NMR Determination of High Temperature Acetic Acid/Water Vapor Phase Equilibria

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Introduction

Acetic acid is one of the most industrially important acids, used widely for the production of vinyl acetate, poly(vinyl acetate) and associated copolymers, and also as solvent for the oxidation of *p*-xylene to terephthalic acid.[1,2] It is also produced as the primary by-product of catalytic hydrothermal oxidation processes, the resulting aqueous solution generally being difficult to separate or dispose of. As a result, this acid has been well studied, particularly as part of multicomponent liquid/vapor mixtures under near-atmospheric conditions. When conducted at elevated temperatures and pressures, however, investigations are hampered by the corrosiveness of the acid towards most reactor alloys, and the rapid increase in pressure towards the critical point, particularly as a binary mixture with water. As a result, data for the acetic acid/water system in the super-atmospheric range are meager.

Nonetheless, several useful studies have been completed. Othmer[2] has published vapor liquid equilibria (VLE) for the acetic acid/water system from 0 to 243°C and 2.7 to 3549 kPa, for which no azeotropic point was found. Ambrose[3] has investigated the vapor pressure of acetic acid up to 141.9°C and 201.7 kPa, and also of the critical point (319.56°C, 5.786 MPa), which has since been of great aid in providing theoretical comparisons to the published experimental data. This is particularly so due to the tendency of the acid to dimerize in the vapor phase.[2] Freeman and Wilson[4,5] have published isothermal data at 99.6, 139.4, 188.9 and 229.7°C for the acetic acid/water system, however, to date the region from 200 to 300°C, and particularly above 243°C, is largely lacking in data. It is within this region that the hydrothermal oxidation processes primarily operate that provided the impetus for the work presented here.

The following study aims to provide phase data in the region of 160 to 300°C and 551 to 7440 kPa, and concurrently illustrates the use of ^{1}H nuclear magnetic resonance (NMR) as a method for the efficient analysis of the two component mixtures.

Methods

A thermostat-controlled Parr 4522 autoclave, rated to 350°C and 13.1 MPa, constructed of Type 316 stainless steel was modified to allow sampling of either the gas or liquid phases in a static system.[6] While coloration of the liquid phase due to minor corrosion of the steel was observed at the higher temperatures and acid concentrations, previous studies have shown that no interference with the VLE data is observed.[2] Pressure was measured by means of a Winters-LF gauge, and temperature via the calibrated autoclave K-type thermocouple. Liquid volumes of 1,000 mL were used with a total autoclave volume of 2,000 mL. The autoclave was purged with argon for 10 min. as a precaution to assist in the removal of gaseous oxidants, and the degassed liquids charged to the vacated autoclave before initiating heating through external jacketed electrical elements. The system was allowed to equilibrate until multiple checks of the temperature and pressure gave identical values,[2] before removing a sample of condensate for analysis. Contact and constant agitation of the phases were achieved via rapid mechanical stirring. The uncertainty in the temperature and pressure readings are ± 1°C (limited to the resolution of the output device) and 10 kPa, respectively, that of the acetic acid concentrations, 3%.

A subsample of the condensate (600 μL) was transferred to a 5 mm (internal dia.) NMR tube, the NMR signal locked using a H_2O/D_2O standard (2 Hz doped) after which the standard was replaced with the sample. A single scan ^{1}H spectrum was obtained, and the ratio of the peak integrations for the exchangeable and nonexchangeable protons calculated. Typical ^{1}H chemical shifts for the two singlet peaks are 4.62 ppm for the exchangeable protons and 1.84 ppm for the nonexchange-

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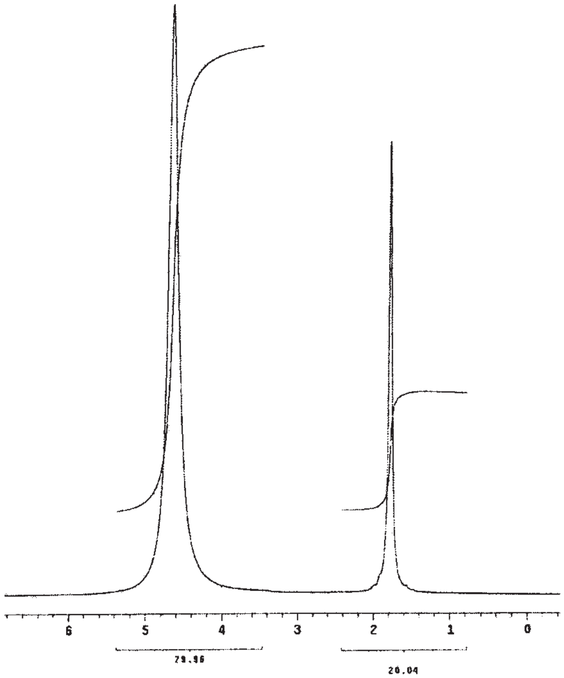

Figure 1. ^{1}H NMR spectrum of acetic acid in water.

able protons (Figure 1). The concentration of acetic acid in the sample was then calculated via a calibration curve obtained with standard solutions of acetic acid in water. Acetic acid (99.8 wt.%) was obtained from Allied Signal, all water used was previously distilled.

Results and Discussion

While not commonly used for such analyses, NMR is suited to the expeditious analysis of small samples. The signal areas of NMR peaks are proportional to the molar ratios of the compounds present, thus, with the optimization of acquisition and processing parameters, the concentrations of both components can be quantified. Signal saturation must be avoided, so that signals with the longest T1 (spin lattice relaxation time) are indeed relaxed. This is achieved by allowing a sufficiently long relaxation time between successive pulses. Additionally, a tip angle of 90 degrees must be used in order to obtain maximum signal intensity.[7] Acetic acid contains three nonexchangeable protons, plus one proton (on the hydroxyl) that is exchangeable with those in water. The two singlet peaks that are observed in a ^{1}H NMR spectrum of a mixture of these two compounds do not overlap, and thus NMR can be used to quantify both components.

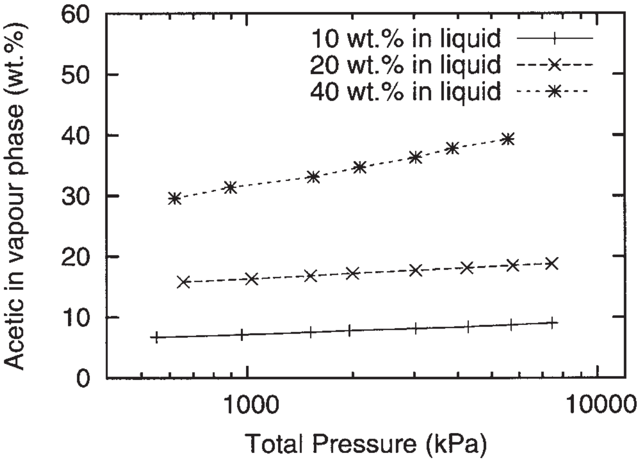

Figure 2. Logarithmic plot of vapor composition vs. total pressure at constant liquid compositions.

The results of the study are presented in Table 1 and Figure 2. In keeping with convention,[2,8,9] the experimental data were correlated according to the linear functions obtained when the logarithm of the vapor concentrations are plotted against the logarithm of the vapor pressure of a reference substance, usually water.

Comparison with existing experimental data is difficult, due to the scarcity of data available under these temperatures and pressures. However, the upper end of those reported by Othmer[2] agree well (Figure 3), particularly for the 10 and 20 wt.% liquid phase data. For the samples covering 40 wt.% in the liquid phase, the last data point as recorded by Othmer does not correlate with the results obtained in the study presented here. While Othmer's data show a decreasing concentration of the acid in the vapor phase with increasing temperature, the current study found a trend towards gradually increasing concentration, matching those found for the 10 and 20 wt.% lines found in the previous work (ibid). No azeotropic point was found, however, and in this the results agree with those of Othmer.

Comparison with theoretical vapor phase concentrations, while possible using the vapor pressure data of Ramsay and Young[8] and Weast[10] with Dalton's law is unsatisfactory, resulting in lower vapor phase concentrations. This is due to the previously noted nonideal behavior of the acid in the gas phase, and particularly its strong tendency to form dimers in this state.

Table 1. Vapor Phase Equilibria Observations

	$x = 10$			$x = 20$			$x = 40$		
T (°C)	P (kPa)	y_{exp}	y	P (kPa)	y_{exp}	y	P (kPa)	y_{exp}	y
160	551	5.0	6.7	655	14.1	15.8	620	29.8	29.6
180	965	7.4	7.1	1030	17.5	16.3	896	32.6	31.4
200	1520	8.0	7.5	1520	17.3	16.8	1550	33.0	33.1
220	1960	8.2	7.8	2000	18.9	17.2	2100	36.1	34.7
240	3030	8.1	8.1	3030	17.5	17.7	3030	37.3	36.3
260	4270	8.1	8.4	4240	18.0	18.1	3860	37.6	37.8
280	5680	8.2	8.7	5750	18.5	18.5	5580	39.0	39.3
300	7440	8.8	9.0	7440	18.0	18.8			

x = liquid (wt.% acetic acid), y_{exp} = vapor, experimental data (wt.% acetic acid), y = vapor, correlated data (wt.% acetic acid).

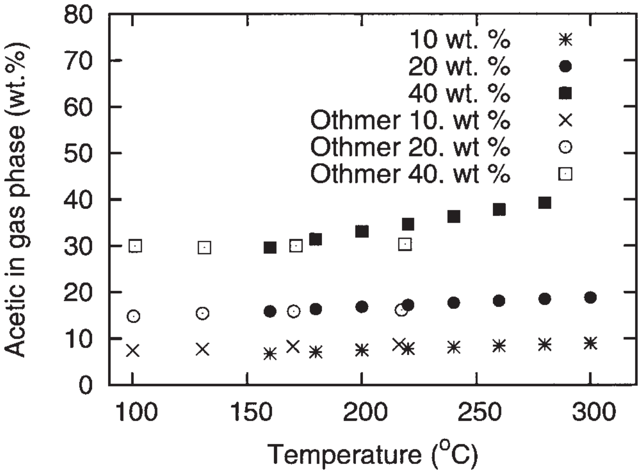

Figure 3. Data obtained in the current study with those of Othmer.[2]

More accurate theoretical predictions would be possible using activity coefficients of the sort reported by Freeman and Wilson[4] however with the exception of one datum at 229°C (ibid) no coefficients for acetic acid above 200°C have been recorded.

In summary: these results, while extending Othmer's work[2] on the vapor phase compositions of the acetic acid/water equilibrium, show primarily that in the region of 200 to 300°C, a gradual increase in the concentration of acetic acid in the vapor phase is observed. No azeotropic point was found under the conditions of the study. As this is the region in which hydrothermal oxidation processes operate, this then allows for a separatory step to be included for the removal of reaction products (of which acetic acid and water form the major part) from homogeneous catalysts.

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