not at temperature extremes of the cloud-point curves demonstrate the inaccuracy of the psuedobinary assumption for this mixture. Despite this, it is interesting to describe qualitatively the shape of the cloud-point curves with the usual equation used to describe the coexistence curve [21, 22]

$$(X_2 - X_1)/X_c = 2B(|T - T_c|/T_c)^{\beta} \quad (1)$$

In Eq. (1) X_1 and X_2 will be, for this analysis, the butyl alcohol concentrations at the two branches of the cloud-point curve at a given temperature, T. X_c is analogous to the critical point in a true binary mixture, the butyl alcohol concentration at the extremum of the cloud-point curve. T_c is the "critical temperature," i.e., the cloud-point extremum temperature.

To accomplish this analysis we plot, in Fig. 4, a double-logarithmic plot of $(X_2 - X_1)/X_c$ versus $|T - T_c|T_c^{-1}$. We find, for tBA concentrations far from the pinched-off region near the critical double point, linear plots implying a power-law behavior and slopes yielding $\beta \simeq \frac{1}{3}$. This is near the normal Ising value found in true binary mixtures [22]. For tBA concentrations near the CDP, however, the plots seem to cross over to exponents that are essentially doubled to $\beta \simeq \frac{2}{3}$. This doubling is expected because our approach to the critical curve is tangential near the CDP [23]. This will cause exponent renormalization, in this case doubling, since the critical curve must be roughly quadratic near the CDP. Similar behavior has been

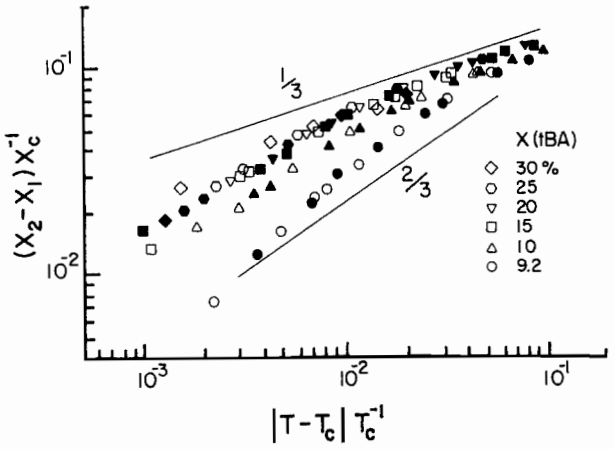

Fig. 4. Width of the cloud-point curve vs reduced temperature for various tBA concentrations. Filled symbols are for lower cloud-point curves; open symbols are for upper curves. Lines with slopes of $\frac{1}{3}$ and $\frac{2}{3}$ are drawn for comparison.

seen in gas–gas systems [24]. In conclusion, while the pseudobinary assumption for this mixture can be shown to be imperfect, it does allow for a qualitative description of the cloud-point curves.

4. CONCLUSION

Cloud-point curves in the mixture tBA, sBA, and water display an interesting variety of miscibility–immiscibility phase change behavior. The effect of adding tBA to the sBA plus water system is very similar to the effect of increasing pressure on the system. This suggests that the delicate interplay of energy and entropy effects on the phase behavior of the system is dependent on the properties of the interaction of the sBA with the water and this interaction can be changed in the same way by either the addition of tBA or the application of pressure. The shape of the cloud-point curves in the pseudobinary assumption is similar to that found in a true binary system with a critical exponent β consistent with the Ising value far from the critical double point and showing exponent doubling near this point.

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