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Density, viscosity and excess parameters of nicotinium dichromate in protic and aprotic solvent media

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ABSTRACT

The densities and viscosities of nicotinium dichromate with DMSO and methanol have been measured at 303.15K. The values are used to calculate the apparent molar volume (V_{ϕ}), limiting molar volume (V_{ϕ}^0), excess molar volume (V_m^E), viscosity deviation ($\Delta\eta$) and excess Gibb's free energy of viscous flow (ΔG^{*E}). The viscosity results have been computed to calculate Falkenhagen coefficient (A) and Jones-Dole B coefficient. The main aim of the study is to correlate the excess properties with molecular interactions present in the solution. The strength of interaction is related to the nature of solvents.

Key words - Nicotinium dichromate, excess properties, apparent molar volume, apparent limiting molar volume, ion-solvent interaction.

INTRODUCTION

The physicochemical properties of solute in mixed solvent are influenced by measurement of density, viscosity and hence the derived parameters will give significant information regarding solute-solvent interaction. Viscosity and density data of solutions give valuable information towards solution theory and molecular dynamics¹⁻⁴. Crookes *et al*⁵ have reported density of solution of NaBF₄ in water to derive concentrative properties of NaBF₄ solution. The apparent molar volume and viscosities of NaCl, NH₄Cl, CaCl₂, CaSO₄, MgSO₄ in pure water, aqueous urea⁶ and sodium molybdate, tungstate in aqueous acetonitrile⁷ and NH₄Cl, NiCl₂, FeCl₃ in DMSO⁸ have been reported. The researchers⁹ have measured the density and viscosity of tris(acetylacetonato)cobalt(III) solution in acetonitrile, dichloromethane, chloroform, tetrachloromethane, benzene, toluene, ethyl benzene, *p*-xylene at different temperatures. Parmer *et al*¹⁰ have measured the viscosity of some metal nitrates in water and in aqueous mixture of DMF at different temperatures to explain the effect of temperature on ion-solvent interaction. The solvation behavior of metal complexes in protic and aprotic solvents is essential for many chemical and industrial application¹¹. Thus an attempt has been made to elucidate the ion-ion interaction and ion – solvent interaction of a stable, non hygroscopic and mild oxidant nicotinium dichromate(NDC)¹². But NDC acts as a reagent for the oxidative determination of amines and aminophosphonates¹³. Only conductance, vibration and thermal behavior of NDC have been reported¹⁴⁻¹⁵. But little work has been done on nicotinium dichromate (NDC). The present work aims at the solvation of NDC in aqueous solutions of DMSO and methanol at 308.25K.

MATERIALS AND METHODS

Nicotinic acid of high purity was used. Potassium dichromate used was Anal R grade. Water used in this study was double distilled. Nicotinium dichromate was prepared by reported method¹⁶. This is characterized by elemental analysis and spectroscopic methods. The solutions are made in aquo-organic mixtures of DMSO and methanol with different compositions. The pycnometer was calibrated by measuring the densities of triple distilled water. The

density of DMSO and methanol were determined with water. The viscosities of different solutions were measured using Ostwald's viscometer at 303.15K and the efflux medium was determined using a digital stop watch. To maintain constant temperature a thermostat with accuracy of $\pm 0.01\text{K}$ was used.

Molar concentration (c) and molal concentration (m) are related by the equation¹⁷,

$$c = md(1 + 0.001mM_2)^{-1} \quad (1)$$

From the density data, the apparent molar volume (V_ϕ) was calculated from the relation¹⁸,

$$V_\phi = 1000(cd_0)^{-1}(d_0 - d) + M_2d_0^{-1} \quad (2)$$

where c is the molar concentration of the solution, M_2 is the molecular mass of the solute, d_0 and d are the densities of pure solvent and solution respectively.

The apparent molar volume thus obtained is found to vary linearly with $c^{1/2}$. The V_ϕ data were fitted by a method of least squares to Masson's equation¹⁹,

$$V_\phi = V_\phi^0 + S_v c^{1/2} \quad (3)$$

Over the range in which the densities are determined, where V_ϕ^0 is the limiting apparent molar volume and S_v is the slope of the plot V_ϕ versus $c^{1/2}$.

The viscosity data of electrolyte solutions both in aqueous and non-aqueous solutions follow the Jones-Dole²⁰ equation,

$$\eta_r = \frac{\eta}{\eta_0} = 1 + Ac^{1/2} + Bc \quad (4)$$

where η_r is the relative viscosity of the solution. η and η_0 are the viscosities of solution and solvent respectively. c is the molar concentration. A is called Falkenhagen and B -coefficient is Jones-Dole coefficient.

The viscosity deviation ($\Delta\eta$), excess molar volume (V_m^E) and excess molar Gibbs free energy of activation of viscous flow (ΔG^{*E}) were determined using the following equations²¹⁻²².

$$\Delta\eta = \eta - \sum_{i=1}^n x_i \eta_i \quad (5)$$

Where x_i is the molefraction of i th component, η_i and η refer to the viscosities of i th pure component and the mixture respectively.

$$V^E = V - \sum_{i=1}^n x_i V_i \quad (6)$$

Where V_i and V represent the molar volume of i th pure component and the mixture respectively

$$\Delta G^{*E} = RT [\ln \eta V - \sum_{i=1}^n x_i \ln(\eta_i V_i)] \quad (7)$$

RESULTS AND DISCUSSION

The experimentally determined values of densities and viscosities of pure solvents have been compared with literature values and presented in Table 1. It is seen that experimental values compare fairly well with the literature values.

Table 1: comparison of Experimental and literature values of densities and viscosities of pure solvents at 303.15K

Pure solvents	ρ (10^{-3} gcm $^{-3}$)		η (mPa.S)	
	Expt.	Lit.	Expt.	Lit.
DMSO	1.0907	1.0905 ²³	1.8405	1.830 ²⁴
methanol	0.7839	0.7818 ²⁵⁻²⁶	0.4928	0.510 ²⁷

The experimental values of density, viscosity, deviation in viscosity, excess molar volume, Gibb's free energy of activation of viscous flow of NDC in aqueous solutions of DMSO and methanol are listed in table 2.

Table 2: The data of density (ρ), viscosity (η), apparent molar volume (V_{ϕ}), viscosity deviation ($\Delta\eta$), excess molar volume (V_m^E) and excess free energy for viscous flow (ΔG^{*E}) for nicotinium dichromate in different mole fractions of DMSO and methanol at 303.15K

Mole Fraction	Concentration (c)	Density (ρ)	viscosity (η)	apparent molar volume (V_{ϕ})	viscosity deviation ($\Delta\eta$)	Excess molar volume (V_m^E)	Excess free energy (ΔG^{*E})
X_{org}	(mole dm $^{-3}$)	(gcm $^{-3}$)	(x10 $^{-1}$ centipoise)	(x10 3 m 3 mol $^{-1}$)	(mPa.s)	(x10 2 cm 3 mol $^{-1}$)	(x10 3 J mol $^{-1}$)
NDC in aqueous solution of DMSO							
	.02	1.0254	1.2406	- 1.1877	0.2163	3.5906	880.37
	.04	1.0292	1.2582	- 0.4932	0.4491	3.5766	885.59
	.06	1.0326	1.2730	- 0.2551	0.4639	3.5641	887.75
.059	.08	1.0363	1.3019	- 0.1405	0.4927	3.5506	892.58
	.02	1.0381	1.5068	- 1.8265	0.6577	3.6783	902.86
	.04	1.0413	1.5557	- 0.7977	0.7066	3.6668	910.26
	.06	1.0451	1.5810	- 0.4646	0.7319	3.6536	913.46
.097	.08	1.0496	1.6518	- 0.3070	0.8027	3.6372	923.43
	.02	1.0512	1.6934	- 2.4855	0.7948	3.4549	895.17
	.04	1.0549	1.8606	- 1.1396	0.9620	3.4389	918.38
	.06	1.0579	1.8456	- 0.6793	0.9470	3.4283	915.58
.144	.08	1.0611	1.9593	- 0.4516	1.0607	3.4173	913.32
NDC in aqueous solution of methanol							
	.02	0.9797	1.1853	1.1112	0.3776	3.7768	873.96
	.04	0.9815	1.1937	0.7065	0.3860	3.7694	875.29
	.06	0.9853	1.2422	0.5380	0.4345	3.7542	884.51
.099	.08	0.9863	1.2622	0.4890	0.4545	3.7502	888.34
	.02	0.9617	1.3004	2.0116	0.4329	3.8373	876.15
	.04	0.9642	1.3593	1.1416	0.4918	3.8268	885.91
	.06	0.9718	1.3997	0.7464	0.5322	3.7952	892.33
.160	.08	0.9763	1.4079	0.6148	0.5404	3.7767	892.65
	.02	0.9557	1.4179	2.3184	0.4673	3.8471	868.36
	.04	0.9564	1.4859	1.3378	0.5353	3.8442	880.17
	.06	0.9592	1.4964	0.9757	0.5458	3.8323	881.22
.228	.08	0.9621	1.5070	0.7934	0.5570	3.8201	882.26

Figure 1 and 2 represent the linear plot of apparent molar volume (V_{ϕ}) with $c^{1/2}$ for DMSO and methanol systems respectively.

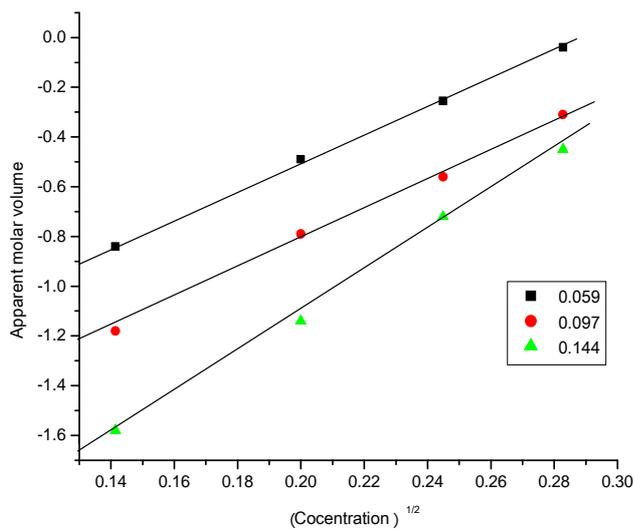


Figure 1: Variation of apparent molar volume (V_{ϕ}) with $C^{1/2}$ for NDC in aqueous solution of DMSO at 303.15K

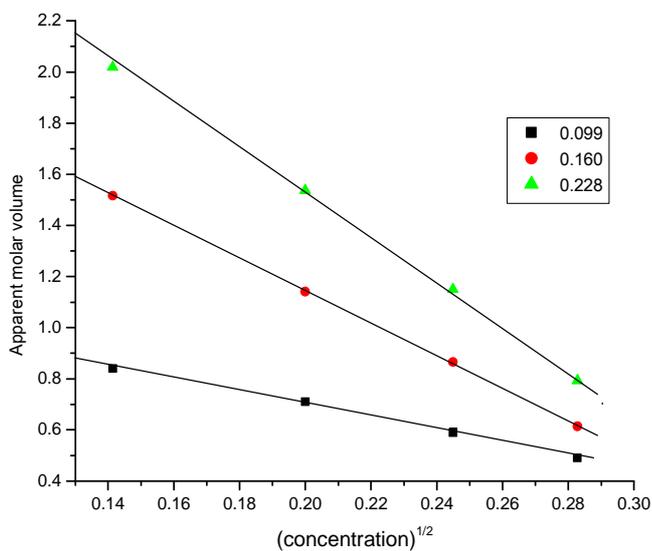


Figure 2: Variation of apparent molar volume (V_{ϕ}) with $C^{1/2}$ for NDC in aqueous solution of methanol at 303.15K

The linear plots of $\eta_r - 1/c^{1/2}$ with $c^{1/2}$ for DMSO and methanol systems are given in Figure 3 and 4 respectively.

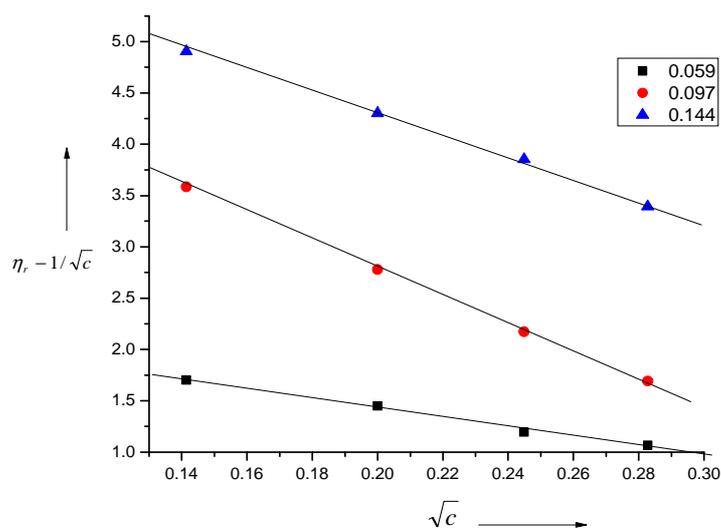


Figure 3: Variation of $\eta_r - 1/\sqrt{c}$ with $C^{1/2}$ for NDC in aqueous solution of DMSO at 303.15K

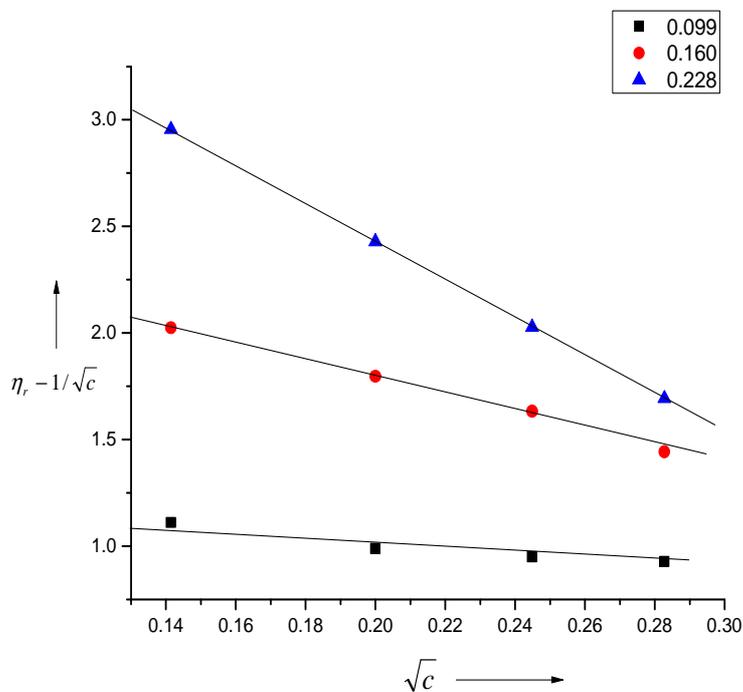


Figure 4: Variation of $\eta_r - 1/\sqrt{c}$ with $C^{1/2}$ for NDC in aqueous solution of methanol at 303.15K

The plots are drawn using least square fitting. The Masson parameters (V_ϕ^0 , S_v) and viscosity parameters (A , B) are tabulated in Table 3.

Table 3: The data of limiting apparent molar volume (V_ϕ^0) and experimental slope (S_v), viscosity coefficients (A, B) for nicotinium dichromate in different mole fractions of DMSO and methanol at 303.15K

Mole Fraction X_{org}	Concentration (C) (mole dm^{-3})	limiting apparent molar volume (V_ϕ^0) ($m^3 mol^{-1}$)	S_v ($m^3 kg^{1/2} mol^{-3/2}$)	A ($dm^{3/2} mol^{-1/2}$)	B ($dm^3 mol^{-1}$)
NDC in aqueous solution of DMSO					
.059	.02	-0.9166	0.2309	1.7617	-0.1584
	.04				
	.06				
	.08				
.097	.02	-1.2713	0.2493	3.7718	-0.4663
	.04				
	.06				
	.08				
.144	.02	-1.6710	0.3640	5.0642	-0.3443
	.04				
	.06				
	.08				
NDC in aqueous solution of methanol					
.099	.02	0.8739	-0.5095	1.0724	-0.0699
	.04				
	.06				
	.08				
.160	.02	1.5745	-0.3443	2.0874	-0.2493
	.04				
	.06				
	.08				
.228	.02	2.1276	-0.1405	3.0342	-0.5543
	.04				
	.06				
	.08				

In both the systems the values of density increase with increasing molar conc. of NDC. This increase is due to the attraction of nicotinium dichromate ion with DMSO and methanol. This increasing trend suggests a moderate electrostatic nature. Molecular interaction is thus responsible for observed increase in density²⁸.

It is found from Table 1 that the values of excess molar volume (V_m^E) in respect to both the systems are positive over the entire range of composition of NDC. The positive values of V_m^E may be attributed to the existence of dispersive interactions between NDC and solvent molecules. V_m^E values decrease with increasing molar concentration of NDC but increase with mole fractions of solvents.

The following observations have been made on V_ϕ values of NDC in aqueous solutions of DMSO and methanol.

- i. The V_ϕ values are negative for DMSO system over the entire range of composition.
- ii. For methanol system the V_ϕ values are positive for DMSO system.
- iii. The magnitude of V_ϕ values in different mole fractions of solvents are in the order

For DMSO system, $NDC_{0.059} > NDC_{0.097} > NDC_{0.144}$

For methanol system, $NDC_{0.228} > NDC_{0.160} > NDC_{0.099}$

From Figure 2 it is seen that limiting apparent molar volume (V_{ϕ}^0) values for NDC in DMSO are negative whereas in methanol mixture these are positive. The negative values decrease with increase in mole fractions of DMSO. The positive values of V_{ϕ}^0 for NDC in methanol indicate the presence of strong ion-solvent interactions. But a sharp decrease in V_{ϕ}^0 values suggest that the strength of ion-solvent interaction is reduced with molar concentration of NDC but increase in these values with mole fractions of methanol refers to solvation around NDC ionic moiety. The S_v values are negative in methanol system but positive for DMSO system. The positive values indicate the presence of ion-ion interaction whereas negative values are associated with hydrophilic effect²⁹. This effect may be due to presence of highly polar group S=O group in DMSO. So solvent-solvent interaction seems to be sufficiently strong in DMSO system.

Viscosity is one of the important property in understanding the molecular interactions occurring in mixtures. Viscosities increases with molar concentration of NDC as observed in Table 1. The increase suggests the existence of ion-solvent interaction. The values of A coefficient are positive showing ion-ion interaction³⁰ while The B -coefficient of Jones-Dole equation indicates the ion-solvent interaction in solutions³¹ and provides useful primary data about the solvation of ions and their effect on the structure of solvent surrounding the solute molecules and has been interpreted as a measure either of structure forming or structure breaking capacity of a solute in solution³² depending on its magnitude. Positive B coefficient shows strong alignment of solvent towards solute which is an ion-solvent interaction parameter and depends upon relative size of ion and solvent molecules. The magnitude of B values is in the order,

$$\text{NDC}_{\text{methanol}} > \text{NDC}_{\text{DMSO}}$$

Viscosity deviations ($\Delta\eta$) are positive for both systems. The positive values of ($\Delta\eta$) can be interpreted in terms of strong interactions between unlike molecules³³. Free energy for viscous flow (ΔG^{*E}) is one of the important parameter regarded as a relative criterion to detect the presence of interactions between unlike molecules³⁴⁻³⁶. The positive values of ΔG^{*E} gives an indication of strength of possible interaction between NDC and solvent which may be related to the size effect of mixing components in these solutions³⁷.

CONCLUSION

The data of density, viscosity and related parameters confirm the presence of strong ion-solvent interaction in methanol system. The strength of ion-solvent interaction depends on concentration of NDC, polarity, structure and mole fraction of solvent. Stronger hydrogen bonding exists in DMSO system having highly polar group S=O group with water indicating solvent-solvent interaction. So it can be concluded that there is a weak ion-solvent interaction in aprotic solvent media but NDC ion interacts more strongly with protic solvent like methanol resulting stronger ion-solvent interaction.

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