

## Interionic Interactions of Nickle Sulphate in Aqueous and Aqueous Methanol Mixtures

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### Abstract

Densities of divalent transition metal sulphate, viz. nickel sulphate (NiSO<sub>4</sub>), were measured in aqueous and aqueous methanol mixtures (10% to 40% v/v) within concentration range (1x10<sup>-3</sup> to 10x10<sup>-3</sup> mol.dm<sup>-3</sup>) at different temperatures (298 to 323 K). The acquired data have been analyzed by using the Masson equation for ascertaining apparent molar volume ( $\phi_v$ ), partial molar volumes ( $\phi_v^\circ$ ) and experimental slopes ( $S_v$ ). The obtained results are interpreted in terms of the ion-ion interaction and ion-solvent interactions. Structure making/breaking capacities of electrolytes have been incidental from the Hepler's criterion i.e.  $\left(\frac{\partial^2 \phi_v^\circ}{\partial T^2}\right)_P$  second derivative of partial molar volume with respect to temperature at constant pressure. Results showed that NiSO<sub>4</sub> in aqueous and aqueous methanol mixtures ranging from 10% to 40% v/v act as structure breaker.

**Keywords:** Apparent molar volume, Ion-ion Interaction, Ion-solvent Interaction, Partial molar volume, Nickel sulphate, Methanol,

### 1. Introduction

Methods of physicochemical analysis have been found to be useful tools in getting sound information about the structure of various liquids and in studying liquid-liquid interactions in binary and ternary mixtures. These physicochemical analyses are based on the dependence of physical properties (additive, constitutive and colligative) on the compositions and external conditions of a liquid mixture. Volumetric characteristics of electrolyte solutions are of elemental importance for the understanding of numerous physicochemical phenomena occurring in the solutions and for the characterization of the interactions between components i.e., solute-solute and solute-solvent. From a practical point of view, the data are useful for the design of mixing, storage, process equipment and in some biochemical and physiological events. Apparent molar volumes of electrolytes provide valuable information about ion-ion, ion-solvent and solvent-solvent interactions. For electroplating of nickel on metallic objects nickel sulphate (NiSO<sub>4</sub>) has been used and also in numerous laboratory experiments [1,2]. It seems to be well established that in the absence of co-ordinatively active anions the 3d<sup>n</sup> transition metal cation (Ni<sup>2+</sup>) exist in the well-defined hexa-solvates of the M(solvent)<sub>6</sub><sup>n+</sup> type (n=2 or 3). It has been found by number of workers that the addition of electrolytes could either break or make the structure of a liquid [3-20].

Methanol is a protic solvent, commercial solvent which is known to be extensively self-associated through hydrogen bonding as its presence in small amount in water alters the solvent structure. It is used as a fuel commonly in racing cars, antifreeze and a denaturant for ethanol, as a solvent in pharmaceutical industry and also for making other chemicals e.g. formaldehyde. Methanol-water mixture is interesting; both from a practical and theoretical point of view, due to bi-functional nature of methanol and extensive formation of hydrogen bonds. As a result, in the areas of experimental and theoretical studies such investigations strongly taken under consideration. Therefore the apparent and partial molar volumes and expansibilities of solute have proven to be very useful tools in elucidating the structural interactions occurring in solution [21, 22]. Tsierkezos and Molinou [23] have reported the electrolytic conductivities of dilute solutions of nickel(II), cadmium(II), magnesium(II), and copper(II) sulfates in binary mixtures of methanol and water at 293.15 K. The results are discussed in terms of limiting molar conductance and the ion-association constants of the electrolytes by conductometric analysis.

The present work investigates the volumetric properties of nickel sulphate to evaluate the structural changes in terms of ion-ion, ion-solvent and solvent-solvent interactions in aqueous and aqueous methanol mixtures. Different variables like concentration, composition of solvent variation and temperatures were also discussed affecting on inter-ionic interactions.

### 2. Experimental

All the glassware used was of Pyrex 'A' grade quality throughout experimental work. Methanol (CH<sub>3</sub>OH) E. Merck of A.C.S HPLC grade having 99 % purity was used for the experimental work. Different compositions (10 % to 40 % v/v) of aqueous methanol were prepared by taking v/v of methanol in a known volume of doubled distilled water. Nickel sulphate hexahydrate (NiSO<sub>4</sub>.6H<sub>2</sub>O; 262.850 g/mol) of E. Merck, 99 % pure was used without further purification. Stock solutions of 0.01mol.dm<sup>-3</sup> NiSO<sub>4</sub> were prepared by dissolving calculated amount in aqueous and aqueous methanol mixtures

ranging from 10 % to 40 % v/v. Solutions in various concentration ranges from  $1 \times 10^{-3}$  to  $8 \times 10^{-3} \text{ mol.dm}^{-3}$  were prepared from stock solutions. The densities of solvent and solutions were measured with relative density bottle having the capacity of  $10 \text{ cm}^3$ . The temperature was kept constant with the help of thermostatic water bath (circulator, model YCW-0.1, R. O. C., Taiwan), having a constant circulation of water to maintain constant temperature during the experimental work. The solutions were kept in thermostatic bath for 15 to 20 minutes to attain constant temperature. Reproducibility of the results was checked by taking each measurement three times.

### 3. Results and Discussion

The density data were observed for the solvent and solutions of divalent transition metal sulfate i.e.  $\text{NiSO}_4$  in aqueous and aqueous methanol mixtures ranging from 10 % to 40 % by volume for concentrations ranging from  $1 \times 10^{-3}$  to  $10 \times 10^{-3} \text{ mol.dm}^{-3}$  at different temperatures 298 to 323 K with the difference of 5 K are tabulated in Table 1 and 2 respectively. Table 1 and 2, represents the values of densities as a function of temperature, concentration and composition of solvent. The respective values of apparent molar volumes ( $\phi_v$ ) of  $\text{NiSO}_4$  were calculated from the densities of the solutions by using the equation (1) [2].

$$\phi_v = \frac{M}{\rho^\circ} - \frac{1000 (\rho - \rho^\circ)}{C \rho^\circ} \quad (1)$$

Where 'M' is the molecular weight of solute, 'C' is the concentration of the  $\text{NiSO}_4$  solution, ' $\rho$ ' is the density of the solution and ' $\rho^\circ$ ' is the density of the solvent.

The results reveal that with the increase in temperature and percent composition of aqueous methanol mixtures density decreased while with the increase in  $\text{NiSO}_4$  concentration increasing trend was observed. This was due to increase in volume of solution by the increased in temperature while by the increased in percent composition of aqueous methanol mixture the number of solute particles decreased as methanol is more bulky than water. As density of a liquid is a simple thermo-physical property which is closely associated with molecular interactions (solute-solute and solute-solvent) that are existing within the system, so it is essential to find out these interionic interaction [24].

With the change of the  $\phi_v$  with the square root of molar (or normal) concentration in 1929, Masson [25] found a valuable, empirical generalization on density data. Scott and Geffcken [26, 27] also examined the  $\phi_v$ 's of electrolytes using this equation and found that it adequately represents the concentration dependence of the  $\phi_v$ 's of electrolytes over a wide range of temperature and concentration. The increased in the partial molar properties was linear when plotted against the square root of the concentration, as expressed in the Masson equation (2) and tabulated in Table 3.

$$\phi_v = \phi_v^\circ + S_v \sqrt{C} \quad (2)$$

Where ' $\phi_v^\circ$ ' is the limiting apparent molar volume or partial molar volume of the solute related to ion – solvent interaction and ' $S_v$ ' is the experimental slope which varies for each electrolyte (empirical constant dependent on charge and salt type) and can be related to ion – ion interactions.

The Plots of  $\phi_v$  versus  $\sqrt{C}$  were linear in all cases as shown in Fig. 1, from the intercept and slope the values of  $\phi_v^\circ$  and  $S_v$  respectively can be obtained. The values of  $\phi_v^\circ$  shown in Table 4, are negative for all solvent composition but decreased with the increase in temperature for aqueous medium (0% v/v aqueous methanol), 30% v/v aqueous methanol mixtures. While reverse behavior was observed for 10 to 20% and 40% v/v aqueous methanol. This indicates that the ion-solvent interactions weakened with the rise of temperature in aqueous and in certain composition of aqueous methanol. In high composition of methanol self association becomes strong by hydrogen bonding causing weak attraction for  $\text{NiSO}_4$ . With the increase of temperature, solvent molecules are loosely attached to solute which expands thus resulting in higher values of  $\phi_v^\circ$  at higher temperature for  $\text{NiSO}_4$ , but with the increase in percent composition of aqueous methanol mixture more electrostrictive solvation occur showing abrupt change [15].

The variation of ' $\phi_v^\circ$ ' with temperature for  $\text{NiSO}_4$  in aqueous and aqueous methanol mixture as shown in Fig. 2, follows the polynomial equation,

$$\phi_v^\circ = \alpha_1 + \alpha_2 T + \alpha_3 T^2 \quad (3)$$

Over the temperature range under the investigation, the co-efficients  $\alpha_i$ 's are evaluated and the following equations are obtained:

For  $\text{NiSO}_4$ ,

$$\phi_v^\circ = 1110 + 20.67 T - 0.090 T^2 \quad (\text{aqueous}) \quad (4)$$

$$\phi_v^\circ = -70601 + 343.1 T - 0.0390 T^2 \quad (10\% \text{ v/v aqueous methanol}) \quad (5)$$

$$\phi_v^\circ = -42987 + 159.2 T - 0.093 T^2 \quad (20\% \text{ v/v aqueous methanol}) \quad (6)$$

$$\phi_v^\circ = -76.96 + 30.11 T - 0.109 T^2 \quad (30\% \text{ v/v aqueous methanol}) \quad (7)$$

$$\phi_v^\circ = -67691 + 320.6 T - 0.349 T^2 \quad (40\% \text{ v/v aqueous methanol}) \quad (8)$$

The partial molar expansibilities;

$$\phi_E^\circ = (\partial \phi_v^\circ / \partial T)_p = \alpha_2 + 2\alpha_3 T \quad (9)$$

Calculated from equation (4-8) in aqueous and aqueous methanol mixtures, are given in Table 5. It was found that from  $\phi_E^\circ$ , the values are increasing with the increase of temperature in aqueous and aqueous methanol. The increase and decrease in  $\phi_E^\circ$  values with the variation in temperature can be used to describe the presence and absence of caging or packing effect, respectively. Caging affect was observed as we move from aqueous to aqueous methanol showing cluster formation or more interactions which disturb with the rise in temperature for all studied system of methanol.

$S_v$  is not the individual decisive factor for determining the structure-making or structure –breaking nature of any solute so in past few years it has been emphasized by different workers that Hepler [28] developed a technique of examining the sign of  $[\partial^2 \phi_v^\circ / \partial T^2]_p$  for various solutes in terms of long range structure-making and structure–breaking capacity of solute using general thermodynamic expression;

$$(\partial C_p / \partial P)_T = -(\partial^2 \phi_v^\circ / \partial T^2)_p = -2\alpha_3 T \quad (10)$$

On the basis of this expression it has been deduced that structure-making solute should have positive value, whereas structure–breaking solute have negative value. In the present alcoholic mixture it is observed from Eq. 4-8 for  $\text{NiSO}_4$ , that  $[\partial^2 \phi_v^\circ / \partial T^2]_p$ , are negative which shows structure-breaking nature of solute ( $\text{NiSO}_4$ ) while in aqueous to aqueous methanol.

#### 4. Conclusion

The density data were observed for the solvent and solutions of  $\text{NiSO}_4$  in aqueous and aqueous methanol mixtures (10%, 20%, 30% and 40% v/v) for concentrations ranging from  $1 \times 10^{-3}$  to  $10 \times 10^{-3}$  mol.dm<sup>-3</sup> at different temperatures 298 to 323 K with the difference of 5 K. The interactions (ion-ion and ion-solvent) of  $\text{NiSO}_4$  in aqueous and aqueous methanol mixtures were described in terms of apparent molar volume and  $S_v$  by using the Masson equation. It is concluded by Hepler's relation that  $\text{NiSO}_4$  act as structure-breaker in aqueous and aqueous methanol mixtures.

#### Acknowledgement

Author (Summyia Masood) is grateful for the research grant provided by the Dean Faculty of Science (DFS), University of Karachi.

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Table 1. Densities ( $\rho^\circ$ ) of aqueous and aqueous methanol mixtures at different temperatures.

Temperature (K)	Densities (gm cm <sup>-3</sup> ) in aqueous and aqueous methanol mixtures				
	0% (v/v)	10% (v/v)	20% (v/v)	30% (v/v)	40% (v/v)
298	1.0100	0.9972	0.9842	0.9806	0.9633
303	1.0090	0.9960	0.9790	0.9755	0.9585
308	1.0085	0.9912	0.9764	0.9733	0.9523
313	1.0055	0.9909	0.9725	0.9674	0.9506
318	1.0035	0.9888	0.9717	0.9611	0.9438
323	1.0025	0.9840	0.9699	0.9600	0.9390

Table 2. Densities ( $\rho$ ) of NiSO<sub>4</sub> in aqueous and aqueous methanol mixtures at different temperatures.

[Salt]x10 <sup>3</sup> (mol.dm <sup>-3</sup> )	Density (gm.cm <sup>-3</sup> ) at different temperatures K					
	298	303	308	313	318	323
	<b>Aqueous</b>					
1.0	1.0122	1.0090	1.0070	1.0050	1.0030	1.0020
2.0	1.0132	1.0092	1.0077	1.0054	1.0033	1.0022
4.0	1.0138	1.0096	1.0080	1.0058	1.0036	1.0026
6.0	1.0140	1.0101	1.0085	1.0060	1.0040	1.0029
8.0	1.0145	1.0103	1.0088	1.0063	1.0045	1.0032
10	1.0150	1.0105	1.0090	1.0065	1.0048	1.0035
	<b>10(% v/v) Aqueous Methanol</b>					
1.0	0.9990	0.9949	0.9933	0.9920	0.9918	0.9912
2.0	0.9992	0.9968	0.9936	0.9925	0.9922	0.9918
4.0	0.9994	0.9972	0.9939	0.9930	0.9926	0.9922
6.0	1.0000	0.9976	0.9943	0.9938	0.9930	0.9926
8.0	1.0002	0.9980	0.9947	0.9942	0.9936	0.9930
10	1.0006	0.9985	0.9950	0.9948	0.9940	0.9938
	<b>20(% v/v) Aqueous Methanol</b>					
1.0	0.9850	0.9825	0.9810	0.9770	0.9760	0.9755
2.0	0.9862	0.9830	0.9826	0.9782	0.9772	0.9745
4.0	0.9875	0.9836	0.9839	0.9795	0.9777	0.9755
6.0	0.9880	0.9855	0.9850	0.9830	0.9785	0.9768
8.0	0.9883	0.9870	0.9860	0.9840	0.9768	0.9751
10	0.9886	0.9800	0.9830	0.9810	0.9750	0.9742
	<b>30(% v/v) Aqueous Methanol</b>					
1.0	0.9765	0.9730	0.9700	0.9650	0.9638	0.9625
2.0	0.9770	0.9742	0.9725	0.9675	0.9637	0.9618
4.0	0.9772	0.9755	0.9736	0.9688	0.9644	0.9632
6.0	0.9788	0.9760	0.9744	0.9692	0.9654	0.9643
8.0	0.9790	0.9770	0.9750	0.9700	0.9666	0.9654
10	0.9799	0.9780	0.9768	0.9721	0.9680	0.9660
	<b>40(% v/v) Aqueous Methanol</b>					
1.0	0.9656	0.9650	0.9520	0.9500	0.9430	0.9420
2.0	0.9660	0.9580	0.9530	0.9523	0.9460	0.9453
4.0	0.9677	0.9590	0.9555	0.9540	0.9470	0.9466
6.0	0.9684	0.9599	0.9577	0.9550	0.9485	0.9472
8.0	0.9690	0.9600	0.9599	0.9575	0.9499	0.9480
10	0.9699	0.9622	0.9600	0.9599	0.9500	0.9490

Table 3. Apparent molar volume ( $\phi_v$ ) of NiSO<sub>4</sub> in aqueous and aqueous methanol mixtures at different temperatures.

[Salt]x10 <sup>3</sup> (mol.dm <sup>-3</sup> )	Apparent molar volume (cm <sup>3</sup> .mol <sup>-1</sup> ) at temperatures K					
	298	303	308	313	318	323
	<b>Aqueous</b>					
1.0	-521.931	-690.932	-790.431	-971.805	-1023.57	-1154.26
2.0	-675.396	-725.619	-840.010	-936.997	-1068.41	-1249.03
4.0	-455.099	-512.537	-589.638	-678.419	-754.509	-897.406
6.0	-384.967	-431.599	-504.528	-605.486	-666.484	-781.862
8.0	-357.327	-397.324	-476.847	-581.452	-618.734	-755.262
10	-233.812	-234.044	-234.160	-234.858	-235.326	-235.561
	<b>10(% v/v) Aqueous Methanol</b>					
1.0	-2082.98	-1804.37	-1389.38	-1046.67	-725.273	-454.421
2.0	-2032.84	-1749.15	-1374.24	-1001.26	-699.990	-418.852
4.0	-1443.69	-1239.61	-950.515	-673.277	-444.630	-238.465
6.0	-1247.31	-1061.40	-799.183	-560.585	-359.510	-169.868
8.0	-1137.84	-967.269	-715.950	-500.454	-300.516	-134.299
10	-236.813	-237.098	-238.247	-238.319	-238.825	-239.990
	<b>20(% v/v) Aqueous Methanol</b>					
1.0	-2979.72	-2485.82	-2094.76	-1664.25	-1368.34	-1003.00
2.0	-2101.28	-1896.92	-1750.28	-1427.55	-1141.51	-804.867
4.0	-1370.94	-1325.94	-1210.44	-990.172	-762.604	-515.292
6.0	-1178.57	-1132.20	-1025.35	-837.518	-643.176	-420.460
8.0	-1047.91	-1027.65	-926.375	-745.755	-573.152	-360.343
10	-241.216	-241.858	-242.828	-243.028	-243.479	-239.941
	<b>30(% v/v) Aqueous Methanol</b>					
1.0	-537.579	-714.659	-819.018	-1010.08	-1068.72	-1205.36
2.0	-695.646	-750.538	-870.389	-973.899	-1115.54	-1304.32
4.0	-468.744	-530.138	-610.963	-705.137	-787.795	-937.135
6.0	-396.509	-446.421	-522.775	-629.333	-695.887	-816.476
8.0	-368.040	-410.969	-494.092	-604.352	-646.031	-788.698
10	-240.822	-242.081	-242.628	-244.108	-245.708	-245.990
	<b>40(% v/v) Aqueous Methanol</b>					
1.0	-2156.29	-1874.96	-1446.13	-1091.05	-759.854	-476.198
2.0	-2104.38	-1817.58	-1430.38	-1043.71	-733.365	-438.924
4.0	-1494.50	-1288.11	-989.342	-701.820	-465.830	-249.894
6.0	-1291.20	-1102.92	-831.828	-584.350	-376.651	-178.009
8.0	-1177.88	-1005.11	-745.196	-521.671	-314.844	-140.735
10	-245.147	-246.375	-247.979	-248.422	-250.212	-251.491

Table 4. Partial molar volumes ( $\phi_v^\circ$ ) and Experimental slopes ( $S_v$ ) for NiSO<sub>4</sub> in aqueous and aqueous methanol mixtures at different temperatures.

Temperature K	temperatures.				
	0%	10%	20%	30%	40%
	$\phi_v^\circ$ (cm <sup>3</sup> .mol <sup>-1</sup> )				
298	-779.2	-3010	-3840	-802.6	-3116
303	-961.0	-2588	-3277	-994.0	-2689
308	-1116	-1990	-2843	-1156	-2072
313	-1327	-1451	-2263	-1379	-1513
318	-1461	-982.3	-1818	-1526	-1029
323	-1685	-566.3	-1290	-1760	-593.4
	$S_v$ (cm <sup>2</sup> .dm <sup>1/2</sup> .mol <sup>-3/2</sup> )				
298	5035	24309	34747	5186	25165
303	6824	20836	28424	7059	21651
308	8020	15934	24141	8310	16584
313	9729	11533	18870	10113	12022
318	10834	7689	15205	11312	8055
323	12404	4285	10821	12953	4491

Table 5. Partial molar expansibilities ( $\phi_E^\circ$ ) for NiSO<sub>4</sub> in aqueous and aqueous methanol mixtures at different temperatures.

Temperature (K)	0%	10%	20%	30%	40%
<b>Partial molar expansibilities '<math>\phi_E^\circ</math>' (<math>\text{cm}^3\text{mol}^{-1}\text{K}^{-1}</math>) for different percent composition (%v/v).</b>					
298	74.31	575.54	214.628	95.074	112.596
303	75.21	579.44	215.558	96.164	109.106
308	76.11	583.34	216.488	97.254	105.616
313	77.01	587.24	217.418	98.344	102.126
318	77.91	591.14	218.348	99.434	98.6360
323	78.81	595.04	219.278	100.52	95.1460
<b><math>(\partial^2\phi_v/\partial T^2)_p</math> (<math>\text{cm}^3\text{mol}^{-1}</math>)</b>					
298	-53.64	-232.44	-55.428	-64.964	-208.004
303	-54.54	-236.34	-56.358	-66.054	-211.494
308	-55.44	-240.24	-57.288	-67.144	-214.984
313	-56.34	-244.14	-58.218	-68.234	-218.474
318	-57.24	-248.04	-59.148	-69.324	-221.964
323	-58.14	-251.94	-60.078	-70.414	-225.454

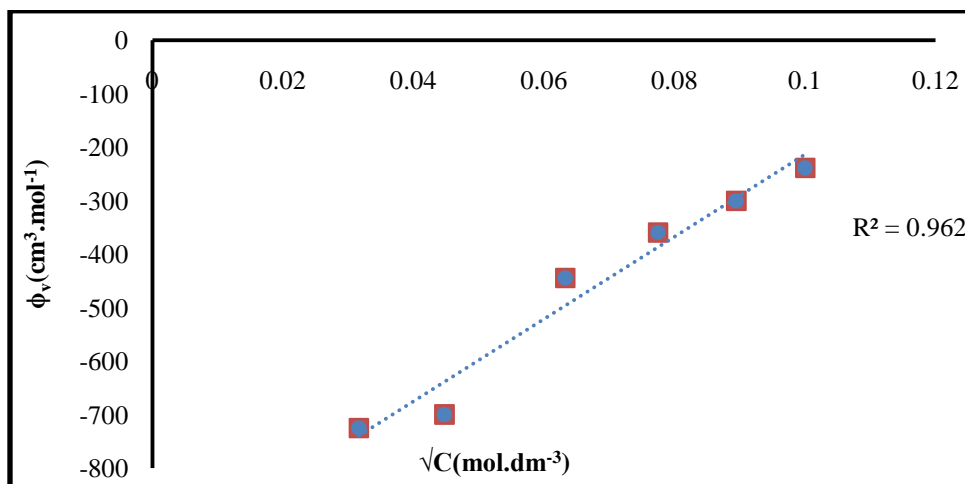


Fig. 1. Plot of apparent molar volumes ( $\phi_v$ ) versus  $\sqrt{C}$  for NiSO<sub>4</sub> in 10% (v/v) aqueous methanol mixtures at 318K.

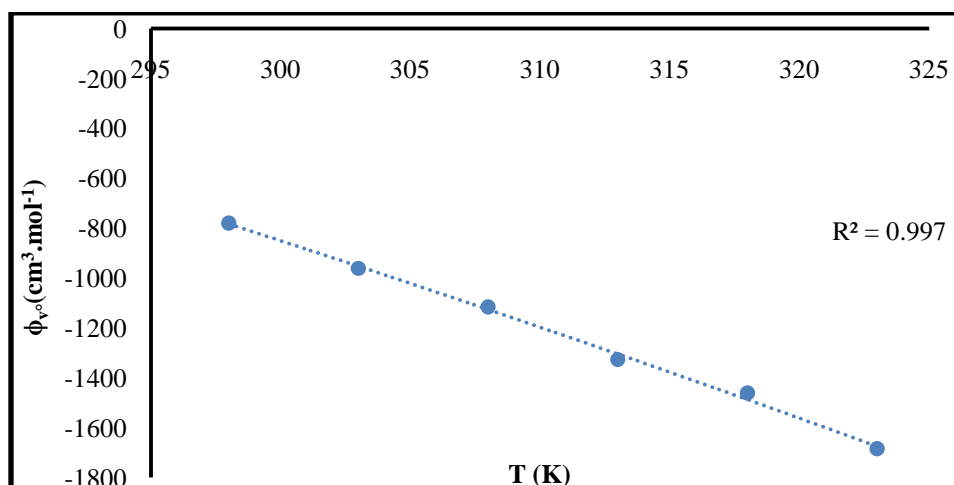


Fig. 2. Plot of partial molar volume ( $\phi_v^\circ$ ) versus temperature for NiSO<sub>4</sub> in aqueous system.