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Ion-solvent Interactions of some Chromium (III) Complexes in Nitromethane and Dimethylsulfoxide Studied Viscometrically at 298.15, 308.15 and 318.15 K

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ABSTRACT

Apparent molal volumes (V_ϕ) and viscosity B-coefficients of NH_4X, $(C_3H_7)_4NX$, $(C_4H_9)_4NX$ (X=$[Cr(NCS)_4(NH_3)_2]^-$) Bu_4NClO_4 and Bu_4NBPh_4 were determined from measured solution density (ρ) and viscosity (η) in Nitromethane (NM) and Dimethyl Sulphoxide (DMSO) at 298.15 K, 308.15 K and 318.15 K at various electrolyte concentrations. The apparent molal volumes were evaluated by Masson equation and were interpreted in terms of ion-solvent and ion-ion interactions. The viscosity data was analyzed by Jones-Dole equation to evaluate viscosity A and B coefficients. The derived parameters were split into the ionic contributions using which viscosity $B_\pm$ coefficients of various ions were evaluated and interpreted in terms of ion-solvent and ion-ion interactions respectively. The A coefficients were in reasonably good agreement with the limiting theoretical values (A_η) calculated using Falkenhagen-Vernon equation. Viscosity $B_\pm$ coefficients confirm the existence of some interactions of the chromium complex and ClO_4^- ion with both NM and DMSO.

Keywords: Ion-solvent interactions, Chromium complexes, Viscosity

INTRODUCTION

Studies on densities (ρ) and viscosities (η) of electrolytes are of great importance in characterizing the thermo physical properties of solutions. Studies on the limiting apparent molar volume and viscosity *B*-coefficients of electrolyte provide us valuable information regarding ion-ion, ion-solvent and solvent-solvent interactions [1-3]. The transport properties of electrolytes in different solvent media are of considerable importance in obtaining information regarding the solvation and association behaviour of ions in solutions. It has been found by a number of workers [4-6] that addition of an electrolyte alters the structure of a liquid in a number of ways. As the viscosity of a liquid depends on the intermolecular forces, the structural aspects of the liquid can be inferred from the viscosity of solutions at various concentrations and temperature.

A survey of literature reveals that many physicochemical studies still need to be carried out for transition metal complexes in organic solvents. The present paper focuses on the ion-association and solvation behaviour of ionic chromium (III) complexes with common anion, $[Cr(NCS)_4(NH_3)_2]^-$ having different cations like tetrapropylammonium and tetrabutylammonium in Nitromethane (NM) and Dimethyl Sulfoxide (DMSO) at T=(298.15 K to 318.15 K) at atmospheric pressure. In this paper we have attempted to report limiting apparent molal isentropic compressibility ($K°_{s,\phi}$), limiting apparent molal volume ($V°_\phi$), experimental slopes (S_v) and viscosity B-coefficients for $(C_4H_9)_4NBPh_4$, $(C_4H_9)_4NClO_4$, $NH_4[Cr(NCS)_4(NH_3)_2]$, $(C_3H_7)_4NX$ and $(C_4H_9)_4NX$ (X= $[Cr(NCS)_4(NH3)_2]^-$) in (NM) and DMSO at 298.15 K, 308.15 K and 318.15 K. Ammonium diamine tetrathiocyanato chromate (III) ($NH_4[Cr(NCS)_4(NH_3)_2]$) (Reinecke's salt) has been prepared in our laboratory. This complex was chosen because of its appreciable solubility in various organic solvents. The dissociation and solvation behaviour of these complexes has not been thoroughly investigated in solution. Therefore, in order to generate some new data and to understand the behaviour of these chromium complexes in non-aqueous solvents, some investigations have been made in NM and DMSO solvents.

EXPERIMENTAL SECTION

Materials

NM and DMSO (Sd. Fine Chemicals Ltd., India) were purified by standard methods [7,8]. The purity of solvents was checked by measuring the density (ρ) and viscosity (η) at 298.15 K. These values are in good agreement with the literature data. Ammonium diamine tetrathiocyanato chromate (III) ($NH_4[Cr(NCS)_4(NH_3)_2]$) (Reinecke's salt) was prepared by the method described in the literature [9] and was purified by recrystallization two times from aqueous solution. This salt was used to prepare all other chromium (III) complexes of $[Cr(NCS)_4(NH_3)_2]^-$ as anion with some tetraalkylammonium cations [10]. The equimolar (0.1 mol) quantities of tetraalkylammonium halides and $NH_4[Cr(NCS)_4(NH_3)_2]$ were separately dissolved in water and mixed to obtain various complexes. These complexes were recrystallized from water at 70°C. The experimental yields obtained for various complexes were between 85-90%.

Bu_4NBPh_4 and Bu_4NClO_4 which were used as reference electrolyte were prepared by the methods described in literature [11]. All salts prepared were characterized by the elemental, chemical and spectroscopic methods.

Solutions

DMSO and NM were chosen as solvent media for the present study. A stock solution for each salt was prepared by mass and the working solutions were prepared by dilution. The mass measurements were done on electronic balance with a precision of ± 0.01 mg.

Density measurements

Densities (ρ) were measured with Anton Parr Digital Densimeter (DSA 5000 densimeter and sound velocity analyzer). Both speed of sound and density are extremely sensitive to temperature, so it was kept constant within ± 1.0×10^{-3} K using the Peltier Method. The reproducibility of density and sound velocity measurements was better than ± 3.0×10^{-6} g/cm^{-3} and ± 0.1 ms^{-1}, respectively. The apparatus was calibrated with double distilled deionized, degassed water and dry air at atmospheric pressure.

Viscosity measurements

Solvent viscosities were measured by means of a suspended-level type Ubbelohde viscometer, calibrated at 298.15 K with triply distilled water and purified hexane, heptane and cyclohexane using density and viscosity values from the literature. A thoroughly cleaned and perfectly dried viscometer filled with experimental liquid was placed vertically in the glass-walled thermostat maintained to ± 0.01 K. After attainment of thermal equilibrium, efflux times of flow were recorded with a stopwatch correct to ± 0.1 s. At least three repetitions of each data reproducible to ± 0.1 s were taken to average the flow times. The uncertainty of viscosity values is ± 0.003 mPa.s^{-1}. The details of the methods and measurement techniques have been described elsewhere. Viscosity (η) of the solution is given by the following equation:

$$\eta = A\rho t - B\rho / t \qquad (1)$$

$$\eta / \rho = (At - B/t) \qquad (2)$$

Where, η/ρ is the kinematic viscosity A and B are the viscometer constants, t is the time of flow in seconds. This equation has been employed in the present investigation for the determination of viscosity of pure liquids and salt solutions.

RESULTS AND DISCUSSION

Viscosities of various chromium (III) complexes have been measured in the concentration range 0.001 to 0.01 m at T=298.15, 308.15 and 318.15 K in NM and DMSO and the values are reported in Tables 1-5. The viscosity data has been analysed by using Jones-Dole equation [12-14] in case where no ion-association were found:

$$\frac{\eta}{\eta_o} = 1 + AC^{½} + BC \qquad (3)$$

And in case where ion-association was found:

$$\frac{\eta}{\eta_o} = 1 + A(C\alpha)^{½} + B(C\alpha) + B'(1-\alpha)C \quad (4)$$

The viscosity *B*-coefficients of the electrolytes have been evaluated by the analysis of viscosity data using Equation 3. For the evaluation of coefficient B, plots of $\left(\frac{\eta}{\eta^o} - 1\right) \Big/ C^{½}$ *vs.* $C^{½}$ were, constructed and were found to be linear over the whole concentration range of electrolyte. The values of $\left(\frac{\eta}{\eta^o} - 1\right) \Big/ C^{½}$ are reported in Tables 1-5. In equation (3) and (4) C is the molar concentration of the electrolyte A and B are constants, characteristics of the solvent and the electrolyte and α is the degree of dissociation respectively. The A coefficient is a measure of ion-ion interaction and can be calculated theoretically from the limiting ionic conductances and the physical properties of the solvent using Falkenhagen-Vernon Equation*:*

$$A_\eta = \frac{0.2577\Lambda_o}{\eta_o(\varepsilon_o T)^{½}\lambda_1^o\lambda_2^o}\left[1 - 0.6863\left(\frac{\lambda_1^o - \lambda_2^o}{\Lambda_o}\right)\right] \qquad (5)$$

Where, λ_1^o and λ_2^o are the limiting ionic conductance for cations and anions and η and ε are the viscosity and dielectric constant of the solvent respectively and T is absolute temperature. The experimental *A*-coefficient values are reported along with the theoretical A_η coefficients calculated using Falkenhagen-Vernon equation. The agreement between the experimental and theoretical *A*-coefficients for all the electrolytes in NM and DMSO has been found to be good.

Ionic B_+ and B_- coefficients

The ionic B_+ and B_- coefficients have been evaluated by splitting viscosity *B*-coefficients into the contribution of individual ions. Gill and Sharma [15] based on the Bu_4NBPh_4 assumption, have suggested a method by which *B*-coefficients of the electrolyte in mixed solvents have been splitted into the contributions of the individual ions based on the following equations;

$$\frac{B_{Ph_4B^-}}{B_{Bu_4N^+}} = \frac{r^3_{Ph_4B^-}}{r^3_{Bu_4N^+}} = \left(\frac{5.35}{5.00}\right)^3 \qquad (6)$$

$$B_{Ph_4B^-} + B_{Bu_4N^+} = B(Bu_4NBPh_4) \qquad (7)$$

Using the equations 6 and 7 the viscosity *B*-Coefficients for Bu_4NBPh_4 electrolyte including some perchlorates were determined. Using ionic B_- coefficients of ClO_4^- in present solvents, the *B*-coefficients for cations of other salts have been calculated and are reported in Table 6.

The values of *B*-coefficients of all salts in NM and DMSO are negative thereby suggesting the presence of weak ion-solvent interactions and these interactions are weakened with rise in temperature in both solvents. The values of *B*-coefficients decrease with a rise in temperature *dB/dT* (positive) suggesting the structure making tendency of salts in organic solvents. The values of *A* coefficients are positive for all the solutions under investigation at all experimental temperatures. These results indicate the presence of strong ion-ion interactions and the interactions further increase with the rise of temperature suggesting decrease in ion- solvation.

Apparent molal volumes (V_ϕ)

The apparent molal volumes (V_ϕ) were determined from the solution densities using the following equation (13) and the values for Bu_4NClO_4, Bu_4NBPh_4, NH_4X, $(C_3H_7)_4NX$ and $(C_4H_9)_4NX$ (X= $[Cr(NCS)_4(NH_3)_2]^-$) in both solvents at different temperatures are reported in Tables 1-5 respectively.

$$V_\phi = \frac{M}{\rho} - \frac{10^3[\rho - \rho_o]}{m\rho\rho_o} \quad (8)$$

Where, *M* is the molar mass of the solute, *m* is molality of the solution, $\rho_\circ$ and ρ are the densities of the solvent and the solution respectively. The limiting apparent molal volume $V°_\phi$ was calculated using a least-squares treatment to the plots of V_ϕ versus $c^{1/2}$ using the following Masson Equation:

$$V_\phi = V°_\phi + S_v c^{1/2} \qquad (9)$$

Where, $V°_\phi$ is the apparent molal volume at infinite dilution and S_v is the experimental slope. Values of $V°_\phi$ and S_v are reported in Table 7. $V°_\phi$ values can be used to interpret ion-solvent interactions. $V°_\phi$ values are positive in both solvents and decreases with rise in temperature which indicates the presence of weak ion-solvent interactions and these interactions are weakened with rise in temperature. S_v values are positive in DMSO whereas negative in NM at all temperatures and decreases with rise in temperature which may be attributed to more violent thermal agitation at higher temperatures, resulting in diminishing the force of ion-ion interactions.

Table 1: Molality (*m*), Density (ρ), Viscosity (η), Apparent molal volume (V_ϕ) and $\alpha=(\eta/\eta_\circ-1)/c^{1/2}$ of Bu_4NClO_4 in NM and DMSO at 298.15, 308.15 and 318.15 K

m (mol/kg^{-1})	ρ (10^{-3} kg/m^{-3})	η (mPa s)	V_ϕ (10^6 m^3/mol^{-3}	α	m (mol/kg^{-1})	ρ (10^{-3} kg/m^{-3})	η (mPa/s)	V_ϕ (10^6 m^3/mol^{-3}	α
NM					**DMSO**				
298.15 K					**298.15 K**				
0.01	1.129685	0.667025	344.25	0.879533	0.01	1.095746	2.051702	279.12	0.448593
0.02	1.129135	0.660404	345.16	0.549838	0.02	1.095709	2.070352	297.13	0.381495
0.03	1.128635	0.645102	344.26	0.312720	0.03	1.095633	2.086418	304.23	0.356722
0.04	1.128145	0.639908	343.68	0.230797	0.04	1.095243	2.109341	314.43	0.364869
0.05	1.128100	0.637660	336.28	0.190920	0.05	1.094829	2.124716	321.00	0.359945
0.06	1.128013	0.633479	331.91	0.147945	0.06	1.094577	2.134173	323.13	0.347451
0.07	1.127952	0.631377	328.49	0.124707	0.07	1.094453	2.145114	323.10	0.341867
0.08	1.127872	0.630536	326.13	0.112069	0.08	1.094190	2.158257	324.59	0.342494
0.09	1.127817	0.629390	324.07	0.099769	0.09	1.094085	2.169219	324.25	0.340748
0.1	1.126562	0.622797	332.20	0.062497	0.1	1.093954	2.183842	324.20	0.345842
308.15 K					**308.15 K**				
0.01	1.116080	0.614789	346.07	3.763448	0.01	1.085788	1.706364	274.16	0.449925
0.02	1.115574	0.608339	346.67	2.563593	0.02	1.085783	1.713905	294.74	0.34954
0.03	1.115116	0.590444	345.67	1.871183	0.03	1.085740	1.718867	302.69	0.302273
0.04	1.114673	0.582702	344.94	1.537460	0.04	1.085337	1.724512	314.41	0.278446
0.05	1.114654	0.578528	337.61	1.334969	0.05	1.084909	1.728855	321.93	0.260538
0.06	1.114602	0.575454	333.18	1.191658	0.06	1.084680	1.731000	324.11	0.243022
0.07	1.114578	0.572551	329.69	1.079647	0.07	1.084540	1.740812	324.58	0.246858
0.08	1.114551	0.564328	327.10	0.947325	0.08	1.084289	1.751690	326.16	0.253599
0.09	1.114529	0.563026	325.04	0.883813	0.09	1.084181	1.765290	326.00	0.265819
0.10	1.113205	0.560100	334.25	0.819019	0.10	1.084061	1.776355	325.99	0.272811
318.15 K					**318.15 K**				
0.01	1.102375	0.553212	345.53	8.374367	0.01	1.07585	1.43777	-370.30	0.579543
0.02	1.101921	0.545622	346.66	5.749101	0.02	1.075847	1.451749	-26.12	0.480067
0.03	1.101498	0.538992	346.27	4.571135	0.03	1.075841	1.46063	88.70	0.428423

0.04	1.101110	0.536873	345.41	3.925118	0.04	1.075449	1.468976	154.56	0.400764
0.05	1.101112	0.531238	338.40	3.429142	0.05	1.074999	1.467094	195.15	0.352543
0.06	1.101038	0.518425	334.79	2.961133	0.06	1.074776	1.47439	218.92	0.343045
0.07	1.100410	0.516832	338.91	2.722759	0.07	1.07464	1.483063	234.81	0.340934
0.08	1.099779	0.512316	342.08	2.495915	0.08	1.074385	1.492825	248.07	0.343505
0.09	1.099511	0.507801	341.15	2.3047	0.09	1.074286	1.502792	256.85	0.347509
0.10	1.099123	0.502734	341.45	2.134899	0.10	1.07418	1.507693	263.94	0.340716

Table 2: Molality (*m*), Density (*ρ*), Viscosity (*η*), Apparent molal volume (V_ϕ) and $\alpha=(\eta/\eta_\circ-1)/c^{1/2}$ of Bu_4NBPh_4 in NM and DMSO at 298.15, 308.15 and 318.15 K

m (mol/kg^{-1})	ρ (10^{-3} kg/m^{-3})	η (mPa/s)	V_ϕ (10^6 m^3/mol^{-3}	α	m (mol/kg^{-1})	ρ (10^{-3} kg/m^{-3})	η (mPa/s)	V_ϕ (10^6 m^3/mol^{-3}	α
NM					**DMSO**				
298.15 K					**298.15 K**				
0.01	1.128698	1.662597	616.40	16.2421	0.01	1.130456	2.000878	-2338.18	0.197730
0.02	1.129135	0.660404	345.16	10.322451	0.02	1.129321	2.005852	-875.71	0.156772
0.03	1.128635	0.645102	344.26	7.985760	0.03	1.128146	2.008155	-386.75	0.134459
0.04	*1.128145*	0.639908	343.68	5.405200	0.04	1.127613	2.013916	-154.88	0.130315
0.05	1.128100	0.637660	336.28	4.274296	0.05	1.126234	2.020857	-1.955	0.131555
0.06	1.128013	0.633479	331.91	3.278962	0.06	1.125479	2.024908	91.75	0.128087
0.07	1.127952	0.631377	328.49	2.308423	0.07	1.124679	2.027454	159.33	0.123259
0.08	1.127872	0.630536	326.13	1.506830	0.08	1.123715	2.031753	211.80	0.122664
0.09	1.127817	0.629390	324.07	0.655108	0.09	1.122459	2.034357	255.43	0.119893
0.1	1.126562	0.622797	332.20	0.871562	0.1	1.121672	2.039722	286.53	0.121955
308.15 K					**308.15 K**				
0.01	1.115864	1.404599	560.43	20.760730	0.01	1.110678	1.830475	-1598.93	1.167363
0.02	1.114893	1.340146	571.36	13.705217	0.02	1.109312	1.832445	-490.55	0.834070
0.03	1.114308	1.233863	564.81	9.871738	0.03	1.108367	1.836122	-132.20	0.693677
0.04	1.113252	1.122218	571.38	7.350505	0.04	1.107819	1.840575	38.95	0.613871
0.05	1.11288	1.056768	564.19	5.944852	0.05	1.106231	1.843035	159.21	0.555872
0.06	1.111653	1.004302	571.36	4.968060	0.06	1.105527	1.847464	227.22	0.518151
0.07	1.112898	0.877653	546.98	3.565433	0.07	1.104278	1.850970	282.53	0.487724
0.08	1.112799	0.770529	542.74	2.519122	0.08	1.103891	1.855531	314.94	0.465719
0.09	1.114136	0.728013	525.93	2.068409	0.09	1.102671	1.857540	348.18	0.443241
318.15 K					**318.15 K**				
0.01	1.102124	1.221310	565.67	29.993517	0.01	1.091564	2.156421	-1511.62	5.647086
0.02	1.101184	1.073700	576.82	17.838841	0.02	1.090672	2.159607	-460.64	4.010632
0.03	1.100609	1.028425	570.65	13.722759	0.03	1.089931	2.162342	-114.30	3.286934
0.04	1.099583	0.939594	577.25	10.450952	0.04	1.088921	2.164413	64.86	2.855205
0.05	1.099208	0.896344	570.34	8.722513	0.05	1.087817	2.166782	174.22	2.562557
0.06	1.098017	0.833791	577.45	7.138977	0.06	1.086138	2.168239	255.72	2.345300
0.07	1.09926	0.748461	552.75	5.560712	0.07	1.085618	2.170769	299.61	2.178614
0.08	1.099174	0.698308	548.45	4.627242	0.08	1.084614	2.173309	337.97	2.045208
0.09	1.100492	0.561186	531.58	2.879912	0.09	1.083671	2.175963	367.33	1.935344

Table 3: Molality (*m*), Density (*ρ*), Viscosity (*η*), Apparent molal volume (V_ϕ) and $\alpha=(\eta/\eta_\circ-1)/c^{1/2}$ of $NH_4[Cr(NCS)_4(NH_3)_2]$ in NM and DMSO at 298.15, 308.15 and 318.15 K

m (mol/kg^{-1})	ρ (10^{-3} kg/m^{-3})	η (mPa/s)	V_ϕ (10^6 m^3/mol^{-3}	α	m (mol/kg^{-1})	ρ (10^{-3} kg/m^{-3})	η (mPa/s)	V_ϕ (10^6 m^3/mol^{-3}	α
NM					**DMSO**				
298.15 K					**298.15 K**				
0.01	1.12891	0.687398	400.37	1.19601	0.01	1.096841	2.13485	182.71	0.8535
0.02	1.12924	0.695547	336.16	0.93450	0.02	1.09811	2.178445	191.68	0.753275
0.03	1.12854	0.704199	315.49	0.83997	0.03	1.099274	2.1982	197.44	0.670234
0.04	1.12956	0.710793	310.68	0.77830	0.04	1.100281	2.213927	203.50	0.618428
0.05	1.12976	0.718975	304.93	0.752518	0.05	1.101422	2.226203	204.81	0.579545
0.06	1.12999	0.730379	300.67	0.75869	0.06	1.102759	2.246382	202.86	0.568761
0.07	1.13037	0.734933	295.91	0.72883	0.07	1.103675	2.253244	206.46	0.538949
0.08	1.13091	0.740817	290.69	0.71367	0.08	1.104913	2.269521	205.73	0.531796
0.09	1.13113	0.752306	289.48	0.73184	0.09	1.105558	2.283348	210.65	0.523603
0.1	1.13143	0.758317	287.85	0.72349	0.1	1.106688	2.299441	210.47	0.521166
308.15 K					**308.15 K**				
0.01	1.11511	0.532121	419.36	1.98543	0.01	1.086859	1.775923	178.05	0.859052
0.02	1.11546	0.534727	346.37	1.44336	0.02	1.088155	1.805648	188.64	0.730698
0.03	1.11575	0.538627	323.60	1.22680	0.03	1.089359	1.811411	194.62	0.615842
0.04	1.11606	0.54400	311.77	1.120102	0.04	1.090389	1.8269337	201.20	0.578692
0.05	1.11645	0.549077	303.34	1.050524	0.05	1.091546	1.837669	202.90	0.545508
0.06	1.11671	0.551341	299.46	0.978768	0.06	1.092905	1.847501	201.08	0.521223
0.07	1.11701	0.557477	296.20	0.955925	0.07	1.093793	1.851518	205.47	0.491269
0.08	1.11726	0.562626	294.25	0.933234	0.08	1.095036	1.858658	204.91	0.474081
0.09	1.11754	0.566811	292.45	0.909752	0.09	1.09567	1.873585	210.23	0.476002
0.1	1.11781	0.574211	291.07	0.913279	0.1	1.096796	1.88307	210.33	0.468913

318.15 K					**318.15 K**				
0.01	1.10135	0.453091	425.26	5.137403	0.01	1.076871	1.482338	-463.82	0.895939
0.02	1.10192	0.458354	341.73	3.752199	0.02	1.078208	1.498137	-133.66	0.712462
0.03	1.10207	0.4636	325.43	3.161451	0.03	1.079442	1.50366	-20.80	0.60402
0.04	1.10237	0.467564	314.13	2.801646	0.04	1.080486	1.508926	39.64	0.541517
0.05	1.10272	0.473705	306.48	2.594319	0.05	1.081691	1.516964	73.02	0.509564
0.06	1.10319	0.479553	299.68	2.444979	0.06	1.083041	1.523946	93.09	0.485071
0.07	1.10353	0.485000	296.35	2.329847	0.07	1.083913	1.53408	113.31	0.476033
0.08	1.10383	0.491904	294.26	2.257992	0.08	1.08516	1.540937	124.33	0.462193
0.09	1.10409	0.496467	292.99	2.177784	0.09	1.085782	1.54959	138.92	0.455736
0.1	1.10448	0.500918	290.85	2.111154	0.1	1.086914	1.558717	146.10	0.452829

Table 4: Molality (*m*), Density (ρ), Viscosity (η), Apparent molal volume (V_ϕ) and $\alpha=(\eta/\eta_\circ -1)/c^{1/2}$ of $Pr_4N[Cr(NCS)_4(NH_3)_2]$ in NM and DMSO at 298.15, 308.15 and 318.15 K

m (mol/kg^{-1})	ρ (10^{-3} kg/m^{-3})	η (mPa/s)	V_ϕ (10^6 m^3/mol^{-3})	α	m (mol/kg^{-1})	ρ (10^{-3} kg/m^{-3})	η (mPa/s)	V_ϕ (10^6 m^3/mol^{-3}	α
NM					**DMSO**				
298.15 K					**298.15 K**				
0.01	1.130255	0.703716	443.47	1.445072	0.01	1.104433	2.017833	-293.77	0.28237
0.02	1.130082	0.709841	451.84	1.088691	0.02	1.104918	2.024648	61.52	0.223015
0.03	1.130652	0.719529	434.99	0.974918	0.03	1.105342	2.030976	181.52	0.199789
0.04	1.13075	0.730439	435.88	0.928369	0.04	1.105999	2.037736	236.58	0.189371
0.05	1.1318	0.740394	421.15	0.898573	0.05	1.106456	2.043122	272.87	0.181029
0.06	1.132108	0.748306	421.15	0.869939	0.06	1.106911	2.04977	297.04	0.178385
0.07	1.132672	0.753299	418.16	0.834273	0.07	1.107372	2.055927	314.18	0.176404
0.08	1.133183	0.761327	416.42	0.823924	0.08	1.107892	2.06245	326.36	0.176152
0.09	1.133633	0.772366	415.56	0.833304	0.09	1.108461	2.070332	335.33	0.178769
0.1	1.134526	0.780627	411.23	0.83044	0.1	1.108933	2.075004	343.29	0.176719
308.15 K					**308.15 K**				
0.01	1.116658	0.583498	445.31	3.089313	0.01	1.087211	2.084231	302.92	2.672978
0.02	1.116558	0.607468	452.68	2.549216	0.02	1.087323	2.091121	378.78	1.91865
0.03	1.117157	0.618929	436.21	2.223188	0.03	1.087613	2.096253	398.94	1.583793
0.04	1.117326	0.63169	436.64	2.06241	0.04	1.087821	2.102588	410.73	1.390107
0.05	1.118403	0.646488	421.98	1.986046	0.05	1.088421	2.111168	410.98	1.26557
0.06	1.118778	0.654557	421.72	1.883499	0.06	1.088861	2.118453	413.39	1.172555
0.07	1.119346	0.671469	419.21	1.88068	0.07	1.089123	2.124281	417.28	1.098394
0.08	1.119913	0.685814	417.28	1.867717	0.08	1.089541	2.130787	418.46	1.040776
0.09	1.120424	0.701304	416.26	1.871392	0.09	1.089871	2.137742	420.21	0.994729
0.1	1.12132	0.723274	412.18	1.923793	0.1	1.090034	2.144989	423.05	0.957079
318.15 K					**318.15 K**				
0.01	1.102976	0.457018	443.51	5.260644	0.01	1.069121	2.326306	368.97	6.917496
0.02	1.102939	0.487081	452.07	4.407505	0.02	1.069621	2.332155	398.43	4.919754
0.03	1.103574	0.513732	436.26	4.095237	0.03	1.070112	2.338687	408.38	4.042919
0.04	1.103799	0.535021	436.81	3.890388	0.04	1.070321	2.344025	419.54	3.51995
0.05	1.10492	0.54851	422.05	3.672855	0.05	1.070843	2.349935	420.60	3.166404
0.06	1.105353	0.571208	421.74	3.651584	0.06	1.071291	2.35464	422.35	2.903598
0.07	1.105945	0.587129	419.56	3.574184	0.07	1.071743	2.360987	423.49	2.704727
0.08	1.106553	0.605181	417.70	3.548534	0.08	1.072121	2.366941	425.14	2.544586
0.09	1.107088	0.613351	416.89	3.432701	0.09	1.07243	2.37298	427.08	2.413045
0.1	1.108031	0.631286	412.71	3.438191	0.1	1.072661	2.378266	429.32	2.30087

Table 5: Molality (*m*), Density (ρ), Viscosity (η), Apparent molal volume (V_ϕ) and $\alpha=(\eta/\eta_\circ -1)/c^{1/2}$ of $Bu_4N[Cr(NCS)_4(NH_3)_2]$ in NM and DMSO at 298.15, 308.15 and 318.15 K

m (mol/kg^{-1})	ρ (10^{-3} kg/m^{-3})	η (mPa/s)	V_ϕ (10^6 m^3/mol^{-3})	α	m (mol/kg^{-1})	ρ (10^{-3} kg/m^{-3})	η (mPa/s)	V_ϕ (10^6 m^3/mol^{-3})	α
NM					**DMSO**				
298.15 K					**298.15 K**				
0.01	1.12972	0.649693	535.28	0.612187	0.01	1.106462	2.097219	-409.91	0.667226
0.02	1.12928	0.638448	533.29	0.310310	0.02	1.107445	2.10614	7.92	0.502178
0.03	1.12886	0.635177	532.24	0.224274	0.03	1.108722	2.112731	138.84	0.428231
0.04	1.12844	0.629825	531.81	0.152966	0.04	1.109367	2.119639	217.18	0.387487
0.05	1.12804	0.620628	531.31	0.073354	0.05	1.110009	2.127935	264.13	0.364448
0.06	1.12762	0.615256	531.30	0.033119	0.06	1.111345	2.138078	285.66	0.352537

0.07	1.12721	0.611171	531.24	0.006828	0.07	1.112561	2.144843	302.34	0.338578
0.08	1.12683	0.605809	530.94	-0.022288	0.08	1.113621	2.152202	316.38	0.329141
0.09	1.12642	0.600262	531.02	-0.050143	0.09	1.114643	2.163422	327.58	0.328252
0.1	1.12605	0.597802	530.78	-0.059595	0.1	1.115129	2.170825	341.01	0.322652
308.15 K					**308.15 K**				
0.01	1.11609	0.567217	541.41	2.739768	0.01	1.088198	1.724397	270.67	0.55548
0.02	1.11568	0.562956	538.60	1.872819	0.02	1.088763	1.732602	368.91	0.426798
0.03	1.11529	0.559838	537.25	1.490666	0.03	1.089482	1.744461	397.09	0.388607
0.04	1.11489	0.554111	536.87	1.229532	0.04	1.090367	1.752939	407.47	0.361313
0.05	1.11450	0.550498	536.56	1.065125	0.05	1.091178	1.761936	414.83	0.34668
0.06	1.11410	0.548186	536.41	0.952171	0.06	1.092267	1.766093	415.61	0.326277
0.07	1.11372	0.543916	536.36	0.846925	0.07	1.093218	1.775207	417.76	0.322157
0.08	1.11337	0.540805	535.95	0.768652	0.08	1.094421	1.783353	416.54	0.318074
0.09	1.11302	0.536709	535.66	0.69539	0.09	1.095523	1.786793	416.47	0.306453
0.1	1.11272	0.533453	535.04	0.637601	0.1	1.096546	1.791625	417.02	0.299545
318.15 K					**318.15 K**				
0.01	1.10234	0.505291	547.01	6.82403	0.01	1.074822	1.37112	-77.42	0.105804
0.02	1.10195	0.500018	544.12	4.705502	0.02	1.075373	1.373614	198.08	0.087337
0.03	1.10161	0.495417	541.88	3.756649	0.03	1.075983	1.37657	288.03	0.083419
0.04	1.10127	0.49147	540.85	3.189968	0.04	1.076279	1.378229	339.79	0.078129
0.05	1.10098	0.488367	539.45	2.808640	0.05	1.076832	1.380218	366.24	0.076182
0.06	1.10069	0.483107	538.56	2.494742	0.06	1.077456	1.382042	382.74	0.074817
0.07	1.10037	0.479982	538.34	2.271769	0.07	1.077971	1.384241	395.84	0.075152
0.08	1.10012	0.477715	537.45	2.099330	0.08	1.078218	1.385328	408.61	0.073017
0.09	1.09989	0.472961	536.59	1.928138	0.09	1.078917	1.387252	413.99	0.073374
0.1	1.09963	0.468518	536.19	1.783893	0.1	1.079457	1.389614	419.67	0.074891

Table 6: Ionic viscosity (B±) coefficients of the Jones-Dole equation for various ions in NM and DMSO at 298.15 K, 308.15 K and 318.15 K

Ion	$B_{\pm}$ ($dm^3.mol^{-1}$)					
	298.15 K		308.15 K		318.15 K	
	NM	DMSO	NM	DMSO	NM	DMSO
NH_4^+	-31.71	-0.25	-35.14	-2.07	-45.51	-8.84
$(C_3H_7)_4N^+$	-32.11	-0.86	-35.53	-7.42	-40.27	-26.08
$(C_4H_9)_4N^+$	-32.69	-0.13	-39.61	-1.35	-54.13	-7.09
BPh_4^-	-40.06	-0.16	-48.52	-1.66	-66.31	-8.69
$[Cr(NCS)_4(NH3)_2]^-$	29.88	-1.26	30.81	0.35	33.19	6.97
ClO_4^-	29.39	-0.245	27.32	0.62	28.09	6.06

Table 7: Limiting apparent molal volume and experimental slopes of Bu_4NClO_4, Bu_4NPh_4B, $NH_4[Cr(NCS)_4(NH_3)_2]$, $Pr_4N[Cr(NCS)_4(NH_3)_2]$ and $Bu_4N[Cr(NCS)_4(NH_3)_2]$ in NM and DMSO at 298.15, 308.15 and 318.15 K

Complex/Salt	$V°_{\phi}$			S_v		
Solvent	NM					
	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K
Bu_4NClO_4	348.86	350.38	348.31	-240.38	-242.91	-149.56
Bu_4NPh_4B	593.1	579.32	584.86	-788.49	-432.56	-428.5
$NH_4[Cr(NCS)_4(NH_3)_2]$	363.63	375.43	377.61	-916.35	-1048.1	-1070.8
$Pr_4N[Cr(NCS)_4(NH_3)_2]$	449.99	451.29	450.21	-418.28	-424.42	-405.05
$Bu_4N[Cr(NCS)_4(NH_3)_2]$	534.07	539.88	546.07	-39.13	-52.17	-109.46
Complex/salt	**$V°_{\phi}$**			**S_v**		
Solvent	**DMSO**					
	298.15 K	308.15 K	318.15 K	298.15 K	308.15 K	318.15 K
Bu_4NClO_4	289.34	285.63	-165.22	439.66	506.27	5303.2
Bu_4NPh_4B	-1460.9	-935.91	-885.62	21557	16146	15740
$NH_4[Cr(NCS)_4(NH_3)_2]$	187.26	182.96	-267.79	261.24	304.96	5069.2
$Pr_4N[Cr(NCS)_4(NH_3)_2]$	-80.22	349.78	386.3	5231.1	903.52	509.71
$Bu_4N[Cr(NCS)_4(NH_3)_2]$	-159.57	334.94	87.79	6157.9	1078.1	4104.7

CONCLUSION

From the perusal of the values of apparent molal volume and viscosity *B*-coefficients it is concluded that all the cations and Ph_4B^- ion show solvophobic interactions with both the solvents at all temperatures. The ion-solvent interactions decrease with increase in the temperature. ClO_4^- and $[Cr(NCS)_4(NH_3)_2]^-$ ions, however, show weak solvation with both NM and DMSO.

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