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Comments On “Liquid−Liquid Equilibria for Water + 2,3-Butanediol + 3-Methyl-1-Butanol with Sodium Sulfate and Sodium Carbonate at 303.15 K” (Sharma, S.; Pandya, G.; Chakrabarti, T.; Khanna, P. *J. Chem. Eng. Data*, 1996, *41*, 306−309)[†]

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In the work of Sharma et al. (1996) and as well as in certain other works on salt effect on LLE, a quaternary (three liquid + one salt) system was considered as a pseudoternary (two liquid + one aqueous salt solution) system and the usual experimental procedure applicable to a true ternary (three liquid) system was merely followed. According to the phase rule, at a given temperature and pressure, a three-component, two-phase system is univariant whereas a four-component, two-phase system is bivariant having many solubility envelopes (Nagata, 1986). The distribution of salt is different in different phase and consideration of a quaternary (three liquid + one salt) system as a pseudoternary (two liquid + one aqueous salt solution) system is therefore wrong and a single pseudosolubility curve cannot exist. To circumvent these situations, one can measure the distribution data alone in salt-containing systems, for example as measured by Eisen and Joffe (1966).

Sharma et al. (1996) reported that the tie line data for the pseudoternary system were obtained by the method used for the ternary system; only 2,3-butanediol concentration was determined, and the complete compositions of the conjugated layers were obtained from the binodal curves. This procedure appears to be wrong. These authors stated that they adopted the procedure followed by Swabb and Mongan (1952) who, however, measured the concentrations of all but one component in the conjugated layers.

Further evidence as to the erroneous measurements are

(i) In the system containing sodium sulfate, the sum of mass fractions is not unity for two readings, at $w_1 = 0.757$ and $w_1 = 0.216$ (Table 2).

(ii) The reported mass fraction of sodium sulfate in aqueous solution, $w_4 = 0.1$. As inferred from the paper, w_4 represents the mass fraction of sodium sulfate in the binary aqueous salt solution. That is, $w_4 = w_s/(w_1 + w_s)$. Our calculations indicate that $w_4 \neq 0.1$ for 5 out of 11 readings reported:

w_1:	0.343	0.216	0.180	0.158	0.133
w_4(calcd):	0.0829	0.0809	0.0863	0.0814	0.0828

(iii) Similarly for the system with sodium carbonate (5), $w_5 \neq 0.1$ for 11 out of 13 readings; the calculated values of w_5 vary from 0.0847 to 0.145. There appears to be typographical error in w_s; for $w_1 = 0.076$, w_s is probably 0.0076.

In conclusion, the data of Sharma et al. (1996) are erroneous, and they should be reinvestigated.

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