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Theoretical foundations of the use of the transcritical state in extraction, separation, and concentration processes. Pathways of transcritical superextraction

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Abstract. **The physicochemical foundations of known fluid supercritical extraction processes and of essentially new transcritical extraction processes in liquid–liquid systems, and in ultramicroheterogeneous systems with a subtransitional dispersed phase in micellar and liquid-crystalline transitions, are discussed via a unified approach based on conclusions of the modern fluctuation theory of phase transitions. It is shown that regions of enhanced selectivity of the phase redistribution exist on the path to the critical point both under supercritical and under subcritical conditions, and that a subcritical selectivity maximum is possible only if the system contains a region in which the classical theory of critical phenomena is applicable. In the selective extraction into both the subcritical and the supercritical phases a weak, universal (physical) selectivity may be accompanied and complemented by stronger specific chemical effects leading to selective complex formation. It is shown that the chemical reaction in the homogeneous phase can be treated as a first-order phase transition close to a second-order phase transition, and accordingly we observe a universal physical superextraction into this phase. The bibliography includes 79 references.**

I. Introduction

Distillation and extraction processes depend on changes in the state of a fluid (gaseous or liquid) heterogeneous system along the equilibrium curve on a phase diagram caused by macrointeractions in the system. Distillation and extraction processes are usually carried out far from the critical point (CP). In two-phase systems the equilibrium curve terminates at the CP, where the difference between the coexisting phases disappears and the concepts of extraction and separation become meaningless (Fig. 1*a*). However, the response of the system to external influences is a maximum at the CP. Near the CP many other unique features of the critical state of matter become apparent due to the anomalous development of fluctuations and to the tendency of their correlation radius to increase towards infinity. Another important property of these systems is the loss of individuality of substances as the critical conditions are approached. The character of these properties is determined by the extent to which critical conditions are approached rather than by the individual character of the substances or even by the type of phase equilibrium. The conjunction of these two features produces uniquely favourable conditions for the realisation of various pathways for extraction, separation, and concentration processes using critical phases, thus creating methods of treatment which use no reagents and therefore emit no waste products.

The aim of this review is to examine by a unified approach the physicochemical foundations of the exploitation of the unique properties of the transcritical state of matter in extraction, separation, and concentration processes. The approach is based

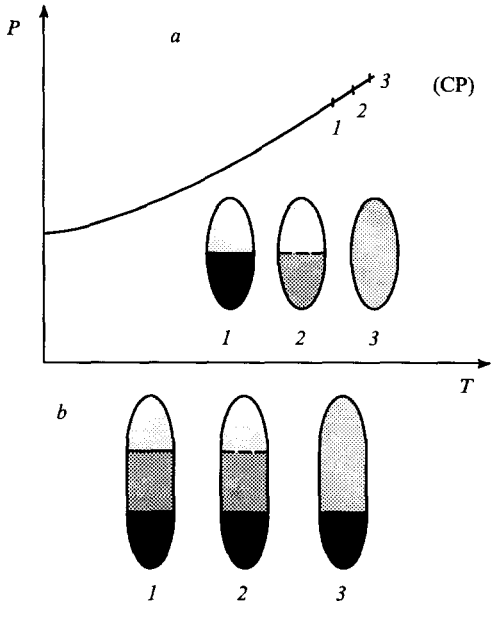


Figure 1. Equilibrium curve of two phases in temperature–pressure coordinates and schemes showing the gradual disappearance of the difference between the phases on approaching the critical point. *a*: (*1*) equilibrium of two noncritical phases; (*2*) equilibrium of two noncritical phases separated by a subcritical interface; (*3*) critical phase; *b*: (*1*) equilibrium of three noncritical phases: (*2*) equilibrium of two subcritical phases with a noncritical phase; (*3*) equilibrium of a critical with a noncritical phase.

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on one of the most important conclusions of the modern theory of critical phenomena and of phase transitions: the existence of a unique and universal driving force[1,2] for the critical phenomena and phase transitions of the second kind.†

An alternative starting point is the postulate first put forward in Landau's classical theory of a continuous and monotonic replacement of one type of phase transition by another.[1] On the path towards the critical phase (or a 'pure' phase transition of the second kind) a phase transition of the first kind becomes increasingly 'weak', and increasingly sensitive to the effect of fluctuations on the character of the transition, i.e. it develops steadily increasing second-order properties.

A third (and very important) consideration is the hypothesis that transcritical and pre-transition phenomena in complex real multicomponent systems can be treated from the standpoint of the modern theory of critical phenomena, developed for the simplest model systems. In the first instance this refers particularly to a specific property of the transcritical state of matter: and enhanced solvent power of the transcritical phases, whose thermodynamic basis and molecular nature are most conveniently examined by considering the simplest two-component binary systems, i.e. critical solutions at infinite dilution. The concept of 'weak' phase transitions of the first kind and the postulate of universality in the properties of substances in the critical region allow the results of an analysis of the enhanced solvent power of critical phases to be applied to a wide range of real transcritical systems whose criticality (or degree of second-order nature) reveals itself not in a 'pure' form but in a form complicated by marked indications of first-order behaviour. A special case of this behaviour is the enhanced solvent power of systems containing an ultramicroheterogeneous dispersed phase.

The properties of the transcritical state can be exploited in extraction, separation, and concentration processes in various ways. In particular, extraction into critical phases from solid surfaces and extraction into critical phases through a noncritical interface have been used in liquid–gas systems. Supercritical fluid extraction processes near the gas–liquid critical point are known. Similar processes have been forecast for liquid–liquid systems. The use in extraction, separation, and concentration processes of the redistribution between phases in the subcritical region through the subcritical interface (Fig. 1*b*) and of the changes in the type of the phase transition under these conditions is new in principle. Processes of this type are known mostly in three-phase systems near the critical homogenisation point of two of the phases. In these processes an increased selectivity, determined by both universal physical effects and specific chemical effects, is observed when the system approaches the critical point, but in the subcritical rather than the supercritical region (in contrast to fluid supercritical extraction). The possibility of similar processes in ultramicroheterogeneous systems has been predicted.

These paths to transcritical superextraction all approach critical conditions, and therefore they can be analysed in terms of a unified concept leading to the prediction of several new phenomena.

II. Enhanced solvent power of critical phases

1. Thermodynamic causes

The thermodynamic causes of the increase in the solvent power as the system approaches the critical point (or a 'pure' phase transition of the second kind) are conveniently discussed in terms of a very simple binary system in which the solvent is a gas. In this case when a pure substance is dissolved in the gas under isothermal conditions (as a function of the gas pressure P) the solubility of the second component (N_2) varies according to the equation

$$\left(\frac{\partial N_2}{\partial P}\right)_{T,s} = \frac{v_2^0 - \left[v - (1-N_2)\dfrac{(\partial P/\partial N_2)_{T,v}}{(\partial P/\partial v)_{T,N_2}}\right]}{(\partial \mu_2/\partial N_2)_{T,P}}, \qquad (1)$$

where μ_2 is the chemical potential of the dissolved substance, v is the molar volume of the solution, and v_2^0 is the molar volume of the pure dissolved substance. The subscript s denotes differentiation along the coexistence curve. Eqn (1) follows from the generalised Gibbs–Duhem equation;[3] it has also been obtained[4] in terms of the quantitative theory of the solvent power of supercritical fluids. This equation describes the increase in the solvent power of a supercritical phase in terms of classical thermodynamics, resulting from the fall to zero of the derivatives $(\partial P/\partial v)_{T,N_2}$ and $(\partial \mu_2/\partial N_2)_{T,P}$ at the critical point. The role of the former of these derivatives is the more marked. Its tendency to zero on the path towards the critical point of the pure solvent depends on the chosen path, and therefore the thermodynamic properties of these solutions (and in particular the partial molar volumes) also depend on the path.[3,5] We note that all these authors[3–5] treat the approach to zero of $(\partial P/\partial v)_{T,N_2}$ near the critical point of the pure solvent under conditions of infinite dilution. Unless these conditions are stipulated the derivative $(\partial P/\partial v)_{T,N_2}$ is nonzero even on the gas–solute critical curve.[3–5] However, according to the modern fluctuation theory of the common nature of all critical phenomena (including phase transitions of the second kind[2]) and of the increased compressibility under all critical conditions[6] the derivative $(\partial P/\partial v)_{T,N_2}$ should decrease even if it does not vanish. This results in a growth of the solvent power of all critical phases. The problem lies in identifying the experimental conditions needed to observe this behaviour (the increased solvent power) experimentally, and the degree of approach towards the critical conditions. These arguments justify the assumption that Eqn (1) is universally applicable.

Let us examine the thermodynamic equations which describe the dependence of the partial molar volumes of the solvent ($\bar{v}_1$) and of the solute ($\bar{v}_2$) on N_1 and N_2 for the simplest two-component system:[7]

$$\bar{v}_1 = v + N_2\frac{(\partial P/\partial N_2)_{T,v}}{(\partial P/\partial v)_{T,N_2}}, \qquad (2)$$

$$\bar{v}_2 = v - N_1\frac{(\partial P/\partial N_2)_{T,v}}{(\partial P/\partial v)_{T,N_2}}. \qquad (3)$$

As it tends towards zero the derivative $(\partial P/\partial v)_{T,N_2}$ is always negative (in keeping with the classical thermodynamic stability conditions). Even more relevant to our problem is the nontrivial question of the sign of the derivative $(\partial P/\partial N_2)_{T,v}$. Under relevant conditions of divergence of the partial molar volumes this sign is assumed[2–5] to be arbitrary, though it has been stated[4] (without any evidence) that 'in practice' the derivative $(\partial P/\partial N_2)_{T,v}$ is positive. Allowing for Eqns (2) and (3) and for the negative sign of $(\partial P/\partial v)_{T,N_2}$, we may conclude that under conditions of divergent $\bar{v}_1$ and $\bar{v}_2$ (v being always finite) the sign of $(\partial P/\partial N_2)_{T,v}$ always agrees with that of the partial molar volume of the solute and is opposite to the sign of the partial molar volume of the solvent. This leads us to the universal thermodynamic conclusion that in keeping with the singularity of the partial molar volume of the solvent and irrespectively of its sign, the molar volume of the solution on the path towards the critical point always decreases. Thus, for negative values of $\bar{v}_1$ this decrease follows from the definition of a partial molar quantity, and for positive values of $\bar{v}_1$ it is produced by the negative value of $\bar{v}_2$ [of course, $(\partial P/\partial N_2)_{T,v} = -(\partial P/\partial N_1)_{T,v}$]. This important property of the molar volume of the solution of the path towards the critical point (i.e. towards the point for a 'pure' phase transition of the

† We shall treat the redistribution between phases as a phase transition of the second kind.

second kind) allows the general thermodynamic reason for the enhanced extraction of a substance into a critical phase to be identified in a specific case.

We note that in the modern theory of phase transitions both phase transitions of the second kind and 'weak' phase transitions of the first kind but close to the second kind are treated as critical phenomena.[2]

If the path to the critical point is examined under isobaric conditions an equation analogous to Eqn(1) can easily be obtained from the same generalised form of the Gibbs–Duhem equation:

$$\left(\frac{\partial N_2}{\partial T}\right)_{P,s} = \frac{-S_2^\circ + \left[S - (1-N_2)\dfrac{(\partial T/\partial N_2)_{P,T}}{(\partial T/\partial S)_{P,N_2}}\right]}{(\partial \mu_2/\partial N_2)_{P,T}} \qquad (4)$$

where S is the entropy of the solution, and S_2° is the molar entropy of the pure solute. This equation was first obtained in the author's laboratory.[8] The derivative $(\partial T/\partial S)_{P,N_2}$ in Eqn (4) plays the same role as $(\partial P/\partial v)_{T,N_2}$ in Eqn (1). Its decrease is the thermodynamic reason for the singularity in the partial molar entropy which enhances the solvent power of the critical phase as the critical point is approached. Equations similar to (2) and (3) can easily be obtained for the entropy, showing that the thermodynamic cause of the enhanced extraction into the critical phases under isobaric conditions is the increase in the molar entropy of the solution on the path towards the critical point. This increase is itself caused by the singularity in the partial molar entropy of the solvent, and is observed irrespectively of the sign of this singularity.

The general condition for a maximum in the isothermal dependence of the solubility on pressure in binary systems takes the form[7]

$$N_1^1(\bar{v}_1 - \bar{v}_1^1) + N_2(\bar{v}_2 - \bar{v}_2^1) = 0, \qquad (5)$$

where the subscripts denote the components and the superscripts denote the phase; the upper bar denotes a partial molar quantity. The presence of extrema on the composition dependence of the partial molar quantities predetermines the presence of extrema on the coexistence curve of the two equilibrium phases, i.e. on the solubility curve.[7] An analogous equation can be obtained for isobaric conditions.

By generalising the dependences described by Eqns (1), (4), and (5) we can establish not only that the solvent power of any critical phase is enhanced but also that the number of solubility maxima in the system is equal to the number of critical points.[8] In the special case of the solubility of an individual substance in a gas the solubility maximum is associated with the presence of a lower critical point in the gas–gas equilibrium, and if an upper critical point is also possible in the gas–gas equilibrium the solvent power of the gas phase should have a second maximum.[7]

2. Increase in the solvent power in 'weak' phase transitions of the first kind

The monotonic nature of the change in the type of the phase transition creates a very large class of so-called 'weak' phase transitions of the first kind, or phase transition of the first kind close to phase transitions of the second kind. The concept of weak phase transitions of the first kind and the widespread occurrence of transitions of this type in practical solutions have stimulated many attempts to find and to characterise various universal dependences in these solutions. The most important of these is the anomalously high response of a substance in the critical state to macroscopic and even to microscopic perturbations.[2] The stipulation of weak phase transitions of the first kind (close to transitions of the second kind) justifies the assumption of a universal enhancement of the solvent power in all cases of more or less clearly displayed second-order properties, i.e. λ-anomalies in the second derivatives of the thermodynamic potential with corresponding S-shaped changes in the first derivatives of the thermodynamic potential (enthalpy, volume, and entropy). The nature of the most important dependences can be determined from the results of studies of critical solutions at infinite dilution.[3]

Several uniquely anomalous dependences, apparently incompatible with classical thermodynamics,[3] have been observed in these solutions and explained in terms of the classical phenomenological theory.[5] The universality postulate suggests that in dilute critical solutions the most clearly marked effects are characteristic of the critical state as a whole, and that these effects should be observed to a greater or lesser extent in all practical critical phases during 'weak' phase transitions of the first kind. Indeed, at the critical point of the pure solvent

$$(\partial P/\partial v)_T = (\partial^2 P/\partial v^2)_T = 0,$$

whence it follows that

$$(\partial V/\partial P)_T = (\partial^2 V/\partial P^2)_T = \infty.$$

The anomalously high compressibility, observed not only in critical solutions at infinite dilution but also in solutions with 'weak' phase transitions of the first kind close to transitions of the second kind, should increase the solvent power. The universality of the anomalous properties of critical solutions at infinite dilution was first postulated in a general form by the writer,[9] and subsequently received independent confirmations.

3. Increased solvent power of ultramicroheterogeneous systems

The enhanced solvent power of systems containing an ultramicroheterogeneous dispersed phase, which increases with the dispersion as a result of changes in the type of the dispersed phase–medium phase transition from the first to the second kind, is of special interest.[10,11] A change in the type of phase transition on the surface of the dispersed phase as the system moves towards the critical point is phenomenologically consistent with Landau's assertion that the curve describing phase transitions of the first kind cannot terminate at a single point and must gradually be converted into a curve for phase transitions of the second kind, so that the two curves have a common tangent.[1] The effect is clearly illustrated in Fig. 2, which shows the dependence of the surface tension on both surfaces of the intermediate phase in a three-phase water–amphiphile–oil system upon the degree of enrichment of the intermediate phase by the components of the lower (water–salt) and the upper (oil) phase. Obviously, in the solubilisation within the droplet of the microemulsion by 'mechanical capture', without any allowance for the change in the type of phase transition and for the effect of this change on the interfacial redistribution, the size and nature of the solubilised volume should be strongly dependent on the type of microemulsion (the inverted microemulsion solubilises the aqueous phase, the normal solubilises the organic phase). This is indeed observed in practice: for surface tensions of 10^{-1}–10^{-2} dyne cm^{-1}, that is corresponding to microemulsion particles in which the intermediate amphiphilic phase is enriched with the components of the water-salt and the organic phase.[12] However, further lowering the surface tension (which corresponds to a decrease in the size of the microemulsion particles[12]), with a gradual transition from an amphiphilic to a micellar microemulsion phase (i.e. at surface tension values in the range 10^{-3}–10^{-5} dyne cm^{-1}), we can see not only an enrichment of the intermediate phase with the components of both the upper and the lower phase but also a decrease in the distance between the curves (see Fig. 2). Thus we observe an increase in the solvent power of the amphiphilic phase even in lyophilic ultramicroheterogeneous systems, with the approach of the 'weak' phase transition of the first kind to a 'pure' phase transition of the second kind. In this case the increase in the degree of criticality of the system is due to the increase in the fluctuations in the surface of the particles (micelles) with decrease in particle size. A thermodynamic driving force for the increased extraction into the micellar phase is provided by anomalies in the compressibility and in the change in the partial molar volumes.

Under isobaric-isothermal conditions the entropy of the ultramicroheterogeneous system increases with the degree of dispersion.[10,11] Allowing for these effects and for the primarily entropic nature of the subcritical redistribution of the components between the phases[13] we may assume that in multicomponent systems under isobaric–isothermal conditions the special properties of the partial molar entropies of the solute in the transcritical phases are the thermodynamic reason for the presence of maxima in the solubility.[10,11]

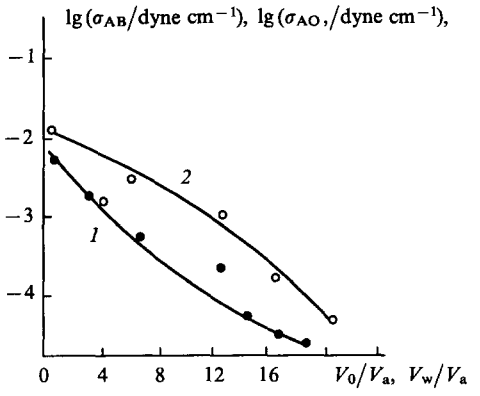


Figure 2. Plots of the surface tension σ in a three-phase system at the interfaces of an intermediate amphiphilic microemulsion-micellar phase with an upper (organic, *1*) and a lower (aqueous salt, *2*) phase against the bulk enrichment of the intermediate phase by the components of the upper (V_w/V_a) and the lower phase (V_0/V_a).[11]

We note that, as shown in Fig. 2, the solvent power of ultramicroheterogeneous systems varies only in the case of lyophilic ultramicroheterogeneous systems. Lyophobic ultramicroheterogeneous systems are thermodynamically unstable, they can be broken down by microscopic perturbations, and their enhanced solvent power can be observed only under conditions specially chosen to stabilise the degree of dispersion, for example by evolving hydrogen at a cathode, by cavitation produced by ultrasonic treatment of the liquids, or by forming Manegold spherical foams (gas emulsions) stabilised by surface-active substances. In all these cases we are dealing with the stabilisation of the gas–liquid interface in a dispersed system at the disappearance boundary of this surface, i.e. at the maximum spread of its fluctuations on the path from a colloidal dispersion to a true solution of a gas in a liquid. In most cases these phenomena have not been discussed from the point of view of changes in the nature of the phase transformation with increasing dispersion, but they can be easily incorporated into the concepts now being developed.

4. Molecular nature of the enhanced solvent power of critical phases

It is important to note that the enhanced solvent power of any critical phase is due to the special properties of partial molar quantities, as can easily be seen by examining the thermodynamics of the simplest binary transcritical systems. The left-hand sides of Eqns (1) and (4) exist only because of the singularity of the partial molar quantities. The signal of the partial molar quantities can be either positive or negative for both the solvent and the solute. The only universal feature is the nature of the decrease (in the critical region) of the molar volume of the solution as a result of the increased compressibility and of the anomalies in the partial molar volume. It has been shown[14] (in the case of critical dilute solution) that the compressibilty extrema correspond to the extrema of the partial molar quantities (Fig. 3). Under the same conditions maxima corresponding to clusters are observed in the solution: these are formations containing up to 10^2 molecules and having a local

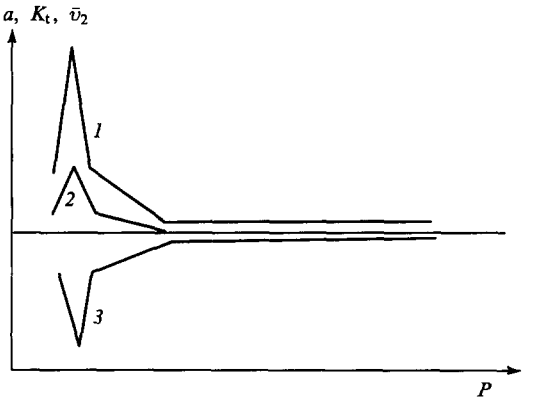


Figure 3. Plots of the size of the clusters (*1*), of the compressibility (*2*), and of the partial molar volumes (*3*) in the CBr_4-CO_2 system at infinite dilution.[14]

density higher than the average for the solution. Until recently the physical nature of the sign of the divergence of the partial molar quantities was not clear, but recent studies using molecular dynamics have thrown some light on the problem. According to Pelsche and Debenedetti[15] the anomaly in the partial molar volumes of a dissolved substance $\bar{v}_2$ is always (irrespectively of its sign) a universal phenomenon, accompanied by an increase in the size of the cluster (a shell surrounding the molecules of solute, with correlated fluctuations of the order parameter). Under these conditions infinitely dilute solutions of a Xe-like Lennard-Jones fluid in a Ne-like Lennard-Jones supercritical fluid show enhanced solvent–solute interactions near the critical point of the solvent, whereas in a 'symmetrical' system (an infinitely dilute solution of a Ne-like Lennard-Jones fluid in a Xe-like Lennard-Jones supercritical fluid) the shells surrounding the solute molecules are depleted of solvent. The stronger solvent–solute interactions correspond to an increased concentration of solvent in the cluster and to a negative divergence of $\bar{v}_2$ (tending to $-\infty$). On the other hand lowering the solvent content of the cluster corresponding to a positive divergence of $\bar{v}_2$ (tending to $+\infty$). In either case the local density of the cluster exceeds the average density of the solvent.

The same universality of the enhanced solvent power of the supercritical phases is observed in the extraction in liquid–liquid systems. Anomalies in the compressibility have been found even in solutions of liquid metals in the supercritical region (Fig. 4).

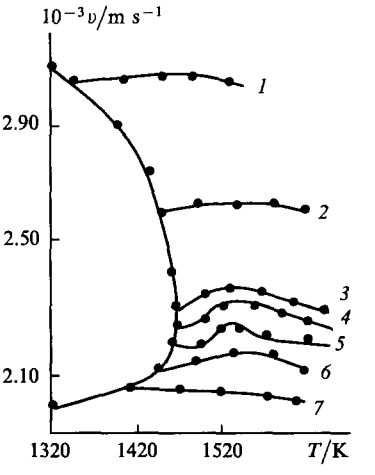


Figure 4. Compressibility anomalies in the critical region of the homogeneous phase-separating Cu–Te system. Plots of the velocity of ultrasound for alloys with an initial concentration of Te of 5 (*1*), 10 (*2*), 16 (*3*), 17.5 (*4*), 18 (*5*), 20 (*6*), and 29 at.% (*7*) (from data by Glazov et al.[16])

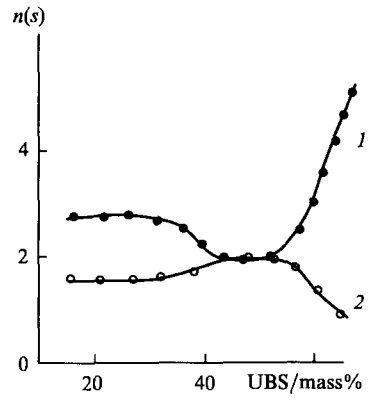


Figure 5. Dependence of the hydration number (*1*) and the solvation number (*2*) of the micelle-forming component uranyl benzenesulfonate (UBS) in the organic phase of the tributyl phosphate–water–UBS system on the concentration of UBS.[18]

The concept of universality in the extraction into micellar and liquid-crystalline phases due to the abundance in these phases of 'weak' transitions of the first kind with a 'diffuse' concentration[17] has provided explanations for several results previously treated as 'anomalous'.[10,11] The molecular nature of the enhanced solvent power of critical phases has been confirmed by a study by NMR of micellar extraction systems.[18] According to these results a region of universality is found in a tributyl phosphate (TBP)–water–uranyl benzenesulfonate (UBS) micellar solution in which the hydration and the solvation number in the hydration–solvation shell of the micelle-forming component become identical (Fig. 5). This means that the solvation shell of the micelle-forming component (in our case uranyl benzenesulfonate) contains both water and the hydrophobic solvent, i.e. that we have a region of universality. These experimental data confirm the validity of the concept of universality in the enhanced solvent power of the micellar phases and in the physical superextraction into these phases. The phenomenon has been called[18] reversible hydration. It confirms the concept of universality on a microscopic scale and contradicts the traditional explanation of solubilisation in the nucleus of a micelle in terms of 'mechanical' trapping of the conjugated phase. The observed solubilisation of both hydrophilic and hydrophobic substances is usually explained by the bicontinuous structures model proposed by Winsor,[19] according to which both normal and reversed-phase micelles are present in the micellar solution.

The concept of universality in the enhanced solvent power of ultramicroheterogeneous systems, produced by the fluctuational nature of the particle surfaces, is consistent with the well-known compression of knots of macromolecules produced by cross-linking within the knots.[20] Enhanced absorption of impurities in highly dispersed aerosols is also known. Evidently this effect becomes more marked as the degree of dispersion and therefore also the role of fluctuations are increased (as in the case of ultramicroheterogeneous liquid–liquid systems). This interpretation follows from the postulated universality of critical phenomena, and agrees well with the higher acidities observed in fog (up to pH 1.6) than in rain.[21] The assumption of fluctuations in critical phenomena allows us to predict other effects due to the development of fluctuations as the size of ultramicroheterogeneous particles is decreased: for example, a maximum in the absorption of CO_2 and SO_2 impurities during the condensation of superheated steam.[8]

5. Dependence of the solvent power of critical phases on the path to the critical state

A thermodynamic paradox, attributed to the 'nonclassicality' of critical phenomena, has been pointed out.[22] The effect of this paradox is that the thermodynamic state at the critical point is not uniquely defined by the conjugation of the available thermodynamic characteristics. This property of binary systems leads to several theoretical anomalies. As reported,[22] these anomalies are not experimentally accessible in liquid–gas systems, but it is thought that they could be observed near the liquid–liquid critical point in the case of two-component systems. We suggest that the ambiguity in the definition of the critical state by a conjunction of thermodynamic characteristics should produce a dependence of the properties of the critical phase on the path by which the critical point is approached.[8]

These dependences have been observed only in very dilute critical solutions. There are no reports of similar effects in concentrated solutions. One method of observing a dependence of the solvent properties of critical phases on the path by which these phases are produced is to study periodic colloid structures, whose composition and structure are known to depend on the method of preparation.[8]

Additional evidence for a dependence of the solvent power of a critical phase on its method of preparation is provided by the fluctuation theory of critical phenomena, according to which the partial derivatives of the concentration with respect to the chemical potential depend both on the degree of approach to the critical point and on the chosen path. In both cases we find a change in the critical index μ (see Anisimov's monograph[2]). Thus, if the critical point is approached by varying the concentration (φ) rather than the temperature the critical index for the surface tension, usually 1.26, takes the value

$$\frac{\mu}{\beta} \approx 3.9 \quad \text{and} \quad \sigma - \sigma_c \sim (\varphi - \varphi_c)^{\mu,\beta},$$

where β is also a critical index.

On the other hand if a concentration region to which the classical approximation applies exists at large distances from the critical point the deviation from the normal value at the critical point becomes less marked:[8,23]

$$\sigma - \sigma_c \sim (\varphi - \varphi_c)^3 \ln[(\varphi - \varphi_c)^{-1}].$$

This behaviour theoretically confirms the dependence of the solvent power of critical phases on the path by which the critical state is approached, since (as reported[10,24]) the σ values near the critical point are related to the solvent power of the critical phase and therefore also to the redistribution between phases. This allows the prediction of additional methods of exploiting the properties of the transcritical state of matter in extraction, separation, and concentration processes.

III. Pathways of transcritical superextraction

1. Superextraction through a noncritical interface

The simplest method of purification and deactivation of various solid surfaces is to use the universal solvent power of the critical phases. These extraction processes can be carried out both by using the macroscopic critical phase, corresponding to the end point of the equilibrium curve, and by relying on microscopic ultramicroheterogeneous lyophilic and lyophobic transcritical systems having a colloidal level of dispersion. Extraction is achieved by introducing into the system (in addition to the critical phase) another, noncritical interface which allows not only the removal but also the separation of the components to be extracted (see Fig. 1*b*). When the macroscopic critical phase is used this path is associated with the development of fluctuations in the volume between the two macroscopic subcritical phases which unite into a single critical phase under critical conditions.

A slightly different path to transcritical superextraction through a noncritical interface is also available: the creation of a critical extracting phase through microscopic critical phenomena in micellar ultramicroheterogeneous systems, in which we can observe the fluctuational erosion of the surface of the microscopic particles, ultimately leading to the fluctuational erosion of the interface between the dispersed phase and the dispersed medium. As in the case of extraction with ultramicroheterogeneous subcritical phases the processes of transcritical superextraction into ultramicroheterogeneous systems through a noncritical interface are usually not treated as subcritical. However, processes of this type are well known in membrane extraction processes in various types of emulsion, in which the formation of nanodispersions plays a controlling role.[25] Nanodispersions are formed with a change in the type of the phase transition on the surface of ultramicroheterogeneous particles, and as a result they not only stabilise a large number of emulsions but they also act as an extractant, able to control even the direction of the extraction process (in particular, they can lower the selectivity of the membrane extraction process in a multiple emulsion).

2. Fluid supercritical extraction processes

Fluid supercritical extraction processes[26] are among the most widely used methods of extraction through a noncritical interface into critical phases. Their main advantage is the ease of control through gradual changes in the gradient of the parameters of state and the physical nature of the extraction (which makes the process totally reversible). In supercritical fluid extraction from solutions the desired components can be isolated in a pure state. Control of the process (for example, the replacement of extraction by re-extraction) is carried out by gradually lowering the pressure, thus lowering the density of the fluid phase (upon which both the capacity and the selectivity of the fluid phase are strongly dependent).

Fluid supercritical extraction processes are used in the extraction, separation, and concentration of organic and of inorganic substances, in the purification of effluent waters, in the regeneration of adsorbents and catalysts, in the removal of toxic substances from soils, etc.[26] Because of the possibility of reagent-free re-extraction these processes offer a promising approach to the development of ecologically clean methods of separating and concentrating substances.[26] The most commonly used extractants are CO_2, ethane, and ethylene i.e. gases with a critical temperature close to 20 °C.[26-28] Other transcritical solvents have been suggested: for example, transcritical water vapour (classified[29] as a 'supersolvent').

Another feature of the fluid supercritical extraction process should be mentioned: in addition to having an anomalously high sensitivity to small changes in the parameters of state these processes are also anomalously sensitive to the presence of a third component (co-solvent) and to the chemical interaction (always quite weak) between the substance to be extracted and this component.[26-28] To produce an acceptable approximation to the experimental data in the physicochemical interpretation of the co-solvent effects in supercritical fluids we must allow for both the physical and the chemical components of the thermodynamic potential.[30] The addition of a co-solvent which interacts with the substance to be extracted can greatly increase the universal physical selectivity of the process as a result of the contribution from the specific chemical selectivity of the additive. If the active co-solvent is an alcohol (which is easily separated from the products) the complete reversibility of the process is retained since only the parameters of state (temperature and pressure) are varied. This feature is important from the point of view of developing technologies free from waste products. The use of fluid supercritical extraction in the technology of inorganic materials[31] (for example, for the separation of mixtures of liquid metals using inert gases as extractants) presents no theoretical difficulties. This would avoid the possibility of chemical decomposition of the extractant in work with very concentrated toxic or radioactive substances.

The extraction of inorganic salts (lanthanides and actinides) can be enhanced by modifying the extractant (CO_2) by additions of methanol with a selective complexing agent. Thus, in the fluid supercritical extraction of lanthanides and actinides from soils, the addition of co-extractants to the fluid superextractant has been suggested: these are compounds able to complex metal salts (dithiocarbamates, fluorinated β-diketones, tributyl phosphate).‡ It was found that tervalent lanthanides (La^{3+}, Eu^{3+}, Lu^{3+}), and also Th^{4+} and UO_2^{2+}, can be efficiently extracted from solid materials by using CO_2 modified by methanol and containing fluorinated β-diketones at 60 °C and 150 bar. It was also found that the addition of small amounts of water to the solid samples greatly increases the effectiveness of the extraction. A strong positive synergism is observed when tributyl phosphate is added together with β-diketones in the fluid supercritical extraction of lanthanides and actinides with CO_2 without modification by methanol. It is important to note that no synergism with tributyl phosphate is observed when the β-diketones do not contain fluorine substituents. Thus, chemical selective complex formation processes play a key role in the universal physical fluid superextraction, as in normal liquid–liquid processes. We note a serious shortcoming of these processes from the standpoint of their application to the extraction and concentration of radioactive substances: the need to work at relatively high pressures. In this context the application of superextraction processes near the critical conditions of liquid–liquid systems (which can be realised at atmospheric pressure) could be of interest.

3. Superextraction processes near the critical conditions for liquid–liquid systems

The possible realisation of supercritical extraction processes at atmospheric pressure near the critical conditions of liquid–liquid systems was theoretically substantiated,[32] and this was also predicted on the basis of the assumed universality of the properties of substances in the critical state.[33,34] More recently a maximum in the solvent power of a binary phase-separating liquid–liquid system near the critical consolute point was observed experimentally,[35] but none was found near the critical point of a ternary mixture.[32] It was shown[36] that the enhanced solvent power of liquid–liquid phases is associated with anomalous activity coefficients under critical conditions and is a universal property of critical phases. The universality is attributed to an increased compressibility. Because of the low compressibility of liquids near the critical phase separation point of a liquid–liquid system the concentration range of the subcritical conditions is very narrow, and therefore the practical possibilities of the method are problematic.[8]

Universal superextraction is more clearly seen in liquid–liquid systems in the case of phase transitions in micellar systems 'diffuse' in concentration, or in the case of abundant phase transitions close to the second kind, as in liquid–crystalline systems.[11,37] In these cases the extraction of substances by the critical liquid phases can reach enormous proportions (up to the complete homogenisation of the phases to be extracted). The increase in the homogenisation with increasing second-order properties of the micellar system (i.e. with decreasing micelle size) is illustrated in Fig. 2. A study of the extraction of uranyl benzenesulfonate by tributyl phosphate has shown[18] that the micellar–liquid-crystalline homogenisation of this system is physically reversible because of the reversibility of the hydration. As can be seen from Fig. 5 at high concentrations of uranyl benzenesulfonate the universality region (equality of the hydration and solvation numbers) disappears, the hydration

‡ See a recently published paper by C W Wai, Y Yen, and F Jean in *Pittsburg Conf. Anal. Chem. and Appl. Spectrosc., Chicago III, 27 Febr.–March 1994, Abstr.* (Chicago, 1994) p. 127

begins to predominate over the solvation, and the highly hydrated organic substance is no longer retained by the organic phase.

By combining the universal physical effects with specific chemical effects we can use the micellar extraction processes in separation and concentration experiments. Thus, the universality of the micellar extraction can be used for concentrating materials when the wanted component (aluminium) is held in the organic phase because of the formation of a complex between aluminium and the phenol–formaldehyde oligomer at the water re-extraction stage.[38] The formation of a complex with the phenol–formaldehyde oligomer in the same micellar extraction–re-extraction process allows gallium to be selectively concentrated and separated from aluminium.[39] Obviously the role of chemical reactions in processes of universal superextraction in liquid–liquid systems at atmospheric pressure is similar to the role of specific interactions with a co-solvent in the fluid supercritical extraction processes discussed above.

4. Universal superextraction processes through a subcritical interface

A new method of exploiting the special features of the transcritical state by using the redistribution of the components through a subcritical interface in the far subcritical region (see Fig. 1) is also of interest. These processes, so far observed only in phase-separating liquid–liquid systems, takes place when the system is moved away from the critical phase separation point, and are apparently unrelated to pretransition phenomena. However, for at least two reasons [the similarity in properties and composition of phases produced by the separation of one phase (usually the aqueous) and based on the same component (water)], these processes are related to the transcritical state of matter and they can be interpreted from this point of view. Detailed studies of three-phase extraction systems have been reported.[40–45] A new type of system, containing a third liquid phase similar in composition and properties to the equilibrium water phase, has been discovered. The third phase is found in ether(diisopropyl etc.)–aqueous hydrochloric acid systems containing metal chlorides both extractable and nonextractable by ether. It was shown[44] that the third phase is formed by the 'reversible extraction' of the ether into the aqueous phase by the hydrogen chloride in the form of the hydrated ether–HCl complex, which is poorly soluble in both water and ether. The second water phase formed under these conditions can extract all the components of the equilibrium water phase (without exception, but to different extents), including those which are poorly extractable or not extractable by ether. This accounts for the closeness of the system to the critical phase separation point.

5. Extraction in three-phase liquid systems near the critical homogenisation point of two of the phases

In this case the critical phase separation point for two subcritical phases is relatively far from the conditions of the experiment, which allows adequate selectivity in the extraction of the various components. For example, the distribution coefficients in the hydrochloric acid medium are greater than 200 for iron, 2–5 for tin and zinc, about 1 for cobalt, and less than 0.1 for nickel. The distribution and separation coefficients are markedly increased by the introduction of complex-formers. Thus, the formation of mixed metal–tin–chlorine complexes with hydrated ether allows the almost complete single-stage extraction of platinum, osmium, and iridium.[42,43] An analysis of these results[40–45] leads to the formulation of two principles of three-phase extraction equilibrium under subcritical conditions.

(1) The phase-forming component (poorly soluble in the phase-separating layer and insoluble or almost insoluble in the non-phase separating layer) becomes concentrated in the third phase, formed by the phase separation of one of the two liquid phases initially at equilibrium in the far subcritical region.

(2) The third liquid phase formed under the far subcritical conditions is an extractant for all the impurities of the separating phase.

The first principle explains the effects of forming a second aqueous phase and a second organic phase in extraction systems containing tributyl phosphate: the latter phase is well known as a concentrate of metal solvate ('red oil') in systems with uranyl nitrate and tributyl phosphate in a paraffin diluent. The extent of extraction of the components into the third phase through a subcritical interface in the far subcritical region is determined by universal physical effects and by highly selective chemical effects. It should be noted that the reported[40–45] enhancement of the extraction power and selectivity of the systems in the redistribution of the components between the phases is a consequence of the location of the system in the subcritical region. This property is independent of the presence in the system of a third (organic) phase, which plays no part in the separation processes.

A similar effect was noted in a study[46–48] of the increased extraction and separation in an extraction system consisting of two equilibrium aqueous phases one of which is strongly depleted of water by the addition of poly(ethylene glycol). In these systems the poly(ethylene glycol) acts not as an extractant but as a complex-former, which allows the formation of two aqueous phases having the same main component and similar compositions. The extraction is achieved by introducing complexing agents into the system. Supplementing the weak physical selectivity effects with clearly marked chemical effects produces results similar to those found in fluid supercritical extraction, but in this case the superextraction processes takes place in the subcritical rather than in the supercritical region.

6. Changes in the character of the phase transition during the redistribution between phases on the path to the critical point

According to Landau's views[1] on phase transitions of the first kind but close to the second, and to Fisher's postulate[49] of a continuous, purely entropic process leading to phase transitions in the critical state, we can formulate some conclusions on the type of changes in the nature of the phase transitions on the path to the critical point. If the redistribution between phases is treated as a phase transition of the first kind it should develop an increasing similarity to phase transitions of the second kind as the system approaches the critical point. The writer first proposed[13] (as a hypothesis) that the role of the entropy should increase along this path, and therefore in the equation

$$\Delta G = \Delta H - T\Delta S, \tag{6}$$

the enthalpic component (ΔH) of the change in the Gibbs free energy (ΔG) should tend to zero faster than the entropy component ($T\Delta S$). Therefore the plots of ΔH and $T\Delta S$ should converge into a single adiabatic curve. If this hypothesis is valid a region of adiabatic redistribution between phases should exist on the path to the critical point (as on the path to any phase transition of the second kind). In multicomponent two-phase systems this redistribution should show a maximum selectivity and a maximum sensitivity to small entropy differences between the redistributed components. In other words a region of adiabatic selectivity of the redistribution between phases should exist on the path to the critical point in multicomponent two-phase systems. The adiabaticity hypothesis was thermodynamically validated,[50] and the adiabaticity of weak phase transitions of the first kind was confirmed in terms of the classical theory of a two-phase flux near a liquid–gas critical point. By using a series expansion of the pressure near the critical point in powers of the difference between the time-dependent and the critical volume it was shown[51] that the equation for the phase equilibrium line coincides with the equation for the critical isentrope. This conclusion confirms the hypothesis of adiabaticity of the redistribution between phases, and it also explains the inconsistency between many experimental data and the adiabaticity hypothesis.

Thus, the specific heat λ-curves near the critical point are symmetrical because of the heat of the transition.[49] Critical solutions at infinite dilution are nonadiabatic.[3] This paradox can be resolved by noting that in a general derivation[51] the conclusion can be valid only if a region in which the classical theory of critical phenomena is applicable exists near the critical point. The classical theory of critical phenomena (region of low Ginzburg numbers) may be valid for conducting liquids[2] (solutions of electrolytes, liquid metals), and also for three-phase fluid systems[52] on the path to the tricritical point. Regions of subcritical adiabaticity of the redistribution between phases can exist only in these cases.[50]

The correctness of this conclusion is convincingly illustrated by considering the energetics of micelle formation. As we know, micelle formation is a weak phase transition of the first kind,[11] and therefore a decrease in the energy steps with temperature can be regarded as an increase in the criticality of the system. As can be seen from Fig. 6, as the criticality of the system is increased a tendency for the ΔG and $T\Delta S$ curves to merge into a single adiabatic curve is found only in electrolyte solutions. Thus the experimental data confirm the theoretical limitations to the possible existence of a subcritical adiabatic binodal.

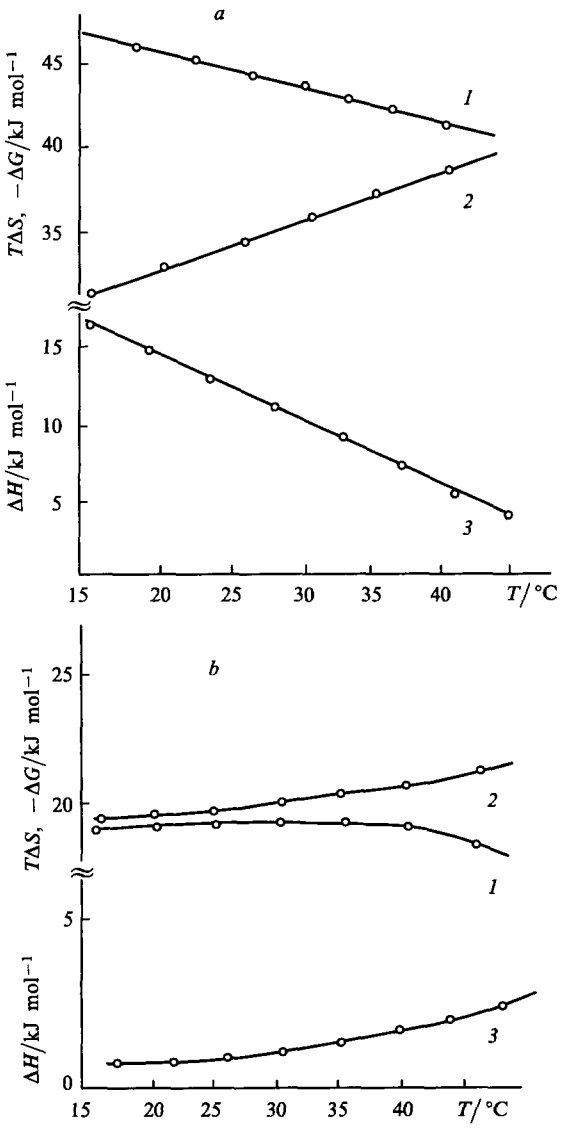


Figure 6. Temperature dependence of the trend towards adiabaticity of the micelle formation in aqueous solutions of nonionogenic SAS in the case of oxyethylated alcohol[53] (*a*) and dodecyltrimethylammonium bromide[54] (*b*): (*1*) $T\Delta S$, (*2*) ΔG, (*3*) ΔH.

7. Subcritical features of partial molar volumes and redistribution between phases

Proof of the existence of maxima in the subcritical selectivity follows from an analysis of the changes in the partial volumes on the path to the critical point. The relationship between extrema in the partial molar volume and in the solubility in critical phases was discussed above, including the simplest case of the solubility of a liquid in a gas.[7] For the far subcritical region it can be shown that because of the asymmetric location of the critical point relative to the coexistence curve we can expect extrema in the partial molar volume $\bar{v}$ and in the corresponding redistribution between phases.[50-55] As is shown in Fig. 7, in volume–composition coordinates the spinodal on the path to the critical point is tangential to a perpendicular to the composition axis at the point R. This point should correspond to an extremum in the partial molar volume $\bar{v}$. This statement becomes self-evident if in the condition for an extremum in the partial molar volume,

$$\left(\frac{\partial \bar{v}_2}{\partial x_2}\right) = 0,$$

$\bar{v}$ is replaced by the derivative of the chemical potential μ_2 with respect to pressure, and the order of the differentiation is changed,

$$\left(\frac{\partial \bar{v}_2}{\partial x_2}\right)_{P,T} = \left[\frac{\partial}{\partial P}\left(\frac{\partial \mu_2}{\partial x_2}\right)_{P,T}\right]_{x_2,T} = 0, \qquad (7)$$

(the subscript 2 denotes a dissolved substance). The condition (7) means that the $(\partial\mu_2/\partial x_2)_{P,T} = 0$ curves are independent of composition at the $\bar{v}$ extremum, i.e. they are tangential to a perpendicular to the composition axis. The spinodal $(\partial\mu_2/\partial x_2)_{P,T} = 0$ is a special case of these curves, and therefore it should also be tangential to the composition axis[50,55] at a point in the $\bar{v}$ extremum. This conclusion has a general thermodynamic significance: the extremum is due to the asymmetry in the position of the critical point on the binodal, and the asymmetry itself is a consequence of the failure of the critical points of the pure components to coincide. Furthermore, in liquid–liquid systems the critical points are usually located asymmetrically on

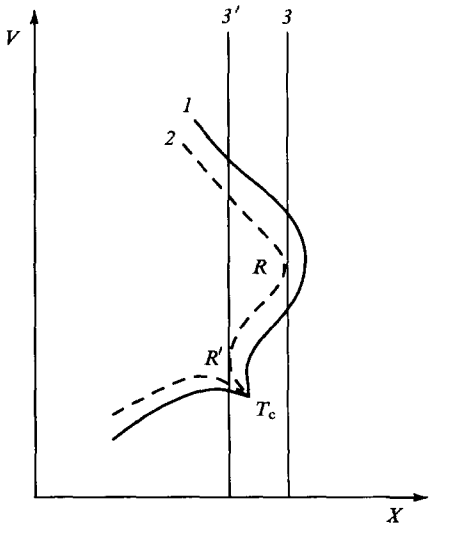


Figure 7. Asymmetry of the position of the critical point on the coexistence curve (*1*), making the spinodal (*2*) tangential to the perpendiculars to the composition axis in volume (V)–composition (X) coordinates at the extremal points R and R' in the far and the near subcritical region respectively (*3* and *3′* are the perpendiculars to the composition axes).[50]

the coexistence curve. The only exception is the rare case of a unit Hundt coefficient.[56] It is important to note that the solubility extrema are an individual characteristic of any binary system. Accordingly, in a multicomponent system the extremum points of the solvent power characterise the region of maximum selectivity in the solvent power of one phase with respect to the components of the other phase. This maximum is associated with the presence of extrema on the coexistence curve, and in general it can be located relatively far from the critical point, in the far subcritical region. However, the presence of extrema in the spinodal, at which the curve is tangential to a perpendicular to the composition axis in volume–composition coordinates (see Fig. 7), and its thermodynamic consequences regarding the distribution between phases, can be noted not only in the far but also in the near subcritical region, in which the theory predicts a singularity of the coexistence curve and of the associated spinodal.[57] The slope of the coexistence curve in the classical region near the critical point is one of the fundamental characteristics of any binary system.[58] The transition to universality (subcritical singularity) again confirms the validity of our proof of the presence of a maximum in the adiabatic selectivity of the subcritical redistribution between phases. The existence, under these conditions, of a region in which the spinodal is tangential to the perpendicular to the composition axis is a geometric necessity, as it is in the far critical region (see Fig. 7). Accordingly, in multicomponent two-phase systems two maxima in the subcritical selectivity should be found on the path to the critical point (in the far and in the near subcritical region respectively).[50]

8. Degree of generality of the predicted features of the transcritical selectivity of the redistribution between phases

According to Cahn[59] the bulk properties of the equilibrium phases in the subcritical region vary in the same sense as their surface properties. By developing and generalising this statement we may conclude that the regions of special features of the surface and of the bulk properties on the path towards the critical point are mutually related: in all cases the regions of changes in the wetting properties correspond to regions of adiabatic selectivity, and vice versa. In particular, in three-phase systems we should observe a maximum selectivity of the extraction into the wetting phase (for an adiabatic redistribution between phases) in the region of Cahn transitions from non-wetting to wetting of the α and β phases by the intermediate phase γ.

The general character of the predicted features is shown in Fig. 8. It can be seen that the curves describing the components of the thermodynamic potential for weak phase transitions of the first kind on the path to the critical path along the coexistence curve are in a symmetrical correspondence with the Nernst heat theorem.[60,61]

However, we should stress the fact that the generality of a subcritical adiabatic selectivity is limited to the case of classical subcritical fluids, i.e. to the existence (on the path to the critical point) of a region in which the classical theory of critical phenomena is applicable. The presence of two (rather than one) regions of subcritical adiabatic selectivity of the phase redistribution in multicomponent systems is also important. This assertion is also confirmed (in terms of the concepts considered here) by the experimentally observed sequence of Cahn transitions on the path to the critical point,[23] possibly related to the presence of several points of intersection of the ΔG and $T\Delta S$ curves in Fig. 8.

The regions of maximum separation (like the regions of the wetting transitions) can be far removed from the critical point along the coexistence curve. Thus, Cahn transitions have been observed several tens of degrees below the critical point.[23] By developing and generalising Cahn's views on the correspondence of surface and bulk properties, we may conclude that a well defined selectivity maximum with almost complete extraction of one of the components, and negligibly small extraction of the others, from the aqueous phase into propane has been observed in this region of Cahn transitions for the fluid extraction of various dyes in the presence of an aerosol of OT (sodium di-2-ethylhexylsulfosuccinate) at 25 °C, i.e. several tens of degrees from the critical point of propane (96.7 °C).[61] In this same region the homogenisation of the two-phase propane–OT aerosol–water system has been observed[62] under conditions which (like the selectivity conditions) depend strongly on the pressure. In this region we are dealing with physical superextraction, but since this superextraction takes place in a subcritical (rather than a critical) phase on the path to the critical point its universality is combined with universality of the maxima in the physical selectivity of the subcritical redistribution between phases whose existence has been predicted,[13] thermodynamically validated,[50] and experimentally demonstrated.[62]

The maximum in the selectivity of the phase redistribution through a subcritical interface into a transcritical region corresponds to the maximum in the selectivity of the extraction of the components of noncritical phases into a supercritical phase through a noncritical interface, i.e. under conditions of normal fluid supercritical extraction (Fig. 9). The existence of this maximum is illustrated in Fig. 9 for the fluid supercritical extraction of terpenes by carbon dioxide.[63] We note that in every case the selectivity maxima are located on the path to the critical path but not in its immediate vicinity. The presence of selective extraction in the region of the pretransition phenomena discussed in modern theories would be fundamentally incompatible with the modern theory of critical phenomena, one of whose main conclusions is the universality of the properties of matter

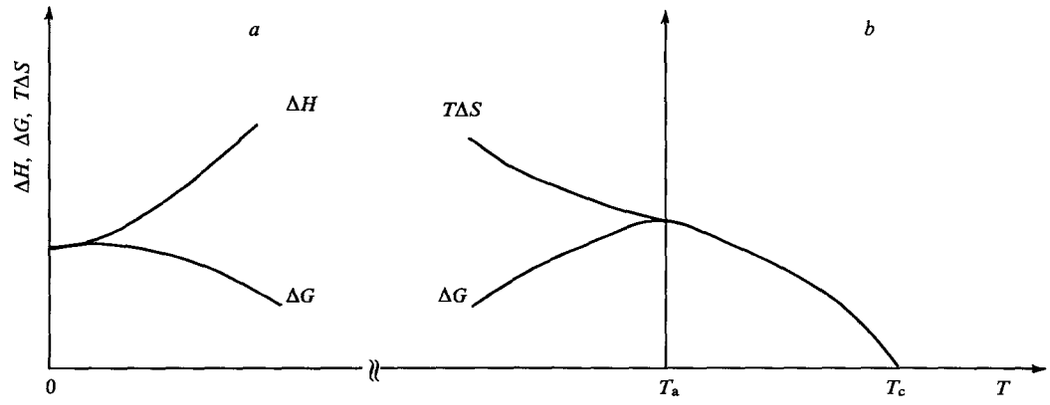


Figure 8. Symmetry of the Nernst heat theorem (*a*) and of the universal subcritical adiabaticity of the redistribution between phases in classical subcritical fluids (*b*). T_c is the critical temperature, T_a is the temperature of the transition to adiabaticity.

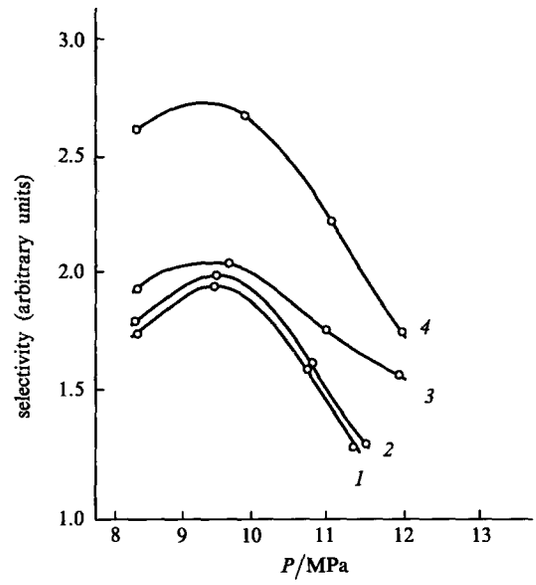


Figure 9. Selectivity in the supercritical region against pressure at different temperatures for the extraction of terpenes by CO_2 (see Ref. 63). (*1*) 40 °C, (*2*) 50 °C; (*3*) 60 °C, (*4*) 70 °C.

under these conditions. This conclusion has been confirmed experimentally[64] by showing that in equilibria between critical and ordinary phases dissolved substances are found in the phases in the same proportions. Another important conclusion is that in both regions of maximum transcritical selectivity (subcritical and supercritical) weak manifestations of universal physical selectivity can be enhanced by marked specific (chemical) effects due to selective complex formation. This is observed also in well known fluid supercritical extraction processes, and in recently described fluid subcritical superextraction processes.

IV. Possibility of subcritical selectivity in ultramicroheterogeneous systems

To conclude this phenomenological discussion of the features of transcritical superextraction we shall make one more observation concerning ultramicroheterogeneous subcritical systems. Wetting transitions accompanied by adiabatic and highly selective redistribution between phases should be found also in ultramicroheterogeneous liquid–liquid and liquid–gas systems on the path to a 'pure' phase transition of the second kind. Indeed, as long as the concept of an interface is meaningful in an ultramicroheterogeneous system it can be treated as a nominal 'wall' (C) with an equilibrium angle of contact, to which Young's law applies:

$$\sigma_{1,2}\cos\theta = \sigma_{1,3} - \sigma_{2,3}. \tag{8}$$

Following Cahn's approach[59] we shall assume that on the path to a 'pure' phase transition of the second kind the different between the interfacial energies $(\sigma_{1,3} - \sigma_{2,3})$ is determined mainly by the compositions of the equilibrium phases (J), and is dependent on temperature as is $(\varphi_2 - \varphi_1)$, i.e. in accordance with the universal scaling relation

$$(\varphi_2 - \varphi_1) \sim t^{\beta}, \tag{9}$$

where β is the critical index, equal to 0.33. On the path to a phase transition of the second kind, as on the path to the critical point, we can use the universal relationship

$$\sigma_{1,2} \sim t^{\mu}, \tag{10}$$

where μ is the critical index, equal to 1.26. From (8)–(10) we find

$$\cos\theta \sim t^{(\beta-\mu)}; \quad \beta - \mu = -0.93. \tag{11}$$

According to Eqn (11) the maximum wetting in a ternary two-phase ultramicroheterogeneous system should be observed at some distance from the phase transition of the second kind, i.e. on the path towards the phase transition, as in the wetting transitions on the path to the critical point in Cahn's original work.[59]

We can arrive at the same result by treating any third component as a nominal 'wall'. In this case on the path to a 'pure' phase transition of the second kind we find a maximum in the wetting of this component, and therefore also a maximum in the adsorption of its ultramicroheterogeneous particles. Since (at least, in three-component systems) the wetting phase is thermodynamically unstable (allowing for possible changes in the masses of the phases) it acts as the extracting phase. The combination of the maximum wetting and the maximum sorption points for various components defines the region of maximum selectivity.[50] Under these conditions the phase redistribution should be approximately adiabatic. In particular, this should be observed near adiabatic micelle formation transitions (see Fig. 6*b*).

V. Chemical reaction in the extractant phase and supercritical extraction into this phase

1. Chemical reaction and the critical phase

As reported,[3] in a critical solution in CO_2 at infinite dilution the apparent constant of the chemical dimerisation reaction ($2NO_2 = N_2O_4$) in the critical phase increases, and tends (if not to infinity) to a finite nonzero value. The thermodynamic dimerisation constant is expressed in terms of the chemical potentials, and therefore it cannot have singularities at the critical point (since the chemical potentials can have singularities only in their higher derivatives[2]).

A similar statement applies to the experimental data (discussed by Tveecrem et al.[65] and interpreted by this author[36]) on the dimerisation of nitrogen dioxide near the liquid–liquid critical point in the perfluorocyclohexane–carbon tetrachloride system. These data suggest the presence of singularities in the activity coefficients under critical conditions. It was shown that the data,[65] however interpreted, confirm the presence of superextraction in the liquid–liquid system near its critical phase separation point. On the other hand the apparent decrease in the rate constant of the chemical reaction under critical conditions is associated not only with anomalies in the activity coefficient but also with the tendency of the diffusion coefficients to vanish under critical conditions.[66]

Thus in micellar systems, in which criticality (fluctuation) conditions are found on the micelle surface rather than in the bulk of the phase, we observe an acceleration of chemical reactions ('micellar catalysis'[67,68]). But the problem of correlating chemical reactions and phase transitions has also other aspects. Thus, the polymerisation of sulfur in many organic solvents leads to the appearance of a new critical phase separation point.[69] Chemical reactions have a similar effect on phase transitions in H-bonded systems. Corrales and Wheeler[69] have examined theoretically other possible types of interaction between chemical reactions and phase transitions (not yet observed experimentally), in which the reaction acts as the driving force of the phase transition.

The possibility of stabilising (or, more strictly, metastabilising) the critical state by inducing a relatively slow chemical reaction in the homogeneous metastable critical phase has been pointed out.[70]

2. The chemical reaction as a weak phase transition of the first kind

The most interesting aspect of the interaction between chemical reactions and phase transitions of the second kind (or critical phenomena) is seen by treating the chemical reaction in the vicinity of the position of equilibrium (the equivalence point) as a

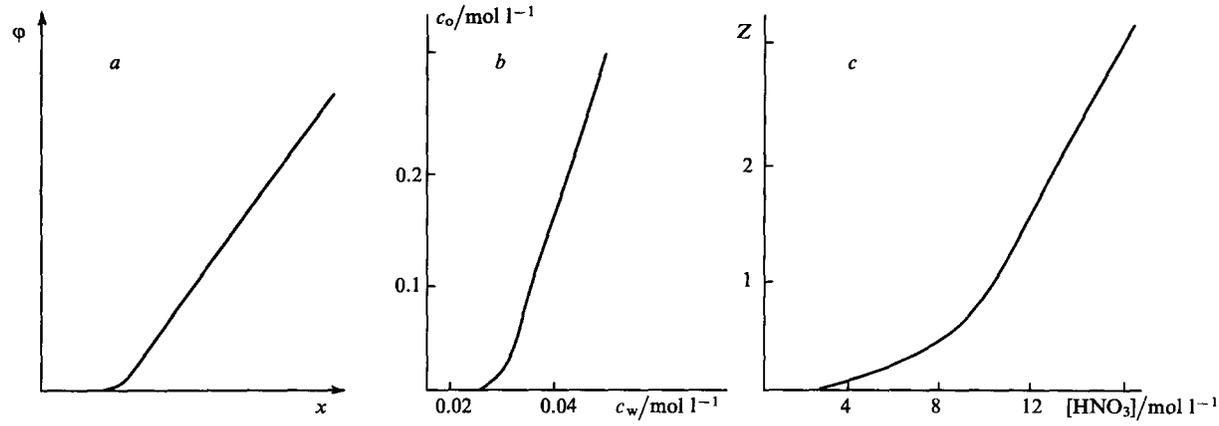


Figure 10. Plots of the concentration of monomers combined into micelles (φ) against the total concentration of monomers x (*a*); of the concentration of copper in the organic phase against its concentration in the aqueous phase in the micellar extraction by tetrachloromethane (*b*); of the concentration ratio of nitric acid and the tributyl phosphate solvate of uranyl nitrate in the organic phase (Z) against the concentration of nitric acid in the aqueous phase in the extraction of nitric acid into the tributyl phosphate solvate of uranyl nitrate (*c*). *a* and *b* from Ref. 11, *c* from Ref. 76.

weak phase transition of the first kind or as a special type of phase transition with marked second-order features. This problem has been examined theoretically[71,72] for the simplest one-dimensional model by studying reactions of the type

$$A \rightarrow X,$$

$$B+X \rightarrow Y+D,$$

$$2X+Y \rightarrow 3X_1,$$

$$X \rightarrow E.$$

It was assumed that the reactions take place near the equilibrium position. Features of transitions of the second kind were detected in the reactions by the reduced perturbation method.

By using Landau's theory it was shown[73] that a chemical reaction can be treated as a phase transition of the second kind even in regions far from equilibrium.

Published data on the superextraction by micellar liquid–crystalline alkylphenol phases at neutral pH values of all the components of conjugated phases are consistent with these theoretical considerations, according to which any manifestation of transitions of the second kind should lead to superextraction in the phase. These results were interpreted[10,11,17] as an indication of supercritical extraction at atmospheric pressure. It was also shown[74,75] that the extraction by metal solvates with tributyl phosphate and other organic extractants produces superstoichiometric supersaturation of the organic phase. The same workers[74,75] have treated the extraction of nitric acid by tributyl phosphate as a physical phenomenon. Rozen and Andrutskii[76] have pointed out the weakness of these conclusions[74,75] on the dimerisation of nitric acid in an organic phase. The formation in the organic phase of mono-, di-, tri-, and tetrasolvates of nitric acid was postulated in order to explain the observed phenomena. However, in this variant four empirical constants are needed to account for the almost linear extraction isotherm (without any indication of saturation) inferred[76] from the published data[74,75] for the dependence of the extraction of nitric acid into the tributyl phosphate solvate of uranyl nitrate on the concentration of nitric acid in the aqueous phase. But it has been shown[10] that similar isotherms without any indication of saturation are observed for micelle formation described as a phase transition of the second kind,[77] and also in the micellar extraction of copper dibutyl phosphate by tetrachloromethane.[10,18]

It can be seen from Fig. 10 that the special features of micelle formation, micellar extraction, and extraction by metal solvates are similar: the extraction into the organic phase shows no sign of saturation (i.e. of a horizontal asymptote for the isotherm). The micelle formation isotherm observed as a phase transition of the first kind which is close to the second kind has exactly the same shape. This experimental fact agrees well with the assertion[78] that many phenomena traditionally treated as chemical are in fact physical effects (in this case effects of universal physical superextraction at atmospheric pressure). The mechanism of this process is still unclear: is it due to a transition of the second kind or (as suggested[79]) is it an experimental observation of anisotropy in the solvates, caused by liquid-crystalline transitions? In any case it is clear that we are dealing with supercritical extraction at atmospheric pressure, but if this extraction is induced by second-order features of a chemical reaction the extractant can be any solvate or other chemical compound in the organic phase, and salts of any metal can be the extracted salts. On the other hand if the superextraction takes place because of the second-order properties of liquid-crystalline transitions only mesogen molecules can be the extractants.

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