

Supporting Information

Density and Viscosity Measurements and Modelling of

CO₂-Loaded and Unloaded Aqueous Solutions of Potassium Lysinate

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1. Uncertainty calculations: concentration of LysK in the solution

The general formula used for the uncertainty calculation of a measured quantity (m) can be written as:

$$u(m) = \sqrt{\left(\frac{u_{RB}}{\sqrt{3}}\right)^2 + \left(\frac{s(m)}{\sqrt{N}}\right)^2} \quad \text{Eq. S1}$$

The first term under square root, u_{RB} , is linked to the accuracy of the instrument, and it corresponds to the so called type-B uncertainty. Regarding the electronic balance used in this work for the preparation of the sampled solutions, u_{RB} is equal to 0.1 mg.

The second term consists in a type-A uncertainty, a statistical term related to the repeatability of the measurement. It is expressed by the so called standard error of the mean, given as the ratio between the estimate standard deviation ($s(m)$) and the square root of the number of repeated measurements (N). In this work $N=3$ and the standard deviation is estimated as it follows:

$$s(m) = \sqrt{\frac{1}{N-1} * \sum_{k=1}^N (m_{i,k} - \bar{m}_i)^2} \quad \text{Eq. S2}$$

Where $m_{i,k}$ is the single measured value and \bar{m}_i is the average of the 3 different repetitions.

When a quantity, for instance the mass of L-lysine $m_{Lys} = m_{flask} + m_{flask + Lys}$, is the result of two different measured values (m_{flask} and $m_{flask + Lys}$), the following formula is used to estimate the propagation of the error and, consequently, the combined uncertainty:

$$u_{comb}(m_{Lys}) = \sqrt{\sum_{i=1}^k \left(\frac{\partial m_{Lys}}{\partial P_j}\right)^2 * u^2(P_j) + \sum_{i=1}^{k-1} \sum_{j=i+1}^k \frac{\partial m_{Lys}}{\partial P_i} * \frac{\partial m_{Lys}}{\partial P_j} * u(P_i, P_j) + (m_{Lys} * u_{purity}(Lys))^2} \quad \text{Eq. S3}$$

Where P_j are the quantities from which m_{Lys} is estimated. Often, $u(P_i, P_j)$, which is the covariance of P_j and P_i , is equal to zero because they can be assumed to be uncorrelated, therefore the combined uncertainty is usually expressed just by the first term.

The term u_{purity} refers to the uncertainty resulting from the purity of the chemical used, and it has been calculated with Eq. S4:

$$u_{purity} = \frac{(1 - Purity\%)}{\sqrt{3}} \quad \text{Eq. S4}$$

What has been said so far has been used to calculate the uncertainty on the total mass of the single compound (L-Lys or KOH) added in the solution. The equimolar amount has been achieved by weight measurements: a residual amount of unreacted Lys/KOH was present in the final solutions, but when it was quantified during calculations it ended up being irrelevant (order of magnitude very low) in the final uncertainty value.

The final concentration level in the aqueous solution is estimated by:

$$w_{\%} = \frac{m_{LysK}}{m_{H_2O \text{ added}} + m_{H_2O \text{ formed}} + m_{LysK}} \quad \text{Eq. S5}$$

The formula written above represents the mass fraction concentration, but the concept is the same even for a molality basis ($\text{mol}_{LysK}/\text{kg}_{H_2O}$). The related combined standard uncertainty ($u_{comb}(w_{\%})$) is calculated via the following expression:

$$u_{comb}(w_{\%}) = \sqrt{\left(\frac{\partial w_{\%}}{\partial m_{LysK}}\right)^2 * u^2(m_{LysK}) + \left(\frac{\partial w_{\%}}{\partial m_{H_2O \text{ formed}}}\right)^2 * u^2(m_{H_2O \text{ formed}}) + \left(\frac{\partial w_{\%}}{\partial m_{H_2O \text{ added}}}\right)^2 * u^2(m_{H_2O \text{ added}})} \quad \text{Eq. S6}$$

2. Uncertainty calculations: CO₂ loading in solution

The CO₂ loading of the solution is defined as the number of moles of carbon dioxide divided by the number of moles of LysK. The procedure to obtain the targeted number of CO₂ moles in solution is described in section 2.1 of the article, and it is calculated with the following formula:

$$n_{CO_2} = V_{vessel} * (\rho_1 - \rho_2) * \frac{1}{MM_{CO_2}} \quad \text{Eq. S7}$$

The uncertainty on this quantity basically depends on the error attributable to the values of the density of CO₂, which can be found from the equation of state employed. Therefore, the uncertainty on the moles of CO₂ is calculated as follows:

$$u(n_{CO_2}) = \sqrt{\left(\frac{\partial n_{CO_2}}{\partial \rho_1}\right)^2 * u(\rho_1)^2 + \left(\frac{\partial n_{CO_2}}{\partial \rho_2}\right)^2 * u(\rho_2)^2} \quad \text{Eq. S8}$$

Then, adding the uncertainty on the moles of LysK, derived in 1, it is possible to calculate the combined uncertainty on the CO₂ loading of the solution with the formula already introduced in 1.

3. Results of the Flucon QVis 01/L quartz viscometer

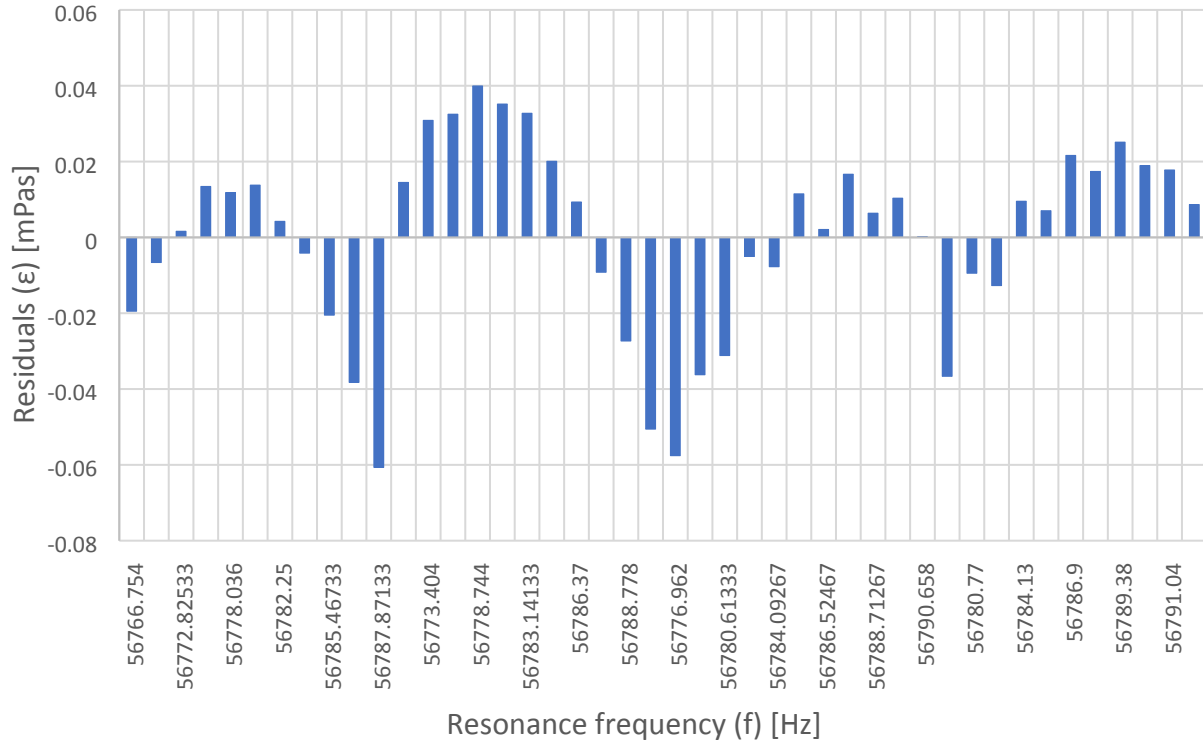


Figure S1: Plot of residuals ($\epsilon = \ln \mu_{exp} - \ln \mu_{calc}$) for the different frequency values encountered during the quartz viscometer calibration

Table S1: Numerical values of the quantities (density and viscosities) and parameters (frequency) used to develop the frequency – viscosity calibration for the quartz viscometer. The values of $u(T)$, $u(P)$, $u(f)$, $u(\rho)$ and $u(\mu)$ represent respectively the standard uncertainty on temperature [K], pressure [kPa], frequency [Hz], density [gcm^{-3}] and viscosity [mPas].

	Temperature [K]	Resonance Frequency [Hz]	Density [gcm^{-3}]	Experimental Viscosity [mPas]	Calculated Viscosity [mPas]
28.3% LysK mass fraction	293.15	56778.53	1.09906	2.89	3.00
	298.15	56780.77	1.09461	2.53	2.56
	303.15	56782.10	1.09022	2.19	2.21
	308.15	56784.13	1.08644	1.95	1.93
	313.15	56785.46	1.08274	1.71	1.70
	318.15	56786.90	1.07963	1.55	1.51
	323.15	56788.13	1.07663	1.38	1.36
	328.15	56789.38	1.07419	1.26	1.23
	333.15	56790.11	1.07190	1.15	1.12
	338.15	56791.04	1.07009	1.05	1.04
	343.15	56791.65	1.06855	0.97	0.96
28.5% LysK mass	293.15	56776.96	1.10076	2.96	3.14
	298.15	56778.48	1.09616	2.59	2.69

fraction	303.15	56780.61	1.09190	2.23	2.30
	308.15	56782.57	1.08797	1.99	2.00
	313.15	56784.09	1.08439	1.74	1.76
	318.15	56785.68	1.08115	1.58	1.56
	323.15	56786.52	1.07825	1.40	1.40
	328.15	56788.02	1.07569	1.29	1.26
	333.15	56788.71	1.07348	1.16	1.15
	338.15	56789.94	1.07159	1.07	1.06
	343.15	56790.66	1.07005	0.98	0.98
43.7% LysK mass fraction	293.15	56769.97	1.15187	7.07	6.96
	298.15	56773.40	1.14682	5.92	5.74
	303.15	56776.08	1.14199	5.00	4.84
	308.15	56778.74	1.13762	4.30	4.13
	313.15	56781.02	1.13360	3.71	3.58
	318.15	56783.14	1.13003	3.25	3.15
	323.15	56784.87	1.12681	2.86	2.80
	328.15	56786.37	1.12404	2.55	2.52
	333.15	56787.72	1.12162	2.27	2.29
	338.15	56788.78	1.11961	2.05	2.10
	343.15	56789.71	1.11798	1.85	1.95
45.0% LysK mass fraction	293.15	56766.75	1.15594	7.63	7.78
	298.15	56769.79	1.15073	6.38	6.42
	303.15	56772.83	1.14585	5.35	5.35
	308.15	56775.61	1.14146	4.59	4.53
	313.15	56778.04	1.13740	3.95	3.90
	318.15	56780.29	1.13382	3.45	3.40
	323.15	56782.25	1.13057	3.02	3.01
	328.15	56783.96	1.12779	2.68	2.70
	333.15	56785.47	1.12535	2.39	2.44
	338.15	56786.77	1.12334	2.15	2.23
	343.15	56787.87	1.12171	1.94	2.06
Standard uncertainties $u(T) = 0.03$ K, $u(P) = 0.4$ kPa, $u(f) = 0.05$ Hz, $u(\rho) = 0.00052$ gcm ⁻³ , $u(\mu) = 0.06$ mPas					

4. Uncertainty analysis of the experimental data

The calculated uncertainty on the measured densities and viscosities is composed of two terms, a type B and a type A uncertainty. As already indicated, u_{RB} is equal to 0.000005 gcm⁻³ for the Anton Paar densimeter and to the 0.5% of the measured value for the LOVIS viscometer. The second term is the standard deviation (s) of the average of three different measurement cycles ($N=3$). Therefore, the uncertainty is determined with the following formula:

$$u = \sqrt{\left(\frac{u_{RB}}{\sqrt{3}}\right)^2 + \left(\frac{s}{\sqrt{N}}\right)^2} \quad \text{Eq. S9}$$

When just one cycle of measurements is performed, the uncertainty on the experimental data corresponds with the uncertainty of the instrument used (u_{RB}).

Uncertainty of viscosity for CO₂ loaded solutions is the combination of two different terms:

$$u = \sqrt{u_1^2 + u_2^2} \quad \text{Eq. S10}$$

The first term (u_1) concerns the calibration with the experimental data coming from the LOVIS viscometer, and it is expressed as the combination of the uncertainty on the experimental data measured with the LOVIS viscometer used for the calibration ($u_{expdata}$) and the deviation between the latters and the values predicted from the model (Δu):

$$u_1 = \sqrt{u_{expdata}^2 + \Delta u^2} \quad \text{Eq. S11}$$

The second term (u_2) is related with the uncertainty of the correlation parameters for the model described by Eq. S12:

$$\ln(\mu/mPas) = A + \frac{B}{T} + C * f + D * f^6 + E/\rho \quad \text{Eq. S12}$$

Therefore, the uncertainty in this correlation can be determined as the combined uncertainty of all the parameters (P_j) on which viscosity depends:

$$u(\ln\mu) = \sqrt{\sum_j \left(\frac{\partial \ln\mu}{\partial P_j} \right)^2 * u(P_j)^2} \quad \text{Eq. S13}$$

Where P_j include both the correlation parameters (A, \dots, E) and the physical quantities T, f and ρ .

5. Uncertainty analysis on the model parameters

The uncertainty estimates for the correlation parameters can be determined from the variance-covariance matrix (V). The elements on the matrix diagonal represent the square of the standard deviation (variances) of the model parameters (P_j), whereas the elements outside the diagonal are the covariances:

$$V_{jj} = \text{var}(P_j), V_{jk} = \text{cov}(P_j, P_k) \quad j, k = 1, \dots, n \quad \text{Eq. S14}$$

The variance-covariance matrix of the model parameters is usually calculated from the Hessian matrix (H) of the likelihood function v at the optimum determined point. For instance, when the objective is to fit experimental data on viscosities, the function v can be expressed as:

$$v = \sum_i v_i = \sum_i (\mu_i^E - \mu_i^C)^2 \quad \text{Eq. S15}$$

Where i represents each experimental point obtained, μ_i^E is the value of the measurements and μ_i^C is the predicted value from the model. The Hessian is the matrix ($n \times n$) of the second-order partial derivatives:

$$H = \left[\sum_i \left(\frac{\partial}{\partial P_j} \left(\frac{\partial v_i}{\partial P_k} \right) \right) \right]_{j,k} \quad \text{Eq. S16}$$

The variance-covariance matrix is then determined from the product between the inverse of the Hessian matrix and the value of the maximum likelihood function divided by the number of degrees of freedom ($df = \text{number of exp. points} - \text{number of model parameters}$):

$$V = \frac{1}{df} * v * H^{-1} = \begin{bmatrix} \sigma^2(P_j) & \text{cov}^2(P_j, P_k) & \dots \\ \text{cov}^2(P_k, P_j) & \ddots & \vdots \\ \vdots & \dots & \sigma^2(P_n) \end{bmatrix} \quad \text{Eq. S17}$$

Taking the square root of the values on the diagonal one can obtain the standard deviations of the parameters P_j .