literature values; Exptl, experimental values.

Substituting Eq. (1) into Eq. (3) and considering $F(t)$ instead of $f(t)$, we get

$$C_p(T) = \frac{F(t)}{mS(T)\,dT/dt} \tag{4}$$

Equation (4) allows the calculation of specific heat values because m is fixed, $S(T)$ has been calculated, $F(t)$ is measured, and the value of $F(t)/S(T)$ is stored by the data acquisition system during the heating of the sample (see Fig. 6). Some differential specific heat measurements were also carried out, using water as the reference substance. Very good agreement was found between the results coming from the absolute procedure and the differential one; the measurements were completed with the absolute method, and the data are reported in Fig. 7 and Table 2.

Kinematic Viscosity

A gravity viscosimeter of the Ubbelohde type is used to obtain the viscosity data. The kinematic viscosity is linearly related to the interval of time during which a fixed amount of fluid passes between two altimetric levels, according to the relation

$$\nu = K\,\Delta t \tag{5}$$

The viscosimeter is placed inside the thermally controlled chamber so the measurements can be performed at fixed and constant temperatures. The relative humidity is maintained in the vicinity of 100% to avoid evaporation from the samples. The temperatures of the samples are not directly measured within the viscosimeter, but they are determined by maintaining thermal equilibrium between the sample and the thermal chamber. The calibration of the viscosimeter is obtained with distilled water in the range of temperatures from 273 to 353 K. It has been further verified that the kinetic energy correction is insignificant for the tested solution in the considered temperature range.

The experimental results and the regression lines are presented in Fig. 8. The numeric values are reported in Table 3.

EXPERIMENTAL UNCERTAINTIES

A detailed discussion of the experimental uncertainties is reported in Refs. 2 and 4. Nevertheless, the main results are summarized in the Appendix and in Table 4, where the nature and extent of the uncertainties are indicated.

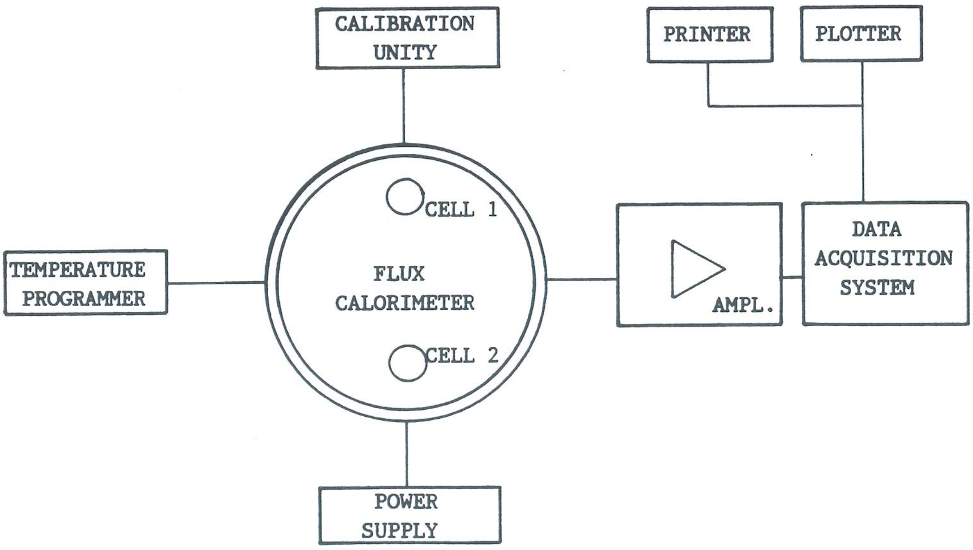

Figure 3. Specific heat measurement: Block diagram of experimental setup.

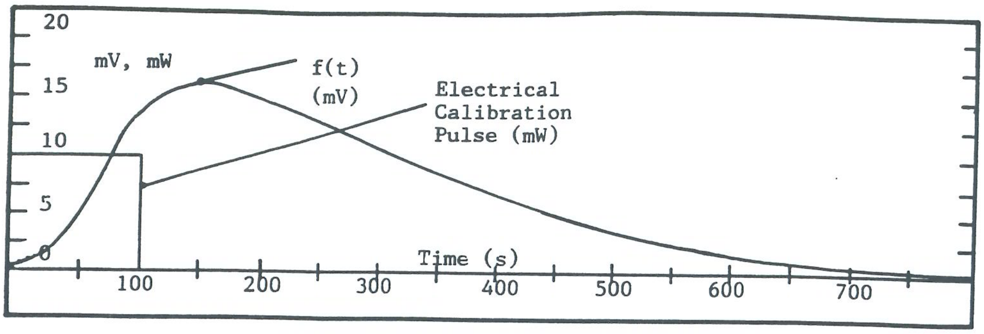

Figure 4. Calibration pulse and heat flow output signal function.

CONCLUSIONS

An experimental investigation was accomplished on water–xylitol mixtures whose vapor pressures, specific heats, and viscosities were measured. The testing facilities proved reliable, and complete sets of data were determined. Measurements of pressure–temperature–concentration relationships, specific heats, and viscosities were carried out for the entire range of concentrations from pure water to saturated solutions. The thermophysical properties of aqueous solutions are not available in the literature on xylitol, so the complete set of data are reported here for the first time.

The experimental *P–T–X* data indicate unsatisfactory characteristics for the use of the mixture within heat transformers, because only a small temperature difference can be obtained, at constant pressure, between the pure refrigerant and the solution in all the investigated temperature ranges. In Fig. 2 the best attainable heat transformer cycle is represented, which has the following characteristics: heat source temperature, 308 K; environment temperature, 298 K; utilizer temperature, 315 K; the last of these is not high enough for applications.

In addition, this mixture exhibited very high viscosity at elevated concentrations and considerable instability at temperatures higher than 373 K or after exposure to light.

APPENDIX

P–T–X Measurements

Temperature The thermoresistance precision is better than ±0.04 K. The reading error is ±0.005 K, so the temperature accuracy is ±0.05 K.

Pressure The zero shifting and the transducer's sensitivity caused by temperature variation are corrected by a computational program [2] that exploits the linear relations between the transducer signal and the pressure. Therefore, in the 0–500 kPa range, the pressure measurement error is due to hysteresis and nonlinearity of the transducer ($< \pm 250$ Pa) and to the resolution of the A/D converter ($< \pm 30$ Pa). The first is less than ±250 Pa; the latter is less than 30 Pa for a 14 bit converter (obtained by dividing the pressure range into 2^{14} discrete intervals).

In the range 0–100 kPa, the pressure measurement error is due to the mechanical manometer, whose accuracy is 0.3% of full scale.

Mass and Concentration Errors in the concentration of the fluid sample are due to weighing and to the free volume above the liquid phase. The absolute weighing error is equal to the scale error ($< \pm 0.02 \times 10^{-3}$ kg). The preparation of the solution includes three operations: first weighing the container alone, then weighing the container first with the solute and then with the solution; so the total concentration error is given by

$$\frac{dX}{X} = \frac{dm_r}{m_r} + \frac{dm_r + dm_a}{m_r + m_a} \tag{6}$$

As the samples of the solution are about 20×10^{-3} kg, the maximum relative error is ±0.9%. The effect of the free volume was estimated assuming that only water is present in the vapor phase and that the perfect gas law is valid [2]. The actual concentration of the mixture is calculated by subtracting the mass of water contained in the vapor phase.

Specific Heat Measurements

Error in specific heat measurements is linked to the errors in determining the mass of the sample, the temperature, and the thermal flux. The last one derives from calibration, calculation, and measurement of the emf generated by the thermocouples.

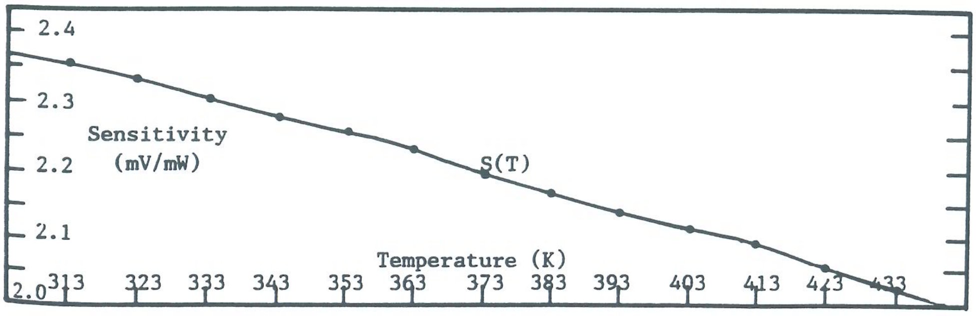

Figure 5. Calibration curve.

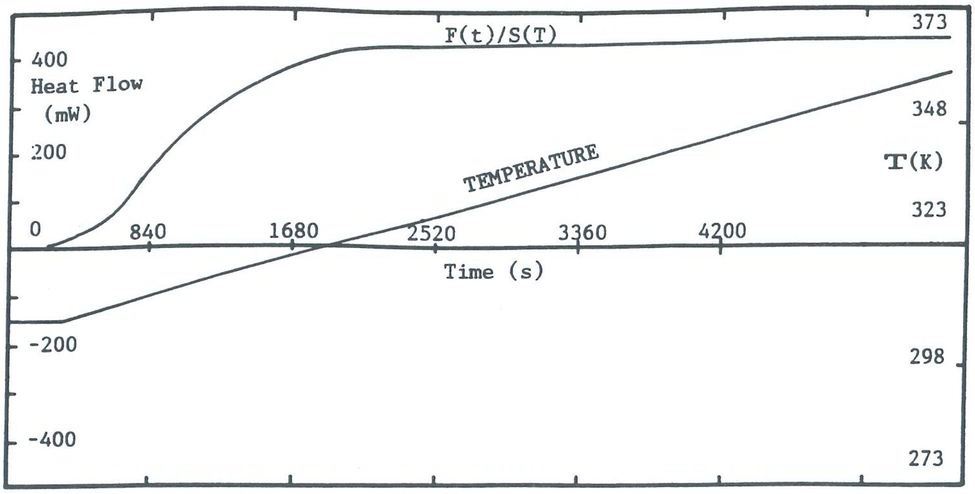

Figure 6. Temperature and heat flow output signal in measure mode.

Calibration Errors Calibration errors are due to measuring the power of the calibration pulse of the emf, to the numerical integrations, and to the interpolation of the regression curve.

Emf Generated by Thermocouples The measurement errors related to the emf generated by the thermocouples were evaluated by comparing the measurements obtained by a fluke 5700A digital calibration voltmeter (10 nV resolution) with those indicated by the instruments. In the range of amplification values used in these experiments, the absolute error is less than ±1 μV within the normal range of application between 0.1 and 70 mV. The calibration pulse was evaluated by measuring both voltage and current at the same time. The deviation from the nominal 10 mW value is less than ±0.05 mW; since the duration of the pulse is 100 s, the absolute error in the measurement of energy is less than ±5 mJ.

Calculation Errors The error due to numerical integration is 0.01% because the program increases the integration step until the difference between two consecutive results is less than 0.01% of the total area. This area, equal to 6000 mV · s, is subtended under the line representing the calorimetric signal resulting from the calibration pulse (see Fig. 4). So the absolute error is less than ±6 μV · s. As the duration of the output signal is equal to 1100 s, the emf measurement gives another absolute error that is less than ±1100 μV · s, so the total error is ±1106 μV · s. The sensitivity function defined by Eq. (2) relates

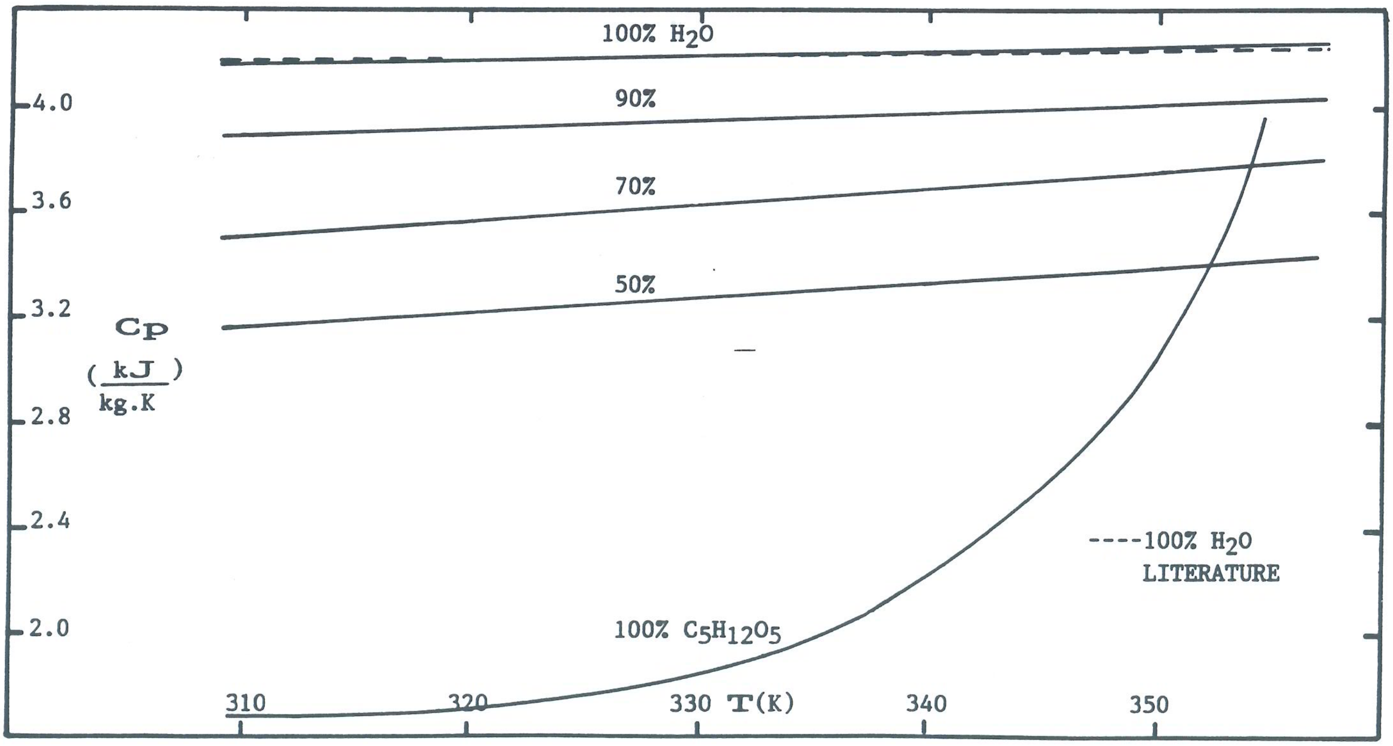

Figure 7. Experimental data on water–xylitol solutions: Specific heat vs. temperature at various concentrations.

Table 2. Specific Heat Data for Water–Xylitol Solutions at Various Temperatures and Concentrations

	Specific Heat C_p [kJ / (kg · K)]					
T (K)	*100% H_2O (Lit)*	*100% H_2O (Exptl)*	*90% H_2O (Exptl)*	*70% H_2O (Exptl)*	*50% H_2O (Exptl)*	*100% $C_5H_{12}O_5$ (Exptl)*
310	4.182	4.172	3.871	3.519	3.144	1.692
315	4.182	4.175	3.885	3.543	3.170	1.698
320	4.182	4.179	3.899	3.568	3.196	1.707
325	4.183	4.182	3.913	3.592	3.221	1.716
330	4.183	4.186	3.927	3.617	3.248	1.801
335	4.184	4.189	3.941	3.641	3.274	2.024
340	4.187	4.193	3.955	3.666	3.300	2.234
345	4.190	4.196	3.969	3.690	3.326	2.560
350	4.192	4.200	3.983	3.715	3.352	3.102
355	4.195	4.203	3.997	3.739	3.378	3.845

the A_u area subtended by the calorimetric signal $f(t)$ and the Q_t area of the calibration pulse. So, after the theory of error propagation [7], the absolute error for the sensitivity can be expressed by

$$e_S = \frac{1}{Q_t^2}\left[(A_u e_t)^2 (Q_t e_u)^2\right]^{1/2} \tag{7}$$

where e_t (= ±5 mJ) is the error in the Q_t area and e_u (±1106 μV · s) is the error in the A_u area. The value of e_s is less than ±12.8 μV/mW; since the average value of the sensitivity is equal to 2280 μV/mW, the relative error is 1.13%. The errors in determining the sensitivity regression function can be reasonably assumed to be of the same order as the errors in the quantity itself, since the deviation from the experimental values is in any case less

Table 3. Kinematic Viscosity Data for Water–Xylitol Solutions at Various Temperatures and Concentrations

	Kinematic Viscosity ν (m^2 / s) × 10^6				
T (K)	*100% H_2O (Lit)*	*100% H_2O (Exptl)*	*70% H_2O (Exptl)*	*50% H_2O (Exptl)*	*30% H_2O (Exptl)*
270	2.025	2.007	—	—	—
275	1.733	1.723	—	—	—
280	1.481	1.476	3.671	—	—
285	1.266	1.266	3.227	9.538	—
290	1.090	1.093	2.824	8.131	—
295	0.952	0.957	2.463	6.865	—
300	0.852	0.858	2.183	5.740	—
305	0.791	0.796	1.864	4.755	10.806
310	0.768	0.771	1.626	3.911	8.895
315			1.430	3.207	7.344
320			1.275	2.643	6.105
325			1.161	2.220	5.135
330			1.089	1.938	4.388
335			1.058	1.796	3.819
340			—	1.795	3.383
345			—	—	3.036
350			—	—	2.732

Table 4. Experimental Uncertainty in Measured Properties

Property	*Measurement Uncertainty*
Pressure	±3 × 10^2 Pa
Concentration	±0.04 × 10^{-3} kg
Temperature	±0.05 K
Specific heat	±0.0361 kJ/(kg · K) (±4%)
Kinematic viscosity	±0.02 × 10^{-6} m²/s (±1%)

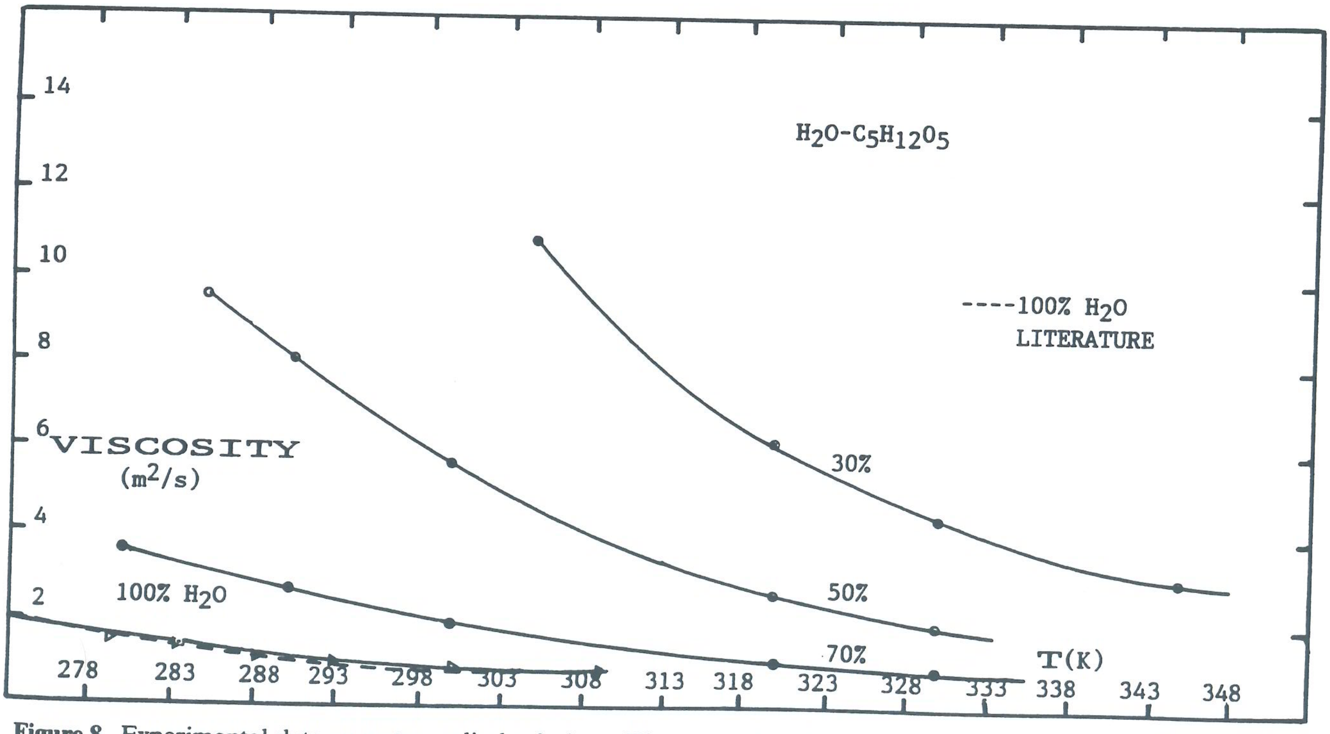

Figure 8. Experimental data on water–xylitol solutions: Kinematic viscosity vs. temperature at various concentrations.

than 0.3%. As the thermal flux (expressed in mW) is the ratio between the calorimetrical signal (in μV) and the sensitivity (in μV/mW), the maximum absolute error can be calculated with a relation similar to (7) and is found to be equal to ± 0.025 mW.

The total error in specific heat can be evaluated from the errors in temperature (± 0.05 K), thermal flux (± 0.025 mW), and mass measurements ($\pm 0.1 \times 10^{-3}$ kg). Applying the theory of error propagation to Eq. (4), the accuracy of the specific heat measurement is determined to be ± 0.0361 kJ/(K · kg) [± 0.0086 kcal/(K · kg)], while the accuracy claimed by the manufacturer is ± 0.005 kcal/(K · kg). The relative error is in the range 2–4%.

Kinematic Viscosity Measurements

The measurement errors of kinematic viscosity derive from the viscosimeter itself (± 0.00001 m^2/s), from errors in temperature measurement (± 0.1 K), and from the operator's reaction time (± 0.1 s). The relative error in kinematic viscosity measurement is in the range $\pm 1\%$.

NOMENCLATURE

C_p	specific heat at constant pressure, kJ/(kg · K)
$f(t)$	heat flow signal in calibration mode, V
$F(t)$	heat flow signal in measuring mode, V
K	viscosimeter constant, m^2/s^2
m	mass of sample, kg
m_a	mass of absorbent in the solution, kg
m_r	refrigerant mass in the solution, kg
P	pressure, Pa
Q	quantity of heat, kJ
Q_t	quantity of heat in calibration mode, kJ
$S(T)$	sensitivity, mV/mW
t	time, s
T	temperature, K

Greek Symbol

ν	kinematic viscosity, m^2/s

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