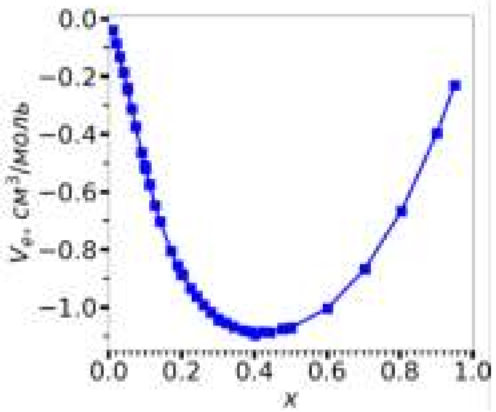
Voronoi analysis of solutions volumetric properties

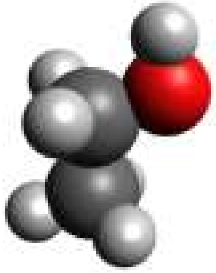
Evgenii Kadtsyn

Novosibirsk

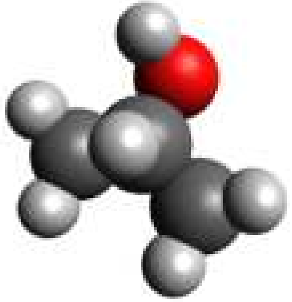
Aqueous alcohol solutions

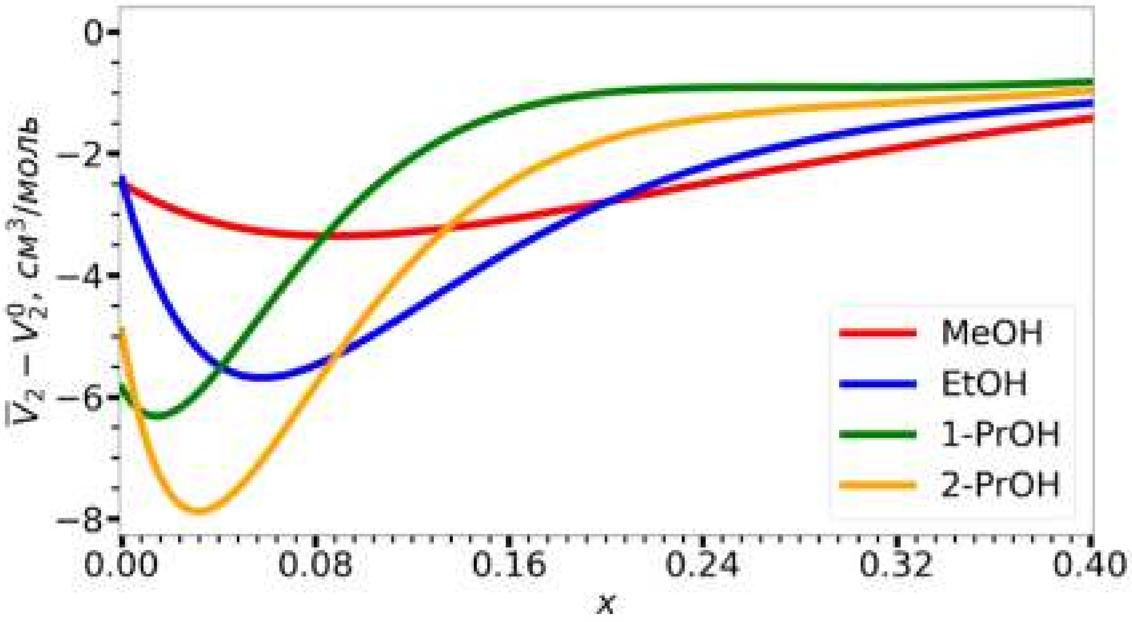



Methanol


Ethanol


1-Propanol

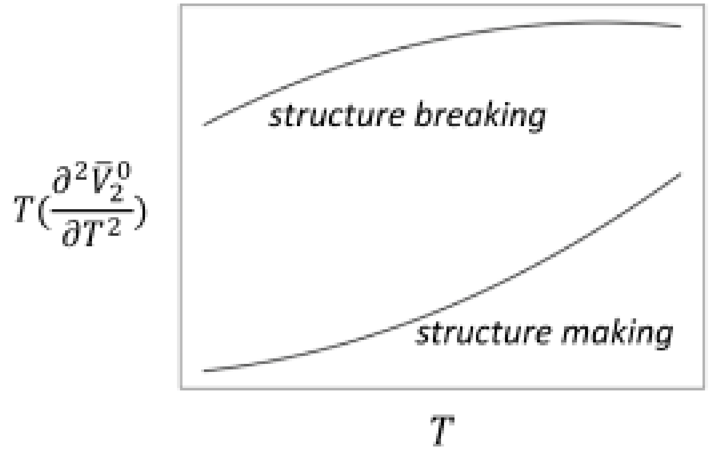

2-Propanol



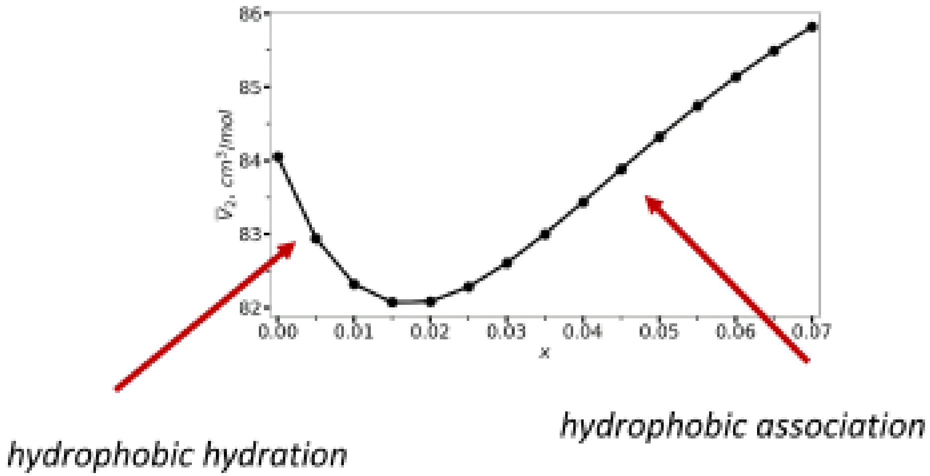
Volumetric properties of solutions

$$\bar{V} = \left(\frac{\partial \bar{G}}{\partial p}\right)_{T,n_i} \qquad \bar{V_i} = \left(\frac{\partial \mu_i}{\partial p}\right)_{T,n_i}$$

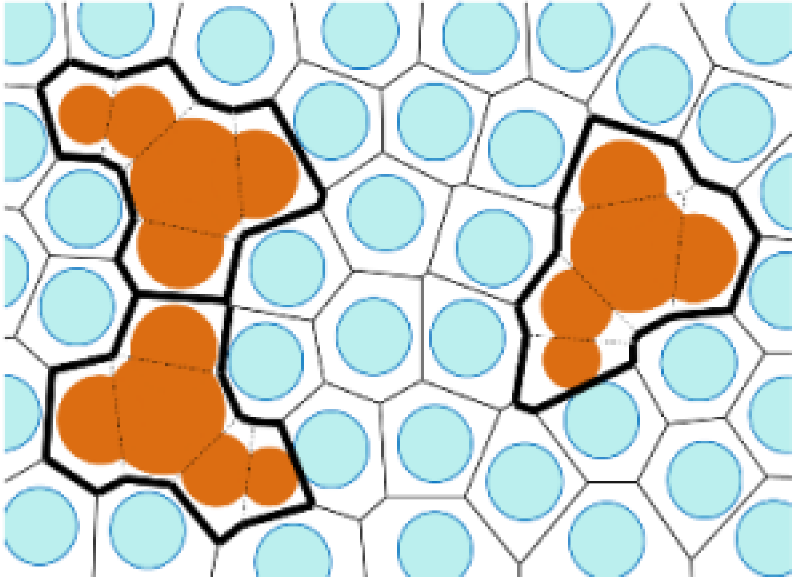
$$\bar{V_i} = \left(\frac{\partial V}{\partial n_i}\right)_{T,p,n_{j\neq i}} \qquad \sum x_i \bar{V_i} = \bar{V}$$



- *Derived from solution density*
- ***Thermodynamics** characteristics*
- *Used in **structural** studies*



Voronoi method



- Voronoi region of an atom is the region which points are closer to this atom than to any other atom of the system
- Voronoi region of a molecule is the union of its atoms' Voronoi regions
- Component's *Voronoi molar volume* is the mean volume for Voronoi regions of component's molecules
- Component Voronoi molar volume is the *real volume* assigned to component molecules in a solution
- Voronoi tessellation divides a solution volume between components

Voronoi molar volumes and volumetric properties of solution

- Voronoi regions form a tessellation
- The sum of Voronoi volumes equals to the system volume

$$V(x) = \sum_i n_i(x)\bar{V}_i^{Vor}(x)$$

$$\bar{V}(x) = (1-x)\cdot V_1^{Vor}(x) + x\cdot V_2^{Vor}(x)$$

$$\rho(x) = \frac{x\cdot M_2 + (1-x)\cdot M_1}{x\cdot V_2^{Vor}(x) + (1-x)\cdot V_1^{Vor}(x)}$$

$$V^E = (1-x)\cdot(V_1^{Vor}(x) - V_1^0) + x\cdot\left(V_2^{Vor}(x) - V_2^0\right)$$

$$V_{\varphi 2} = V_2^{Vor}(x) + (V_1^{Vor}(x) - V_1^0)\frac{(1-x)}{x}$$

$$\overline{V_2} = V_2^{Vor} + (1-x)(x\cdot\frac{dV_2^{Vor}}{dx} + (1-x)\cdot\frac{dV_1^{Vor}}{dx})$$

All volumetric properties for solutions can be expressed via components' Voronoi molar volumes

Simulation details

- Methanol, ethanol – interval 1-40%
- 1-propanol, 2-propanol – interval 1-20%
- Step of 1% in each case

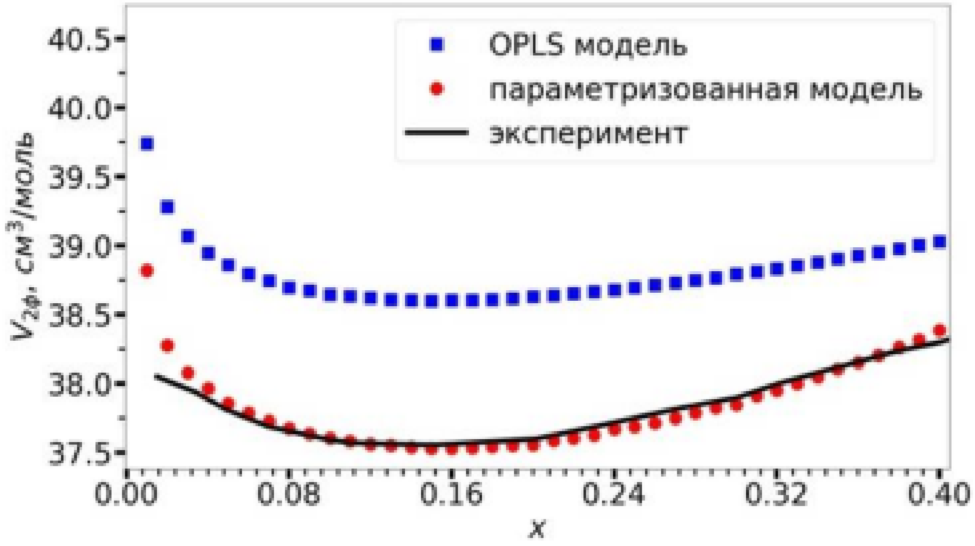
<u>Gromacs 5.0.7</u>

T=300K

p=1 бар

- Alcohols – OPLS-AA derived concentration dependent charge scaling
- Water – TIP4P-2005

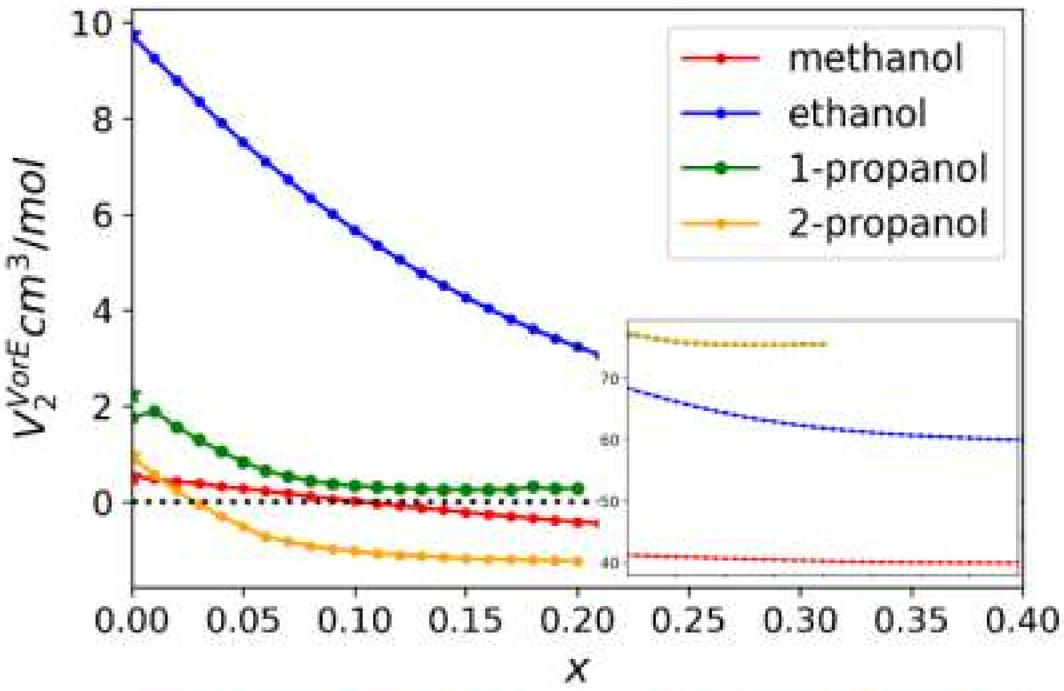
100ns for each simulation

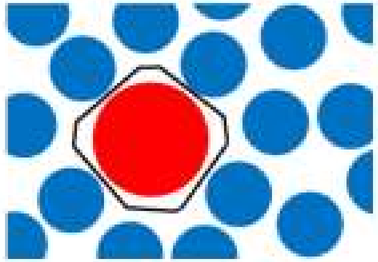


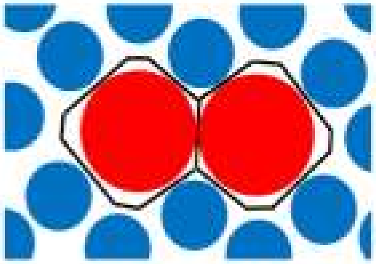
methanol apparent volume

Components' Voronoi molar volumes

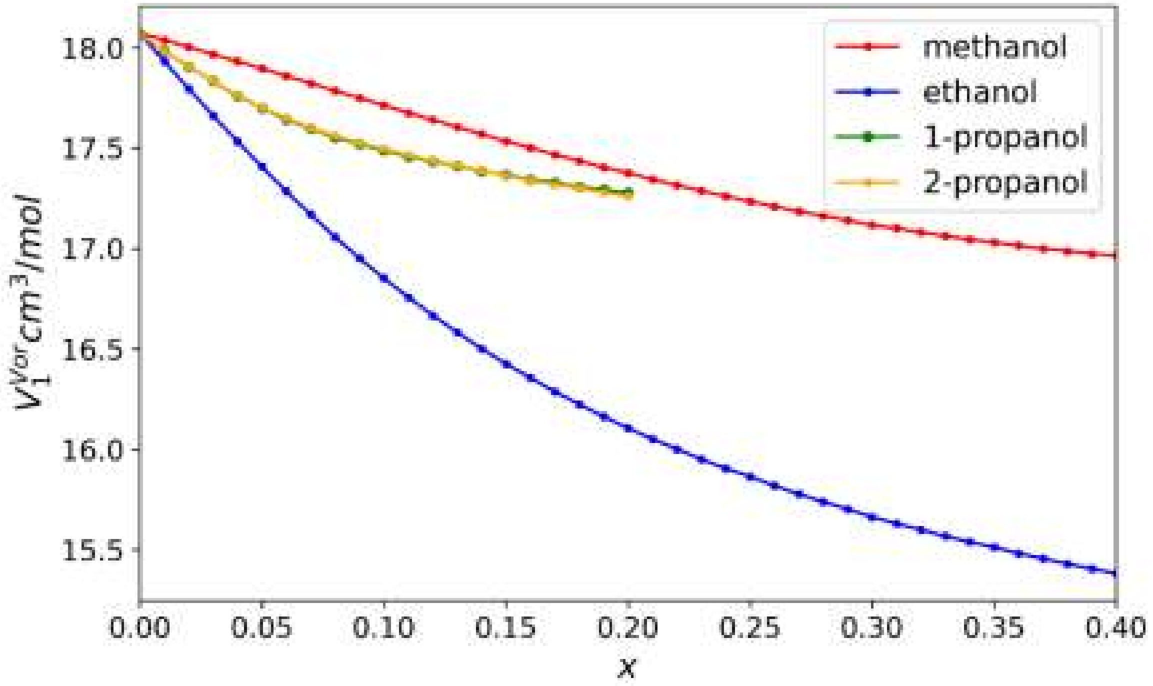
solute

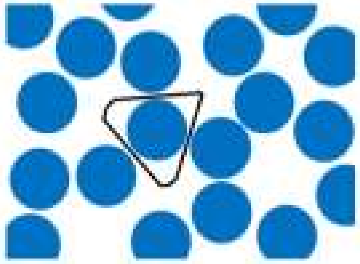


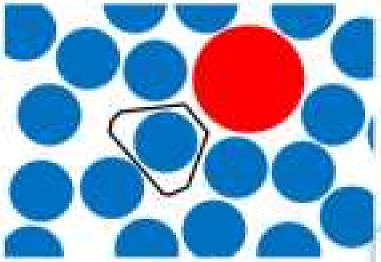




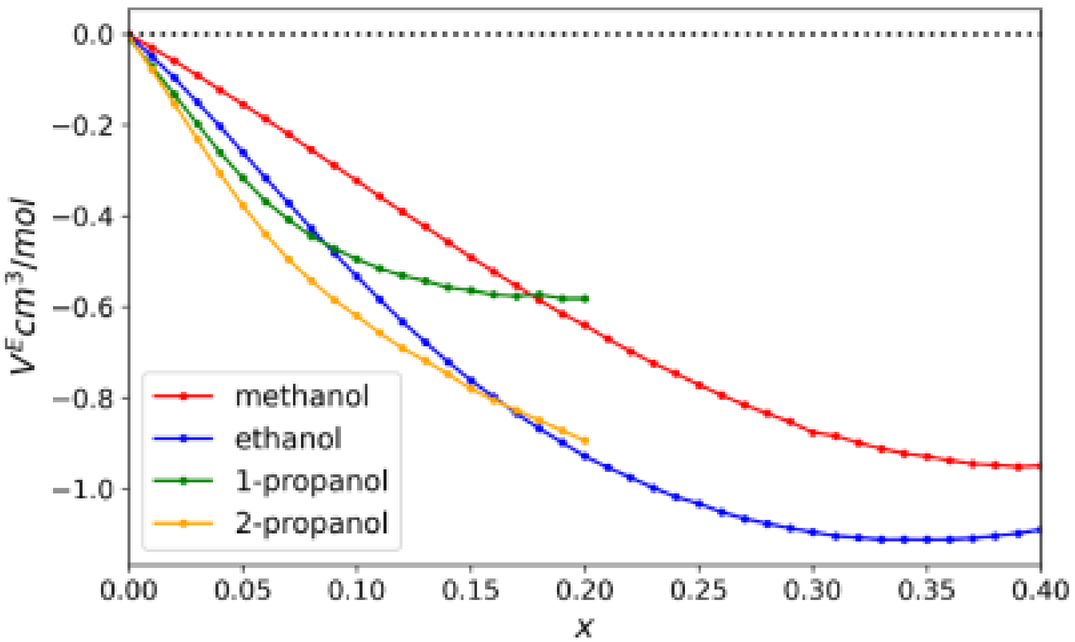
solvent

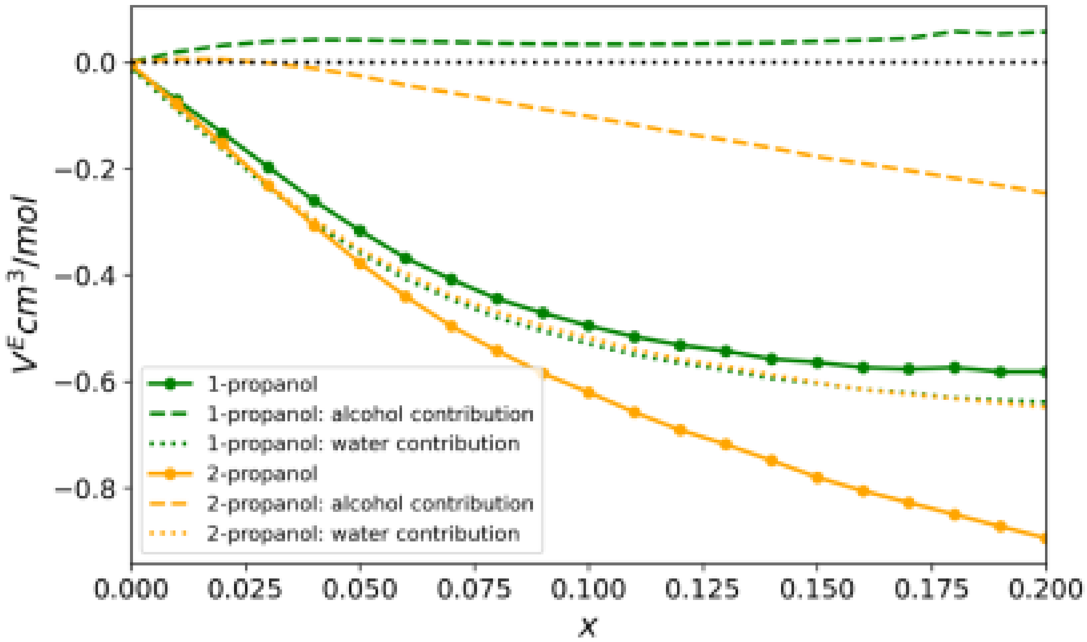






Excess molar volume



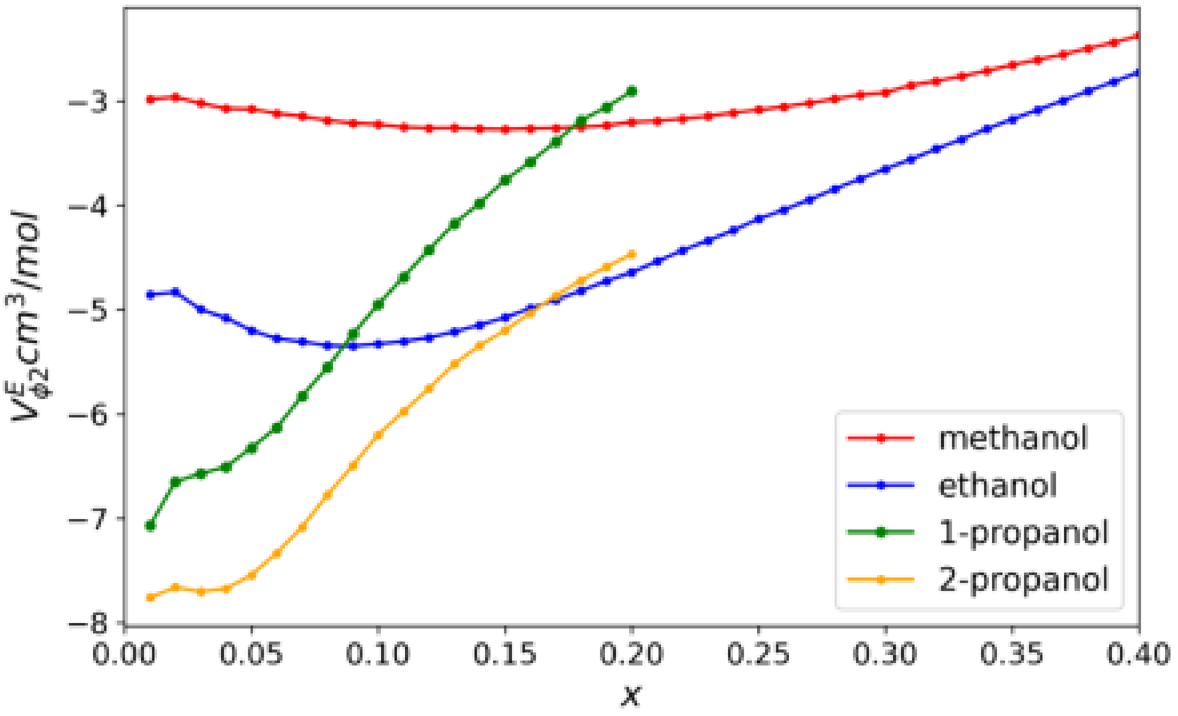


$$V^E = (1-x)\cdot(V_1^{Vor}(x) - V_1^0) + x\cdot\left(V_2^{Vor}(x) - V_2^0\right)$$

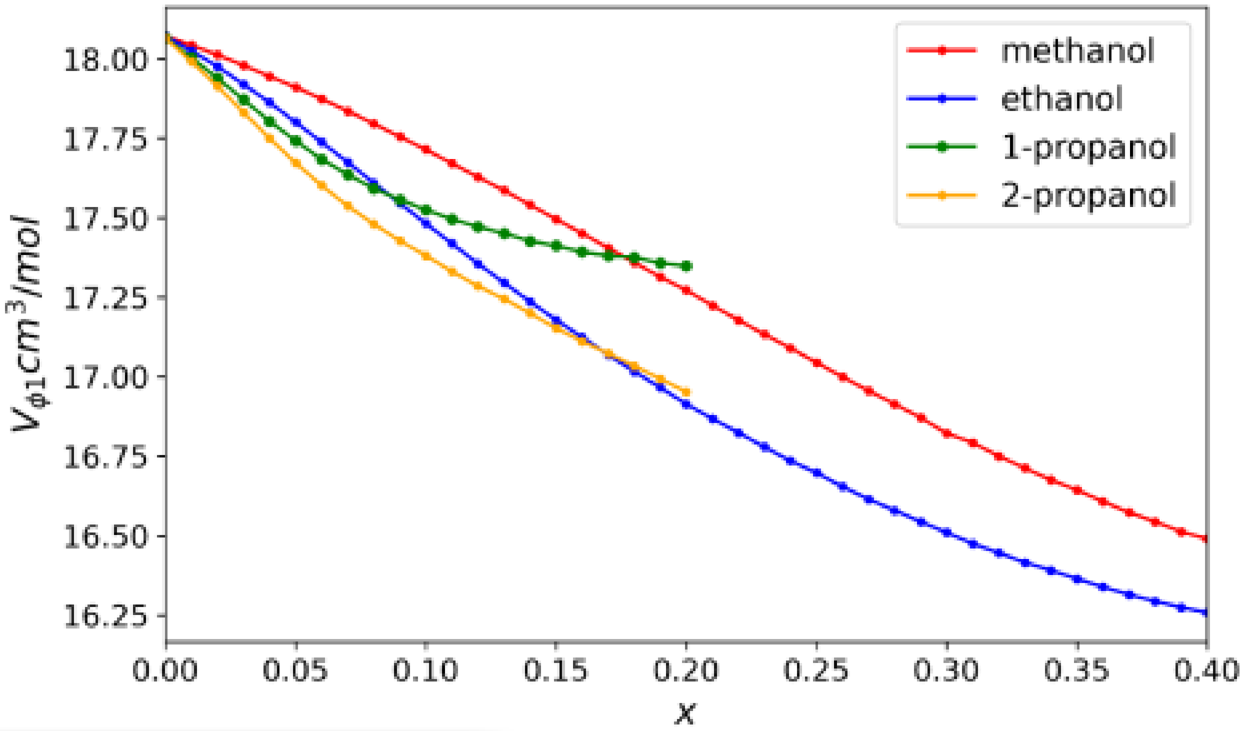
solvent contribution *solute contribution*

Apparent molar volume

solute

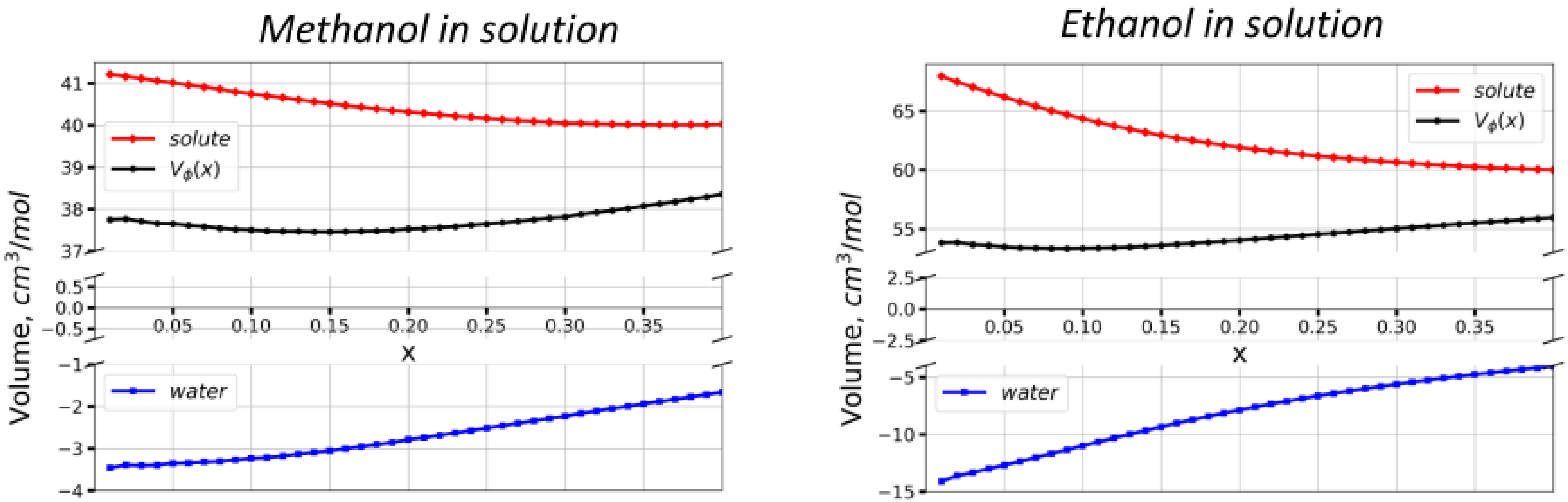


solvent



$$V_{\varphi \mathrm{i}} = \frac{V - n_\mathrm{j} V_\mathrm{j}^0}{n_\mathrm{i}}$$

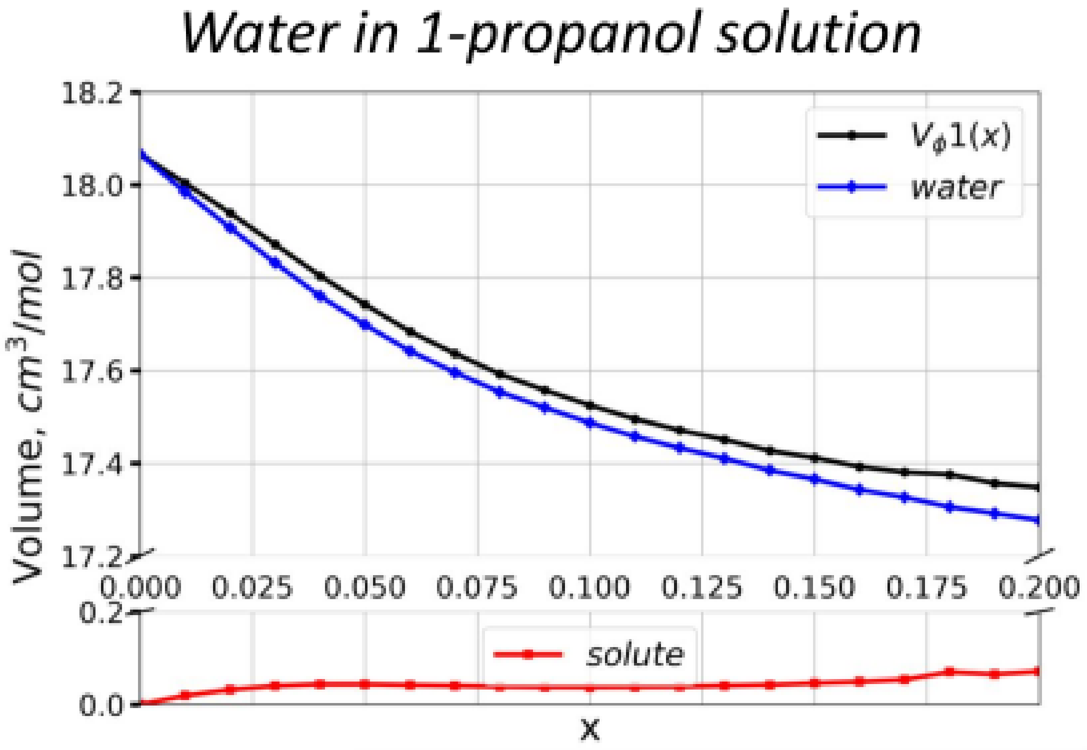
Apparent molar volume: components contributions

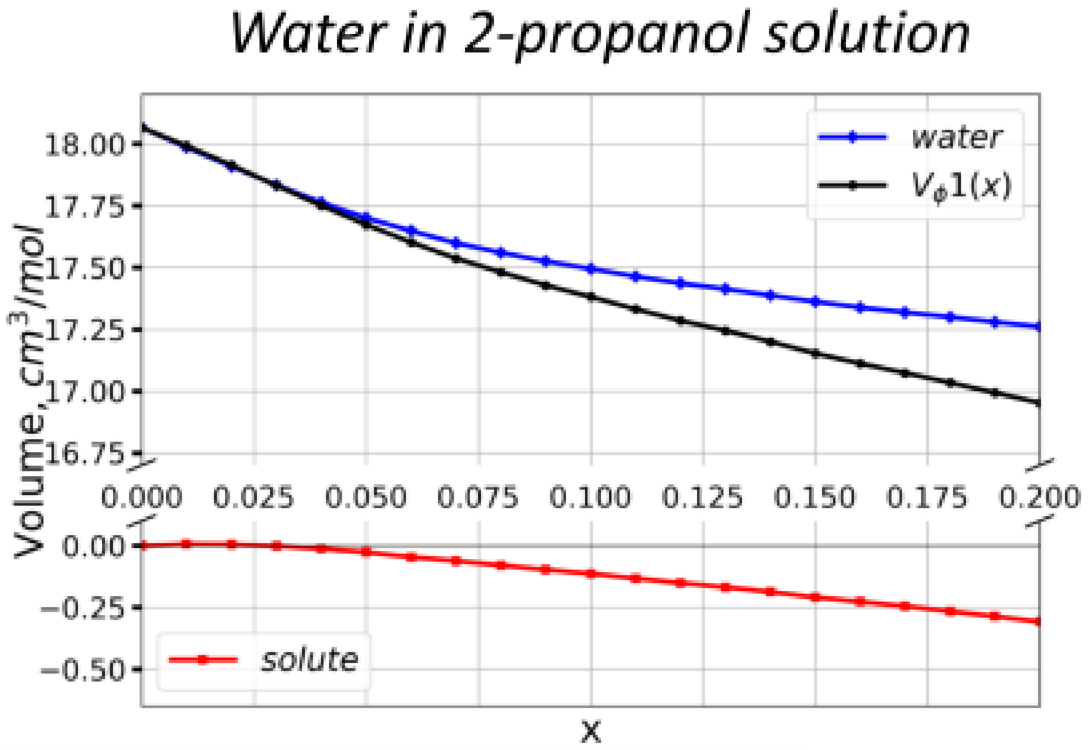


$$V_{\varphi 2} = V_2^{Vor}(x) + (V_1^{Vor}(x) - V_1^0)\frac{(1-x)}{x}$$

solute contribution *solvent contribution*

Apparent molar volume: components contributions



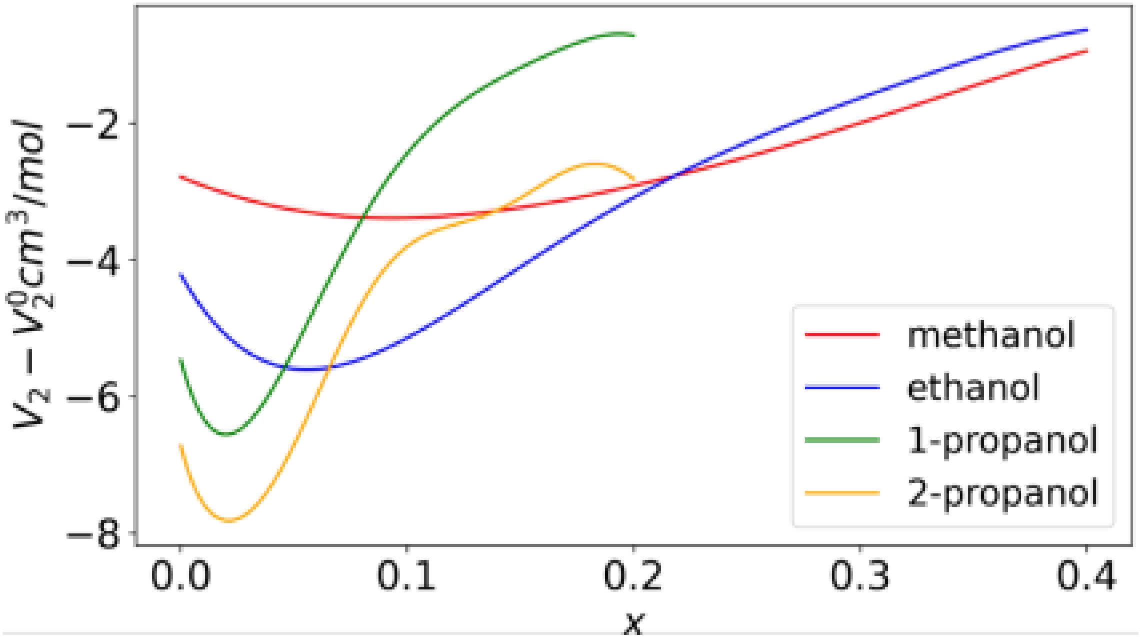


$$V_{\varphi 1} = V_1^{Vor}(x) + (V_2^{Vor}(x) - V_2^0)\frac{x}{(1-x)}$$

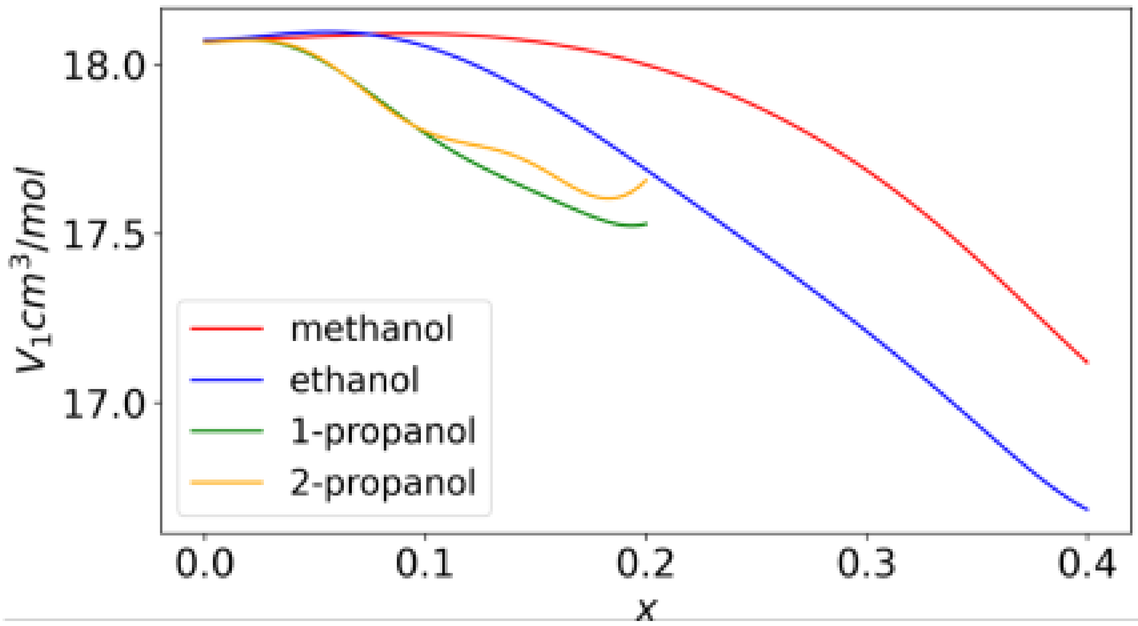
solvent contribution *solute contribution*

Partial molar volume

solute



solvent



$$\bar{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,p,n_{j\neq i}} = \left(\frac{\partial \mu_i}{\partial p}\right)_{T,n_i}$$

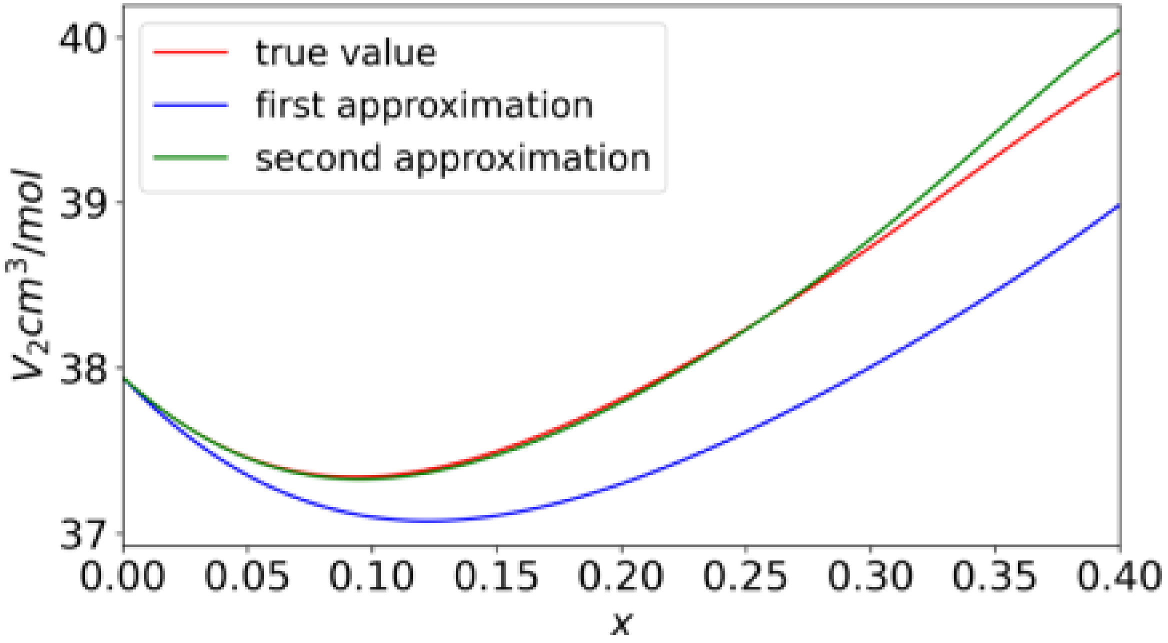
Partial molar volume

$$\overline{V_2} = V_2^{Vor} + (1-x)(x \cdot \frac{dV_2^{Vor}}{dx} + (1-x) \cdot \frac{dV_1^{Vor}}{dx})$$

$$\overline{V_2} = V_2^{Vor} + \frac{dV_1^{Vor}}{dx} + x\left(\frac{dV_2^{Vor}}{dx} - 2 \cdot \frac{dV_1^{Vor}}{dx}\right) + x^2\left(\frac{dV_1^{Vor}}{dx} - \frac{dV_2^{Vor}}{dx}\right)$$

$$\overline{V_2} \approx V_2^{Vor} + x\frac{dV_2^{Vor}}{dx} + (1-2x)\frac{dV_1^{Vor}}{dx}$$

$$\overline{V_2} \approx V_2^{Vor} + \frac{dV_1^{Vor}}{dx}$$



methanol in solution

Partial molar volume: components contributions

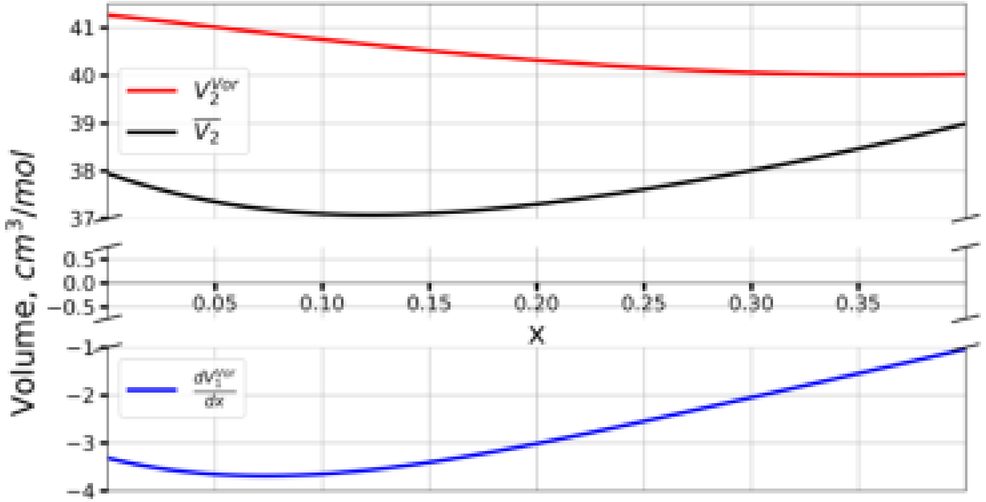
$$\overline{V_2} \approx V_2^{Vor} + \frac{dV_1^{Vor}}{dx}$$

geometric volume (solute contribution)

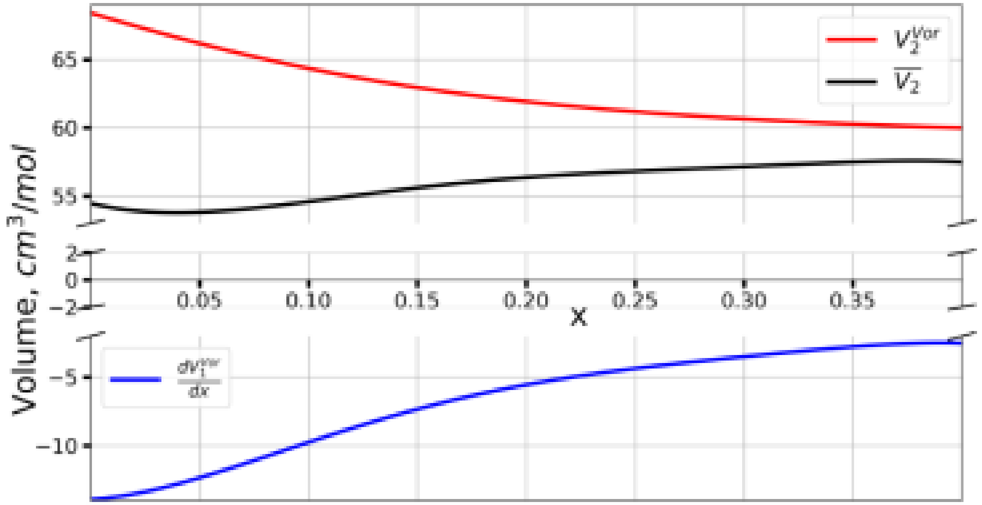
solvent volume change (solvent contribution)

Partial volume of a *solute* is the sum of its geometric volume and the *solvent* volume change

methanol in solution



ethanol in solution



Partial molar volume: components contributions

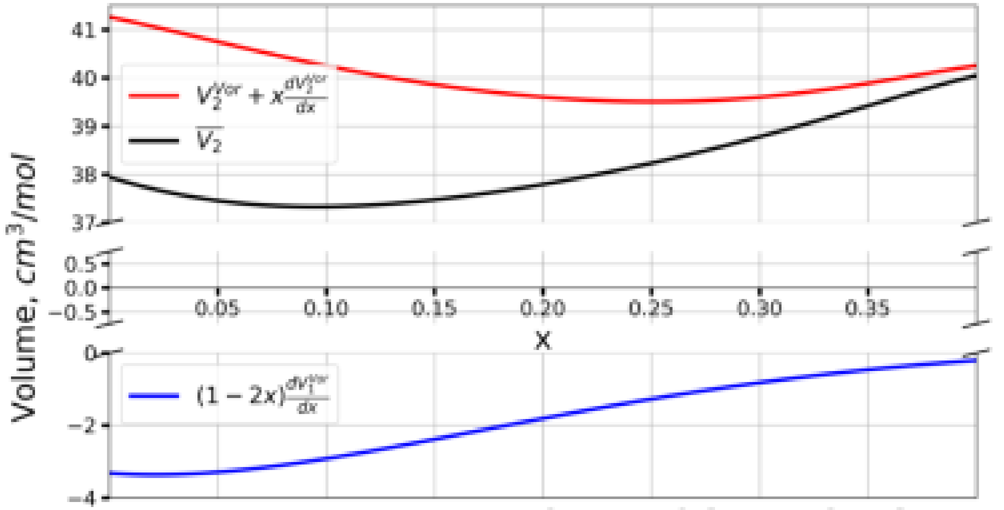
$$\overline{V_2} \approx V_2^{Vor} + x\frac{dV_2^{Vor}}{dx} + (1-2x)\frac{dV_1^{Vor}}{dx}$$

solute contribution *solvent contribution*

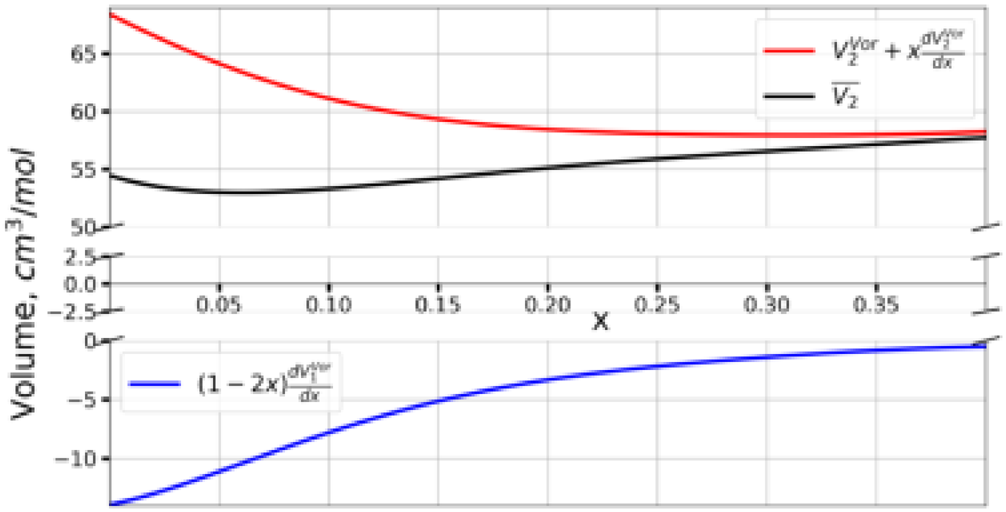
In second order approximation:

- solvent contribution includes its concentration as weight factor
- solute-solute influence is accounted in form of solute volume change

methanol in solution



ethanol in solution

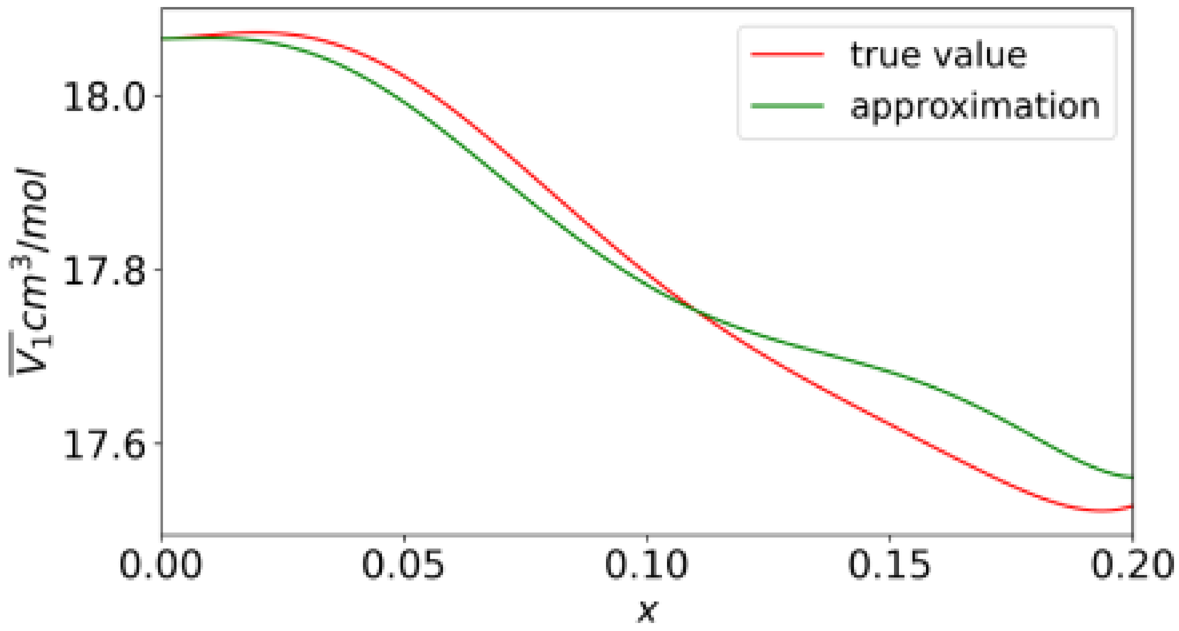


Partial molar volume

$$\bar{V_1}(x) = V_1^{Vor}(x) - x\left((1-x)\cdot\frac{dV_1^{Vor}(x)}{dx} + x\cdot\frac{dV_2^{Vor}(x)}{dx}\right)$$

$$\bar{V_1}(x) = V_1^{Vor}(x) - x\frac{dV_1^{Vor}(x)}{dx} + x^2\left(\frac{dV_1^{Vor}}{dx} - \frac{dV_2^{Vor}}{dx}\right)$$

$$\bar{V_1}(x) \approx V_1^{Vor}(x) - x\frac{dV_1^{Vor}(x)}{dx}$$



1-propanol in solution

A possible way to explain effects

$\langle n_f \rangle$

$V_1^{Vor\,0}$

$V_1^{Vor\,0} + \Delta V_1^{Vor}$

$$V_1^{Vor} = V_1^{Vor\,0} + \frac{x}{1-x}\langle n_f \rangle \Delta V_1^{Vor}$$

$$V_{\varphi 2} = V_2^{Vor}(x) + \langle n_f \rangle \Delta V_1^{Vor}$$

A mean solute impact to a solvent volume

A solvent contribution to solute's apparent volume

The minimun on the apparent volume is related to the change of solute impact to a solvent

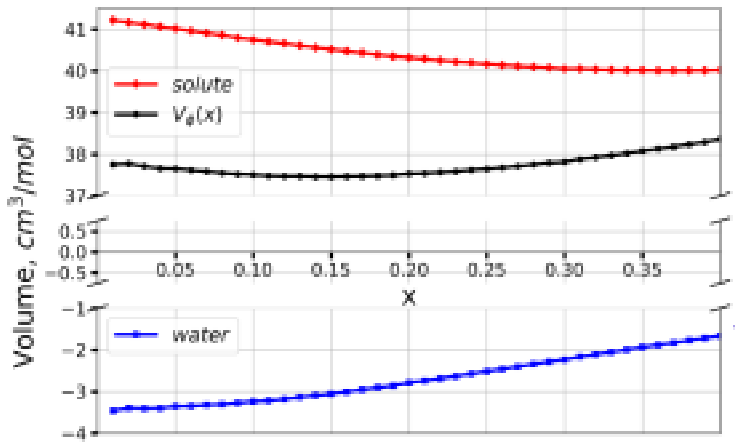
$\overline{V_2} \approx V_2^{Vor} + \langle n_f \rangle \Delta V_1^{Vor} + \frac{x}{1-x}\frac{d}{dx}(\langle n_f \rangle \Delta V_1^{Vor})$ - first order approximation

$\overline{V_2} \approx V_2^{Vor} + \langle n_f \rangle \Delta V_1^{Vor} + x\frac{d}{dx}(V_2^{Vor} + \langle n_f \rangle \Delta V_1^{Vor})$ - second order approximation

A possible way to explain effects

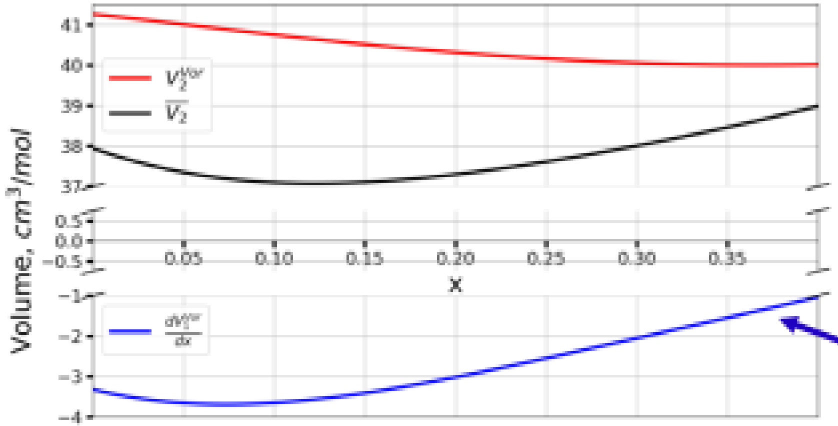
methanol in solution

apparent volume



$\langle n_f \rangle \Delta V_1^{Vor}$

partial volume



$$\frac{x}{1-x}\frac{d}{dx}\left(\langle n_f \rangle \Delta V_1^{Vor}\right)$$

We can consider a two-state model with hydrated and non-hydrated water molecules with constant volumes. The solute's impact factor on the solvent $\langle n_f \rangle \Delta V_1^{Vor}$ is determined then by hydration number $\langle n_f \rangle$ only.

The minimum on the apparent and partial volumes is defined then by decrease of hydration number related to an association process.

Summary

- Excess molar volume is defined mostly by solvent. Pure solute's volumes must be considered in it's analysis
- Apparent and partial volumes of a solute values is defined by solute's volume, but their features strongly affected by solvents contribution
- Apparent and partial volumes of a solvent is close to it's Voronoi volumes. Solute's volume affect must be included in an analysis.
- Minima on apparent and partial volume curves can be connected with solute hydration number decrease.
- Voronoi analysis provide insights into volumetric properties behavior

Thank you for attention!