

Supporting Information

Exploring the Solubility and Solvation Thermodynamics of Coumarin in a Range of Aqua-Organic Solvents

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1. Theoretical

1.1 Calculations of thermodynamic parameters

The Gibbs energy of solutions ($\Delta G_{sol}^0(i)$) (shown in Table 3) on a molal scale for different solvent mixtures at various temperatures was calculated using equation 2, similar to previous studies [1-3].

$$\Delta G_{sol}^0(i) = -RT \ln S \quad (2)$$

In this theoretical study, the experimental saturated solubility of coumarin is denoted by 'S' and measured in mol·kg⁻¹. It is important to emphasize that the mole fractions of coumarin in different compositions of the aqueous DMF/DMSO/ACN solvent systems, as determined from the solubility values presented in Table 2, are found to be negligibly small. Additionally, the activity coefficients of non-polar coumarin in these solvent systems are assumed to be unity, a common practice for non-electrolytes and organic solvent systems [1, 3]. This assumption is

considered reasonable due to the insignificance of the factor involving the ratio of activity coefficients (represented as 'sol' for the aqueous solution of DMF/DMSO/ACN) in determining transfer free energies, which is the primary focus of our investigation. It is expected that this factor has a negligible impact on the transfer free energies due to the small values associated with it.

To get the precise value of $\Delta G_{sol}^0(i)$ and to count the effect of temperature on $\Delta G_{sol}^0(i)$ the method of least squares is used in the form of equation 3 [1, 3].

$$\Delta G_{sol}^0(i) = a + bT + cT \ln T \quad (3)$$

where T is the temperature in Kelvin scale. The values of coefficients a, b, and c are shown in Table 4. Transfer Gibbs energies, ΔG_t^0 and entropies ΔS_t^0 of coumarin molecules from H₂O to H₂O-DMF/DMSO/ACN mixtures were calculated at 298.15 K on mole fraction scale by using the following equations 4, 5 & 6.

$$\Delta G_t^0(i) = {}_s \Delta G_{sol}^0(i) - {}_R \Delta G_{sol}^0(i) \quad (4)$$

$$\text{i.e. } \Delta G_t^0(i) = (a_s - a_R) + (b_s - b_R)T + (c_s - c_R)T \ln T - RT \ln(M_s / M_R) \quad (5)$$

and

$$\Delta S_t^0(i) = (b_R - b_s) + (c_R - c_s)(1 + \ln T) + R \ln(M_s / M_R) \quad (6)$$

here the subscript 's' for H₂O /DMF/DMSO/ACN mixtures, 'R' for H₂O, M_s and M_R is the molar mass of the H₂O +DMF/DMSO/ACN and pure H₂O respectively. The computed $\Delta G_t^0(i)$ and $T\Delta S_t^0(i)$ values of coumarin are offered in Table 4 & 5. The calculated values show uncertainties in $\Delta G_t^0(i)$ and $\Delta S_t^0(i)$ are about $\pm 0.07 \text{ kJ}\cdot\text{mol}^{-1}$ and $2.5 \text{ kJ}\cdot\text{mol}^{-1}$, respectively.

Now $\Delta E_t^0(i)$ (where E=G or S) may be ascribed as the sum of the following terms (assuming dipole induced dipole term to be very small)[4].

$$\text{i.e. } \Delta E_t^0(i) = \Delta E_{t,cav}^0(i) + \Delta E_{t,d-d}^0(i) + \Delta E_{t,ch}^0(i) \quad (7)$$

In this study, we consider the transfer energy contribution of two main effects: the cavity effect ($\Delta E_{t,cav}^0(i)$) and the dipole-dipole interaction effect ($\Delta E_{t,d-d}^0(i)$). The cavity effect accounts for the energy associated with the creation of cavities required for introducing coumarin into both pure water (H₂O) and water mixed with DMF/DMSO/ACN solvents. The dipole-dipole interaction effect represents the energy resulting from the interactions between coumarin and the

solvent molecules. Additionally, $\Delta X_{t,cav}^0(i)$ includes all other effects, such as those originating from short-range dispersion interactions, hydrophilic or hydrophobic hydration, and structural effects. Here $\Delta X_{t,cav}^0(i)$ values are computed by well established Scaled particle theory (SPT) of R.A. Pierotti [4, 5]. In this theory, the solute molecule (coumarin) and solvent molecules are treated as equivalent hard-sphere models, with their respective diameters considered as important parameters [6]. Here the hard-sphere diameter for mixed solvent, σ_s for a particular composition of solvent mixture is calculated according to Graziano [7] (Table S1):

The determination of the hard-sphere diameter (σ_s) for a particular composition of the solvent mixture is essential for our study. To achieve this, we employ the methodology proposed by Graziano [7]. The detailed calculation procedure and results can be found in Table S1, which is provided as supplementary material accompanying this study. By applying the approach outlined in Graziano's work, we are able to calculate the appropriate hard-sphere diameter (σ_s) specifically tailored for the mixed solvent system under investigation. This diameter parameter plays a crucial role in our analysis and allows us to accurately account for the characteristics and interactions within the solvent mixture.

$\sigma_s = \text{mole fraction of water} \times \text{hard-sphere diameter of water} + \text{mole fraction of DMF/DMSO/ACN} \times \text{hard-sphere diameter of DMF/DMSO/ACN}$.

Now replacing actual term of E we have calculated $\Delta G_{d-d}^0(i)$ and ${}_s\Delta S_{d-d}^0(i)$ using Keesom-orientation expression[8] as:

$$\Delta G_{t,d-d}^0(i) = ({}_s\Delta G_{d-d}^0(i) - {}_R\Delta G_{d-d}^0(i)) \quad (8)$$

$$\text{and } \Delta S_{t,d-d}^0(i) = ({}_s\Delta S_{d-d}^0(i) - {}_R\Delta S_{d-d}^0(i)) \quad (9)$$

For ${}_s\Delta G_{d-d}^0(i)$ in a solvent S, as given below:

$${}_s\Delta G_{d-d}^0(i) = -(8\Pi/9)N^2\mu_s^2\mu_x^2\sigma_{s-x}^{-3}(kT)^{-1}V_s^{-1} = A/TV_s \quad (10)$$

Where $A = -(8\Pi/9)N^2\mu_s^2\mu_x^2\sigma_{s-x}^{-3}(k)^{-1}$

$\Pi = 22/7$, $V_s = M_s/d_s = \text{molar volume of solvent}$, $M_s = \text{molar mass of binary solvent}$, $d_s = \text{density of binary solvent}$, $k = \text{Boltzmann constant}$. $N = \text{Avogadro's number}$, μ_s, μ_x are the dipole moment of binary solvent and coumarin molecules respectively (Table 5 & Table S1).

The dipole moment of the mixed binary solvent system in a particular composition is calculated as[6]: $\mu_s = \mu$ of reference solvent (H₂O) \times mole fraction of H₂O + μ of co-solvent (DMF/DMSO/ACN) \times mole fraction of co-solvent (DMF/DMSO/ACN).

σ_{s-x} represents the distance at which the attractive and repulsive interactions between the solvent and solute molecules are equal and is generally equal to $\frac{1}{2}(\sigma_s + \sigma_x)$ where σ_s and σ_x are the hard sphere diameters of binary solvent and coumarin respectively (Table S1)

Here $\Delta S_{d-d}^0(i)$ can be written as follows:

$${}_s \Delta S_{d-d}^0(i) = -\{\delta_s \Delta G_{d-d}^0(i) / \delta T\}_p \quad (11)$$

$$\text{i.e. } T_s \Delta S_{d-d}^0(i) = {}_s \Delta G_{d-d}^0(i) [1 + T\alpha] [4] \quad (12)$$

where α is the isobaric thermal coefficient²³ of the mixed solvent and represented by eq 13 as:

$$\alpha = (\delta \ln V_s / \delta T)_p = -(\delta \ln d_s / \delta T) \quad (13)$$

As in the earlier studies[4, 7, 9], in order to get the $\Delta E_{t,d-d}^0(i)$ term on the mole fraction scale, $\Delta E_{t,d-d}^0(i)$ was again multiplied by X_{sl} , which is the actual mole fraction of the organic binary solvent in the vicinity of the coumarin for the contribution of dipole-dipole interaction which was estimated using the equation 14 as follow[4];

$$X_{s1} = X_s (\mu_s / \sigma_s^3) / (\mu_R / \sigma_R^3) \quad (14)$$

On the other hand $\Delta E_{t,ch}^0(i)$ values of amino acids were calculated after the subtraction of $\Delta E_{t,cav}^0(i)$ and $\Delta E_{t,d-d}^0(i)$ from the total i.e. $\Delta E_t^0(i)$. The values of $\Delta E_{t,cav}^0(i)$, $\Delta E_{t,d-d}^0(i)$ and $\Delta E_{t,ch}^0(i)$ are presented in Table 5.

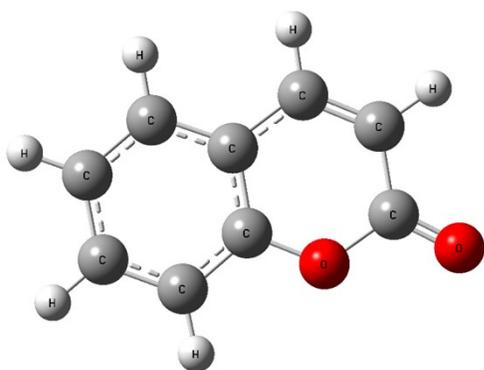
Table S1. Solvent parameters (mole fraction of cosolvent (z_s), water (z_R), apparent mol. weight of electrolyte solvent (M_s), apparent density (d_s), apparent molar volume (V_s), apparent solvent diameter (σ_s), σ_{s-x} , μ_s , and apparent isobaric thermal coefficients (α) and apparent dipole moment (D) of the H₂O +DMF/DMSO/ACN systems at 298.15 K[#]

Wt % of solvent (s)	Mole fraction (z_s)	Mole fraction (z_R)	Molar mass (M_s) ($\text{g}\cdot\text{mol}^{-1}$)	$10^3 d_s$ ($\text{kg}\cdot\text{m}^{-3}$)	σ_{s-x} (nm)	σ_s (nm)	Dipole Moment (μ_s) (Debye)	α ($\times 10^{-3}$) (K^{-1})
100% H ₂ O	1.0000	0.0000	18.0153	0.9970	0.3500	0.2740	1.8310	0.257
20% DMF	0.9420	0.0580	21.2096	0.9939	0.3565	0.2870	2.0277	0.301
40% DMF	0.8589	0.1411	25.7863	0.9895	0.3658	0.3056	2.2813	0.363
60% DMF	0.7301	0.2699	32.8800	0.9827	0.3803	0.3345	2.6206	0.459
80% DMF	0.5035	0.4965	45.3599	0.9707	0.4056	0.3852	3.0982	0.631
100% DMF	0.0000	1.0000	73.0900	0.9440	0.4620	0.4980	3.8200	1.009
100% H ₂ O	1.0000	0.0000	18.0153	0.9970	0.3500	0.2740	1.8310	0.257*
20%DMSO	0.9455	0.0545	21.2913	0.9939	0.3559	0.2858	1.9438	0.296
40%DMSO	0.8668	0.1332	26.0223	0.9895	0.3645	0.3029	2.1066	0.353
60%DMSO	0.7430	0.2570	33.4646	0.9827	0.3779	0.3298	2.3627	0.442
80%DMSO	0.5202	0.4798	46.8582	0.9707	0.4021	0.3781	2.8237	0.602
100%DMSO	0.0000	1.0000	78.1300	0.9440	0.4585	0.4910	3.9000	0.982
100% H ₂ O	1.0000	0.0000	18.0153	0.9970	0.3500	0.2740	1.8310	0.257*
20% ACN	0.9011	0.0989	20.2934	0.9761	0.3568	0.2876	1.9901	0.369
40% ACN	0.7736	0.2264	23.2304	0.9490	0.3656	0.3051	2.1953	0.513
60% ACN	0.6030	0.3970	27.1599	0.9131	0.3774	0.3288	2.4698	0.706
80% ACN	0.5326	0.4674	28.7816	0.8983	0.3823	0.3385	2.8561	0.786
100% ACN	0.0000	1.0000	41.0500	0.7860	0.4190	0.4120	3.4400	1.388

$u(T)^{\#} = 0.10 \text{ K}$ [u for standard uncertainty]; Coumarin has a diameter of 0.456 nm and a dipole moment of 5.257 Debye [DFT data, 10]. The hard sphere diameters of DMF, DMSO, ACN, and water are 0.498 nm, 0.491 nm, 0.412 nm, and 0.274 nm, respectively [11, 12, 13]. The dipole moments of DMF, DMSO, ACN, and water are 3.82 D, 3.90 D, 3.45 D, and 1.831 D, respectively [22, 29]. Furthermore, the isobaric thermal coefficient of DMF, DMSO, ACN, and water are 1.009×10^{-3} , 0.982×10^{-3} , 1.388×10^{-3} , and 0.257×10^{-3} , respectively [13,14].

1.2 Density Functional Theory:

Structure of coumarin, was optimized in density functional theory (DFT) using the Gaussian 09 software [10] Computation was performed using B3LYP hybrid functional and 6-31G+(d,p) basis set. The ball and stick model of the ground state optimized geometries has been represented in Fig 1.



Calculation Type = FOPT
Version: Gaussian 09W software
Calculation Method = RB3LYP
Basis Set = 6-31+G(d,p)
Charge = 0
Spin = Singlet
Total Energy (RB3LYP) = -497.05238818 a.u.
RMS Gradient Norm = 0.00000343 a.u.
Dipole Moment = 5.2567 Debye
Point Group = C1

Fig S1. Structure of coumarin determined by Density Functional Theory.

1.3. UV-Vis spectrum:

The absorption spectrum of coumarin in water, Acetonitrile, DMF, DMSO shows two absorption maxima in the wavelength range 270-275 nm and 310-312 nm. From the comparative UV-Vis spectrum of coumarin in water, pure solvents and aqueous solvents (Fig.S2a-S2c), it is clear that absorption peaks at 270-275 and 310-312 nm remain almost unaltered which is indicative of the fact that there is no specific chemical change during the transfer of solid coumarin into the solution phase. Slight changes in the peak position and intensity appeared due to different polarity of the solvents used. It is important to mention here that the clean absorption spectrum in various solvent system also support the purity of the understudying compound.

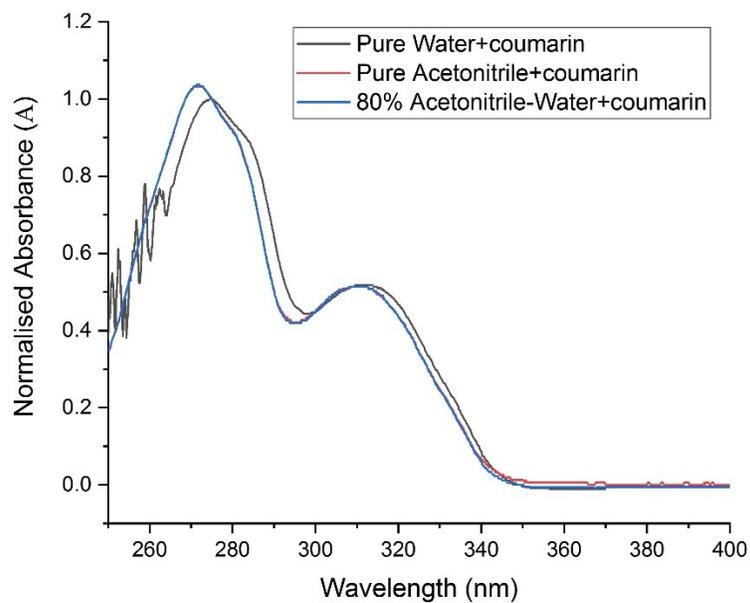


Figure S2(a). Comparative UV-Vis spectrum of coumarin in water, pure acetonitrile and aqueous acetonitrile (ACN)

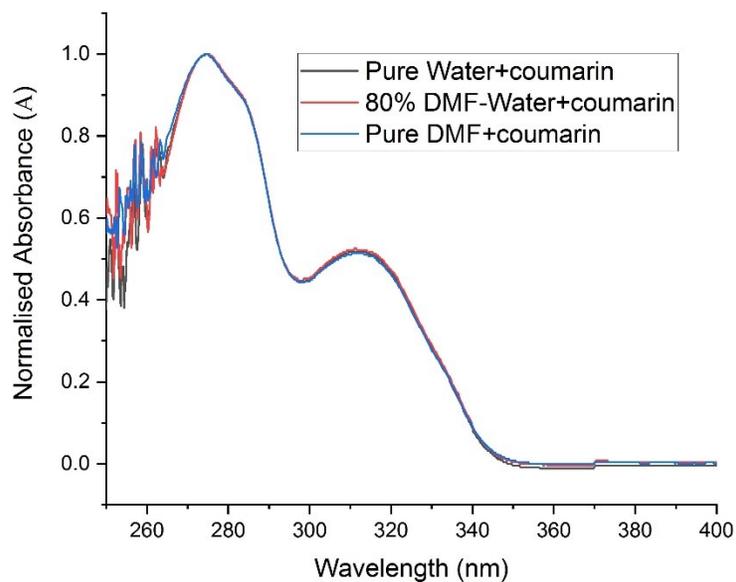


Figure S2(b). Comparative UV-Vis spectrum of coumarin in water, pure DMF and aqueous DMF

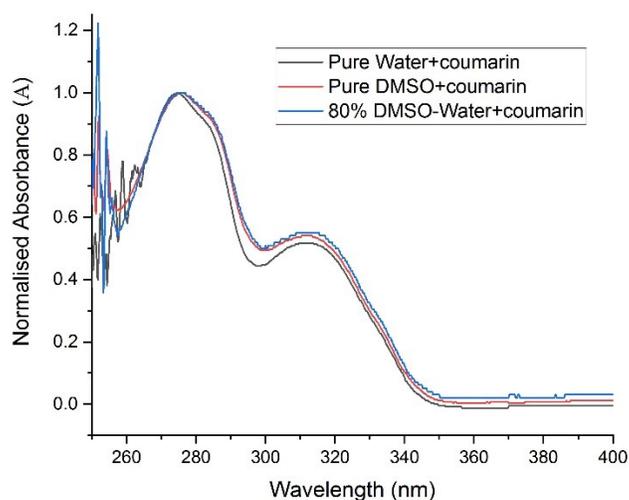


Figure S2(c). Comparative UV-Vis spectrum of coumarin in water, Pure DMSO and aqueous DMSO

1.3 Mole Fraction Solubility of Coumarin in Aqueous-Organic Solvent System

Mole fraction solubility of coumarin in aqueous -DMF, aqueous-DMSO and aqueous-ACN at different temperatures was calculated as follows:

$$\text{Mole fraction solubility } (x_S) = \frac{(m_1/M_1)}{(m_1/M_1 + m_2/M_2 + m_3/M_3)} \quad (1)$$

where, 1, 2 and 3 refer to coumarin, water and DMF/DMSO/ACN solvents, respectively. Here m_1 and M_1 are the solubility of coumarin in gram and the molar mass of coumarin, m_2 and M_2 weight taken, and molar mass of water, and m_3 and M_3 weight taken, and molar mass of DMF/DMSO/ACN solvents, respectively.

Table S2. Solubility of coumarin in aqueous -DMF, aqueous-DMSO and aqueous-ACN at different temperatures in mole fraction scale of solvent mixtures at pressure 0.1MPa^b

Mole fraction [cosolvents]	Mole fraction solubility (x_S) x 10 ³				
	288.15 K [#]	293.15 K [#]	298.15 K [#]	303.15 K [#]	308.15 K [#]
X_{DMF}					
0.0000	0.095	0.205	0.322	0.351	0.546

0.0580	1.021	1.244	1.785	2.419	2.716
0.1411	4.574	5.011	6.841	8.942	9.254
0.2699	15.847	20.427	29.768	40.352	41.009
0.4965	85.371	93.002	113.634	143.273	147.951
1.0000	228.141	240.154	260.277	283.003	283.224

x_{DMSO}

0.0000	0.095	0.205	0.322	0.351	0.546
0.0545	0.262	0.504	0.670	0.791	1.025
0.1332	0.739	1.229	1.697	1.943	2.396
0.2570	2.657	4.126	5.921	6.414	7.048
0.4798	30.783	42.983	56.555	70.542	77.815
1.0000	137.689	232.832	251.245	273.095	278.922

x_{ACN}

0.0000	0.095	0.205	0.322	0.351	0.546
0.0989	0.402	0.623	0.935	1.222	1.414
0.2264	1.030	1.169	1.628	2.096	22.906
0.3970	1.670	2.765	28.448	31.382	51.526
0.4674	71.460	83.355	86.637	89.158	92.239
1.0000	109.270	117.374	131.882	134.977	153.003

$u(T)^{\#} = 0.10 \text{ K}$ [u for standard uncertainty]; and $u_r(S) = 0.001$ and $u_r(p)^b = 0.02 \text{ MPa}$
[u_r = relative uncertainty]

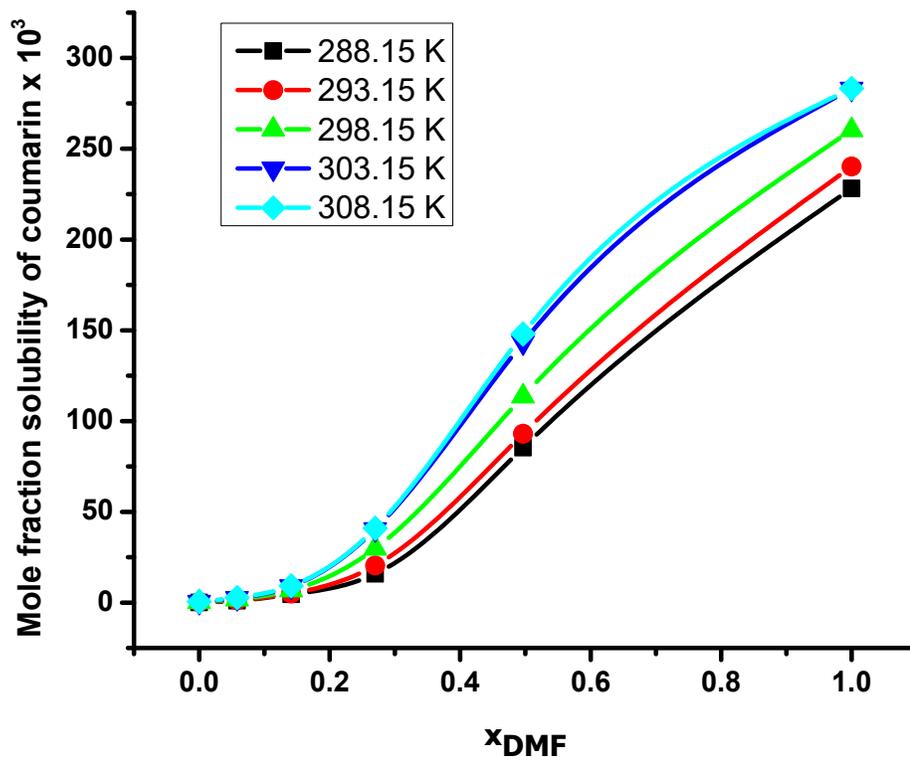


Figure S 3(a) Mole fraction solubility of coumarin in various temperatures (288.15 to 308.15 K) in pure water and with the variation of mole fraction concentration of *N, N*-dimethylformamide (x_{DMF}).

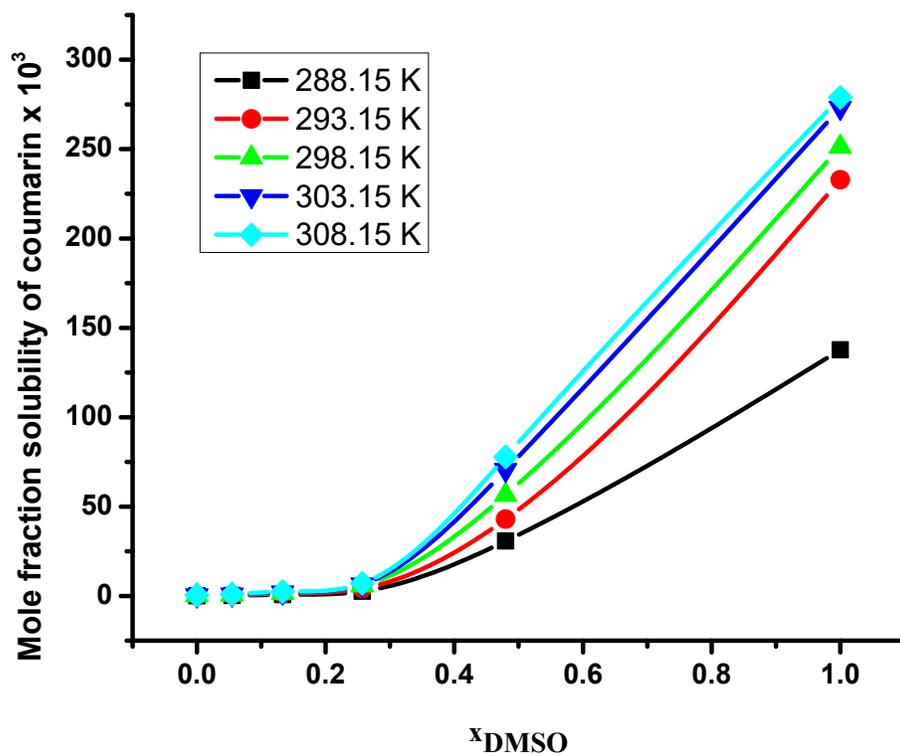


Figure S 3(b) Mole fraction solubility of coumarin in various temperatures (288.15 to 308.15 K) in pure water and with the variation of mole fraction concentration of dimethylsulfoxide (x_{DMSO}).

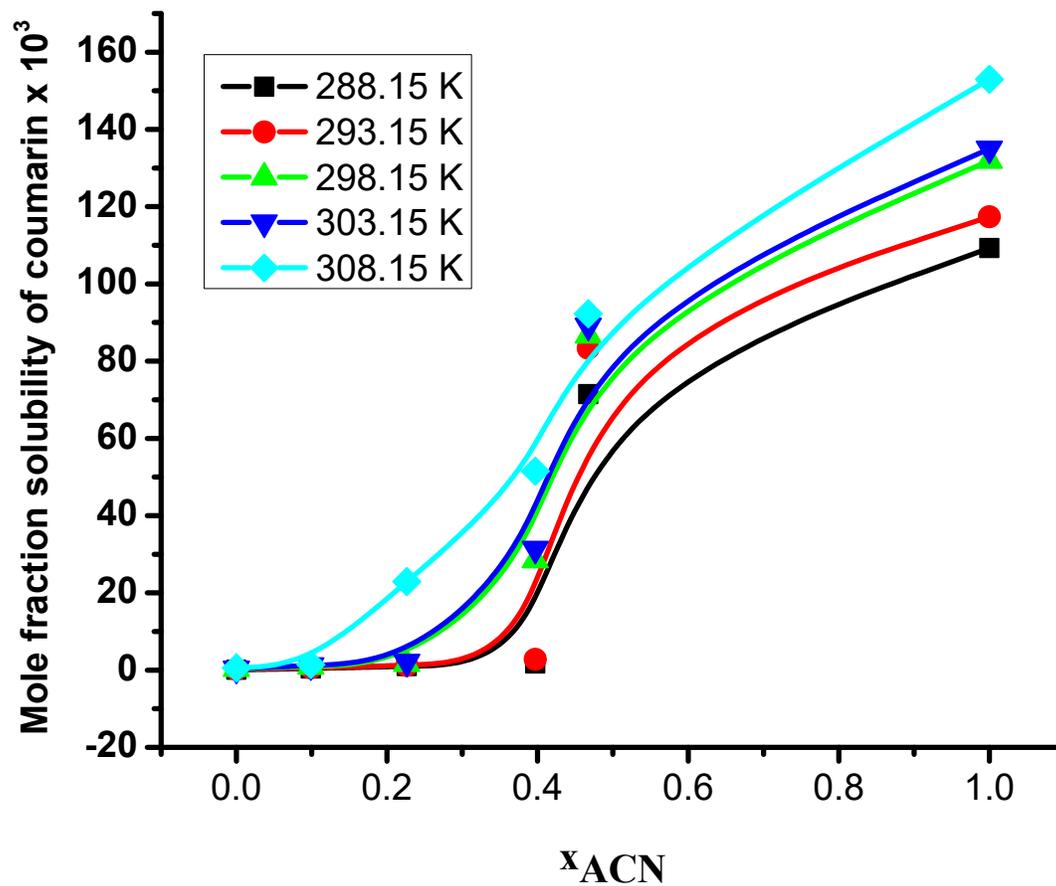


Figure S3 (c) Mole fraction solubility of coumarin in various temperatures (288.15 to 308.15 K) in pure water and with the variation of mole fraction concentration of acetonitrile (x_{ACN}).

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