

## BINARY LIQUIDS UNDER ABSOLUTE NEGATIVE PRESSURE

Attila R. IMRE

KFKI Atomic Energy Research Institute  
H-1525 Budapest, POB 49, Hungary  
Tel.: +36-1-392-2222/1117 or 13-23, Fax: +36-1-392-2299  
e-mail: imre@sunserv.kfki.hu

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### Abstract

We would like to give a brief review concerning liquid-liquid equilibrium in binary liquid mixtures under absolute negative pressure. Although negative pressure states are metastable ones, they can be maintained long enough to make phase equilibrium measurements. Several phenomena concerning liquid-liquid equilibrium can be seen only – or can be seen better – under negative pressure; these are briefly reviewed here.

*Keywords:* liquid, binary, negative pressure, phase equilibrium.

### 1. Introduction

Some physical quantities – like mass, volume etc. – can be only positive; others – like acceleration, electrical charge etc. – can be either negative or positive. For temperature the situation is not entirely clear; for a middle school student, temperature can be negative or positive (on Celsius scale), but in high school one should learn about the absolute Kelvin scale where temperature (for normal systems) can be only positive.

In kinetic-molecular approach pressure was introduced as applied force per surface area, when the force was generated by particles rebounding from the wall. In this approach pressure was always positive and therefore zero was a natural endpoint for it: less particles mean smaller pressure, zero particle means zero pressure. Although this approach – that the pressure is proportional to the number-density of particles – is strictly true only in ideal gases, somehow most of us accepted that pressure cannot be negative.

Physicians and engineers are often using the term “negative pressure” for pressures below atmospheric (but still above zero), therefore for most of us ‘negative pressure’ is just a lousy term for vacuum.

In reality negative pressure exists, and – at least for solids and liquids – it is really negative [1]. It can be easily demonstrated even in a classroom by a single piece of chalk with one end fixed. Let us assume that the cross section of the chalk is 1 cm × 1 cm (*Fig. 1*). As atmospheric pressure is 100000 Pa, the force generated by the atmospheric pressure in the un-pulled chalk at the shaded ‘A’ surface is +10 N along the  $x$ -axis. We can easily pull the chalk with 10 N into the other

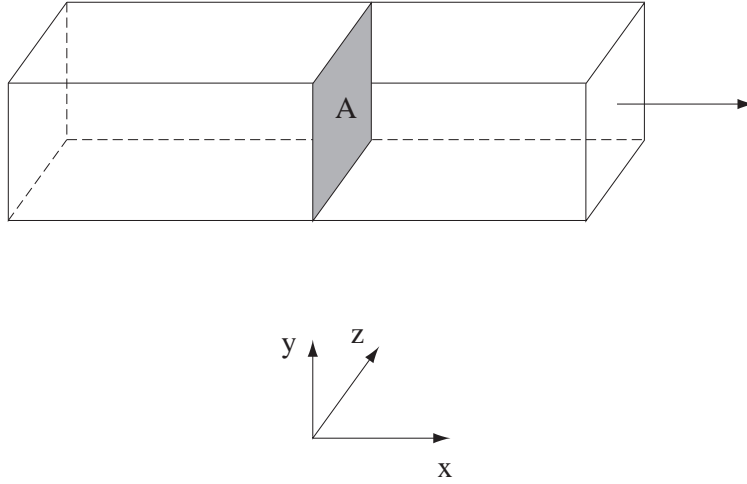


Fig. 1. Demonstration of negative pressure in solid materials (see text)

direction, creating  $10 - 10 = 0$  N force; i.e. 0 Pa pressure at ‘A’. Using bigger forces (like 20 N), we can generate negative ‘pressure’ (–1 bar) along the  $x$ -axis in the chalk. As pressure is a  $3 \times 3$  tensor in condensed matters, we have to pull the chalk simultaneously along the  $y$  and  $z$  axes with the same force, generating an isotropic diagonal  $\mathbf{P}$  matrix with negative ( $p_{xx} = -1$  bar,  $p_{yy} = -1$  bar and  $p_{zz} = -1$  bar) elements. The scalar pressure is  $p = 1/3 \text{Tr}(\mathbf{P})$  (and it can be defined only in isotropic diagonal  $P$  tensors), i.e. the pressure in the chalk is –1 bar. It is a little bit difficult to imagine the same experiment with liquids, but it can be done too (see later), and in that case the hydrostatic pressure will be negative; liquids under negative pressure are often referred to as ‘stretched liquids’ or ‘liquids under tension’.

Huygens was the first to make experiments with stretched liquids under negative pressure, without knowing that he generated negative pressure [2]. He tried to reproduce Torricelli’s experiment, using a mercury-filled glass tube with one end closed and the open end immersed into mercury. When he raised the closed end the mercury usually dropped back to the approx. 76 cm level, but occasionally the approx. 1.5 m long tube remained completely filled with mercury (Fig. 2). Boyle and Papen also tried this experiment, but as the result was irreproducible they gave up after a while [2]. This phenomenon was re-discovered more than one and half century later by Donny [3]. He explained it with the adhesion between the glass wall and the mercury and with the cohesion in the mercury; i.e. in this experiment the mercury column was held by the glass and pulled by the gravitation, generating approx. –1 bar negative pressure at the top in the mercury (Fig. 2).

Negative pressure states can be found in nature; they have important role in the xylem transport of trees [4, 5, 6], stretched liquid can be found in mineral inclusions [7] and negative pressure can be measured under the sucker of the octopus [8].

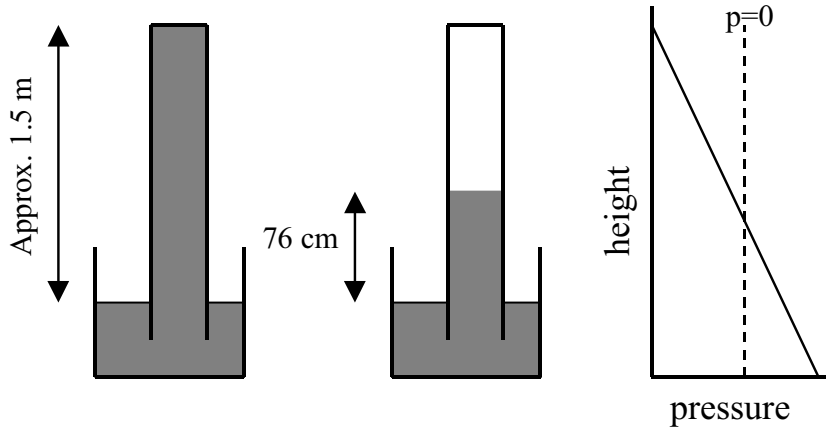


Fig. 2. The experiments of Huygens and Torricelli, see text

Several books have been written about this topic [3, 9, 10, 11, 12], also there are some recent reviews [1, 13] as well as a homepage dedicated to related researches [14].

There are several ways to produce negative pressure like spinning a Z-shaped liquid-filled (open-ended) tube, where negative pressure will be generated by the ‘centrifugal’ force or by using intense sound (or ultrasound) in a liquid, where – when the sound amplitude is big enough – positive pressure peaks can be followed by negative ones, or by using the thermal expansion difference of liquids and solids in a completely liquid-filled solid container [1, 3, 12]. Liquids can withstand only limited negative pressures – when applying bigger negative pressure than their ‘tensile strength’ they will cavitate. Water – being a strong liquid – can be stretched down to almost  $-150$  MPa [15], while liquid  $^4\text{He}$  can withstand only less than  $-1$  MPa [13]. Moderate negative pressures (for example several megapascals in water) can be maintained even for days [16] – for long enough time to make measurements under these conditions. Negative pressure states and overheated states are closely related (see Fig.3); they are two – seemingly different – manifestations of the huge metastable region located below the vapour pressure curve.

Although for liquids,  $p = 0$  does not have any special meaning (therefore their physical-chemical behaviours do not change abruptly by crossing  $p = 0$ ), there are several phenomena which cannot be seen too often at positive pressures. In this paper we would like to give a brief review about some phenomena concerning liquid-liquid phase equilibrium in binary liquids under negative pressure.

## 2. Liquid-Liquid Equilibrium

Mixing any two liquids we might face three different situations: i.: the two liquids can be totally incompatible, i.e. we cannot get a homogeneous mixture of them, ii.:

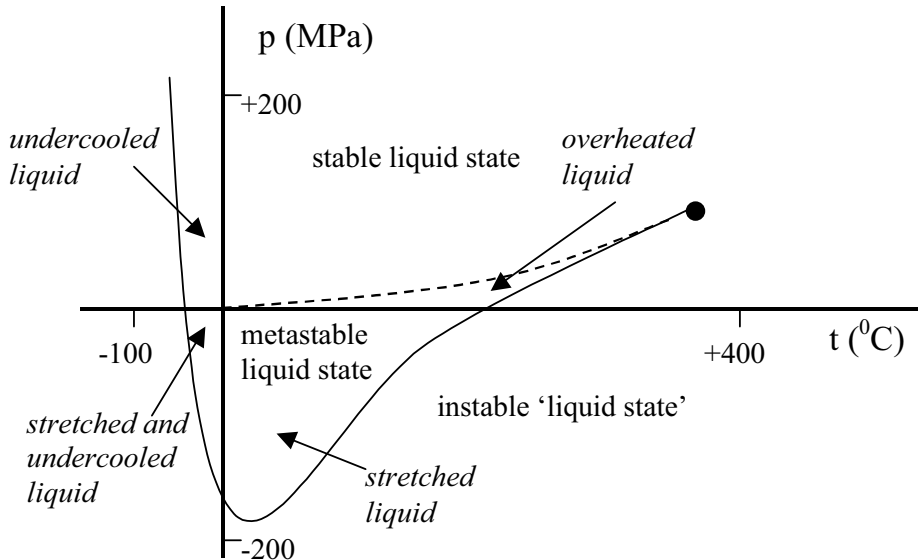


Fig. 3. Schematic phase diagram (fluid states) of water, showing that overheated and stretched states are related; they are parts of the big metastable region located below the vapour pressure curve (dashed line). The border between stable liquid states and metastable liquid states is the vapour pressure line (dashed); the border between metastable and unstable liquid states is the spinodal line (solid). Vapour-liquid critical point is marked by a big black dot.

the two liquids can be completely miscible, i.e. their mixture will be homogeneous at every pressure, temperature etc., iii.: the two liquids can be partially soluble, i.e. their mixture will be homogeneous at a certain temperature, but on changing the temperature the mixture will exhibit liquid-liquid phase transition and phase separation, resulting in two liquid phases (none of them will be pure *A* or *B*; one of them will be '*A*'-rich, the other one will be '*B*'-rich). A good example for partially miscible compounds are certain polymer solutions, like polystyrene+cyclohexane; for very long chain polystyrene, the mixture is heterogeneous below 307 K, homogeneous in the range of 307 – 486 K and will split into two phases again above 486 K [17]. These kinds of solutions are called weakly interacting solutions; a general concentration-temperature diagram of these kinds of systems can be seen in Fig. 4a, lines *A* and *B*. The system has one homogeneous region (between lines *A* and *B*) and two heterogeneous ones (below line *A* and above line *B*). Two special points are marked in the figure; UCST (Upper Critical Solution Temperature) and LCST (Lower Critical Solution Temperature). Upper and lower means that they

are on the maximum or in the minimum of the binodal curve; in case of weakly interacting solutions, the upper one (UCST) is actually located below the lower one (LCST).

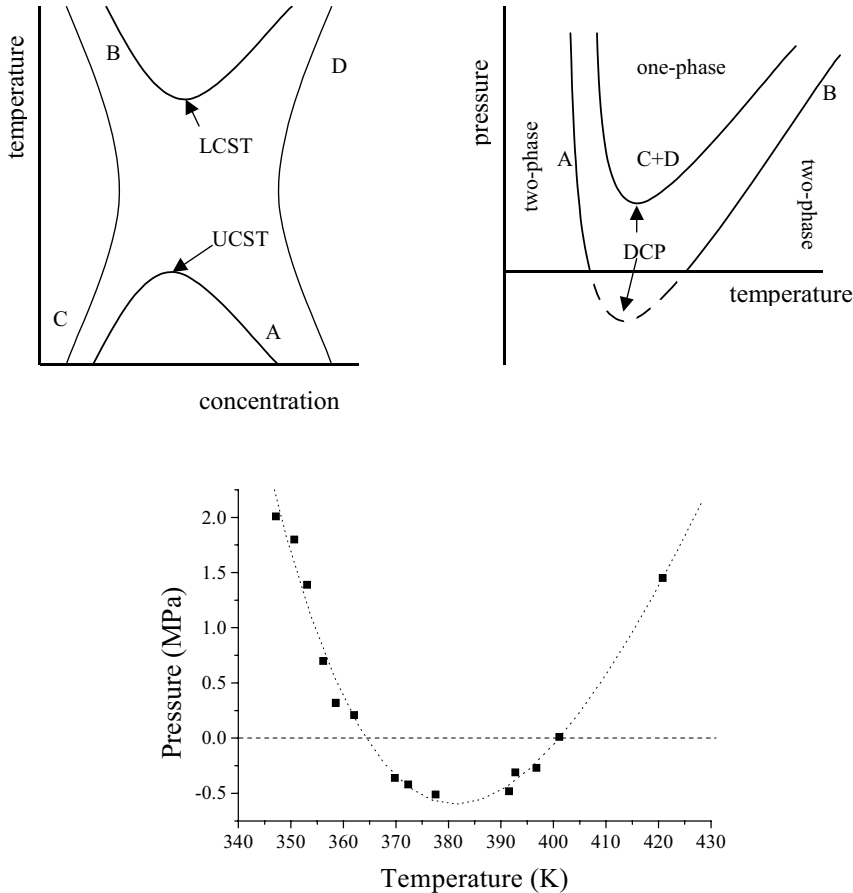


Fig. 4. Schematic representation of the concentration-temperature (a) and temperature-pressure diagram (b) of weakly interacting systems. For further explanation see text. c: Liquid-liquid phase equilibrium in polystyrene+propionitrile solution ( $M_w = 22000$ , 20.1 w%) [20, 22].

A typical pressure dependence can be seen in Fig. 4b with UCST (represented by line A) decreasing with pressure and LCST (represented by line B) increasing with pressure (more detailed description of these dependencies can be found for example in Ref. [18]). It is known that for a few solutions (like polystyrene

in acetone) this kind of dependence (and the one represented by lines *A* and *B* in *Fig. 4a*) can be seen only with low molecular weight polymer. With longer polystyrene chains the two branches will join (forming a joined UCST-LCST) then split again into two parts, forming a so-called hourglass configuration (*Fig. 4a*, lines *C* and *D*). In this case the system has two homogeneous regions (previously it had only one), left from line *C* and right from line *D*, and only one heterogeneous one, between lines *C* and *D*. Concerning the pressure dependence, the lower ends of the two branches will move closer and closer, finally forming a distorted parabolic-shaped critical curve with a double critical point (DCP) at the minimum (*Fig. 4b* line *C+D*). DCP is also called Critical Pressure Minimum. From this scenario one can see clearly that actually the DCP was not ‘formed’ by the merging of the UCST and LCST, but rather emerged from the metastable region (i.e. below the vapour pressure curve). Therefore it is quite trivial to extend the UCST (line *A*) and LCST (line *B*) below  $p = 0$  (see dashed line). This extension has been proposed decades ago by WOLF [19], but experimentally proved only much later on polystyrene solution [20, 21, 22, 23]. An experimental example of this extensibility can be seen in *Fig. 4c* [20, 22].

For polymer mixtures usually only one branch can be seen while the other one can be masked by freezing or by polymer degradation. In a couple of blends we can see only UCST, and for great surprise the UCST will almost always increase with pressure, i.e. while in typical polymer mixtures pressure can increase solubility (pushing UCST lower), in polymer blends the effect is usually just the opposite. As there is no clear border between polymer mixtures (blends) and polymer solutions (mixture of some polymer with long-chain alkanes can be considered as polymer solution but also as mixtures of that polymer with polyethylene, polyethylene being a very long alkane) this difference made the theoretical description very hard. Recently it has been shown that having a polymer (with fixed chain length) plus another chain molecule (with variable length), we can see solution-like behaviour (UCST decreasing with pressure) when short chains are used but blend-like behaviour (UCST increasing with pressure) when longer chains are used. This was shown to be a result of the curved shape of the UCST. As it can be seen in *Fig. 5a*, the UCST curve has an extremum, the so-called Critical Temperature Minimum (CTM) which is general for binary solutions [24, 25]. The position of this CTM governs the effect of pressure under ‘normal’ (i.e.  $p > 0$ ) circumstances; when CTM is below  $p = 0$ , we can see UCST increasing with pressure, when CTM is above  $p = 0$  but located at moderate pressure, we can see curved UCST and finally when CTM is well above  $p = 0$ , we can see UCST decreasing with pressure. The location of CTM is governed by the chain length of the components; an experimental example (CTM shifting below  $p = 0$  with increasing chain-length of one of the components) can be seen in *Fig. 5b*.

There is another class of solutions, the so-called strongly interacting ones, like polyethyleneglycol+water. A general concentration-temperature diagram – a closed loop – of these kinds of systems can be seen in *Fig. 6a*. As it can be seen, in these systems the UCST is below LCST. Very famous examples of these systems are the group of the aqueous solutions of various methylpyridines.

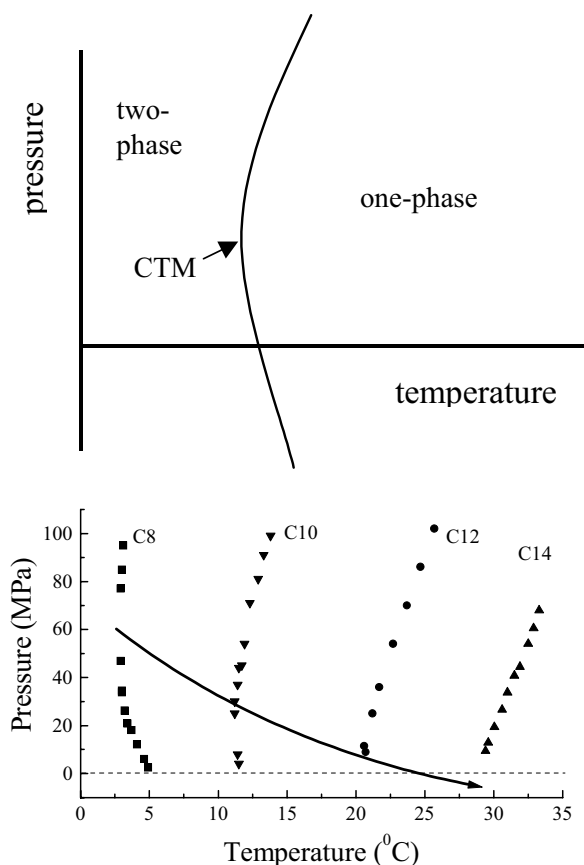
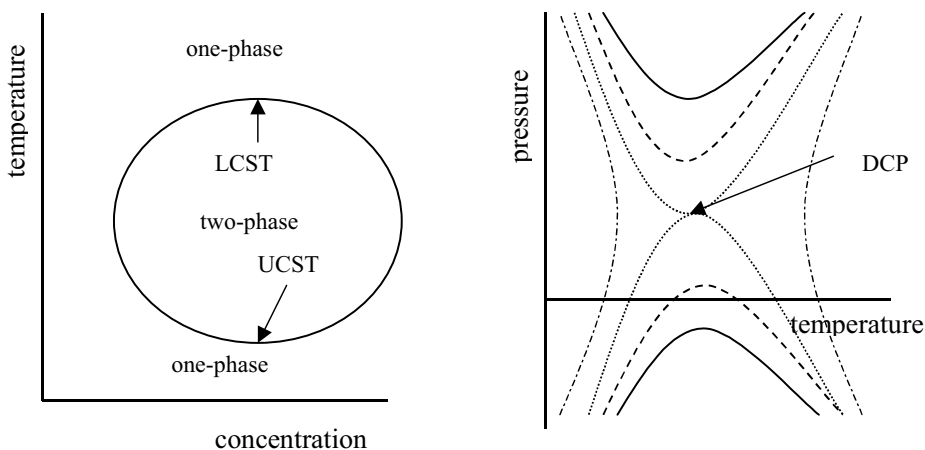


Fig. 5. a: Schematic representation of a curved UCST with Critical Temperature Maximum (CTM). b: The movement of the CTM with chain-length in various oligostyrene ( $M_w = 1241$ )/alkane systems. C8, C10, C12 and C14 represents *n*-octane, *n*-decane, *n*-dodecane and *n*-tetradecane, respectively [24].

2-methylpyridine (2 MP), 3-methylpyridine (3 MP) with water and 4-methylpyridine (4 MP) are always homogeneous at atmospheric pressure, although they have a two-phase region at high pressures, at or above 300 MPa [26]. Replacing the water with heavy water (HW), the 4 MP/HW system remains homogeneous at atmospheric pressure, but the 2 MP/HW and the 3 MP/HW systems will split into two homogeneous phases. Similar effect can be seen by adding salt to the aqueous solutions [26]. This behaviour can be easily understood by looking at the schematic temperature-pressure diagram (Fig. 6b). 2 MP/HW exhibits a phase diagram like the one represented by dashed lines in Fig. 6b; a liquid-liquid equilibrium line at

high pressure and another one mainly below  $p = 0$ , only its top can be seen under normal ( $p > 0$ ) circumstances. Approaching this top by increasing the pressure (or approaching the minimum of the high-pressure branch by decreasing the pressure, the closed loop in *Fig. 6b* will shrink into one point, then disappear. The 3 MP/HW system can be represented by the dash-dotted lines; it seems that the high pressure and low pressure branches (dashed lines) merged (dotted lines) then formed an hour-glass configuration. For 4 MP/HW we can see only the high-pressure branches, although it is definitely lower than in 4 MP/water. From this diagram it is clearly seen that for 4 MP/HW and for all three solutions with light water the low pressure branch is below  $p = 0$  and the small ‘hill’ of 2 MP/HW is only the top of an ‘iceberg’ hiding into the stretched liquid region. For the 2 MP/water and 3 MP/water systems, replacing water gradually by HW, we can lift up that hiding branch. The same effect can be achieved by adding salt into the aqueous solutions [26].

Although the existence of this kind of hiding solubility branches has been known for at least half of a century [27], they have not been reached yet, probably because they are hiding in the deeper region of metastability, where the liquid is too fragile and therefore these states cannot be reached easily.



*Fig. 6.* a: Schematic concentration-temperature phase diagram of ‘strongly interacting’ binary mixtures exhibiting a closed-loop (also called immiscibility island). b: Schematic temperature-pressure diagrams of various methylpyridines in water and in heavy water (see text).



### 3. Conclusions

Negative pressure states for liquids are metastable, but existing and experimentally accessible states. In binary liquid mixtures, several phenomena concerning liquid-liquid miscibility can be seen only (or can be seen better) under negative pressures, such as the merging of UCST and LCST branches or the existence of the Critical Temperature Maximum on the UCST in weakly interacting binary mixtures, or the existence of a low pressure solubility branch (often hiding completely below  $p = 0$ ) in some systems, like the aqueous solution of the different methylpyridines.

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