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The Selection of Azeotropes at Ambient Pressure Drying of Aerogels

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The representation of phase states in the multicomponent systems by graphical images is used for estimation of the LV ($x_L = x_V$) azeotrope influence on SLV and $L = V$ equilibria. These theoretical investigations occurred from complications arising at an ambient pressure drying (APD) synthesis of transparent and crack-free bulk silica aerogels. During the empiric selection of azeotropic mixtures, the negative azeotropes advantage over positive ones for this goal is determined and substantiated in theory. As shown, the forecast must base not only on the critical points of components ($L = V$), in which liquid and vapour become indistinguishable, but also on the triple points of components (SLV —crystal—liquid—vapour). Using the P – T – x phase diagrams, the prediction of ways to reach a supercritical region at the ambient pressure is done. A good agreement between the theoretical results and experimental data is revealed.

Представлення фазових рівноваг у багатокомпонентних системах методом графічного зображення використовувалося для оцінки впливу азеотропу LV ($x_L = x_V$) на рівноваги SLV та $L = V$. Дані теоретичні дослідження виконувалися через виникнення ускладнень при синтезі прозорих і бездефектних кремнійових аерогелів способом атмосферного сушіння (APD). При емпіричному відборі азеотропних сумішей було визначено і теоретично обґрунтовано перевагу використання негативних азеотропів над позитивними задля зазначеної мети. Показано, що прогноза має бути основою не лише на критичних точках компонентів $L = V$, в яких рідина і пар стають нерозрізненими, але й на потрійних точках компонентів SLV (кристал—рідина—пар). У даній роботі з використанням P – T – x -фазових

діяграм показано можливість досягнення надкритичної області за атмосферного тиску. Виявлено хорошу відповідність між теоретичними та експериментальними результатами.

Представление фазовых равновесий в многокомпонентных системах методом графического изображения использовано для оценки влияния азеотропа LV ($x_L = x_V$) на равновесия SLV и $L = V$. Данные теоретические исследования выполнялись по причине возникновения сложностей при синтезе прозрачных и бездефектных кремниевых аэрогелей способом атмосферной сушки (APD). При эмпирическом отборе азеотропных смесей определено и теоретически обосновано преимущество использования негативных азеотропов над положительными для этой цели. Показано, что прогноз должен быть основан не только на критических точках компонентов $L = V$, в которых жидкость и пар становятся неразличимыми, но и на тройных точках компонентов SLV (кристалл–жидкость–пар). В данной работе с использованием P – T – x -фазовых диаграмм показана возможность достижения сверхкритической области при атмосферном давлении. Обнаружено хорошее соответствие между теоретическими и экспериментальными результатами.

Key words: nanostructures, sol–gel synthesis, azeotrope, critical point.

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1. INTRODUCTION

The remarkable material, nanostructure silica aerogel, was first created by S. Kistler in 1931 [1] but saw just a little development for these years. Wide applications of this material that possess high specific surface area, high porosity, low density, low dielectric constant, and excellent heat insulation properties [2, 3], terminates complications of its production. There are many research works concerning aerogel properties and manufacture. The most attention is paid to drying of aerogels to make the production of these materials more profit making.

Common procedure for transparent silica aerogels production in our case included two-step sol–gel process using tetraethyl orthosilicate (TEOS) (Aldrich, USA), as a silica precursor and isopropanol (Junsei, Japan) as a solvent. Isopropanol was exchanged than with *n*-butanol (Junsei), and the gel surface was modified using 5% volume solution of trimethylchlorosilane (TMCS) (Alfa Aesar) in *n*-butanol. Next, the solvent was exchanged in some steps with binary azeotropes like pore fluids.

Actually, the process of aerogels obtaining by azeotropic mixtures evaporation on the final stages of ambient pressure drying has not been reported in the literature. Authors [4] used the water–ethanol azeotrope as the solvent just in prime stage of synthesis for the production of low-density silica gel. This material was prepared by the classical two-step sol–gel method developed by Deshpande, Brinker and Scherer

[5, 6], which includes the ambient pressure drying stage. This process demonstrated the existence a greater total pore volumes and more mesopores $> 50 \text{ \AA}$ in samples in comparison with the supercritical drying one. The main purpose of the azeotrope using [7] was to bind water inside pores after sol–gel process, because their appearance finally leads to increasing of the capillary pressure and then, during the thermal drying, to the cracking of aerogels.

Authors of [8] used azeotrope mixtures of water and *n*-butanol-saturated hydrocarbon (hexane, heptane, octane or nonane) for the first time on the stage of washing. In three steps, gels were washed successively with a 3:1 mixture of *n*-butanol and a saturated hydrocarbon, with a 1:1 mixture of *n*-butanol and a saturated hydrocarbon, finally, with only the saturated hydrocarbon. *Per se*, they had used azeotrope water, which necessarily remains inside of aerogel pores after sol–gel process. Further, in the process of the choice of other suitable azeotropic mixtures, first we could attempt to predict ways to get in a supercritical region at ambient pressure. Physical properties data of azeotropic mixtures were given from Azeotrope Databank by J. W. Ponton and by book of John A. Dean [9]; we used the results of investigations of the negative azeotrope for the methanol–propanal system in the methanol-rich region [10].

2. THEORY

This prediction was made using the well-known method of the phase diagrams, which is the graphical representation of the equilibria between the thermodynamically distinct phases. The main design principles were created by Van der Waals [11]. Then, this method was highly developed and it is a very powerful tool for predicting the state of a system under different conditions [12]. It was determined with the accumulation of experimental material that the prognosis can be based not only on the critical points of components, in which liquid and vapour become indistinguishable, but also on the triple points of components at which three phases (solid, liquid and vapour) of that substance coexist in thermodynamical equilibrium. In most cases, the phenomenon of azeotropy [13] is examined only within the framework of the liquid–vapour equilibrium *LV* and its characteristic features. Usually, there are extremes on the $T-x$ isobars of the boiling or on $P-x$ isotherms of the evaporation. In addition, the interaction between azeotropic and solid–liquid equilibria *SL* for several binary organic systems was investigated [14]. It was just the partial investigations, but for the extensions of thermodynamic models, a reliable knowledge of the phase equilibria behaviour as a whole is required. The experimental determination of the gas solubility in the liquid phase along the *SLV* solid–liquid–vapour equilibrium line of some binary system was established, and these data plotted as $P-T$ and $T-x$

projections of the SLV -equilibrium line [15].

However, within the framework of the P – T – x -phase diagram of the binary systems (where P —pressure, T —temperature, x —an independent co-ordinate of composition), the contiguity line of liquid L and vapour V surfaces corresponds to the LV azeotrope (more precisely $x_L = x_V$). This line does not need to be a straight line; furthermore, it is a segment, limited from one side by the surface of SLV monovariant equilibrium of crystal–liquid–vapour, and from the other side, in the simplest case, by the $L = V$ curve, connecting the critical points of pure components. The most obvious case relates to the P – T projection of P – T – x phase diagram. If layering of liquid and equilibrium with participation of the crystalline phase and fluid is absent, the azeotrope $x_L = x_V$ is enclosed between VLS (SLV) and $L = V$ lines (see Fig. 1). Certainly, the presence of azeotrope influences VLS (SLV) and $L = V$ line shapes. From the other side, the existence of extremes on these lines is necessary, but insufficient condition for existence of the azeotrope. We would set constant P , T co-ordinates for the triple and critical points of components A and B , and examine the interrelation of the azeotrope $x_L = x_V$ on the SL monovariant line and the $L = V$ critical curve.

3. RESULTS AND DISCUSSION

We can use, for the convenience, P – T projections and T – x key isobaric sections for the analysis of different variants. We should take into the consideration the fact that order of phases at the heterogeneous equilibria is very important and agree that it will be certain increase of the B component content.

I. The positive azeotrope appears in the A – B system and components are mutually soluble without restriction in all of phase states.

A and B triple points for pure components, also K_A and K_B critical points are marked on the P – T projection (Fig. 1, a). The positions of critical points are specially chosen [11].

AK_A and BK_B lines correspond to evaporation of liquids based on pure components. Lines going out from A and B points straight up to the direction of high temperatures represent the melting, and the ones move away to the direction of low temperatures correspond to the sublimation of crystals based on pure components. The AB curve is the only monovariant line of binary system and consists of two parts: AN_{LV} , with the LVS order of phases, and BN_{LV} , with the VLS order of ones. In the N_{LV} conditional non-variant point, being near to P_{\max} , a maximum of pressure of the monovariant curve, compositions of liquid and vapour are identical, and from it, the $x_L = x_V$ line of azeotrope begins, which is stopped in the K_{AZ} critical point placed near-by a maximum of pressure of the $K_A K_B$ critical curve.

Dashed lines on the P – T projection (Fig. 1, a) are imaged isobars and

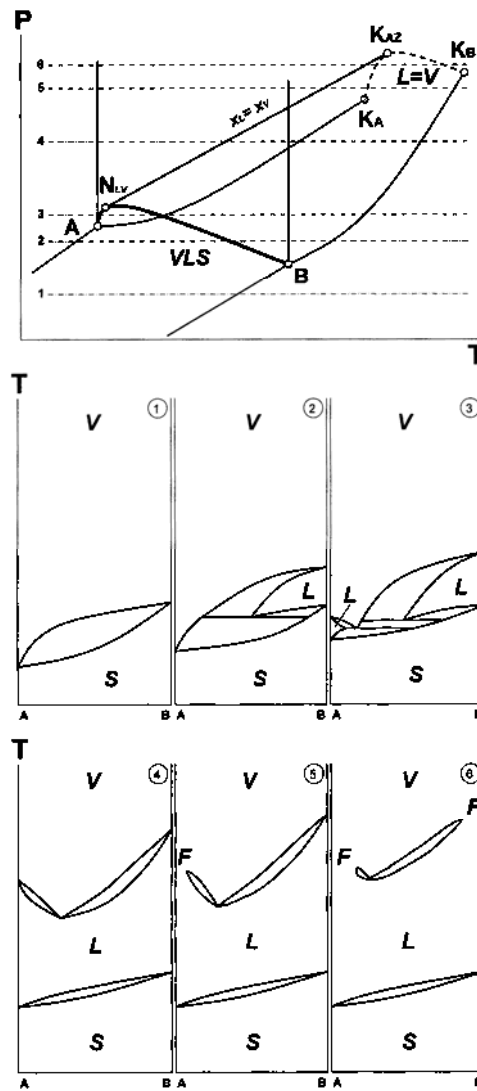


Fig. 1.

their proper $T-x$ isobaric sections (Fig. 1, b). Let us consider six key isobars.

1. There is only the sublimation of the continuous solid solution S at $P_1 < P_B$ and, in the same time, vapour V enriched by the B component.

2. The solid solution S begins to melt from the $P_B < P_2 < P_A$ interval at constant pressures, area of liquid L , enriched by the B component, appears on the $T-x$ section and the node of the VLS three-phase equilibrium arises.

3. Due to the melting of the solid solution on basis of the A compo-

nent, the second local area of liquid L and another LVS node appear in $P_A < P_3 < P_{NLV}$ interval.

4. Finally, typical $T-x$ isobars for positive azeotropes with a minimum of the pressure in the LV equilibrium appear at $P_{NLV} < P_4 < P_{KA}$.

5. With the further increasing of pressure, fluid F appears at the beginning, for compositions enriched by the A component in the interval $P_{KB} < P_5 < P_{KAZ}$.

6. Then, fluid F appears for compositions enriched by the B component under achievement the $P_{KB} < P_6 < P_{KAZ}$ interval of pressure.

Further, with the growth of pressure, areas of fluids extend, but, firstly, the minimum disappears at P_{KAZ} , and then, at P_{max} , the equilibrium LV disappears for $K_A K_B$, and the area of fluid F becomes continuous.

Evidently, in the case of positive-azeotropes using, it is possible to reach the fluid area only at pressures higher than P of the critical points of constituent components.

II. The positive azeotrope appears in the $A-B$ system and components restrictedly mutually soluble in the crystalline state.

It should be noted that triple and critical points for pure components remain on the $P-T$ projection (Fig. 2, *a*), and, accordingly, some lines are stored too: the evaporation, the melting and the sublimation lines for pure components, and the $K_A K_B$ critical curve. There are four monovariant lines: $S_A LV$, VLS_B , $S_A VS_B$, and $S_A LS_B$ appeared in place of one monovariant line of the two-component system. The mutual solubility in the crystalline state is insignificant; therefore, vapour pressure in the $S_A VS_B$ equilibrium is an additive summation of vapour pressures for pure components. The invariant equilibrium in the $N(S_A VLS_B)$ point has the eutectic character and the $x_L = x_V$ azeotrope line starts in the N_{LV} invariant point on the AN line. There is the change of the order phases $S_A LV \Leftrightarrow S_A VL$ in the N_{LV} point, which is near-by a maximum of the pressure. We can analyse $T-x$ -isobar sections (Fig. 2, *b*).

Similar to the previous case (Fig. 1, *a*), the dashed lines mark isobars on the $P-T$ projection, and their $T-x$ -isobaric sections are resulted on (Fig. 2, *b*).

1. There is only the sublimation of the S_A and S_B limited solid solution at $P_1 < P_B$. There is the only $S_A VS_B$ node.

2. The solid solution based on the B component begins melting at constant pressures from the $P_B < P_2 < P_A$ interval and, accordingly, the area of liquid L , enriched by the B component, appears on the $T-x$ -isobaric section. Furthermore, another node of the VLS_B three-phase equilibrium appears.

3. The second local area of liquid L , due to the melting of the solid solution based on the A component, and the third node $S_A LV$ appear in the $P_A < P_3 < P_N$ interval.

4. Finally, $S_A VS_B$ and VLS_B equilibria disappear and $S_A LS_B$ and $S_A VL$ ones appear in the $P_{NLV} < P_4 < P_{KA}$ interval due to the presence of the

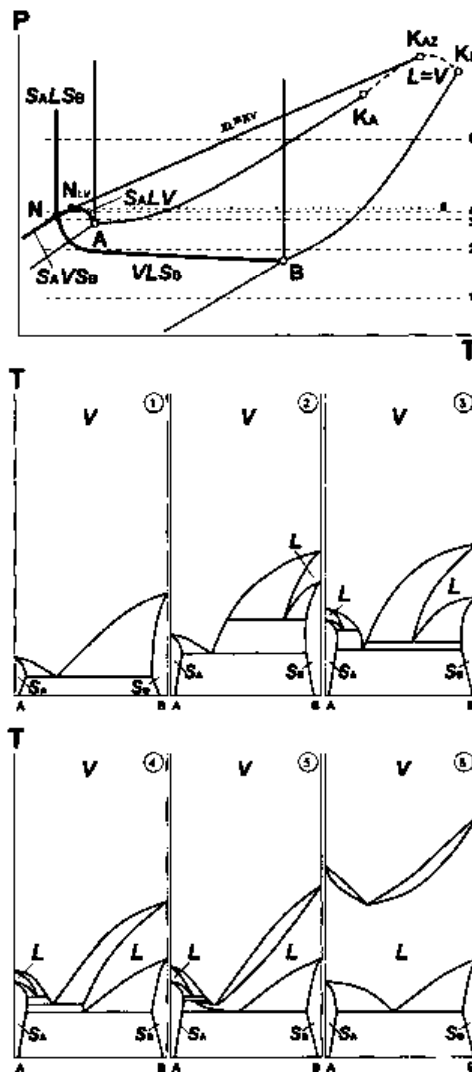


Fig. 2.

$x_L = x_V$ azeotrope.

5. An interesting $T-x$ isobar exists in a very narrow interval of pressures. At the further increasing of the pressure in the $P_{NLV} < P_5 < P_{max}$ interval, two nodes are realized with the same order of phases $S_A L V$, and a minimum of the pressure appears in the $L V$ divariant equilibrium.

6. Then, the $T-x$ isobar acquires characteristic for the positive azeotropes shape with a minimum of the pressure in the equilibrium at the $P_{NLV} < P_6 < P_{KA}$ interval. Unlike the cross-section (Fig. 1, b, 6), fusion is in the equilibrium not with the continuous solid solution, but with two

limited ones on basis of A and B components.

Further, the areas of fluids are broadening with the growth of the pressure, and in the beginning, at P_{KAZ} , a minimum disappears, and then, at P_{\max} for $K_A K_B$, the LV equilibrium disappears, and the area of fluid F becomes continuous.

Then, fluid F appears with growth of pressures for compositions enriched by the A component, then for compositions enriched by the B component, and, finally, the area of fluid F becomes continuous (Fig. 1).

III. The negative azeotrope appears in the A – B system and components mutually soluble without restriction in all of the phase states.

Existence of the negative azeotrope, in this case, is related to the presence of a minimum of the pressure (P_{\min}) on the monovariant AB curve [3]. More complex variant (Fig. 3, a), with P_{\min} and T_{\max} on the AB curve has shown on P – T projection. The monovariant line consists of three parts: AN_{LV} with the VLS order of phases, $N_{LV}N_{SV}$ with the LVS order of ones, and BN_{SV} with the LSV order of phases. Compositions of liquid and vapour are identical in the N_{LV} conditional invariant point, and the $x_L = x_V$ azeotrope line of the azeotrope begins from this point. Compositions of crystal and vapour are identical in the N_{SV} conditional invariant point, and the $x_S = x_V$ line of the congruent sublimation of crystal begins from this point, get-away toward low pressures. The condition of obligatory congruent sublimation of binary crystals explains the statistical predominance of positive azeotropes (Fig. 1), in which this condition is absent, in the comparison with negative ones.

Let us consider key T – x isobars (Fig. 3, b , 1–6).

1. There is only the congruent sublimation of the continuous solid solution S in the absence of liquid L at $P_1 < P_{NLV}$.

2. The local area of liquid L , capable to evaporate, appears from the $P_{NLV} < P_2 < P_{NSV}$ interval at the constant pressures. At the same time, there are two azeotropes: along with the congruent sublimation of the solid solution S , there is the congruent evaporation of liquid L , richer in the A component. There are the VLS and LVS nodes of the three-phase equilibria.

3. The solid solution S halts the congruent sublimation in the $P_{NSV} < P_3 < P_B$ interval, and for the high-temperature node, it changes the order of phases to LSV on the T – x cross-section.

4. The pressure of the B triple point ($P_B < P_4 < P_A$) is exceeded and the area L spreads to the B component.

5. T – x -isobars with a minimum of pressure in the LV equilibrium, characteristic for negative azeotropes, appear at $P_{NLV} < P_5 < P_{KAZ}$.

6. The $(T-x)_6$ isobar ($P_{KAZ} < P_6 < P_{KA}$) holds the greatest interest, because fluid F appears in the wide interval of concentrations, at pressures below the critical points pressures for pure components.

At the further increase of the pressure ($P_{KA} < P < P_{KB}$), fluid F first spreads to the A component, and then, under reaching the $P > P_{KB}$ in-

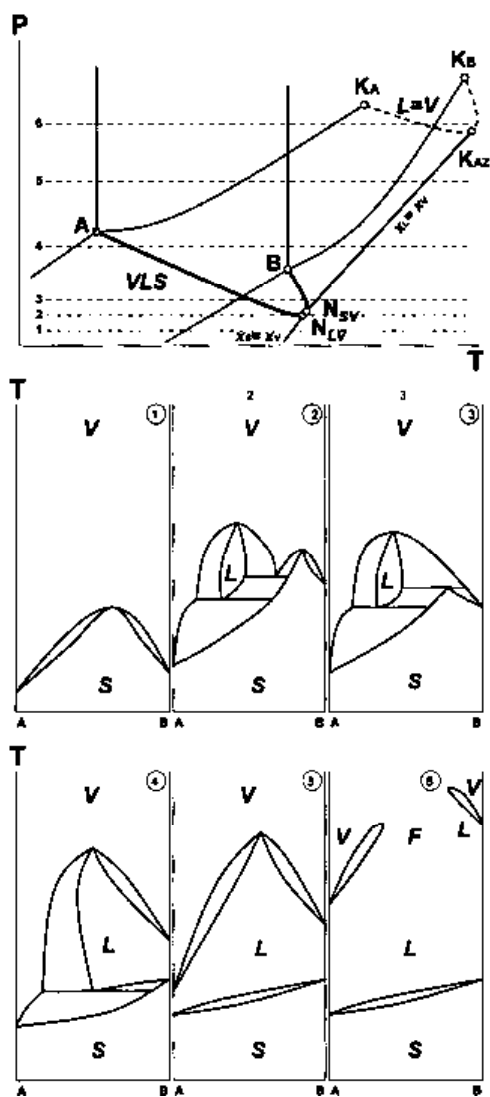


Fig. 3.

terval, the area of fluid becomes continuous.

The systems with the limited mutual solubility in the crystalline state and the systems, in which compounds appear, are of particular interest.

IV. The negative azeotrope and the crystalline phase based on the *AB* compound, which sublimates and melts congruently, appears in the *A-B* system.

On the *P-T* projection (Fig. 4, *a*), except for the triple and critical points for pure components, invariant points of eutectic equilibria are

present: N_1 ($VS_A LS_{AB}$) and N_2 ($S_{AB} LS_B V$), and N_{LV} , N_{SV} , N_{SL} conditional invariant points. Accordingly, the monovariant lines appear. Two of them are co-sublimation of two crystalline phases $VS_A S_{AB}$ and $S_{AB} S_B V$ (get-away toward low pressures from N_1 and N_2), also $S_A LS_{AB}$ and $S_{AB} LS_B$ co-melting lines (vertical ones spreading toward high pressures from N_1 and N_2), and three lines of crystal-liquid-vapour: AN_1 ($VS_A L$), $N_1 N_2$ (VLS_{AB}) and BN_2 ($LS_B V$). The $N_1 N_2$ monovariant line with the change of phases order: $VLS_{AB} \leftrightarrow VS_{AB} L \leftrightarrow S_{AB} VL \leftrightarrow S_{AB} LV$ in points N_{SL} , N_{SV} , and N_{LV} , from which $x_{SAB} = x_L$, $x_{SAB} = x_V$, and $x_L = x_V$ azeotropes lines start, is of particular interest.

Mutual solubility of A and B components in the crystalline state is insignificant. We can consider T - x -isobaric sections (Fig. 4, b).

1. There is the incongruent sublimation of S_A and S_B limited solid solutions, and the congruent sublimation of the S_{AB} binary crystalline phase at $P_1 < P_{N_2}$. There two nodes exist: $VS_A S_{AB}$ and $S_{AB} S_B V$.

2. The solid solution, rich in the A component, begins to melt at constant pressures from the $P_{N_2} < P_2 < P_B$ interval. The area of liquid L appears and instead of the $S_{AB} S_B V$ node $S_{AB} LS_B$, $LS_B V$ and $S_{AB} LV$ nodes appear on the T - x section.

3. The area of liquid L spreads to B component, and the $LS_B V$ node disappears in the $P_B < P_3 < P_{N_1}$ interval.

4. Then, liquid L rich with the B component begins the congruent evaporation, besides, the P_{N_1} pressure is exceeded and liquid L rich with the A component appears at $P_{NLV} < P_4 < P_{NSV}$.

5. An interesting T - x isobar exists in $P_{NSV} < P_5 < P_{NSL}$ narrow interval of pressures. The binary crystalline phase melts incongruently, liquid L rich with the B component evaporates congruently, aiming to unite with liquid L based on the A component.

6. The T - x isobar acquires a characteristic form for negative azeotropes with a minimum of the pressure at $P_6 > P_{NSL}$. There is the congruent melting of the AB binary phase at low temperatures.

Further, with increase of pressures, fluid F appears, similar to the previous case.

4. CONCLUSION

It is clear that the graphical phase-diagrams method makes possible to improve experimental information concerning the equilibrium states. Usually, it is used in the research and industrial development to save large amounts of time and resources by reducing the experimental work and by making thermodynamic predictions available especially for the multicomponent systems.

It has ascertained experimentally that the application of positive azeotropes initially could not be very successful, because the pressure above them is higher than above pure components in isothermal conditions.

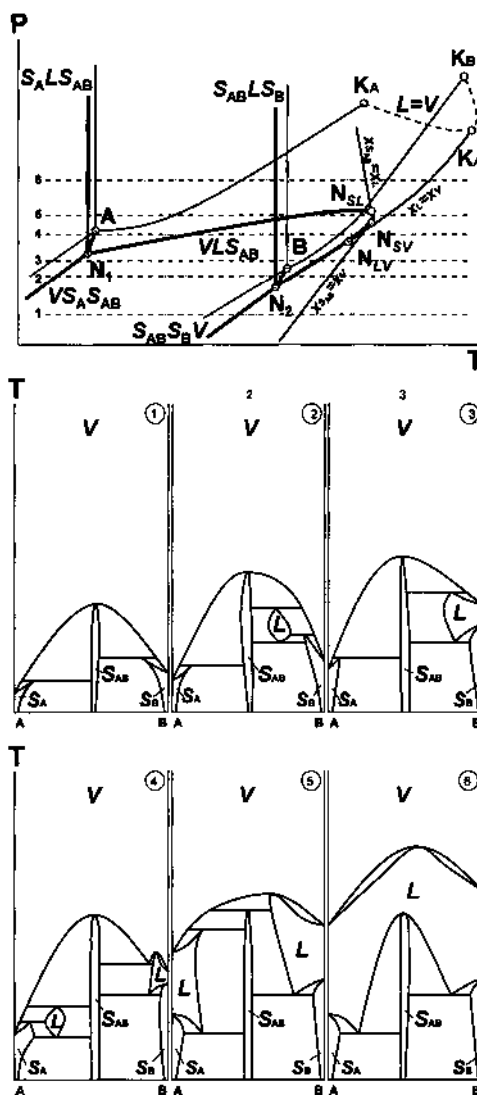


Fig. 4.

Apparently, it is possible to get in the supercritical region for negative azeotropes at pressures below critical points of pure components. We have used some binary negative azeotropic mixtures like pore fluids in our experimental work and obtained transparent, crack-free bulk samples of silica aerogels. It would pay to try other compounds for aerogels production, such as triple azeotropic mixtures. We are sure that there will be a great number of the additional phenomena related to the presence of the third component. As it has been noticed earlier, the sys-

tems that possess the limited mutual solubility in the crystalline state and those, in which the chemical compounds appear, are of significant practical interest. It is possible to expect the considerable decline of the evaporation pressure of liquid–vapour azeotrope, as compared to the evaporation of liquid components. Such systems exist, but they are scantily known now.

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