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Short communication

Volumetric properties of the water + 3-(dimethylamino) propylamine (DMAPA) mixture at atmospheric pressure from 283.15 to 353.15 K

Christophe Coquelet, Alain Valtz, Xavier Courtial, Dominique Richon*

Centre Energétique et Procédés, Ecole Nationale Supérieure des Mines de Paris, CEP/TEP, CNRS FRE 2861,
35 rue Saint Honoré, 77305 Fontainebleau, France

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Abstract

Densities of the water + 3-(dimethylamino) propylamine (DMAPA) binary system were measured at atmospheric pressure over the whole range of compositions at temperatures from 283.15 to 353.15 K using Anton Paar digital vibrating glass tube densimeter. The density of this system has been found an increasing function of water composition and a decreasing function of temperature. Excess molar volumes have been correlated using Redlich–Kister equations. Sets of parameters have been determined from experimental data to obtain correlations in the measurement range uncertainty. Partial molar volumes on the whole concentration range have been determined using Redlich–Kister parameters.

Keywords: Binary system; 3-(Dimethylamino) propylamine (DMAPA); Density; Excess molar volume; Partial molar volume; Modelling; Redlich–Kister equation

1. Introduction

3-(Dimethylamino) propylamine (DMAPA) is utilised for the manufacture of pharmaceuticals, cationic surfactants, dyes, adhesives, coatings, polyurethanes, additives for fuels and lubricants rubber and water treatment chemicals. This molecule is used as special surfactant because it is not corrosive and does not react with other additives. Moreover, it is highly biodegradable. The production of DMAPA is growing up. Data about this amine are consequently of high interest and also in order to improve general knowledge about amines and water binary mixtures. This study is a continuation of work handled in our laboratory [1–6]. Nevertheless, only Valkovskaya *et al*. [7] experimental data concerning this binary system are available in literature. For these reasons it was decided to start a campaign of density measurements.

Density of the water (1) + DMAPA (2) binary mixture was measured in the temperature range (283.15–353.15 K) for the whole composition range to assess composition and temperature effects.

Redlich–Kister [8] model is used to represent excess molar volumes and to calculate partial molar volumes and partial molar volumes at infinite dilution.

2. Experimental

DMAPA [$C_5H_{14}N_2$, CAS number: 109-55-7] was purchased from Aldrich with certified purity >99% (GC). Ultra pure water is produced with Direct-Q model from Millipore. DMAPA and water were carefully degassed before use and mixtures were prepared gravimetrically under vacuum. The apparatus used for density measurements is Anton Paar digital vibrating glass tube densimeter (model DMA5000), with a certified precision of 10^{-5} g cm^{-3}. Eq. (1) relates density ρ (g cm^{-3}) as a function of vibrating period τ (s^{-1}) with constant parameters a and b.

$$\rho = a + b\tau^2 \tag{1}$$

a and b constants were determined at 293.15 K using dry air and (bidistilled/degassed) water. Reliable density data are available for these two reference compounds, respectively, in [9] and [10]. Preparation and loading of mixtures into the vibrating tube is the following: empty 20 cm^3 glass bottles were closed air-tight with a septum and then evacuated with the help of a vacuum pump using a syringe needle introduced through the septum. Each empty bottle was weighed, and then the less volatile com-

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* Corresponding author. Tel.: +33 1 6469 4965; fax: +33 1 6469 4968.
E-mail address: dominique.richon@ensmp.fr (D. Richon).

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ponent, freshly degassed by vacuum distillation, introduced by means of a syringe. After weighing the bottle loaded with the first component, the more volatile one was added similarly and then the bottle was weighed again. All weighing were performed using a balance with 0.0003 g accuracy. Taking into account uncertainties on density measurements of pure compounds and mixtures, the maximum uncertainty on excess molar volume v^E ($cm^3\ mol^{-1}$) is estimated to be within ±0.005 $cm^3\ mol^{-1}$.

3. Results

Measured densities for pure DMAPA reported in Table S1 (Supplementary data) have been fitted using Eq. (2) from Daubert *et al.* [11]. ρ^*_{cor} are the densities of pure DMAPA ($g\ cm^{-3}$) determined by the correlation.

$$\rho^*_{cor} = \frac{A}{B^{(1+(1-T/Tc)^C)}} \times \frac{M}{1000} \tag{2}$$

where T is the temperature in Kelvin, Tc the critical temperature of the species and M is the molar mass of pure compound ($g\ mol^{-1}$). A, B and C are the adjusted parameters (the best obtained values are: $A = 8139.227\ cm^3\ g^{-1}$; $B = 28.862$; $C = -0.084$). No value for DMAPA critical temperature was found, and then it has been estimated using Joback [12] and Lydersen [13] methods. Joback [12] method leads to 588.58 K and Lydersen [13] method to 587.57 K. These two values are quite similar; we chose arbitrarily intermediate value, i.e. 588 K.

DMAPA density data are represented within 0.06% (bias value close to 0). Valkovskaya *et al.* [7] have reported pure DMAPA densities at 288, 298 and 308 K along with mixture density data. Relative deviations between their densities and those calculated through Eq. (2) using the previous parameters are less than 0.4% but all positive.

Excess molar volumes are calculated with Eq. (3).

$$v^E = v - x_1 v_1^* - x_2 v_2^* \tag{3}$$

where x_i is the molar composition, v the molar volume of the solution ($cm^3\ mol^{-1}$) and v_i^* is molar volume of pure component i ($cm^3\ mol^{-1}$). By introducing the density ρ, Eq. (3) can be written as:

$$v^E = \left[\frac{x_1 M_1 + x_2 M_2}{\rho}\right] - \frac{x_1 M_1}{\rho_1^*} - \frac{x_2 M_2}{\rho_2^*} \tag{4}$$

ρ_2^* is the experimental pure DMAPA densities data from Table S1 (Supplementary data), ρ_1^* the pure water densities data from Tables produced by Bettin and Spieweck [10] and ρ is the experimental DMAPA + water densities of the mixture (Table S2 (Supplementary data)). Mixture densities are compared with Valkovskaya *et al.* [7] data in Fig. 1. Excess molar volumes, corresponding to lowest and highest temperatures, are plotted in Fig. 2.

Redlich–Kister equation [8] was applied to correlate excess molar volumes:

$$v^E = x_1 x_2 \sum_i A_i (x_1 - x_2)^i \tag{5}$$

with $i \leq 9$.

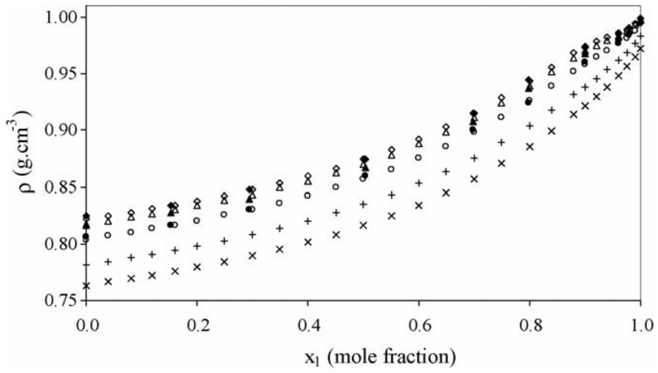

Fig. 1. Density of H_2O (1) + DMAPA (2) as a function of water mole fraction at atmospheric pressure. Our measurements performed at: 288.15 K (◇), 298.15 K (△), 308.15 K (○), 333.15 K (+) and 353.15 K (×), and Valkovskaya *et al.* [7] data at atmospheric pressure: at 288 K (◆); 298 K (●); 303 K (▲).

The Redlich–Kister coefficients (A_i) that determined at each studied temperature are presented in Table 1. The number of parameters has been established to reach a standard deviation, σ ($cm^3\ mol^{-1}$), lower than 0.005 (experimental uncertainty).

According to Table 1, Redlich–Kister [8] parameters number decreases with temperature (from 10 at 283.15 K to 6 at 353.15 K). The partial molar volume ($cm^3\ mol^{-1}$) ($\overline{v_i}$) of each component i has been calculated using Eq. (6), with V, the volume of the mixture (cm^3).

$$\overline{v_i} = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_j} \tag{6}$$

Differentiating Eq. (3) with respect to n_i and combining the result to Eq. (6) leads to equations for the partial molar volumes of DMAPA and water:

$$\overline{v_1} = v^E + v_1^* - x_2 \left(\frac{\partial v^E}{\partial x_2}\right)_{T,P} \tag{7}$$

$$\overline{v_2} = v^E + v_2^* - x_1 \left(\frac{\partial v^E}{\partial x_1}\right)_{T,P} \tag{8}$$

Expression of partial molar volumes (Eqs. (9) and (10)) are obtained by differentiating Redlich–Kister [8] equation (Eq. (5)) with respect to x_i and substitution in Eqs. (7) and (8). Excess

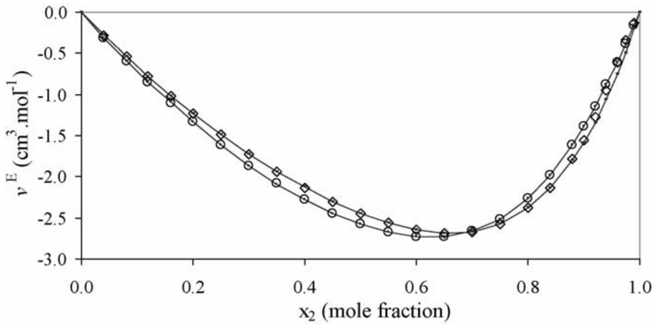

Fig. 2. Excess molar volume (v^E) for the H_2O (1) + DMAPA (2) binary system as a function of water composition. (◇) 283.15 K and (○) 353.15 K. Solid line: calculated values from Redlich–Kister [8] equation with parameters given in Table 1.

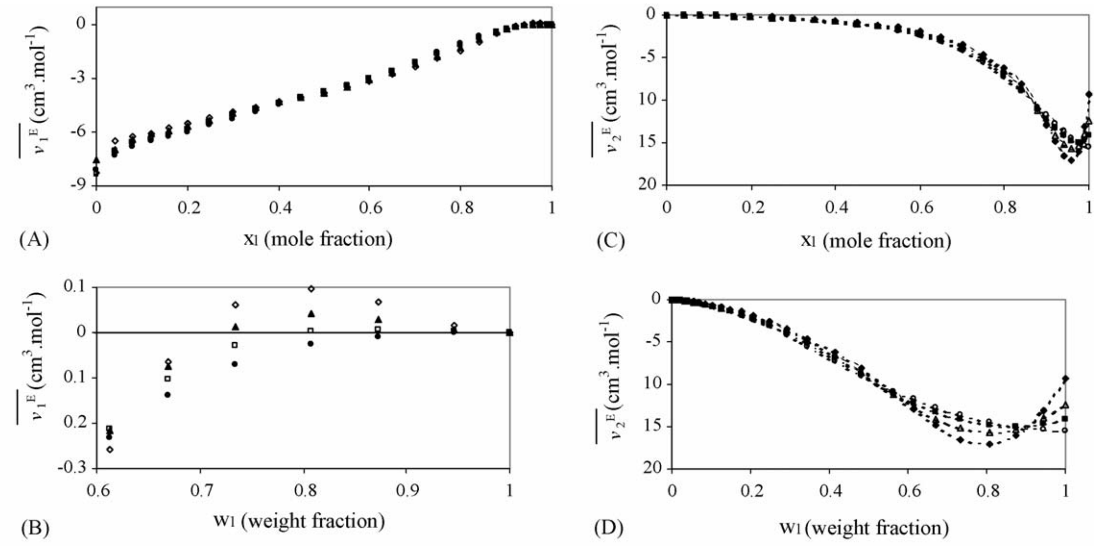

Fig. 3. Excess partial molar volume as a function of water (mole and mass) composition. (A and B) $\overline{v_1^E}$— (◇) 283.15 K; (▲) 303.15 K; (□) 328.15 K; (●) 353.15 K. (C and D) $\overline{v_2^E}$— (♦) 283.15 K; (△) 303.15 K; (■) 328.15 K; (○) 353.15 K. Dotted lines are for displaying trends.

partial molar volumes ($\overline{v_i^E}$) (cm^3 mol^{-1}) (Eqs. (11) and (12)) are plotted in Fig. 3.

$$\overline{v_1} = v_1^* + x_2^2 \sum A_n (1-2x_2)^n + 2x_2^2 (1-x_2) \sum n A_n (1-2x_2)^{n-1} \quad (9)$$

$$\overline{v_2} = v_2^* + (1-x_2)^2 \sum A_n (1-2x_2)^n - 2x_2 (1-x_2)^2 \sum n A_n (1-2x_2)^{n-1} \quad (10)$$

$$\overline{v_1^E} = x_2^2 \sum A_n (1-2x_2)^n + 2x_2^2 (1-x_2) \sum n A_n (1-2x_2)^{n-1} \quad (11)$$

$$\overline{v_2^E} = (1-x_2)^2 \sum A_n (1-2x_2)^n - 2x_2 (1-x_2)^2 \sum n A_n (1-2x_2)^{n-1} \quad (12)$$

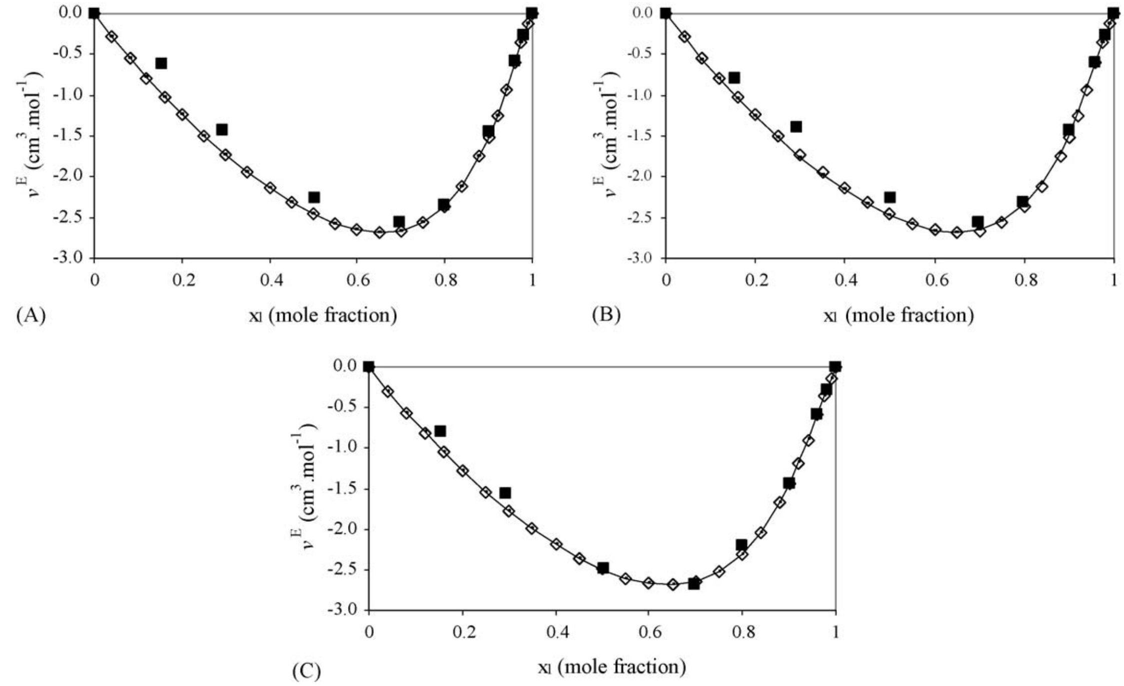

Fig. 4. v^E literature data comparison. (A) 288.15 K, (B) 298.15 K and (C) 308.15 K. (■) Valkovskaya *et al.* [7] and (◇) this work. Black line: calculated with Redlich–Kister [8] equation involving parameters from Table 1.

Table 1
Values of Redlich–Kister [8] coefficients (A_i) and of σ at different temperatures

T (K)	A_0 ($cm^3 mol^{-1}$)	A_1 ($cm^3 mol^{-1}$)	A_2 ($cm^3 mol^{-1}$)	A_3 ($cm^3 mol^{-1}$)	A_4 ($cm^3 mol^{-1}$)	A_5 ($cm^3 mol^{-1}$)	A_6 ($cm^3 mol^{-1}$)	A_7 ($cm^3 mol^{-1}$)	A_8 ($cm^3 mol^{-1}$)	A_9 ($cm^3 mol^{-1}$)	σ ($cm^3 mol^{-1}$)
283.15	−9.7832	−5.2949	−4.7526	−2.5451	6.1407	6.9592	−19.6347	−22.3997	19.0185	22.5239	0.0038
288.15	−9.8129	−5.2059	−4.4679	−2.3888	4.6812	6.2266	−15.1121	−19.1638	15.3693	19.4966	0.0033
293.15	−9.8443	−5.3083	−4.3945	1.1510	4.9294	−11.0744	−14.8952	13.0242	14.8510		0.0046
298.15	−9.8797	−5.2122	−4.2338	0.8145	4.2975	−9.3488	−12.3319	11.4164	12.5130		0.0040
303.15	−9.9214	−5.1245	−4.0518	0.5679	3.4618	−7.9753	−9.4802	10.1077	10.0526		0.0035
308.15	−9.9806	−5.0669	−3.1156	0.6232	−2.7717	−7.6735	4.9928	9.7409			0.0048
313.15	−10.0178	−4.9933	−3.1330	0.3531	−2.1160	−6.3796	4.3146	8.4958			0.0040
318.15	−10.0613	−4.9329	−3.1181	0.1619	−1.6513	−5.2440	3.7985	7.3559			0.0033
323.15	−10.1023	−4.8718	−3.1306	0.0022	−1.1414	−4.3594	3.2514	6.4566			0.0027
328.15	−10.1437	−4.8210	−3.0943	−0.1464	−0.7545	−3.5878	2.7748	5.6831			0.0023
333.15	−10.1854	−4.5973	−2.9860	−2.4697	−0.8440	3.4168	2.8424				0.0049
338.15	−10.2231	−4.5773	−2.9740	−2.2845	−0.4748	3.1825	2.3995				0.0043
343.15	−10.2590	−4.5601	−2.9628	−2.1366	−0.1297	2.9860	1.9760				0.0037
348.15	−10.2843	−4.5370	−3.3403	−2.0668	1.7963	2.9299					0.0045
353.15	−10.3156	−4.5314	−3.2296	−1.9162	1.7018	2.6996					0.0037
283.15*	−9.7892	−5.3532	−4.1853	−1.6442							0.0041
283.15**	−9.7847	−5.2302	−4.3534	−2.7482	0.5194	1.8294					0.0047

Density was measured at atmospheric pressure.

* Parameters determined from experimental value corresponding to densities below 0.8 (mole fraction).

** Parameters determined from experimental value corresponding to densities below 0.9 (mole fraction).

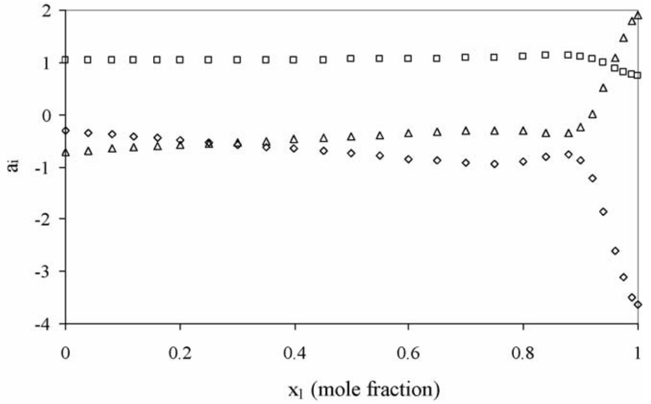

Fig. 5. Evolution of a_i parameters from Eq. (17). (□) a_0, (△) $a_1 \times 10^3$ and (○) $a_2 \times 10^6$.

The partial molar volumes at infinite dilution (Eqs. (13) and (14)) and the excess partial molar volumes at infinite dilution ($\overline{v_i^{\infty}}$) ($cm^3 mol^{-1}$) (Eqs. (15) and (16)) are presented in Table S3 (Supplementary data).

$$\overline{v_1^{\infty}} = v_1^* + \sum A_n(-1)^n \quad (x_1 \to 0) \tag{13}$$

$$\overline{v_2^{\infty}} = v_2^* + \sum A_n \quad (x_2 \to 0) \tag{14}$$

$$\left(\overline{v_1^{\mathrm{E}}}\right)^{\infty} = \sum A_n(-1)^n \quad (x_1 \to 0) \tag{15}$$

$$\left(\overline{v_2^{\mathrm{E}}}\right)^{\infty} = \sum A_n \quad (x_2 \to 0) \tag{16}$$

4. Discussion

All v^{E} values are negative, a characteristic of completely miscible systems. v^{E} of liquid mixtures is complex function of size and shape of the involved molecules and of intermolecular forces.

Excess molar volumes calculated from Valkovskaya *et al.* [7] mixture density data are compared with ours in Fig. 4. Better agreement is found in water rich region than in DMAPA's. These deviations in DMAPA rich region could be explained by deviations occurring in DMAPA densities from both sources. Perhaps Valkovskaya *et al.* [7] have used water containing DMAPA instead of free water DMAPA.

From Table 1, we note the number of Redlich–Kister [8] parameters needed to reach standard deviation, σ, lower than 0.005 decreases with temperature. In fact, at the lower temperatures, mixture composition has important effect and especially on water rich side as pointed out by lower numbers of necessary parameters to fit mixture densities when water compositions above 0.8 or 0.9 are not included in data fitting (see examples for 283.15 K reported in Table 1).

This allows us pointing out special behaviour of this system for water compositions in this region and especially for the lowest temperature.

Two different temperature behaviours are exhibited (from Table S4 (Supplementary data)):

- One where DMAPA excess partial molar volume presents a minimum for water composition between 0.95 and 1, this behaviour is observed from 283.15 to 343.15 K.
- Another where DMAPA excess partial molar volume decreases with water composition, this behaviour is observed at 348.15 and 353.15 K.

To quantify influence of temperature at the various compositions, a new data treatment is done: for each composition, mixture composition is maintained constant and temperature is considered as a variable (Eq. (17)).

$$\rho(T)_{x_i} = \sum_{i=0}^{2} a_i T^i \tag{17}$$

Evolution of a_i parameters as a function of water composition is presented in Fig. 5. For $x_1 < 0.88$, parameters do not depend so much on temperature but for $x_1 > 0.88$ each parameter is highly temperature dependent. $x_1 = 0.88$ corresponds to DMAPA weight fraction close to 0.50.

For the lowest temperature, when DMAPA molecules are added to water, water excess partial molar volumes increase slightly whereas DMAPA excess partial molar volumes decrease strongly (Fig. 3). In fact, when organic molecules are added to water, the hydrocarbon parts of the molecules are surrounded by a large number of water molecules, structurally arranged to form a kind of cages. Long DMAPA hydrocarbon chain needs big water cage. Increasing DMAPA concentration requires more and more cages. Cages tends to group together in order to form huge structure which offers minimal area between water and DMAPA molecules. However, introduction of DMAPA modifies water structure and the length of H-bonding between water molecules close to DMAPA molecule. Water partial molar volume increases (Fig. 3) and leads to a decreasing of local water density. This phenomenon is a characteristic of hydrophobic interactions.

If quantities of DMAPA still increase, chemical interaction due to association between DMAPA and water (N–H···O type) has higher effect than hydrophobic interaction (as displayed by decrease of $\overline{v_2^{\mathrm{E}}}$ negative value).

Thermal agitation seems to inhibit hydrophobic interactions ($\overline{v_2^{\mathrm{E}}}$ minimal value for infinite dilution). Table S4 (Supplementary data) presents at different temperatures the compositions for which $\overline{v_2^{\mathrm{E}}}$ presents a minimum ($\overline{v_2^{\mathrm{E}}}_{\mathrm{min}}$). It can be seen that $\overline{v_2^{\mathrm{E}}}_{\mathrm{min}}$ increases with temperature to reach constant values, pointing out the influence of thermal agitation against hydrophobic effect. Water molecules do not have enough time to create between themselves together enough H-bonds to surround DMAPA molecules. Consequently, adding more DMAPA to water, decreases and increases partial molar volumes of water and DMAPA, respectively.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2006.04.016.

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