Chemical Equilibrium and Critical Phenomena: Solubility of Indium Oxide in Isobutyric Acid + Water Near the Consolute Point[†]

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We have determined the solubility, s, of indium oxide in the liquid mixture isobutyric acid + water along the critical isopleth at temperatures above the upper critical solution temperature near 299 K. When plotted in van't Hoff form with $\ln s$ vs $1/T$, the measurements of solubility lie on a straight line for values of the absolute temperature, T, which are sufficiently in excess of the critical solution temperature, T_c. The sign of the slope, $(\partial \ln s/\partial(1/T))$, indicates that the enthalpy of dissolution is endothermic. When the temperature is within 1 K of T_c, however, the slope departs from its constant value and appears to diverge toward negative infinity. The principle of critical point universality predicts that a divergence in $(\partial \ln s/\partial(1/T))$ is to be expected for T near T_c in those cases where the stoichiometry of the dissolution reaction involves both components of the solvent; moreover, the Gibbs−Helmholtz equation predicts that if the enthalpy of solution is endothermic, the sign of the divergence should be negative. Both of these predictions are confirmed by the experimental data.

Introduction

In the case of a binary liquid mixture with a miscibility gap, the opposite sides of the coexistence curve in the temperature vs mole fraction phase diagram converge at the consolute point.[1] The temperature at the point of convergence is called the critical solution temperature. If the coexistence curve is concave *down*, the critical temperature is an *upper* critical solution temperature (UCST), while if it is concave *up*, the critical temperature is a *lower* critical solution temperature (LCST). At the consolute point, the distinction between the coexisting liquid phases disappears.

The consolute point is a member of a class of critical points where certain thermodynamic properties tend to infinity as the temperature approaches the critical temperature.[2,3] According to the *principle of critical point universality*,[4,5] isomorphic behavior of thermodynamic properties at critical points is expected to occur in phenomena as diverse as the liquid−vapor transition of pure liquids,[6−11] the liquid−liquid transition in mixtures,[2,3,8,10] the Curie point transition in ferromagnetic materials,[6,7] the lambda line of liquid helium,[7] and the normal conducting to superconducting transition in superconductors.[7]

The application of the principle of critical point universality to binary liquid mixtures is due to Griffiths and Wheeler.[2] Following the lead of Fisher,[12] Griffiths and Wheeler[2] divide the thermodynamic variables into two classes called *fields* and *densities*, respectively. In a system at thermodynamic equilibrium, a field has a uniform value across all coexisting phases. Examples of field variables include the pressure, P, the absolute temperature, T, the chemical potential of each component, and also the Gibbs energy of reaction, ΔG, which is the stoichiometric coefficient weighted linear combination of chemical potentials. By contrast, a density variable has a different value in each coexisting phase. Examples of density variables include the entropy, the molar volume, and the composition variables represented by the mass fractions of the various components.

To apply the principle of critical point universality to the dissolution of a metal oxide in isobutyric acid + water close to the upper critical solution temperature, we consider the following stoichiometric relation

$$(1/x)\mathrm{M}_x\mathrm{O}_y(\mathrm{c}) + Z\mathrm{HA}(\mathrm{aq}) + (6 - (Z/2))\mathrm{H_2O}(\mathrm{aq}) \rightarrow \mathrm{M(H_2O)_6}^{Z+}(\mathrm{aq}) + Z\mathrm{A}^-(\mathrm{aq}) \quad (1)$$

in which the generic oxide, $\mathrm{M}_x\mathrm{O}_y$, reacts with isobutyric acid, HA, to form the hexahydrate metal cation,[13] $\mathrm{M(H_2O)_6}^{Z+}$, and the isobutyrate anion, A^-. Here "c" in parentheses refers to the crystalline phase, while "aq" denotes the water-based solvent mixture. We denote the solubility of the metal in the liquid by s, which is the solute to solvent mass ratio expressed in units of grams of metal per gram of solvent.

According to Griffiths and Wheeler,[2] critical effects can manifest themselves in thermodynamic derivatives that involve the differentiation of a density variable with respect to a field variable. An example is $(\partial s/\partial T)_e$, where the subscript, e, refers to chemical equilibrium.[14,15] There are two distinguishable cases: (1) When the experimental conditions are such that the fixed thermodynamic variables consist of fields and two or more densities, the derivative of a density with respect to a field is expected be a smooth function of the temperature as T approaches the critical temperature, T_c. That is to say, there is no observable critical effect. (2) When fewer than two densities are held fixed, the derivative of a density with respect to a field should go to infinity as $|T - T_c|^{-x}$, where x is called the critical exponent. If only *one* density is held fixed, the value of x is of the order of *tenth*, and the derivative is said to diverge *weakly*.[2] If *no* densities are held fixed, the value of x is of the order of

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unity, and the derivative is said to diverge *strongly*.[2] The exact value of the critical exponent, x, depends upon the direction of approach to the critical point reckoned with respect to the direction of the liquid−liquid coexistence curve plotted in the space spanned by the fields.[2] The liquid−liquid coexistence curve in a binary mixture is, incidentally, a markedly symmetric function of the fields, T and P.[16]

In the case of a chemically reactive liquid mixture at equilibrium under ordinary laboratory conditions, the fixed thermodynamic variables are T, P, and the mass fractions of any inert components that may be part of the system. A component is considered to be inert if it is not involved in at least one chemical reaction. Since the dissolution reaction in eq 1 involves both components of the solvent, the mixture contains *no* inert components. In the absence of inert components, the thermodynamic derivative, $(\partial s/\partial T)_e$, can be identified with $(\partial s/\partial T)_{P,\Delta G=0}$, where $\Delta G = 0$ is the criterion for dissolution equilibrium.[14,15] Since no densities are held fixed, $(\partial s/\partial T)_{P,\Delta G=0}$ is expected to approach infinity strongly as T approaches T_c.[15]

When solubility data collected *outside* the critical region are plotted in the form ln s vs $1/T$, the van't Hoff law predicts that the slope, $(\partial \ln s/\partial(1/T))_{P,\Delta G=0}$, should be a constant. As T approaches T_c, however, the critical behavior of $(\partial s/\partial T)_{P,\Delta G=0}$ forces $(\partial \ln s/\partial(1/T))_{P,\Delta G=0}$ to depart from its expected constant value. At temperatures *inside* the critical region, $(\partial \ln s/\partial(1/T))_{P,\Delta G=0}$, goes to *positive* infinity, if the dissolution is *exothermic,* and it goes to *negative* infinity, if the dissolution is *endothermic*.[15] We will demonstrate that the latter prediction applies in the case of the dissolution of indium oxide in isobutyric acid + water (UCST) as the consolute point is approached in the one-phase region along the critical isopleth.

Experimental Section

Isobutyric acid was obtained from Aldrich (lot #07710 PB) and used as received. Water was once distilled from a glass system. The binary solvent mixture was prepared at the critical mass fraction of 0.388 isobutyric acid[17] by weighing. Indium oxide was obtained from Fisher (lot #19529 PD) and used as received.

To maintain a constant temperature in our experiments, we employed a 14 dm^3 water bath heated by a submerged 60 W light bulb powered by a Cole Parmer, 115 V Variable Output, model G-02149-20 controller connected to a Philadelphia Roto-Stat differential thermoregulator. The temperature of the bath was read with a precision of 0.007 K by using a magnifying glass to observe the gradations on a long mercury-in-glass thermometer. The 24 h stability of the water bath temperature was better than 0.01 K.

To start a solubility experiment, 0.15 dm^3 of the isobutyric acid + water mixture, prepared at the critical composition, was transferred to the reaction vessel, which was a 3 cm i.d. × 25 cm long flat bottom, Pyrex test tube. A magnetic stirring bar and 0.66 g of indium oxide were added to the reaction vessel. The vessel was then closed with a stopper. Visual observation of critical opalescence in this mixture indicated that the critical temperature was 299.12 K.

The contents of the reaction vessel were stirred for 24 h. The stirrer was turned off, and the mixture was left to stand undisturbed for an additional 24 h to permit the suspended solid to separate from the liquid by gravitational sedimentation. At the end of the 24 h period of sedimentation, a 2 cm^3 aliquot of the supernatant liquid was extracted with a serological pipet. The aliquot was diluted with 5 cm^3 of an aqueous solution of 20 g of nitric acid in 1 kg of water to prevent precipitation of dissolved metal ions. The thermostat temperature was adjusted to the next value, and the process of stirring followed by standing was repeated. By using this experimental procedure, the solubility, s, could be tracked along the critical isopleth of the mixture. The concentration of In^{3+} dissolved in each sample was determined in the laboratories of Sentinel, Inc. using a ThermoFisher iCAP 6000 inductively coupled plasma spectrometer equipped with iTEVA software. Some of the samples were diluted before analysis with acidified water to keep the measured concentrations within the linear range of the spectrometer. All standardizations, standard checks, and sample analyses conformed to the specifications of U.S. Environmental Protection Agency method 6010.

Table 1. Temperature Dependence of the Solubility of In_2O_3 in 0.388 Mass Fraction Isobutyric Acid in Water[a]

T/K	s/s^o
299.10	7.26 ± 0.11
299.35	6.56 ± 0.10
299.55	7.53 ± 0.11
299.75	11.25 ± 0.17
299.95	13.80 ± 0.21
300.20	19.88 ± 0.30
300.77	27.02 ± 0.41
301.69	32.91 ± 0.49
303.47	42.18 ± 0.63
305.22	57.07 ± 0.86
308.80	73.1 ± 1.1
312.40	97.8 ± 1.5
315.96	126.7 ± 1.9

[a] The estimated error in T is ± 0.007 K.

For temperatures *outside* the critical region, we assume that the ions on the right-hand side of eq 1 are sufficiently dilute as to make their activity coefficients unity and that the water and isobutyric acid are each in such excess as to make their activities independent of the solubility of the metal. Under these conditions, the van't Hoff law may be applied in the form[15]

$$\ln(s/s^o) = -\frac{A}{T} + B \qquad (2)$$

where $A = \Delta_{sol}H^o/(Z + 1)R$ and B are constants; R is the gas law constant; $\Delta_{sol}H^o$ is the standard molar enthalpy of solution; and $s^o = 10^{-9}$ is the solute standard state.

For temperatures *inside* the critical region, the Gibbs−Helmholtz equation predicts that the slope of the van't Hoff plot can be calculated using[15]

$$\left(\frac{\partial \ln s}{\partial(1/T)}\right)_{P,\Delta G=0} = -T\Delta_{sol}H\left(\frac{\partial \ln s}{\partial \Delta G}\right)_{T,P} \qquad (3)$$

The condition for dissolution equilibrium at constant T and P is $\Delta G = 0$; the condition for stability of the dissolution equilibrium is $(\partial \ln s/\partial \Delta G)_{T,P} > 0$.[15] Being the positive definite derivative of a density with respect to field, $(\partial \ln s/\partial \Delta G)_{T,P}$ must diverge toward positive infinity as $T \rightarrow T_c$. Since the enthalpy of solution in the critical region, $\Delta_{sol}H$, is bounded,[15] eq 3 indicates that the slope of the van't Hoff plot in the critical region should go to *negative* infinity when the dissolution is *endothermic* ($\Delta_{sol}H > 0$) and should go to *positive* infinity when the dissolution is *exothermic* ($\Delta_{sol}H < 0$).[15]

The measured values of the solubility of In_2O_3 as a function of temperature along the critical isopleth of isobutyric acid + water are listed in Table 1. The same data have been plotted in

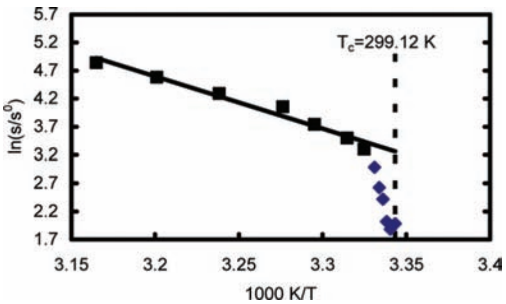

Figure 1. Van't Hoff plot of the dependence of the solubility, s/s^o, where $s^o = 10^{-9}$ for In_2O_3 in 0.388 mass fraction isobutyric acid in water as a function of the absolute temperature, T. Points represented by *squares* were used to determine the slope and intercept of the van't Hoff line. Points represented by *diamonds* were considered to lie within the critical region.

van't Hoff form in Figure 1. The values of s corresponding to the seven highest temperatures in Table 1 were fitted to eq 2 by the method of least-squares.[18] The least-squares values of the constants were $A/K = 9320 \pm 740$ and $B = 34.4 \pm 2.4$ with linear correlation coefficient,[18] $R^2 = 0.9698$. A plot of eq 2 forms the straight line in Figure 1. The figure reveals that for temperatures substantially above critical the slope of this van't Hoff line is negative; hence, In_2O_3 dissolves endothermically in isobutyric acid + water. At temperatures just above the critical temperature at 299.12 K, however, the solubility is suppressed, and the van't Hoff slope, $(\partial \ln s/\partial(1/T))_{P,\Delta G=0}$, becomes increasingly negative as $1/T$ increases in agreement with eq 3 and the principle of critical point universality. Table 1 suggests that the critical region for dissolution of indium oxide in isobutyric acid + water extends over the temperature range, (299.12 to 300.20) K, which is a little more than 1 °C.

Discussion and Conclusions

Binary liquid mixtures with phase diagrams having a consolute point are plentiful; the list includes several hundred pairs exhibiting a LCST and several thousand pairs exhibiting an UCST.[19] The solvent power of these liquids permits them to be used to study the effect of the critical point not only on the net rate of reaction[20−28] but also on the position of chemical equilibrium.[15,29]

Greer et al. studied the position of the NO_2 dimerization equilibrium in perfluoromethylcyclohexane + carbon tetrachloride (UCST) as a function of temperature along the critical isopleth.[29] Because the mixture was confined to a closed vessel with a space above the liquid to accommodate the vapors of the volatile components, the reaction was *heterogeneous*. The position of equilibrium was monitored by the making measurements of the dielectric constant of the liquid phase. Greer et al. reported a 4 % shift in the position of equilibrium as the temperature approached the critical value.[29]

The dissolution of In_2O_3 in isobutyric acid + water involves a solid in equilibrium with a liquid and so is also a *heterogeneous* reaction. Both components of the solvent take part in the overall stoichiometry of the dissolution reaction ($x = 2$, $y = 3$, and $Z = +3$ in eq 1). Because of this, the mass fractions of all of the liquid phase components are functions of the field variables, T and P; hence, there are no fixed density variables, and $(\partial \ln s/\partial(1/T))_{P,\Delta G=0}$ measured along the critical isopleth appears to diverge in the critical region. The sign of the divergence is negative because the enthalpy of solution of indium oxide in isobutyric acid + water is endothermic.

The dissolution reaction of In_2O_3 in isobutyric acid + water can be compared with the dissolution reactions of MnO_2 and Al_2O_3 in this solvent mixture.[15] Like In_2O_3, manganese dioxide dissolves *endothermically* along the critical isopleth, and $(\partial \ln s/\partial(1/T))_{P,\Delta G=0}$ appears to diverge toward *negative* infinity. In contrast to both In_2O_3 and MnO_2, aluminum oxide dissolves *exothermically* along the critical isopleth, and $(\partial \ln s/\partial(1/T))_{P,\Delta G=0}$ appears to diverge toward *positive* infinity. At the atomic level, both indium and aluminum exhibit the +3 oxidation state in their oxides, whereas manganese exhibits a +4 oxidation state in MnO_2. The occurrence of a critical solubility effect, be it positive or negative, should be independent of the oxidation state, as long as the dissolution reaction is consistent with the principle of critical point universality.

Thermodynamic theories of the supercritical dissolution of solids have been worked out by Procaccia and Gitterman,[30] by Gitterman,[31] and by Levelt-Sengers and collaborators.[32] A Kirkwood−Buff solution theory has been introduced by Cochran et al.,[33] while a decorated lattice gas model has been proposed by Nielson and Levelt-Sengers,[34] and a molecular dynamics approach has been developed by Chialvo and DeBenedetti.[35] The thermodynamic treatment outlined in Section II above concentrates on the equilibrium between just two phases and is in this respect very close in both spirit and detail to the theories of Levelt-Sengers et al.[32] and Gitterman.[31] The main new feature, which we have considered, is the role of the dissolution reaction in restricting the number of fixed density variables.

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