Ion Exchange at the Critical Point of Solution

James Baird [C, S], Jonathon Savoy and Joshua Lang
Department of Chemistry, University of Alabama in Huntsville, Huntsville, AL, U.S.A.
bairdj@uah.edu

The opposite sides of the liquid-liquid coexistence curve describing a mixture of isobutyric acid (IBA) + water converge to an upper consolute point at an acid concentration of 4.4 M and a temperature near 26 C. Isobutyric acid is a weak acid, which ionizes in water to form hydronium ion and isobutyrate ion. When a sample of IBA + water at a temperature above 26 C comes into equilibrium with an ion exchange resin in the hydroxide form, isobutyrate ion exchanges with the hydroxide ion. The amount of acid exchanged is proportional to the difference between the initial acid concentration and the concentration remaining after equilibrium. We have determined the amount of acid adsorbed as a function of the initial acid concentration for isotherms at 27, 29, 31, and 38 degrees. The data collected along the 38 C isotherm lie on a straight line when plotted according to the Langmuir adsorption equation. By contrast, each of the Langmuir plots associated with the isotherms at 27, 29, 31 degrees, respectively, exhibits a maximum at an equilibrium acid concentration near 4.4 M. These maxima indicate that isobutyrate ion is increasingly rejected by the resin as the critical point is approached. At 27 C, which is the isotherm closest to critical, the uptake of isobutyrate ion is smaller by a factor of 100 than would be expected on the basis of a straight line Langmuir plot. Using Donnan ion exchange theory, we derive an equation linking the swelling pressure in the resin to the osmotic pressure in the exterior liquid phase. We find that the maximum exhibited by the Langmuir plots has its origin in the divergence in the osmotic compressibility as the critical point is approached. The latter is a common feature of the consolute point of a binary liquid mixture.