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Molecular Interionic Interaction Studies of Benzimidazolium Dichromate and 2-Methyl Imidazolium Dichromate in Water and DMSO + Water at Different Temperatures

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Abstract: *Density and viscosity of benzimidazolium dichromate and 2-methyl imidazolium dichromate have been determined in water and aqueous mixtures of dimethyl sulphoxide (DMSO) (10, 20, 30, 40 and 50% by volume) at 298.15, 303.15, 308.15 and 313.15K. From the experimental data, the related parameters such as: apparent molar volume (V_φ); limiting apparent molar volume (V_φ^0) and their associated constant (S_v); transfer volume (ΔV_φ^0) from water to aqua organic solution of DMSO; and B-coefficients of Jones-Dole equation were evaluated. Such parameters vary as a power series of temperature. The molecular interactions such as ion-ion, ion-solvent and solvent-solvent are identified and discussed in the light of structure making and structural-breaking behaviour of Cr-complex in the solvent mixture.*

Keywords: Benzimidazolium dichromate, 2-methyl imidazolium dichromate, ion-solvent interaction, DMSO

1. INTRODUCTION

Knowledge of ion-solvent interactions in aqueous and non-aqueous media is of considerable fundamental and technological importance. Accurate knowledge of the physico-chemical properties of solutions has great relevance in theoretical and applied areas of research. Such properties are functionally dependent on temperature and composition of solutions. The potentialities of non-aqueous solvents in thermodynamic, kinetic and analytical techniques in organic and inorganic synthesis as well as industrial applications have well been recognised.[1,2]

Dimethyl sulphoxide (DMSO) is aprotic and is strongly associated due to highly polar S=O group. The study of DMSO is important because of its utilisation in a broad range of applications in medicine.[3] It easily penetrates biological membranes, facilitates chemical transport into biological tissue and is well known for its protective effects on biological systems.[4] It is also used as an anti-inflammatory agent. Additionally, it has been utilised as an *in-situ* free radical scavenger for various cancer treatments.[5] The unique properties of DMSO also give rise to its wide use as a solvent.

Many drugs contain an imidazole ring such as antifungal drugs and nitro-imidazole.[6–9] The substituted imidazole derivatives are valuable in treatment of many systemic fungal infections.[10]

The experimental measurement of density and viscosity and the derived parameters such as apparent molar volume and transfer volume of such systems will provide some significant information regarding the state of interactions in solution. Studies of solutions have been carried out by many researchers.[11–13] Ionic association and electrostatic interactions are the primary factors that must be considered in solution. In view of the above-mentioned importance, an attempt has been made to elucidate the molecular interactions of Cr complexes of substituted imidazole in water and aqueous solutions of DMSO at 298.15, 303.15, 308.15 and 313.15K. The aim of the present study is to generate new information on ion-ion, ion-solvent and solvent-solvent interactions that are interesting from chemical and biological point of view.

2. EXPERIMENTAL

DMSO is spectroscopic reagent (SR) grades of minimum assay of 99.9% obtained from SD Fine Chemicals, India, which is used as such without further purification. Deionised water was distilled and used. Benzimidazolium dichromate and 2-menthyl imidazolium dichromate were prepared as reported in literature.[14] The density was determined using specific gravity bottle by relative measurement method with accuracy of ± 0.1 mg. An Ostwald's viscometer (10 ml) was used for the viscosity measurement and efflux time was determined using a digital stopwatch. To maintain the temperature constant, a thermostat with accuracy of ± 0.01K was used. An ice bath with a stirrer was equipped to maintain the temperature below room temperature. The densities and viscosities of benzimidazolium dichromate and 2-methyl imidazolium dichromate were evaluated at different compositions between 0.01 and 0.05 m in water and in DMSO + H_2O mixtures in the range 10–50% (v/V) of DMSO.

All the binary aqueous mixtures of DMSO were prepared by v/V ratio in terms of mole fraction and the solutions of complexes were made by weight, and the conversion of molality (m) into molar concentration (c) was done using the standard expression:

$$C = md\,(1+0.001mM_2)^{-1} \tag{1}$$

where d is the solution density and M_2 is the molecular weight of the complex.

The apparent molar volume (V_φ) is calculated as

$$V_\varphi = 1000(d_0\text{-}d)(cd_0)^{-1} + M_2 d_0^{-1} \quad (2)$$

where d_0 is the density of the pure solvent.

The limiting apparent molar volume (V_Φ) is calculated by Masson's equation,

$$V_\varphi = V_\varphi^0 + S_v c^{½} \quad (3)$$

Transfer volume ($\Delta V\varphi^0$) of each complex from water to aqueous DMSO solution were calculated using the equation as:

$$\Delta V_\varphi^{\ 0} = V_\varphi^{\ 0}{}_{\text{(in aqueous DMSO)}} - V_\varphi^{\ 0}{}_{\text{(in water)}} \quad (4)$$

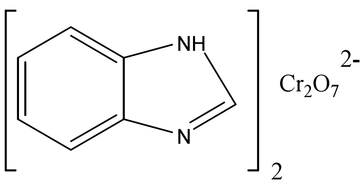
The entire viscosity data have been analysed using the Jones–Dole equation:[15]

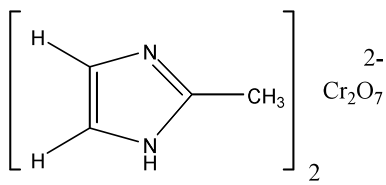
$$\eta_r = 1 + Ac^{1/2} + Bc \quad (5)$$

where A is known as Falkenhagen coefficient, which characterises the ionic interaction and B is Jones-Dole or viscosity B- Coefficient, which depends on the size of the solute and nature of solute-solvent interactions.

3. RESULTS AND DISCUSSION

The structures of benzimidazolium dichromate and 2-methyl imidazolium dichromate are as follows:





(Benzimidazolium dichromate) (2-methylimidazolium dichromate)

The experimental values of density (d) and viscosity (η) for the solutions of Cr complexes, i.e., benzimidazolium dichromate and 2-methyl imidazolium dichromate in water and DMSO + H_2O (10, 20, 30, 40, 50% by weight of DMSO) at 298.15, 303.15, 308.15 and 313.15K are tabulated in Table 1 and Table 2 respectively. The values of apparent molar volume (V_ϕ), limiting apparent molar volume (V_ϕ^0) and associated constant (Sv) for both the system in water and DMSO + H_2O at different temperatures are listed in Table 3 and Table 4, while the transfer volume (ΔV_ϕ^0), A and B are tabulated in Table 5.

It is evident from Table 1 that the values of density and viscosity increased with the increase in molar concentration of Cr Complexes. The increase in density was due to the shrinkage in the volume, which was caused by the presence of solute molecules. An increase in density may be attributed to the structure maker of the solvent due to the added solute. Viscosity is a measure of cohesiveness or rigidity present between either ions or ion-solvent or solvent-solvent molecules present in the solution. The values of viscosity (η) increased with the increase in complex concentration in all the system, but decreased with the rise in temperature. This increasing trend indicated the existence of molecular interaction occurring in these systems, while the decreasing nature was due to greater thermal agitation and reduction of attractive forces between the ions.

The apparent molar volume (V_ϕ) decreased with molar concentrations of both the systems observed in Table 3 and 4. The values of V_ϕ of benzimidazolium dichromate in water are positive and increase with the rise in temperature. The higher value of V_ϕ is obtained for benzimidazolium dichromate solution as compared to 2-methyl imidazolium dichromate indicating that strong molecular association is found in benzimidazolium dichromate. Such values of V_ϕ suggest that ionic and hydrophobic interactions are occurring in such system, indicating presence of ion-solvent interactions. This may also support the possibility of stacking interaction between Cr metal and water.

But in case of DMSO + H_2O mixtures, the values of V_φ are all negative over the entire range of concentrations of benzimidazolium dichromate and 2-methyl imidazolium dichromate. These negative values indicate the electrostrictive salvation of ions.[16,17] The values of V_φ increased with increase in concentration of complex and decrease with increase in mole fraction of DMSO indicating the solvent-solvent interactions in DMSO having high polar S=O group. However, a reverse trend was obtained for water.

Table 1: The values of density (d) and viscosity (η) for benzimidazolium dichromate in water and DMSO + water at different temperatures.

Mole fraction (X_{org})	Concentration (c) mole dm^{-3}	Density (d) kg m^{-3}				Viscosity (η) centipoise			
		298.15K	303.15K	308.15K	313.15K	298.15K	303.15K	308.15K	313.15K
Benzimidazolium dichromate in water									
	0.0098	992.51	988.43	985.11	978.14	0.7388	0.7044	0.6698	0.6358
	0.0198	998.54	992.58	986.30	979.45	0.7462	0.7094	0.6766	0.6409
	0.0298	1007.3	1001.1	991.44	981.91	0.7496	0.7144	0.6792	0.6430
	0.0396	1007.8	1001.7	992.94	982.54	0.7525	0.7191	0.6856	0.6515
	0.0494	1008.5	1003.3	995.17	984.77	0.7571	0.7239	0.6899	0.6559
Benzimidazolium dichromate in DMSO + water									
0.027	0.0099	1017.0	1009.7	1001.8	994.10	0.8828	0.8186	0.7541	0.6889
	0.0197	1017.3	1009.8	1002.7	994.39	0.8940	0.8267	0.7615	0.6962
	0.0295	1019.5	1011.5	1003.6	995.84	0.9068	0.8397	0.7734	0.7033
	0.0392	1019.7	1011.9	1004.3	996.18	0.9111	0.8438	0.7768	0.7094
	0.0488	1019.8	1012.5	1005.1	997.98	0.9186	0.8507	0.7837	0.7166
0.059	0.0100	1003.0	1022.7	1014.8	1006.0	1.2621	1.1863	1.0165	0.8450
	0.0200	1030.6	1022.8	1015.6	1007.2	1.3599	1.1960	1.0294	0.8600
	0.0298	1032.3	1024.2	1016.2	1007.6	1.3682	1.2090	1.0350	0.8701
	0.0397	1032.5	1024.9	1017.3	1009.1	1.3612	1.2265	1.0493	0.8500
	0.0495	1032.8	1025.5	1019.3	1011.2	1.4302	1.2502	1.0782	0.8904
0.097	0.0110	1041.9	1034.1	1025.4	1017.4	1.3234	1.2378	1.1084	0.9634
	0.0202	1043.2	1035.0	1026.6	1018.5	1.3825	1.2462	1.1125	0.9725
	0.0302	1044.0	1036.0	1027.5	1019.3	1.3899	1.2591	1.1227	0.9817
	0.0401	1045.3	1036.9	1028.5	1020.3	1.3907	1.2265	1.1325	0.9907
	0.0500	1046.2	1038.0	1029.5	1021.2	1.4001	1.2502	1.1401	1.0101
0.144	0.0130	1051.0	1047.7	1040.2	1030.6	1.8902	2.2512	1.5200	1.1550
	0.0250	1057.0	1047.8	1041.6	1031.9	1.9211	2.2900	1.5316	1.1715
	0.0308	1057.3	1049.5	1043.4	1032.3	1.9403	2.3213	1.5601	1.1750
	0.0407	1058.5	1050.6	1044.6	1033.8	1.9500	2.3387	1.5791	1.1950
	0.0510	1058.9	1051.1	1.0503	1041.1	1.9902	2.3601	1.6011	1.2201
0.201	0.0140	1068.8	1060.5	1052.7	1042.8	2.7219	2.2556	1.7819	1.3119
	0.0207	1069.8	1061.3	1053.6	1044.0	2.7479	2.2659	1.7980	1.3279
	0.0309	1071.0	1062.3	1054.6	1044.6	2.7527	2.2772	1.8212	1.3327
	0.0414	1071.7	106.33	1056.0	1046.3	2.7721	2.2862	1.8308	1.3606
	0.0517	1072.6	1064.2	1058.8	1056.0	2.7873	2.2964	1.8429	1.3772

Table 2: The values of density (d) and viscosity (η) for 2-methylimidazolium dichromate in water and DMSO + water at different temperatures.

Mole fraction (X_{org})	Concent-ration (c) mole dm^{-3}	Density (d) kg m^{-3}				Viscosity (η) centipoise			
		298.15K	303.15K	308.15K	313.15K	298.15K	303.15K	308.15K	313.15K
2-methylimidazolium dichromate in water									
	0.0100	1004.6	1000.1	995.17	991.92	0.8259	0.7496	0.6846	0.6174
	0.0200	1006.7	1002.5	998.74	994.63	0.8297	0.7604	0.6907	0.6203
	0.0300	1008.3	1004.7	1001.2	997.58	0.8351	0.7901	0.7276	0.6208
	0.0398	1010.9	1007.6	1004.2	1000.9	0.8377	0.8202	0.7284	0.6279
	0.0497	1013.0	1010.1	1007.2	1004.3	0.8418	0.8293	0.8001	0.6300
2-methylimidazolium dichromate in DMSO + water									
0.027	0.0101	1017.7	1013.9	1010.0	1006.2	0.9766	0.8798	0.8138	0.7448
	0.0202	1019.3	1015.8	1012.2	1008.6	0.9814	0.9082	0.8348	0.7528
	0.0303	1022.7	1019.3	1015.1	1010.9	0.9848	0.9122	0.8388	0.7628
	0.0403	1023.4	1019.6	1016.4	10132	0.9912	0.9168	0.8399	0.7678
	0.0502	1024.3	1021.4	1018.6	1015.6	0.9971	0.9172	0.8452	0.7752
0.059	0.0103	1031.4	1028.4	1023.0	1018.4	1.2050	1.1402	1.0793	1.0110
	0.0205	1032.3	1029.3	1025.2	1020.8	1.2201	1.1593	1.0895	1.0254
	0.0307	1036.3	1032.3	1027.2	1023.8	1.2450	1.1710	1.0100	1.0321
	0.0409	1037.2	1033.1	1029.4	1025.5	1.2509	1.1891	1.1182	1.0428
	0.0510	1038.9	1038.4	1031.6	1027.8	1.2611	1.1901	1.1285	1.0633
0.097	0.0104	1043.2	1039.1	1035.0	1030.6	1.3857	1.2694	1.1496	1.0194
	0.0208	1045.8	1041.4	1036.9	1032.4	1.3934	1.2898	1.1592	1.0496
	0.0312	1050.7	1045.3	1039.7	1034.3	1.3997	1.3078	1.2107	1.1231
	0.0414	1051.0	1046.1	1041.1	1036.1	1.4087	1.3100	1.2225	1.1332
	0.0517	1053.5	1048.6	1043.5	1038.1	1.4167	1.3378	1.2389	1.1476
0.144	0.0105	1058.2	1053.9	1048.1	1042.5	1.6271	1.6281	1.5735	1.5309
	0.0210	1059.6	1054.3	1050.2	1043.8	1.6900	1.6415	1.5963	1.5422
	0.0315	1063.2	1057.8	1054.3	1047.3	1.7401	1.6792	1.6108	1.5536
	0.0419	1063.8	1059.6	1055.9	1049.1	1.7511	1.6917	1.6324	1.5701
	0.0523	1066.7	1059.9	1057.2	1052.9	1.7739	1.7198	1.6745	1.6208
0.201	0.0107	1071.4	1066.0	1060.4	1054.9	2.1270	2.0188	1.8875	1.7673
	0.0213	1073.6	1068.3	1062.9	1057.6	2.1670	2.0435	1.9232	1.8033
	0.0319	1075.2	1070.0	1064.7	1059.6	2.2468	2.1188	1.9882	1.8490
	0.0425	1078.4	1072.7	1068.0	1062.7	2.2475	2.1278	1.9904	1.8723
	0.0530	1080.8	1075.6	1070.3	1065.2	2.2877	2.1575	1.0265	1.9080

Table 3: The values of apparent molar volume (V_ϕ), limiting apparent molar volume $(V_\phi{}^0)$ of benzimidazolium dichromate and 2-methylimidazolium dichromate in water and DMSO-water at different temperatures.

Mole fraction	Concent-ration (*c*) mole dm^{-3}	Apparent molar volume $(V_\phi)\times10^{-3} m^3mol^{-1}$				Limiting apparent molar volume $(V_\phi{}^0)$ m^3mol^{-1}			
		298.15K	303.15K	308.15K	313.15K	298.15K	303.15K	308.15K	313.15K
Benzimidazolium dichromate in water									
	0.0098	0.5152	0.9668	1.0841	1.4585				
	0.0198	0.3723	0.7642	0.8387	1.1513				
	0.0298	0.2749	0.5421	0.6815	0.9250	0.53	1.05	1.12	1.51
	0.0396	0.1869	0.3826	0.5173	0.7181				
	0.0494	0.1342	0.2705	0.3932	0.5855				
Benzimidazolium dichromate in DMSO + water									
0.027	0.0099	–0.8851	–0.4138	–0.2595	–0.2430				
	0.0197	–0.5797	–0.2847	–0.1184	–0.2897				
	0.0295	–0.3193	–0.1041	–0.1030	–0.3053	–0.77	–0.4	–0.26	0.23
	0.0392	–0.1402	–0.0857	–0.1859	–0.3102				
	0.0488	–0.0379	–0.0287	–0.3114	–0.3131				
0.059	0.0100	–1.6784	–0.9239	–0.8564	–0.5964				
	0.0200	–1.2237	–0.7194	–0.6531	–0.3281				
	0.0298	–0.7291	–0.5198	–0.3137	–0.1923	–1.72	–0.98	–0.81	–0.51
	0.0397	–0.4493	–0.3021	–0.1577	–0.1025				
	0.0495	–0.2819	–0.1802	–0.0817	–0.0418				
0.097	0.0110	–2.2784	–1.5325	–1.4669	–0.9688				
	0.0202	–1.6103	–1.2502	–1.1796	–0.8794				
	0.0302	–1.3077	–0.8935	–0.6804	–0.4760	–2.47	–1.63	–1.47	1.14
	0.0401	–0.8509	–0.5886	–0.4286	–0.2776				
	0.0500	–0.5362	–0.4103	–0.2803	–0.1558				
0.144	0.0130	–2.7291	–2.6028	–1.9141	–2.0945				
	0.0250	–2.1374	–1.7092	–1.5853	–1.5204				
	0.0308	–1.5094	–1.3182	–1.1801	–1.2183	–2.80	2.32	–1.91	–2.26
	0.0407	–1.1055	–0.9095	–0.8103	–1.0602				
	0.0510	–0.7704	–0.6544	–0.6735	–0.4453				
0.201	0.0140	–4.0164	–2.7599	–2.4196	–2.8847				
	0.0207	–3.0160	–2.7140	–1.8440	–2.0943				
	0.0309	–2.9134	–1.6986	–1.5258	–1.5808	–4.5	–2.88	–2.54	–2.93
	0.0414	–1.3519	–1.1986	–1.0747	–1.1846				
	0.0517	–0.8016	–0.8945	–0.8301	–0.8150				

(*continued on next page*)

Mole fraction	Concent-ration (c) mole dm^{-3}	Apparent molar volume $(V_{\phi})\times 10^{-3}$ m^{3}mol^{-1}				Limiting apparent molar volume (V_{ϕ}^{0}) m^{3}mol^{-1}			
		298.15K	303.15K	308.15K	313.15K	298.15K	303.15K	308.15K	313.15K
		2-methylimidazolium dichromate in water							
	0.0100	–0.1441	0.1913	0.1885	0.2857				
	0.0200	–0.0753	0.0356	0.1582	0.2270				
	0.0300	0.0259	0.0548	0.1380	0.1923	–1.52	0.06	2.02	2.99
	0.0398	0.3138	0.0780	0.1228	0.1597				
	0.0497	0.5863	0.0882	0.1132	0.1349				
		2-methylimidazolium dichromate in DMSO + water							
0.027	0.0101	–0.9235	–0.8643	–0.6212	–0.4683				
	0.0202	–0.6425	–0.6223	–0.4791	–0.3240				
	0.0303	–0.4689	–0.4062	–0.3233	–0.2463	–0.98	–0.82	–0.62	–0.47
	0.0403	–0.2754	–0.2177	–0.1814	–0.1418				
	0.0502	–0.1639	–0.1639	–0.1129	–0.1084				
0.059	0.0103	–1.6784	–1.4847	–1.2072	–1.2315				
	0.0205	–1.2450	–1.1277	–0.9164	–0.9524				
	0.0307	–0.9281	–0.8226	–0.7132	–0.6657	–1.51	–1.5	–1.28	–1.3
	0.0409	–0.6042	–0.5435	–0.4952	–0.4485				
	0.0510	–0.4425	–0.3211	–0.3655	–0.3295				
0.097	0.0104	–1.9872	–2.1851	–2.0363	–1.7575				
	0.0208	–1.5644	–1.6384	–1.5171	–1.3349				
	0.0312	–1.2653	–1.2283	–1.1511	–1.0002	–2.13	–2.22	–2.11	–1.81
	0.0414	–0.9266	–0.8492	–0.7737	–0.7023				
	0.0517	–0.7146	–0.6518	–0.5906	–0.5265				
0.144	0.0105	–2.9425	–2.7594	–2.5302	–2.7546				
	0.0210	–2.2438	–2.1106	–2.0133	–2.1159				
	0.0315	–1.6765	–1.6076	–1.5562	–1.6569	–3.07	–2.88	–2.69	–2.91
	0.0419	–1.2174	–1.1596	–1.1114	–1.0163				
	0.0523	–0.9552	–0.8601	–0.8430	–0.8010				
0.201	0.0107	–3.3591	–3.2590	–2.8564	–2.8384				
	0.0213	–2.6322	–2.4393	–2.3303	–2.2173				
	0.0319	–2.0769	–1.9753	–1.8689	–1.7883	–3.51	–3.29	–3.09	–3.01
	0.0425	–1.5694	–1.4488	–1.3863	–1.3136				
	0.0530	–1.2043	–1.1399	–0.0801	–1.0244				

It is also clear from Table 3 that the values of limiting apparent molar volume (V_{φ}^{0}) are positive for benzimidazolium dichromate (Figure 1) and negative for 2-methyl imidazolium dichromate in water (Figure 2) as shown in Table 4, at different temperatures. The positive value of V_{ϕ}^{0} indicates strong solute-solute interactions. The values of V_{φ}^{0} in benzimidazolium dichromate increased approximately 2 times with the increase in temperature. In case of aqueous solution of 2-methyl imidazolium dichromate, the value of V_{φ}^{0} was negative at lower temperature, but turned positive with increase in temperature.

This clearly indicates that the solute-solute interaction was becoming more prominent in 2-methyl imidazolium dichromate with the increase in temperature.

Table 4: Values of transfer volume (ΔV_{φ}^{0}) and experimental slope (S_v) of benzimidazolium dichromate and 2-methylimidazolium dichromate at different temperatures.

Mole fraction	Transfer volume (ΔV_{φ}^{0}) m^3mol^{-1}				S_v $m^3kg^{1/2}mol^{-3/2}$			
	298.15K	303.15K	308.15K	313.15K	298.15K	303.15K	308.15K	313.15K
Benzimidazolium dichromate in water								
					–0.1584	–0.2867	–0.3443	–0.4040
Benzimidazolium dichromate in DMSO + water								
0.027	–1.3	–1.45	–1.38	–1.29	0.1228	0.5543	–0.4452	–0.4877
0.059	–2.25	–2.03	–1.93	–2.02	0.2493	0.4877	0.3057	0.4040
0.097	–3.0	–2.68	–2.59	–2.12	0.3443	0.3153	0.2867	0.1944
0.144	–3.33	–3.37	–3.03	–3.77	0.3839	0.2309	0.1763	0.1051
0.201	–5.03	–4.93	–3.56	–4.14	0.5543	0.1405	0.1409	0.0978
2-methylimidazolium dichromate in water								
					0.3640	0.1405	–0.2126	–0.1944
2-methylimidazolium dichromate in DMSO + water								
0.027	–0.37	–0.11	–0.19	–0.24	0.1584	0.1944	0.1228	0.0524
0.059	–0.16	–0.57	–0.47	–1.07	0.2679	0.2661	0.2309	0.2126
0.097	–0.78	–1.29	–1.30	–1.58	0.2867	0.3640	0.4040	0.2867
0.144	–1.72	–1.95	–1.88	–1.68	0.4663	0.4663	0.4877	0.4452
0.201	–1.98	–2.36	–2.28	–2.78	0.4877	0.5095	0.5317	0.4663

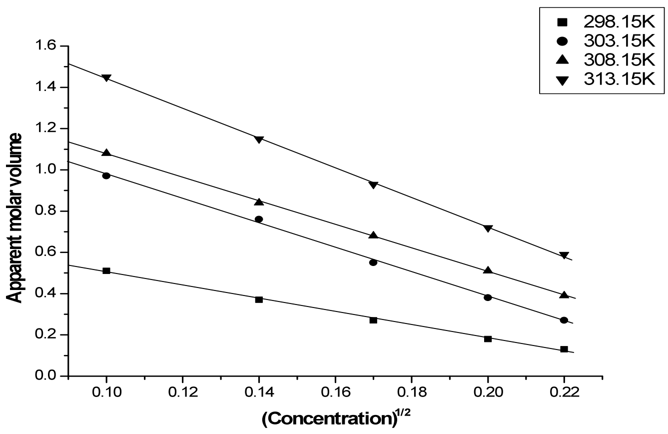


Figure 1: Variation of apparent molar volume (V_{φ}) with $c^{1/2}$ for benzimidazolium dichromate in water at different temperatures.

Table 5: Values of A and B coefficients of Jone-Dole equation in benzimidazolium dichromate and 2-methylimidazolium dichromate at different temperatures.

Mole fraction	A dm$^{3/2}$ mol$^{-1/2}$				B dm^{3}mol^{-1}			
	298.15K	303.15K	308.15K	313.15K	298.15K	303.15K	308.15K	313.15K
Benzimidazolium dichromate in water								
	–1.34	–0.94	–0.81	–0.23	0.3839	0.2867	0.2679	0.1584
Benzimidazolium dichromate in DMSO + water								
0.027	–4.5	–4.78	–4.77	–4.28	0.1763	0.2309	0.3443	0.4452
0.059	–3.1	–2.95	–4.02	–3.59	0.1563	0.1584	0.3249	0.3284
0.097	–2.6	–2.73	–3.53	–3.11	0.1051	0.1404	0.2679	0.2867
0.144	–0.5	–2.25	–2.01	–2.17	0.0524	0.1405	0.1944	0.2309
0.201	3.7	2.31	–0.63	–1.26	–0.1763	–0.1051	0.1051	0.1409
2-methylimidazolium dichromate in water								
	–7.2	–6.51	–7.5	–4.52	0.3640	0.6009	0.4050	0.2126
2-methylimidazolium dichromate in DMSO + water								
0.027	–4.08	–3.7	–4.37	–4.52	0.2119	0.2309	0.3057	0.3001
0.059	–3.2	–2.80	–3.82	–2.71	0.2126	0.2309	0.2679	0.1588
0.097	–2.6	–2.52	–3.21	–2.27	0.1944	0.2126	0.2493	0.1407
0.144	–1.3	–1.1	–1.58	–2.21	0.1228	0.1584	0.1763	0.0349
0.201	0.7	1.31	1.01	1.74	0.0349	–0.0349	0.0699	–0.0641

The value of V_φ^0 became more negative with the increase in mole fraction of DMSO, showing increase in ion-solvent interaction in solution of benzimidazolium dichromate, but it increased with increase in temperature. The ion-solvent interaction is much weaker in benzimidazolium dichromate at an increased temperature. But having more negative value of V_φ^0 means that the 2-methyl imidazolium dichromate ion-solvent interaction is more prominent as compared to benzimidazolium dichromate. The values of Sv were negative for benzimidazolium dichromate and positive for 2-methyl imidazolium dichromate. A very strong ion-ion interaction is observed in benzimidazolium dichromate having negative Sv values and less complexation formation. But in case of 2-methylimidazolium dichromate, the positive Sv values suggest that the presence of ion-solvent interaction, which decreases at higher temperature is confirmed by negative Sv values. The negative values of V_ϕ^0 and positive Sv values for both the complexes are shown in Figure 3 and 4 respectively.

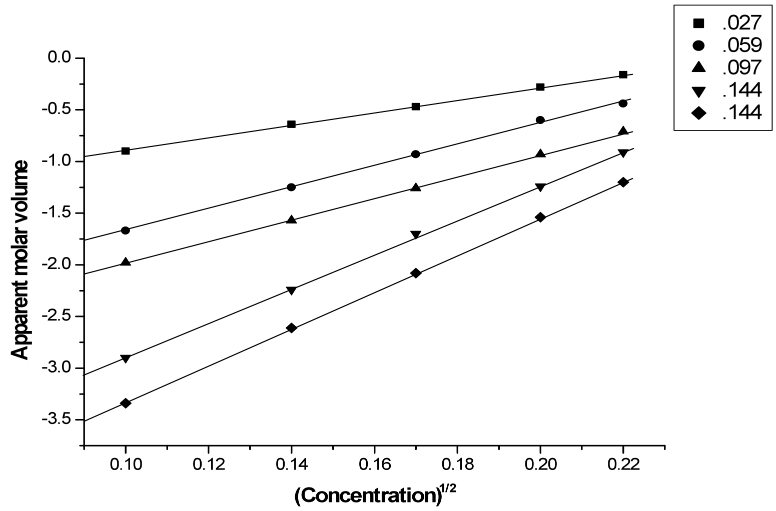


Figure 2: Variation of apparent molar volume (V_φ) with $c^{1/2}$ for 2-methyl imidazolium dichromate in water at different temperatures.

From the magnitudes of V_φ^0 and Sv, it has been shown that ion-solvent interaction dominated the ion-ion interactions in 2-methyl imidazolium dichromate in water as compared to benzimidazolium dichromate. In aqua-organic solutions, ion-solvent interaction is much stronger in 2-methyl imidazolium dichromate than benzimidazolium dichromate. This was confirmed with the V_φ^0 and Sv values.

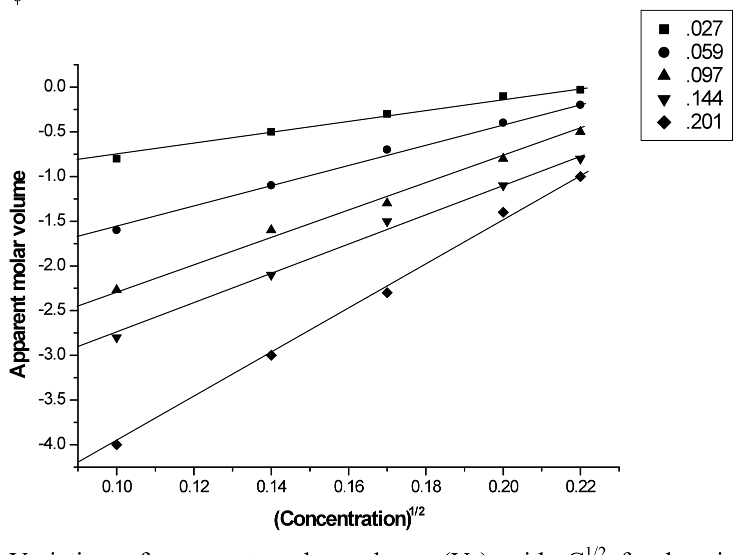


Figure 3: Variation of apparent molar volume (V_φ) with $C^{1/2}$ for benzimidazolium dichromate at different mole fractions of DMSO at 298.15K.

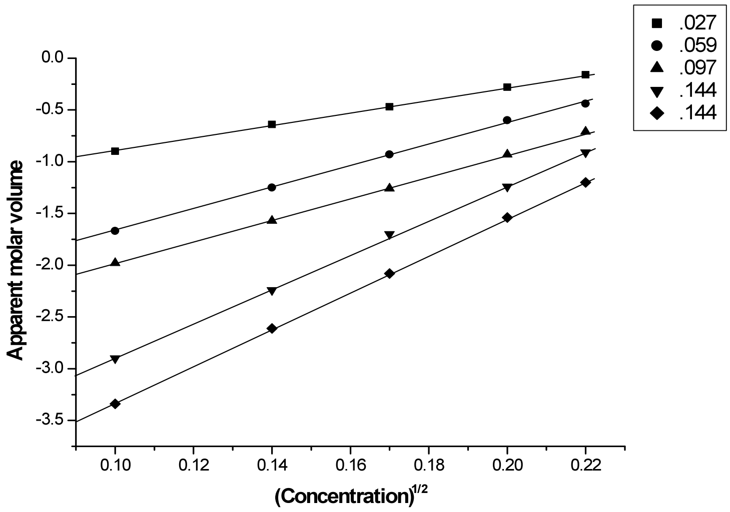


Figure 4: Variation of apparent molar volume (V_φ) with $C^{1/2}$ for 2-methylimidazolium dichromate at different mole fractions DMSO at 298.15K.

According to co-sphere model,[18,19] hydrophilic-ionic group of interaction contribute positively whereas ionic hydrophobic group contribute negatively to the transfer volume studies (ΔV_φ^0) of ion-ion interactions. It is noticed from Table 5 that the $\Delta V_\varphi°$ values were negative in both systems and decreased with rise in temperature. This clearly suggests that the latter types of interactions are dominating over the former. The calculated values suggest that the ion-ion interaction is much weaker in 2-methyl imidazolium dichromate, having less negative values than benzimidazolium dichromate both in water and aqua-organic solvents.

From Table 5, it is also observed that the values of A (Falkenhagen Coefficient) are negative in both systems since A is a measure of ionic interaction. B-coefficient is also known as a measure of order or disorder introduced by the solute into the solvent. It is also a measure of solute-solvent interaction and relative size of the solute and solvent molecules. The values of B-coefficient are positive in both the Cr complexes. Such type of results is also shown by Eyring.[20] In water and aqua-organic solvent 2-methyl imidazolium dichromate is having higher positive values of B-coefficient than that of benzimidazolium dichromate. So benzimidazolium dichromate in water and aqua-organic solvent having less positive B-coefficient and low negative A values suggest the larger of ion-ion interaction and weaker ion-solvent interaction.

4. CONCLUSION

The present investigation of molecular interactions of both the Cr complexes in water and DMSO + water at varying temperatures can be summarised as follows. In the present system, 2-methyl imidazolium dichromate is an effective structure-maker in aqueous medium over benzimidazolium dichromate. The transfer volume studies, which predict the solute-solute interaction, suggest the ionic-hydrophobic interaction exists in the systems under study. At lower temperature, the transfer volume was positive for 2-methyl imidazolium dichromate but became negative with the increase in mole fraction of DMSO. A very strong ion-ion interaction is noticed in the benzimidazolium dichromate solution. The ion-solvent interaction was stronger in 2-methyl imidazolium dichromate system. The elevation of temperature led to the weakening of molecular associations in the present system due to thermal dispersion forces. The presence of bulkier group in the system reduced the ion-solvent interaction. From the experimental data, it can be concluded that the ion-solvent interaction of 2-methylimidazolium dichromate was stronger than benzimidazolium dichromate in aqueous DMSO of the order:

2-methyl imidazolium dichromate > Benzimidazolium dichromate

Probability of steric effect of benzimidazolium dichromate reduces the possibility of ion-solvent interaction.

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6. REFERENCES

1. Kaminsky, M. (1957). Ion-solvent and viscosity of strong electrolyte solutions. *Discuss. Faraday Soc.*, 24,171–179.
2. Nandi, D. & Hozra, D. K. (1989). Viscosities of alkali metal chlorides and bromides in 2-methoxy ethanol at 25 and 35°C. *J. Chem. Soc. Faraday Trans.*, 85, 4227–4235.
3. Jacob, S. W., Rosenbanm, E. E. & Wood, D. C. (1971). *Dimethyl sulphoxide.* New York: Marcel Dukker.
4. Lal, J. T. et al. (1995). Exess partial molar enthalpies, entropies, Gibbs energies and volumes in aqueous dimethyl sulphoxide. *J. Sol. Chem.*, 24(1), 89–102.

5. Scaduto, R. C. (1995). Oxidation of DMSO and methanesulfinic acid by hydroxyl radical. *Free Radic. Biol. Med.*, 18(2), 271–277.
6. Katritzky, A. R. & Rees, C. W. (eds.) (1984). *Comprehensive heterocyclic chemistry*. Oxford: Pergamon Press.
7. Grimmett, M. R. (1997). *Imidazole and benzimidazolium synthesis*. San Diego: Academic Press.
8. Brown, E. G. (1998). *Ring nitrogen and key biomolecules*. Boston: Kluwer Academic Press.
9. Pozharskii, A. F. et al. (1997). *Heterocycles in life and society*. New York: John Wiley & Sons.
10. Shargel, L., Mutnick, A. H., Souney, P. F. & Swanson, L. N. (2006). *Comprehensive pharmacy review, 6th ed*. New York: Lippincott Williams & Wilkins.
11. Kannappan, V. & Vinayagam, S. C. (2006). Ultrasonic investigation of ion-solvent interactions in aqueous and non-aqueous solutions of transition and inner transition metal ions. *Ind. J. Pure Appl. Phys.*, 44, 670–676.
12. Ravicharan, S. & Ramanathan, K. (2010). Ultrasonic investigations of $MnSO_4$, $NiSO_4$, and $CuSO_4$ in aqueos polyvinyl alcohol solution at 303K. *Rasayan J. Chem.*, 3(2), 375–384.
13. Parmer, M. L., Sharma, P. & Guleria, M. K. (2009). A comparative study of partial molar volumes of some hydrated and anhydrous salts of transition metal sulphates and magnesium sulphate in water at different temperatures. *Ind. J. Chem.*, 48A, 57–62.
14. Ramaiah K. et al. (2002). Synthesis and structural elucidation of novel benzimidazoles and chromium(VI) reagent. *Ind. J. Chem.*, 41B(10), 2136–2144.
15. Jones, G. & Dole, M. (1929). The viscosity of aqueous solutions of strong electrolytes with special reference to barium chloride. *J. Am. Chem. Soc.*, 51(10), 2950–2964.
16. Nishikawa, S., Mashima, M. & Yasunuga, T. (1975). Ultrasonic absorption mechanism in an aqueous solution of n-propyl alcohol. *Bull. Chem. Soc. Jpn.*, 48(2), 661–665.
17. Murthy, N. M. & Subrahmanyam, S. V. (1977). Structure of aqueous isomeric butyl alcohols, sound velocity studies. *Bull. Chem. Soc. Jpn.*, 50(10), 2589–2593.
18. Hakin, A. W. et al. (1994). Apparent molar heat capacities and volumes of some aqueous solutions of aliphatic amino acids at 288.15, 298.15, 313.15K. *Can. J. Chem.,* 72(2), 362–368.
19. Gurney, R. W. (1953). *Ionic processes in solutions*. New York: McGraw-Hill.
20. Eyring, H. & Kincaid, J. F. (1939). The liquid state. *J. Chem. Phys.*, 43(1), 37–40.