# DENSITIES AND RELATIVE PERMITTIVITIES OF BINARY MIXTURES CONTAINING DIPROPYLENE GLYCOL MONOMETHYL ETHER

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Relative permittivities ($\varepsilon$) and densities ($\rho$) of numerous binary mixtures of dipropylene glycol monomethyl ether (1)+propylene glycol mono *n*-butyl ether (2) and dipropylene glycol monomethyl ether (1)+dipropylene glycol mono *n*-butyl ether (2) at five temperatures, between (293.15 and 313.15) K, are reported. The excess molar volumes ($V^E$) and the relative permittivity deviations ($\Delta\varepsilon$) were calculated from these experimental data. The results are discussed in terms of intermolecular interactions in the bulk of studied the binary mixtures.

## Introduction

Systematic investigations of intermolecular interactions and the internal structures of mixed binary liquid mixtures continue to be an area of interest in physical chemistry. Regarding structural studies, review of the literature shows that for the analysis of this type of effect in liquid solvent mixtures it is possible to apply a wide range of spectral methods, thermochemical methods, as well as studies on intensive macroscopic properties of solutions (such as relative permittivity, density, etc.) carried out at different temperatures [1, 2].

As a part of our experimental program on the measurements of physicochemical properties and studies on internal structures of binary liquid mixtures, in which alkoxyalcohol is one of the two constituents [3–7], we present here the relative permittivities and the densities for the dipropylene glycol monomethyl ether (DPM)+propylene glycol mono *n*-butyl ether (PnB) and dipropylene glycol monomethyl ether+dipropylene glycol mono n-buthyl ether (DPnB) mixtures, at different temperatures. We calculated the excess molar volumes and the deviations in the relative permittivities, which were fitted to the Redlich–Kister equation [8].

## Results and discussion

The experimental data of relative permittivity ($\varepsilon$) and density ($\rho$) obtained from the measurements of the pure solvents and for the analysed binary mixtures at all investigated temperatures are summarized in Tables 1 and 2.

From the measured densities the excess values of molar volumes $V^E$ of the mixtures, at the each investigated temperature, were fitted to the equation:

$$V^E = x_1 M_1(\rho^{-1} - \rho_1^{-1}) + x_2 M_2(\rho^{-1} - \rho_2^{-1}) \qquad (1)$$

where $M_1$ and $M_2$ are the molar masses of the pure components and $\rho_1$, $\rho_2$ and $\rho$ are the densities of the pure species (1) and (2), and that of the mixtures at different temperatures, respectively.

The deviation of the relative permittivity from a mole fraction average was calculated by:

$$\Delta\varepsilon = \varepsilon - (x_1\varepsilon_1 + x_2\varepsilon_2) \qquad (2)$$

where $\varepsilon_1$, $\varepsilon_2$ and $\varepsilon$ are the relative permittivities of the pure species (1) and (2), and that of the mixtures at different temperatures, respectively.

Excess volume and deviations of relative permittivity were fitted by a Redlich–Kister type equation [8]:

$$V^E/\text{cm}^3\ \text{mol}^{-1}$$

$$\Delta\varepsilon = x_1(1 - x_1)\sum_{j=0}^{k} a_j(2x_1 - 1)^j \qquad (3)$$

The parameters $a_j$ of Eq. (3) were evaluated by the least-squares method. The values of these parameters, at each studied temperature, with standard deviation $\sigma(V^E)$ and $\sigma(\Delta\varepsilon)$ are summarized in Table 3.

The standard deviation values were obtained from

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**Table 1** Experimental relative permittivity for DPM+PnB and DPM+DPnB binary mixtures

| | DPM+PnB | | | | | | DPM+DPnB | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\varepsilon$ | | | | | | $\varepsilon$ | | | | |
| | 293.15 | 298.15 | 303.15 | 308.15 | 313.15 | | 293.15 | 298.15 | 303.15 | 308.15 | 313.15 |
| $x_1$ | K | | | | | $x_1$ | K | | | | |
| 0.0000 | 8.19 | 7.90 | 7.79 | 7.55 | 6.98 | 0.0000 | 7.71 | 7.48 | 7.30 | 7.08 | 6.93 |
| 0.0402 | 8.06 | 7.83 | 7.75 | 7.54 | 7.01 | 0.0501 | 7.81 | 7.59 | 7.41 | 7.19 | 7.05 |
| 0.0812 | 7.96 | 7.75 | 7.71 | 7.53 | 7.02 | 0.1001 | 7.92 | 7.70 | 7.52 | 7.31 | 7.16 |
| 0.1659 | 7.90 | 7.67 | 7.65 | 7.50 | 7.05 | 0.2000 | 8.15 | 7.91 | 7.73 | 7.52 | 7.36 |
| 0.2543 | 7.85 | 7.67 | 7.64 | 7.48 | 7.10 | 0.3000 | 8.41 | 8.17 | 7.98 | 7.74 | 7.57 |
| 0.3470 | 7.85 | 7.66 | 7.62 | 7.46 | 7.10 | 0.4000 | 8.67 | 8.41 | 8.21 | 7.96 | 7.77 |
| 0.4431 | 7.93 | 7.75 | 7.69 | 7.51 | 7.17 | 0.5000 | 8.96 | 8.68 | 8.46 | 8.20 | 8.00 |
| 0.5004 | 8.15 | 7.96 | 7.88 | 7.66 | 7.36 | 0.5511 | 9.11 | 8.83 | 8.60 | 8.33 | 8.13 |
| 0.5442 | 8.15 | 7.96 | 7.88 | 7.66 | 7.36 | 0.6000 | 9.26 | 8.97 | 8.74 | 8.46 | 8.26 |
| 0.6004 | 8.33 | 8.14 | 8.04 | 7.79 | 7.51 | 0.6501 | 9.42 | 9.13 | 8.89 | 8.61 | 8.39 |
| 0.6499 | 8.53 | 8.32 | 8.20 | 7.95 | 7.68 | 0.7000 | 9.59 | 9.28 | 9.05 | 8.76 | 8.54 |
| 0.7609 | 9.07 | 8.86 | 8.71 | 8.44 | 8.21 | 0.7500 | 9.76 | 9.45 | 9.22 | 8.93 | 8.70 |
| 0.8774 | 9.73 | 9.49 | 9.33 | 9.09 | 8.86 | 0.8000 | 9.94 | 9.63 | 9.39 | 9.09 | 8.86 |
| 0.9380 | 10.16 | 9.94 | 9.75 | 9.47 | 9.22 | 0.8990 | 10.32 | 10.00 | 9.75 | 9.43 | 9.18 |
| 0.9750 | 10.49 | 10.20 | 9.98 | 9.66 | 9.40 | 0.9500 | 10.53 | 10.19 | 9.94 | 9.61 | 9.34 |
| 1.0000 | 10.76 | 10.40 | 10.12 | 9.77 | 9.49 | 1.0000 | 10.76 | 10.40 | 10.12 | 9.77 | 9.49 |

$$\sigma = \left[ \frac{\sum (X_{\text{exptl}} - X_{\text{calcd}})^2}{N - p} \right]^{1/2} \qquad (4)$$

where $N$ is the number of experimental points, $p$ is the number of parameters, $X_{\text{exptl}}$ and $X_{\text{calcd}}$ are the experimental and calculated properties, respectively.

The variations of $V^E$ and $\Delta\varepsilon$ *vs*. the mole fraction of DMP at 298.15 K are presented in Figs 1 and 2, respectively.

Figure 1 shows that the excess molar volumes are negative for all the investigated systems, with a minimum positioned always nearly $x_{\text{DPM}} \approx 0.50$ for DPM+PnB, and nearly $x_{\text{DPM}} \approx 0.50$ for DPM+DPnB binary mixtures. The negative values of $V^E$ over the all mole fraction may be attributed mainly to the association through intermolecular hydrogen bonds between DPM and PnB or DPnB.

As suggested by other authors [10–13], the alkoxyalcohols exist as associated structures in the liquid state. The association may be due to the intermolecular hydrogen bond formation between the ether oxygen atom and the –OH group. This association may also be through the hydrogen bonding of alkoxyalcohols –OH groups. The magnitude of $V^E$ is the result the specific interactions in analysed binary mixtures [9, 14]. The specific interactions results from disruption of the DPM, PnB and DPnB structure through breaking of hydrogen bonds, as well as weakening of the interactions between molecules, formation of new

hydrogen bonds between ME and PnB or DPnB, and other complex-forming interactions.

The results obtained in this work seem to indicate that the respective stable intermolecular complexes of the DPM·PnB and DPM·DPnB types would be formed in the studied binary mixtures of dipropylene glycol monomethyl ether+propylene glycol mono *n*-butyl ether and dipropylene glycol monomethyl ether+dipropylene glycol mono *n*-butyl ether.
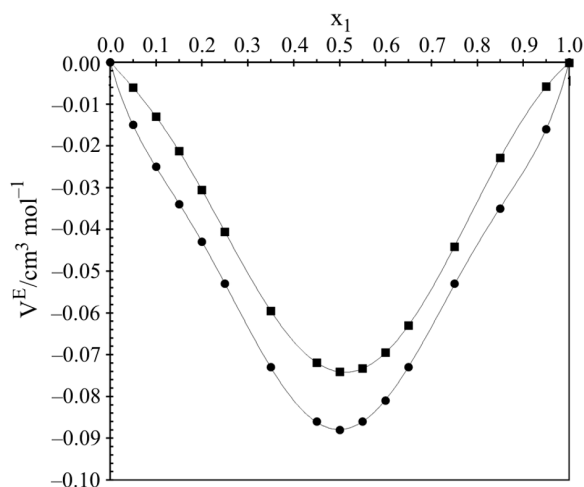


**Fig. 1** Plot of $V^E$ as a function of composition for ● – DPM+PnB and ■ – DPM+DPnB at 298.15 K

**Table 2** Experimental density for DPM+PnB and DPM+DPnB binary mixtures

| $x_1$ | DPM+PnB $\rho$/g cm$^{-3}$ | | | | |
|---|---|---|---|---|---|
| | 293.15 K | 298.15 K | 303.15 K | 308.15 K | 313.15 K |
| 0.0000 | 0.87927 | 0.87447 | 0.87050 | 0.86577 | 0.86131 |
| 0.0402 | 0.88255 | 0.87770 | 0.87366 | 0.86890 | 0.86439 |
| 0.0812 | 0.88586 | 0.88099 | 0.87688 | 0.87208 | 0.86754 |
| 0.1659 | 0.89265 | 0.88772 | 0.88350 | 0.87863 | 0.87401 |
| 0.2543 | 0.89970 | 0.89470 | 0.89035 | 0.88544 | 0.88074 |
| 0.3470 | 0.90706 | 0.90201 | 0.89753 | 0.89256 | 0.88777 |
| 0.4431 | 0.91460 | 0.90950 | 0.90489 | 0.89985 | 0.89498 |
| 0.5004 | 0.91905 | 0.91391 | 0.90922 | 0.90415 | 0.89922 |
| 0.5442 | 0.92241 | 0.91725 | 0.91249 | 0.90740 | 0.90244 |
| 0.6004 | 0.92671 | 0.92150 | 0.91666 | 0.91153 | 0.90653 |
| 0.6499 | 0.93045 | 0.92522 | 0.92032 | 0.91515 | 0.91010 |
| 0.7609 | 0.93879 | 0.93349 | 0.92843 | 0.92320 | 0.91805 |
| 0.8774 | 0.94749 | 0.94212 | 0.93689 | 0.93158 | 0.92634 |
| 0.9380 | 0.95198 | 0.94657 | 0.94126 | 0.93593 | 0.93063 |
| 0.9750 | 0.95470 | 0.94928 | 0.94391 | 0.93856 | 0.93323 |
| 1.0000 | 0.95651 | 0.95108 | 0.94570 | 0.94034 | 0.93500 |

| $x_1$ | DPM+DPnB $\rho$/g cm$^{-3}$ | | | | |
|---|---|---|---|---|---|
| | 293.15 K | 298.15 K | 303.15 K | 308.15 K | 313.15 K |
| 0.0000 | 0.91879 | 0.91665 | 0.91404 | 0.90879 | 0.90545 |
| 0.0501 | 0.92026 | 0.91799 | 0.91526 | 0.91001 | 0.90658 |
| 0.1001 | 0.92176 | 0.91936 | 0.91653 | 0.91126 | 0.90776 |
| 0.2000 | 0.92489 | 0.92223 | 0.91919 | 0.91390 | 0.91023 |
| 0.3000 | 0.92820 | 0.92527 | 0.92199 | 0.91669 | 0.91285 |
| 0.4000 | 0.93169 | 0.92847 | 0.92493 | 0.91962 | 0.91561 |
| 0.5000 | 0.93533 | 0.93179 | 0.92800 | 0.92268 | 0.91848 |
| 0.5511 | 0.93726 | 0.93355 | 0.92961 | 0.92428 | 0.91998 |
| 0.6000 | 0.93913 | 0.93525 | 0.93117 | 0.92585 | 0.92144 |
| 0.6501 | 0.94110 | 0.93704 | 0.93282 | 0.92748 | 0.92297 |
| 0.6999 | 0.94309 | 0.93886 | 0.93448 | 0.92915 | 0.92453 |
| 0.7500 | 0.94515 | 0.94074 | 0.93620 | 0.93086 | 0.92613 |
| 0.7999 | 0.94727 | 0.94267 | 0.93797 | 0.93262 | 0.92777 |
| 0.8999 | 0.95172 | 0.94671 | 0.94169 | 0.93633 | 0.93124 |
| 0.9500 | 0.95407 | 0.94886 | 0.94366 | 0.93830 | 0.93308 |
| 1.0000 | 0.95651 | 0.95108 | 0.94570 | 0.94034 | 0.93500 |

Similar conclusions can be drawn from the analysis of the relative permittivity deviations. Figure 2 shows that the relative permittivity deviations are also negative for each binary system, with a minimum lying always nearly $x_1 \approx 0.55$ for DPM+PnB, and nearly $x_1 \approx 0.55$ for DPM+DPnB binary mixtures. As evidenced from the calculations, the relative permittivity deviations decrease with an increase in the temperature (Tables 1 and 3).

The study of this extrathermodynamic parameter for binary liquid systems represents a unique tool for investigating the formation of intermolecular complexes, and provides a valuable aid for determining their stoichiometry and their relative thermostability.

**Table 3** Parameters $a_j$ of Eq. (3), and standard deviations $\sigma(\Delta\varepsilon)$ or $\sigma(V^E)$ for DPM+PnB and DPM+DPnB binary mixtures

| DPM+PnB | | | | | | |
|---|---|---|---|---|---|---|
| | $a_0$ | $a_1$ | $a_2$ | $a_3$ | $a_4$ | $\sigma$ |
| *T*/K | | | 293.15 | | | |
| $\Delta\varepsilon$ | −5.7804 | −0.6194 | 1.9565 | −0.3512 | −4.2079 | $7.0\cdot10^{-3}$ |
| $V^E$/cm$^3$ mol$^{-1}$ | −0.3643 | 0.0132 | 0.3511 | −0.0140 | −0.4582 | $3.7\cdot10^{-4}$ |
| *T*/K | | | 298.15 | | | |
| $\Delta\varepsilon$ | −5.2021 | −0.6095 | 1.5094 | 0.1056 | −1.8830 | $14.0\cdot10^{-3}$ |
| $V^E$/cm$^3$ mol$^{-1}$ | −0.3508 | 0.0061 | 0.3668 | −0.0187 | −0.4053 | $8.4\cdot10^{-4}$ |
| *T*/K | | | 303.15 | | | |
| $\Delta\varepsilon$ | −4.6921 | −0.9452 | 1.4198 | 0.7677 | −0.4526 | $15.0\cdot10^{-3}$ |
| $V^E$/cm$^3$ mol$^{-1}$ | −0.3345 | 0.0045 | 0.3745 | −0.0273 | −0.3318 | $9.8\cdot10^{-4}$ |
| *T*/K | | | 308.15 | | | |
| $\Delta\varepsilon$ | −4.3274 | −1.5094 | 1.5514 | 1.6996 | 0.5975 | $9.0\cdot10^{-3}$ |
| $V^E$/cm$^3$ mol$^{-1}$ | −0.3215 | −0.0021 | 0.3947 | −0.0234 | −0.3145 | $5.4\cdot10^{-4}$ |
| *T*/K | | | 313.15 | | | |
| $\Delta\varepsilon$ | −3.9233 | −1.4870 | 2.4627 | 1.9418 | −0.0759 | $11.0\cdot10^{-3}$ |
| $V^E$/cm$^3$ mol$^{-1}$ | −0.3074 | −0.0073 | 0.3838 | −0.0117 | −0.2448 | $6.8\cdot10^{-4}$ |
| DPM+DPnB | | | | | | |
| | $a_0$ | $a_1$ | $a_2$ | $a_3$ | $a_4$ | $\sigma$ |
| *T*/K | | | 293.15 | | | |
| $\Delta\varepsilon$ | −1.1164 | −0.2042 | −0.1341 | −0.0591 | −0.1905 | $3.0\cdot10^{-3}$ |
| $V^E$/cm$^3$ mol$^{-1}$ | −0.3138 | −0.0451 | 0.3271 | 0.0657 | −0.1661 | $4.4\cdot10^{-4}$ |
| *T*/K | | | 298.15 | | | |
| $\Delta\varepsilon$ | −1.0318 | −0.2450 | −0.0643 | −0.0041 | 0.1061 | $4.0\cdot10^{-3}$ |
| $V^E$/cm$^3$ mol$^{-1}$ | −0.2965 | −0.0292 | 0.3138 | 0.0412 | −0.1259 | $4.8\cdot10^{-4}$ |
| *T*/K | | | 303.15 | | | |
| $\Delta\varepsilon$ | −0.9837 | −0.3145 | 0.1641 | 0.2195 | 0.1167 | $4.0\cdot10^{-3}$ |
| $V^E$/cm$^3$ mol$^{-1}$ | −0.2842 | −0.0174 | 0.3182 | 0.0189 | −0.0960 | $5.4\cdot10^{-4}$ |
| *T*/K | | | 308.15 | | | |
| $\Delta\varepsilon$ | −0.9138 | −0.3108 | 0.4845 | 0.2176 | −0.0122 | $2.0\cdot10^{-3}$ |
| $V^E$/cm$^3$ mol$^{-1}$ | −0.2712 | −0.0243 | 0.3528 | 0.0274 | −0.1273 | $4.8\cdot10^{-4}$ |
| *T*/K | | | 313.15 | | | |
| $\Delta\varepsilon$ | −0.8335 | −0.3245 | 0.5696 | 0.2926 | 0.0740 | $2.0\cdot10^{-3}$ |
| $V^E$/cm$^3$ mol$^{-1}$ | −0.2591 | −0.0300 | 0.3781 | 0.0036 | −0.1286 | $4.0\cdot10^{-4}$ |

The position of the relative minima in the plots of $\Delta\varepsilon$ *vs.* $x_1$, could be taken as the true composition of these intermolecular complexes [1, 2, 9, 15].

On the base of comparison of $\Delta\varepsilon$ values in studied liquid mixtures in the composition regions corresponding to their maximum deviation from ideality, it is possible to deduced that:

$$|\Delta\varepsilon_{DPM+PnB}| > |\Delta\varepsilon_{DPM+DPnB}|$$

Therefore, it is necessary to assume that the energetic stability of intermolecular complexes DPM·PnB and DPM·DPnB changes in the identical way.

From the experimental values of relative permittivities ($\varepsilon_{12}$) (Table 1), the temperature coefficients of the relative permittivity, denoted $\alpha_{12}$, viz.:

$$\alpha_{12} = \frac{1}{\varepsilon}\left[\frac{d\varepsilon}{d(1/T)}\right] \quad (4)$$

at 298.15 K, were calculated (Fig. 3).

The composition range of liquid binary mixtures within which $\alpha_{12}$ or its excess attain their highest values should be interpreted (as shown in Räetzsch *et al.*'s thermodynamic considerations [16]) as a region characterized by maximal intermolecular interactions between two different components of the given binary liquid mixture.

For all studied mixtures, the $\alpha_{12}$ *vs.* $x_1$ curves are W-shaped, being negative at the ends and positive at $x_1$ from about 0.20 to 0.80. In the case of all studied mixtures, we observed the tendency to achieve the maxi-
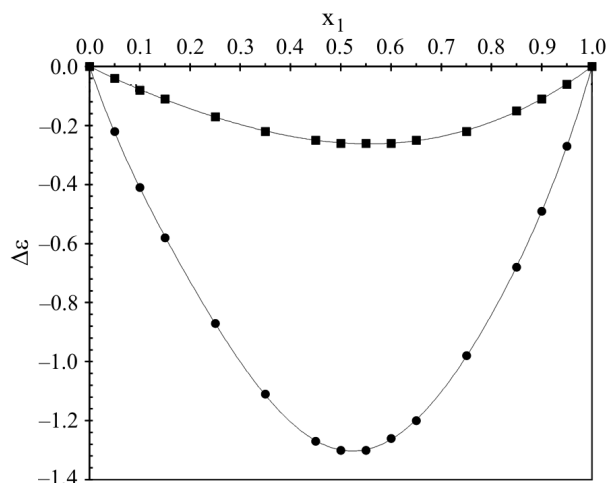
**Fig. 2** Plot of $\Delta\varepsilon$ as a function of composition for
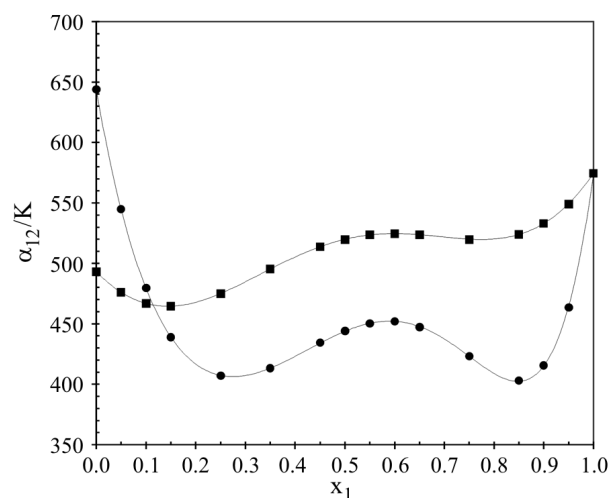● – DPM+PnB and ■ – DPM+DPnB at 298.15 K



**Fig. 3** Plot of $\alpha_{12}$ as a function of composition for
● – DPM+PnB and ■ – DPM+DPnB at 298.15 K

mum by the function $\alpha_{12}$ at ca. $x_1 \approx 0.55$. This effect can be accounted for by maximal intermolecular interactions between DPM and PnB or DPnB molecules, which lead to the formation of stable DPM·PnB and DPM·DPnB intermolecular complexes [1–3].

The conclusions to be drawn from presented results are that:

• The probable compositions of the intermolecular complexes are in DPM+PnB=1:1 and; in DPM+DPnB=1:1 mole reactions, over the measured temperature range.
• Most likely, complexes of DPM with PnB are energetically the most stables.

## Experimental section

### *Materials*

DPM, PnB and DPnB (Fluka, purum, GC>98%) were used. All solvents were further purified by the methods reported by Riddick *et al*. [17]. The mixtures were prepared by weighing with an accuracy $\pm 1 \cdot 10^{-4}$ g. The conversions to molar quantities were based on the relative atomic mass table (1985), issued by IUPAC in 1986. The uncertainty in the mole fractions is less than $1 \cdot 10^{-4}$. All the liquids were stored in a dry-box over $P_2O_5$, and were degassed by ultrasounds just before the experiments.

### *Measurements*

Solvent densities were measured with a bicapillary type Lipkin pycnometer, with a capacity of ca. 90 cm$^3$. Double distilled, deionized and degassed water with a specific conductance of $1 \cdot 10^{-7}$ $\Omega^{-1}$ cm$^{-1}$ was used for the calibration. The maximum error in the density measurements was $4 \cdot 10^{-5}$ g cm$^{-3}$.

The relative permittivity measurements were carried out at 3 MHz, using a bridge of the type OH-301 (made in Radelkis, Hungary). The thermostatic stainless steel measuring cell was of C3 ($1 < \varepsilon < 25$) type. The cell was calibrated with standard pure liquids, such as acetone, butan-1-ol and dichloromethane. All these solvents were of spectrograde quality or higher. The relative permittivity for the standards were taken [1, 10]. The accuracy in the relative permittivity measurements was $\pm 0.02$.

In all the physical property measurements, a Haake model DC-30 thermostat was used at a constant digital temperature control of $\pm 0.01$ K.

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