Experimental Determination and Representation of Binary and Ternary Diagrams of N-Hexacosane, N-Octacosane and N-Heptane

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EXPERIMENTAL DETERMINATION AND REPRESENTATION OF BINARY AND TERNARY DIAGRAMS OF *n*-HEXACOSANE, *n*-OCTACOSANE AND *n*-HEPTANE

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DÉTERMINATION EXPÉRIMENTALE ET REPRÉSENTATION DES DIAGRAMMES BINAIRES ET TERNAIRES DU n-HEXACOSANE, n-OCTACOSANE ET n-HEPTANE

L'accumulation des dépôts dans les conduites est un problème majeur lors de l'exploitation et du transport des bruts paraffiniques. La limitation de ces dépôts ou leur élimination par des méthodes telles que l'addition de produits chimiques, le raclage ou le réchauffage des conduites augmentent les coûts de production. Une meilleure connaissance du phénomène permettrait d'ajuster les schémas de production mis en œuvre et donc de limiter les coûts.

Des modèles thermodynamiques peuvent être utilisés pour calculer la température de cristallisation commençante et la quantité de dépôts solides en fonction de la température. Dans ces modèles, le fluide est représenté comme un mélange de corps purs ou de « pseudo-constituants » (qui représentent eux-mêmes plusieurs constituants purs). Pour décrire le comportement thermodynamique de ces mélanges, il est nécessaire d'avoir des données sur les constituants purs ainsi que sur leurs mélanges mais ces données sont rares dans la littérature lorsque l'on s'intéresse aux composés lourds.

Ce travail consiste en l'étude de mélanges de n-paraffines lourdes : le n-hexacosane (noté C_{26}) et le n-octacosane (noté C_{28}) dans le n-heptane (noté C_7). Nous présentons ici la solubilité du C_{26}, du C_{28} et du mélange équimolaire de C_{26} et C_{28} dans le C_7, ainsi qu'une coupe isotherme (T = 303,15 K) du diagramme ternaire. Les résultats expérimentaux sont restitués de façon satisfaisante par un calcul utilisant des expressions simples de l'énergie de Gibbs d'excès (NRTL et Redlich-Kister). Ce travail permet d'envisager la modélisation du comportement de systèmes complexes en utilisant uniquement des coefficients d'interaction binaires.

EXPERIMENTAL DETERMINATION AND REPRESENTATION OF BINARY AND TERNARY DIAGRAMS OF n-HEXACOSANE, n-OCTACOSANE AND n-HEPTANE

Accumulation of waxy deposits is a commonly occurring problem during exploitation and transportation of paraffinic crude oils. Limitation of these undesirable solids or removal by methods such as addition of chemical inhibitor, scrapping or heat tracing of flowlines, increase production costs. A better knowledge of this

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phenomenon will make it possible to adjust process operating parameters and limit the operating costs.

Thermodynamic models can be used in order to calculate the wax appearance temperature and the amount of solid deposit versus temperature. In these models, the crude oil is represented as a mixture of pure or "pseudo-components" (which content several pure components). To describe the thermodynamic properties of those mixtures, data on pure components and on their mixtures are necessary but they are very scarce for heavy components in the literature. This work is devoted to the study of a mixture of heavy components including two heavy n-alkanes (n-hexacosane, denoted C_{26} and n-octacosane, denoted C_{28}) and a solvent (n-heptane denoted C_7).

Measurements of solubility of C_{26} and C_{28} and of equimolar mixture of C_{26} and C_{28} in C_7, and an isothermal ternary diagram of the mixture of the three components at 303 K are presented. Their calculations using simple expressions of Gibbs molar energy (NRTL and Redlich-Kister) are in good agreement with experimental data. The work allows to consider calculating complex systems with the only use of binary interaction coefficients.

DETERMINACIÓN EXPERIMENTAL Y REPRESENTACIÓN DE LOS DIAGRAMAS BINARIOS Y TERNARIOS DEL n-HEXACOSANO, n-OCTACOSANO Y n-HEPTANO

La acumulación de sedimentos en las canalizaciones constituye un importante problema durante la operación y el transporte de los crudos parafínicos. La limitación de estos sedimentos o sencillamente su eliminación, por aplicación de métodos, como, por ejemplo, la adición de productos químicos, el raspado o el calentamiento de las canalizaciones, vienen a aumentar los costes de producción. Así, un mejor conocimiento del fenómeno permitiría ajustar los esquemas de producción implementados y, por ende, limitar los costes.

Existe la posibilidad de utilizar modelos termodinámicos para calcular la temperatura de cristalización en su etapa inicial y el volumen de sedimentos sólidos en función de la temperatura. En estos modelos, el fluido está representado como una mezcla de cuerpos puros o de "seudocomponentes" (que representa a su vez varios componentes puros. Para describir el comportamiento termodinámico de estas mezclas, es preciso disponer de los datos acerca de los componentes puros, así como de sus mezclas, pero tales datos figuran en muy contados casos en la literatura profesional cuando se trata de conocer los componentes pesados.

Este trabajo consiste en estudiar las mezclas de n-parafinas pesadas a saber : el n-hexacosano (referencia C_{26}) y el n-octacosano (referencia C_{28}) en el n-heptano (referencia C_7). Presentamos en este trabajo la solubilidad del C_{26}, del C_{28} y de la mezcla equimolar de C_{26} y C_{28}, en el C_7, así como una fracción isoterma (T = 303,15 K) del diagrama ternario. Los resultados experimentales se restituyen de forma satisfactoria mediante un cálculo en que se utilizan expresiones simples de la energía de Gibbs de exceso (NRTL y Redlich-Kister). Este trabajo permite contemplar la modelización del comportamiento de sistemas complejos utilizando únicamente los coeficientes de interacción binarios.

INTRODUCTION

Accumulation of waxy deposits is a commonly occurring problem during exploitation and transportation of paraffinic crude oils. Limitation of these undesirable solids or removal by methods such as addition of chemical inhibitor, scrapping or heat tracing of flowlines, increase production costs. A better knowledge of this phenomenon will make it possible to adjust process operating parameters and limit the operating costs. Thermodynamic models can be used in order to calculate the wax appearance temperature and the amount of solid deposit versus temperature. In these models, the fluid is represented as a mixture of pure or pseudo-components (which content several pure components). To describe the thermodynamic properties of those mixtures, data on pure components and on their mixtures are necessary but they are very scarce for heavy components in the literature. This work is devoted to the study of a mixture of heavy components including two heavy *n*-alkanes (*n*-hexacosane, denoted C_{26} and *n*-octacosane, denoted C_{28}) and a solvent (*n*-heptane denoted C_7). The assessment of the thermodynamic properties of such a mixture should increase the reliability of the calculations of complex systems.

1 EXPERIMENTS

1.1 Solubility

A simple thermal analysis device constructed in our laboratory was used to determine the solubility. A sample of known composition was introduced in an iron steel crucible. It was first heated until melting, and then slowly cooled. The actual measurement then began, by heating the sample at a temperature rate of 1 K/min. The apparatus was tested by measuring the melting temperature of the pure *n*-alkanes C_{26} and C_{28}. Results were in good agreement with those of the literature ($\Delta T < 0.3$ K) [1] and [2].

1.2 Isothermal diagram

The following sequence was used to determine the isothermal diagram (C_{26}: C_{28}: C_7) at T = 303.15 K: the desired amount of C_{26}, C_{28} and C_7 was introduced in a seringe and melted. It was maintained in a thermostatic bath at a constant temperature (T = 303.15 K) during at

least 1 hour, to ensure phase equilibrium. The liquid phase was picked through a filter (∅ 0,45 µm), and the remaining wet solid was dissolved in cyclohexane. Both solutions (containing the wet solid and the liquid) were analysed by gas chromatography. A mass balance, assuming that the solid is a binary mixture of C_{26} and C_{28}, and doesn't contain C_7, leads to the determination of the liquid and dry solid compositions.

2 RESULTS AND DISCUSSION

2.1 Binary systems

2.1.1 Solubility

Measured solubility of C_{26} and C_{28} in C_7 in a temperature range from 290 K to 350 K are shown in Figure 1, with those of Domanska [3] for the C_{28} in C_7. Our data are in good agreement with the literature values. As expected, the solubility of C_{26} is higher than that of C_{28}.

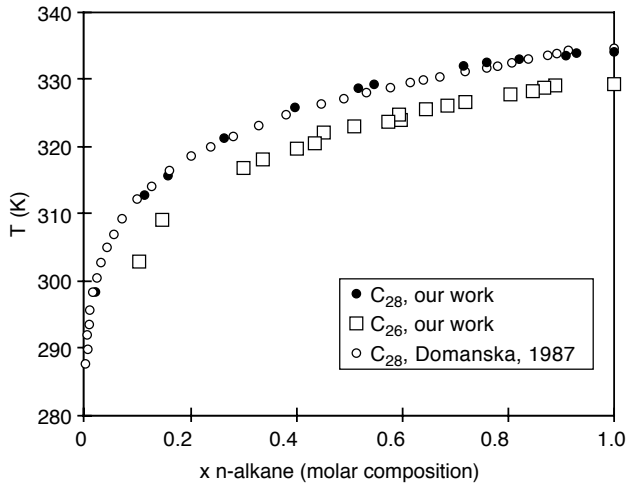

Figure 1

Solubility of C_{26} and C_{28} in C_7. Experimental results and literature.

2.1.2 Experimental activity coefficient

The activity coefficients γ of C_{26} and C_{28} have been calculated using the standard thermodynamic relationship for equilibrium between a pure solid component and a liquid:

$$\gamma = \frac{1}{x} \exp\left(-\frac{\Delta G(T)}{RT}\right)$$

where x is the molar composition of the liquid
T is the equilibrium temperature
$\Delta G(T)$ is the melting Gibbs energy
R is the universal gas constant
$= 8.31441\ J \cdot mol^{-1} \cdot K^{-1}$

$\Delta G(T)$ has been calculated in terms of enthalpy and entropy, leading to the following expression:

$$\Delta G(T) = Cp^s \left[T_{tr} - T\left(1 + \ln\frac{T_{tr}}{T}\right)\right] + L_{tr}\left(1 - \frac{T}{T_{tr}}\right) + Cp^{RII}\left[T_m - T_{tr} - T\ln\frac{T_m}{T_{tr}}\right] + L_m\left[1 - \frac{T}{T_m}\right] + Cp^{liq}\left[T\left(1 + \ln\frac{T_m}{T}\right) - T_m\right]$$

In the above equation, T_m and L_m are respectively the temperature and the enthalpy of melting of the solid, T_{tr} and L_{tr} are the temperature and enthalpy of solid-solid transition, Cp^s, Cp^{RII} and $Cp^{liq.}$ the heat capacities of respectively the low temperature solid phase, the rotator phase and the liquid. Cp^s has been represented using Einstein'model [4].

The properties of the pure component (C_{26} or C_{28}) were obtained from previous measurements [5], and are listed in Table 1. N and θ are the Eintein's model parameters.

The evolution of the activity coefficient versus composition is represented in Figure 2.

TABLE 1

Thermodynamic properties of pure C_{26}, C_{28} or in phase β"

	Cp^s		$Cp^{\beta"}$		Cp^{RII}	$Cp^{liq.}$	T_{tr}	L_{tr}	T_m	L_m	$T_{\beta"->liq.}$	$L_{\beta"->liq.}$
	N	θ / K	N	θ / K	/J·mol^{-1}·K^{-1}	/J·mol^{-1}·K^{-1}	/K	/kJ·mol^{-1}	/K	/kJ·mol^{-1}	/K	/kJ·mol^{-1}
C_{26}	165.6	1553	194.5	1553	1363	850	325.9	32.9	329.4	58.7	327.0	82.0
C_{28}	161	1553	194.5	1553	1374	930	330.5	33.4	333.9	61.9	332.4	88.0

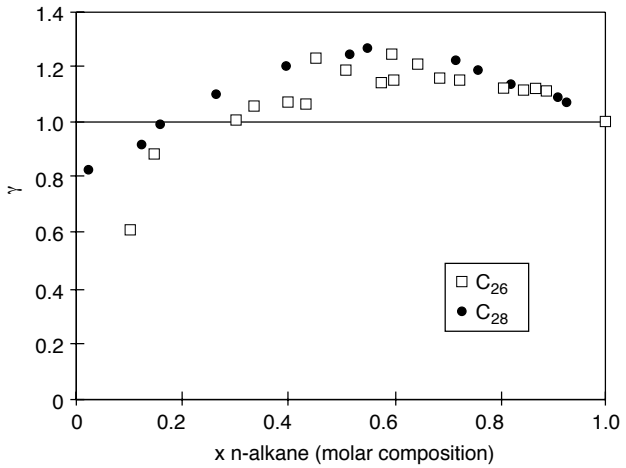

Figure 2

Activity coefficient of C_{26} and C_{28} in C_7 versus molar composition.

It shows an atypical behaviour: $\gamma > 1$ for low C_7 composition, and $\gamma < 1$ for higher C_7 compositions. This phenomenon indicates a trend to association for high heavy *n*-alkane concentrations (C_{26} or C_{28}) and to demixion for lower concentrations.

2.1.3 Calculated activity coefficients

The activity coefficient γ is related to the Gibbs molar partial excess energy by the well-known relation:

$$g_i^e = RT \ln \gamma_i$$

Two expressions of the Gibbs excess molar energy have been used [6] (NRTL and Margules):

$$\text{NRTL: } \frac{g^e}{RT} = x_{C_{26}} x_{C_{28}} \left(\frac{\tau_{21} G_{21}}{x_{C_{26}} + x_{C_{28}} G_{21}} + \frac{\tau_{12} G_{12}}{x_{C_{26}} G_{12} + x_{C_{28}}} \right)$$

$$\text{with } \tau_{12} = \frac{\Delta g_{12}}{RT}\,;\, \tau_{21} = \frac{\Delta g_{21}}{RT}$$

and $\ln G_{12} = -\alpha\tau_{12}$; $\ln G_{21} = -\alpha\tau_{21}$ ($\alpha = 0.4$ [7])

the index 1 corresponds to C_{26} and the index 2 to C_{28}.

$$\text{Margules: } g^e = x_{C_{26}} x_{C_{28}} \left[A + B \left(x_{C_{26}} - x_{C_{28}} \right) \right]$$

The parameters (reported in Table 2) have been fitted on the experimental curves of the activity coefficient γ.

TABLE 2

Parameters of the g^e equations

	Margules		NRTL	
	A	*B*	Δg_{ij}	Δg_{ji}
$C_{26} + C_7$	–154	1956	9978	–3008
$C_{28} + C_7$	650	1635	9749	–2620

Both expressions lead to a good representation of the experimental solubility curves, as it can be seen in Figure 3, even if results are slightly better with NRTL. The mean temperature deviation ΔT between calculated and experimental solubilities are given in Table 3.

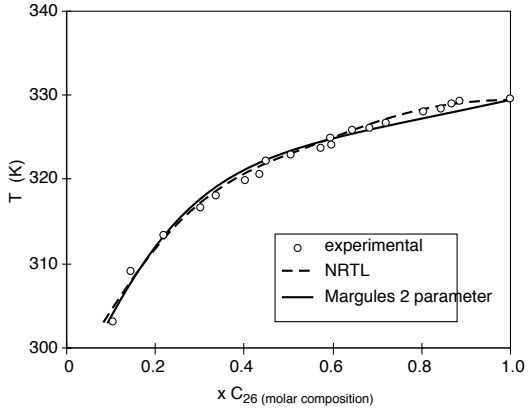

Figure 3

Solubility of C_{26} in C_7. Experimental and calculated results.

TABLE 3

Mean temperature deviation on the solubility results of C_{26} and C_{28} in C_7

	Margules	NRTL
$C_{26} + C_7$	0.70	0.46
$C_{28} + C_7$	0.60	0.16

It is always lower than 0.7 K. ΔT is calculated using the following expression:

$$\Delta T = \frac{1}{n} \sum_i^n \left| T_i^{\text{calc}} - T_i^{\text{exp}} \right|$$

with T_i^{calc} calculated temperature corresponding to the solubility point *i*

T_i^{exp} experimental temperature corresponding to the solubility point *i*

n number of experimental solubility points.

2.2 Ternary system

2.2.1 Results

Solubility of the equimolar mixture of C_{26} and C_{28} in C_7 is presented in Figure 4. The isothermal diagram at T = 303.15 K is presented in Figure 5.

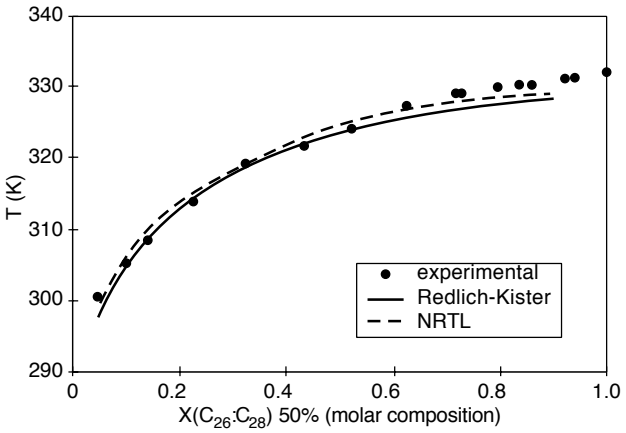

Figure 4

Solubility of equimolar mixture of C_{26}: C_{28} in C_7. Experimental and calculated results.

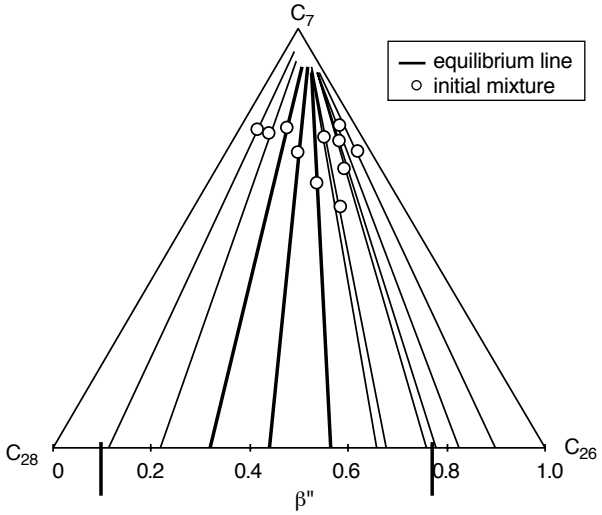

Figure 5

Isothermal ternary diagram at T = 303.15 K. Experimental results.

Additionnal X-ray diffraction measurements made on the solid phase in equilibrium with the ternary liquid mixture have showed that this solid has the same structure as the initial binary (C_{26}: C_{28}) mixture. Chromatographic results indicate that the solid is a binary mixture of C_{26} and C_{28}; its composition is not the initial one [5]. Its structure is orthorhombic, denoted β", distinct from the pure *n*-alkanes. This point will be taken into consideration in the diagram calculation. It is also observed that the solubility of C_{26} is higher when a small amount of C_{28} is added.

It is probably due to the formation of the orthorhombic intermediate solid phase β", more soluble than the pure C_{26}: the structure of the β" phase presents a conformational disorder which increases the solubility of the solid.

2.2.2 Representation

Uniformity of the chemical potential in liquid and solid phases leads to the following system, allowing the calculation of the diagram:

$$\begin{cases} RT \ln\left(\dfrac{X_{C_{26}}}{x_{C_{26}}}\right) = \Delta G_{C_{26}}^{\beta"\rightarrow liq.}(T) + g_{C_{26}}^{e,liq.}\left(x_{C_{26}}\right) - g_{C_{26}}^{e,\beta"}\left(X_{C_{26}}\right) \\ RT \ln\left(\dfrac{X_{C_{28}}}{x_{C_{28}}}\right) = \Delta G_{C_{28}}^{\beta"\rightarrow liq.}(T) + g_{C_{28}}^{e,liq.}\left(x_{C_{28}}\right) - g_{C_{28}}^{e,\beta"}\left(X_{C_{28}}\right) \end{cases}$$

with x_i composition of the liquid phase

X_i composition of the solid phase

$\Delta G_i^{\beta"\rightarrow liq.}(T)$ Gibbs energy of melting of *i* from the solid β" to the liquid

$g_i^{e,liq.}$ Gibbs excess molar partial energy of *i* in the liquid

$g_i^{e,\beta"}$ Gibbs excess molar partial energy of *i* in the solid β".

$\Delta G_i^{\beta"\rightarrow liq.}(T)$ is calculated for each pure *n*-alkane, with the following expression:

$$\Delta G_i^{\beta"\rightarrow liq.}(T) = Cp^{\beta"}\left[T_{\beta"\rightarrow liq.} - T\left(1 + \ln\frac{T_{\beta"\rightarrow liq.}}{T}\right)\right] + L_{\beta"\rightarrow liq.}\left[1 - \frac{T}{T_{\beta"\rightarrow liq.}}\right] + Cp^{liq.}\left[T\left(1 + \ln\frac{T_{\beta"\rightarrow liq.}}{T}\right) - T_{\beta"\rightarrow liq.}\right]$$

$T_{\beta''\rightarrow liq.}$ and $L_{\beta''\rightarrow liq.}$ are the hypothetical temperature and heat of transition from the solid β" to the liquid, $Cp^{\beta''}$ is the heat capacity of the phase β". Values have been determined from thermodynamical measurements [5], and are reported in Table 1.

Different expressions of the Gibbs excess energy (g^e) have been used to represent the liquid phase or the solid phase:

– Solid phase (binary mixture of C_{26} and C_{28}):
a two parameters Margules expression has been used. The parameters (A and B) have been determined from the study of the binary diagram (C_{26}: C_{28}) [5].

$$g^e = X_{C_{26}} X_{C_{28}} \left[A + B\left(X_{C_{26}} - X_{C_{28}} \right) \right]$$

– Liquid phase (ternary mixture of C_{26}, C_{28} and C_7):
two models have been used, NRTL and Redlich-Kister which is equivalent to Margules when applied to multicomponent systems, with the following assumptions:
- the mixture of C_{26} and C_{28} in the liquid state is an ideal solution ($g^e = 0$). This point has been verified by Achour [8], for the binary system C_{26}: C_{24};
- ternary interactions are neglected.

The g^e equations are finally:

$$\text{NRTL: } \frac{g^e}{RT} = \sum_{i=1}^{3} x_i \frac{\sum_{j=1}^{3} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{3} G_{ki} x_k}$$

with $\Delta g_{23} = \Delta g_{32} = 0$ and $\alpha = 0.4$

Redlich-Kister:

$$g^e = x_1 x_2 [A_{12} + B_{12} (x_1 - x_2)] + x_2 x_3 [A_{23} + B_{23} (x_2 - x_3)] + x_3 x_1 [A_{31} + B_{31} (x_3 - x_1)]$$

In these equations, $i = 1$ for C_{26}, $i = 2$ for C_{28} and $i = 3$ for C_7.

The calculation leads to a good representation of both solubility curves and the isothermal diagram; the calculated solubility of binary mixtures of C_{26} and C_{28} in C_7 is presented in Figure 4 together with experimental points. Table 4 shows the mean percentage deviation $\Delta x(\%)$ between experimental and calculated compositions of the liquid phase (isothermal diagram). $\Delta x(\%)$ has been calculated using the following expression:

$$\Delta x(\%) = \frac{1}{n} \sum_{i}^{n} \frac{\left| x_i^{calc.} - x_i^{exp} \right|}{x_i^{exp}} \times 100$$

with $x_i^{calc.}$ calculated liquid phase molar composition

x_i^{exp} experimental liquid phase molar composition

n number of experimental points.

In all cases, results are satisfactory. The hypothesis of negligible ternary interactions seems to be valid.

TABLE 4

Mean percentage deviation between experimental and calculated liquid phase of the isothermal ternary diagram (T = 303.15 K)

	Redlich-Kister	NRTL
C_7	1.8%	0.6%
C_{26}	20.8%	7.2%
C_{28}	11.8%	5.9%

CONCLUSION

The solubility curves of C_{26}, C_{28} and mixtures of C_{26} and C_{28} have been determined in *n*-heptane, as well as an isothermal diagram of the 3 components. Experimental results have been represented using simple expressions of the Gibbs excess energy (NRTL and Margules). The ternary system (solubilities and isothermal diagram) has been calculated from binary solubility parameters, taking into consideration the formation of an intermediate solid phase between C_{26} and C_{28}. Ternary interactions have been neglected. Results are good, for both solubilities and the isothermal diagram.

This work allows to consider calculating complex systems with the only use of binary interaction coefficients.

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