Reply to Comments by W. E. Acree, Jr. on *J. Chem. Eng. Data* 2008, *53*, 1367−1370

Hong-Kun Zhao*

College of Chemistry and Chemical Engineering, YangZhou University, Yangzhou, Jiangsu, 225002, People's Republic of China

The comments by Acree[1] on the paper by Zhao et al.[2] provide many constructive suggestions. In that comment, Acree presents a method for assessing the internal consistency of experimental data used in Schreinemaker's wet residue method.[1] This comment appears to be reasonable. However, there are problems with the method suggested.

1. Acree indicates that Schreinemaker's wet residue method is only as good as the experimental data used to construct the tie lines. One question is how to confirm the equilibrium solid phase, dried directly, or washed, dried, and then analyzed. For multicomponent systems (e.g., $Na_2SO_4 + H_2O_2 + H_2O^3$), it is very difficult to identify the equilibrium solid phase directly (in this system, the adduct $Na_2SO_4 \cdot H_2O_2$ or $Na_2SO_4 \cdot H_2O_2 \cdot 0.5H_2O$ can be formed, which depends on the concentration of H_2O_2). However, Schreinemaker's wet residue method is a valid method to construct the solid−liquid phase diagram of the ternary system. It is not only as good as the experimental data (composition of equilibrium liquid phase not "wet" solid phase) used to construct the tie lines but also a very valid method to identify the equilibrium solid phases.[4,5]

2. Acree[1] presents a calculation method to assess whether or not the measured values obey "the conservation of mass". However, the phase diagram can be used not only for qualitative but also for a quantitative description of the system, and that can form a basis for calculating material balances.[4] These quantitative relationships are represented graphically by two rules, the straight line rule and the lever rule. "The conservation of mass" proposed by Acree[1] is a lever rule in nature. This method, initially proposed by Schreinemaker, has been used in solid−liquid phase diagrams of multicomponent systems for many many years.[4,6] The internal inconsistencies in the experimental data (the compositions of the "wet" residue and the equilibrium liquid phase) can be found in many papers.[7−9]

It is well-known that, strictly speaking, the mass and the composition of the liquid phase, the original mixture, and the wet solid and dry solid must obey the lever rule and the straight line rule. In a ternary phase diagram, when a pure solid is formed, the composition of the other component in the "dry" solid phase must be zero. In fact, there always exist some errors in the experiments. Any expert in the field is aware of the fact. The errors (positive errors or negative errors) result from the fact that the mass and the composition of the liquid phase, original mixture, and wet solid do not obey the straight line rule and the level rule strictly. That is to say a straight line drawn through a pair of points representing such compositions on a phase diagram may not pass through the composition of the pure solid exactly. The numerical values of the composition of the other component calculated according to the lever rule and the straight line rule are often not zero. It is not possible that all the calculated numerical values are zero. The tie-lines fixed by the compositions of equilibrium solution and moist wet solid were extrapolated algebraically to the line of 100 % pure component, and the errors can be calculated. The errors of analysis and synthesis, which are probably quite small, are greatly multiplied by the extrapolation.[7−9]

3. To construct the multicomponent solid−liquid phase diagram, any two of the following three compositions, liquid phase, original mixture, and wet solid, are needed. In our investigation,[2] the equilibrium liquid phase and wet solid phase are employed to determine the pure solid phase. Acree indicates that the experimental data employed in the method are flawed, and that is the reason for Acree's comment. I recognized the point in our experiments. The so-called "flaw" mainly results from experimental uncertainties. This uncertainty is not avoidable during the experiment. In our paper[2] ("in Figures 1, 2, and 3, along the solubility curve S_1C_1, S_2C_2, or S_3C_3, linking the composition points of the liquid phase and moist solid phase and an extension thereof, the point of intersection of these tie-lines is approximately the solid-phase component for *o*-nitrobenzoic acid on a wet basis"),[2] we only say "approximately", not "exactly". The ± 0.1 % precision that we gave is the analytical results using HPLC, not the experimental uncertainty.

4. The compositions of wet solid phase determined by Schreinemaker's wet residue method have experimental uncertainties that are estimated to be about 3 %. However, from the engineering point of view, the experimental uncertainty is acceptable in determining the phase diagram of multicomponent systems.

A simple example is given below to illustrate the experimental uncertainty in the measured data of the phase diagram for the multicomponent system. For mathematical convenience, I have also assumed 100 g total of each phase, so that the mass percentages become the mass of each chemical. The calculation method is the same as described in ref 1. The solubility of the system potassium sulfate + hydrogen peroxide + water at 20 °C[3] and the calculated results are all given in Table 1.

From Table 1, only a single solid, K_2SO_4, is present in the equilibrium solid phase. The mass of H_2O_2 in the "dry" solid is nonzero. Many similar examples can be found in the published papers.[7−30]

There are several possible reasons the various uncertainties might affect composition determination of the liquid phase. Acree[1] indicates that the liquid phase compositions may be wrong. I claim that the liquid phase compositions and equilibrium tie line of the liquid phase published in ref 2 are correct. In our experiment, there are no overlaps in the chromatographic peaks for *o*-nitrobenzoic acid and *m*-nitrobenzoic acid. Filtration was carries out at the studied temperatures, and a filter pore size of 0.22 μm (Isopore) was used during the separation process. When some filtrate was obtained, the filter unit was placed into a ice−water mixture. A very small amount of solvent

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* Corresponding author. E-mail: hkzhao@zzu.edu.cn. Tel.: +86 514 87975568. Fax: +86 514 87975244.

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evaporated from the filtered solid residue. This is a possible reason that leads to an inaccurate quantification of the composition of the "wet" solid phase. It is very difficult to reproduce the "wet" composition; however, the tie lines of equilibrium liquid composition and the equilibrium solid phase can easily be reproduced.

Table 1. System Potassium Sulfate (1) + Hydrogen Peroxide (2) + Water (3) at 20 °C (Solubility Data Were Taken from Reference)

liquid phase		moist solid phase				
K_2SO_4 (100 w_1)	H_2O_2 (100 w_1)	K_2SO_4 (100 w_1)	H_2O_2 (100 w_1)	solid phase	mass of 1 in "dry" solid	mass of 2 in "dry" solid
10.00	0.00	98.2	0.00	K_2SO_4	98.0	0
13.78	4.12	87.5	0.63	K_2SO_4	85.5	0.034
16.78	8.35	91.4	1.00	K_2SO_4	89.7	0.152
19.40	12.10	86.0	0.61	K_2SO_4	82.21	−1.76
23.12	15.57	89.7	2.00	K_2SO_4	86.57	0.108
23.89	18.45	91.0	2.33	K_2SO_4	88.24	0.196
24.83	20.11	93.6	1.89	K_2SO_4	91.57	0.24
28.31	24.12	90.7	3.36	K_2SO_4	87.17	0.35
31.41	28.17	95.7	1.81	K_2SO_4	93.77	0.075
35.93	33.66	94.0	3.05	K_2SO_4	90.52	−0.22
41.09	39.29	93.0	4.75	K_2SO_4	88.29	0.244
44.36	43.85	81.5	6.60	K_2SO_4	36.73	−37.66

In determining the compositions of the wet residue based on Schreinemaker's method, filter operation was already used to obtain the wet solid phase. This method can be found in published papers.[16−18]

Acree indicates that: "Reporting data as the mass fraction for the "wet" solid phase hides inconsistencies. I recommend that if authors report their experimental solid−liquid compositional data on the "wet" solid phase basis they should also include the mass fractions calculated on the "dry" solid phase basis. One can quickly spot the internal inconsistencies in the experimental data by noting how large the nonzero positive and nonzero negative masses are." I do not believe that reporting data as the mass fraction for the "wet" solid phase hides any inconsistencies because the reported data (compositions of equilibrium liquid and wet solid phase) should obey the lever rule and the straight line rule. The tie-lines fixed by the compositions of equilibrium solution and moist wet solid were extrapolated algebraically, and then any inconsistency can be obtained. Papers reporting the experimental solid−liquid compositional data on the "wet" solid phase basis have been published.[7−30] Many papers do not include the mass fractions calculated on the "dry" solid phase basis.[10−29]

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