SOME INTERESTING PROPERTIES OF VAPOR–LIQUID OR LIQUID–LIQUID COEXISTENCE CURVES FOR IONIC AND NON-IONIC FLUIDS *

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(Received 5 April 1988)

ABSTRACT

   Comparisons are made between the recently measured coexistence curves for ionic fluids with the well-known features of such curves for non-ionic fluids. Both vapor–liquid curves for pure fluids and liquid–liquid curves for mixtures are considered. Further comparisons are then made with recently developed theory for each type of fluid.

INTRODUCTION

   In recent years, the exact pattern of a coexistence curve very close to the critical point has been widely studied experimentally and related to theory. In contrast, the present work will emphasize simple patterns which are followed to good approximation over a wide range of temperature and often over the entire range from the critical temperature to the triple-point temperature. It is the molecular properties controlling the wide-range behavior which are important chemically. The details very close to the critical point, while of theoretical interest, involve very small differences in chemical potential which would be trivial for most chemical purposes. While each of these patterns has been noted before empirically, it is interesting to compare the behavior of an ionic fluid with that of a neutral-molecule fluid and to make comparisons with theory in each case. Primary emphasis will be given to vapor–liquid equilibria for pure fluids, but comparisons will be made to liquid–liquid coexistence curves for both ionic and non-ionic systems.

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* Dedicated to Professor Edgar F. Westrum, Jr., who carried out his Ph.D. research with me in 1941–1944, on the occasion of his 70th birthday. It is a pleasure to participate in honoring Professor Westrum for his great contributions to calorimetry.

HISTORICAL SUMMARY

The first generalization was that of the "law of rectilinear diameters" of Cailletet and Mathias in 1886 [1,2]. It is expressed in the equation

$$(\rho_{r,l} + \rho_{r,v})/2 = 1 + A(1 - T_r) \tag{1}$$

where $\rho_{r,l}$ and $\rho_{r,v}$ are the reduced densities of liquid and vapor, respectively, T_r is the reduced temperature and A is a substance-dependent constant. While there is no exact and rigorous theoretical justification for this principle, and indeed, some theoretical basis exists for a small departure near the critical point, there is very extensive empirical support for eqn. (1).

Shortly after the development of the Schrödinger quantum mechanics, it was possible to put van der Waals' "principle of corresponding states" on a sound theoretical basis and to select a set of real fluids that should conform accurately [3,4]. This set, the "simple fluids" Ar, Kr, Xe, CH_4, does indeed show good conformity, and from a study of this group Guggenheim [5] demonstrated that their coexistence curve was represented by eqn. (1) with $A = 3/4$ and eqn. (2)

$$(\rho_{r,l} - \rho_{r,v}) = B(1 - T_r)^\beta \tag{2}$$

with $B = 7/2$ and $\beta = 1/3$. Equations (1) and (2) hold in good approximation over the entire liquid range of the simple fluids which extends to about 0.56 in T_r. B is undoubtedly a substance-dependent parameter in general and has larger values for fluids such as CO_2, n-heptane, and H_2O which still conform quite well to eqns. (1) and (2) over the same range of T_r down to about 0.6. One was tempted to hope that the exponent $\beta = 1/3$ might be exact in theory, but this does not appear to be true. Indeed, any mathematically analytical equation of state (EOS) can be expanded in a Taylor series about the critical point, and one then finds the leading term for the coexistence curve has the form of eqn. (2) but the exponent 1/2 [6]. Any EOS which yields $\beta = 1/3$ is non-analytic and gives divergences in certain properties, such as C_v, at the critical point. The modern theory for fluids with short-range forces predicts limiting behavior near the critical point following eqn. (2) with an irrational exponent $\beta = 0.325$ [7]. But this theory is valid only very near the critical point and offers no basis for the value $\beta = 1/3$ over the wide range of temperature.

Equations (1) and (2) can be combined to yield for the liquid and vapor, respectively

$$\rho_{r,l} = 1 + A(1 - T_r) + (B/2)(1 - T_r)^\beta \tag{3}$$

$$\rho_{r,v} = 1 + A(1 - T_r) - (B/2)(1 - T_r)^\beta \tag{4}$$

For liquid–liquid coexistence curves for two-component non-ionic systems, one substitutes the mole fractions x' and x'' for $\rho_{r,l}$ and $\rho_{r,v}$ in eqns. (1)–(4)

and finds rather good agreement over a substantial range of reduced temperature for $\beta = 1/3$ [8]. Again, the constants A and B are system-specific.

IONIC FLUIDS

It is only recently that any quantitative information has become available for the coexistence curves for reasonably simple ionic fluids. For the alkali halides, the temperatures are too high for measurement by currently available methods [9]. Buback and Franck [10] reported measurements for NH_4Cl which is clearly ionic (NH_4^+, Cl^-) in the liquid. The vapor at subcritical densities is primarily $NH_3 + HCl$, rather than the ion pairs which dominate alkali halide vapors. It is this difference for the vapor that reduces the critical temperature to 882°C and makes quantitative measurements feasible. In their published paper Buback and Franck do not offer an equation for the coexistence curve, but in Buback's thesis [11] it is reported that the data fit eqns. (1)–(4) over the entire range of temperature with $\beta = 1/2$, $A = 1.23$ and $B = 4.75$. That A and B differ from the values 0.75 and 3.50 for simple fluids is not surprising, but the value $\beta = 1/2$ is most interesting since that is the value for a classical or analytical EOS.

Very recently de Lima, Schreiber and the present author [12,13] found a clearly ionic liquid–liquid system, tetra-n-butylammonium picrate in chloroheptane with a critical point at 141.2°C (414 K) and 0.085 mole fraction picrate. It follows eqns. (1)–(4) (with reduced mole fractions of the picrate replacing reduced densities) and with $\beta = 1/2$, $A = 2.2$ and $B = 6.1$. Agreement is good over an 80°C temperature range down to the triple point with the solid picrate. The value of 1/2 for β is the result of particular interest, although the conformity to the simple equation over a wide range of temperature is also significant.

THEORY FOR NON-IONIC FLUIDS

It would seem desirable to transform eqns. (1)–(4) to a general equation of state. As a direct transformation, however, this is not possible. Rather, one must make the calculation in the reverse direction from EOS to coexistence curve. Indeed, there is extensive material in the literature concerning complex equations of state which yield coexistence curves approximating eqns. (1)–(4). The complexity of these equations makes further interpretation at the molecular level very difficult, but there are recent Monte Carlo simulations for the Lennard–Jones (LJ) model [14–16] that yield a coexistence curve which can be compared directly with experimental
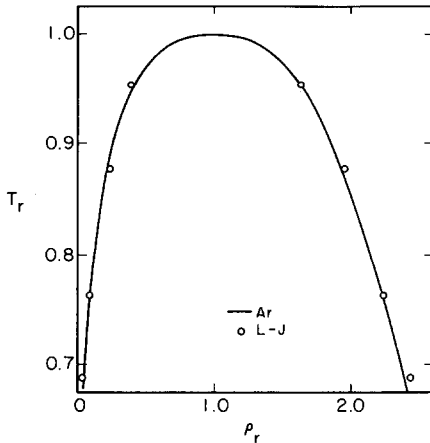
Fig. 1. Reduced coexistence curve for argon (solid line) [17] and points for Monte Carlo calculations for the Lennard–Jones potential [14]. On the scale of the figure, the curve for argon is indistinguishable from that for eqns. (1)–(4) with the parameters $\beta = 1/3$, $A = 3/4$ and $B = 7/2$.

data. This model assumes an R^{-12} repulsive potential and an R^{-6} attractive potential.

The most recent calculation and the one best determining the LJ coexistence curve is that of Panagiotopoulos [14]. The calculated vapor and liquid densities are shown as circles in Fig. 1, along with a solid curve for the experimental measurements for argon [17]. The agreement is well within the statistical uncertainties of the Monte Carlo calculations. This pattern conforms quite clearly to $\beta = 1/3$ over the entire temperature range and to the values $A = 3/4$, $B = 7/2$ selected by Guggenheim for eqns. (1)–(4) as stated above.

THEORY FOR LONG-RANGE FORCES

While there have been efforts to derive the coexistence curve theoretically for a model ionic fluid [18,19], these are too crude for meaningful comparison with eqns. (1)–(4). Other models, with all particles of the same type, have been studied with interparticle potentials of longer range than the R^{-6} function applicable to real neutral molecules. Lebowitz and Penrose [20] showed rigorously that for very long-range potentials the van der Waals attractive term $-a\rho^2$ for the pressure is correct (a being a constant). For the compressibility factor, this becomes

$$Z = P/\rho RT = Z^{\text{rep}} - a\rho/RT \qquad (5)$$

where Z^{rep} is the function arising from short-range repulsive forces. Assuming that Z^{rep} is an analytic function of ρ and T, the full equation is analytic

and the coexistence curve must show $\beta = 1/2$ in the limit as the critical point is approached. Other properties show classical behavior, e.g. C_v remains finite, etc.

For interparticle potentials depending on R^{-n} with $n < 6$, there is less complete theory [21,22] which indicates classical behavior for n less than 4.5 in three-dimensional space. The interionic forces have $n = 1$, which is $\ll 4.5$, but there is substantial ion-pairing and clustering near the critical point. Hence, no unambiguous conclusion can be drawn, but the potential between an ion and a rotating dipole has $n = 4$, which is < 4.5. Hence, a large component of the interparticle forces in a near-critical ionic system is long range with respect to the 4.5 dividing value. Thus, it is not surprising to find that the exponent $\beta = 1/2$ appears to pertain to the two ionic systems which have been studied. These measurements do not preclude a departure from the $\beta = 1/2$ pattern very close to the critical point.

For the case of hard spheres, Z^{rep} has been evaluated exactly for low densities and by Monte Carlo or molecular dynamics simulations for high densities [23]. Carnahan and Starling [24] showed that a relatively simple function fits these results quite accurately

$$Z^{rep} = \left(1 + y + y^2 - y^3\right)/\left(1 - y\right)^3 \tag{6}$$

$$y = \pi\sigma^3\rho/6 \tag{7}$$

Here, σ is the hard sphere diameter. The substitution of this expression into eqn. (5) yields an equation of state which can be designated CSvdW (Carnahan–Starling–van der Waals)

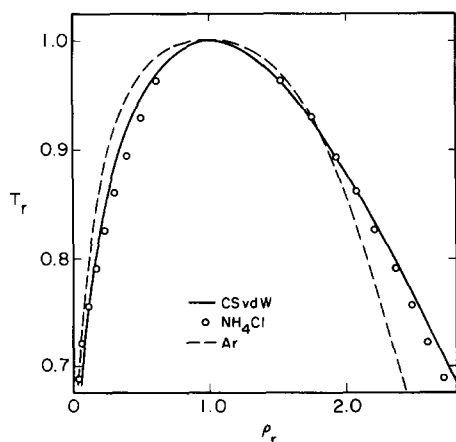$$Z = \left(1 + y + y^2 - y^3\right)/\left(1 - y\right)^3 - a\rho/RT \tag{8}$$

Fig. 2. Reduced coexistence curves for the Carnahan–Starling–van der Waals (CSvdW) model (solid line) and for argon (dashed line) and measured points for NH$_4$Cl [10,11]. The CSvdW curve is very nearly the same as that for eqns. (1)–(4) with the parameters $\beta = 1/2$, $A = 1.25$ and $B = 4.90$.

The resulting coexistence curve is shown in Fig. 2 as a solid line. It is practically indistinguishable from the curve of eqns. (1)–(4) with $A = 1.25$ and $B = 4.90$. The measured points for NH_4Cl, shown as circles, follow almost the same pattern. The dashed curve for argon has a distinctly different pattern corresponding to $\beta = 1/3$ instead of $\beta = 1/2$ and to smaller values of A and B.

While the agreement of NH_4Cl properties with the CSvdW equation is close for the coexistence curve, this is not general. Indeed, the critical compressibility factor Z_c is 0.359 for CSvdW, whereas for NH_4Cl it is 0.95 on the basis of two moles of fluid per mole NH_4Cl. This corresponds to the state of the vapor which is $NH_3 + HCl$ at low density. The density of fluid NH_4Cl has not been measured except on the coexistence curve.

DISCUSSION

For non-ionic fluids, the pattern very near the critical point defined by $\beta = 0.325 \approx 1/3$ arises from very long-range fluctuations. The appearance of the $\beta = 1/3$ pattern at lower temperatures must arise from a different source since the Monte Carlo calculations were made for a limited number of particles (300 or 500) and do not include fluctuations of longer range. Also, the Ising lattice, which has the same near-critical limiting behavior ($\beta = 0.325$), shows quite a different pattern at lower temperatures [25], corresponding to $\beta < 0.3$. This is shown in Fig. 3 where the third power of $(\rho_1 - \rho_v)$ or the magnetization M is shown as a function of reduced temperature. From eqn. (2) one notes that if $\beta = 1/3$ one obtains a straight line on this plot. The constants are adjusted to yield the same ordinate at
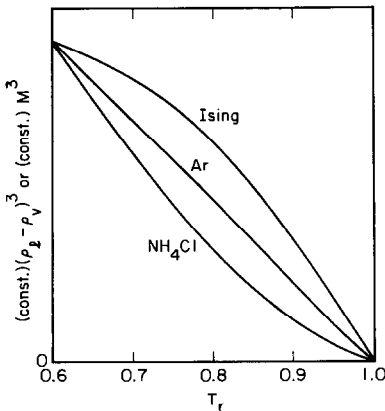

Fig. 3. Comparison of Ising lattice properties with those of Ar and NH_4Cl. Although both Ar and Ising show little curvature and finite slope near the critical point, in agreement with $\beta = 1/3$, their patterns over a wide range of temperature are quite different.

$T_r = 0.6$ for each curve in Fig. 3. The line for Ar is nearly straight over the entire range of reduced temperature. For the Ising lattice, the line becomes straight near the critical point which indicates the same $\beta \approx 1/3$ limiting behavior, but the pattern away from the critical region is very different from Ar. Thus, the Ising lattice does not conform to eqn. (2), and if one defines a local β, it is much smaller than $1/3$.

It appears that the differences in coexistence curve (or lattice magnetization) pattern are related to the range of interparticle forces in both near-critical and wide-ranging regions. In the former the essential phenomenon is long-range fluctuations and there are just the two patterns, $\beta = 0.325$ or $\beta = 1/2$, as discussed above. Over a wide range of temperature we see three patterns in Fig. 3. For R^{-6} potentials (Ar) one has $\beta \approx 1/3$ over the entire range of T_r. The Ising lattice has only nearest neighbor forces, which are shorter in range, and departs from the Ar pattern in the direction of $\beta < 1/3$. NH_4Cl shows a departure in the opposite direction which agrees with its longer-range interparticle potential.

On a strictly quantitative basis, the conformity of many systems (but not the Ising lattice) to eqns. (1)–(4) is only approximate over the long range of temperature. Also, there is a great need for further theory and simulation calculations in order to better understand ionic fluids. Nevertheless, this clear trend of effective β with range of interparticle potential is very interesting and should be included in one's thinking about phase separation in fluids.

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