Short Communication

Comments Concerning ''Equilibrium Phase Diagram of the Ternary 2-Nitrobenzoic Acid + 3-Nitrobenzoic Acid + Acetone System at 283.15 and 313.15 K''

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In a recent paper published in this journal Zhao et al.[1] reported the equilibria phase diagram of the ternary 2-nitrobenzoic acid (1) + 3-nitrobenzoic acid (3) + acetone (3) system at both 283.15 and 313.15 K. Schreinemaker's wet residue method was used to determine the concentrations of the liquid and solid phases. The experimental methodology involved filtering the wet solid residue from an equilibrated saturated solution (the authors state aqueous solution, which I believe should read acetone 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 to point to errors that go undetected when experimental data is reported on the "wet" solid phase basis. In Tables 1 and 2, I have reproduced the authors' experimental solubility data for the ternary 2-nitrobenzoic acid (1) + 3-nitrobenzoic acid (2) + acetone (3) system measured at 283.15 and at 313.15 K. For the third experimental data point in Table 1, the composition of the "wet" solid phase is reported to be 2.55 mass% of 2-nitrobenzoic acid and 70.39 mass% of 3-nitrobenzoic acid, respectively. The remaining 27.06 mass% would be acetone 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 2-nitrobenzoic acid and 3-nitrobenzoic acid absorbed onto the solid residue along with acetone.

Through mass balance concentrations, it is possible to subtract the amount of 2-nitrobenzoic acid and 3-nitrobenzoic that would have been absorbed onto the solid residue along with the 27.06 mass% of acetone. For mathematical convenience, I have assumed 100 g total of each phase, so that the mass percentages become the mass of each chemical.

$$\text{mass of 2-nitrobenzoic acid in ''dry'' phase}$$
$$= \text{mass of 2-nitrobenzoic acid in ''wet phase}} - \left(\frac{\text{mass of acetone in solid phase}}{\text{mass of acetone in liquid phase}} \right)$$
$$\times \text{ mass of 2-nitrobenzoic acid in liquid phase} \qquad \text{(Eq 1)}$$

$$\text{mass of 3-nitrobenzoic acid in ''dry'' phase}$$
$$= \text{mass of 3-nitrobenzoic acid in ''wet phase}} - \left(\frac{\text{mass of acetone in solid phase}}{\text{mass of acetone in liquid phase}} \right)$$
$$\times \text{ mass of 3-nitrobenzoic acid in liquid phase} \qquad \text{(Eq 2)}$$

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 third line of Table 1 into Eq 1 and 2, I calculate that the mass of 2-nitrobenzoic acid in the solid phase, calculated on a dry phase basis, would be −2.46 g, and that the mass of 3-nitrobenzoic acid would be 56.978 g. Clearly, the negative mass of −2.46 is meaningless as one cannot have a negative mass% for chemical

compositions. The negative numerical value does provide an indication of the likely experimental uncertainty associated with the reported values.

There are several problems with the mass% compositions that the authors report for the solubilities in the ternary 2-nitrobenzoic acid (1) + 3-nitrobenzoic acid (2) + acetone (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, and ninth mixture in Table 2. Using the authors reported experimental data, combined with the mass constraints given by Eq 1 and 2, 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 in Tables 1 and 2 that should be zero according to the equilibrium solid phase reported in the Zhao et al.'s paper.[1] The mass fraction of composition of the "dry" solid phase is calculated by

Table 1 Experimental solubility data for the system 2-nitrobenzoic acid (1) + 3-nitrobenzoic acid (2) + acetone (3) system at 283.15 K

Liquid phase, mass%		"Wet" solid phase, mass%		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 w1	100 w2	100 w1	100 w2				
0.00	34.36	0.00	83.43	16.57	65.64	0.00*	74.76
5.91	31.78	2.82	81.77	15.41	62.31	1.36*	73.91
11.01	29.49	2.55	70.39	27.06	59.50	−2.46*	56.98
16.84	28.18	8.53	64.91	26.56	54.98	0.39*	51.30
21.88	27.76	11.76	60.50	27.74	50.36	−0.29*	45.21
28.22	25.30	15.33	60.52	24.15	46.48	0.67*	47.37
29.57	24.23	49.53	31.33	19.14	46.20	37.28	21.29
29.79	24.97	42.69	21.40	35.91	45.24	19.04	1.58*
30.46	19.29	43.36	15.87	40.77	50.25	18.65	0.22*
33.49	11.91	52.42	8.71	38.87	54.60	28.58	0.23*
36.14	9.06	51.29	7.25	41.46	54.80	23.95	0.40*
36.47	5.54	57.46	3.64	38.90	57.99	33.00	−0.08*
38.89	2.61	63.13	1.93	34.94	58.50	39.90	0.37*
40.87	0.01	84.65	0.00	15.35	59.12	74.04	0.00*

The asterisks indicate those values that should be zero according to the equilibrium solid phase reported in the Zhao et al.'s paper

Table 2 Experimental solubility data for the system 2-nitrobenzoic acid (1) + 3-nitrobenzoic acid (2) + acetone (3) system at 313.15 K

Liquid phase, mass%		"Wet" solid phase, mass%		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 w1	100 w2	100 w1	100 w2				
0.00	51.69	0.00	75.83	24.17	48.31	0.00*	49.97
5.42	46.09	3.55	64.99	31.46	48.49	0.03*	35.09
12.34	42.41	8.54	58.19	33.27	45.25	−0.53*	27.01
16.69	40.16	10.87	60.30	28.83	43.15	−0.28*	33.47
19.46	36.71	6.78	79.17	14.05	43.83	0.54*	67.40
25.03	36.34	10.58	74.20	15.22	38.63	0.72*	59.88
27.66	35.41	14.43	66.02	19.55	36.93	−0.21*	47.27
30.56	33.26	20.21	57.07	22.72	36.18	1.02*	36.18
31.06	32.90	31.86	47.33	20.81	36.04	13.93	28.33
31.98	31.59	49.95	23.90	26.15	36.43	26.99	1.22*
32.35	29.18	42.82	24.75	32.43	38.47	15.55	0.15*
33.13	25.49	60.74	14.99	24.27	41.38	41.31	0.04*
36.14	22.69	56.59	15.02	28.39	41.17	31.67	−0.63*
37.82	18.01	58.32	11.86	29.82	44.17	32.79	−0.30*
40.00	12.80	44.26	11.54	44.20	47.20	6.80	−0.45*
43.07	8.48	59.16	6.22	34.62	48.45	28.38	0.16*
46.08	5.12	55.33	4.37	40.30	48.80	17.28	0.14*
51.19	0.00	63.21	0.00	36.79	48.81	24.63	0.00*

The asterisks indicate those values that should be zero according to the equilibrium solid phase reported in the Zhao et al.'s paper

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

and

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

dividing the mass of each nitrobenzoic acid derivative by the total mass of the dry solid. The mass% that is calculated for 2-nitrobenzoic acid, based on the -2.46 g mass is $100 w_1 = -4.31$, and does not equal zero as would be required if only 3-nitrobenzoic acid were present. Reporting data as the mass% for the "wet" solid phase hides the inconsistencies of this nature. I suggest that if authors insist on reporting their experimental solid–liquid compositional data on the "wet" solid phase basis that they also 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.

Based on my analysis of the $w_{1,\text{dry}}$ and $w_{2,\text{dry}}$ values calculated from the masses in the seventh and eighth columns of Tables 1 and 2, I believe that a more realistic estimate of the experimental uncertainty in the measured data of Zhao et al. is ± 3 to 4 mass%. This is much larger than the $\pm 0.1\%$ precision that the authors gave.

My estimate takes into account how far the "dry" solid mass% compositions are from zero in order for only one crystalline material to be present.

The best indication of the composition of the solid phase does not come from the chromatographic analysis data reported in the Zhao et al.'s paper.[1] Rather, Lettre[2] previously determined the phase diagram of binary 2-nitrobenzoic acid + 3-nitrobenzoic acid, 2-nitrobenzoic acid + 4-nitrobenzoic acid, and 3-nitrobenzoic acid + 4-nitrobenzoic acid mixtures based on melting point versus binary mixture composition measurements. The melting point measurements showed the binary systems to be simple eutectics, with no mixed crystal or molecular compound formation. The chromatographic analysis of Zhao et al. is in accord with the published binary 2-nitrobenzoic acid + 3-nitrobenzoic acid phase diagram, provided that one is willing to accept negative mass fractions and mass fractions in the "dry" solid phase as large as $w = 0.077$ (eighth data point in Table 1) to mean that the

chemical is absent from the "dry" solid phase.

References

1. H.-K. Zhao, Q.-H. Zhang, R.-R. Li, D.-S. Zhang, and Q.-S. Qu, Equilibrium Phase Diagram of the Ternary 2-Nitrobenzoic Acid-3-Nitrobenzoic Acid–Acetone System at 283.15 and 313.15 K, *J. Phase Equilibr. Diff.*, 2008, **29**(4), p 333-336
2. H. Lettre, Isomorphism of Organic Compounds. V. Nitrobenzoic Acids and Substituted Benzoic Acids, *Berichte der Deutschen Chemischen Gesellschaft [Abteilung] B, Abhandlungen*, 1940, **73B**, p 386-390

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