Specific Heats and Enthalpies of Mixing of Amine−H_2O and Amine−H_2O−NaCl Mixtures

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Specific heats of mixtures of dimethylisopropylamine (*N*,*N*-dimethyl-2-propanamine) or diisopropylamine (*N*-(1-methylethyl)-2-propanamine) and water and of dimethylisopropylamine and water saturated with NaCl were measured in a temperature range from 272 to 280 K at atmospheric pressure. The specific heats of the three systems all obtained maximum values in the amine weight fraction range (salt free) of 0.1 to 0.4. The enthalpies of mixing of dimethylisopropylamine or diisopropylamine and water were determined as a function of the amine concentration in the mixture. The mixing of water and the amines was strongly exothermic. The highest measured enthalpies of mixing per gram of mixture were −105 $J\cdot g^{-1}$ for dimethylisopropylamine−H_2O at an amine weight fraction of 0.49 and −81 $J\cdot g^{-1}$ for diisopropylamine−H_2O at an amine weight fraction of 0.60.

Introduction

In industry, soluble inorganic salts such as NaCl, whose solubility possesses a weak temperature dependence, are often separated from water by evaporative crystallization. The evaporation of water in these processes consumes considerable energy. To reduce the energy consumption in the production of such inorganic salts, drowning out crystallization by the addition of an organic antisolvent could be an interesting alternative. Dimethylisopropylamine and diisopropylamine are suitable antisolvents for the crystallization of NaCl, because they reduce NaCl solubility and they can be separated from the water phase by a temperature-induced liquid−liquid phase split (Zijlema et al., 1995).

To set up an energy balance over the process, specific heats of the binary amine−H_2O mixtures and of the ternary amine−H_2O mixtures saturated with NaCl need to be known. Also, the enthalpy of mixing of the amines and water in the crystallizer is of great importance to the overall energy consumption. Since these data are not available in the literature and their values cannot be predicted with great accuracy, they need to be determined experimentally. In this work, the specific heats of mixtures of diisopropylamine or dimethylisopropylamine and water and of dimethylisopropylamine and water saturated with NaCl, as well as the enthalpies of mixing of water and diisopropylamine or dimethylisopropylamine, are presented.

Experimental Section

Chemicals. The chemicals were dimethylisopropylamine (or DMiPA; $C_5H_{13}N$, Fluka purum, ≥98%), diisopropylamine (or DiPA; $C_6H_{15}N$, Elf Atochem, ≥99%), and pharmaceutical grade sodium chloride (Akzo Nobel). Demineralized water with a conductivity of less than 4 $mS\cdot cm^{-1}$ was used in all the experiments. In these experiments the amine concentration is expressed as a salt-free mass fraction $w_{amine} = m_{amine}/(m_{amine} + m_{H_2O})$.

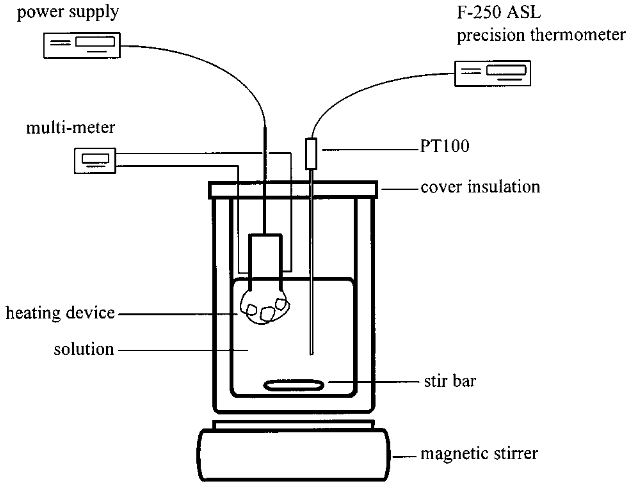

Figure 1. Experimental setup.

Apparatus and Procedures. All experiments were carried out in a covered stainless steel Dewar vessel (Figure 1). A small hole in the vessel cover ensured atmospheric pressure during the experiments. A magnetic stirrer and a stir bar provided agitation, and the temperature of the vessel contents was measured with an ASL-F250 precision thermometer (0.01 K accuracy, 0.002 K repeatability). All experiments were carried out in a thermostated room which was kept at temperatures of −268 to 278 K, depending upon the temperature of the experiment.

The specific heats were determined by heating the amine−water or amine−water−salt solutions with an electrical heating device (Figure 2). The device consisted of a Cr−Ni wire ($D \approx 0.4$ mm, 11 $\Omega\cdot m^{-1}$) which at both ends was attached to a stainless steel pin (AISI-316SS, D $\approx$ 2 mm). During the experiments the Ni−Cr wire was fully immersed in the solution. The stainless steel pins were attached to copper wire which was connected to a power supply (ES 030-4, Delta Electronics). The electrical heat input was controlled by the power supply. The electrical current through the Cr−Ni wire was kept at a constant

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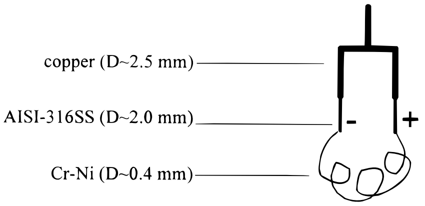

Figure 2. Heating device.

value, and the potential difference over the wire adjusted itself to the given current set point value. The potential difference over the Ni−Cr wire was measured locally, and the electrical power input was calculated from $P_{el} = V \cdot I$, in which V is the measured potential difference and I is the current through the Ni−Cr wire. During the experiments the electrical power input was kept at a value between 7 and 9 W, at which solution temperature changes were measurable and yet no insulating gas layer formed at the Ni−Cr wire−solution interface. Experiments showed that the heat exchange between the Dewar vessel contents and the surroundings could be neglected. An enthalpy balance could be set up for the solution in the vessel during an experiment

$$\frac{dH}{dt} = P_{el} \quad \text{with} \quad dH = mC_{p,m}\,dT \tag{1}$$

in which $C_{p,m}$ is the specific heat at constant pressure ($J \cdot g^{-1} \cdot K^{-1}$). These equations can be used for the calculation of the specific heat from the experimental data. All specific heats were determined in the temperature range 272 to 280 K (solution temperature) at atmospheric pressure.

The enthalpy of mixing experiments were carried out in the same experimental setup, except in these experiments the electrical heating device was removed. At the start of the experiments the Dewar vessel, the amine, and the water were in thermal equilibrium with their surroundings. First, the vessel was filled with the amine. The temperature of the amine inside the Dewar vessel T_1, as well as the temperature of the water in the Erlenmeyer flask T_2, was measured. The water was added to the Dewar vessel under stirring, and the temperature rise due to mixing was recorded. It took approximately 5 s for the liquid to reach its final constant temperature value T_m. The enthalpies of mixing were calculated from the following equation:

$$\Delta H_{mix} = \frac{(m_1 C_{p,m1} T_1 + m_2 C_{p,m2} T_2) - (m_1 + m_2) C_{p,m(1+2)} T_m - C_{p,D}(T_m - T_1)}{(m_1 + m_2)} \tag{2}$$

in which ΔH_{mix} is the enthalpy of mixing ($J \cdot g^{-1}$), m is the component mass (g), T is the temperature (K), $C_{p,m}$ is the specific heat ($J \cdot g^{-1} \cdot K^{-1}$), and $C_{p,D}$ is the specific heat of the Dewar vessel ($J \cdot K^{-1}$). The subscripts 1 and 2 refer to the amine and the water, respectively. Since in all experiments the total volume of the mixture in the vessel was kept constant at a value of approximately 400 mL, a correction for the heat loss to the Dewar vessel wall could be made. The specific heat of the vessel wall was determined in separate experiments and proved to be 68 $J \cdot K^{-1}$ (liquid volume inside the vessel ca. 400 mL).

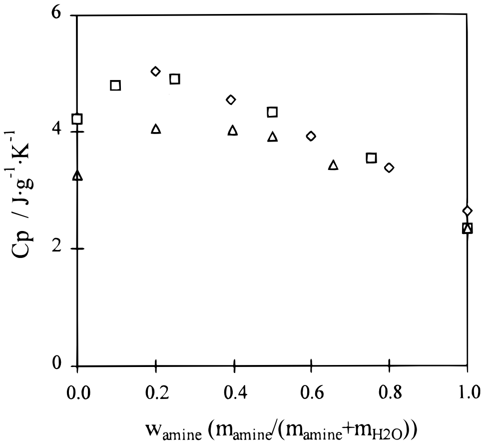

Figure 3. Experimentally determined specific heats of (◇) diisopropylamine−H_2O; (□) dimethylisopropylamine−H_2O; (△) dimethylisopropylamine−H_2O saturated with NaCl.

Table 1. Specific Heats of Dimethylisopropylamine−H_2O Mixtures

$w_{DMiPA}/m_{DMiPA}/(m_{H_2O} + m_{DMiPA})$	T_{range}/K	$C_{p,m}/J \cdot g^{-1} \cdot K^{-1}$
0	277	4.26 ± 0.07
0.0995	275−277	4.80 ± 0.08
0.2492	273−274	4.90 ± 0.05
0.4998	272−273	4.33 ± 0.05
0.7550	272−272	3.55 ± 0.03
1	277−279	2.32 ± 0.07

Table 2. Specific Heats of DiisoPropylAmine-H_2O Mixtures

$w_{DiPA}/m_{DiPA}/(m_{H_2O} + m_{DiPA})$	T_{range}/K	$C_{p,m}/J \cdot g^{-1} \cdot K^{-1}$
0	277	4.26 ± 0.07
0.2015	276−277	5.04 ± 0.03
0.3928	276−277	4.55 ± 0.02
0.5996	275−276	3.92 ± 0.03
0.8001	275−277	3.37 ± 0.03
1	277−279	2.63 ± 0.02

Table 3. Specific Heats of Mixtures of Dimethylisopropylamine and H_2O Saturated with NaCl

$w_{DMiPA}/m_{DMiPA}/(m_{H_2O} + m_{DMiPA})$	T_{range}/K	$C_{p,m}/J \cdot g^{-1} \cdot K^{-1}$
0	278	3.26[a]
0.1998	274−276	4.06 ± 0.07
0.3993	277−278	4.03 ± 0.07
0.5003	278−280	3.92 ± 0.08
0.6565	276−277	3.44 ± 0.06
1	277−279	2.32 ± 0.07

[a] Value from Kaufmann, 1960.

Results and Discussion

The results of the specific heat measurements of the binary mixtures of dimethylisopropylamine or diisopropylamine and water are displayed in Figure 3 and in Tables 1 and 2. The specific heats of dimethylisopropylamine−H_2O and diisopropylamine−H_2O reach maximum values of 4.90 and 5.04 $J \cdot g^{-1} \cdot K^{-1}$ at amine concentrations of 0.2492 and 0.2015, respectively. The specific heat of pure water was measured at 277 K; the measurement deviated +1.2% from a literature value of 4.21 $J \cdot g^{-1} \cdot K^{-1}$ (Marsh, 1987).

The results of the specific heat measurements on mixtures of dimethylisopropylamine and water saturated with sodium chloride are displayed in Table 3 and in Figure 3. As a result of the presence of NaCl, both the negatively charged stainless steel pin and the connected Cr−Ni wire were subject to corrosion. The measured specific heats reached a maximum value of 4.06 $J \cdot g^{-1} \cdot K^{-1}$ at an amine concentration of 0.1998.

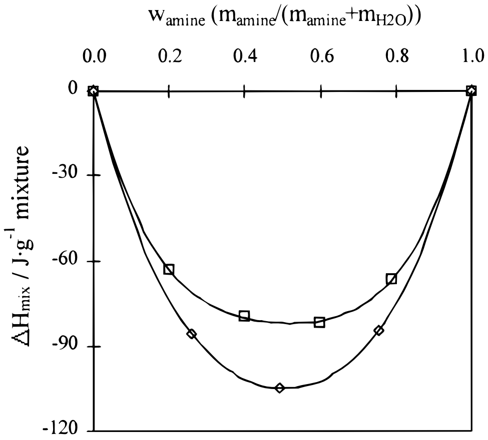

Figure 4. Enthalpies of mixing of the (◇) dimethylisopropylamine−H_2O and the (□) diisopropylamine−H_2O systems in J·g^{-1} (mixture) versus the weight fraction of amine.

Table 4. Enthalpies of Mixing of Dimethylisopropylamine and H_2O

$w_{DMiPA}/m_{DMiPA}/(m_{H_2O} + m_{DMiPA})$	T_{range}/K	ΔH_{mix}/J·g^{-1} (mixture)
0.2579	275−291	-85.6 ± 1.0
0.4916	275−298	-105.0 ± 1.2
0.7533	275−297	-84.5 ± 0.7

Table 5. Enthalpies of Mixing of Diisopropylamine and H_2O

$w_{DiPA}/m_{DiPA}/(m_{H_2O} + m_{DiPA})$	T_{range}/K	ΔH_{mix}/J·g^{-1} (mixture)
0.1986	276−288	-63.2 ± 0.6
0.3964	277−293	-79.6 ± 0.6
0.5990	277−296	-81.5 ± 0.7
0.7894	277−295	-66.5 ± 0.7

The results of the enthalpy of mixing measurements are displayed in Figure 4 and in Tables 4 and 5. For the calculation of enthalpies of mixing, the experimentally determined specific heats of the amine and of the amine−H_2O mixtures were used and were considered to be temperature independent in the temperature range at which the experiments were carried out. The specific heat of pure water was taken from the literature (Marsh, 1987). The results show that the mixing process is strongly exothermic. This indicates that the amine−water interactions are strong compared to the water−water and amine−amine interactions. For dimethylisopropylamine−H_2O, the highest measured enthalpy of mixing was −105 J·g^{-1} (mixture) at an amine concentration of 0.4916, corresponding to a temperature rise of approximately 23 K. For diisopropylamine−H_2O the highest enthalpy of mixing was −81 J·g^{-1} (mixture) measured at an amine concentration of 0.5990, corresponding to a temperature rise of approximately 19 K.

Conclusions

Specific heats of the binary dimethylisopropylamine−H_2O and diisopropylamine−H_2O systems and of the ternary dimethylisopropylamine−H_2O system saturated with NaCl have been measured as a function of the amine concentration. The specific heats of the three systems obtained maximum values in the amine weight fraction range of 0.1−0.4. The enthalpies of mixing of the amines and water were determined as a function of the mixing ratio. The mixing process was strongly exothermic, demonstrating the nonideal behavior of the amine−H_2O mixtures. The highest measured enthalpies of mixing were −105 J·g^{-1} for dimethylisopropylamine−H_2O at an amine concentration of 0.4916 and −81 J·g^{-1} for diisopropylamine−H_2O at an amine concentration of 0.5990.

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