Solubility of Acetamide, Propionamide, and Butyramide in Water at Temperatures between (278.15 and 333.15) K

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The aqueous solubilities of acetamide, propionamide, and butyramide were measured from (278.15 to 333.15) K at intervals of 5.00 K using the gravimetric method. The temperature dependence of the solubility of acetamide, propionamide, and butyramide in water is described by the van't Hoff equation. Linear van't Hoff plots were found for amides in water, and the differential enthalpy of solution was calculated.

Introduction

Thermodynamic properties of biological solutes in aqueous solutions have received increased attention in the last years to obtain a better understanding of the interactions in water and their role on the conformational stability of proteins. In particular, solubility data of binary nonelectrolyte solutions are required to describe their thermodynamic behavior and are useful in the elucidation of solute−solute and solute−water interactions as well as in the design of industrial separation and purification processes.

The amides can be used as model systems for the study of complex biochemical systems as peptides and proteins in solution. However, studies with amides in aqueous solution at temperatures different from 298.15 K are very scarce.[1−8] The solubility of acetamide in water has been reported previously, showing that solubility increases with temperature,[9] but for propionamide and butyramide no experimental solubility data in water at temperatures different from 298.15 K have been found in literature.

In this work the effect of temperature on the solubilities of acetamide, propionamide, and butyramide is studied. The amides were selected taking into account that the length of the hydrocarbon chain increases with the number of CH_2 groups. The solubility was measured by gravimetry at temperatures between (278.15 and 333.15) K, and the results are compared with literature data. The temperature dependence of the solubility of acetamide, propionamide, and butyramide in water is described by the van't Hoff equation, and the differential heat of solution was calculated from van't Hoff plots.

Experimental Section

Materials. The materials used in this work were acetamide from Merck, > 99 % (certificate of analysis: 99.9 % for lot no. S4157443), propionamide from Aldrich, > 97 % (certificate of analysis: 99.9 % for lot no. 01621HE), and butyramide from Fluka, > 98 % (certificate of analysis: 99.7 % for lot no. 433980/1). All of the materials were used without further purification since their mass fraction purity is higher than 99.0 %. The amides were dried under vacuum and were kept in desiccators before use. Water was doubly distilled, degassed, and treated according to literature.[10]

Apparatus and Procedure. The solubility cell used in this work has been described previously.[11,12] The apparatus has a plexiglas unit containing four glass tubes of 10 mL uniformly distributed. The cell is stirred by a turbine stirrer at 60 rpm and is held in a constant temperature bath for the necessary time to reach equilibrium at each temperature. The temperature is controlled with a Lauda E100 circulator with temperature control to 0.1 K. A refrigerator unit is used to work below room temperature.

To determine the time to reach equilibrium, the less soluble solute, butyramide, was added in excess to tubes containing a volume of 5 mL of water. Samples of the saturated solution were taken at (2, 4, 6, 8, and 12) h by means of a small glass syringe. The longer equilibrium time at the working temperatures was 6 h for butyramide in aqueous solutions. Experimentally, it was confirmed that this time was adequate to reach equilibrium in the case of acetamide and propionamide; thus, it was selected as the equilibrium time to complete the saturation of the aqueous phase for the systems considered.

When saturation was reached, samples of 2 mL were transferred to 5 mL glass flasks and were dried in an Arthur H. Thomas vacuum oven at 323.15 K. The mass of the compounds was determined by weight using a Precisa balance XR 205SM-DR with the uncertainty of $\pm 3 \cdot 10^{-5}$ g in the range between (0 and 92) g. To check the method used, weighed small samples of the pure amides were dried in the vacuum oven at 323.15 K under the same conditions of which the saturated solutions were dried and then weighed again. No differences in mass were detected showing that amides do not evaporate at the conditions of the experiment. Measurements were made at temperatures between (278.15 and 333.15) K.

Results and Discussion

Experimental data obtained in this work and literature data for the mole fraction solubility of aqueous solutions of acetamide, propionamide, and butyramide between (278.15 and 333.15) K at intervals of 5.00 K are presented in Table 1. Each value of solubility is the average of two independent measurements. The calculated uncertainty in mole fraction solubility is ± 0.0001.

The values for solubility are in agreement with the results presented by other authors who have studied acetamide[9] as a function of temperature and butyramide at 298.15 K.[13] No

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Table 1. Solubility x_2 of Acetamide, Propionamide, and Butyramide in Water

T	$10^2\ x_2$		
K	acetamide	propionamide	butyramide
278.15	30.87	13.36	1.63
283.15	34.24	16.29	2.10
	34[a]		
288.15	37.09	19.45	2.60
293.15	40.17	23.15	3.31
	0.40[a]		
298.15	44.31	27.57	4.42
			$2.3 \cdot 10^2$ [b]
303.15	47.75	31.53	5.75
	48[a]		
308.15	51.49	37.08	7.24
313.15	55.63	39.99	8.95
	56[a]		
318.15	59.13	45.03	10.89
323.15	63.08	48.59	13.05
	63[a]		
328.15	67.73	52.70	15.24
333.15	72.13	56.78	17.48
	72[a]		

[a] Ref 9. [b] Ref 13 (reported value in $g \cdot L^{-1}$).

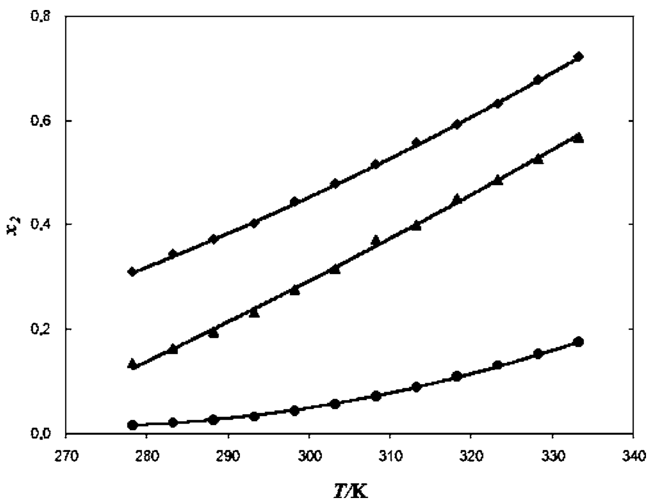

Figure 1. Solubility (x) of amides in water vs temperature (T): ◆, acetamide; ▲, propionamide; ●, butyramide.

results have been found in literature for butyramide at different temperatures or for propionamide. The solubility of amides in water increases with temperature and at constant temperature decreases as chain length increases (Figure 1).

According to the van't Hoff equation, the differential enthalpy of solution (ΔH_{sol}^{dif}) is obtained from the slope of a ln x_2 versus $1/T$ plot. The equation is applicable when the change of the activity coefficients with concentration near the saturation point is small.[14]

$$\frac{\partial \ln x_2}{\partial(1/T)} = \frac{\Delta_{sol}H_{dif}}{R} \tag{1}$$

where x_2 is the mole fraction, R is the universal gas constant, and T is the absolute temperature.

The temperature dependence of the solubility of acetamide, propionamide, and butyramide in water is well-described by the van't Hoff equation. Linear van't Hoff plots with negative slope were obtained for the amide−water systems as is shown in Figure 2. The differential enthalpy of solution for acetamide ($\Delta_{sol}H_{dif} = 11.83$ kJ·mol^{-1}), propionamide ($\Delta_{sol}H_{dif} = 20.36$ kJ·mol^{-1}), and butyramide ($\Delta_{sol}H_{dif} = 34.37$ kJ·mol^{-1}) are positive indicating that the processes are endothermic.

In this work, new data were measured for the solubility of acetamide, propionamide, and butyramide in water at several

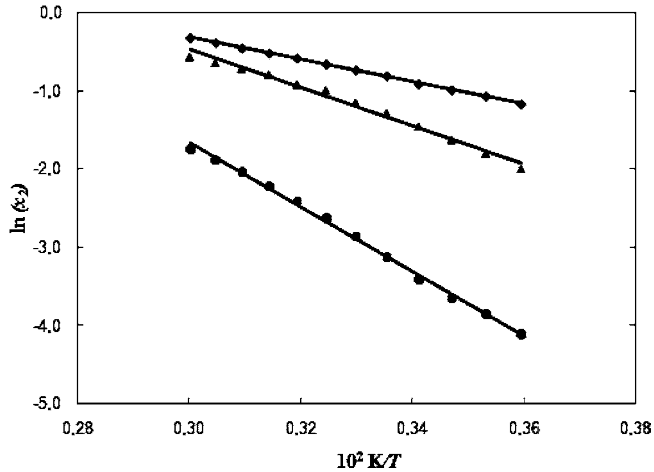

Figure 2. van't Hoff plot for the amide + water system: ◆, acetamide; ▲, propionamide; ●, butyramide.

temperatures. In general, the solubility of amides in water increases with temperature and decreases as the number of methylene groups in the alkyl chain increases as the result of apolar group interactions mediated by water. The hydrophobic behavior shown by aliphatic amides follows the same trend shown in other thermodynamic properties.[7,8]

Literature Cited

(1) Lilley, T. H. Interactions in solutions: The interplay between solute solvation and solute-solute interactions. *Pure Appl. Chem.* **1994**, *66*, 429–434.
(2) Lu, Y.; Wang, X.; Su, G.; Lu, J. Calorimetric and volumetric studies of the interactions of formamide with alkan-1-ol in water at 298.15 K. *Thermochim. Acta* **2003**, *406*, 233–239.
(3) Cabani, S.; Gianni, P.; Mollica, V.; Lepori, L. Group contributions to the thermodynamic properties of non-ionic organic solutes in dilute aqueous solution. *J. Solution Chem.* **1981**, *10*, 563–595.
(4) Zaichikov, A. M.; Manin, N. G. Thermochemical Study of Solvation of Aliphatic Carboxamides in Aqueous Formamide Solutions. *Russ. J. Gen. Chem.* **2001**, *71*, 679–688.
(5) Zielkiewicz, J. Excess Molar Volumes and Excess Gibbs Energies in N-Methylformamide + Water, or + Methanol, or + Ethanol at the Temperature 303.15 K. *J. Chem. Eng. Data* **1998**, *43*, 650–652.
(6) Lu, Y.; Cheng, Q.; Liu, M.; Han, Y.; Lou, X.; Lu, J. Calorimetric and volumetric studies of the interactions of butyramide in aqueous carboxylic acid solutions at 298.15 K. *Thermochim. Acta* **2002**, *386*, 103–110.
(7) Romero, C. M.; González, M. E. Effect of the temperature on the behavior of osmotic and activity coefficients of amides in aqueous solutions. *J. Therm. Anal. Calorim.* **2008**, *92*, 705–710.
(8) Romero, C. M.; González, M. E.; Lamprecht, I. Enthalpy of dilution of aliphatic amides in aqueous solutions at temperatures between 293.15 and 308.15 K. *Thermochim. Acta* **2009**, *488*, 49–53.
(9) Seidell, A. *Solubilities of organic compounds*; D. Van Nostrand Company: New York, 1943.
(10) Weissberg, A.; Rossiter, B. *Physical methods of chemistry*; Wiley-Interscience: New York, 1957.
(11) Blanco, L. H.; Sanabria, N. R.; Dávila, M. T. Solubility of 1,3,5,7-tetra azatricyclo[3.3.1.13,7]decane (HMT) in water from 275.15 to 313.15 K. *Thermochim. Acta* **2006**, *450*, 73–75.
(12) Blanco, L. H.; Sanabria, N. R. Solubility of 1,3,6,8-Tetraazatricyclo [4.4.1.13,8]dodecane (TATD) in water at temperatures between 275 and 303 K. *J. Chem. Eng. Data* **2007**, *52*, 2288–2290.
(13) Yalkowsky, S. H.; He, Y. *Handbook of aqueous solubility data*; CRC Press: Boca Raton, FL, 2003.
(14) Letcher, T. M.; Battino, R. An introduction to the understanding of solubility. *J. Chem. Educ.* **2001**, *78*, 103.

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