

LIQUID-LIQUID PHASE EQUILIBRIUM OF POLYMER SOLUTIONS AND POLYMER BLENDS UNDER POSITIVE AND NEGATIVE PRESSURE*

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Abstract In this paper we would like to give a brief review about the extensibility of the liquid-liquid locus into the negative pressure region. Negative pressure states are hardly explored; most researchers believe that the pressure scale ends at $p = 0$. We would like to show that this is not true, the $p = 0$ point is not a special point for liquids, it can be “easily” crossed. We are going to give a few example, where the extension of liquid-liquid locus for polymer blends and solutions below $p = 0$ gives us some interesting results, like the merging of UCST and LCST branches in weakly interacting polymer solutions or the reason why most UCST blends exhibit pressure induced immiscibility. Also, we will see what happens with the immiscibility island of aqueous polymer solutions when — reaching the critical molar mass — it “disappears”.

Keywords Pressure, Negative pressure, Polymer, Solubility, Phase transition

INTRODUCTION

Some physical quantities (like acceleration or charge, *etc.*) can be either positive or negative, while some others (like mass, length, *etc.*) cannot be negative. For most scientists pressure seems to fit into the second category: decreasing the pressure from an initial positive value, one can approach $p = 0$ by increasing the volume of the system, but cannot cross it and cannot reach any negative values.

However this is not the case. Thermodynamics does not exclude the possibility of the existence of $p < 0$ states in condensed matter (*i.e.* in liquids and solids)^[1–3]. While positive pressure can be realised by pushing, negative pressure can be generated by pulling — even in liquids.

Although Toricelli's famous experiment is taught everywhere even at the middle-school level, only a very few people heard about the similar experiment of Huygens done less than two decades later. In the Toricelli experiment one has to fill a long (> 76 cm) glass tube (closed at one end) with mercury, then turn the tube upside down, while the open end is immersed in mercury. Doing this experiment at sea level, the mercury column has to drop down to 76 cm — above the mercury there is the Toricelli vacuum (practically $p = 0$), within the mercury column the pressure changes linearly with the height from zero to atmospheric (Fig. 1a). That happened for Toricelli and that happens for us — almost all the time. But sometimes the mercury column was observed to stick — it did not fall to 76 cm (Fig. 1b). This happened a few times for Huygens, using an approx. 1.5 m long tube^[4]. He conducted several experiments, but after a few years he just gave up this research — he faced a non-reproducible phenomenon, unexplainable with the knowledge of his Age. The phenomenon was rediscovered and explained only one and a half-century later by Donny^[5].

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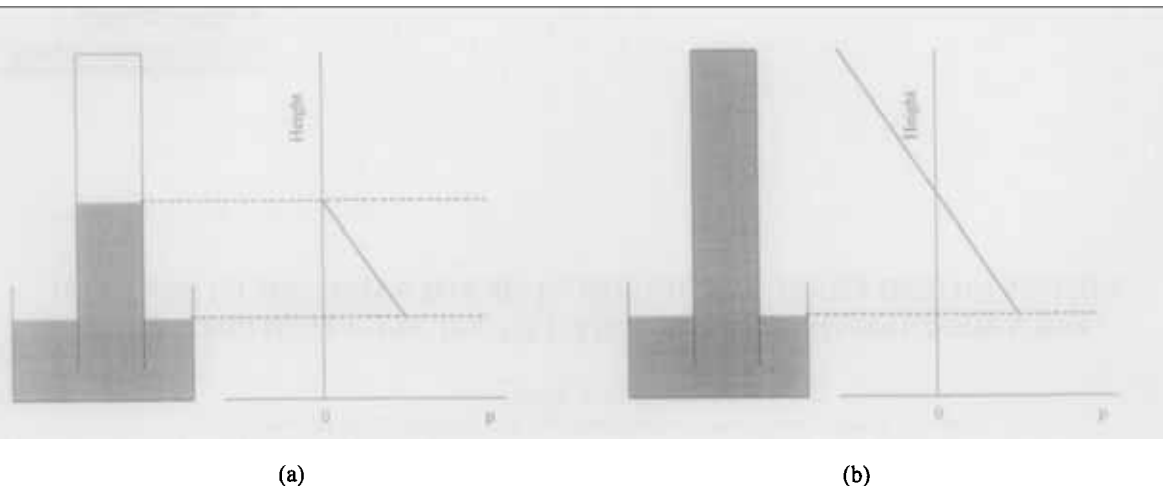


Fig. 1 a) Schematic model of Toricelli's famous experiment; b) Huygens' experiment for the demonstration of the existence of negative pressure in liquids (see text)

The sticking of the mercury was caused by the adhesion; the adhesion kept the mercury at the wall, and the upper part of the mercury column (above 76 cm) was stretched by the weight of the rest of the column. Since the hydrostatic pressure is proportional to the height, the pressure in the upper part of the liquid has to be below $p = 0$ — in the experiment of Huygens, the pressure at the top was approximately -1 bar.

Negative pressure states^[2, 5–9] for liquids are metastable states, very closely related to superheated states; in both cases the liquid is metastable with respect to the liquid-vapour phase transition, only in the second case the metastable region has been reached by heating, while in the first case it has been reached by stretching. Metastability means that for some perturbation the liquid can show a sudden liquid-vapour phase transition (boiling or cavitation) and the pressure will jump back to the vapour pressure, which is a positive quantity. $p = 0$ is not a special point for liquids; the special point (or rather line) is the vapour pressure line, where the stable liquid became metastable.

A schematic phase diagram of water can be seen in Fig. 2 (after Ref. [10]). One can see that the region of super heated liquids is only a small segment of the metastable states; most of this metastable region is below $p = 0$. Water can be stretched; it can endure even -100 MPa^[7, 10], but on increasing the stretch, sooner or later the liquid will give up and will relax by cavitation. The theoretical limit is the so-called spinodal line (solid line in Fig. 2). In real experiments cavitation happens much before the spinodal due to the heterogeneous or homogeneous nucleation of bubbles. "Dirty" liquids can withstand only very small negative pressures (or cannot withstand any negative pressure); cavitation will happen on solid contaminations or microbubbles will act as nuclei soon after going below the vapour pressure.

Liquids under negative pressure can be found in the nature. The liquids (sap) in plants are under moderate negative pressure, at least in some plants (especially in trees) — this negative pressure helps to overcome the problem that by vacuum water can be sucked only up to 10 meters, while some trees can reach a ten times greater height^[11]. Also, negative pressure can be found in the liquid inclusion of crystals^[12], including artificial ones — like mercury inclusions in artificial diamonds^[13]. The negative pressure in inclusions can reach the -100 MPa value. Negative pressure can be generated by an octopus under its liquid-filled sucker; the value of this pressure can be in the 0 to -3 bar range^[14]. Also, by the sudden pull of a joint (for example in our fingers) the liquid between the two bones can be suddenly stretched, then relax by cavitation — emitting a cracking noise and causing some damage. Positive pressure waves (like the big ones generated by earthquakes) reflected from a liquid/solid or liquid/gas interface can generate quite big rarefaction waves with negative pressure.

Although $p = 0$ is not a special point for liquids, there are some phenomena which can be seen (or can be seen better) under negative pressure. In this paper we are reviewing what happens with liquid-liquid phase equilibrium in binary polymeric liquids (polymer solutions and polymer blends) below $p = 0$ (for reviews, see Refs. [15–19]).

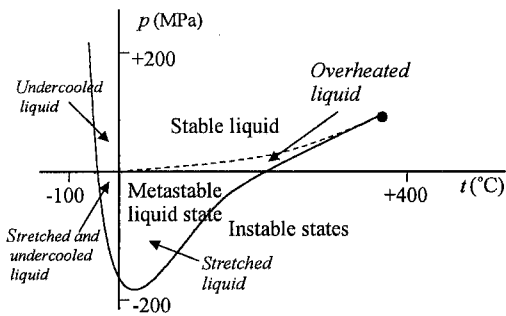


Fig. 2 Schematic phase diagram of water (after [10])

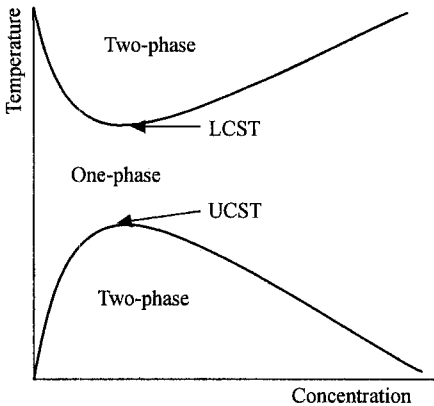


Fig. 3 Schematic representation of the liquid-liquid equilibrium in weakly interacting binary polymer solutions and blends

LIQUID-LIQUID PHASE EQUILIBRIUM IN WEAKLY INTERACTING POLYMERIC LIQUIDS

Although most of the polymers are solid materials, polymer solutions can show liquid-liquid phase transition, when the previously homogeneous solution will split into a polymer-rich and a polymer-lean parts. Schematic representation of the liquid-liquid equilibrium (at constant pressure) in weakly interacting binary polymer solutions (like most polystyrene or polyethylene solutions) can be seen in Fig. 3^[20]. At constant (usually atmospheric) pressure liquid-liquid phase transition can be induced by cooling and/or by heating. The two liquid-liquid loci have two extrema; one of them is the so-called Upper Critical Solution Temperature (UCST), while the other one is the so-called Lower Critical Solution Temperature (LCST). For most polymer solution, both branches can be seen^[21], although in some system the low-temperature one can be masked by freezing or the high temperature one can be masked by polymer degradation. In polymer blends usually only one of these branches can be seen — probably the miscibility gap is much wider and therefore one of the branches is always masked.

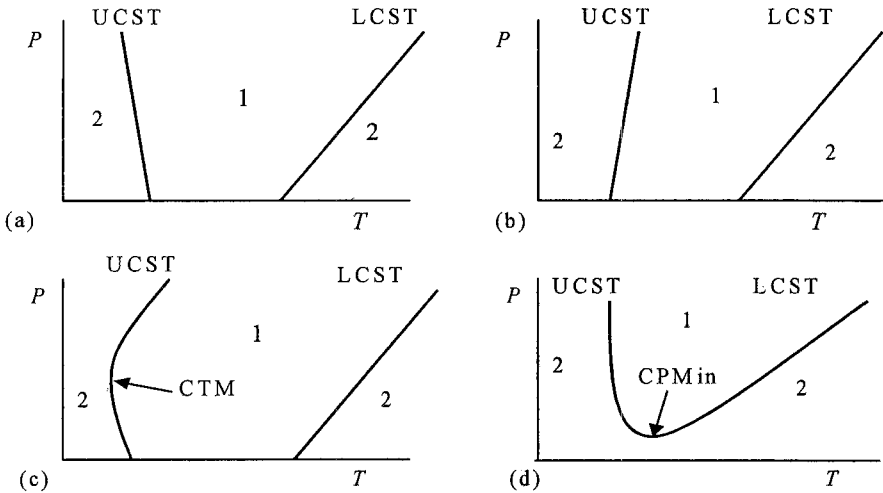


Fig. 4 Pressure dependences of weakly interacting polymer solutions (see text)

Concerning the pressure dependence on solubility (or miscibility), mostly the movement of the LCST and UCST has been studied. The behavior of the LCST is “simple”, because it always increases with increasing pressure, *i.e.* in (temperature, pressure) space it can be represented by a mainly straight line with positive slope.

The behavior of the UCST is more difficult: sometimes it can be represented also by a straight line, but the slope of that line can be either positive or negative; sometimes it can be curved with an extremum or it can even join to the LCST, forming a minimum (see Fig. 4). The two possible extrema (they are double critical points) can be marked as CTM (Critical Temperature Minimum) and as CPMIn (Critical Pressure Minimum) (according to some recent simulations and experimental results with short-chain solution, there is a third extremum, a Critical Pressure Maximum, CPM_{ax}, located at very high temperatures, usually well-above the degradation temperature^[22–24]).

These four kinds of UCST might remind us of the old tale about the elephant and the three blind men. For the first man (touching the tusk) the elephant is a long and hard animal, for the second one (touching the trunk) the elephant is a long and soft animal while for the third one (touching the ear) the elephant is a flat and soft animal. Probably these four distinct kinds of UCSTs and the LCST can be described by one general pressure dependence. There are two crucial points to reach this general dependence. First, we have to accept that the liquid-liquid solubility branch can be extended into the region of negative pressures. Extensibility of UCST and LCST and their merging at negative pressure has been proved experimentally by Imre and Van Hook^[15, 25, 26] and later by Rebelo *et al.*^[19, 27]. Experimental examples can be seen in Fig. 5. According to these results, the virtually separated UCST and LCST are not two really separate phenomena, only two sides of one phenomenon. In this way, two virtually different dependences (Figs. 4a and 4d) are the same, only in the first case the CPMIn is located below $p = 0$.

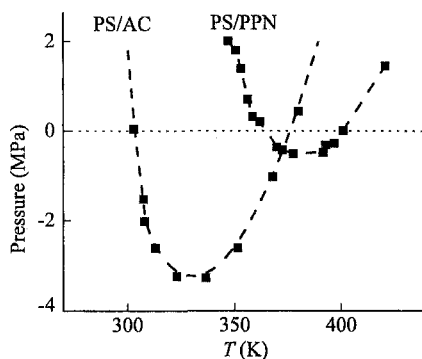


Fig. 5 Extensibility of the UCST and LCST branches in polystyrene/propionitrile ($M_w = 22000$, 20.1 wt%^[25]) and in polystyrene/acetone ($M_w = 16600$, 18 wt%^[27]) solutions

Here we would like to stop a little bit and describe how one can measure liquid-liquid phase transition under negative pressure. Although there are several methods to generate negative pressure, most of them produce negative pressure only for a short time. The method used by Huygens would be good to produce long-lasting negative pressure, but to reach -1 MPa in an aqueous solution one needs a 100 meter long, thermostated tube - so this method is not very useful.

The method used by Imre and Van Hook^[25, 26] and Rebelo *et al.*^[19, 27] was the so-called Berthelot method. Schematic representation of this method and the way to use it for liquid-liquid phase transition measurements can be seen in Figs. 6 and 7. In the first step a heavy-walled glass capillary has to be filled (almost completely) with the degassed liquid and the capillary has to be flame-sealed under vacuum (while the solution is frozen) (Fig. 6a and the corresponding point in Fig. 7). Going back to room-temperature, we have to get a liquid-filled capillary with a tiny bubble. At this stage the pressure in the capillary is equal to the vapour pressure of the solution. In the next step we have to heat the system up. The liquid will expand and at a certain temperature (T_f , filling temperature) the bubble will disappear. At this point the pressure is approximately $p_{\text{vap}}(T_f)$. Continuing the heating, the capillary will be over-pressurized. To eliminate all micro-bubbles, it is recommended to heat the system up (*i.e.* overpressurize it), but one has to be careful not to blow it up. The pressure at this stage can be

calculated from the constant volume thermal pressure coefficient ($\Gamma = (dp/dT)_{V = \text{const}}$) of the liquid in the following way:

$$p(T) = p^{\text{vap}}(T_f) + \int_{T_f}^T \Gamma(T, p) dT \tag{1}$$

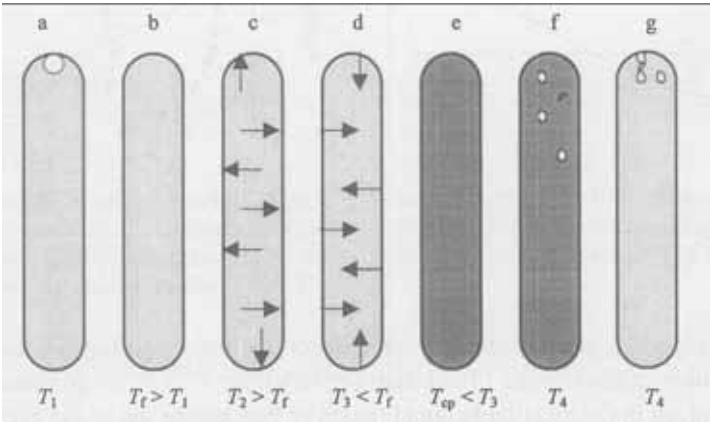


Fig. 6 The Berthelot-method to generate negative pressure (see text)

Although the volume of the heavy-wall capillary is not constant, since the experimental temperature range is only a few K, one can use this method to get a fairly good estimation.

On cooling the system back, to the filling temperature again, one can expect the appearance of the initial bubble, but this is not the case. Having a clean system with good adhesion between the wall and the liquid, there will be no bubble appearance in this stage. One can cool down the system even a few K below T_f without getting bubbles. During the cooling due to the big thermal expansion coefficient difference between the glass and the liquid, the liquid tries to shrink faster than the capillary. But this shrinking is prevented by the adhesion, i.e. the liquid will soon be stretched. The actual pressure can be estimated by Eq. (1). A typical value for Γ is a few bar/K, i.e. during a few K cooling the system can reach negative pressure down to a few MPa. During the cooling, the isochor of the system can cross the cloud point curve (see Fig. 7). At that point the initially almost transparent liquid will be white. Knowing the corresponding temperature one can calculate the corresponding pressure and in this way one point of the cloud point curve can be determined. On further cooling the liquid will cavitate and the pressure will jump back to the vapour pressure almost immediately. This is a very remarkable event: the cavitation will cause an audible click and then the white liquid will turn back to transparent in less than a second.

Unfortunately one sealed sample can give us only one point of the cloud point curve. Since the sample preparation is pretty time-consuming, to determine the whole cloud point curve of one particular solution might take weeks or even months.

After this proof of the extensibility of UCST and LCST below $p = 0$, the next step will be easier: one has to accept the movement of the CTM with changing chain length. Having a CTM below $p = 0$ one will see (under normal laboratory conditions, i.e. when $p > 0$) a UCST with positive slope (Fig. 4b). Having CTM above $p = 0$ but still in the experimental range, one can see a curved UCST (Fig. 4c), while with CTM located on very high pressure, only a UCST with negative slope can be seen (Fig. 4a). In this way, we can explain one more “mystery”, namely that in polymer solutions miscibility can be increased by pressure (UCST decreases with increasing pressure), while in polymer blends, pressure cannot be used as “compatibilizer”, because UCST increases with increasing pressure. An experimental example, showing the chain length dependence of the location of the CTM can be seen in Fig. 8, showing that with changing chain-length in an oligomer-mixture one can see solution-like behavior (with shorter chains) and blend-like behavior (with longer chains)^[28].

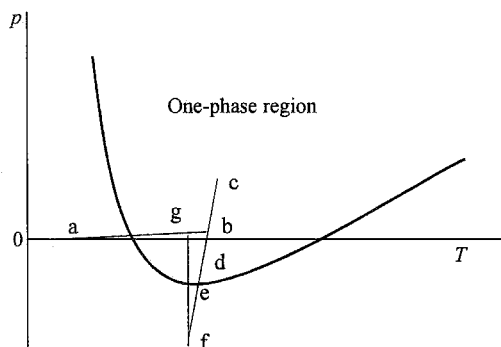


Fig. 7 Schematic representation of the different stages of the process to generate negative pressure in a solution by the Berthelot method and its use to determine cloud points

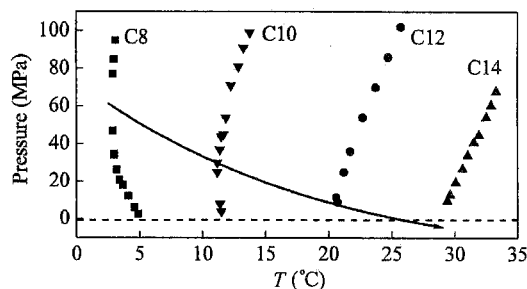


Fig. 8 Movement of the CTM (marked by a heavy arrow) with increasing chain-length in oligostyrene/oligoethylene mixture from positive to negative pressures C8—C14 indicate alkanes from octane to tetradecane^[28]

Finally, we can propose a general pressure dependence for the liquid-liquid locus of polymer solutions which exhibits two double critical points (TCM and TPMin) (Fig. 9)^[27, 29–31]. Sometimes one or both double critical points can be hidden in the metastable liquid region or they can be out of the experimental range causing “different kinds” of pressure dependences shown in Fig. 4. This general pressure dependence can be extended to describe polymer blends too. In that case CPMIn is always below $p = 0$ while CTM goes below $p = 0$ by increasing the chain length^[28, 32]. Experimental evidence for this kind of critical lines (exhibiting two critical points) has been found by Imre and Van Hook^[29] in polystyrene/1,4-*trans*-dimethylcyclohexane (PS/DMCH) and by Rebelo *et al.* in polystyrene/acetone (PS/AC) solutions^[27] (see Fig. 10). We have to mention here that while in the first system both double critical points were found at positive pressures, in the PS/AC case the CPMIn was located at negative pressure (see Fig. 5).

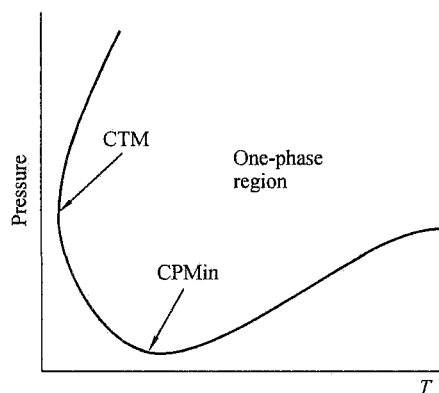


Fig. 9 General pressure dependence of the liquid-liquid locus in weakly interacting binary polymeric liquids (solutions and blends)

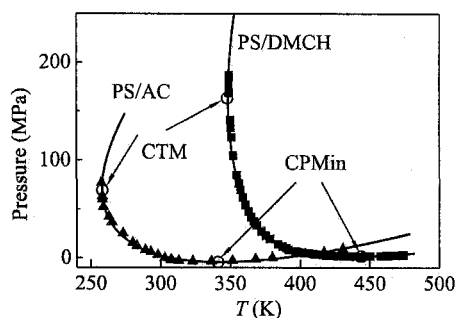


Fig. 10 Liquid-liquid critical lines of polystyrene/1,4-*trans*-dimethylcyclohexane (PS/DMCH, $M_w = 575000$, 7 wt%)^[29] and polystyrene/acetone (PS/AC, $M_w = 16600$, 18 wt%)^[27] solutions exhibiting two double critical points

LIQUID-LIQUID PHASE EQUILIBRIUM IN STRONGLY INTERACTING POLYMERIC LIQUIDS

Aqueous polymer solutions (like PNIPAM/water or PEG/water) exhibit totally different phase behaviors. A crucial difference is that for this kind of solutions high molecular mass polymers are more miscible than the shorter chains. In a concentration-temperature plot they exhibit an immiscibility island — outside of that island

the system is homogeneous, while inside it splits into two phases. The corresponding pressure dependence is also different. Schematic temperature-pressure and temperature-concentration diagrams can be seen in Fig. 11. As well as in the weakly interacting system, there are two critical points, a LCST and a UCST, but in this case at least LCST is below UCST. It can be seen that starting with a high molar mass polymer, solutions have two separated miscibility branches in a temperature-pressure diagram (Fig. 11a), one at low temperature and one at high temperature. Decreasing the molar mass, these two branches become closer and closer, and finally somewhere between the states in Fig. 11(b) and (c), they will merge, forming a double critical point. During this time their representation in the concentration-pressure diagram will be still an island, changing shape and size. Decreasing the molar mass further, the critical lines separate again, but in this time they will form a high-pressure and a low-pressure branch (Fig. 11c). Further decreasing the molar mass, the top of the low-pressure branch will become closer and closer to $p = 0$ (simultaneously the miscibility island on the concentration-temperature diagram will become smaller and smaller). Reaching $p = 0$, the low-pressure branch virtually disappears (*i.e.* at moderate positive pressures we cannot induce phase separation) (Fig. 11d) — but extrapolating the movement of the critical lines we can conclude that that branch simply shifted into the negative pressure region (Fig. 11e).

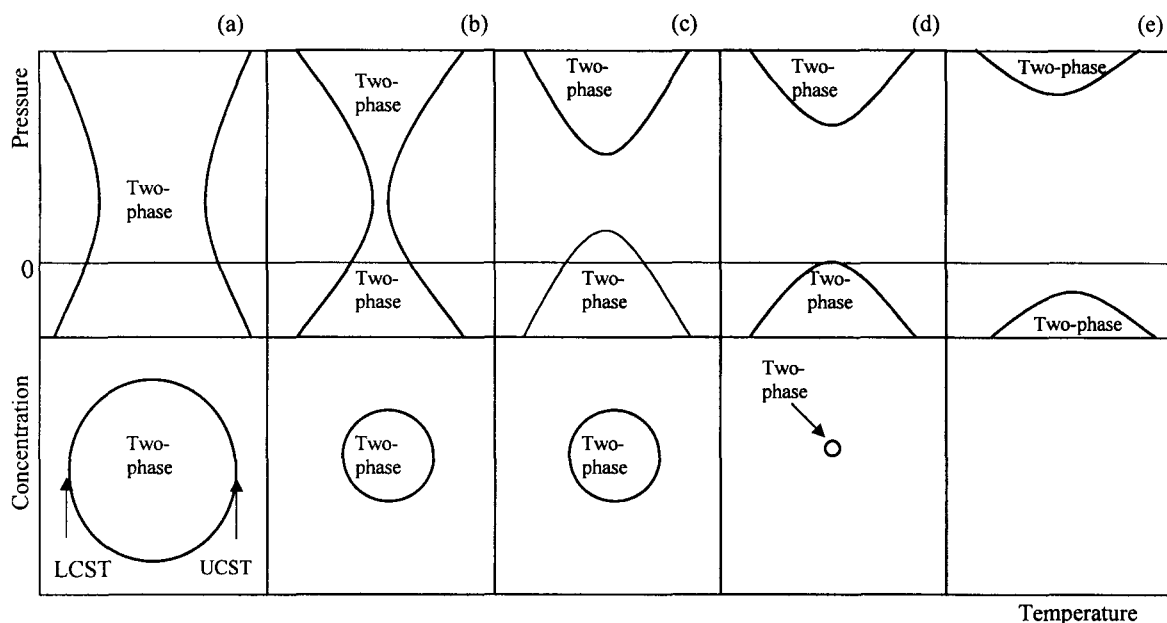


Fig. 11 Liquid-liquid loci for strongly interacting polymer solutions in temperature-pressure and temperature-concentration diagrams. Molar mass decreases from (a) to (e) (see text)

Up to now there is no experimental evidence for the existence of the liquid-liquid critical branch in strongly interacting polymer solutions below $p = 0$. But there is a similar case: the ternary system of different methylpyridines (2, 3 and 4) in methylpyridine+water+heavy water (MP/W/HW)^[33]. In that case we can get all kinds of phase diagrams represented in Fig. 11; however, instead of changing the molar mass, one can change the methylpyridines (from 2 to 3 to 4) and/or the W/HW ratio. For 3MP/W/HW system one can see the “disappearance” of the critical line from the positive pressure region. Very recently this missing branch has been found by Rebelo *et al.*^[18] on tracking the miscibility curves down to -25 MPa.

CONCLUSION

It is a common misbelief that the pressure scale has a lower end at $p = 0$; liquids can endure remarkably high negative pressures for macroscopic times (even for days). Although the $p = 0$ point is not a special point for liquids, the extension of our experiments, theories or models below this point might give us some unexpected

result or we can get answers for long-unanswered questions.

In this paper the extensibility of the liquid-liquid locus into the negative pressure region has been demonstrated. It was shown that for weakly interacting polymer solutions and blends virtually separated UCST and LCST merge below $p = 0$, forming a double critical point. The phenomenon why most of the polymer solutions can exhibit pressure induced miscibility while most polymer blends exhibit pressure induced immiscibility can be explained by the existence of a second double critical point. While for most solvents this point is located at positive pressures, for long-chain blends it can shift below $p = 0$. Indications that for completely water-soluble polymers a two-phase region might hide below $p = 0$ have been given.

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