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Supplementary material

SUPPLEMENTARY MATERIAL TO

Experimental measurements and modelling of solvent activity and surface tension of binary mixtures of poly(vinyl pyrrolidone) in water and ethanol

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TABLE S-I. Measured densities of PVP solutions and parameters of Eq. (1) at various temperatures; the densities are given as mean ± standard deviation

T / °C	*a*	*b*	*c*	*ARE*	ρ_{exp} / g cm^{-3}				*RMSE*	R^2
					w = 0.1	*w* = 0.2	*w* = 0.3	*w* = 0.45		
K25 + water										
20	0.977	–0.551	1.93	–0.0051	0.937 ± 0.001	0.955 ± 0.001	0.976 ± 0.001	1.122 ± 0.001	0.01521	0.9892
25	0.973	–0.530	1.90	–0.0058	0.935 ± 0.002	0.955 ± 0.001	0.975 ± 0.001	1.121 ± 0.001	0.01621	0.9878
30	0.972	–0.531	1.89	–0.0052	0.934 ± 0.001	0.953 ± 0.002	0.974 ± 0.002	1.119 ± 0.001	0.01534	0.9890
35	0.970	–0.525	1.88	–0.0051	0.932 ± 0.002	0.951 ± 0.001	0.972 ± 0.001	1.116 ± 0.001	0.01520	0.9890
40	0.968	–0.524	1.88	–0.0058	0.930 ± 0.001	0.950 ± 0.001	0.970 ± 0.001	1.115 ± 0.002	0.01621	0.9878
45	0.967	–0.544	1.92	–0.0057	0.928 ± 0.001	0.947 ± 0.001	0.967 ± 0.001	1.113 ± 0.002	0.01595	0.9881
50	0.964	–0.531	1.88	–0.0053	0.926 ± 0.001	0.945 ± 0.001	0.965 ± 0.001	1.109 ± 0.001	0.01567	0.9882
55	0.962	–0.525	1.87	–0.0055	0.924 ± 0.001	0.943 ± 0.001	0.963 ± 0.001	1.106 ± 0.001	0.01553	0.9883
K40 + water										
20	0.974	–0.506	1.86	–0.0042	0.938 ± 0.001	0.957 ± 0.001	0.981 ± 0.001	1.125 ± 0.001	0.01378	0.9912
25	0.971	–0.499	1.86	–0.0043	0.936 ± 0.001	0.956 ± 0.001	0.980 ± 0.001	1.125 ± 0.002	0.01418	0.9909
30	0.972	–0.518	1.88	–0.0045	0.935 ± 0.001	0.954 ± 0.001	0.977 ± 0.001	1.122 ± 0.001	0.01439	0.9905

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TABLE S-I. Continued

T / °C	a	b	c	ARE	ρ_{exp} / g cm^{-3} w = 0.1	w = 0.2	w = 0.3	w = 0.45	$RMSE$	R^2
					K40 + water					
35	0.968	–0.493	1.83	–0.0045	0.933 ± 0.001	0.953 ± 0.001	0.976 ± 0.001	1.119 ± 0.001	0.01437	0.9903
40	0.965	–0.486	1.82	–0.0044	0.931 ± 0.001	0.951 ± 0.002	0.974 ± 0.002	1.116 ± 0.001	0.01423	0.9904
45	0.963	–0.480	1.80	–0.0044	0.929 ± 0.001	0.949 ± 0.001	0.972 ± 0.002	1.113 ± 0.001	0.01410	0.9905
50	0.961	–0.486	1.80	–0.0048	0.927 ± 0.001	0.947 ± 0.001	0.969 ± 0.002	1.110 ± 0.001	0.01457	0.9897
55	0.959	–0.486	1.80	–0.0049	0.925 ± 0.001	0.945 ± 0.001	0.967 ± 0.002	1.108 ± 0.002	0.01457	0.9897
					K25 + ethanol					
20	0.80	–0.63	2.34	–0.0200	0.755 ± 0.001	0.787 ± 0.001	0.807 ± 0.001	0.994 ± 0.001	0.02508	0.9819
25	0.79	–0.60	2.31	–0.0189	0.751 ± 0.001	0.784 ± 0.001	0.806 ± 0.001	0.993 ± 0.001	0.02440	0.9832
30	0.79	–0.60	2.31	–0.0190	0.747 ± 0.000	0.780 ± 0.002	0.802 ± 0.002	0.989 ± 0.001	0.02440	0.9832
35	0.78	–0.60	2.30	–0.0200	0.742 ± 0.001	0.776 ± 0.001	0.798 ± 0.001	0.986 ± 0.001	0.02480	0.9829
40	0.78	–0.59	2.27	–0.0180	0.739 ± 0.002	0.772 ± 0.001	0.795 ± 0.001	0.980 ± 0.002	0.02365	0.9841
45	0.78	–0.61	2.30	–0.0170	0.737 ± 0.001	0.768 ± 0.002	0.792 ± 0.001	0.977 ± 0.003	0.02265	0.9853
50	0.78	–0.60	2.28	–0.0170	0.733 ± 0.001	0.765 ± 0.001	0.787 ± 0.001	0.971 ± 0.001	0.02372	0.9836
55	0.77	–0.61	2.31	–0.0170	0.730 ± 0.000	0.761 ± 0.001	0.784 ± 0.001	0.969 ± 0.000	0.02313	0.9846
					K40 + ethanol					
20	0.723	0.230	0.890	–0.0684	0.766 ± 0.001	0.774 ± 0.001	0.898 ± 0.001	1.001 ± 0.002	0.04199	0.9531
25	0.719	0.245	0.877	–0.0713	0.763 ± 0.001	0.771 ± 0.001	0.897 ± 0.001	1.000 ± 0.003	0.04293	0.9518
30	0.705	0.315	0.770	–0.0732	0.756 ± 0.000	0.767 ± 0.001	0.896 ± 0.001	0.997 ± 0.001	0.04384	0.9512
35	0.703	0.328	0.728	–0.0722	0.754 ± 0.001	0.766 ± 0.001	0.893 ± 0.000	0.992 ± 0.001	0.04291	0.9519
40	0.702	0.314	0.743	–0.0797	0.753 ± 0.001	0.762 ± 0.002	0.891 ± 0.001	0.988 ± 0.001	0.04492	0.9467
45	0.699	0.314	0.730	–0.0813	0.750 ± 0.001	0.758 ± 0.001	0.887 ± .001	0.982 ± 0.002	0.04546	0.9443
50	0.691	0.353	0.669	–0.0829	0.745 ± 0.001	0.755 ± 0.001	0.885 ± 0.003	0.979 ± 0.003	0.04555	0.9448
55	0.686	0.353	0.681	–0.0841	0.740 ± 0.000	0.750 ± 0.000	0.881 ± 0.002	0.976 ± 0.003	0.04588	0.9449

TABLE S-II. Measured viscosities of PVP solutions and parameters of Eq. (2) at various temperatures; the viscosities are given as mean ± standard deviation

T / °C	a'	b'	c'	d'	ARE	η_{exp} / mPa s				R^2
						w = 0.1	w = 0.2	w = 0.3	w = 0.45	
K25 + water										
20	–293	5488	–29874	53494	–1.8×10^{-12}	10.5 ± 0.4	37.6 ± 1.5	109.2 ± 4.3	1002 ± 22.6	1.00
25	–239	4500	–24344	43395	–3.5×10^{-12}	10.4 ± 0.1	33.9 ± 1.5	91.2 ± 3.0	810.2 ± 23.0	1.00
30	–185	3503	–18857	33736	–0.31×10^{-12}	9.9 ± 0.3	30.6 ± 1.1	79.0 ± 2.5	646.3 ± 29.2	1.00
35	–138	2647	–14243	25824	2.4×10^{-12}	9.3 ± 0.2	27.6 ± 1.3	70.8 ± 2.5	521.6 ± 15.3	1.00
40	–107	2081	–11220	20508	2.2×10^{-12}	8.8 ± 0.2	23.9 ± 0.9	60.7 ± 1.3	425.7 ± 11.0	1.00
45	–83	1633	–8828	16368	–0.29×10^{-12}	8.1 ± 0.2	21.2 ± 0.5	54.2 ± 2.7	355.7 ± 7.9	1.00
50	–54	1111	–6108	11870	1.7×10^{-12}	7.7 ± 0.1	18.8 ± 0.7	50.1 ± 1.9	290.9 ± 6.9	1.00
55	–48	977	–5194	9840	3.3×10^{-12}	7.2 ± 0.2	18.0 ± 0.5	43.1 ± 1.9	236.4 ± 3.8	1.00
K40 + water										
20	–371	7074	–39495	71794	–9.7×10^{-10}	13.2 ± 0.2	38.4 ± 2.0	135.2 ± 3.2	1357 ± 28.5	1.00
25	–261	5029	–27988	51272	–1.5×10^{-10}	12.5 ± 0.4	34.6 ± 1.1	112.3 ± 4.5	1005.8 ± 15.0	1.00
30	–210	4119	–23205	42734	–0.63×10^{-10}	12.0 ± 0.2	26.8 ± 2.4	90.4 ± 2.8	808.0 ± 15.1	1.00
35	–177	3475	–19573	36080	–0.20×10^{-10}	10.7 ± 0.3	23.6 ± 1.1	78.0 ± 3.3	710.9 ± 19.8	1.00
40	–117	2349	–13219	24784	–0.98×10^{-10}	9.9 ± 0.1	21.7 ± 0.8	66.6 ± 0.9	521.1 ± 10.3	1.00
45	–93	1887	–10655	20235	–0.81×10^{-10}	9.1 ± 0.3	19.8 ± 0.1	60.3 ± 2.1	442.3 ± 11.4	1.00
50	–82	1657	–9256	17461	–8.71×10^{-10}	8.3 ± 0.1	18.6 ± 0.6	53.2 ± 0.8	380.2 ± 7.0	1.00
55	–66	1347	–7473	14086	–0.75×10^{-10}	7.8 ± 0.2	16.9 ± 0.3	45.6 ± 1.5	310.3 ± 3.4	1.00
K25 + ethanol										
20	–285	5458	–30095	54301	–1.1×10^{-12}	13.9 ± 0.2	37.0 ± 2.0	109.9 ± 3.2	1025.0 ± 30.1	1.00
25	–220	4244	–23462	42930	–0.52×10^{-12}	12.2 ± 0.4	33.3 ± 1.1	100.3 ± 4.5	850.4 ± 16.3	1.00
30	–176	3407	–18803	34581	–2.8×10^{-12}	11.2 ± 0.2	29.9 ± 2.1	87.6 ± 2.8	700.9 ± 15.1	1.00
35	–136	2704	–15159	28334	–0.09×10^{-12}	10.9 ± 0.3	24.9 ± 1.1	75.7 ± 3.3	592.9 ± 19.8	1.00

TABLE S-II. Continued

T / °C	a'	b'	c'	d'	ARE	η_{exp} / mPa s				R^2
						w = 0.1	w = 0.2	w = 0.3	w = 0.45	
					K25 + ethanol					
40	–101	2041	–11388	21506	–0.26×10^{-12}	10.0 ± 0.1	23.1 ± 1.0	66.4 ± 0.9	470.6 ± 9.5	1.00
45	–87	1748	–9601	17899	–0.2×10^{-12}	9.1 ± 0.3	21.3 ± 0.3	56.2 ± 2.3	386.2 ± 11.4	1.00
50	–51	1092	–6158	12150	0.58×10^{-12}	8.3 ± 0.1	17.8 ± 0.6	50.0 ± 0.9	300.1 ± 7.0	1.00
55	–56	1158	–6435	12340	–0.84×10^{-12}	7.9 ± 0.2	17.0 ± 0.3	45.6 ± 1.5	286.7 ± 4.0	1.00
					K40 + ethanol					
20	–382	7174	–39190	69001	31×10^{-13}	12.3 ± 0.3	37.0 ± 1.5	106.0 ± 4.3	1198.0 ± 36.5	1.00
25	–295	5576	–30373	53665	36×10^{-13}	11.8 ± 0.1	33.9 ± 1.5	92.5 ± 3.0	953.3 ± 31.3	1.00
30	–241	4571	–24890	44196	–25×10^{-13}	11.2 ± 0.3	31.0 ± 1.5	83.4 ± 2.5	803.0 ± 29.2	1.00
35	–180	3434	–18699	33612	5.2×10^{-13}	10.0 ± 0.1	27.7 ± 1.3	74.8 ± 2.5	641.7 ± 15.3	1.00
40	–135	2639	–14537	26577	6.0×10^{-13}	9.6 ± 0.2	19.2 ± 0.9	65.5 ± 1.3	530.3 ± 10.8	1.00
45	–111	2156	–11650	21105	0.26×10^{-13}	8.8 ± 0.2	23.5 ± 0.5	56.8 ± 2.5	423.1 ± 7.9	1.00
50	–84	1671	–9134	16840	–5.3×10^{-13}	8.2 ± 0.1	22.7 ± 0.7	49.6 ± 1.9	352.7 ± 6.9	1.00
55	–61	1232	–6685	12551	2.6×10^{-13}	7.7 ± 0.2	18.2 ± 0.5	45.6 ± 1.9	283.1 ± 5.5	1.00

Thermodynamic model for solvent activity

A thermodynamic model based on the Eyring absolute rate theory was proposed to calculate the activity of solvents in binary PVP polymer solutions.[1] Generally, measuring the viscosity and density of polymer solutions are much easier than measuring the solvent activity. For this reason, in this model, the viscosity and density of the polymer solution were used to calculate the solvent activity.

According to the Eyring viscosity model, the viscosity of a liquid solution is calculated by the following equation:[2,3]

$$\ln(\eta \upsilon) = \sum_i x_i \ln(\eta_i \upsilon_i) + \frac{g^{*E}}{RT} \tag{S-1}$$

where η, υ, η_i and υ_i are the viscosity, molar volume of the solution, viscosity of pure component i and molar volume of pure component i, respectively. X_i is the molar fraction of component i in the mixture, T is the absolute temperature, R is the gas constant and g^{*E} is the excess Gibbs energy of viscous flow required to move the fluid particles from a stable state to an activated state.

There is an equivalence relationship between the excess Gibbs energy (g^*) and the equilibrium excess Gibbs free energy of mixing (g):

$$\frac{g^E}{RT} = \ln(\eta\upsilon) - \sum_i x_i \ln(\eta_i \upsilon_i) \tag{S-2}$$

The first and second terms on the right-hand side of Eq. (2) are related to the real viscosity of the solution and the ideal viscosity of the solution, respectively.

In this paper, dimensionless terms were used instead of the real and ideal viscosity as follows:

$$\frac{g^E}{RT} = \frac{(\eta\upsilon)}{(\eta_R \upsilon_R)} - \sum_i \frac{x_i(\eta_i \upsilon_i)}{\eta_R \upsilon_R} \tag{S-3}$$

where η_R and υ_R are the viscosity and molar volume of a reference component, respectively. In this work, component 2 was selected as the reference component. Thus:

$$\frac{g^E}{RT} = \frac{(\eta\upsilon)}{(\eta_2 \upsilon_2)} - \sum_{i=1}^{2} \frac{x_i(\eta_i \upsilon_i)}{\eta_2 \upsilon_2} \tag{S-4}$$

$$\frac{g^E}{RT} = \left(\frac{\eta\upsilon}{\eta_2 \upsilon_2}\right) - \left(\frac{x_1 \eta_1 \upsilon_1}{\eta_2 \upsilon_2}\right) - \left(\frac{x_2 \eta_2 \upsilon_2}{\eta_2 \upsilon_2}\right) \tag{S-5}$$

Hence, the viscosity and density values of components 1 and 2 are required to calculate the excess Gibbs free energy by Eq. (S-5). The density and viscosity of the solutions that were used to verify the model were measured experimentally and fitted by quadratic equations.

On the other hand, activity coefficient of the solvent (γ_1) can be expressed as a function in terms of the excess Gibbs energy:

$$RT \ln \gamma_1 = g^E + (1 - x_1)\frac{\partial g^E}{\partial x_1} \tag{S-6}$$

$$\ln \gamma_1 = \frac{g^E}{RT} + \frac{(1 - x_1)}{RT}\frac{\partial g^E}{\partial x_1} \tag{S-7}$$

With respect to the relationship between a_1 (activity of the solvent) and γ_1 (activity coefficient of the solvent) ($a_1 = x_1\gamma_1$), by determining the term $\partial g^E/\partial x_1$ and substituting the term $\partial g^E/\partial x_1$ into Eq. (S-7), one obtains the following relation:

$$\ln a_1 = \left(\frac{\eta \upsilon}{\eta_2 \upsilon_2}\right) - \left(\frac{x_1 \eta_1 \upsilon_1}{\eta_2 \upsilon_2}\right) - \left(\frac{x_2 \eta_2 \upsilon_2}{\eta_2 \upsilon_2}\right) + \frac{(1-x_1)}{RT}\frac{\partial g^E}{\partial x_1} + \ln x_1 \tag{S-8}$$

$$\frac{g^E}{RT} = \left(\frac{\left(a' + b'w + c'w^2 + d'w^3\right)\left(\dfrac{m_1 x_1 + m_2 x_2}{a + bw + cw^2}\right)}{\eta_2 \upsilon_2}\right) - \left(\frac{x_1 \eta_1 \upsilon_1}{\eta_2 \upsilon_2}\right) - \left(\frac{x_2 \eta_2 \upsilon_2}{\eta_2 \upsilon_2}\right) \tag{S-9}$$

$$w_2 = \frac{m_2(1-x_1)}{m_1 x_1 + m_2(1-x_1)}$$

$$\ln a_1 = \left(\frac{(a' + b'w + c'w^2 + d'w^3)\left(\dfrac{m_1 x_1 + m_2 x_2}{a + bw + cw^2}\right)}{\eta_2 \upsilon_2}\right) - \tag{S-10}$$

$$- \left(\frac{x_1 \eta_1 \upsilon_1}{\eta_2 \upsilon_2}\right) - \left(\frac{x_2 \eta_2 \upsilon_2}{\eta_2 \upsilon_2}\right) + \frac{(1-x_1)}{RT}\frac{\partial g^E}{\partial x_1} + \ln x_1$$

This model can predict the solvent activity in binary mixtures by using experimental density and viscosity values.

Thermodynamic model for surface tension

A thermodynamic model based on the Butler Equation[4] for the prediction of the surface tension of binary polymer solutions is presented. For calculating the surface tension of a polymer solution, it is assumed that one phase is configured at the surface. The chemical potential of component 1 in the bulk of a non-electrolyte binary solution is expressed as follows:

$$\mu_{1\mathrm{b}} = \mu_{1\mathrm{b}}^0 + RT \ln a_{1\mathrm{b}} \tag{S-11}$$

where $\mu_{1\mathrm{b}}^0$ and $a_{1\mathrm{b}}$ are the standard chemical potential and the activity of component 1 in the bulk phase, and *R* and *T* are the gas constant and temperature, respectively.

The chemical potential of component 1 at the surface phase can be calculated using the following equation:

$$\mu_{1\mathrm{s}} = \mu_{1\mathrm{s}}^0 + RT \ln a_{1\mathrm{s}} - \sigma A_1 \tag{S-12}$$

where $\mu_{1\mathrm{s}}^0$ is the standard chemical potential at the surface, and σ and $a_{1\mathrm{s}}$ are the surface tension of the solution and the activity of component 1 at the surface phase, respectively, while A_1 is the molar surface area (cm^2 mol^{-1}) of component 1 in solution.

The following equation is used for the pure components:

$$\mu_{1s}^{0} - \mu_{1b}^{0} = \sigma A_1 \tag{S-13}$$

where A_1 and σ_1 are the molar surface area and surface tension of component 1, respectively.

At equilibrium, the chemical potential of component 1 in the bulk and surface phases are equivalent:

$$\mu_{1s} = \mu_{1b} \tag{S-14}$$

By combining the above equations, the following equation is obtained:

$$\sigma A_1 = \sigma_1 A_1 + RT \ln \frac{a_{1s}}{a_{1b}} \tag{S-15}$$

The activity of component 1 in both the bulk and surface phases is achieved using the activity coefficients:

$$\sigma A_1 = \sigma_1 A_1 + RT \ln \frac{x_{1s}\ \gamma_{1s}}{x_{1b}\ \gamma_{1b}} \tag{S-16}$$

where x_{1b}, x_{1s}, γ_{1b} and γ_{1s} and are the mole fraction of component 1 in the bulk, the mole fraction of component 1 at the surface, the activity coefficient of component 1 in the bulk and the activity coefficient of component 1 at the surface, respectively. Equation (S-16), which is known as the Butler Equation, could be written as the following:[4]

$$\sigma = \sigma_1 + \frac{RT}{A_1} \ln \frac{x_{1s}\ \gamma_{1s}}{x_{1b}\ \gamma_{1b}} \tag{S-17}$$

The molar surface area is determined by the UNIFAC method as follows:

$$A_i = 2.5 \times 10^9 \sum \upsilon_k Q_k \tag{S-18}$$

where Q_k and υ_k are the UNIFAC parameter and the number of group k, respectively. Here, 2.5×10^9 is a normalization factor.

To calculate the activity of each component at the surface and in the bulk of a binary liquid mixture, the Flory–Huggins Equation[5] is used:

$$\ln a_1 = \ln \varphi_1 + (1 - \frac{\upsilon_1}{\upsilon_2})\varphi_2 + \chi_1 \varphi_2^2 \tag{S-19}$$

$$\ln a_2 = \ln \varphi_2 + (1 - \frac{\upsilon_2}{\upsilon_1})\varphi_1 + \chi_2 \varphi_1^2 \tag{S-20}$$

where a_1 and a_2 are the solvent activity and polymer activity, φ_1 and φ_2 are the volume fraction of the solvent and polymer, υ_1 and υ_2 are the partial molar volume of the solvent and polymer, respectively, and χ_1 and χ_2 are the interaction parameters between the polymer and the solvent.

A polymer molecule consists of r elements. Theoretically, the volume of a polymer element is equal to the volume of a solvent molecule.[6] Thus, the volume of one mole of polymer is r times larger than the volume of one mole of solvent:

$$\frac{\upsilon_2}{\upsilon_1} = r \tag{S-21}$$

The interaction parameter is obtained from the following equation:

$$\chi_1 = \frac{(\delta_1 - \delta_2)^2 \upsilon_1}{RT} \tag{S-22}$$

Equation (S-17) can be written for component 1 and 2 according to the following assumptions:

$$\begin{gathered} A_1 = A_2 = A \\ \gamma_{1s} = \gamma_{1b} = 1 \\ (\sigma_2 - \sigma_1) + \frac{RT}{A} \ln \frac{x_{1b}}{x_{2b}} + \frac{RT}{A} \ln \frac{x_{2s}}{x_{1s}} = 0 \end{gathered} \tag{S-23}$$

If the first and second terms of Eq. (S-23) are equal to C_{12}, the following equation is obtained:

$$x_{2s} = x_{1s} \exp(-C_{12} \frac{A}{RT}) \tag{S-24}$$

Therefore, the mole fraction of the components at the surface, the activity coefficient at the surface, and finally, the surface tension of the solution are obtained using Eq. (S-15).

TABLE S-III. Activity of water for various solutions of K25 and K40 in water and ethanol at different temperatures and mass fractions; experimental activities are given as the mean ± standard deviation; *OAARE*: overall average absolute relative error

w	$a_{1\mathrm{Exp}}$[a]	$a_{1\mathrm{Model}}$	*RMSE*	*RE*	*AARE*	w	$a_{1\mathrm{Exp}}$[a]	$a_{1\mathrm{Model}}$	*RMSE*	*RE*	*AARE*
K25–water (T = 45 °C)						K40–water (T = 45 °C)					
0.1	0.9999 ± 0.0001	0.9999		0.0000		0.1	0.9999 ± 0.0001	0.9999		0.0000	
0.2	0.9999 ± 0.0001	0.9990		0.0900		0.2	0.9999 ± 0.0001	0.9975		0.2400	
0.3	0.9999 ± 0.0000	0.9950	0.0078	0.4900	0.51	0.3	0.9999 ± 0.0000	0.9930	0.0092	0.6900	0.65
0.45	0.9997 ± 0.0003	0.9850		1.4704		0.45	0.9998 ± 0.0001	0.9830		1.6803	

TABLE S-III. Continued

w	$a_{1\mathrm{Exp}}$[a]	$a_{1\mathrm{Model}}$	*RMSE*	*RE*	*AARE*	w	$a_{1\mathrm{Exp}}$[a]	$a_{1\mathrm{Model}}$	*RMSE*	*RE*	*AARE*
K25–water (T = 55 °C)						K40–water (T = 55 °C)					
0.1	0.9999 ± 0.0001	0.9999		0.0000		0.1	0.9999 ± 0.0001	0.9999		0.0000	
0.2	0.9999 ± 0.0001	0.9998		0.0100		0.2	0.9999 ± 0.0000	0.9980		0.1900	
0.3	0.9999 ± 0.0001	0.9970	0.0056	0.2900	0.35	0.3	0.9999 ± 0.0000	0.9940	0.0080	0.5900	0.57
0.45	0.9998 ± 0.0002	0.9890		1.0802		0.45	0.9998 ± 0.0001	0.9850		1.4803	
K25–ethanol (T = 45 °C)						K40–ethanol (T = 45 °C)					
0.1	0.9999 ± 0.0001	0.9999		0.0000		0.1	0.9999 ± 0.0001	0.9998		0.0100	
0.2	0.9999 ± 0.0001	0.9997		0.0200		0.2	0.9999 ± 0.0001	0.9996		0.0300	
0.3	0.9999 ± 0.0000	0.9980	0.0026	0.1900	0.17	0.3	0.9999 ± 0.0001	0.9986	0.0034	0.1300	0.21
0.45	0.9998 ± 0.0002	0.9950		0.4800		0.45	0.9998 ± 0.0002	0.9931		0.6701	
K25–ethanol (T = 55 °C)						K40–ethanol (T = 55 °C)					
0.1	0.9999 ± 0.0001	0.9997		0.0200		0.1	0.9999 ± 0.0001	0.9998		0.0100	
0.2	0.9999 ± 0.0001	0.9996		0.0300		0.2	0.9999 ± 0.0001	0.9997		0.0200	
0.3	0.9999 ± 0.0000	0.9988	0.0017	0.1100	0.12	0.3	0.9999 ± 0.0000	0.9987	0.0032	0.1200	0.19
0.45	0.9999 ± 0.0001	0.9967		0.3200		0.45	0.9999 ± 0.0001	0.9936		0.6300	
OAARE = 0.35											

TABLE S-IV. Surface tensions of various solutions of K25 and K40 in water and ethanol at different temperatures and mass fractions; experimental surface tensions are given as the mean ± standard deviation; *OAARE*: overall average absolute relative error

T °C	σ_{exp} mN m^{-1}	σ_{model} mN m^{-1}	*RE*	*RMSE*	*AARE*	T °C	σ_{exp} mN m^{-1}	σ_{model} mN m^{-1}	*RE*	*RMSE*	*AARE*
w = 0.1											
K25–water						K40–water					
20	61.0 ± 0.4	62.48	–2.426			20	58.7 ± 0.2	63.01	–7.342		
25	60.9 ± 0.5	61.76	–1.412			25	57.6 ± 0.4	61.85	–7.379		
30	60.3 ± 0.4	61.05	–1.244			30	57.1 ± 0.3	60.90	–6.655		

TABLE S-IV. Continued

T °C	σ_{exp} mN m^{-1}	σ_{model} mN m^{-1}	*RE*	*RMSE*	*AARE*	*T* °C	σ_{exp} mN m^{-1}	σ_{model} mN m^{-1}	*RE*	*RMSE*	*AARE*
w = 0.1											
K25–water						K40–water					
35	58.4 ± 0.8	60.33	–3.305	1.5120	2.48	35	56.6 ± 0.2	60.10	–6.184	4.2710	7.66
40	57.6 ± 0.8	59.52	–3.333			40	55.6 ± 0.2	59.50	–7.014		
45	57.8 ± 0.2	58.80	–1.730			45	54.5 ± 0.3	58.78	–7.853		
50	56.0 ± 0.8	57.98	–3.536			50	53.2 ± 0.3	57.96	–8.947		
55	55.4 ± 0.3	56.97	–2.834			55	51.8 ± 0.2	56.94	–9.923		
K25–ethanol						K40–ethanol					
20	25.0 ± 0.4	24.13	3.480			20	24.8 ± 0.2	23.97	3.345		
25	24.3 ± 0.4	22.93	5.638			25	24.1 ± 0.2	23.0	4.564		
30	23.5 ± 0.4	22.16	5.702			30	23.4 ± 0.2	22.15	5.342		
35	23.1 ± 0.2	21.56	6.667	1.6956	7.09	35	22.7 ± 0.4	21.47	5.418	1.0316	4.49
40	22.7 ± 0.1	21.18	6.696			40	22.2 ± 0.4	21.06	5.135		
45	22.6 ± 0.1	20.77	8.097			45	21.5 ± 0.3	20.65	3.953		
50	22.5 ± 0.2	20.37	9.467			50	21.2 ± 0.3	20.18	4.811		
55	22.3 ± 0.2	19.85	10.986			55	20.3 ± 0.3	19.61	3.399		
w = 0.2											
K25–water						K40–water					
20	58.0 ± 0.2	61.29	–5.672			20	57.0 ± 0.2	62.25	–9.210		
25	57.3 ± 0.2	60.55	–5.671			25	56.3 ± 0.2	60.84	–8.063		
30	56.5 ± 0.2	59.81	–5.858			30	55.8 ± 0.4	59.71	–7.007		
35	55.1 ± 0.2	59.08	–7.223	4.0389	7.38	35	55.2 ± 0.2	58.89	–6.684	4.5306	8.32
40	53.9 ± 0.4	58.24	–8.051			40	54.2 ± 0.4	58.23	–7.435		
45	53.0 ± 0.2	57.40	–8.301			45	53.1 ± 0.1	57.49	–8.267		
50	52.0 ± 0.2	56.56	–8.769			50	51.8 ± 0.1	56.64	–9.343		

TABLE S-IV. Continued

T °C	σ_{exp} mN m^{-1}	σ_{model} mN m^{-1}	*RE*	*RMSE*	*AARE*	T °C	σ_{exp} mN m^{-1}	σ_{model} mN m^{-1}	*RE*	*RMSE*	*AARE*
					w = 0.2						
		K25–water						K40–water			
55	50.7 ± 0.2	55.53	–9.526			55	50.3 ± 0.3	55.61	–10.55		
		K25–ethanol						K40–ethanol			
20	23.5 ± 0.2	23.75	–1.063			20	23.1 ± 0.1	23.42	–1.385		
25	23.2 ± 0.3	22.57	2.715			25	22.5 ± 0.3	22.35	0.666		
30	22.9 ± 0.2	21.85	4.585			30	22.0 ± 0.3	21.55	2.045		
35	22.2 ± 0.1	21.29	4.099	1.2760	4.91	35	21.4 ± 0.2	20.95	2.102	0.4420	1.61
40	22.0 ± 0.2	20.90	5.000			40	21.2 ± 0.1	20.53	3.160		
45	21.8 ± 0.3	20.51	5.917			45	20.5 ± 0.4	20.09	2.000		
50	21.7 ± 0.2	20.03	7.695			50	20.2 ± 0.4	19.61	2.920		
55	21.6 ± 0.1	19.37	10.324			55	19.2 ± 0.3	18.94	1.354		
					w = 0.3						
		K25–water						K40–water			
20	56.8 ± 0.4	59.90	–5.457			20	54.5 ± 0.2	61.38	–12.62		
25	56.3 ± 0.4	59.15	–5.062			25	54.0 ± 0.1	59.80	–10.74		
30	55.2 ± 0.4	58.38	–5.760			30	53.5 ± 0.4	58.53	–9.401		
35	54.0 ± 0.3	57.62	–6.703	6232	6.76	35	53.1 ± 0.2	57.47	–8.229	5.2131	9.86
40	53.0 ± 0.2	56.86	–7.283	3.		40	52.2 ± 0.1	56.70	–8.620		
45	52.3 ± 0.2	56.00	–7.074			45	51.3 ± 0.2	56.00	–9.161		
50	50.8 ± 0.1	55.14	–8.543			50	50.1 ± 0.5	55.06	–9.900		
55	50.0 ± 0.1	54.08	–8.160			55	49.0 ± 0.2	54.01	–10.22		
		K25–ethanol									
20	22.9 ± 0.2	23.38	–2.096								
25	22.6 ± 0.1	22.30	1.327								

TABLE S-IV. Continued

T °C	σ_{exp} mN m^{-1}	σ_{model} mN m^{-1}	RE	$RMSE$	$AARE$
		w = 0.3			
		K25–ethanol			
30	22.3 ± 0.2	21.53	3.452		
35	21.7 ± 0.2	20.95	3.456	1.0423	3.86
40	21.5 ± 0.3	20.53	4.511		
45	21.2 ± 0.1	20.10	5.188		
50	20.9 ± 0.1	19.59	6.267		
55	20.8 ± 0.1	18.97	8.798		
$OAARE$ = 5.69					

Statistical analysis

1. Relative error

$$RE = \left(\frac{X_{\rm exp} - X_{\rm cal}}{X_{\rm exp}}\right) \times 100$$

2. Average relative error

$$ARE = \frac{1}{n}\sum_{i=1}^{n}(RE)$$

3. Average absolute relative error

$$AARE = \frac{1}{n}\sum_{i=1}^{n}\left|RE\right|$$

4. Root mean squared error

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(X_{\rm exp} - X_{\rm cal})_i^2}$$

5. Standard deviation

$$SD = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(X_i - \overline{X})^2}$$

where X_i is the amount of each data, $\overline{X}$ is the average of the data points, and n is the number of data points.

6. Coefficient of determination

$$R^2 = 1 - \sum_{i=1}^{n}[X_{\mathrm{exp}} - X_{\mathrm{cal}}]_i^2 \Big/ \sum_{i=1}^{n}[X_{\mathrm{exp}} - \overline{X}]_i^2$$

with:

$$\overline{X} = \frac{1}{n}\sum_{i=1}^{n}[X_{\mathrm{exp}}]_i$$

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