

Study of the polythermal diagram water–sodium sulphate–piperidine

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Abstract Two isothermal sections of the isobaric ternary system $\text{H}_2\text{O}-\text{Na}_2\text{SO}_4-\text{C}_5\text{H}_{10}\text{NH}$ were determined by isoplethic thermal analysis at 293 and 323 K. The compositions of the aqueous and organic invariant liquids, respectively L1 and L2, as well as that of the critical point, were characterized for each isotherm. The temperature of the invariant reaction was obtained by controlled flow thermal analysis and the temperature of the demixing ending, by interpolation of the monovariant lines. All these informations allowed us to establish the isobaric polythermal diagram of the $\text{H}_2\text{O}-\text{Na}_2\text{SO}_4-\text{C}_5\text{H}_{10}\text{NH}$ system, for the temperature range 293–323 K, as well as a qualitative representation of the monovariant curves. This system is then characterized by a wide miscibility gap, three crystallization domains, and four-three-phase invariant domains. The relevant exploitation of this diagram so permits us to deduce the demixing temperature leading to the optimal transfer of the organic compounds in the light phase and also the composition of the organic phase recovered after this first step of extraction.

Keywords Ternary system · Miscibility gap · Piperidine · Sodium sulphate · Water

Introduction

The salting out by the use of soda is often used as an early step in a purification strategy. In industries like in laboratories, this process is useful to separate compounds with different polarity.

Our laboratory studies now the *N*-aminopiperidine synthesis and extraction process. This hydrazine is produced by the reaction between the hydroxylamine-*O*-sulfonic acid and a large excess of piperidine. During the synthesis, sulphuric acid is released, this latter catching two piperidine equivalents to form a salt. Before the steps of recycling, it will be thus necessary to neutralize this salt in order to release piperidine at molecular state. Indeed, during the neutralization of this piperidine salt by soda addition, a demixing phenomenon appears due to the dessicant power of the sodium sulphate thus produced. The optimization of this step requires then the study of the polythermal ternary system $\text{H}_2\text{O}-\text{Na}_2\text{SO}_4-\text{C}_5\text{H}_{10}\text{NH}$.

So, this work focuses on the study of conditions of extraction and concentration of the piperidine reagent in diluted aqueous medium after soda addition. This way is more interesting than a distillation is unsuited to this level for the two following reasons: two piperidine equivalents trapped in the sulphate salt and a too large excess of water to be distilled.

Experimental

Piperidine (99%) and sodium sulphate (99%) were obtained from Acros. All chemicals were used without any further purification and double distilled, deionized water was used.

Two isothermal sections of the ternary system $\text{H}_2\text{O}-\text{Na}_2\text{SO}_4-\text{C}_5\text{H}_{10}\text{NH}$ were determined at atmospheric pressure

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by isoplethic thermal analysis [1, 2] (ITA) at 293 and 323 K. ITA is a synthetic method of isobaric thermal analysis. Its principle is based on the measurement of the thermal effects linked to the system transformations (phase appearance or disappearance), when its composition is modified.

The mixture is maintained under quasi-isothermal conditions and the temperature variations, about some hundredths of degree, are represented according to the global composition of the system. Experimental points were determined by the following method, already described in the literature [3]:

Pure water is added to a ternary mixture M of known composition, maintained under isobaric and isothermal conditions. The global composition of the mixture evolves thus along the line joining the representative points of M and H₂O into the plane of compositions. The temperature variations are so recorded as a function of the volume v of water added, which leads to a thermogram similar to that illustrated in Fig. 1.

The crossing of each equilibrium domain has a specific variation law and each break in this variation corresponds to a change in the number or the nature of the phases in equilibrium.

Flow controlled thermal analysis (FCTA), designed at the laboratory, allows us to determine the temperature of the isobaric ternary invariants. Formerly called enthalpymeter [4], the new generation of FCTA does not use any more mechanical mixing.

A known composition sample is slowly heated. The sample temperature is recorded as a function of time. Any modification of the number or the nature of phases results in a breakpoint on the straight line $T = f(t)$, the presence of a plateau corresponding then to an invariant equilibrium.

This technique permits to avoid supercooling phenomena, which often appear during the cooling. Moreover,

metastable equilibria can be eliminated by suitable thermal treatments.

Apparatus description [5, 6]: The experiments are carried out using a device with controlled heat flow, in the temperature range 173–423 K. The main feature of this apparatus lies in a control of the heat flow to the heating of the sample, which results so in a higher resolution power.

Figure 2 represents the overall device of the apparatus and the measuring cell.

The sample tube A is introduced inside two coaxial cylindrical furnaces B and C.

The furnace B is enslaved to the sample in such a way that the temperature deviation between A and B remains always constant. The furnace C acts as an adiabatic screen towards the external medium ($T_C - T_B = 0$ K).

This device is composed of the following elements:

- A laboratory tube A in stainless steel containing a thimble devoted to the thermocouple location. The sealing is ensured by the tightening of a screw plug on a Viton disc. It contains approximately 6 cm³ of the product.
- Two furnaces B and C were built starting cylindrical brass tubes and fixed via insulators in stumatite. A bell jar D, made of pyrex glass, covers the furnace-laboratory tube unit; it is used as an adiabatic enclosure. Nitrogen,

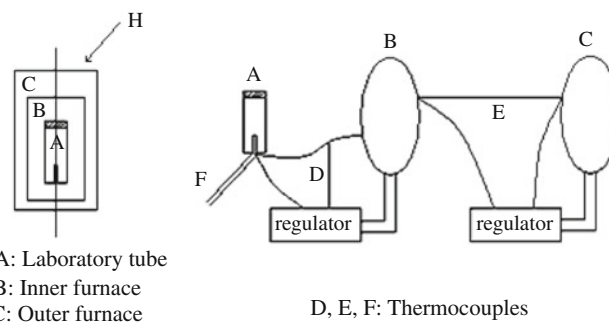


Fig. 2 FCTA regulation and measurement device

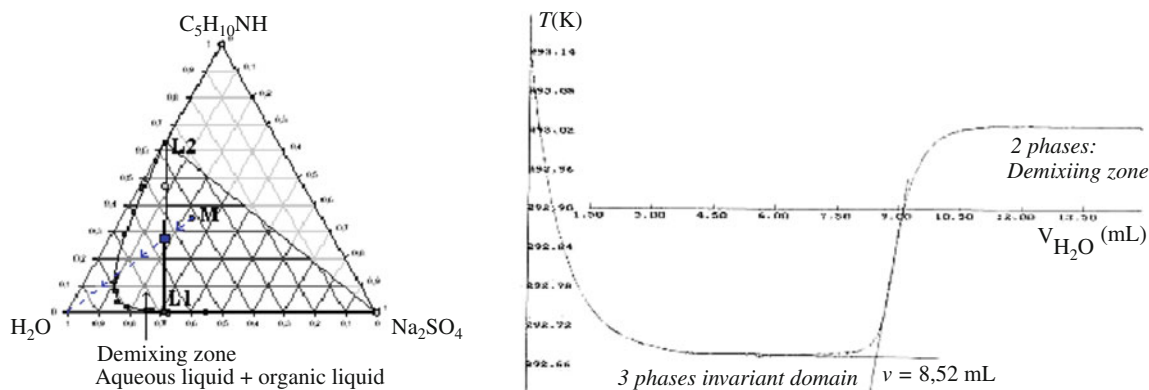


Fig. 1 ITA Thermogram (H₂O–Na₂SO₄–C₅H₁₀NH ternary system at $T = 313$ K and $P = 1$ atm)

cooled by liquid air, can be introduced directly at the sample level by an injector H. The control cluster, electronics, as well as the various cooling and vacuum inlets are gathered on the support E.

The temperature difference between the sample and the inner furnace B is maintained constant thanks to a differential thermocouple chromel–alumel F, which controls the furnace heating via a thermal regulator. In the same way, a second regulator permits to maintain the two furnaces B and C at the same temperature.

The tube containing the sample to analyze is put in place. The pyrex bell jar is set up on the apparatus and a primary vacuum is carried out in the enclosure (close to the water vapor pressure at the room temperature).

After a heating/cooling cycle, the temperature regulators are activated. If no thermal phenomenon occurs, the sample warms up linearly. However, the curve corresponding to a monovariant displacement of a solid–liquid equilibrium is not linear due to variations of the liquid and solid quantities.

Critical line of the miscibility gap was obtained by the generalized diameter method [3]. Four tie-lines were titrated for each isotherm. For these tie-lines (i), four points P_i obtained satisfy the relation:

$$\vec{P}_i = w_{1i} \cdot \vec{L}_{1i} + w_{2i} \cdot \vec{L}_{2i}$$

where w_{1i} and w_{2i} represent respectively the mass fractions of the liquid phases of compositions \vec{L}_{1i} and \vec{L}_{2i} . The value of w corresponding to the best correlation coefficient is chosen to then define the coordinates of the critical point by intersection with the binodal.

Results and discussion

Isotherms 298 and 313 K were the subject of a previous paper [3]. In the aim to establish the polythermal ternary diagram $\text{H}_2\text{O}-\text{Na}_2\text{SO}_4-\text{C}_5\text{H}_{10}\text{NH}$, two new isotherms 323 and 293 K were also determined. ATI was used to delimit the various equilibrium domains. The compositions of the invariant liquids L1, L2, and L3 were obtained by chemical titration and those of the critical point of the miscibility gap by the generalized diameter method.

Figures 3 and 4 represent, respectively, the isobaric isotherms 323 and 293 K of the ternary system $\text{H}_2\text{O}-\text{Na}_2\text{SO}_4-\text{C}_5\text{H}_{10}\text{NH}$, and Tables 1 and 2 collect the associated experimental compositions, expressed in mass fractions.

The ternary system studied is delimited by three binary systems. The $\text{Na}_2\text{SO}_4-\text{C}_5\text{H}_{10}\text{NH}$ system is known between 293 and 323 K (α coordinates in this work; Cf Table 1). In the temperature field studied, the piperidine is totally miscible in water. On the other hand, two hydrates are present in the binary mixture $\text{H}_2\text{O}-\text{Na}_2\text{SO}_4$ [7, 8]: a metastable

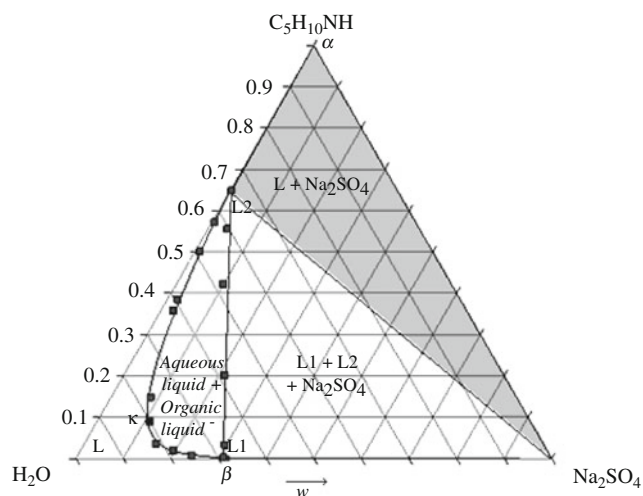


Fig. 3 Ternary system $\text{H}_2\text{O}-\text{Na}_2\text{SO}_4-\text{C}_5\text{H}_{10}\text{NH}$: isotherm 323 K ($P = 1$ bar)

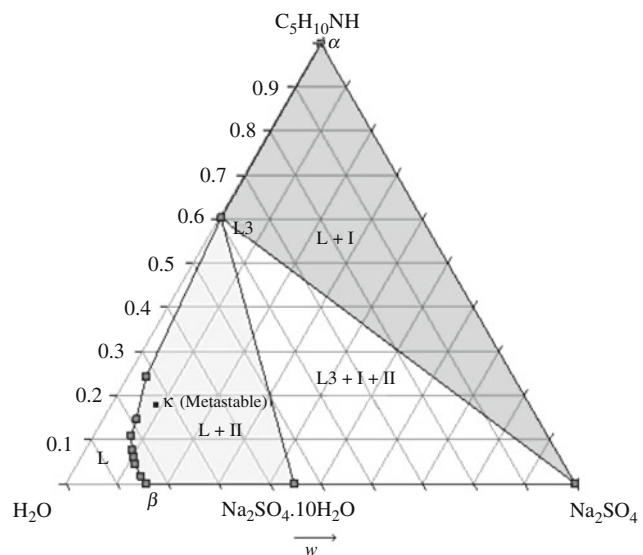


Fig. 4 Ternary system $\text{H}_2\text{O}-\text{Na}_2\text{SO}_4-\text{C}_5\text{H}_{10}\text{NH}$: isotherm 293 K ($P = 1$ bar). Solid phase I: Na_2SO_4 ; Solid phase II: $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$

Table 1 Solubility of sodium sulphate in piperidine

w (Na_2SO_4)/%	T/K
0.104	293
0.101	298
0.080	313
0.075	323

heptahydrate and a stable decahydrate (Glauber salt) which undergoes a peritectic decomposition at 305.4 K.

The isotherm 323 K is characterized by the existence of a miscibility gap in the crystallization area of the anhydrous sodium sulphate. The liquid–liquid two-phase equilibrium

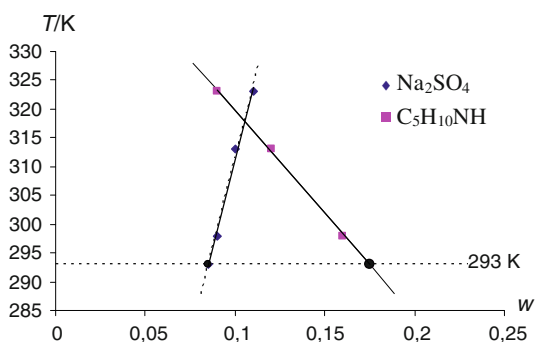
Table 2 Isotherm 323 K determined by ATI, chemical analysis^a or generalized diameter method^b

w (C ₅ H ₁₀ NH)	w (Na ₂ SO ₄)	Phenomenom
0	0.317	β
0.002	0.309	Aqueous invariant liquid L1 ^a
0.008	0.240	Binodal
0.022	0.194	Binodal
0.036	0.151	Binodal
0.09	0.11	Critical point κ^b
0.148	0.082	Binodal
0.358	0.026	Binodal
0.385	0.021	Binodal
0.501	0.010	Binodal
0.572	0.005	Binodal
0.033	0.297	Limit tie-line L1–L2
0.202	0.212	Limit tie-line L1–L2
0.421	0.099	Limit tie-line L1–L2
0.555	0.041	Limit tie-line L1–L2
0.648	0.002	Organic invariant liquid L2 ^a
0.99925	0.00075	α

domain is delimited by the limit tie-line L1–L2 and the critical point κ . One of the Na₂SO₄ liquidus is almost merged with the limiting binary system C₅H₁₀NH–H₂O, the other is also confounded with the aqueous invariant liquid L1. Consequently, the two-phase domain L + Na₂SO₄ in the aqueous side is not easily observable.

At 293 K, two solid phases, the anhydrous and the decahydrated sodium sulphates crystallize. The demixing phenomenon was not observed. To confirm this result, Fig. 5 shows the variations of the piperidine and sodium sulphate mass fractions of each critical point, according to the isotherm temperature (Table 3).

Critical points κ		
w (C ₅ H ₁₀ NH)	w (Na ₂ SO ₄)	T /K
0.16	0.09	298 [3]
0.12	0.10	313 [3]
0.09	0.11	323

**Fig. 5** Variations of the piperidine and sodium sulphate mass fractions of each critical point according to the isotherm temperature. Extrapolation at 293 K**Table 3** Isotherm 293 K determined by ATI, chemical analysis^a or generalized diameter method^b

w (C ₅ H ₁₀ NH)	w (Na ₂ SO ₄)	Phenomenom
0	0.441	Na ₂ SO ₄ ·10H ₂ O
0	0.157	β
0.017	0.139	Na ₂ SO ₄ ·10H ₂ O liquidus
0.045	0.112	Na ₂ SO ₄ ·10H ₂ O liquidus
0.062	0.100	Na ₂ SO ₄ ·10H ₂ O liquidus
0.077	0.092	Na ₂ SO ₄ ·10H ₂ O liquidus
0.110	0.073	Na ₂ SO ₄ ·10H ₂ O liquidus
0.146	0.065	Na ₂ SO ₄ ·10H ₂ O liquidus
0.17	0.085	Critical point κ^b (metastable)
0.243	0.036	Na ₂ SO ₄ ·10H ₂ O liquidus
0.603	0.003	Organic invariant liquid L3 ^a
0.99896	0.00104	α

These points are practically aligned and by extrapolation, we can determine the critical point composition of the demixing binodal at 293 K:

$$w(\text{Na}_2\text{SO}_4) = 0.085; w(\text{C}_5\text{H}_{10}\text{NH}) = 0.17.$$

This critical point κ is located inside the L + Na₂SO₄·10H₂O two-phase domain, which corresponds to the most stable domain at 293 K (Fig. 4). We will not thus observe any more the demixing phenomenon, which leads to a metastable equilibrium.

We use the right-angled trihedron as reference axis system for the representation of the isobaric polythermal ternary diagram.

In order to define the positions of the monovariant curves according to the temperature, the mass coordinates of all the experimental points belonging to these monovariant lines were gathered in Table 4.

At 313 [3] and 323 K, we note that the miscibility gap is based on the anhydrous sodium sulphate crystallization domain, whereas at 298 K [3], it is based on that of the decahydrated sodium sulphate. To determine exactly the invariant reaction temperature, we recorded the FCTA thermogram of a ternary mixture titrating

Table 4 Mass coordinates of the experimental points belonging to the monovariant curves

w (Na ₂ SO ₄)	w (C ₅ H ₁₀ NH)	Invariant liquid	T/K
0.309	0.002	L1	323
0.314	0.001	L1	313
0.170	0.045	L1	298
0.003	0.648	L2	323
0.002	0.628	L2	313
0.026	0.385	L2	298
0.0011	0.696	L3	298
0.0033	0.603	L3	293

40 wt% Na_2SO_4 and 4 wt% $\text{C}_5\text{H}_{10}\text{NH}$, composition chosen to maximize the amplitude of the phenomenon. The heating curves underline the existence of an invariant reaction at 302.5 K, characterized by the following equilibrium:



with, $\Lambda 1$ and $\Lambda 2$, respectively, the aqueous and organic invariant ternary liquids at 302.5 K.

Figure 6 represents the theoretical scheme of the invariant reaction at 302.5 K, with the fourphasic reaction involved:

The three-phase domains involved are:

- $\Lambda 1 + \Lambda 2 + \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
- $\Lambda 2 + \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{Na}_2\text{SO}_4$
- $\Lambda 1 + \Lambda 2 + \text{Na}_2\text{SO}_4$
- $\Lambda 1 + \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} + \text{Na}_2\text{SO}_4$

The compositions of these invariant liquids, at 302.5 K, were determined by chemical analysis. The ending temperature of the demixing gap was extrapolated at

296.5 ± 0.5 K, as well as the critical point K composition at this temperature, via the projection of the organic, aqueous, and critical monovariant lines. These results are given in Table 5.

The gathering of all these experimental data permits to build a perspective view of the polythermal diagram H_2O – Na_2SO_4 – $\text{C}_5\text{H}_{10}\text{NH}$, in the temperature range 293–323 K (Fig. 8). To simplify the 3D representation of this ternary diagram, Fig. 7 shows, separately, the various two-phase and three-phase domains.

Eight different domains are observed:

- two anhydrous sodium sulphate $\text{L} + \text{Na}_2\text{SO}_4$ crystallization domain,
- a decahydrated sodium sulphate $\text{L} + \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystallization domain,
- three-three-phase domains : $\text{L}3 + \text{Na}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{L}1 + \text{L}2 + \text{Na}_2\text{SO}_4$ and $\text{L}1 + \text{L}2 + \text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$,
- the miscibility gap aqueous liquid + organic liquid,
- and a single-phase domain L .

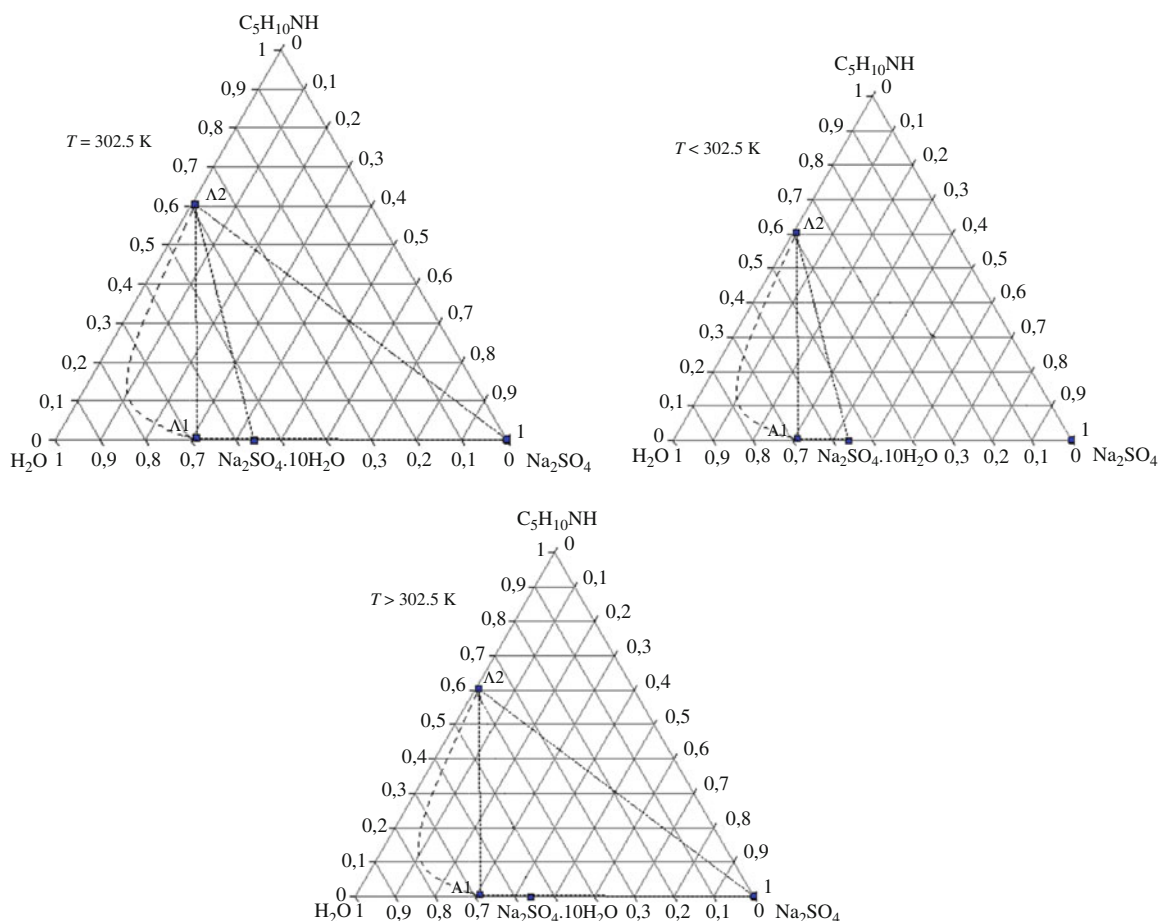
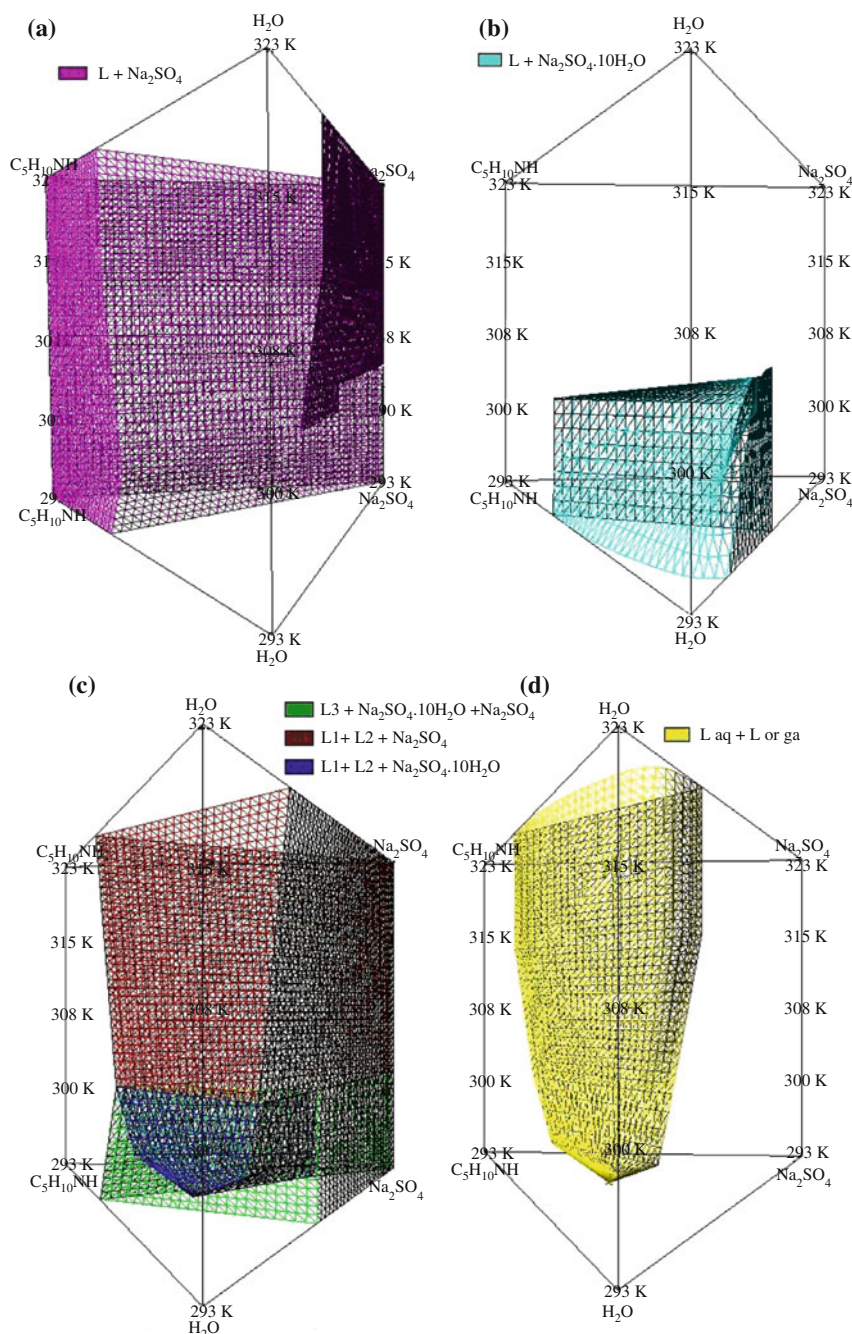


Fig. 6 Invariant reaction at 302.5 K. Illustrations at $T < 302.5$ K and $T > 302.5$ K

Table 5 Mass coordinates of the invariant liquids $\Lambda 1$, $\Lambda 2$ and the critical point

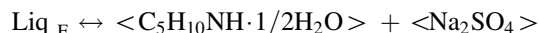
Phenomenon	$w(\text{Na}_2\text{SO}_4)$	$w(\text{C}_5\text{H}_{10}\text{NH})$	T/K
$\Lambda 1$	0.309	0.004	302.5
$\Lambda 2$	0.007	0.603	
K	0.085	0.16	296.5 ± 0.5

Figure 9 shows the vertical section I- Na_2SO_4 linking the anhydrous sodium sulphate to the critical point K of the miscibility gap.

Fig. 7 Various equilibrium domains of the ternary polythermal diagram H_2O – Na_2SO_4 – $\text{C}_5\text{H}_{10}\text{NH}$ between 293 and 323 K, $P = 1$ bar (mass coordinates)

The compilation of all these results permits to roughly draw the orthogonal projection, on the compositions plane, of all the monovariant curves (Fig. 10), but does not give access to the coordinates of the ternary invariant.

The existence of a quasi-binary section Na_2SO_4 – $\text{C}_5\text{H}_{10}\text{NH} \cdot 1/2\text{H}_2\text{O}$ is strongly suspected [9], with the following eutectic invariant reaction:



However, it remains an uncertainty between the eutaxy $E1$ and the close peritaxy.

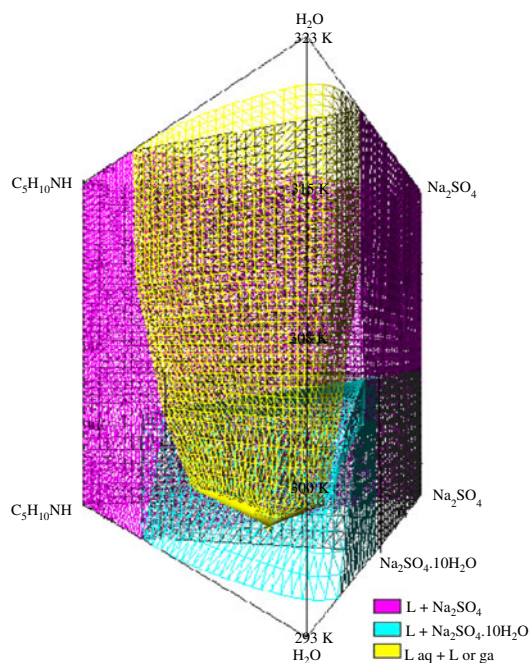


Fig. 8 Polythermal diagram $H_2O-Na_2SO_4-C_5H_{10}NH$ between 293 and 323 K; $P = 1$ bar

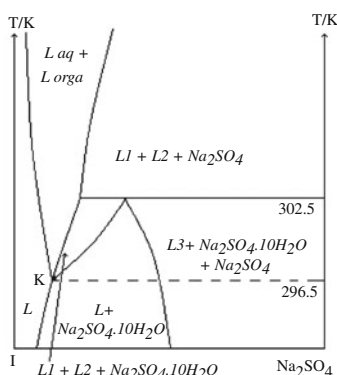


Fig. 9 Vertical section $I-Na_2SO_4$ ($I: w(C_5H_{10}NH) = 0.176$; $w(H_2O) = 0.824$); $P = 1$ bar

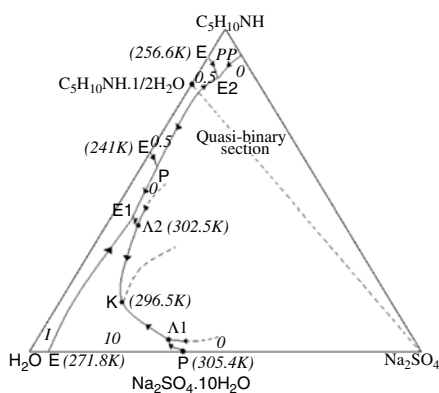


Fig. 10 Monovariant curves projection on the compositions plane 0: Na_2SO_4 domain; 10: $Na_2SO_4 \cdot 10H_2O$ domain; 0.5: hemihydrate of $C_5H_{10}NH$ domain; I ice domain

Conclusions

Two isotherms (293 and 323 K) of the ternary diagram $H_2O-Na_2SO_4-C_5H_{10}NH$ were established by ITA and chemical titration at atmospheric pressure. The invariant temperature at 302.5 K was obtained by FCTA experiment. The end of the demixing gap was extrapolated thanks to the critical line at 296.5 K, via the projection of the organic, aqueous, and critical monovariant lines.

All these information allowed us to determine the polythermal diagram $H_2O-Na_2SO_4-C_5H_{10}NH$ in the temperature range 293–323 K, as well as a qualitative representation of the monovariant curves of this system. Its relevant exploitation is essential for the process optimization of the hydrazine extraction and purification. This extraction process rests on successive operations of demixing before the distillation step.

The hydrazine extraction is similar to that of piperidine because this latter, by its excess concentrations in the reaction liquors, drives the hydrazine by solvent effect.

Demixing at temperatures lower than 302.5 K is not interesting. Indeed, the crystallization of the decahydrate of Na_2SO_4 decreases the piperidine concentration in the organic invariant liquid L2.

We underline that the two isotherms 313 and 323 K have similar demixing features: thus it does not seem relevant, from an energetic point of view, to implement a separation by demixing beyond these temperatures.

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