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Comments & Replies

Comments on Solid−Liquid Phase Equilibrium and Phase Diagram for the Ternary *o*-Nitrobenzoic Acid + *m*-Nitrobenzoic Acid + Ethanol System

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A polemic is given in response to the recently published paper of Zhao and co-workers [*J. Chem. Eng. Data* **2008**, *53*, 1367−1370].

In a recent paper published in this Journal, Zhao et al.[1] reported the equilibria phase diagram of the ternary *o*-nitrobenzoic acid (1) + *m*-nitrobenzoic acid (2) + ethanol (3) system at (273.15, 283.15, and 293.15) K determined using Schreinemaker's wet residue method. Briefly, the experimental methodology involved filtration to remove the wet solid residue from an equilibrated saturated solution and then analyzing the collected liquid and solid phases by high performance liquid chromatography. The authors reported the concentrations as mass % for the "wet" solid phase.

The purpose of the present communication is not to criticize the published paper by Zhao and co-workers. Rather, I want to present a method that journal readers and reviewers can use in assessing the internal consistency of experimental data used in Schreinemaker's wet residue method. The practice of reporting the experimental data on the "wet" solid phase basis does not readily allow one to detect internal inconsistencies that might be present in the measured values. The method presented here does quickly allow one to check the experimental values. Once identified, suspected data points need to be redetermined so that more accurate experimental values are published.

In Tables 1 to 3, I have reproduced the authors' experimental solubility data for the ternary *o*-nitrobenzoic acid (1) + *m*-nitrobenzoic acid (2) + ethanol (3) system measured at (273.15, 283.15, and 293.15) K, respectively. For the ninth experimental data point in Table 1, the composition of the "wet" solid phase is reported to 25.76 mass % of *o*-nitrobenzoic acid and 13.08 mass % of *m*-nitrobenzoic acid, respectively. The remaining 61.16 mass % would be ethanol that would have been adsorbed onto the filtered solid residue from the saturated solution. The solid residue was analyzed "wet", and the chromatographically measured concentrations would include the amounts of *o*-nitrobenzoic acid and *m*-nitrobenzoic acid coabsorbed onto the solid residue along with ethanol.

Through mass balance concentrations, it is possible to subtract the amount of *o*-nitrobenzoic acid and *m*-nitrobenzoic that would have been absorbed onto the solid residue along with the 61.16 mass % of ethanol. For mathematical convenience, I have assumed 100 g total of each phase, so that the mass percentages become the mass of each chemical.

$$\text{mass of } o\text{-nitrobenzoic acid in ``dry'' phase} = \text{mass of } o\text{-nitrobenzoic acid in ``wet'' phase} - \left(\frac{\text{mass of ethanol in solid phase}}{\text{mass of ethanol in liquid phase}}\right) \cdot \text{mass of } o\text{-nitrobenzoic acid in liquid phase} \quad (1)$$

$$\text{mass of } m\text{-nitrobenzoic acid in ``dry'' phase} = \text{mass of } m\text{-nitrobenzoic acid in ``wet'' phase} - \left(\frac{\text{mass of ethanol in solid phase}}{\text{mass of ethanol in liquid phase}}\right) \cdot \text{mass of } m\text{-nitrobenzoic acid in liquid phase} \quad (2)$$

The individual masses will change depending on the number of grams assumed; however, the final calculated mass fraction composition of the "dry" solid phase is independent of the number of grams assumed. Substituting numerical values from the ninth line of Table 1 into eqs 1 and 2, I calculate that the mass of *o*-nitrobenzoic acid in the solid phase, calculated on a dry phase basis, would be 13.32 g and that the mass of *m*-nitrobenzoic acid would be 0.77 g. Clearly, the mass of 0.77 g is not zero, as should be the case if only crystalline *o*-nitrobenzoic acid was present. The nonzero numerical value does provide an indication of the likely experimental uncertainty associated with the reported values.

As noted above, the numerical values of the individual masses depend on the total grams of solid residue assumed. The mass fraction, however, is independent of the total grams of solid residue assumed. The mass fraction of composition of the "dry" solid phase is calculated by

$$w_{1,\text{dry}} = \frac{\text{mass of component 1 in the ``dry'' solid}}{\text{mass of component 1 in the ``dry'' solid phase} + \text{mass of component 2 in the ``dry'' solid phase}} \quad (3)$$

and

$$w_{2,\text{dry}} = \frac{\text{mass of component 2 in the ``dry'' solid}}{\text{mass of component 1 in the ``dry'' solid phase} + \text{mass of component 2 in the ``dry'' solid phase}} \quad (4)$$

dividing the mass of each nitrobenzoic acid derivative by the total mass of the dry solid. The mass percent that is calculated for *m*-nitrobenzoic acid, based on the 0.77 g mass, is 100 w_1 =

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Table 1. Experimental Solubility Data for the System *o*-Nitrobenzoic Acid (1) + *m*-Nitrobenzoic Acid (2) + Ethanol (3) at 273.15 K

liquid phase mass fraction		"wet" solid phase mass fraction		mass of acetone in "wet" solid	mass of acetone in liquid phase	mass of chemical 1 in "dry" solid	mass of chemical 2 in "dry" solid
100 w_1	100 w_2	100 w_1	100 w_2				
0.00	25.59	0.00	54.45	45.55	74.41	0.00*	38.79
2.74	24.13	2.20	41.80	56.00	73.13	0.10*	23.32
5.66	23.08	3.64	50.99	45.37	71.26	0.04*	36.30
8.25	21.93	5.93	44.69	49.38	69.82	0.10*	29.18
9.58	21.47	5.36	52.15	42.49	68.95	−0.54*	38.92
11.81	21.28	8.53	39.79	51.68	66.91	−0.59*	23.35
13.74	20.52	26.63	44.39	28.98	65.74	20.57	35.34
14.13	16.64	45.29	10.78	43.93	69.23	36.32	0.22*
14.48	14.33	25.76	13.08	61.16	71.19	13.32	0.77*
14.50	13.29	38.11	9.92	51.97	72.21	27.67	0.36*
15.56	8.87	51.61	5.02	43.37	75.57	42.68	−0.07*
16.69	4.82	42.12	3.88	54.00	78.49	30.64	0.56*
17.93	0.00	65.41	0.00	34.59	82.07	57.85	0.00*

Table 2. Experimental Solubility Data for the System *o*-Nitrobenzoic Acid (1) + *m*-Nitrobenzoic Acid (2) + Ethanol (3) at 283.15 K

liquid phase mass fraction		"wet" solid phase mass fraction		mass of acetone in "wet" solid	mass of acetone in liquid phase	mass of chemical 1 in "dry" solid	mass of chemical 2 in "dry" solid
100 w_1	100 w_2	100 w_1	100 w_2				
0.00	31.66	0.00	74.99	25.01	68.34	0.00*	63.40
2.98	29.94	1.02	71.17	27.81	67.08	−0.22*	58.76
7.03	29.64	5.32	45.51	49.17	63.33	−0.14*	22.50
10.47	27.34	3.14	76.55	20.31	62.19	−0.28*	67.62
14.54	25.89	6.39	67.42	26.19	59.57	0.00*	56.04
19.69	24.74	11.09	55.77	33.14	55.57	−0.65*	41.02
22.71	24.46	16.90	45.79	37.31	52.83	0.86*	28.52
23.34	24.17	46.50	30.12	23.38	52.49	36.10	19.35
23.56	23.59	46.10	17.24	36.66	52.85	29.76	0.88*
24.21	20.71	37.08	16.96	45.96	55.08	16.88	−0.32*
25.50	14.94	53.61	9.46	36.93	59.56	37.80	0.20*
28.29	8.02	66.49	3.69	29.82	63.69	53.24	−0.07*
29.14	4.28	49.54	3.12	47.34	66.58	28.82	0.08*
31.94	0.00	61.35	0.00	38.65	68.06	43.21	0.00*

Table 3. Experimental Solubility Data for the System *o*-Nitrobenzoic Acid (1) + *m*-Nitrobenzoic Acid (2) + Ethanol (3) at 293.15 K

liquid phase mass fraction		"wet" solid phase mass fraction		mass of acetone in "wet" solid	mass of acetone in liquid phase	mass of chemical 1 in "dry" solid	mass of chemical 2 in "dry" solid
100 w_1	100 w_2	100 w_1	100 w_2				
0.00	38.56	0.00	75.24	24.76	61.44	0.00*	59.70
3.91	36.08	2.76	54.46	42.78	60.01	−0.03*	28.74
5.87	34.65	3.06	61.35	35.59	59.48	−0.45*	40.62
9.16	33.22	6.80	48.13	45.07	57.62	−0.36*	22.15
12.43	31.93	6.05	69.73	24.22	55.64	0.64*	55.83
15.58	30.34	9.64	58.45	31.91	54.08	0.45*	40.55
20.25	28.76	14.26	50.13	35.61	50.99	0.12*	30.04
24.32	27.64	18.57	44.97	36.46	48.04	0.11*	23.99
28.79	26.48	42.71	42.67	14.62	44.73	33.30	34.02
29.28	23.83	47.03	17.96	35.01	46.89	25.17	0.17*
30.61	20.33	40.12	17.63	42.25	49.06	13.76	0.12*
31.29	16.54	49.88	12.74	37.38	52.17	27.46	0.89*
32.76	11.57	60.31	6.49	33.20	55.67	40.77	−0.41*
34.53	7.49	62.49	4.31	33.20	57.98	42.72	0.02*
37.78	0.00	64.08	0.00	35.92	62.22	42.27	0.00*

5.46 and does not equal zero as would be required if only *o*-nitrobenzoic acid were present. Reporting data as the mass % for the "wet" solid phase hides inconsistencies of this nature. I suggest that if authors plan on reporting their experimental solid−liquid compositional data on the "wet" solid phase basis that they may wish also to include the percentages calculated on the "dry" solid phase basis as well. One can quickly spot the internal inconsistencies in the experimental data by noting how large the nonzero positive and nonzero negative masses are.

There are several problems with the mass percent compositions that the authors report for the solubilities in the ternary *o*-nitrobenzoic acid (1) + *m*-nitrobenzoic acid (2) + ethanol (3) system. The authors indicate that only a single solid is present in the equilibrium solid phases, except for the seventh mixture in Table 1, eighth mixture in Table 2, and ninth mixture in Table 3. Using the authors' reported experimental data, combined with the mass constraints given by eqs 1 and 2 above, I calculate both nonzero positive and nonzero negative masses for the nitrobenzoic acid derivative that the authors state is absent in the solid phase. I have indicated with an asterisk (*) those values that should be zero according to the equilibrium solid phase reported in the Zhao et al. paper.[1] Several of the numerical values are nearly zero, and several are not. The computation method suggested here identifies those experimental values that are not sufficiently close to zero so that the values can be redetermined. On the basis of my analysis of the $w_{1,\mathrm{dry}}$ and $w_{2,\mathrm{dry}}$ values calculated from the masses in the seventh and eighth columns of Tables 1 to 3, I believe that a more realistic estimate of the experimental uncertainty in the measured data of Zhao et al. is ± 3 to 4 mass percent. This is much larger than the ± 0.1 % precision that the authors gave. My estimate takes into account how far the "dry" solid mass percent compositions are from zero in order for only one crystalline material to be present.

I have focused my analysis on the solid phase composition as this is where the internal inconsistencies are noticeable. Schreinemaker's wet residue method is only as good as the measured experimental data used to draw the equilibrium tie lines. I do not know of any simple method to check the composition of the saturated liquid solutions given only the information in the published paper. The liquid phase compositions may be correct, or the values may be wrong. One can examine the authors' experimental methodology and speculate on possible errors that might have occurred. I can think of several possible reasons for the observed inconsistencies and have rationalized how each error might affect composition determination of the liquid phase. First, there could have been considerable overlap in the chromatographic peaks for *o*-nitrobenzoic acid and *m*-nitrobenzoic acid, making accurate quantification difficult. The concentrations were determined using HPLC analysis. Overlapped peaks would affect both the calculated and solid phase concentrations as the same analysis method was used to quantify the equilibrium concentrations. Filtration was used to separate the wet solid residue from the liquid solution. The filtration process was likely performed at ambient room temperature, which is different than the equilibrium temperatures studied. Depending on the filtration method (vacuum filtration, gravitational filtration), sufficient time may have elapsed for a change in the solution temperature. A better experimental procedure would have been to remove a small sample of the saturated liquid solution while the sample was still being held at constant temperature. The removed sample could then be analyzed and the results compared with the values obtained from the filtered saturated liquid solution. A changing solution temperature would affect the liquid phase compositions. Third, evaporation of solvent from the filtered solid residue may have led to an inaccurate quantification of the composition of the "wet" solid phase. This error would probably not affect the reported liquid phase compositions. Fourth, as suggested by a Reviewer, the solid residue and filter can act as a sorbent for the analytes and retain much more than expected (solution going through is not saturated). Fifth, as noted by a Reviewer, no filter pore size was given in the paper by Zhao et al. Normally (0.1 or 0.2) μm is considered to separate dissolved and particle fraction in solution. Anyway, there can be some particles that pass the filter. Sixth, there may be undetected computational, typographical, and/or typesetting errors associated with the published values. Irrespective of the source(s) of the solid phase inconsistencies, Journal Readers need to be aware of the problems found when the published "wet" phase values are put on the "dry" solid phase basis. With the aforementioned knowledge, one is in a better position to assess the experimental data reported in the paper by Zhao and co-workers.[1]

Literature Cited

(1) Zhao, H.-K.; Zhang, Q.-H.; Li, R.-R.; Ji, H.-Z.; Meng, X.-C.; Qu, Q.-S. Solid-liquid phase equilibrium and phase diagram for the ternary *o*-nitrobenzoic acid + *m*-nitrobenzoic acid + ethanol system. *J. Chem. Eng. Data* **2008**, *53*, 1367–1370.

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