Refined Flow Microcalorimetric Setup for Measurement of Mixing Enthalpies at High Dilutions: Determination of Infinite Dilution Dissolution Enthalpies of Some Alkanol and Ether Solutes in Water

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A refined flow microcalorimetric setup with a fully automatic control of the entire experimental sequence has been designed for accurate measurement of mixing enthalpies of highly dilute aqueous solutions as a function of composition and, in turn, for reliable determination of the solute's infinite dilution dissolution enthalpies ($\Delta_{\text{sol}}H_1^\infty$). The instrument and procedure were extensively tested, and their performance was verified using various microcalorimetric standards and further test reactions that involved the dissolutions of 1-propanol at eight temperatures from (283.15 to 318.15) K, of 1-butanol at 298.15 K, of 2-hexanol at five temperatures from (288.15 to 318.15) K and the dilutions of 10 % mass fraction aqueous 1-propanol and 2 mol·kg^{-1} sucrose solutions at 298.15 K. It was found that even for viscous solute media (viscosity 7 mPa·s) of limited aqueous solubility (mole fraction 0.002), $\Delta_{\text{sol}}H_1^\infty$ could be determined with a combined standard uncertainty of 1 % or lower. The microcalorimeter was employed to determine $\Delta_{\text{sol}}H_1^\infty$ for further oxygenated solutes for which these data are lacking or insufficient, namely, for 2-pentanol, 3-methyl-1-butanol, and 3-methyl-2-butanol at 298.15 K, for 1-methoxy-2-propanol at four temperatures from (288.15 to 318.15) K, for diethyl ether at five temperatures from (283.15 to 303.15) K, and for dimethoxymethane at seven temperatures from (288.15 to 318.15) K. The measurements of $\Delta_{\text{sol}}H_1^\infty$ as a function of temperature enabled us to derive reliable values of infinite dilution dissolution heat capacities.

Introduction

Accurate calorimetric measurements of minute heat effects accompanying a highly asymmetric mixing of two liquids are needed to determine reliable limiting values of the solute's partial molar excess enthalpy at infinite dilution. This thermodynamic quantity, corresponding to the dissolution enthalpy at infinite dilution $\Delta_{\text{sol}}H_1^\infty$, drives the effect of temperature on fluid-phase equilibria in highly dilute solutions and provides valuable information on molecular interactions of involved components. Data on $\Delta_{\text{sol}}H_1^\infty$ are essential for establishing and checking the consistency of the temperature dependences of limiting activity coefficients, Henry's law constants, and solubilities, for calculating solvation and transfer enthalpies used to rationalize molecular interaction energetics, and for estimating parameters in solution models or molecular simulations.

Dissolution enthalpies of organic solutes in water are of special interest due to the environmental, industrial, and biological significance of such systems. In spite of their importance, available $\Delta_{\text{sol}}H_1^\infty$ data for aqueous solutes are not ample and are mostly confined to the single temperature of 298.15 K. Existing data, gathered over the past 30 to 40 years, were obtained essentially in only a few laboratories using specialized batch, flow, or titration calorimetric arrangements. The most notable results in this direction were achieved by I. Wadsö and co-workers,[1] in Lund during the 1980s, who developed the most precise instruments and obtained the most accurate $\Delta_{\text{sol}}H_1^\infty$ values for both easily and slightly soluble liquids and as a function of temperature. Currently, due to more popular calorimetric themes, reports of new $\Delta_{\text{sol}}H_1^\infty$ measurements are scarce, sharply contrasting with the demands.

In our previous works on this topic,[2,3] we implemented, together with our French cooperation partners, two older flow mixing calorimeters (Picker and LKB 2107) and obtained $\Delta_{\text{sol}}H_1^\infty$ data for a number of aqueous solutes. In this work, we describe our own refined flow microcalorimetric arrangement and respective procedure for determination of infinite dilution dissolution enthalpies of aqueous solutes based on an isothermal microcalorimeter, model 4400, from Calorimetry Science Corp. (Provo, USA). We report on thorough testing and calibration of the entire system and demonstrate its performance and applicability. In addition, we present new accurate $\Delta_{\text{sol}}H_1^\infty$ results for some selected aqueous alkanols and ethers for which these data have been missing.

Experimental

Materials. The organic substances used in this study were of the highest purity grade commercially available. The liquid samples were dried by 0.4 nm molecular sieves (except for 1-propanol), but otherwise they were used without purification. Their sources and purity grades are listed as follows: 1-propanol, Aldrich, > 99.7 %, anhydrous; 1-butanol, Merck, 99.9 %; 2-pentanol, Aldrich, 98 %; 3-methyl-1-butanol, Aldrich, 99+ %; 3-methyl-2-butanol, Aldrich, 98 %; 2-hexanol (racemic), Aldrich, 99 %; 1-methoxy-2-propanol, Fluka, > 99 %; diethyl ether, Penta (Czech Republic), p.a. 99.7 %; dimethoxymethane, Aldrich, 99.9 %; sucrose, Lachema (Czech Republic), p.a. Water used as solvent was distilled and subsequently treated by a Milli-Q Water Purification System (Millipore, Milford, USA). Before the measurement, each liquid was partially degassed by

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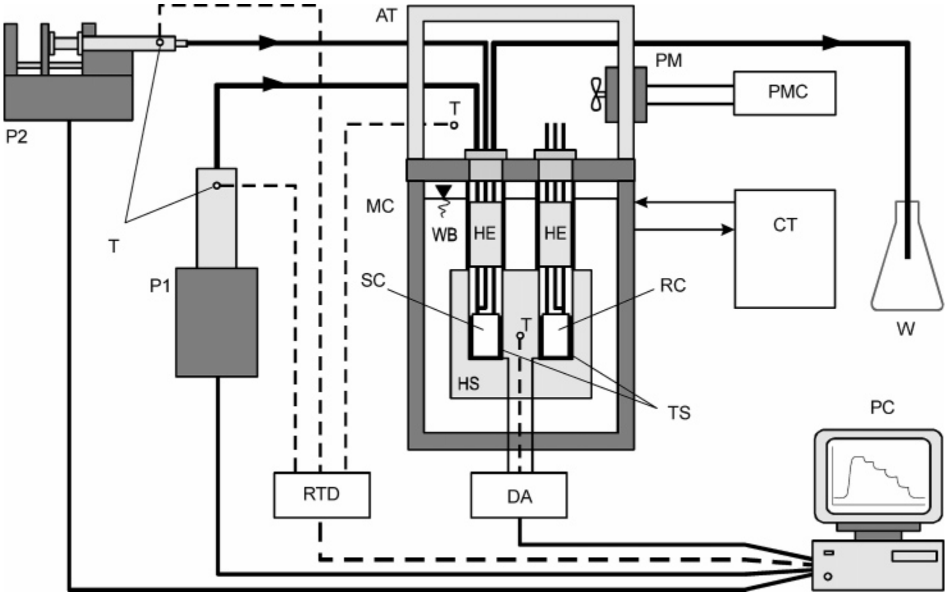

Figure 1. Schematic diagram of calorimetric setup: AT, air thermostat; CT, cooling thermostat; DA, differential amplifier; HE, heat exchanger; HS, heat sink; MC, microcalorimeter; P1, HPLC syringe pump (400 mL); P2, syringe pump (8 mL); PC, computer for data acquisition and setup control; PM, Peltier cooler/heater module with fan; PMC, Peltier module controller; RC, reference cell; RTD, RTD measuring card; SC, sample cell; T, temperature sensor; TS, thermoelectric sensors; W, waste bottle; WB, ultrastable termostating water bath.

repeatedly filtering it through a glass frit under a vacuum into a flask placed in a warm ultrasonic bath.

Apparatus. The model 4400 isothermal microcalorimeter (CSC, Provo, USA), on which the present calorimetric setup is based, is of a differential heat conduction type, incorporating two test wells (sample and reference) in a large aluminum heat sink which is immersed in an ultrastable thermostating bath (± 0.5 mK over 24 h). The microcalorimeter is characterized by a thermal power sensitivity of 0.1 μW and a time constant of 300 s. Equipped with twin flow mixing cells (model 4442), this instrument has been successfully used by us earlier,[4] in a flow arrangement with two HPLC syringe pumps, to measure excess enthalpy H^E throughout the entire composition range for some highly exothermic mixtures. For the present application, however, modifications and refinements of this previous setup were necessary.

First, to attain sufficiently low concentrations, a highly asymmetric pumping system which would deliver accurately very small mass flow rates of one component was required. Second, because a level of thermal power to be detected in the dilute range experiments (100 μW) is 2 to 3 orders of magnitude smaller than that in our previous work, the signal stability is critical and had to be improved to ensure precision. Third, because of the slow calorimetric response and the need for averaging the signal for long periods of time, a fully automatic control of the entire experimental process was needed.

A schematic diagram of the refined flow mixing microcalorimeter assembly designed for determination of $\Delta_{\mathrm{sol}}H_1^{\infty}$ of aqueous solutes is given in Figure 1. The pumping system consisted of two high-quality syringe pumps, a model HPP 5001 of 400 mL capacity from Laboratorní Přístroje (Praha, Czech Republic), and a model PHD 2000 from Harvard Apparatus (Holliston, MA) equipped with an 8 mL stainless steel syringe, which were employed to feed the solvent water and a solute, respectively, into the inlets of the sample cell of the calorimeter. Stainless steel capillaries (1/16 in. o.d.) with standard Swagelok and/or HPLC PEEK fittings were used for connections. The flow rates of the HPP 5001 pump can be set within the range from (0.01 to 0.99) mL·min^{-1} with the resolution of 0.01 mL·min^{-1} and were calibrated by flowing water through the system while timing and then weighing the delivered amount. Replicates showed flow rate repeatability within 0.3 %. The PHD 2000 pump was capable of delivering low flow rates down to 0.025 μL·min^{-1}. Its accuracy specified by the manufacturer was 0.35 %, and we verified it at the flow rate of 1 μL·min^{-1} by the procedure used to calibrate the HPP 5001 pump. The temperatures of the liquids contained in the syringe barrels of the pumps were continuously monitored by attached micro Pt-100 resistance thermometers, and the recorded values were used to evaluate accurate mass flow rates of the components.

As a modification to improve the stability of the calorimetric signal, the lid of the calorimeter, together with the inlet and outlet tubes of the cells, and the entire lid of the calorimeter bath were incorporated into a precise, ad hoc constructed air thermostat with a Peltier cooler/heater module which maintained their temperature to be the same as that of the calorimeter to better than 0.1 K. In preliminary explorations, we found that the signal fluctuations and the baseline zero-offset were related to the fluctuations in the room temperature and its difference from the calorimeter temperature, respectively, and we clearly identified that a thermal bridge between the thermostating part of the mixing cell and the calorimeter lid was responsible for the problem. The external thermostating described above provided an efficient remedy. Concerning the absolute setting of the calorimeter bath temperature, it was done with an uncertainty of ± 10 mK against an ASL precision Pt-25 resistance thermometer and a F26 resistance bridge having a calibration (ITS-90) traceable to the National Physical Laboratory (Teddington, UK).

The reference cell that serves to compensate for electronic noise and any heat flux due to temperature fluctuations in the heat sink was left empty. The differential signal from the calorimeter test wells thus corresponded to the rate of heat production from the sample cell itself. The signal was calibrated using a Joule effect produced by a built-in calibration heater on the pure solvent water. As shown in Figures 2 and 3, the calibration constant exhibited consistent dependence on both the flow rate and temperature. Regular checks of the calibration proved its excellent long-term stability which was within 0.1 % over a period of 1 year.

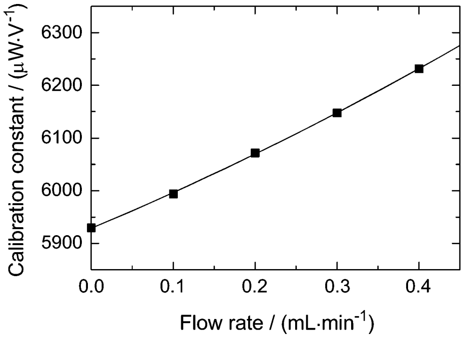

Figure 2. Calibration constant as a function of the total flow rate at 298.15 K.

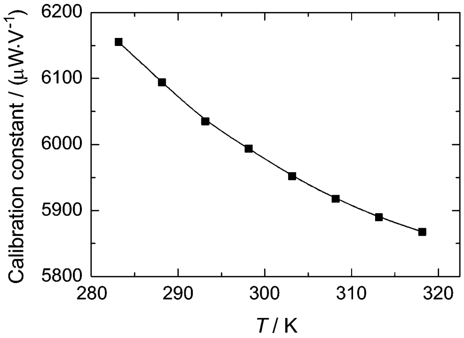

Figure 3. Calibration constant as a function of temperature at the total flow rate of 0.1 mL·min^{-1}.

Data acquisition and setup control were entirely accomplished by a PC. The HPP 5001 pump was interfaced with the computer through a National Instruments PCI 6503 board (24 TTL DIO), whereas for connecting the PHD 2000 pump, its built-in RS232 interface was used. The measurement of various temperatures (e.g., syringe cylinders, calorimeter lid, ambient air) with Pt-100 sensors was provided by means of a National Instruments SC 2042 RTD measuring card connected to a National Instruments PCI 6013 multifunctional I/O board. The calorimetric signal and its calibration were handled by a Keithley PIO-12 digital I/O board, as supplied by CSC. This hardware system along with a new custom-made program interface enabled us to fully automate the measurement sequence for determination of $\Delta_{sol}H_1^\infty$.

Procedure. In a typical experimental run, the excess enthalpy H^E was determined for six compositions within the range of solute mole fractions x_1 from 0.01 down to 0.0005, proceeding from the higher to the lower composition. For each particular solute, however, the composition interval examined was individual, depending on the molar volume and aqueous solubility of the solute. Regular measurements were conducted at the solvent water flow rate of 0.1 mL·min^{-1} and solute flow rates selected typically from the range (3 to 0.2) μL·min^{-1} so that sufficient dilution was attained. This level of flow rates was found in test experiments as optimal: it was low enough to provide a sufficiently long residence time ensuring complete mixing even for solutes partially miscible with water but still high enough to suppress the effect of back diffusion into the solute feeding tube and to give sufficiently large thermal effects of mixing compared to the parasite ones due to heat leaks, adsorption, etc. The calorimetric signal for each composition was recorded usually for 5 h; shorter recording times were used only for well-soluble solutes when pumped at relatively higher flow rates. The baseline signal was recorded for 3 h, as both the initial and the final step of the experimental run. A typical run thus lasted from (32 to 36) h. Signals corresponding to mixing were averaged over integral multiples of the rotation period of the solute pump screw to compensate for mechanical imperfections of the pump. The infinite dilution dissolution enthalpy $\Delta_{sol}H_1^\infty$ was determined by linear extrapolation of the quantity $H^E/(x_1x_2)$ as a function of x_1 to infinite dilution. The following equation

$$H^E/(x_1x_2) = A + Bx_1 \tag{1}$$

was fitted to measured data by the weighted least-squares method yielding $\Delta_{sol}H_1^\infty = A$. In cases when no trend of $H^E/(x_1x_2)$ values with respect to composition was observed ($B = 0$), $\Delta_{sol}H_1^\infty$ was obtained as a weighted average of $H^E/(x_1x_2)$ values. The weights in the treatment were given by the standard uncertainties of data points as estimated by the error propagation law from the standard deviations of signal fluctuations and the standard uncertainties in flow rates of components. For the evaluation of $\Delta_{sol}H_1^\infty$, data from all experimental runs corresponding to a given temperature were merged and processed simultaneously.

Results and Discussion

Due to the smallness of heat effects investigated, microcalorimetric measurements can easily be impaired by systematic errors. To minimize the risk of such errors, we subjected our setup and procedure to extensive examinations and verified their performance by several standardized chemical tests.

Quality of Calorimetric Signal. Concerning the quality of the calorimetric signal, the following characteristics were generally observed. The long-term drift (over 24 h) of the baseline at a flow of 0.1 mL·min^{-1} of water was less than 1 μW, with fluctuations being several tenths of microwatts. Thanks to the air thermostatization of the calorimeter lid, the sensitivity of the baseline signal to the ambient temperature diminished about 25 times, and thus the effect of common changes in ambient temperature were hardly identifiable at a flow rate of 0.1 mL·min^{-1}. The baseline change over a long experimental run (36 h) was typically within 2 μW, even if heat-of-mixing effects as high as 10 mW were measured and/or solutes partially miscible with water were studied. Signals corresponding to thermal effects of mixing (for characteristic patterns, see Figure 4) exhibited effectively no drift but, as expected, more appreciable fluctuations than the baselines. Expressed by the signal relative standard deviation, these fluctuations were from about (1 to 2) % under favorable conditions, i.e., for solutes with high solubility in water (e.g., 1-propanol) pumped at a higher flow rate (e.g., 3 μL·min^{-1}) yielding relatively high thermal effects (> 500 μW). At lower solute flow rates and/or smaller thermal effects, the signal relative standard deviation usually increased, up to threefold at 0.2 μL·min^{-1} and/or thermal effects smaller than 200 μW. For solutes easily soluble in water, the calorimetric signal exhibited a nearly perfect periodicity reflecting the rotation of the screw of the solute pump. For solutes of limited miscibility with water, the periodicity of the signal was observed to break, the signal stability deteriorating considerably when the solubility limit was approached.

Dissolution of 1-Propanol in Water. To verify the correct performance of our microcalorimetric setup and procedure, we determined $\Delta_{sol}H_1^\infty$ of 1-propanol in water as a primary check. In isothermal microcalorimetry, the dissolution of 1-propanol in water serves as a standard test reaction,[5,6] especially useful for testing asymmetric flow arrangements. We carried out the measurements at eight temperatures in the range from (283.15 to 318.15) K with a step of 5 K. Results and their comparison

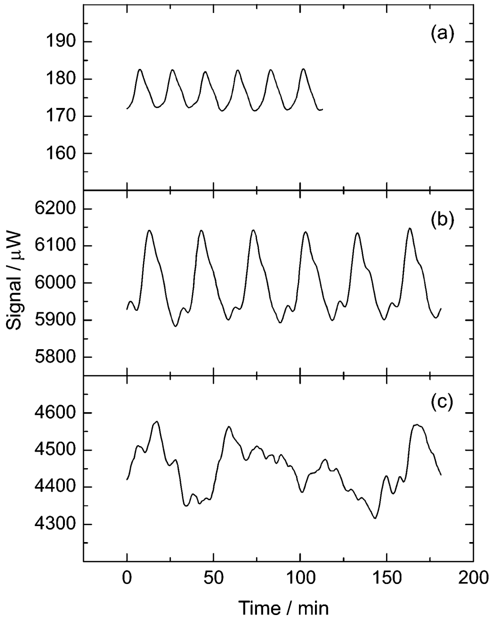

Figure 4. Calorimetric signal records over time periods corresponding to six revolutions of the driving screw of the PHD 2000 pump for mixing (a) 10 % mass fraction aqueous 1-propanol, 4 μL·min^{-1} with water, 100 μL·min^{-1} at 298.15 K, signal average 176.2 μW, signal standard deviation 3.6 μW; (b) 1-propanol, 2.5 μL·min^{-1} with water, 100 μL·min^{-1} at 293.15 K, signal average 5995 μW, signal standard deviation 78 μW; (c) 2-pentanol, 2.5 μL·min^{-1} with water, 100 μL·min^{-1} at 298.15 K, signal average 4444 μW, signal standard deviation 58 μW.

with reference data are given in Table 1. With the exception of 298.15 K, the obtained $\Delta_{\mathrm{sol}}H_1^{\infty}$ values at each temperature come from duplicate runs. At 298.15 K, five replicated runs were taken, to confirm the measurement repeatability. The standard deviations $s(\Delta_{\mathrm{sol}}H_1^{\infty})$ reported in Table 1 are based on the fits of measured $H^{\mathrm{E}}/(x_1x_2)$ data with eq 1. As seen, the values of $s(\Delta_{\mathrm{sol}}H_1^{\infty})$ for 1-propanol amount to 0.3 % or less, indicating a high degree of repeatability and extrapolation precision. Excellent agreement (within 1 %) of the obtained $\Delta_{\mathrm{sol}}H_1^{\infty}$ values with the highly reliable and accurate recommended $\Delta_{\mathrm{sol}}H_1^{\infty}$ data proves the absolute accuracy of our measurements and suggests that the combined standard uncertainty of our $\Delta_{\mathrm{sol}}H_1^{\infty}$ values for 1-propanol can be estimated as 0.5 %. The quality of the results for 1-propanol is additionally demonstrated by Figure 5. Here, the dissolution heat capacity $\Delta_{\mathrm{sol}}C_{p,1}^{\infty}$, inferred from the SIMFIT2 model equation[7]

$$\Delta_{\mathrm{sol}}H_1^{\infty} = RT_0[B - C\exp(D\tau)(D\tau - 1)] \qquad (2)$$

where $\tau = T/T_0$; $T_0 = 298.15$ K; and $B = 7.6813$, $C = -53.6391$, and $D = -2.8712$ are adjustable parameters fitted to the present $\Delta_{\mathrm{sol}}H_1^{\infty}$ data, is compared with the literature heat capacity measurements and existing recommendations. Apparently, the accuracy and extent of the obtained $\Delta_{\mathrm{sol}}H_1^{\infty}$ data for 1-propanol allow us to evaluate accurately not only $\Delta_{\mathrm{sol}}C_{p,1}^{\infty}$ but also its temperature dependence.

Dilution of 10 % Mass Fraction 1-Propanol Solution in Water. The heat evolved in the dissolution of 1-propanol was quite large. To verify our calorimetric setup also for determination of much smaller thermal effects, we additionally measured the heat accompanying the dilution of 10 % mass fraction (1.849 mol·kg^{-1}) 1-propanol solution in water, a reaction which has been proposed as a convenient test for such cases.[5,6] In our experiment, conducted at 298.15 K, we were diluting the solution of 1-propanol of initial molality $m_{\mathrm{i}} = 1.849$ mol·kg^{-1} pumped at 1 μL·min^{-1} in a stream of water of 100 μL·min^{-1}. This process resulted in a highly dilute solution with the final molality of $m_{\mathrm{f}} = 0.01626$ mol·kg^{-1} and a very small thermal power of about 45 μW. Two replicated measurements agreeing within 1 % gave the average $\Delta_{\mathrm{dil}}H = -1654$ J·mol^{-1}. The enthalpy change for this dilution calculated from recommended data expressed by the equation[6]

$$\Delta_{\mathrm{dil}}H(m_{\mathrm{i}} \rightarrow m_{\mathrm{f}}) = h_{xx}(m_{\mathrm{f}} - m_{\mathrm{i}}) + h_{xxx}(m_{\mathrm{f}}^2 - m_{\mathrm{i}}^2) \qquad (3)$$

where $h_{xx} = 558$ J·kg·mol^{-2} and $h_{xxx} = 158$ J·kg^2·mol^{-3}, is $\Delta_{\mathrm{dil}}H = -1563$ J·mol^{-1}. To assess the observed difference, one needs to consider uncertainties of the two values. The uncertainty reported for the recommended value is 44 J·mol^{-1}, and that for our result, which we inferred by the error propagation from the observed signal fluctuations and the uncertainty of pumping, is still larger, amounting to 60 J·mol^{-1}. Consequently, the difference between the present result and the recommended value might be well accounted for by the combined uncertainty. In this context, it is noteworthy that recent precise measurements of Olofsson et al.[17] carried out by two calorimetric techniques (batch solution and titration) have also indicated that the dilution of 1-propanol could be slightly more exothermic than the existing recommendation, and these researchers concluded that it would be highly desirable to improve the accuracy of the interaction coefficients in eq 3.

Dilution of a Concentrated Aqueous Sucrose Solution in Water. A necessary condition for flow mixing calorimetry measurements to be correct is that the mixing process must be entirely completed in the mixing cell. As a stringent test of mixing efficiency, measurement of the enthalpy of dilution of aqueous sucrose solutions and comparison of results with well-established standard data have been recommended.[5,6] Concentrated sucrose solutions are very viscous, and to mix them with water can be difficult especially for flow calorimeters without stirring. In this work, these dilution experiments were performed at 298.15 K on a 2 mol·kg^{-1} aqueous sucrose solution (viscosity 5.53 mPa·s)[18] and at two dilution ratios, mixing 10 μL·min^{-1} or 5 μL·min^{-1} of the sucrose solution with 100 μL·min^{-1} of solvent water. These dilutions were accompanied by a quite small thermal power of about 230 μW and 120 μW, respectively. All the measurements were carried out with freshly prepared sucrose solutions to avoid the risk that they would be impaired by bacterial growth. As seen from Table 2, the results obtained compare favorably with recommended standard data[6] thus proving correct performance of the calorimetric system even for viscous solute media.

Dissolution of 1-Butanol in Water. In addition to the dissolution of 1-propanol, the dissolution of 1-butanol in water can also be considered as a convenient test reaction. For both these solutes, highly accurate $\Delta_{\mathrm{sol}}H_1^{\infty}$ values were measured by Hallén et al.[8] and recommended data consistent with other infinite dilution thermodynamic properties have been established.[7] Owing to the limited miscibility of 1-butanol with water (mole fraction aqueous solubility of 1.91 % at 298.15 K),[19] the dissolution of 1-butanol provides even a more severe test, making more demands especially on flow mixing calorimetric systems. The present measurements were carried out in five experimental runs at 298.15 K. As seen from Table 1, the result is in perfect agreement with the reference data.

Dissolution of 2-Hexanol in Water. To increase the difficulty of the dissolution test still more, we examined additionally the dissolution of 2-hexanol in water at several temperatures in the range from (288.15 to 318.15) K. The demands of this system on the mixing efficiency are really high because the viscosity

Table 1. Experimental Dissolution Enthalpies at Infinite Dilution in Water, $\Delta_{sol}H_1^\infty$, Together with Their Standard Uncertainties,[a] $s(\Delta_{sol}H_1^\infty)$, Number of Experimental Runs, n, Range of Mole Fractions, x_1, Covered by Measurements, and Comparison with Literature Data

T	$\Delta_{sol}H_1^\infty$	$s(\Delta_{sol}H_1^\infty)$			$\Delta_{sol}H_1^\infty$/(kJ·mol^{-1}) (lit.)		
K	kJ·mol^{-1}	kJ·mol^{-1}	n	range of x_1	recommended data		other data
				1-Propanol			
283.15	−13.45	0.04	2	0.001−0.007	−13.43[6]	−13.47[7]	
288.15	−12.20	0.04	2	0.001−0.007	−12.31[6]	−12.33[7]	
293.15	−11.11	0.02	2	0.001−0.007	−11.22[6]	−11.23[7]	
298.15	−10.12	0.01	5	0.001−0.012	−10.16[6]	−10.16[7]	
303.15	−9.12	0.03	2	0.001−0.007	−9.13[6]	−9.12[7]	
308.15	−8.12	0.01	2	0.001−0.007	−8.13[6]	−8.10[7]	
313.15	−7.14	0.01	2	0.001−0.007	−7.16[6]	−7.12[7]	
318.15	−6.16	0.02	2	0.001−0.007	−6.21[6]	−6.17[7]	
				1-Butanol			
298.15	−9.28	0.03	5	0.0004−0.005		−9.28[7]	−9.27[8]
				2-Pentanol			
298.15	−12.15	0.04	2	0.0008−0.005			−11.82[9]
				3-Methyl-1-butanol			
298.15	−8.23	0.05	4	0.0008−0.003			
				3-Methyl-2-butanol			
298.15	−12.61	0.04	2	0.0008−0.005			
				2-Hexanol			
288.15	−14.78	0.09	2	0.0004−0.0013			
298.15	−10.94	0.07	3	0.0006−0.0014			−10.81[9]
308.15	−7.52	0.04	2	0.0004−0.0011			
313.15	−5.53	0.07	3	0.0006−0.0014			
318.15	−4.09	0.03	2	0.0004−0.0011			
				1-Methoxy-2-propanol			
288.15	−20.67	0.04	2	0.0009−0.0055			
298.15	−19.10	0.02	2	0.0009−0.0064			
308.15	−17.40	0.02	2	0.0009−0.0064			
318.15	−15.71	0.02	2	0.0009−0.0064			
				Diethyl Ether			
283.15	−23.10	0.09	2	0.0009−0.0052			
288.15	−22.00	0.08	2	0.0009−0.0052			
293.15	−20.83	0.08	2	0.0009−0.0052			
298.15	−19.66	0.08	3	0.0009−0.0052			−19.26[10]
303.15	−18.24	0.08	3	0.0009−0.0052			
				Dimethoxymethane			
288.15	−11.81	0.1	2	0.0005−0.003			
293.15	−11.09	0.1	2	0.0005−0.003			
298.15	−10.54	0.1	2	0.0005−0.003			
303.15	−9.78	0.1	2	0.0005−0.003			
308.15	−9.24	0.09	2	0.0005−0.003			
313.15	−8.57	0.08	2	0.0005−0.003			
318.15	−7.91	0.08	2	0.0005−0.003			

[a] Inferred from fits of $H^E/(x_1x_2)$ vs x_1. The combined standard uncertainty involving contributions from all possible sources of error can be estimated to 0.5 % for 1-propanol and to 1 % or lower for other solutes studied.

of 2-hexanol at 288.15 K is 7.24 mPa·s (ref 20) and its mole fraction aqueous solubility at 318.15 K is as low as 0.2 % (ref 21). Our experiments showed that correct results could be obtained only at concentrations well below saturation. The situation is illustrated in Figure 6 where the measured $H^E(x_1)$ data at 313.15 K, obtained in a broader mole fraction range extending above the solubility limit, are plotted. From these data, one can clearly identify three regimes: (A) complete mixing at the lowest concentrations exhibiting practically linear $H^E(x_1)$, (B) two-phase flow at the concentrations higher than the solubility exhibiting also a linear $H^E(x_1)$ dependence, and (C) a transitional regime of intermediate mole fractions. Apparently, when the mole fraction increases and approaches the solubility limit, the driving force of the dissolution decreases, making the dissolution process slower. As a result, the mass transfer is not completed within the residence time and the heat effect measured is thus smaller than the true one. In general, correct $\Delta_{sol}H_1^\infty$ values can be obtained only from data of regime A, i.e., here, from measurements for concentrations not

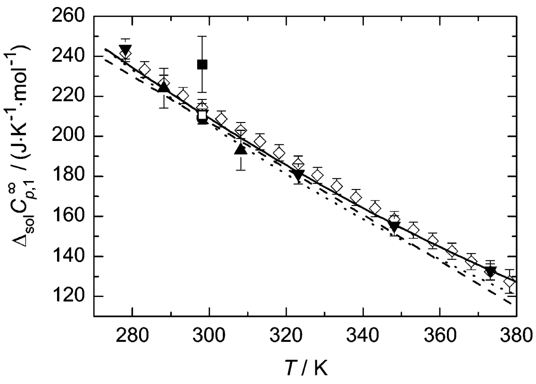

Figure 5. Dissolution heat capacity at infinite dilution for 1-propanol in water as a function of temperature. Experimental values: ■, Arnett et al.;[11] ●, Jolicoeur and Lacroix;[12] ▲, Benson and D'Arcy;[13] ▼, Makhatadze and Privalov;[14] ◇, Origlia-Luster and Woolley;[15] □, Fenclová et al.;[16] full line, recommendation;[7] dashed line, from $\Delta_{sol}H_1^\infty(T)$ recommendation;[6] dotted line, from fit of the present $\Delta_{sol}H_1^\infty$ data by eq 2.

Table 2. Enthalpies of Dilution, $\Delta_{dil}H$, Measured in This Work for a Concentrated Aqueous Sucrose Solution of Initial Molality, m_i, Diluted to Its Final Molality, m_f, Number of Experimental Runs, n, and Comparison with Recommended Data

m_i	m_f		$\Delta_{dil}H/(J\cdot mol^{-1})$	
$mol\cdot kg^{-1}$	$mol\cdot kg^{-1}$	n	this work	recommended[6]
2.000	0.1312	4	−964	−952
2.000	0.06778	2	−995	−988

exceeding roughly half of the solubility limit. Note also that attempts to determine the solubility by extrapolating from the complete dissolution and two-phase flow regimes give only its semiquantitative lower estimates because the heat effects measured for the two-phase flow regime are lower than the true ones.

Experiments in regime A used to determine $\Delta_{sol}H_1^{\infty}$ of 2-hexanol in this work required pumping the solute at the lowest practical flow rates, i.e., from (0.2 to 0.9) $\mu L\cdot min^{-1}$. The signal fluctuations observed for this system were irregular and significantly larger than for other systems studied, leading to a higher uncertainty of the obtained $\Delta_{sol}H_1^{\infty}$ values. Direct comparison of the present $\Delta_{sol}H_1^{\infty}$ measurements for 2-hexanol (see Table 1) is possible to only a single existing literature value at 298.15 K, which indicates a very good agreement. As seen from Figure 7, essential support for the reliability of our results for 2-hexanol comes further from their consistency with homologous $\Delta_{sol}H_1^{\infty}$ and $\Delta_{sol}C_{p,1}^{\infty}$ trends in 2-alkanol and 1-alkanol series. The value of $\Delta_{sol}C_{p,1}^{\infty}$ for 2-hexanol, obtained from a linear fit of the present $\Delta_{sol}H_1^{\infty}(T)$ data, amounts along with its standard uncertainty (358 ± 7) $J\cdot K^{-1}\cdot mol^{-1}$.

Dissolution of Other Alkanols or Ether Solutes in Water. Having thoroughly verified our microcalorimeter setup and procedure, we employed them to determine $\Delta_{sol}H_1^{\infty}$ for further aqueous oxygenated solutes for which these data are missing or insufficient. The measurements were carried out, namely, for 2-pentanol, 3-methyl-1-butanol, and 3-methyl-2-butanol at 298.15 K, for 1-methoxy-2-propanol at four temperatures from (288.15 to 318.15) K, for diethyl ether at five temperatures from (283.15 to 303.15) K, and for dimethoxymethane at seven temperatures from (288.15 to 318.15) K. The results are summarized in Table 1. No comparison to literature data can be done except for 2-pentanol and diethyl ether at 298.15 K; here, the agreement with only single literature values available is fairly good, within (2 to 3) %. The present $\Delta_{sol}H_1^{\infty}$ measurements contribute to a systematic effort which is now underway in our laboratory to establish reliable temperature dependences of limiting activity coefficients and Henry's law constants for branched pentanols, ethers, and alkoxyalkanols. Analogous studies for 1-alkanols (C1−C5) and branched (C3−C4) alkanols have been recently presented.[7,22]

The measurements of $\Delta_{sol}H_1^{\infty}$ as a function of temperature were performed with the aim to obtain reliable values of infinite dilution dissolution heat capacities. The values of $\Delta_{sol}C_{p,1}^{\infty}$ with their standard uncertainties derived from the linear fit of $\Delta_{sol}H_1^{\infty}(T)$ data for 1-methoxy-2-propanol, diethyl ether, and dimethoxymethane are (166 ± 2) $J\cdot K^{-1}\cdot mol^{-1}$, (241 ± 7) $J\cdot K^{-1}\cdot mol^{-1}$, and (129 ± 2) $J\cdot K^{-1}\cdot mol^{-1}$, respectively. Possibilities for comparison of these values with literature data are rather limited. Fair agreement can be noted with the older, less precise results of Cabani et al.[23] for diethyl ether (250 $J\cdot K^{-1}\cdot mol^{-1}$) and dimethoxymethane (111 $J\cdot K^{-1}\cdot mol^{-1}$) obtained for rather insufficiently dilute solutions by adiabatic C_p calorimetry. For diethyl ether, noteworthy is the excellent agreement with the value 242 $J\cdot K^{-1}\cdot mol^{-1}$ obtained at 298.15 K from very recent C_p measurements of Slavík et al.,[24] even though these investigators targeted mainly elevated temperature and pressure conditions.

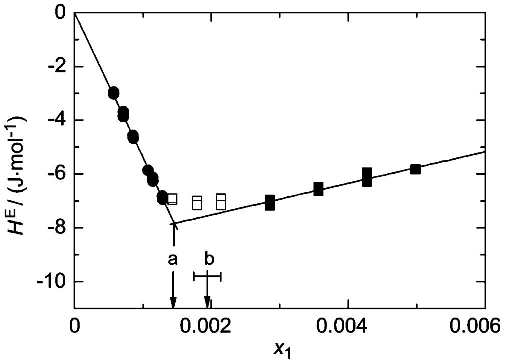

Figure 6. Experimental excess enthalpy H^E for dilute solutions of 2-hexanol (1) with water (2) at 313.15 K measured with the present flow microcalorimetric setup as a function of mole fraction x_1 in the composition range involving the solubility limit. Data from: ●, regime A; ■, regime B; □, regime C. a, solubility estimated from the present $H^E(x_1)$ data; b, experimental solubility with its standard uncertainty.[21]

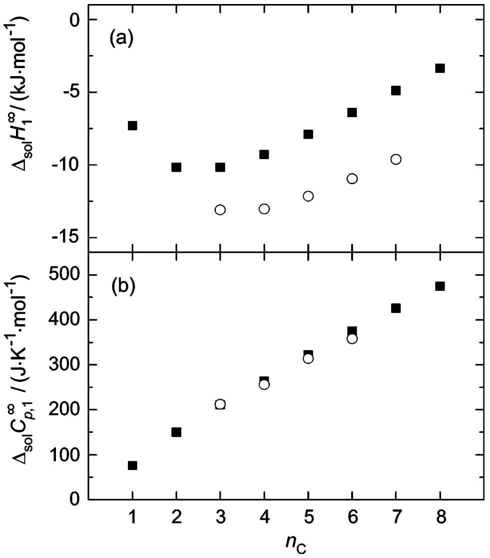

Figure 7. Dissolution enthalpy $\Delta_{sol}H_1^{\infty}$ (a) and heat capacity $\Delta_{sol}C_{p,1}^{\infty}$ (b) at 298.15 K in 1-alkanol (■) and 2-alkanol (○) homologous series as a function of the number of carbon atoms of alkanol, n_C. Data are from the following sources: both $\Delta_{sol}H_1^{\infty}$ and $\Delta_{sol}C_{p,1}^{\infty}$ for (C1−C5) 1-alkanols from ref 7; for (C6−C8) 1-alkanols from ref 8; and for (C3−C4) 2-alkanols from ref 22. $\Delta_{sol}H_1^{\infty}$ for 2-pentanol and 2-hexanol are from this work and for 2-heptanol is from ref 9. $\Delta_{sol}C_{p,1}^{\infty}$ for 2-pentanol is from ref 16 and for 2-hexanol is from this work.

In conclusion, the performance of the newly refined flow microcalorimetric setup we designed for determinations of $\Delta_{sol}H_1^{\infty}$ of aqueous liquid organic solutes was thoroughly examined and verified using various microcalorimetric standards and other test mixtures. The relative standard uncertainty of these determinations appears to be 1 % or better. It was demonstrated that accurate results can be obtained even for quite viscous solutes of appreciably limited miscibility with water like 2-hexanol. Measurements of $\Delta_{sol}H_1^{\infty}$ as a function of temperature, which can be easily done in the range from (283.15 to 318.15) K, are precise enough to allow the derivation of reliable values of infinite dilution dissolution heat capacity. Also, heat-of-mixing effects producing a low thermal power (< 100 μW) can be measured accurately. Such effects are often encountered in dilution processes or, as the prospective application may be, when mixing dilute solutions of two chemically interacting solutes. The present measurement procedure is rather time consuming, but its full automation compensates for this drawback. A large solvent consumption limits, however, this technique in its possible extension to nonaqueous systems. In this work, our microcalorimetric setup was employed to determine $\Delta_{\mathrm{sol}}H_1^{\infty}$ for some selected aqueous alkanols and ethers for which these data were missing or insufficient but urgently needed for establishing the temperature dependences of limiting activity coefficients and Henry's law constants of these solutes. Currently, the instrument is already in routine use in our laboratory for continuing $\Delta_{\mathrm{sol}}H_1^{\infty}$ determinations; some further oxygenates are now under study within task-specific projects aiming at reliable characterization of their infinite dilution thermodynamic behavior.

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