Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Physico-chemical investigation of highly concentrated potassium acetate solutions towards applications in electrochemistry

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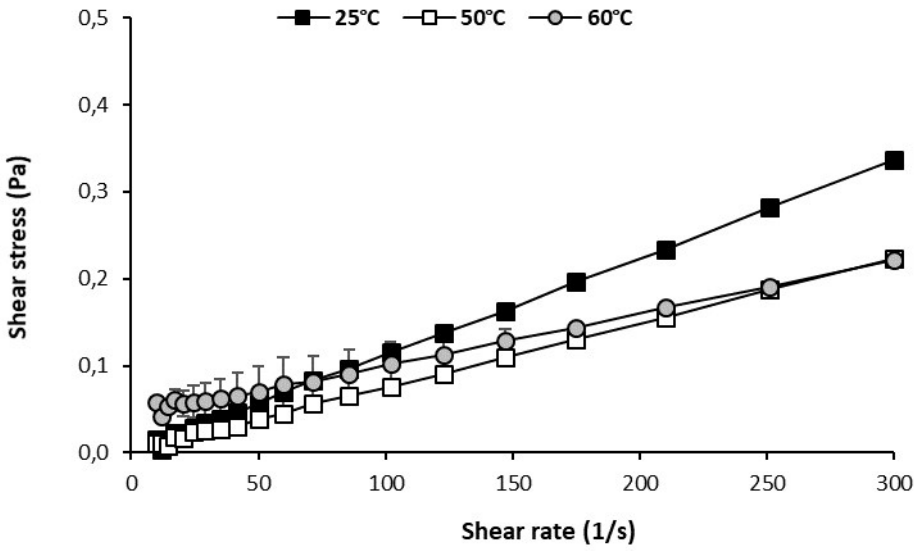

Figure S1 Flow curve of the sample KAC-1 at different temperature values (mean values ± s.d., n=3)

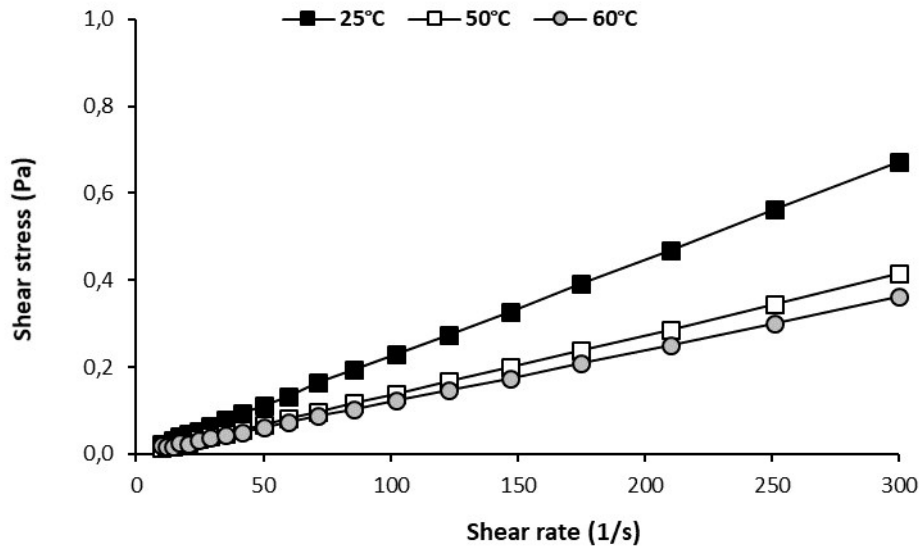

Figure S2 Flow curve of the sample KAC-5 at different temperature values (mean values ± s.d., n=3)

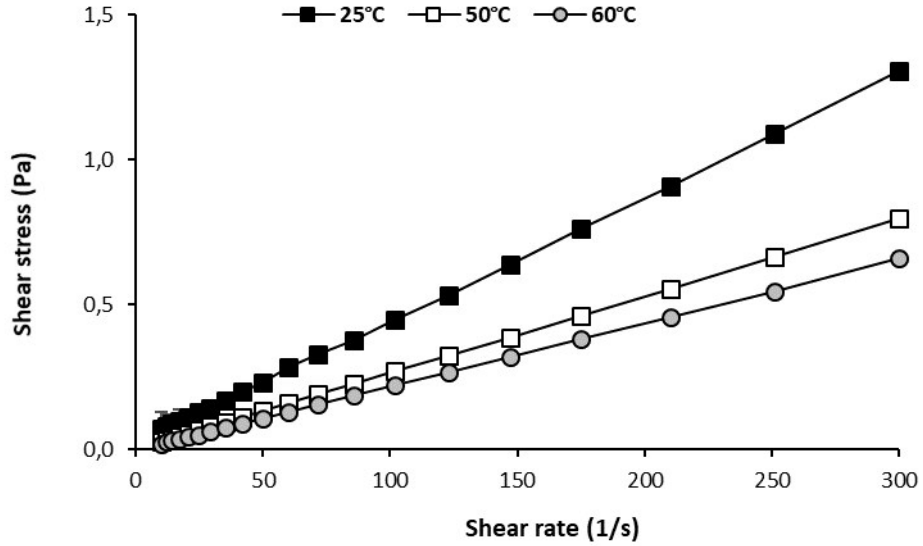

Figure S3 Flow curve of the sample KAC-10 at different temperature values (mean values ± s.d., n=3)

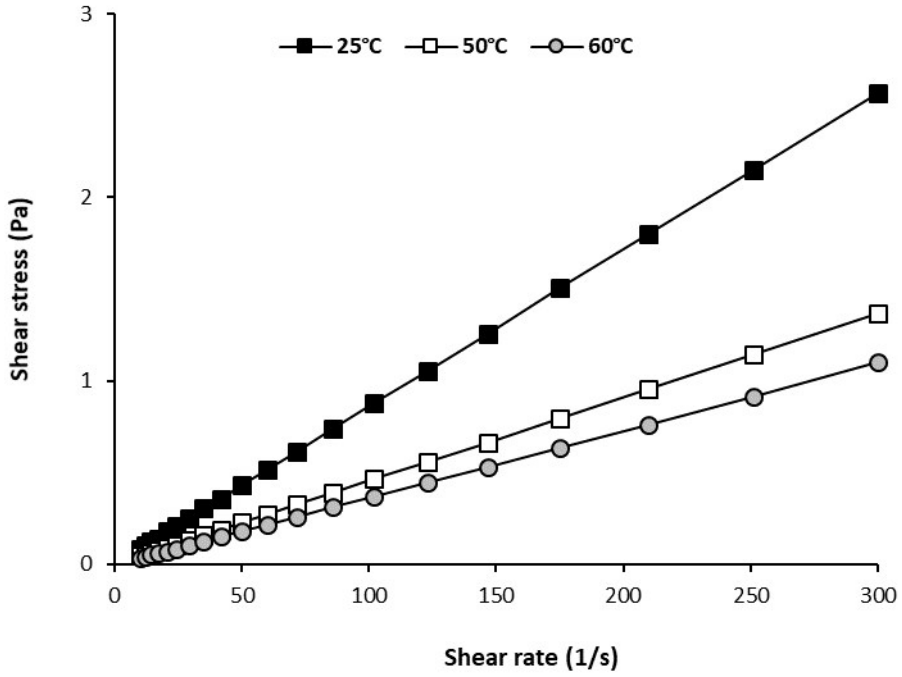

Figure S4 Flow curve of the sample KAC-15 at different temperature values (mean values ± s.d., n=3)

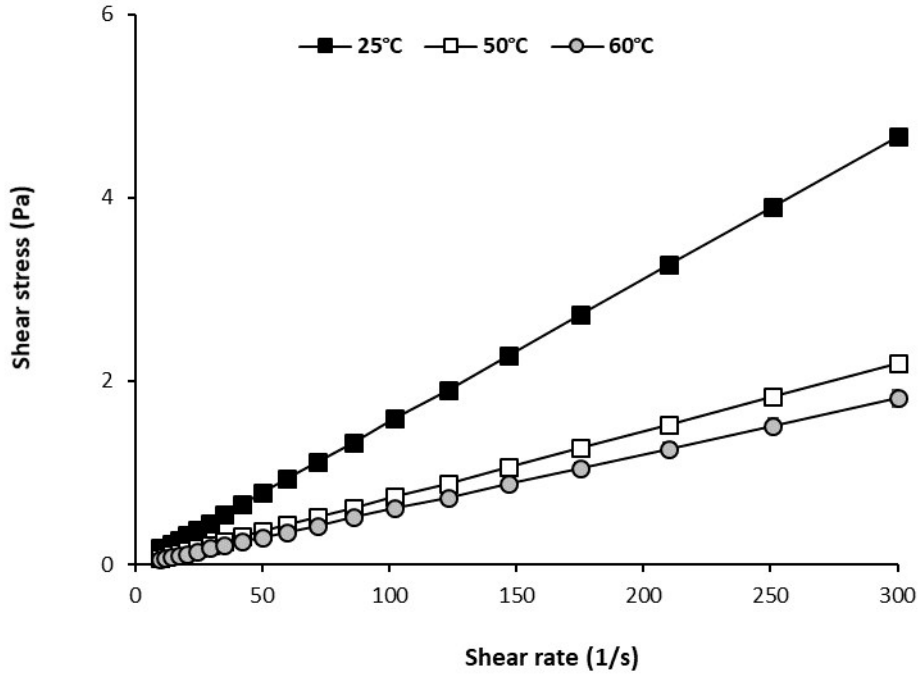

Figure S5 Flow curve of the sample KAC-20 at different temperature values (mean values ± s.d., n=3)

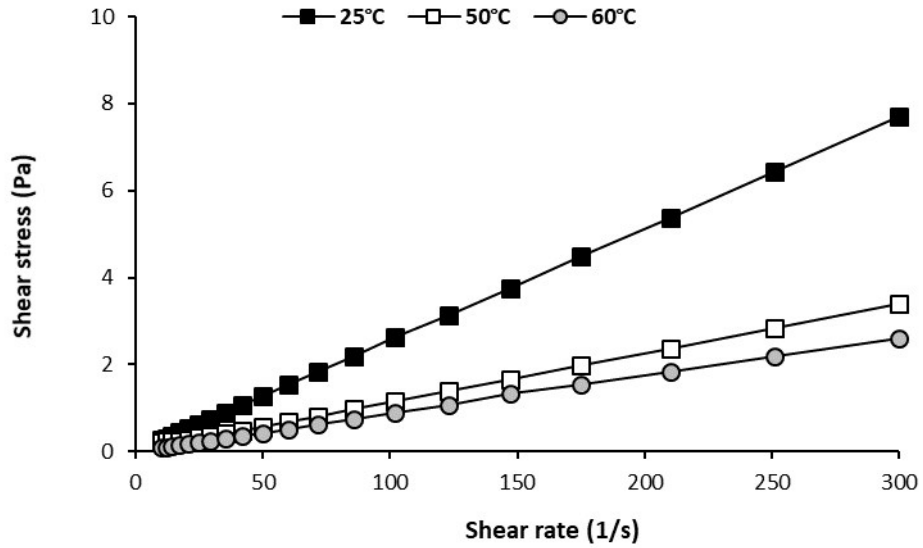

Figure S6 Flow curve of the sample KAC-25 at different temperature values (mean values ± s.d., n=3)

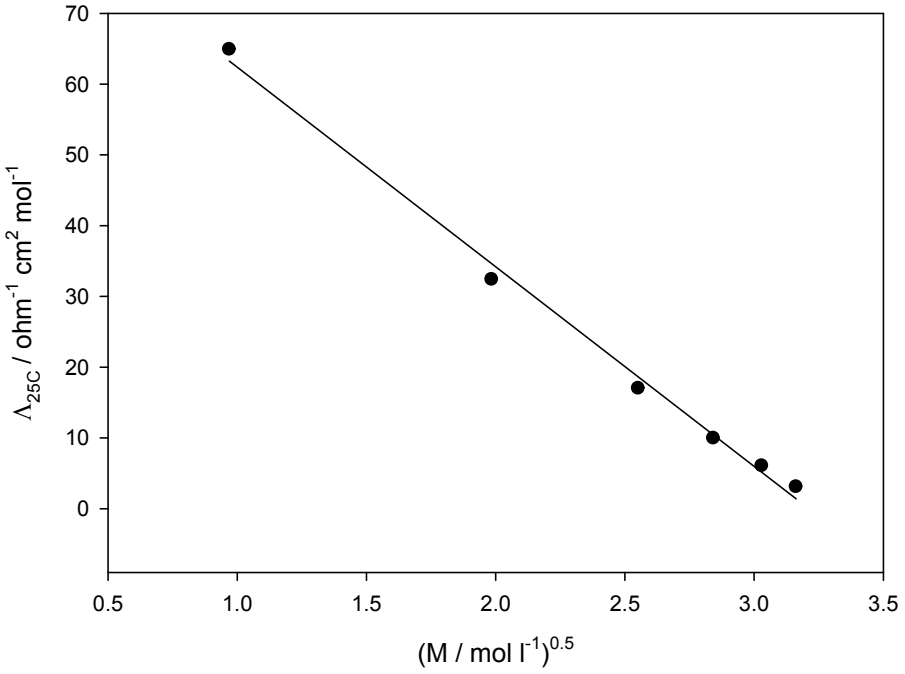

Figure S7 Molar conductivity vs. the square root of the molarity of the KAC solutions. The full line is a linear best-fit ($R^2 > 0.99$). The molar conductivity at infinite dilution at 25°C is Λ_0 = 90.6 ohm^{-1} cm^2 mol^{-1}.

M mol kg-1	**pH**	**Anodic water decomposition** V vs. SHE	**Cathodic water decomposition** V vs. SHE
1	6.88	-0.39	0.84
5	7.72	-0.44	0.79
10	8.57	-0.49	0.74
15	9.20	-0.52	0.71
20	9.57	-0.54	0.68
25	9.82	-0.56	0.67

Table S1: Experimental pH values of the solution and thermodynamic stability limits of water decomposition at 25°C. Decomposition values have been calculated using the corresponding Nernst equations.

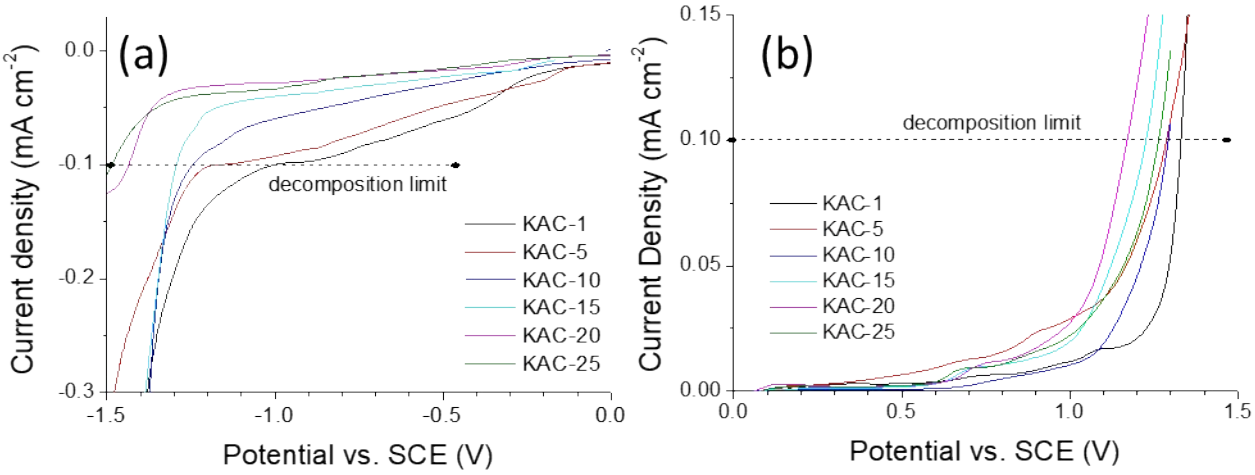

Figure S8. Cathodic and anodic LSV for the determination of the solutions decomposition limits.

ν_{max} cm^{-1}	**Relative Intensity**	**Assignment**
470	2.7	ρCO_2
622	4.9	ωCO_2
651	14	δCO_2
924	84	νCC
1018	1.9	ρCH_3
1345	18	δCH_3
1412	43	$\nu_s CO_2$
1576	6.3	$\nu_{as} CO_2$
1667	3.6	δH_2O
2672*	2.1	n.a.
2747*	1.5	n.a.
2849*	8.4	n.a.
2932	100	$\nu_s CH_3$
2979	29	$\nu_{as} CH_3$
3240 (b)	15	$\nu_s H_2O$
3420 (b)	20	$\nu_{as} H_2O$

Table S2: Experimental Raman frequencies of sample KAC-25, relative intensities are normalized with respect to the most intense peak at 2932 cm-1. Peaks assignment is taken from references (1) and (2). The abbreviations represent the following: b, broad; ρ, rocking; ω, wagging; δ, bending; ν, stretching; s, symmetric; as, asymmetric. Peaks marked with an asterisk miss of unambiguous and definite assignments. They have been already observed in previous works[1] and are likely due to overtones and/or combination of vibrational modes.

Parameters	**Exponential fit:** $a + b\ exp(-kC)$	**Logistic model fit:** $a + L/[1 + exp(-k(C - C_0))]$
a (cm^{-1})	1415.5	31.9
b (cm^{-1})	0.226	n.a.
k (Kg/mol)	$8.58 \cdot 10^{-2}$	0.251
L (cm^{-1})	n.a.	4.43
C_0 (mol/kg)	n.a.	13.0

Table S3: Fitting results of the exponential and logistic functions used to fit respectively peak maximum position and FWHM of the $\nu_s CO_2$ Raman peak as a function of KAC molality. For the sake of simplicity we used the same parameter labels, *a* and *k,* in the two fitting models. Importantly, these values are not connected each other, i.e. the two starting values and the two growth rates are independents.

References

1. W. Rudolph W, Irmer G. Raman spectroscopic studies and DFT calculations on NaCH 3 CO 2 and NaCD 3 CO 2 solutions in water and heavy water. RSC Advances. 2015;5(28):21897–908.

2. Carey DM, Korenowski GM. Measurement of the Raman spectrum of liquid water. J Chem Phys. 1998 Feb 15;108(7):2669–75.