Supporting Information

Volumetric, Viscometric and [1]H NMR Studies on Caffeine, Theophylline and Theobromine in Aqueous Solutions of $MgCl_2$ at Temperatures, T = (288.15 to 318.15) K and at Pressure, p =101.3 kPa

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Table S1. Partial Molar Volumes at Infinite Dilution, $V_{2,\phi}^{\circ}$, and experimental slope, S_v of Xanthine Solutes in aqueous $MgCl_2$ Solutions from T = (288.15 to 318.15) K.

I / mol·kg^{-1}	$V_{2,\phi}^{\circ}\cdot 10^6$/m^3·mol^{-1}($S_V$ /m^3·kg·mol^{-2})			
	T/K = 288.15	298.15	308.15	318.15
		Caffeine		
0.00000	140.30[a] (-35.11)	144.02[a] (-28.30)	147.88[a] (- 40.94)	152.06[a] (- 41.56)
0.29997	155.67 (-17.62)	158.47 (-14.66)	161.48 (-12.53)	164.89 (-19.81)
0.74997	154.56 (-16.87)	157.60 (-19.37)	160.58 (-19.27)	163.69 (-23.53)
1.49985	153.68 (-19.69)	156.58 (-17.36)	159.46 (-11.89)	162.55 (-18.49)
2.24982	151.87 (-22.94)	154.59 (-12.32)	157.61 (-10.27)	160.68 (-15.56)
2.99967	149.59 (-20.51)	152.56 (-17.80)	155.67 (-17.13)	158.51 (-14.48)
		Theophylline		
0.00000	126.43[a] (-84.00)	129.91[a] (-92.25)	131.48[a] (-73.22)	133.72 [a] (-69.66)
0.29997	140.53 (-23.02)	144.70 (-21.80)	147.23 (-46.71)	150.02 (-38.69)
0.74997	140.14 (-37.59)	144.15 (-41.31)	146.90 (-40.50)	149.70(-31.56)
1.49985	138.54 (-44.58)	142.59 (-28.05)	145.36 (-36.75)	148.52 (-52.04)
2.24982	136.41 (-23.11)	140.42 (-32.39)	143.49 (-24.79)	146.71(-27.98)
2.99967	134.60 (-34.08)	138.70 (-40.43)	141.51 (-32.10)	144.54(-38.48)
		Theobromine		
0.00000	126.40[a] (-75.15)	129.31[a] (-94.12)	131.95[a] (-71.92)	133.42 [a] (-82.32)
0.29997	140.60 (-72.25)	145.06 (-77.78)	149.50 (-63.18)	152.39 (-72.59)
0.74997	140.13 (-70.93)	144.04 (-88.37)	147.41 (-62.44)	149.70 (-69.87)
1.49985	138.47 (-63.69)	142.36 (-81.59)	145.91 (-64.65)	148.19 (-69.61)
2.24982	136.49 (-64.66)	140.74 (-79.76)	144.47 (-61.35)	146.79 (-77.53)
2.99967	134.06 (-70.33)	138.35 (-70.37)	142.62 (-67.60)	145.56 (-63.61)

[a] Reference[34]. Standard deviations for fitting of equation 3 lie in the range of ± (0.003 to 0.11)·10^6 m^3·mol^{-1} (0.68 level of confidence).

Table S2. Values of Constants of Equation (5) for Xanthine Solutes in aqueous $MgCl_2$ Solutions.

I /mol·kg^{-1}	$a\cdot 10^6$/ m^3·mol^{-1}	$b\cdot 10^6$/ m^3·mol^{-1}·K^{-1}	$c\cdot 10^6$/ m^3·mol^{-1}·K^{-2}	R^2
		Caffeine		
0.29997	207.11	-0.618	0.0015	0.9999
0.74997	83.10	0.198	0.0002	0.9999
1.49985	112.26	0.007	0.0005	0.9999
2.24982	147.21	-0.236	0.0009	0.9999
2.99967	33.70	0.496	-0.0003	0.9998
		Theophylline		
0.29997	-264.98	2.401	-0.0035	0.9963
0.74997	-227.68	2.148	-0.0030	0.9983

1.49985	-159.61	1.676	-0.0022	0.9974
2.24982	-142.48	1.537	-0.0020	0.9990
2.99967	-205.58	1.948	-0.0027	0.9979
		Theobromine		
0.29997	-334.01	2.778	-0.0039	0.9985
0.74997	-323.62	2.776	-0.0041	0.9997
1.49985	-324.82	2.767	-0.0040	0.9992
2.24982	-405.67	3.272	-0.0048	0.9994
2.99967	-287.12	2.434	-0.0034	0.9989

I is the ionic strength of aqueous $MgCl_2$ Solutions.

Table S3. Partial Molar Expansibilities, $(\partial V_{2,\phi}^{\square}/\partial T)_P$, and Second-Order Derivatives $(\partial^2 V_{2,\phi}^{\square}/\partial T^2)_P$ of Xanthine Solutes in aqueous $MgCl_2$ Solutions from T = (288.15 to 318.15) K.

I mol·kg^{-1}	T/K = 288.15	$(\partial V_{2,\phi}^{\square}/\partial T)\cdot 10^6$/ m^3·mol^{-1}·K^{-1} 298.15	308.15	318.15	SD	$(\partial^2 V_{2,\phi}^{\square}/\partial T^2)_P\cdot 10^6$ m^3·mol^{-1}·K^{-2}
			Caffeine			
0.29997	-0.664	-0.633	-0.603	-0.572	0.042	0.0030
0.74997	0.192	0.196	0.199	0.203	0.042	0.0004
1.49985	-0.007	0.002	0.012	0.021	0.051	0.0010
2.24982	-0.262	-0.245	-0.227	-0.210	0.021	0.0001
2.99967	0.506	0.500	0.493	0.486	0.092	-0.0007
			Theophylline			
0.29997	2.505	2.436	2.367	2.298	0.425	-0.0069
0.74997	2.239	2.179	2.118	2.057	0.293	-0.0061
1.49985	1.743	1.698	1.654	1.609	0.373	-0.0045
2.24982	1.596	1.557	1.517	1.478	0.244	-0.0039
2.99967	2.028	1.975	1.921	1.868	0.338	-0.0053
			Theobromine			
0.29997	2.896	2.817	2.739	2.660	0.342	-0.0079
0.74997	2.898	2.817	2.736	2.655	0.121	-0.0081
1.49985	2.888	2.808	2.727	2.647	0.208	-0.0081
2.24982	3.417	3.320	3.223	3.127	0.199	-0.0097
2.99967	2.535	2.468	2.400	2.333	0.293	-0.0067

SD is the standard deviation.

Table S4. Viscosity B-coefficients and dB/dT Values of Xanthine Solutes in aqueous $MgCl_2$ Solutions from T = (288.15 to 318.15) K.

I /mol·kg^{-1}		$B\cdot 10^3$ (m^3· mol^{-1})			dB /dT (m^3·K^{-1}·mol^{-1})
	T/K = 288.15	298.15	308.15	318.15	
		Caffeine			
0.00000	0.407[a]	0.541[a]	0.612[a]	0.717[a]	0.0100
0.29997	0.401	0.525	0.587	0.685	0.0091
0.74997	0.397	0.513	0.578	0.675	0.0090
1.49985	0.381	0.496	0.558	0.657	0.0089
2.24982	0.362	0.479	0.537	0.631	0.0087
2.99967	0.331	0.442	0.505	0.603	0.0088
		Theophylline			
0.00000	0.374[a]	0.493[a]	0.563[a]	0.634[a]	0.0085
0.29997	0.364	0.476	0.540	0.606	0.0079
0.74997	0.353	0.466	0.530	0.595	0.0079
1.49985	0.337	0.449	0.510	0.575	0.0078
2.24982	0.323	0.432	0.492	0.554	0.0075
2.99967	0.300	0.413	0.472	0.535	0.0076
		Theobromine			

0.00000	0.376[a]	0.497[a]	0.567[a]	0.635[a]	0.0085
0.29997	0.362	0.478	0.543	0.605	0.0079
0.74997	0.346	0.461	0.527	0.590	0.0080
1.49985	0.326	0.443	0.507	0.570	0.0080
2.24982	0.310	0.428	0.495	0.559	0.0081
2.99967	0.300	0.418	0.483	0.546	0.0080

[a]Reference[34]. Standard deviations for fitting in eq 10 lie in the range of (0.005 to 0.500)$\cdot 10^{-3}\cdot$ $m^3\cdot mol^{-1}$ and the standard deviation in dB/dT lie in the range of (0.0040-0.0500) $m^3\cdot K^{-1}\cdot mol^{-1}$ (0.68 level of confidence).

Table S5. *D*-coefficient Values of Xanthine Solutes in aqueous NaCl and $MgCl_2$ Solutions from *T* = (288.15 to 318.15) K.

Solutes	$D\cdot 10^3(m^3\cdot mol^{-2}\cdot kg)$			
	T/K = 288.15	T/K = 298.15	T/K = 308.15	T/K = 318.15
		NaCl		
Caffeine	-0.189	-0.310	-0.378	-0.459
Theophylline	-0.173	-0.219	-0.258	-0.295
Theobromine	-0.179	-0.211	-0.276	-0.293
		$MgCl_2$		
Caffeine	-0.057	-0.065	-0.067	-0.068
Theophylline	-0.052	-0.053	-0.057	-0.060
Theobromine	-0.053	-0.051	-0.051	-0.050

Table S6. $B/V_{2,\phi}$ Values for Xanthine Solutes in aqueous $MgCl_2$ Solutions.

I /mol·kg^{-1}	$B/V_{2,\phi}$			
	T/K = 288.15	298.15	308.15	318.15
		Caffeine		
0.00000	2.90	3.76	4.14	4.72
0.29997	2.58	3.31	3.64	4.15
0.74997	2.57	3.26	3.60	4.12
1.49985	2.48	3.17	3.50	4.04
2.24982	2.38	3.10	3.41	3.93
2.99967	2.21	2.90	3.24	3.80
		Theophylline		
0.00000	2.96	3.79	4.28	4.74
0.29997	2.59	3.29	3.67	4.04
0.74997	2.52	3.23	3.61	3.97
1.49985	2.43	3.15	3.51	3.87
2.24982	2.37	3.08	3.43	3.78
2.99967	2.23	2.98	3.34	3.70
		Theobromine		
0.00000	2.97	3.84	4.30	4.76
0.29997	2.57	3.30	3.63	3.97
0.74997	2.47	3.20	3.58	3.94
1.49985	2.35	3.11	3.47	3.85
2.24982	2.27	3.04	3.43	3.81
2.99967	2.24	3.02	3.39	3.75

Table S7. NMR Chemical Shifts, δ of Xanthine Solutes in Water and in Aqueous $MgCl_2$ Solutions at T = 298.15 K under p = 101.3 kPa.

Solute protons		^{1}H NMR				
δ / ppm	water	I = 0.299997 mol·kg^{-1}	I = 0.74997 mol·kg^{-1}	I = 1.49985 mol·kg^{-1}	I = 2.24982 mol·kg^{-1}	I = 2.99967 mol·kg^{-1}
			Caffeine			
δ H(1)	3.229	3.410	3.397	3.379	3.378	3.360
δ H(3)	3.062	3.233	3.219	3.200	3.200	3.180
δ H(7)	3.727	3.848	3.835	3.819	3.818	3.800
δ H(8)	7.738	7.808	7.799	7.790	7.790	7.779
			Theophylline			
δ H(1)	3.213	3.250	3.240	3.222	3.195	3.176
δ H(3)	3.404	3.442	3.432	3.415	3.388	3.370
δ H(8)	7.868	7.911	7.907	7.897	7.878	7.865
			Theobromine			
δ H(3)	3.242	3.273	3.262	3.254	3.234	3.221
δ H(7)	3.798	3.829	3.818	3.812	3.788	3.779
δ H(8)	7.726	7.762	7.757	7.757	7.742	7.741

The standard deviation in the chemical shift values, δ is < 0.004 ppm.

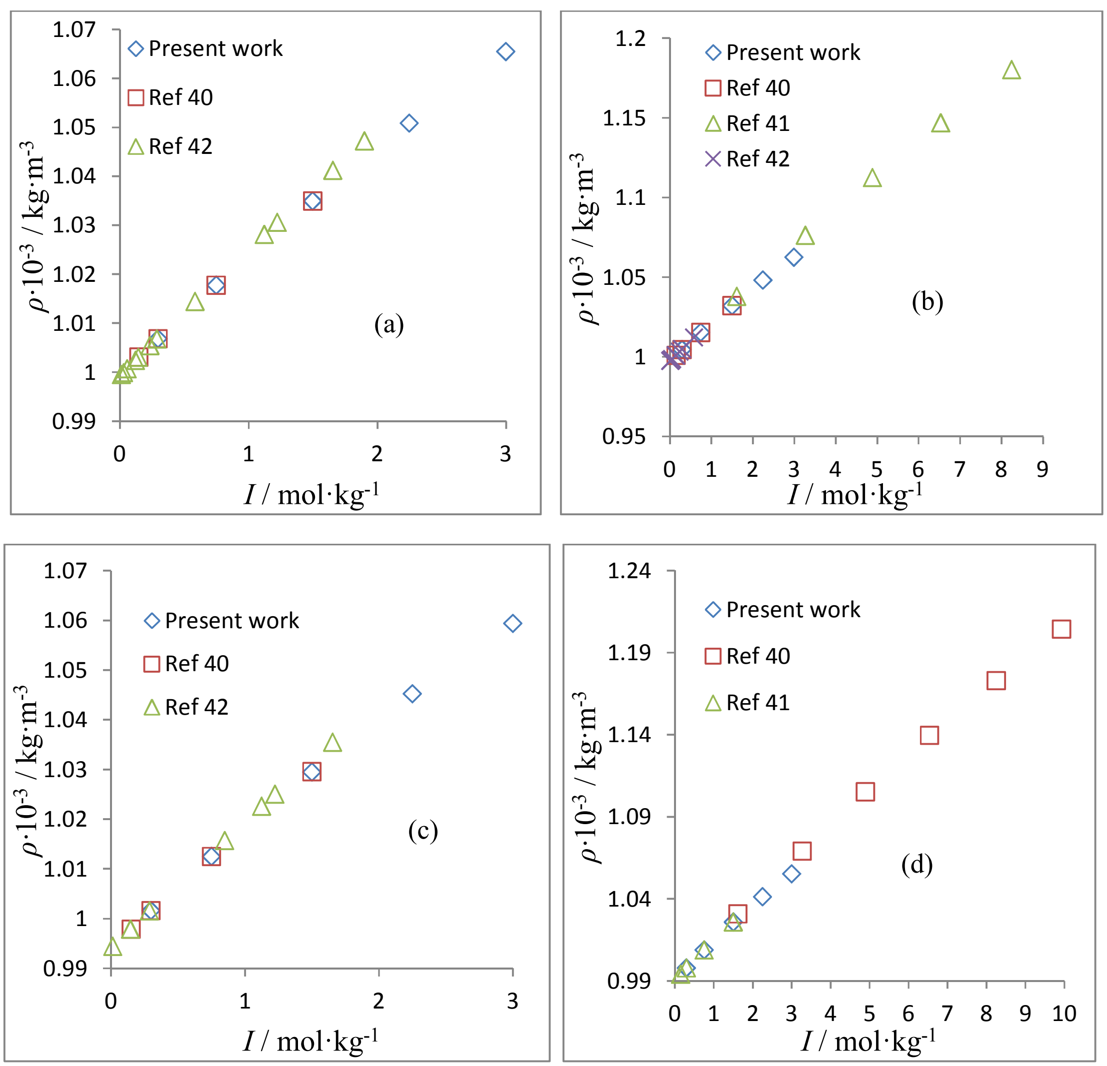


Figure S1.Comparison of density, ρ, data for aqueous $MgCl_2$ solutions at (a) T = 288.15 K, (b) 298.15 K, (c) 308.15 K, (d) 318.15 K.

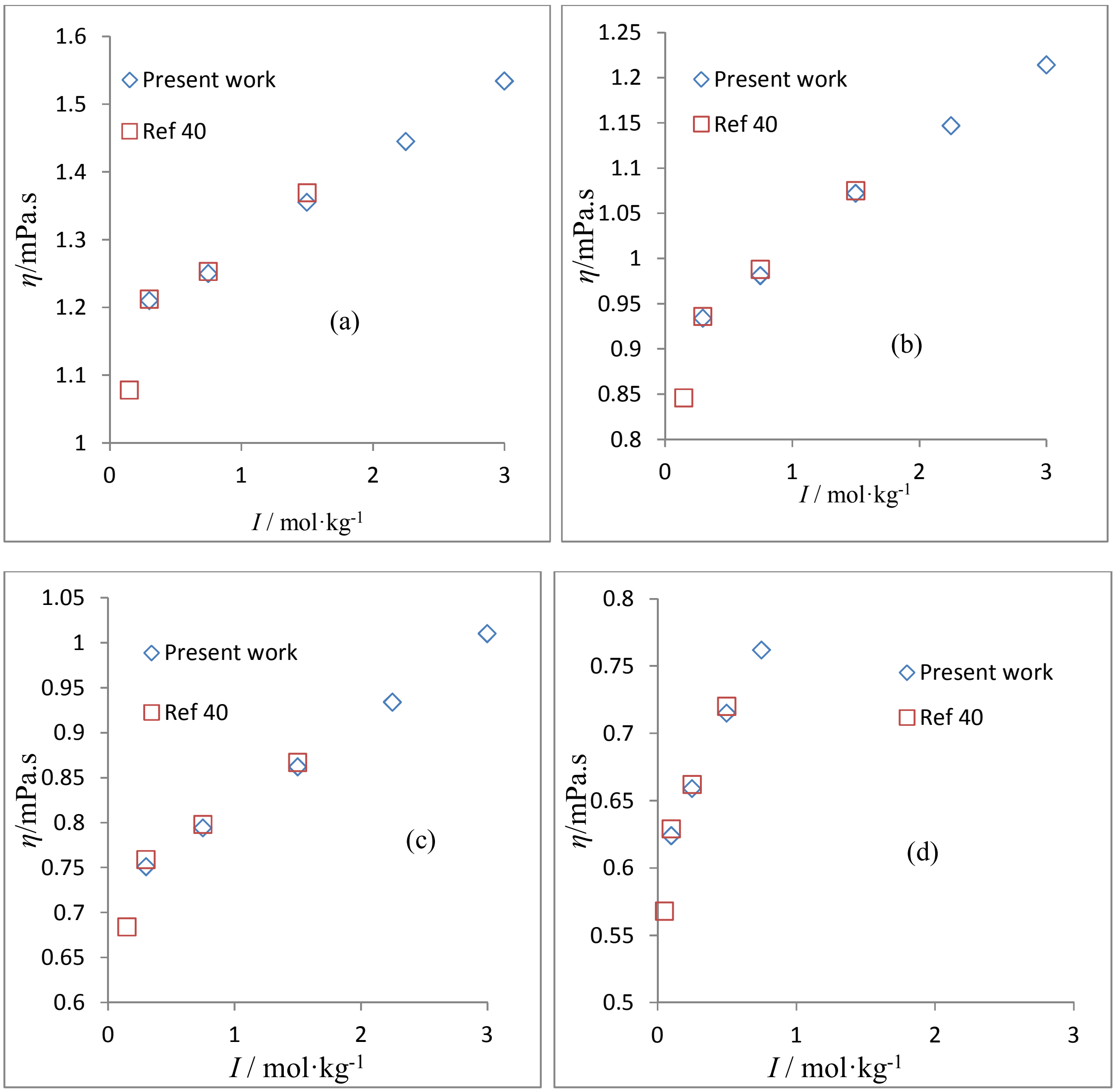


Figure S2.Comparison of viscosity, η, data for aqueous $MgCl_2$ solutions at (a) T = 288.15 K, (b) 298.15 K, (c) 308.15 K, (d) 318.15 K.

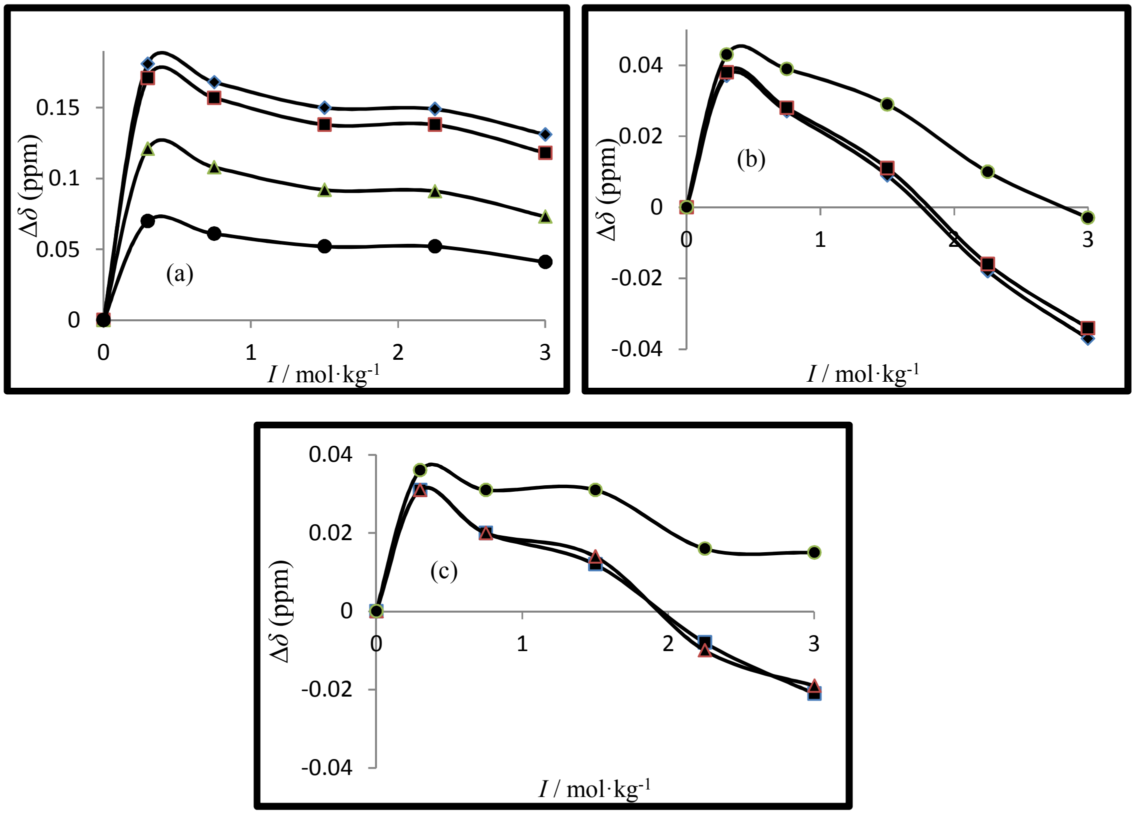
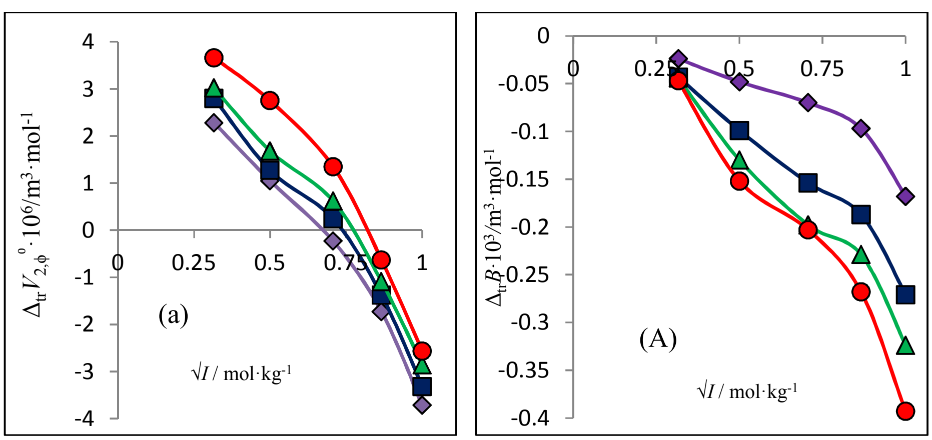


Figure S3. Change in chemical shift of different protons (◆, 1H; ■, 3H; ▲, 7H; ●, 8H), $\Delta\delta$, versus ionic strength of $MgCl_2$, I, of (a) caffeine (b) theophylline, (c) theobromine.



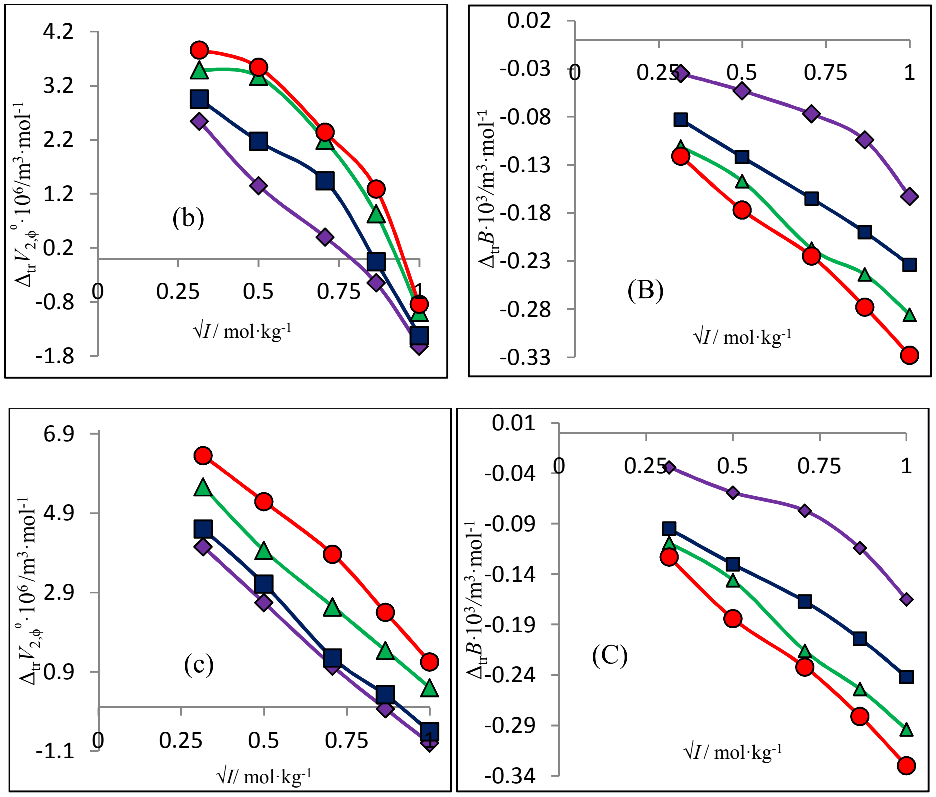


Figure S4. Partial molar volume of transfer, at infinite dilution, $\Delta_{tr}V_{2,\phi}^{0}$ and viscosity *B*-coefficients of transfer, $\Delta_{tr}B$ versus square root of ionic strength, $\sqrt{I}$ of aqueous NaCl solution[34] of (a/A) caffeine (b/B) theophylline (c/C) theobromine at ♦, 288.15 K; ■, 298.15 K; ▲, 308.15 K; ●, 318.15 K.