Supporting Information

Solubility of Biocompounds 2,5-furandicarboxylic acid and 5-formylfuran-2-carboxylic acid in binary solvent mixtures of water and 1,4-dioxane

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Table S1 Calculation of solubility parameters δ for FFCA by Fedors' method along with molar volume[a].

Group	number	Δe^{a} cal·mol^{-1}	V cm^{3}·mol^{-1}
-CH=	2	1030	
-C=O	1	4150	
-COOH	1	6600	
-O-	1	800	96.4[b]
>C=	2	1030	
Five rings	1	750	
conjugate	2	400	
∑		17220.00	

$$\delta_{\text{solute}} = \left(\frac{\sum_i \Delta e_i}{V} \right)^{0.5} = 27.30 \text{ MPa}^{0.5},$$

[a] cited from （Du, C.B.; Luo, Y.L.; Huang, C.Y.; Li, R.R. The solubility measurement and thermodynamic models correlation of baclofen in twelve pure organic solvents. J. Chem. Eng. Data, 2022, 67: 2655-2661.

[b] obtained from ACD/Labs.

The calculation of preferential solvation parameters of FDCA/FFCA in binary mixtures of 1,4-dioxane+water

The preferential solvation parameter $\delta_{1,3}$ could also be calculated by the inverse Kirkwood-Buff integrals (IKBI) method [1], as presented in Eqs.(1) to (5):

$$\delta_{1,3} = x_{1,3}^{L} - x_1 = -\delta_{2,3} \quad (1)$$

$$\delta x_{1,3} = \frac{x_1 x_2 \left(G_{1,3} - G_{2,3}\right)}{x_1 G_{1,3} + x_2 G_{2,3} + V_{cor}} \quad (2)$$

$$G_{1,3} = RT\kappa_T - \overline{V_3} + \frac{x_2 \overline{V_2} D}{Q} \quad (3)$$

$$G_{2,3} = RT\kappa_T - \overline{V_3} + \frac{x_1 \overline{V_1} D}{Q} \quad (4)$$

$$V_{cor} = 2522.5\left[r_3 + 0.1363\left(x_{1,3}^{L}\overline{V}_1 + x_{2,3}^{L}\overline{V_2}\right)^{1/3} - 0.085\right]^3 \quad (5)$$

In above equations, the isothermal compressibility of mixed solvent (κ_T) could be calculated with the equation of $\kappa_T = x_1\kappa_{T,1}^{o} + x_2\kappa_{T,2}^{o}$, x_i and $\kappa_{T,i}^{o}$ are volume fraction and isothermal compressibility of pure solvent *i*. [2]. $\overline{V_1}$, $\overline{V_2}$ and $\overline{V_3}$ are the partial molar volume of solvents and solute. $\overline{V_1}$ and $\overline{V_2}$ are cited from the reported values and $\overline{V_3}$ values are obtained from ACD/Labs (97.3 $cm^3 \cdot mol^{-1}$ and 96.4 $cm^3 \cdot mol^{-1}$ for FDCA and FFCA, respectively). V_{cor} is the correlation volume and listed in Table S2, r_3 is molecular radius of solute and calculated by $r_3 = \left(\frac{3\times10^{21}V_3}{4\pi N_{AV}}\right)^{1/3}$. The function *D* is the derivative of the standard molar Gibbs energies of transfer ($\Delta_{tr}G_{(3,2\rightarrow1+2)}^{o}$) of solute from pure water to binary mixtures with respect to the proportion of 1,4-dioxane, presented in Eq. (6). The function *Q* is the second derivative of the excess molar Gibbs energy of mixing (G_{1+2}^{Exc}) with respect to the water composition in mixtures, presented in Eq. (7) [2].

$$D = \left(\frac{\partial \Delta_{tr}G_{(3,2\rightarrow1+2)}^{o}}{\partial x_1}\right)_{T,P} \quad (6)$$

$$Q = RT + x_1 x_2 \left[\frac{\partial^2 G_{1+2}^{Exc}}{\partial x_2^2}\right]_{T,p} \quad (7)$$

The standard molar Gibbs energies of transfer ($\Delta_{tr}G^{o}_{(3,2\rightarrow1+2)}$) of solute could be calculated according to regular polynomials in the fifth degree, as presented in Eq. (8).

$$\Delta_{tr}G^{0}_{3,2\rightarrow1+2} = RT\ln\left(\frac{x_{3,2}}{x_{3,1+2}}\right) = a + bx_1 + cx_1^2 + dx_1^3 + ex_1^4 + fx_1^5 \qquad (8)$$

The equation coefficients and *D* values were listed in Table S3 and Table S4. The values of $G_{1,3}$ and $G_{2,3}$ were listed in Table S5. $\delta x_{1,3}$ can be obtained by iterative calculation of (1), (2) and (5), and the results were tabulated in Table S2.

(1) Rodrigueza, G.A.; Delgadoa, D.R.; Fleming, M. Preferential solvation of indomethacin and naproxen in ethyl acetate + ethanol mixtures according to the IKBI method. Phys. Chem. Liq. 2014, 52, 533-545.

(2) Jimenez, D.M.; Cardenas, Z.J.; Delgado, D.R.; Pena, M.A.; Martinez, F. Solubility temperature dependence and preferential solvation of sulfadiazine in 1, 4-dioxane+ water co-solvent mixtures. Fluid Phase Equilibr. 2015, 397, 26-36.

Table S2. Correlation volume V_{cor} and the preferential solvation parameters $\delta_{1,3}$ of FDCA and FFCA in binary water + 1,4-dioxane mixtures with different solvent mixing ratio at 303.15 K.

x_1	V_{cor}		$100\delta_{1,3}$	
	FDCA	FFCA	FDCA	FFCA
0.00	574.40	571.45	0.00	0.00
0.05	586.90	583.37	-3.06	-3.09
0.10	647.93	648.80	-2.85	-2.57
0.15	729.96	729.07	-1.02	-0.84
0.20	811.53	804.72	0.97	0.74
0.25	887.12	873.37	2.67	1.92
0.30	956.78	936.84	4.04	2.82
0.35	1021.97	997.34	5.17	3.56
0.40	1084.56	1057.00	6.16	4.30
0.45	1145.96	1116.92	7.13	5.14
0.50	1204.95	1175.15	7.97	5.90
0.55	1248.99	1218.92	7.62	5.51
0.60	1250.44	1225.04	3.72	2.00
0.65	1225.75	1215.07	-2.39	-2.87
0.70	1230.56	1237.00	-6.03	-5.08
0.75	1263.34	1284.15	-7.31	-5.12
0.80	1309.09	1340.55	-7.47	-4.33
0.85	1362.50	1399.56	-6.92	-3.24
0.90	1423.06	1458.41	-5.66	-2.08
0.95	1493.24	1516.02	-3.48	-0.96
1.00	1576.69	1570.92	0.00	0.00

Table S3. Gibbs energy of transfer ($kJ \cdot mol^{-1}$) of FDCA and FFCA in 1,4-dioxane (1) + water (2) mixtures at 303.15 K.

x_1	FDCA	FFCA
0.00	0	0
0.20	-8.279	-7.919
0.40	-11.132	-10.069
0.60	-11.799	-10.560
0.80	-11.271	-10.183
1.00	-7.295	-8.912

Table S4. *D* values (kJ· mol^{-1}) of FDCA and FFCA in 1,4-dioxane (1) + water (2) mixtures at 303.15 K.

x_1	FDCA	FFCA
0.00	-62.17	-67.53
0.05	-50.56	-50.76
0.10	-40.44	-37.58
0.15	-31.75	-27.42
0.20	-24.44	-19.74
0.25	-18.42	-14.06
0.30	-13.57	-9.95
0.35	-9.77	-7.04
0.40	-6.87	-4.98
0.45	-4.71	-3.50
0.50	-3.10	-2.35
0.55	-1.85	-1.36
0.60	-0.71	-0.39
0.65	0.55	0.66
0.70	2.19	1.82
0.75	4.50	3.08
0.80	7.77	4.38
0.85	12.34	5.62
0.90	18.54	6.64
0.95	26.73	7.22
1.00	37.29	7.13

Table S5. $G_{1,3}$ and $G_{2,3}$ values ($cm^3 \cdot mol^{-1}$) of solute (3) in 1,4-dioxane (1) + water (2) mixtures at 303.15 K.

x_1	$G_{1,3}$		$G_{2,3}$	
	FDCA	FFCA	FDCA	FFCA
0.00	-542.20	-579.72	-96.148	-95.25
0.05	-432.72	-433.16	-176.89	-176.31
0.10	-358.63	-339.20	-230.76	-220.35
0.15	-305.19	-275.74	-268.75	-244.27
0.20	-265.45	-231.92	-296.92	-257.33
0.25	-235.21	-201.36	-319.11	-265.41
0.30	-212.10	-180.26	-338.48	-272.98
0.35	-194.67	-166.18	-358.41	-284.18
0.40	-182.03	-157.44	-382.74	-302.98
0.45	-173.12	-152.32	-415.18	-332.07
0.50	-165.57	-147.81	-451.49	-364.62
0.55	-151.98	-136.38	-448.71	-355.54
0.60	-120.13	-108.15	-284.91	-198.14
0.65	-81.22	-77.35	43.573	73.06
0.70	-62.61	-67.28	304.17	237.64
0.75	-59.81	-70.19	460.06	285.96
0.80	-62.79	-76.19	578.64	285.55
0.85	-68.10	-82.14	696.16	266.01
0.90	-75.00	-87.27	830.33	236.84
0.95	-83.89	-91.44	989.35	198.62
1.00	-95.44	-94.54	1180.2	149.32