Improving ethylene glycol transport properties by caffeine –

thermodynamic and computational evidence

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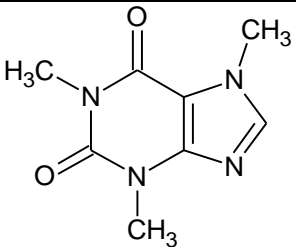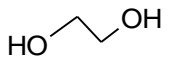[2]*Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia*

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Table S1. Provenance, purity, and structure of the used chemicals.

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Chemical Name	Source	CAS Number	Mass Fraction Purity	Structure
Caffeine	Sigma-Aldrich	58-08-2	≥ 0.99	
Ehylene glycol	Sigma-Aldrich	107-21-1	≥ 0.99	

Table S2. Molality, (m) and density, (ρ) of caffeine + ethylene glycol solutions in the temperature range from T = (288.15 to 343.15) K at p = $1 \cdot 10^5$ Pa.

m / (mol·kg^{-1})	ρ / (g·cm^{-3})											
T / (K)	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15	343.15
0.0000	1.116743	1.113266	1.109773	1.106266	1.102743	1.099201	1.095640	1.092056	1.088449	1.084817	1.081158	1.077645
0.0090	1.117059	1.113582	1.110089	1.106580	1.103057	1.099515	1.095950	1.092362	1.088753	1.085115	1.081453	1.077933
0.0181	1.117377	1.113898	1.110403	1.106892	1.103371	1.099828	1.096260	1.092666	1.089055	1.085412	1.081746	1.078219
0.0268	1.117680	1.114199	1.110698	1.107185	1.103666	1.100122	1.096552	1.092952	1.089339	1.085690	1.082021	1.078488
0.0358	1.117989	1.114504	1.110998	1.107482	1.103966	1.100422	1.096848	1.093241	1.089628	1.085971	1.082300	1.078761
0.0461	1.118345	1.114855	1.111342	1.107823	1.104312	1.100766	1.097190	1.093575	1.089960	1.086295	1.082621	1.079075
0.0542	1.118621	1.115126	1.111606	1.108084	1.104577	1.101030	1.097451	1.093829	1.090213	1.086542	1.082866	1.079315

Standard uncertainties are: $u(\rho)$ = $8.2 \cdot 10^{-5}$ g·cm^{-3}, $u(m)$ = $3.5 \cdot 10^{-4}$ mol·kg^{-1}, $u(T)$ = 0.01 K;

Relative standard uncertainty: $u_r(p)$=0.015.

Table S3. Fitting parameters of the plot representing density as a function of the temperature (eq. S1) for each caffeine molality (m), the standard deviation (σ) of the fit with the regression coefficient (R^2).

m / (mol·kg^{-1})	b_o / (g·cm^{-3})	$b_1 \cdot 10^6$ / (g·cm^{-3}·K^{-1})	σ	R^2
0.0000	1.32212	-7.122	0.00241	0.99994
0.0090	1.32258	-7.127	0.00332	0.99994
0.0181	1.32306	-7.132	0.00704	0.99993
0.0268	1.32352	-7.138	0.01539	0.99993
0.0358	1.32400	-7.144	0.01765	0.99993
0.0461	1.32455	-7.150	0.02417	0.99993
0.0542	1.32499	-7.156	0.03074	0.99992

The coefficients obtained from equation S1:

$$\rho = b_o + b_1 T \qquad (S1),$$

where b_o is intercept, and b_1 is slope presented in Table S3.

Table S4. Fitting parameters of the plot representing density as a function of the caffeine molality (m) (eq. S2), for each temperature, the standard deviation (σ) of the fit with the regression coefficient (R^2).

T / (K)	$c_o \cdot 10^{-2}$ / (g·cm^{-3})	c_1 / (g·kg·cm^{-3}·mol^{-1})	σ	R^2
288.15	3.465	1.11675	0.00147	0.99999
293.15	3.431	1.11327	0.00182	0.99997
298.15	3.379	1.10978	0.00167	0.99993
303.15	3.351	1.10628	0.00158	0.99992
308.15	3.382	1.10275	0.00149	0.99995
313.15	3.372	1.09921	0.00180	0.99994
318.15	3.340	1.09565	0.00174	0.99995
323.15	3.269	1.09207	0.00168	0.99993
328.15	3.253	1.08846	0.00173	0.99993
333.15	3.180	1.08483	0.00168	0.99991
338.15	3.149	1.08117	0.00175	0.99992
343.15	3.079	1.07766	0.00159	0.99993

The coefficients obtained from equation S2:

$$\rho = c_o + c_1 m \qquad (S2),$$

where c_o is intercept, and c_1 is slope presented in Table S4.

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Table S5. Values of thermal expansion coefficient, (α_p), for caffeine + ethylene glycol solutions for each caffeine molality (*m*) in the temperature range from T = (288.15 to 343.15) K at $p = 1 \cdot 10^5$ Pa.

m / (mol·kg^{-1})	$\alpha_p \cdot 10^4 / (\text{K}^{-1})$											
T / (K)	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15	343.15
0.0000	6.38	6.40	6.42	6.44	6.46	6.48	6.50	6.52	6.54	6.57	6.59	6.61
0.0090	6.38	6.40	6.42	6.44	6.46	6.48	6.50	6.52	6.55	6.57	6.59	6.61
0.0181	6.38	6.40	6.42	6.44	6.46	6.48	6.51	6.53	6.55	6.57	6.59	6.61
0.0268	6.39	6.41	6.43	6.45	6.47	6.49	6.51	6.53	6.55	6.57	6.60	6.62
0.0358	6.39	6.41	6.43	6.45	6.47	6.49	6.51	6.53	6.56	6.58	6.60	6.62
0.0461	6.39	6.41	6.43	6.45	6.47	6.50	6.52	6.54	6.56	6.58	6.60	6.63
0.0542	6.40	6.42	6.44	6.46	6.48	6.50	6.52	6.54	6.56	6.59	6.61	6.63

Table S6. Apparent molar volume, (V_ϕ), partial molar volume of ethylene glycol ($\overline{V_1}$) and partial molar volume of caffeine, ($\overline{V_2}$), in caffeine + ethylene glycol mixture in the temperature range from $T = (288.15$ to $343.15)$ K at $p = 1 \cdot 10^5$ Pa.

m / (mol·kg^{-1})	V_ϕ / (cm^3·mol^{-1})											
T / (K)	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15	343.15
0.0090	145.60	145.96	146.33	146.89	147.27	147.65	148.40	149.17	149.76	150.73	151.43	152.50
0.0181	145.59	146.05	146.51	147.06	147.35	147.78	148.49	149.35	149.93	150.86	151.61	152.68
0.0268	145.68	146.16	146.78	147.34	147.59	148.04	148.71	149.61	150.20	151.15	151.88	152.93
0.0358	145.71	146.25	146.92	147.51	147.73	148.16	148.85	149.79	150.33	151.34	152.05	153.08
0.0461	145.71	146.31	147.03	147.63	147.79	148.25	148.91	149.88	150.43	151.45	152.15	153.18
0.0542	145.77	146.41	147.19	147.79	147.93	148.39	149.06	150.05	150.60	151.63	152.32	153.33

m / (mol·kg^{-1})	$\overline{V_1}$ / (cm^3·mol^{-1})											
0.0090	55.5793	55.7528	55.9282	56.1055	56.2848	56.4661	56.6497	56.8356	57.0239	57.2148	57.4085	57.5956
0.0181	55.5792	55.7527	55.9279	56.1052	56.2845	56.4659	56.6494	56.8352	57.0236	57.2145	57.4081	57.5953
0.0268	55.5791	55.7525	55.9275	56.1048	56.2842	56.4655	56.6491	56.8349	57.0232	57.2141	57.4077	57.5950
0.0358	55.5790	55.7522	55.9271	56.1043	56.2839	56.4651	56.6488	56.8344	57.0228	57.2136	57.4073	57.5945
0.0461	55.5789	55.7519	55.9265	56.1036	56.2834	56.4646	56.6483	56.8338	57.0222	57.2129	57.4066	57.5939
0.0542	55.5788	55.7516	55.9259	56.1031	56.2830	56.4641	56.6479	56.8332	57.0217	57.2124	57.4061	57.5934

m / (mol·kg^{-1})	$\overline{V_2}$ / (cm^3·mol^{-1})											
0.0090	145.66	146.12	146.63	147.20	147.50	147.91	148.64	149.48	150.05	151.05	151.74	152.79
0.0181	145.68	146.26	146.93	147.51	147.68	148.15	148.82	149.78	150.34	151.31	152.04	153.08
0.0268	145.78	146.43	147.29	147.88	148.00	148.49	149.11	150.13	150.69	151.69	152.41	153.43
0.0358	145.83	146.56	147.51	148.13	148.19	148.68	149.31	150.40	150.91	151.97	152.66	153.65
0.0461	145.85	146.65	147.70	148.34	148.33	148.84	149.44	150.57	151.08	152.17	152.85	153.83
0.0542	145.92	146.78	147.91	148.56	148.51	149.03	149.63	150.80	151.31	152.40	153.07	154.04

Standard uncertainties are: $u(\rho) = 8.2 \cdot 10^{-5}$ g·cm^{-3}, $u(m) = 3.5 \cdot 10^{-4}$ mol·kg^{-1}, $u(T) = 0.01$ K, $u(V_\phi) = 5.6 \cdot 10^{-3}$ cm^3·mol^{-1}; $u(\overline{V_2}) = 6.9 \cdot 10^{-3}$ cm^3·mol^{-1};

Relative standard uncertainty: $u_r(p)=0.015$.

*calculated by eq (S3)

** calculated by eq (S4 and S5)

From the experimental densities the apparent molar volumes, (V_ϕ), were calculated using the equation:

$$V_\phi = \frac{1000(\rho_1 - \rho)}{m\rho\rho_1} + \frac{M_2}{\rho} \qquad \text{(S3)},$$

The partial molar volumes of ethylene glycol ($\bar{V}_1$) and caffeine ($\bar{V}_2$) were calculated using the equations:

$$\bar{V}_1 = \frac{M_1}{\rho_1} - \frac{M_1 m^{3/2}}{2000}\left(\frac{\partial V_\phi}{\partial \sqrt{m}}\right)_{T,p,n_2} \qquad \text{(S4)},$$

$$\bar{V}_2 = \frac{\sqrt{m}}{2}\left(\frac{\partial V_\phi}{\partial \sqrt{m}}\right)_{T,p,n_1} + V_\phi \qquad \text{(S5)},$$

In equations S3 to S5 m (mol·kg^{-1}) represents molality of caffeine, ρ (g·cm^{-3}) the experimental density of the solution, ρ_1 (g·cm^{-3}) the experimental density of the ethylene glycol, M_1 and M_2 (g·mol^{-1}) are molar masses of ethylene glycol and of caffeine, respectively. Calculated values of the apparent molar volumes and partial molar volumes for investigated systems are given in the Table S6.

Table S7. Fitting coefficients a_o, a_1 and a_2 of apparent molar volumes, (V_ϕ), of the caffeine + ethylene glycol mixtures (eq. 4), with the regression coefficient (R^2).

a_o / (cm$^3\cdot$mol^{-1})	a_1 / (cm$^3\cdot$mol$^{-1}\cdot$K^{-1})	a_2 / (cm$^3\cdot$mol$^{-1}\cdot$K^{-2})	R^2
261.05	-0.8373	-0.00151	0.9980

Table S8. Values of the limiting apparent molar expansibilities, (E_ϕ^o) of the caffeine + ethylene glycol solutions (eq. 5) in the temperature range from T = (288.15 to 343.15) K.

E_ϕ^o / (cm$^3\cdot$mol$^{-1}\cdot$K^{-1})

T / (K)	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15	343.15
	0.02715	0.04215	0.05716	0.07214	0.08715	0.1022	0.1172	0.1322	0.1473	0.1622	0.1771	0.1922

Table S9. Viscosity of caffeine + ethylene glycol solutions in the temperature range from T = (288.15 to 343.15) K at p = 1·10^5 Pa.

m / (mol·kg^{-1})	η / (mPa·s)											
T / (K)	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15	343.15
0.0000	26.343	20.857	16.909	13.831	11.444	9.590	8.126	6.933	5.973	5.188	4.535	4.016
0.0090	26.253	20.794	16.863	13.792	11.410	9.550	8.092	6.902	5.956	5.172	4.514	3.994
0.0181	26.186	20.751	16.800	13.766	11.364	9.528	8.070	6.890	5.923	5.144	4.495	3.978
0.0268	26.136	20.688	16.758	13.717	11.341	9.492	8.048	6.866	5.903	5.130	4.479	3.962
0.0358	26.047	20.636	16.714	13.674	11.300	9.464	8.019	6.833	5.886	5.102	4.460	3.941
0.0461	25.981	20.570	16.656	13.626	11.272	9.426	7.982	6.805	5.859	5.087	4.439	3.925
0.0542	25.939	20.526	16.628	13.590	11.231	9.403	7.965	6.785	5.845	5.061	4.416	3.910

Standard uncertainties: $u(T)$ = 0.01 K, $u(m)$ = 3.5·10^{-4} mol·kg^{-1};
Relative standard uncertainties: $u_r(\eta)$ = 0.002, $u_r(p)$ = 0.015.

Table S10. Values of viscosity, shear stress, shear rate and revolution per minute of spindle (RPM), at molality of caffeine $m = 0.0542$ mol·kg^{-1} and at $T = 298.15$ K and $p = 1\cdot10^5$ Pa.

RPM	η / (mPa·s)	Shear stress / (N·m^{-2})	Shear rate / (s^{-1})
105	16.59	2.340	138.6
120	16.62	2.681	158.4
135	16.71	3.030	178.2
140	16.74	3.150	184.8
150	16.68	3.363	198.0
160	16.79	3.607	211.2

Standard uncertainties: $u(T) = 0.01$ K;
Relative standard uncertainties: $u_r(\eta) = 0.002$, $u_r(p) = 0.015$.

Table S11. Thermodynamics parameters of viscous flow values in the temperature range from T = (288.15 to 343.15) K.

Parameters	T / (K)											
	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15	343.15
Caffeine + ethylene glycol												
$\bar{V}_2^o$ / (cm^3·mol^{-1})	145.46	145.64	145.72	146.23	146.76	147.10	147.90	148.53	149.17	150.05	150.79	151.91
$\bar{V}_1^o$ / (cm^3·mol^{-1})	55.58	55.75	55.93	56.11	56.28	56.47	56.65	56.84	57.02	57.21	57.41	57.60
$\Delta\mu_1^{o\neq}$ / (kJ·mol^{-1})	19.66	19.44	19.26	19.09	18.92	18.78	18.65	18.53	18.41	18.31	18.22	18.15
$\Delta\mu_2^{o\neq}$ / (kJ·mol^{-1})	12.98	11.83	10.88	9.44	9.21	8.14	7.47	5.59	5.01	2.30	1.39	1.08
Caffeine + water*												
$\bar{V}_2^o$ / (cm^3·mol^{-1})	141.05	141.99	142.93	143.59	144.45	145.20	-	-	-	-	-	-
$\bar{V}_1^o$ / (cm^3·mol^{-1})	18.02	18.03	18.05	18.07	18.09	18.12	-	-	-	-	-	-
$\Delta\mu_1^{o\neq}$ / (kJ·mol^{-1})	9.60	9.44	9.29	9.16	9.04	8.93	-	-	-	-	-	-
$\Delta\mu_2^{o\neq}$ / (kJ·mol^{-1})	77.7	79.3	82.1	84.2	86.4	88.0	-	-	-	-	-	-

*Results taken from work of *Vraneš* et al. [69]

Table S12. Refractive index, (n_D) of caffeine + ethylene glycol solutions in the temperature range from T = (288.15 to 343.15) K at p = $1 \cdot 10^5$ Pa.

m / (mol·kg^{-1})	n_D											
T / (K)	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15	343.15
0.0000	1.43335	1.43190	1.43046	1.42901	1.42751	1.42601	1.42450	1.42295	1.42138	1.41979	1.41824	1.41669
0.0090	1.43358	1.43215	1.43070	1.42922	1.42772	1.42619	1.42466	1.42311	1.42153	1.41995	1.41842	1.41685
0.0181	1.43378	1.43235	1.4309	1.42943	1.42791	1.42639	1.42486	1.42330	1.42173	1.42017	1.41862	1.41706
0.0268	1.43398	1.43254	1.43109	1.42961	1.42810	1.42657	1.42501	1.42343	1.42188	1.42030	1.41877	1.41723
0.0358	1.43420	1.43273	1.43127	1.42979	1.42830	1.42680	1.42520	1.42362	1.42205	1.42049	1.41896	1.41741
0.0461	1.43445	1.43299	1.43153	1.43007	1.42854	1.42699	1.42541	1.42383	1.42227	1.42071	1.41918	1.41760
0.0542	1.43464	1.43317	1.43171	1.43022	1.42870	1.42716	1.42556	1.42395	1.42242	1.42088	1.41934	1.41777

Standard uncertainties are: $u(n_D)$ = $5.2 \cdot 10^{-4}$, $u(m)$ = $3.5 \cdot 10^{-4}$ mol·kg^{-1}, $u(T)$ = 0.01 K;

Relative standard uncertainty: $u_r(p)$ = 0.015.

Table S13. Fitting parameters of the plot representing refractive index as a function of the temperature (eq. S6) for each caffeine molality (m), the standard deviation (σ) of the fit with the regression coefficient (R^2).

m / (mol·kg⁻¹)	e_o	e_1 / (K⁻¹)	σ	R^2
0.0000	1.52100	-3.037	0.00338	0.99986
0.0090	1.52173	-3.054	0.00327	0.99989
0.0181	1.52188	-3.052	0.00684	0.99990
0.0268	1.52238	-3.063	0.01289	0.99991
0.0358	1.52268	-3.066	0.01547	0.99990
0.0461	1.52327	-3.078	0.02071	0.99991
0.0542	1.52357	-3.081	0.03001	0.99993

The coefficients obtained from equation S6:

$$n_D = e_o + e_1 T \tag{S6},$$

where e_o is intercept, and e_1 is slope from S6 equation, and presented in Table S13.

Table S14. Fitting parameters of the plot representing refractive index as a function of the caffeine molality (m) (eq. S7), for each temperature, the standard deviation (σ) of the fit with the regression coefficient (R^2).

| T / (K)	f_o	f_1 / (kg·mol⁻¹)	σ	R^2
288.15	1.433	1.11675	0.02370	0.99988
293.15	1.432	1.11327	0.02307	0.99945
298.15	1.430	1.10978	0.02272	0.99949
303.15	1.429	1.10628	0.02237	0.99937
308.15	1.428	1.10275	0.02201	0.99987
313.15	1.426	1.09921	0.02145	0.99951
318.15	1.424	1.09565	0.01973	0.99973
323.15	1.423	1.09207	0.01871	0.99927
328.15	1.421	1.08846	0.01934	0.99959
333.15	1.420	1.08483	0.02008	0.99920
338.15	1.420	1.08117	0.00203	0.99976
343.15	1.417	1.07766	0.01999	0.99968

The coefficients obtained from equation (S7):

$$n_D = f_o + f_1 m$$ (S7),

where f_o is intercept, and f_1 is slope presented in Table S14.

Table S15. Refraction molar values, (R_m), of caffeine + ethylene glycol solutions in the temperature range from T = (288.15 to 343.15) K at p = $1 \cdot 10^5$ Pa.

m / (mol·kg^{-1})	R_m / (cm^3·mol^{-1})											
T / (K)	288.15	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15	343.15
0.0000	14.455	14.458	14.461	14.464	14.466	14.468	14.470	14.471	14.472	14.473	14.475	14.475
0.0090	14.475	14.478	14.481	14.484	14.486	14.487	14.488	14.489	14.490	14.491	14.493	14.493
0.0181	14.494	14.497	14.500	14.503	14.504	14.506	14.507	14.508	14.509	14.511	14.513	14.513
0.0268	14.512	14.516	14.519	14.521	14.523	14.524	14.525	14.525	14.527	14.528	14.530	14.531
0.0358	14.532	14.534	14.537	14.540	14.542	14.544	14.543	14.544	14.545	14.547	14.549	14.550
0.0461	14.554	14.557	14.560	14.563	14.564	14.565	14.565	14.566	14.567	14.569	14.571	14.571
0.0542	14.571	14.574	14.577	14.579	14.581	14.582	14.581	14.581	14.583	14.586	14.588	14.588
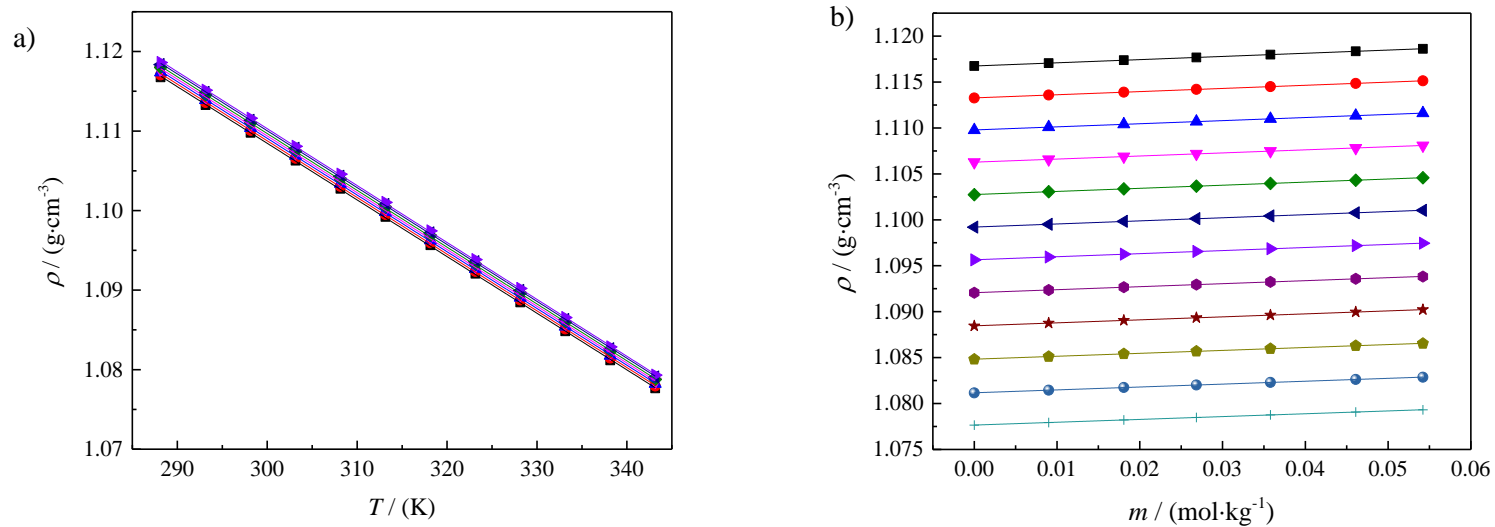
**Figure S1**. Variation of density, (ρ), for caffeine + ethylene glycol solutions as a function of:

a) temperature, at different caffeine molality, (m): = (■) 0.0000, (●) 0.0090, (▲) 0.0181, (▼) 0.0268, (◆) 0.0358, (◄) 0.0461 and (►) 0.0542;

b) molality, at different temperatures, (T): = (■) 288.15; (●) 293.15; (▲) 298.15; (▼) 303.15; (◆) 308.15; (◄) 313.15; (►) 318.15; (⬣) 323.15; (★) 328.15; (⬠) 333.15; (●) 338.15 and (+) 343.15 K. The points represent experimental values while lines are fitts obtained using eqs. S1 and S2.
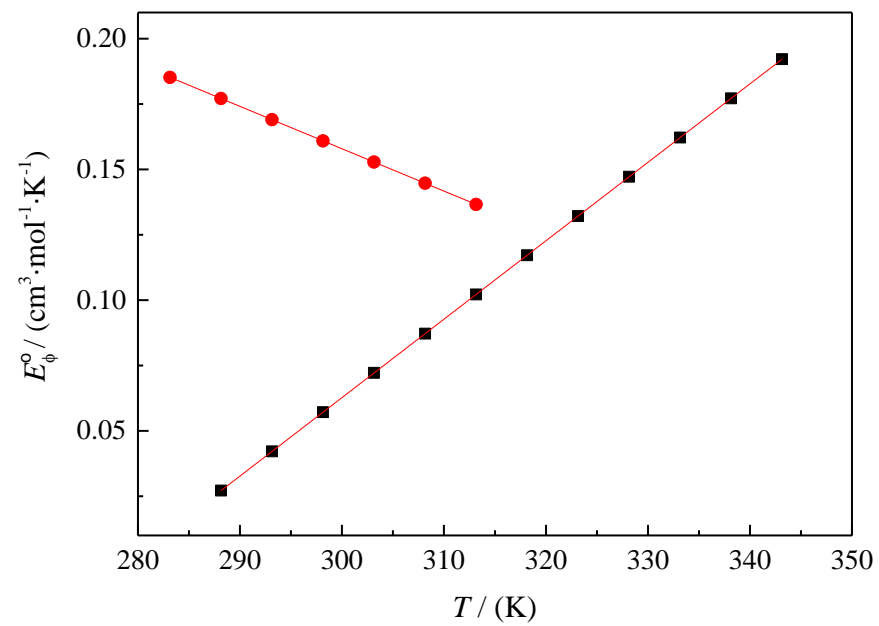
Figure S2. Variation of the limiting apparent molar expansibility, (E_ϕ^o) of caffeine in: (●) aqueous solutions [64] and (■) ethylene glycol solutions with a temperature.
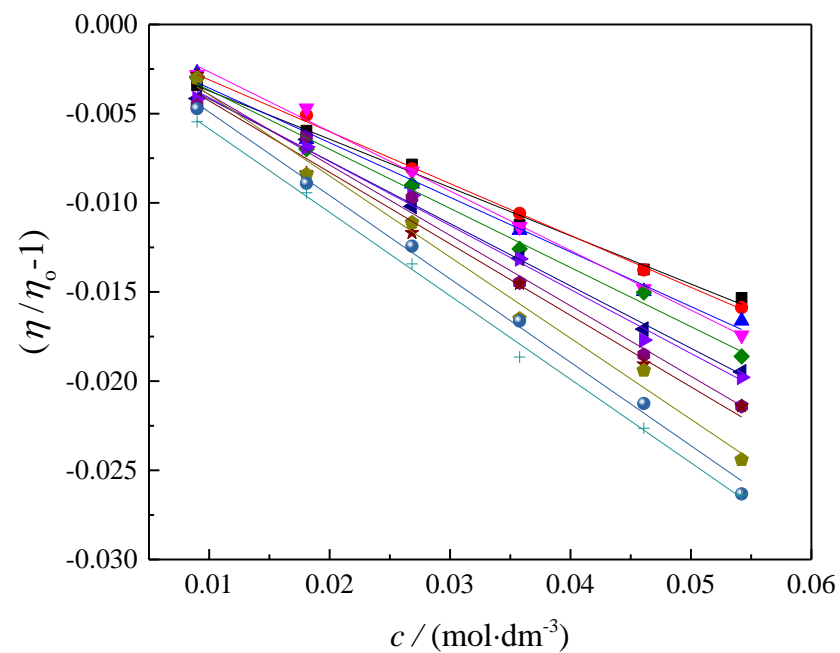
a)
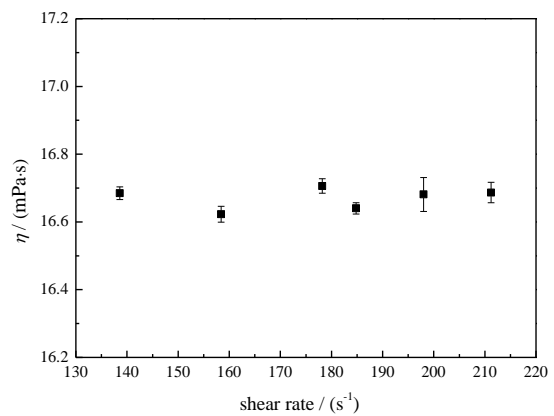
b)
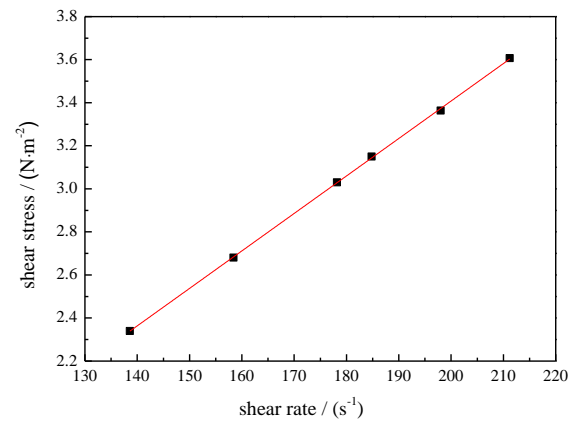
Figure S3. a) Changes of viscosity values with shear rate along with error bars, for caffeine + ethylene glycol solutions, at molality of caffeine $m = 0.0542$ mol·kg^{-1} and at $T = 298.15$ K and b) flow curve, showing shear stress as a function of shear rate.

Figure S4. Plot of reduced viscosity, ($\frac{\eta}{\eta_o}-1$), against concentration, (*c*), of the caffeine + ethylene glycol mixture, at different temperatures: T = (■) 288.15; (●) 293.15; (▲) 298.15; (▼) 303.15; (◆) 308.15; (◀) 313.15; (▶) 318.15; (⬟) 323.15; (★) 328.15; (⬠) 333.15; (●) 338.15 and (+) 343.15 K. The points represent experimental values and lines represent values calculated from eq. (7).
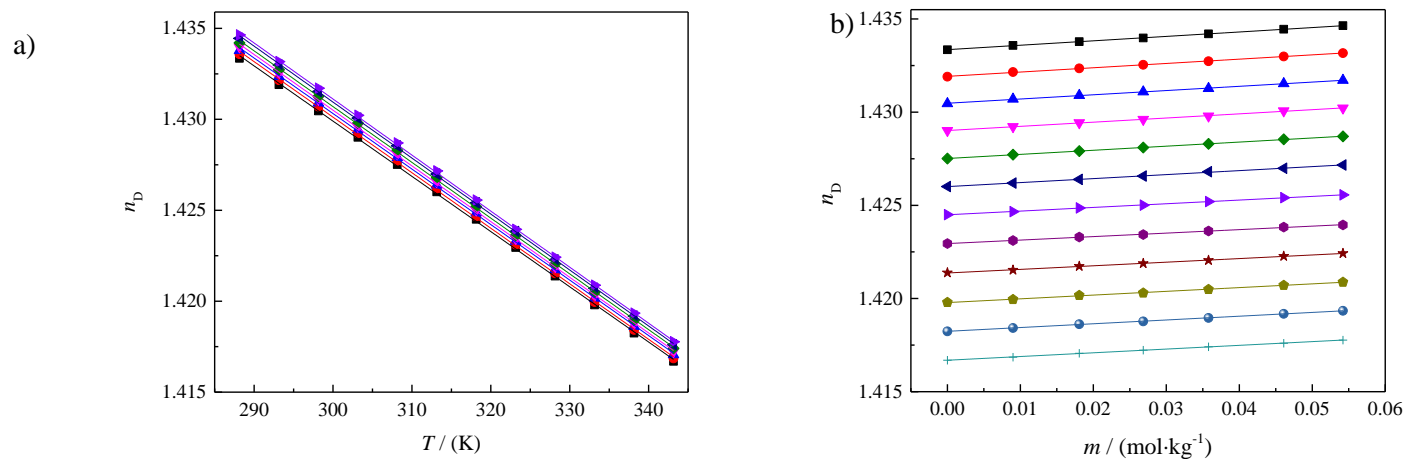
Figure S5. Variation of refractive index, (n_D), for caffeine + ethylene glycol solutions as a function of:

a) temperature, at different caffeine molality, (m): = (■) 0.0000, (●) 0.0090, (▲) 0.0181, (▼) 0.0268, (◆) 0.0358, (◀) 0.0461 and (▶) 0.0542;

b) molality, at different temperatures, (T): = (■) 288.15; (●) 293.15; (▲) 298.15; (▼) 303.15; (◆) 308.15; (◀) 313.15; (▶) 318.15; (⬣) 323.15; (★) 328.15; (⬠) 333.15; (●) 338.15 and (+) 343.15 K. The points represent experimental values, while the lines represents fitts obtaned by eq. S6 and S7.
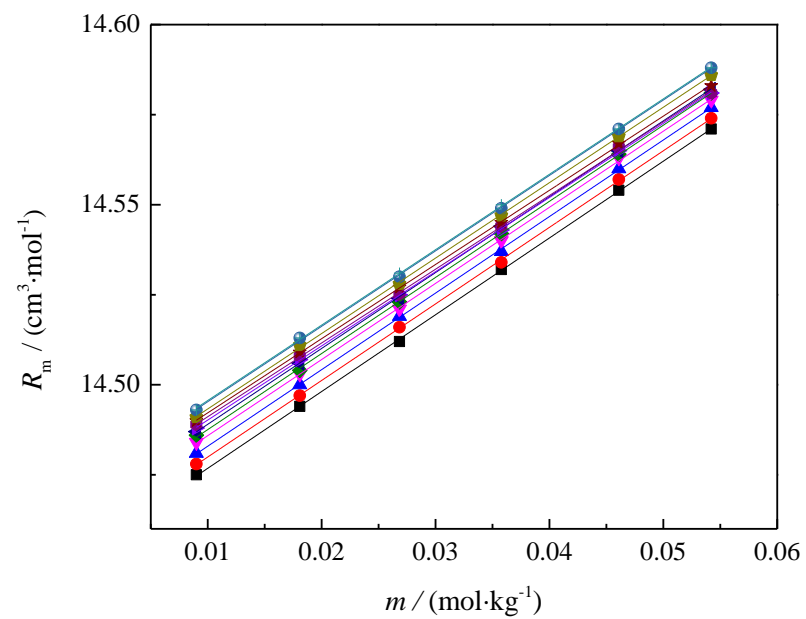
Figure S6. The dependence of the molar refractive index, (R_m), on caffeine molality, (m), in caffeine + ethylene glycol solutions at different temperatures: $T =$ (■) 288.15; (●) 293.15; (▲) 298.15; (▼) 303.15; (◆) 308.15; (◀) 313.15; (▶) 318.15; (●) 323.15; (✳) 328.15; (⬟) 333.15; (●) 338.15 and (+) 343.15 K. The points are experimental values, while the lines represents fitts obtained by eq. S7.