Near-Critical Solutions and Supercritical Solubility - a Century of Experiments

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One of the foci of John O'Connell's work is the correlation of thermodynamic properties of dilute solutions over wide ranges of pressure and temperature, including the solvent's near- and supercritical regime [1].

Such properties were also of interest over a century ago, when Van der Waals formulated the first binary-mixture equation of state that produced phase separation and both vapor-liquid and liquid-liquid critical points, see [2]. The first reliable measurements in fluid mixtures near critical points were performed by Kamerlingh Onnes graduate student Kuenen in Leiden, in the early 1890s, see [2]. He understood profoundly how large the effects of small impurities can be on density measurements performed near a solvent critical point.

Initiated into Gibbs's phase theory by Van der Waals, the Amsterdam chemistry professor Bakhuis Roozeboom and his school systematically measured phase diagrams of unary, binary and ternary systems in fluid and solid phases [3] – Smits and Wuite, for instance, studied the solubility of sodium sulfate up to the water critical point in 1909. The Amsterdam chemists were familiar with the phenomenon of supercritical solubility.

The work of the Dutch School was of great interest to the Moscow physical chemistry professor Krichevskii (1901-1993), whose large group of experimental collaborators, mostly women PhDs, landed several "firsts" through the 20th century, such as gas-gas equilibrium and the asymmetric tricritical point, see [2]. In the 1960s, to Krichevskii's initial disbelief, he and his collaborators found evidence of the path-dependence of the partial molar volume of the solvent and the divergence of that of the solute near the solvent critical point [4]. One of Krichevskii's collaborators, Rozen, was able to explain these effects correctly in 1976 [5].

Many of the historic results were rediscovered when supercritical fluids became a topic of widespread interest in chemical engineering in the 1980s, see [6]. John O'Connell's work in this area might be characterized as exploiting the properties of the direct correlation function integral, which does not vary strongly and is reasonably well-behaved near critical points, to keep the strong divergences of infinite-dilution partial molar properties under control.

[1] A.V. Plyasunov, E.L. Shock and J.P. O'Connell, Corresponding-states correlations for estimating partial molar volumes of nonelectrolytes at infinite dilution in water over extended temperature and pressure ranges, Fluid Phase Equilibria, **247** (2006) 18, and references therein.

[2] Johanna Levelt Sengers, *How Fluids Unmix; Discoveries by the School of Van der Waals and Kamerlingh Onnes*, Koninklijke Akademie van Wetenschappen, Amsterdam (2002). ISBN 90-6984-357-9. Also Chicago University Press.

[3] H.W. Bakhuis Roozeboom, (and members of his school), Die Heterogene Gleichgewichte vom Standpunkte der Phasenlehre, Vieweg & Sohn, Braunschweig. Volumes I–III (1901-1918).

[3] N.E. Khazanova and E.E. Kominskaya, Partial molar volumes in the ethane-carbon dioxide system near the critical points of the pure components, Russ. J. Phys. Chem, **45** (1971) 1485.

[5] A.M. Rozen, The unusual properties of solutions in the vicinity of the critical point of the solvent, Russ. J. Phys. Chem. **50** (1976) 1381.

[6] J.M. H. Levelt Sengers, Thermodynamics of solutions near the solvent's critical point, Chapter 1 in *Supercritical Fluid Technology: Reviews in Modern Theory and Applications,* T.J. Bruno and J.F. Ely, Editors, CRC Press, Boca Raton (1991).