Solubility of *N*-Hydroxyphthalimide in Binary Acetic Acid + Water Solvent Mixtures at (293.2 to 363.2) K

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Experimental solubilities are reported for *N*-hydroxyphthalimide (NHPI) dissolved in binary acetic acid + water solvent mixtures in the temperature range of (293.2 to 363.2) K. The mole fraction of water in the solvent mixtures x_{water} ranges from 0 to 0.5882. The experimental results show that the solubility of NHPI in the range of 10^{-2} to 10^{-3} mole fraction increases significantly with an increase in temperature and x_{water}. The solubility data were correlated by a modified Buchowski equation, and the parameters h and λ were regressed, which gave good agreement with all experimental data.

Introduction

N-Hydroxyphthalimide (NHPI) is an important radical catalyst that can promote the oxidation of a variety of hydrocarbons with molecular oxygen in the presence or absence of transition metal salts under mild conditions.[1−3] Oxidation of methyl aromatic hydrocarbons, notably, toluene, *p*-xylene, and pseudocumene, is of great scientific, technological, and commercial importance. One of the most successful commercial applications is the production of carboxylic acids by liquid-phase oxidation of methyl aromatic compounds with air using a Co−Mn−Br catalyst system (cobalt acetate, manganese acetate, and hydrogen bromide) in acetic acid (HOAc) medium.[4−6] Since a bromide ion in the catalyst system is highly corrosive and can result in the formation of poisonous brominated byproducts, a bromide-free catalyst system may be an attractive opinion. The catalyst system of NHPI combined with transition metal salts is an interesting choice. As Ishii et al.[1] reported, NHPI combined with cobalt acetate and manganese acetate is an effective bromide-free catalyst system used in the aerobic oxidation of toluene, xylene, and pseudocumene. The efficacy of the catalyst system is due to the fact that the catalytic cycles of NHPI and transition metal (Me) become coupled to produce synergistic results.

With respect to catalyst activation, the use of aqueous acetic acid as the solvent is a good choice for the NHPI−Me-catalyzed aerobic oxidation of methyl aromatic hydrocarbons. Because of the formation of water during the oxidation, the actual solvent is acetic acid and water mixtures. However NHPI is not very soluble in acetic acid or water at mild reaction temperatures, but the solubility increases with an increase in the reaction temperature. Therefore, solubility data for NHPI in acetic acid + water is important for determination of NHPI catalyst concentration at different reaction temperatures. The purpose of this work is to report solubilities of NHPI in binary acetic acid + water solvent mixtures at several temperatures. The data are correlated by a modified Buchowski equation, which gave good agreement with all experimental data.

Experimental Methods

N-Hydroxyphthalimide (>99 %) obtained from the Hangzhou Chemical Reagent Co. was used without any further purification. Demineralized water and analytical-grade acetic acid were also obtained from the Hangzhou Chemical Reagent Co.

Excessive solute (NHPI) and solvent (acetic acid + water) were placed in a sealed glass bottle (100 mL) and allowed to equilibrate in a water bath at a preset temperature with periodic agitation for at least 48 h (often longer). The water bath temperature was controlled within ± 0.1 K of the desired temperature with a thermoelectric controlling system. The bottle was sealed by a rubber stopper to prevent evaporation of the solvent. Attainment of equilibrium was verified both by repetitive measurements after 48 h and by approaching equilibrium from supersaturation by pre-equilibrating the solutions at a higher temperature.

The experimental runs were carried out under five solvent composition conditions at eight temperatures {i.e., $x_{\text{water}} = n_{\text{water}}/(n_{\text{water}} + n_{\text{HOAc}}) = (0, 0.1493, 0.2703, 0.4545, \text{and } 0.5882)\ \text{mol}\cdot\text{mol}^{-1}$ and $T = (293.2, 303.2, 313.2, 323.2, 333.2, 343.2, 353.2, \text{and } 363.2)$ K}. At each experimental temperature, a part of saturated NHPI solutions, viz., the clear upper portion of the solution, was transferred through a 10 mL syringe into a 100 mL volumetric flask. The syringe wall was washed by methanol at least four times to remove the crystallized solute to the volumetric flask, which was diluted quantitatively with methanol to 100 mL. The amount of NHPI in the volumetric flask was determined by high-performance liquid chromatography (HPLC) analysis using the external reference method and was carried out using an Agilent 1100.

In this work, the solubility was defined as the mole fraction of solute in the saturated solution. Thus, the solubility of NHPI in binary acetic acid + water solvent could be determined from

$$x = \frac{n_{\text{NHPI}}}{n_{\text{NHPI}} + n_{\text{water}} + n_{\text{HOAc}}} \qquad (1)$$

where x stands for the mole fraction of a solute NHPI in the saturated solution; n_{NHPI}, n_{water}, and n_{HOAc} are the molar concentrations of NHPI, water, and acetic acid in the solution sample. When n_{NHPI} was determined by HPLC and x_{water} was known, x_{exp} (the experimental NHPI solubilities) were calculated from eq 1 and are listed in Table 1. Numerical values represent the average of between four and eight independent determina-

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Table 1. Solubilities of NHPI in Binary Acetic Acid + Water Solvent Mixtures[a]

T	$x_{\mathrm{water}} = 0$		$x_{\mathrm{water}} = 0.1493$		$x_{\mathrm{water}} = 0.2703$		$x_{\mathrm{water}} = 0.4545$		$x_{\mathrm{water}} = 0.5882$	
K	x_{exp} ($\times 10^{-3}$)	x_{cal} ($\times 10^{-3}$)	x_{exp} ($\times 10^{-3}$)	x_{cal} ($\times 10^{-3}$)	x_{exp} ($\times 10^{-3}$)	x_{cal} ($\times 10^{-3}$)	x_{exp} ($\times 10^{-3}$)	x_{cal} ($\times 10^{-3}$)	x_{exp} ($\times 10^{-3}$)	x_{cal} ($\times 10^{-3}$)
293.2	2.98	3.01	2.82	2.81	2.79	2.80	2.75	2.78	3.05	3.08
303.2	3.94	3.94	3.87	3.85	3.98	3.98	4.07	4.12	4.66	4.63
313.2	5.04	5.07	5.10	5.18	5.53	5.52	6.03	5.97	6.76	6.80
323.2	6.58	6.46	6.81	6.86	7.54	7.53	8.47	8.47	9.79	9.76
333.2	8.16	8.14	9.11	8.96	10.0	10.1	12.0	11.8	13.8	13.7
343.2	10.3	10.2	11.6	11.6	13.6	13.4	16.2	16.1	19.1	18.9
353.2	12.7	12.6	15.0	14.8	17.7	17.4	22.1	21.6	25.8	25.7
363.2	15.5	15.5	18.7	18.7	22.5	22.5	28.7	28.7	34.3	34.3

[a] The x_{exp} stands for the experimental solubility (in mole fractions of the solute). The x_{cal} stands for the calculated solubility (in mole fractions of the solute) from eqs 2 and 3.

tions, with the measured values being reproducible to within ± 2.0 %.

Results and Discussion

The Buchowski equation (eq 2), which is used particularly for solid−liquid equilibrium systems, is applicable to describe most solution behavior as was suggested first by Buchowski et al.[7] Although only two parameters (λ and h) are involved, this equation is thermodynamically correct and gives an excellent description of experimental data without considering the activity coefficients of the components:

$$\ln\left(1 + \frac{\lambda(1 - x)}{x}\right) = \lambda h\left(\frac{1}{T} - \frac{1}{T_{\mathrm{m}}}\right) \tag{2}$$

In eq 2, T is the absolute temperature of solid−liquid equilibrium; x stands for the mole fraction of a solute NHPI in the saturated solution, which was defined by eq 1; T_{m} is the melting temperature of the solute NHPI, $T_{\mathrm{m}} = 513.7$ K from ref 8; λ and h are two parameters. As the Buchowski equation is effective only for constant solvent composition, the values of λ and h change with different solvent composition. We assumed that the parameters λ and h were quadratic polynomial functions of x_{water} as described in eq 3:

$$\lambda = a_1 {x_{\mathrm{water}}}^2 + b_1 x_{\mathrm{water}} + c_1$$

$$h = a_2 {x_{\mathrm{water}}}^2 + b_2 x_{\mathrm{water}} + c_2 \tag{3}$$

Equations 2 and 3 were used to correlate the experimental solubility of NHPI (x_{exp}) at different solvent compositions of $x_{\mathrm{water}} = (0, 0.1493, 0.2703, 0.4545, \text{and } 0.5882)$ mol·mol^{-1} and in the temperature range from (293.2 to 363.2) K. For comparison with the experimental values of this work (x_{cal}), the calculated solubility from eqs 2 and 3 at different x_{water} and temperatures conditions is listed in Table 1 together with x_{exp}. The comparison between the calculated results x_{cal} and the experimental data x_{exp} is also shown in Figure 1.

The values of the six parameters a_1, b_1, c_1, a_2, b_2, and c_2 in eq 3, which were regressed using a nonlinear optimization method, are listed in Table 2 together with the average relative deviation between the experimental and calculated values. The average relative deviation σ is defined as

$$\sigma = \left[\frac{i}{n}\sum_{i=1}^{n}\left(\frac{x_{\mathrm{exp}} - x_{\mathrm{cal}}}{x_{\mathrm{exp}}}\right)^2\right]^{1/2} \tag{4}$$

where x_{exp} is the experimental solubility of NHPI, n is the number of experimental points, and x_{cal} is the solubility calculated from eqs 2 and 3. The calculated solubility values of NHPI are also given in Table 1 and Figure 1. It can be seen that the obtained agreement is in general satisfactory. The average relative deviation of the simulated value and the experimental data is < 5 %.

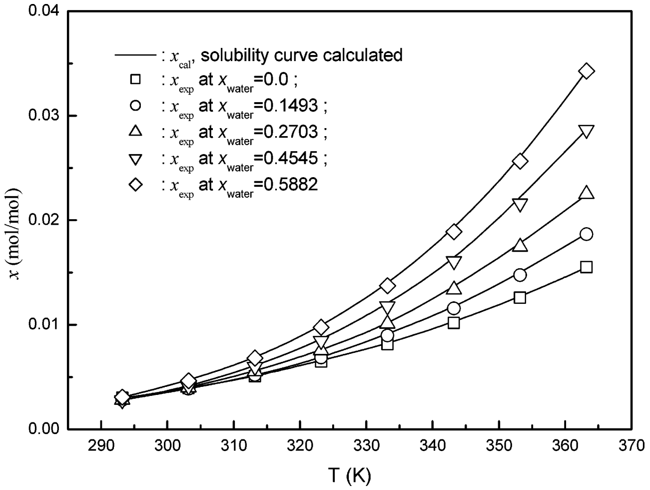

Figure 1. x_{exp}, experimental solubilities of NHPI in aqueous acetic acid, compared with x_{cal}, the calculated solubility from eqs 2 and 3.

Table 2. Quadratic Polynomial Parameters in Equation 3 and σ

x_{water}	a_{i}	b_{i}	c_{i}
$i = 1$	0.4050	0.1086	0.04955
$i = 2$	67272	−105110	53142
σ	0.03251		

From Figure 1 and Table 1, the experimental values of the solubilities of NHPI in the range of 10^{-2} to 10^{-3} mole fraction show good agreement with the calculated solubilities correlated by a modified Buchowski equation. The solubilities of NHPI increase significantly with increasing temperature and x_{water}. The experimental solubility and correlation equation in this work can provide essential data for the study of NHPI−Me-catalyzed aerobic oxidation in aqueous acetic acid solvent.

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