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Ion exchange at the critical point of solution

J.D. Savoy[a], J.K. Baird[a,b,c,*], J.R. Lang[a,b]

[a] Department of Chemistry, University of Alabama in Huntsville, Huntsville, AL 35899, United States
[b] Materials Science Graduate Program, University of Alabama in Huntsville, Huntsville, AL 35899, United States
[c] Department of Physics, University of Alabama in Huntsville, Huntsville, AL 35899, United States

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ABSTRACT

A mixture of isobutyric acid (IBA) + water has an upper critical point of solution at 26.7 °C and an IBA concentration of 4.40 M. We have determined the Langmuir isotherms for the hydroxide form of Amberlite IRN-78 resin in contact with mixtures of IBA + water at temperatures, 27.0, 29.0, 31.0 and 38.0 °C, respectively. The Langmuir plot at 38.0 °C forms a straight line. At the three lower temperatures, however, a peak in the Langmuir plot is observed for IBA concentrations in the vicinity of 4.40 M. We regard this peak to be a critical effect not only because it is located close to 4.40 M, but also because its height becomes more pronounced as the temperature of the isotherm approaches the critical temperature. For concentrations in the vicinity of the peak, the data indicate that the larger isobutyrate ion is rejected by the resin in favor of the smaller hydroxide ion. This reversal of the expected ion exchange reaction might be used to separate ions according to size. Using the Donnan theory of ion exchange equilibrium, we link the swelling pressure to the osmotic pressure. We show that the peak in the Langmuir plot is associated with a maximum in the "osmotic" energy. This maximum has its origin in the concentration derivative of the osmotic pressure, which goes to zero as the critical point is approached.

1. Introduction

In the case of pairs of liquids which exhibit a miscibility gap, the liquid–liquid coexistence curve plotted in the form of temperature, T vs. mole fraction, X, often ends in an extremum, called the critical point of solution. As illustrated in Fig. 1a and b, the extremum can be a maximum or a minimum. The coordinates of the extremum are known as the critical solution temperature, T_c^o, and the critical composition, X_c^o, respectively. The vertical line, $X = X_c^o$, defines the critical isopleth, while the horizontal line, $T = T_c^o$, defines the critical isotherm. When the extremum is a minimum, T_c^o corresponds to a lower critical solution temperature (LCST), whereas when it is a maximum, T_c^o corresponds to an upper critical solution temperature (UCST). In either case, the two components form a single liquid phase on the convex side of the phase boundary but partition themselves into two immiscible liquid layers separated by a meniscus on the concave side [1].

Binary liquid mixtures with miscibility gaps have found application in separations science in the phase transfer (PTE) method of solvent extraction [2]. In this method, the single liquid phase, which exists on the convex side of a UCST is used as the solvent for the solutes that are to be separated. After a rapid temperature quench into the two phase region, the solutes partition themselves between the immiscible liquid layers. The PTE method avoids emulsification, which often slows phase separation in conventional solvent extractions [3].

In pursuit of applications of binary liquid mixtures in separation science [4], we have examined the interaction of Amberlite IRN-78 resin in the hydroxide form with a mixture of isobutyric acid (IBA) + water (UCST). IBA + water was chosen not only because it ionizes to form the isobutyrate ion, which can exchange with the hydroxide ion, but also because its critical point of solution is located conveniently at temperature 26.7 °C and mole fraction $X_c^o = 0.11$ IBA (38.8 mass% IBA or about 4.40 M) [5]. We focus our attention on the interactions between the resin and the liquid on the one phase side of the IBA + water phase diagram. We show that the "osmotic" energy in the resin rises rapidly near the critical point. Experimentally, we find that this rise causes the resin to reject the larger ion (isobutyrate, $A^- = (CH_3)_2CHCOO^-$) in favor of the smaller ion (hydroxide, OH^-). This reversal of the expected ion exchange reaction could be used to separate ions according to size.

Using the Donnan ion exchange theory, plus an equation linking the swelling pressure to the osmotic pressure, we explain

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* Corresponding author at: 301 Sparkman Drive Huntsville, AL 35899, United States.

E-mail addresses: jds0013@uah.edu (J.D. Savoy), bairdj@uah.edu (J.K. Baird), joshua.r.lang@gmail.com (J.R. Lang).

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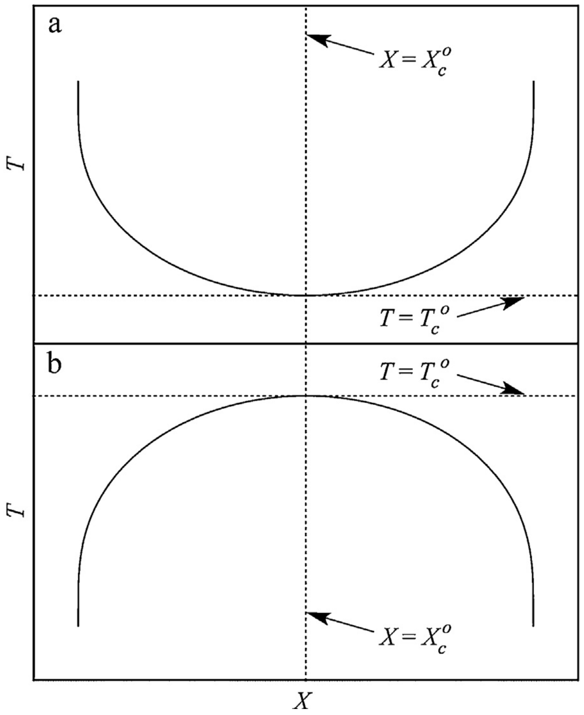

Fig. 1. Phase diagram for a binary liquid mixture that exhibits a lower (a) and upper (b) critical point of solution. The critical values of the temperature, T, and the mole fraction, X, are T_c^o and X_c^o, respectively. A single liquid phase exists on the convex side of the coexistence curve while two immiscible liquid phases are in equilibrium on the concave side.

our experimental results in terms of the osmotic pressure, whose derivative with respect to concentration is known to have a zero near a critical point of solution. A list of symbols, which are used in critical point theory, osmotic pressure theory, and Donnan ion exchange theory, can be found in Appendix A.

2. Experiment

2.1. Materials and methods

Isobutyric acid was obtained from Sigma–Aldrich and used as received. Water was distilled once from a glass system. The binary mixture of IBA + water was prepared at various acid concentrations by weighing. The water bath, the stirring equipment, and the thermostat were as previously described [6]. The temperature was determined with a long mercury in glass thermometer, which was supplemented by an E.H. Sargent Beckmann differential thermometer as needed. Visual detection of critical opalescence and the disappearance of the meniscus indicated that the critical solution temperature of the binary mixture was $T_c^o = 26.7\,^\circ\mathrm{C}$.

Amberlite IRN-78 anion exchange resin in the hydroxide form was purchased from SUPELCO and used as received. The ion exchange capacity of this resin was $Q = 1.28$ eq/L. The harmonic mean size of the resin beads was 0.566 mm.

Table 1
Data for Amberlite IRN-78 resin in the hydroxide form in equilibrium with aqueous isobutyric acid at temperature, T. The initial acid concentration is c_{HA}, the equilibrium acid concentration is c_{HA}^L. The initial mass of resin is $m = 8$ g, while the mass of acid taken up by the resin is x.

$T(^\circ\mathrm{C})$	$c_{\mathrm{HA}}(M)$	$c_{\mathrm{HA}}^L(M)$	$x(\mathrm{g})$	$m(\mathrm{g})$	$\left(c_{\mathrm{HA}}^L m/x\right)\ (\mathrm{mol/L})$
27					
	0.47	0.07	1.62	8.03	0.35
	1.05	0.49	2.29	8.02	1.70
	2.05	1.21	3.40	8.00	2.85
	2.82	1.96	3.49	8.02	4.52
	3.06	2.14	3.89	8.00	4.40
	3.67	2.91	3.21	8.03	7.28
	4.15	3.42	2.96	8.01	9.27
	4.25	3.46	3.34	8.01	8.30
	4.83	3.84	4.01	7.99	7.65
	4.74	4.13	2.58	8.01	12.83
	5.01	4.94	0.30	8.01	133.51
	5.44	5.23	0.85	8.00	49.34
	7.01	5.74	5.15	8.01	8.93
29					
	0.52	0.15	1.56	8.01	0.77
	1.48	0.78	2.96	7.99	2.10
	2.23	1.33	3.81	8.01	2.80
	3.13	2.33	3.38	8.00	5.51
	4.18	3.96	0.93	8.08	34.38
	4.61	4.48	0.55	8.02	65.31
	5.57	5.30	1.14	8.00	37.15
	6.85	6.01	3.70	8.06	13.09
31					
	0.47	0.09	1.54	8.03	0.48
	1.05	0.49	2.27	8.02	1.73
	2.05	1.16	3.61	8.00	2.57
	2.82	2.04	3.16	8.02	5.18
	3.06	2.23	3.51	8.00	5.08
	3.67	3.01	2.79	8.03	8.66
	4.15	3.43	2.92	8.01	9.42
	4.74	4.17	2.41	8.01	13.85
	5.01	4.34	2.83	8.01	12.26
	5.44	4.57	3.53	8.00	10.37
	5.70	4.74	3.89	8.00	9.75
	7.01	6.00	4.09	8.01	11.73
38					
	0.47	0.09	1.55	8.03	0.47
	1.05	0.48	2.41	8.02	1.60
	2.05	1.24	3.28	8.00	3.02
	2.82	1.89	3.77	8.02	4.02
	3.06	2.10	4.06	8.00	4.14
	3.67	3.01	2.79	8.03	8.66
	4.15	3.34	3.28	8.01	8.15
	4.25	3.42	3.51	8.01	7.81
	4.74	4.02	3.05	8.01	10.57
	5.70	4.98	2.92	8.00	13.66

To begin an experiment, 50 mL of aqueous IBA at a concentration, c_{HA}, was introduced into a 250 mL Erlenmeyer flask. To this mixture were added 8 g of resin. The Erlenmeyer flask was then placed in a water bath with the temperature fixed, gently agitated, and then let stand for 24 h in order to reach equilibrium. At the end of 24 h, several 2 mL aliquots of the supernatant liquid were harvested with a serological pipet. The acid content of each aliquot was determined by titration against standardized sodium hydroxide with phenolphthalein as the indicator. Based upon the average of multiple titrations, the concentration of acid in equilibrium with the resin at the end of the experiment was determined and denoted as c_{HA}^L. The mass of IBA measured in grams, x, taken up by the resin was computed using the formula,

$$x = \left(c_{\mathrm{HA}} - c_{\mathrm{HA}}^L\right) V_S M_{\mathrm{HA}} \tag{1}$$

where $V_s = 0.05$ L is the volume of IBA + water mixture, and $M_{\mathrm{HA}} = 88.1$ g/mol is the molar mass of IBA. With the temperature fixed, the experiment was then repeated starting with a new concentration, c_{HA}, of IBA.

In this way, the masses of IBA taken up by the resin from solutions having starting concentrations lying in the range from $c_{\mathrm{HA}} = 0.47$ M to $c_{\mathrm{HA}} = 7.0$ M were determined along isotherms at 27.0, 29.0, 31.0 and 38.0 °C, respectively. We let $m = 8$ g denote the initial mass of the resin in each experiment. Using this notation, the data are listed in Table 1 in the form of $c_{\mathrm{HA}}^L m/x$ vs. c_{HA}^L. These variables were chosen because when plotted with $c_{\mathrm{HA}}^L m/x$ on the ordinate and c_{HA}^L is on the abscissa, a straight line often results [7]. This line served as the "background" for assessing the size of any