Critical Solubility Behavior of Electrolytes in Water-Based Binary Liquid Mixtures with a Consolute Point

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The opposite sides of the coexistence curve of a binary liquid mixture with a miscibility gap converge at a consolute point where certain of the thermodynamic derivatives go to infinity [1]. Among the derivatives exhibiting divergent behavior is the slope of a van't Hoff plot of the solubility of a solid in dissolution equilibrium with a mixture [2]. If the dissolution is endothermic, the slope diverges toward negative infinity. If exothermic, it diverges toward positive infinity. As predicted by the principle of critical point isomorphism [1], the divergent slope behavior is expected to be universal in cases where one or fewer composition variables are fixed. This condition is automatically satisfied in the case of chemically inert solute. Given that there are more than 1000 pairs of liquids with a consolute point, the phenomenon should be readily observable. By contrast, when a solid dissolves by chemical reaction, it is possible for more than one composition variables to be fixed. The exact number can be ascertained by a counting procedure based on the Gibbs phase rule. In agreement with the isomorphism principle, the divergent slope effect disappears if two or more composition variables are fixed [2]. Ordinarily, this restriction does not place a severe limitation on observing a divergent slope effect, however. The phenomenon is observed, for example, in the case of many salts and metal oxides dissolving by reaction with hydronium ion to form electrolytes in a mixture of isobutyric acid + water near its consolute point at 26 °C [2].

References:

[1] R. B. Griffiths and J. C. Wheeler, Phys. Rev. A 2, 1047 (1970).

[2] J. K. Baird, J. D. Baker, B. Hu, J. R. Lang, K. E. Joyce, A. K. Sides, and R. D. Richey, J. Phys. Chem. B 119, 4041 (2015).