Molar volume, viscosity and conductance studies of nickel sulphate in water and aqueous mannitol

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Abstract : Molar volume, viscosity and conductance of nickel sulphate in water and 2, 4 and 6 wt. % of aqueous mannitol solutions have been evaluated from density, viscosity and conductance data respectively at temperatures 303.15, 308.15, 313.15 and 318.15 K. The solute-solvent interactions for nickel sulphate in water and various compositions of aqueous mannitol have been inferred from ϕ_v^0, B-coefficient of Jones-Dole equation and Λ_m^0 values. The structure making/breaking behaviour of nickel sulphate is inferred from the sign of $[\partial^2 \phi_v^0/\partial T^2]_p$, dB/dT and temperature coefficient of Walden product i.e. $d(\Lambda_m^0 \eta_0)/dT$ values. It has been found that nickel sulphate behaves as structure-breaker in water and structure-maker in 2, 4 and 6 wt. % of aqueous mannitol solutions from molar volume, viscosity and conductance studies. The energy of activation for nickel sulphate in different composition of aqueous mannitol have also been calculated from conductance and viscosity data.

Keywords : Molar volume, viscosity, conductance, nickel sulphate-water-mannitol system.

Introduction

The study of apparent molar volumes of electrolytes at infinite dilution, B parameter of Jones-Dole equation and their dependence on temperature, molar conductance at infinite dilution and Walden product studies can furnish useful information on the nature of solute-solvent interactions. The behaviour of electrolytes in aqueous carbohydrates and carbohydrates containing small quantity of ions which are present in body fluids have recently been subject of interest[1-7]. Increasing concern over the toxicity of metals in environment has led to increase research activity to indentify the fate of these metal ions in the organisms. Nickel is an essential trace element for several hydrogenase and ureases enzymes. Its deficiency in food slows down the functioning of liver in chicks. It is highly toxic to plants and moderately toxic to mammals. The nickel requirement for adults should not exceed 25–35 mg/day, as it disturbs Mg and Zn metabolism. Nickel is carcinogenic if present in higher concentration in biological system. The study of nickel sulphate in water and 2, 4 and 6 wt. % of aqueous mannitol at 303.15, 308.15, 313.15 and 318.15 K temperature was carried out to understand the nature of solute-solute and solute-solvent interactions by measuring the density, molar volume, molar conductance and viscosity of their solutions.

Experimental

Water used for solutions had specific conductance in range $0.1–1.0 \times 10^{-6}$ Ω^{-1} cm^{-1}. Nickel sulphate and mannitol (AnalaR) were dried over anhydrous calcium chloride for more than 48 h and used as such. All the solutions were prepared by weight and conversion of molality to molarity was done by using the standard expression[8]. The concentration range of $NiSO_4.7H_2O$ in water and 2, 4 and 6 wt. % aqueous mannitol solutions was 0.01 to 0.12 M. The density was measured with the help of DSA (Density and Sound Analyser) 5000, Antor Paar, GmbH, Garz, Austria. Viscosity was determined with the help of capillary type Viscometer[9]. The conductance was measured with the help of calibrated Digital conductivity meter, CM 180, Elico Limited. All measurements were made in a water bath maintained at 30, 35, 40, 45 °C (± 0.05).

Results and discussion

The apparent molar volume of nickel sulphate in water and 2, 4 and 6 wt. % of aqueous mannitol solutions have been calculated from density data (Table 1) by using eq. (1),

$$\phi_v = \frac{M_2}{d^o} - \frac{1000(d - d^o)}{mdd^o} \qquad (1)$$

Table 1. Densities, apparent molar volumes, relative viscosities and molar conductance of nickel sulphate in different compositions of aqueous mannitol at different temperatures

Concentration, $C \times 10^2$ (mol L^{-1})	Density, d (g cm^{-3})	Apparent molar volume, ϕ_v (cm^3 mol^{-1})	Relative viscosity (η/η_o)	Molar conductance Λ_m (Ω^{-1} cm^2 mol^{-1})
		Water		
Temp. = 303.15 K	d_o = 0.995670		η_o = 0.79730 cP	
0.9946	0.997435	105.30	1.00542	150.81
1.9872	0.999175	106.36	1.01216	140.90
3.9659	1.002608	107.80	1.02497	128.60
5.9359	1.005986	108.94	1.03879	119.61
7.8972	1.009321	109.87	1.05229	111.43
9.8496	1.012614	110.70	1.06583	104.57
11.7932	1.015879	111.36	1.08008	98.36
Temp. = 308.15 K	d_o = 0.994060		η_o = 0.71900 cP	
0.9930	0.995807	107.55	1.00430	161.12
1.9839	0.997535	108.32	1.01005	151.22
3.9593	1.000947	109.53	1.02264	138.91
5.9260	1.004314	110.43	1.03562	128.25
7.8841	1.007645	111.15	1.04938	120.50
9.8333	1.010934	111.86	1.06275	113.90
11.7738	1.014203	112.37	1.07692	107.02
Temp. = 313.15 K	d_o = 0.992240		η_o = 0.65260 cP	
0.9912	0.993973	109.47	1.00373	171.51
1.9803	0.995690	110.09	1.00943	161.59
3.9520	0.999092	110.92	1.02204	149.29
5.9151	1.002456	111.58	1.03467	140.32
7.8696	1.005794	112.06	1.04854	130.88
9.8154	1.009095	112.57	1.06164	123.28
11.7525	1.012375	112.96	1.07518	116.57
Temp. = 318.15 K	d_o = 0.990250		η_o = 0.59720 cP	
0.9892	0.991982	110.14	1.00304	181.96
1.9763	0.993699	110.71	1.00822	177.10
3.9441	0.997102	111.49	1.02074	159.73
5.9034	1.000469	112.11	1.03372	149.08
7.8540	1.003803	112.64	1.04672	141.33
9.7961	1.007112	113.07	1.05977	133.73
11.7295	1.010395	113.45	1.07329	127.03
		2% Aqueous mannitol		
Temp. = 303.15 K	d_o = 1.002160		η_o = 0.84128 cP	
1.0013	1.004095	86.48	1.00604	129.83
2.0007	1.005950	90.31	1.01266	124.96
3.9934	1.009558	94.50	1.02679	115.19
5.9774	1.013019	98.10	1.03988	107.07
7.9528	1.016428	100.36	1.05491	100.59
9.9188	1.019727	102.66	1.06797	95.78
11.8751	1.022932	104.86	1.08132	90.95

Table-1 (contd.)

Temp. = 308.15 K	d_o = 1.000390			η_o = 0.75668 cP	
0.9995	1.002350		84.48	1.00579	150.07
1.9973	1.004240		87.81	1.01222	135.18
3.9867	1.007876		92.80	1.02568	130.43
5.9675	1.011342		97.05	1.03903	122.33
7.9394	1.014722		100.06	1.05237	115.88
9.9022	1.018017		102.57	1.06568	110.08
11.8552	1.021218		104.89	1.07860	104.60
Temp. = 313.15 K	d_o = 0.998176			η_o = 0.68143 cP	
0.9974	1.000186		80.11	1.00584	160.42
1.9930	1.002110		84.24	1.01198	150.52
3.9785	1.005799		90.02	1.02492	138.24
5.9556	1.009319		94.51	1.03776	125.93
8.8067	1.014241		99.19	1.05482	114.69
9.8832	1.016070		100.55	1.06332	110.29
11.8325	1.019261		103.40	1.07561	103.95
Temp. = 318.15 K	d_o = 0.996586			η_o = 0.62318 cP	
0.9958	0.998615		78.67	1.00577	180.76
1.9899	1.000577		81.85	1.01149	165.83
3.9726	1.004309		87.98	1.02318	151.03
5.9472	1.007906		92.03	1.03437	139.56
7.9127	1.011305		96.34	1.04584	128.91
9.8691	1.014615		99.66	1.05768	120.58
11.8159	1.017832		102.53	1.06906	112.56

4% Aqueous mannitol

Temp. = 303.15 K	d_o = 1.009241			η_o = 0.88601 cP	
1.0083	1.011169		85.22	1.00766	119.01
2.0147	1.013022		88.79	1.01466	114.16
4.0212	1.016585		93.87	1.02766	106.93
6.0188	1.020036		97.18	1.04183	99.69
8.0067	1.023313		100.81	1.05558	94.92
9.9852	1.026552		103.22	1.06845	91.14
11.9537	1.029701		105.45	1.08189	87.00
Temp. = 308.15 K	d_o = 1.007513			η_o = 0.79488 cP	
1.0066	1.009472		82.60	1.00762	139.08
2.0114	1.011353		86.32	1.01451	129.26
4.0147	1.014950		92.03	1.02717	122.05
6.0091	1.018391		96.28	1.04108	113.16
7.9940	1.021701		99.85	1.05426	106.33
9.9693	1.024921		102.74	1.06672	100.31
11.9344	1.028039		105.38	1.07982	95.52
Temp. = 313.15 K	d_o = 1.005566			η_o = 0.72049 cP	
1.0047	1.007553		80.34	1.00743	149.29
2.0076	1.009449		84.72	1.01443	144.45
4.0073	1.013069		90.93	1.02685	127.27
5.9982	1.016535		95.32	1.04027	118.37

Table-1 (contd.)

7.9795	1.019836	99.38	1.05286	110.28
9.9509	1.023030	102.73	1.06539	103.51
11.9126	1.026165	105.33	1.07829	97.38
Temp. = 318.15 K	d_o = 1.003215		η_o = 0.65431 cP	
1.0024	1.005228	78.40	1.00718	169.59
2.0030	1.007149	82.83	1.01428	159.76
3.9984	1.010822	88.99	1.02636	142.56
5.9850	1.014305	93.97	1.03872	130.33
7.9621	1.017621	98.35	1.05056	121.83
9.9297	1.020845	101.74	1.06196	112.79
11.8874	1.023991	104.52	1.07373	105.15

6% Aqueous mannitol

Temp. = 303.15 K	d_o = 1.016660		η_o = 0.94130 cP	
1.0157	1.018585	83.48	1.00907	108.29
2.0295	1.020434	87.10	1.01636	103.48
4.0504	1.023979	92.45	1.02941	96.29
6.0621	1.027363	96.66	1.04409	92.38
8.0638	1.030615	100.22	1.05726	88.05
10.0556	1.033794	102.93	1.06955	84.53
12.0372	1.036900	105.21	1.08269	81.41
Temp. = 308.15 K	d_o = 1.014906		η_o = 0.84176 cP	
1.0140	1.016852	81.86	1.00890	128.20
2.0261	1.018715	85.83	1.01615	118.46
4.0437	1.022280	91.56	1.02928	111.28
6.0523	1.025715	95.38	1.04266	104.09
8.0508	1.028955	99.53	1.05590	98.13
10.0398	1.032170	102.12	1.06822	92.63
12.0179	1.035235	104.96	1.08044	87.37
Temp. = 313.15 K	d_o = 1.012967		η_o = 0.75504 cP	
1.0121	1.014948	78.90	1.00860	148.20
2.0223	1.016824	83.97	1.01608	133.51
4.0364	1.020430	89.88	1.02882	121.40
6.0414	1.023860	94.52	1.04145	114.21
8.0364	1.027119	98.78	1.05397	108.26
10.0217	1.030310	101.87	1.06612	101.78
11.9962	1.033365	104.92	1.07854	96.70
Temp. = 318.15 K	d_o = 1.010743		η_o = 0.68798 cP	
1.0099	1.012742	77.71	1.00844	158.43
2.0179	1.014645	82.83	1.01568	148.66
4.0279	1.018278	88.69	1.02774	134.07
6.0289	1.021748	93.28	1.04007	122.74
8.0198	1.024992	98.19	1.05224	113.47
10.0015	1.028230	101.05	1.06406	104.98
11.9724	1.031315	104.10	1.07578	97.72

where d^o is the density of solvent, d is the density of solution, m is the molality of solution and M_2 is the molecular weight of nickel sulphate. Errors in ϕ_v were calculated from eq. (2),

$$\Delta\phi_v = (2\Delta d/d^2)(1000/m + M_2) \tag{2}$$

Eq. (2) assumes error to be associated with the density of solution (d) and solvent (d^o). Moreover, errors associated with determination of solution concentration are not the limiting factor while calculating the apparent molar volumes. The error in apparent molar volume as derived from eq. (2) was estimated to range from ± 0.06 cm^3 mol^{-1} at 0.01 M concentration to ± 0.10 cm^3 mol^{-1} at 0.12 M concentration. The densities of various solutions of nickel sulphate in water and 2, 4 and 6 wt. % of aqueous mannitol obey Root's equation and justify the use of Masson's eq. (3) for the estimation of the limiting apparent molar volume,

$$\phi_v = \phi_v^o + S_v\sqrt{C} \tag{3}$$

where ϕ_v^o and S_v are calculated from the intercept and slope from the extrapolation of the plots of ϕ_v versus $\sqrt{C}$. The values of limiting apparent molar volume and slopes S_v are recorded in Table 2. The slope S_v in Masson's equation may be attributed to be as a measure of ion-ion or solute-solute interactions[10-12], low and positive values accounts for weak solute-solute interactions in water and 2, 4 and 6 wt. % of aqueous mannitol solutions. There is a decrease in inter ionic interactions with increase in tem-

perature for nickel sulphate in water, which may be due to more solvation of metal ions with rise in temperature and increase in inter ionic interaction with increase in the temperature for nickel sulphate in 2, 4 and 6 wt. % of aqueous mannitol solutions, which may be due the decrease in solvation of metal ions.

The ϕ_v^o is a measure of solute-solvent interactions[13]. The ϕ_v^o values for nickel sulphate in water are higher than ϕ_v^o values for nickel sulphate in 2, 4 and 6 wt. % of aqueous mannitol solutions, which indicates that solute-solvent interactions are more in water than in aqueous mannitol solutions. The ϕ_v^o values for nickel sulphate in water increases with increase in temperature and it may be due to decrease in hydrogen bonding between water molecules with increase in temperature, thus making more free water molecules available for solvation of metal ions and hence solute-solvent interactions increases with increase in temperature. On the other hand ϕ_v^o values for nickel sulphate in 2, 4 and 6 wt. % of aqueous mannitol decreases with increase in temperature and it may be due to increase in moleculer interactions in water-mannitol system due to extensive hydrogen bonding and thus making less free water molecules available for solvation of metal ions and consequently solute-solvent interactions

Table 2. Limiting apparent molar volume (ϕ_v^o), S_v, apparent molar expansibility (ϕ_E^o) and excess molar volume ($\Delta\phi_v^o$) of nickel sulphate in different compositions of aqueous mannitol at different temperatures

Mannitol wt. %	Temp. (T) (K)	ϕ_v^o (cm^3 mol^{-1})	S_v (cm^3 L$^{1/2}$ mol$^{-3/2}$)	ϕ_E^o (cm^3 mol^{-1} K^{-1})	$\Delta\phi_v^o =$ (ϕ_v^o NiSO$_4$ in aq mannitol $- \phi_v^o$ NiSO$_4$ in water)
0	303.15	102.83	0.249	0.682	–
0	308.15	105.54	0.200	0.483	–
0	313.15	108.06	0.143	0.284	–
0	318.15	108.78	0.137	0.085	–
2	303.15	79.57	0.739	-0.858	-23.26
2	308.15	76.03	0.845	-0.766	-29.51
2	313.15	70.85	0.952	-0.674	-37.21
2	318.15	68.23	0.995	-0.582	-40.55
4	303.15	77.03	0.828	-0.815	-25.80
4	308.15	73.20	0.937	-0.695	-32.34
4	313.15	70.19	1.027	-0.575	-37.87
4	318.15	67.56	1.080	-0.455	-41.22
6	303.15	74.47	0.895	-0.507	-28.36
6	308.15	72.48	0.939	-0.482	-33.06
6	313.15	68.68	1.052	-0.457	-39.38
6	318.15	66.94	1.081	-0.432	-41.84

decreases with increase in temperature.

The temperature dependence of ϕ_v^0 for nickel sulphate in water and 2, 4 and 6 wt. % of aqueous mannitol solutions can be expressed as :

$$\phi_v^0 = -1932.65 + 12.747T - 0.0199T^2 \qquad (4)$$
$$= (NiSO_4.7H_2O \text{ in water})$$

$$\phi_v^0 = 1185.32 - 6.436T + 0.0092T^2 \qquad (5)$$
$$= (NiSO_4.7H_2O \text{ in 2 wt. \% aq. mannitol})$$

$$\phi_v^0 = 1426.90 - 8.091T + 0.012T^2 \qquad (6)$$
$$= (NiSO_4.7H_2O \text{ in 4 wt. \% aq. mannitol})$$

$$\phi_v^0 = 457.99 - 2.023T + 0.0025T^2 \qquad (7)$$
$$= (NiSO_4.7H_2O \text{ in 6 wt. \% aq. mannitol}) \cdot$$

where T is the temperature in Kelvin.

The limiting apparent molar expansibility, $\phi_E^0 = (\partial \phi_v^0/\partial T)_p$, calculated for nickel sulphate from eqs. (4), (5), (6) and (7) are given in Table 2. The values of ϕ_E^0 decreases with increase in temperature for nickel sulphate in water, indicates the absence of "caging effect[14]" and its behaviour is just like common electrolytes[15,16]. The increase in ϕ_E^0 values with increase in temperature for nickel sulphate in aqueous mannitol, indicates the presence of "caging effect[14]" and its behaviour is just like symmetrical tetra-alkyl ammonium salts and like cupric chloride in aqueous mannitol[6].

The structure making/breaking capacity of nickel sulphate may be interpreted with the help of Hepler's reasoning[17], i.e. on the basis of sign of $(\partial^2 \phi_v^0/\partial T^2)_p$. It has been shown from general thermodynamic eq. (8),

$$(\partial \overline{C}_p^0/\partial P)_p = -T(\partial^2 \phi_v^0/\partial T^2)_p \qquad (8)$$

where $\overline{C}_p^0$ is the partial molar heat capacity at infinite dilution. From eq. (8), it is clear that structure making electrolytes should have a positive value of $(\partial^2 \phi_v^0/\partial T^2)_p$ and structure breaking electrolytes should have negative value of $(\partial^2 \phi_v^0/\partial T^2)_p$. For nickel sulphate in water sign of $(\partial^2 \phi_v^0/\partial T^2)_p$ has been found to be negative and for nickel sulphate in 2, 4 and 6 wt. % of aqueous mannitol sign of $(\partial^2 \phi_v^0/\partial T^2)_p$ has been found to be positive, which suggests that nickel sulphate acts as structure breaker in water and structure maker in 2, 4 and 6 wt. % of aqueous mannitol solutions.

The limiting excess molar volume of nickel sulphate

for different compositions of mannitol have been estimated from eq. (9),

$$\Delta \phi_v^0 \text{ (excess)} = \phi_v^0 (A) - \phi_v^0 (B) \qquad (9)$$

where $\phi_v^0 (A)$ is the limiting apparent molar volume of nickel sulphate in different compositions of aqueous mannitol and $\phi_v^0 (B)$ is the limiting apparent molar volume of nickel sulphate in water. The negative value of excess molar volume of nickel sulphate in aqueous mannitol solution may be attributed to the decrease in solute-solvent interactions at infinite dilution.

Viscosity studies :

The viscosity data (Table 1) has been analyzed on the basis of Jones-Dole equation[18],

$$\eta_s/\eta_0 = 1 + A\sqrt{C} + BC \qquad (10)$$

where η_s and η_0 are viscosities of solution and solvent respectively, C is the molar concentration and A and B are constants. The values of A and B have been determined from the intercept and slope of linear plots of $\eta_s/\eta_0 - 1/\sqrt{C}$ versus $\sqrt{C}$. The values of A and B of different solutions are recorded in Table 3.

Parameter A of Jones-Dole equation represents the contribution from solute-solute interactions[19]. The values of A, shows that ion-ion interactions for nickel sulphate in water decreases with increase in temperature, which may be due to more solvation of metal ions. The ion-ion interactions in case of nickel sulphate in aqueous mannitol solutions increases with increase in temperature and composition of mannitol, which may be due to decrease in solvation of metal ions with increase in temperature and composition.

The B parameter which measures the structure making/breaking capacity of an electrolyte in a solution also contain a contribution from structural effects and is responsible for solute-solvent interactions in a solvent[20]. It has been emphasized by a number of workers that dB/dT is more important criteria[21] for determining solute-solvent interactions, as positive B-coefficient obtained from aqueous mannitol can be interpreted as merely due to large size ion. Viscosity study of a number of electrolytes has shown that structure-maker will have negative dB/dT and structure-breaker will have positive dB/dT. The temperature effect on nickel sulphate in water shows a posi-

Table 3. Values of parameters of Jones-Dole equation, limiting molar conductance, Λ_m^o and Walden product for nickel sulphate in different compositions of aqueous mannitol at different temperatures

Mannitol wt.%	Temp. (T) (K)	A (L mol^{-1})$^{1/2}$	B (L mol^{-1})	Λ_m^o (Ω^{-1} cm^2 mol^{-1})	$\Lambda_m^o\,\eta_o$ (Ω^{-1} cm^2 mol^{-1} poise)
0	303.15	−1.80	0.728	171.5	1.38
0	308.15	−3.29	0.744	182.6	1.31
0	313.15	−3.80	0.749	193.8	1.26
0	318.15	−4.64	0.760	206.9	1.24
2	303.15	−1.19	0.723	147.1	1.23
2	308.15	−1.18	0.700	164.2	1.24
2	313.15	−0.74	0.659	183.6	1.25
2	318.15	−0.10	0.586	206.2	1.28
4	303.15	0.94	0.656	132.6	1.17
4	308.15	1.16	0.634	155.8	1.23
4	313.15	1.24	0.619	172.6	1.24
4	318.15	1.71	0.573	196.2	1.27
6	303.15	2.80	0.606	118.9	1.12
6	308.15	2.92	0.587	143.1	1.20
6	313.15	3.00	0.567	164.2	1.23
6	318.15	3.05	0.544	183.7	1.26

tive sign of dB/dT and a negative sign of dB/dT in 2, 4 and 6 wt. % of aqueous mannitol thereby showing that nickel sulphate behaves as structure-breaker in water and structure-maker in 2, 4 and 6 wt. % of aqueous mannitol solutions.

The effect of temperature on the viscosity is given by eq. (11),

$$\eta = A\,e^{E\eta/RT} \tag{11}$$

where A is a constant and E_η is the activation energy for the viscous flow[22] and other symbols have their usual significances. The values of E_η for nickel sulphate in water and 2, 4 and 6 wt. % of aqueous mannitol solutions were calculated from the slope of the linear plots of log η versus $1/T$ and are given in Table 4.

Table 4. Values of E_η and E_Λ for nickel sulphate in different compositions of aqueous mannitol

% Composition of aqueous mannitol	E_η (kJ mol^{-1})	E_Λ (kJ mol^{-1})
0.04 m		
0	15.31	10.81
2	15.95	13.80
4	16.01	13.43
6	16.67	17.41

Table-4 (contd.)

	E_η	E_Λ
0.06 m		
0	15.36	11.49
2	16.05	12.37
4	16.06	13.73
6	16.73	15.61
0.08 m		
0	15.39	12.24
2	16.09	12.24
4	16.09	11.25
6	16.76	13.43
0.10 m		
0	15.43	12.99
2	16.19	11.25
4	16.17	10.13
6	16.79	12.37
0.12 m		
0	15.52	13.67
2	16.31	10.20
4	16.20	10.20
6	16.80	10.13

Conductance studies :

The limiting molar conductance Λ_m^o for nickel sulphate in water and 2, 4 and 6 wt. % of aqueous mannitol

solutions were obtained by extraploating the linear plots of Λ_m (Table 1) versus $\sqrt{C}$ to zero concentration. The limiting molar conductance for nickel sulphate in water and 2, 4 and 6 wt. % aqueous mannitol solutions at 303.15, 308.15, 313.15 and 318.15 K temperatures are recorded in Table 3, shows that limiting molar conductance increases with increase in temperature, which may be due to increase in ionic mobility of free Ni^{2+}, SO_4^{2-} ions at infinite dilution.

Since in the state of infinite dilution, the motion of an ion is limited solely by its interaction with surrounding solvent molecules, there are no other ions with in a finite distance. Therefore evaluation of Λ_m^o should give equally reliable information regarding ion-solvent interactions[23]. Greater value of Λ_m^o may therefore be interpreted as a measure of greater ion-solvent interactions. The order of solute-solvent interactions for nickel sulphate in aqueous mannitol solutions follow as : water > 2 wt. % aq. mannitol > 4 wt. % aq. mannitol > 6 wt. % aq. mannitol. It
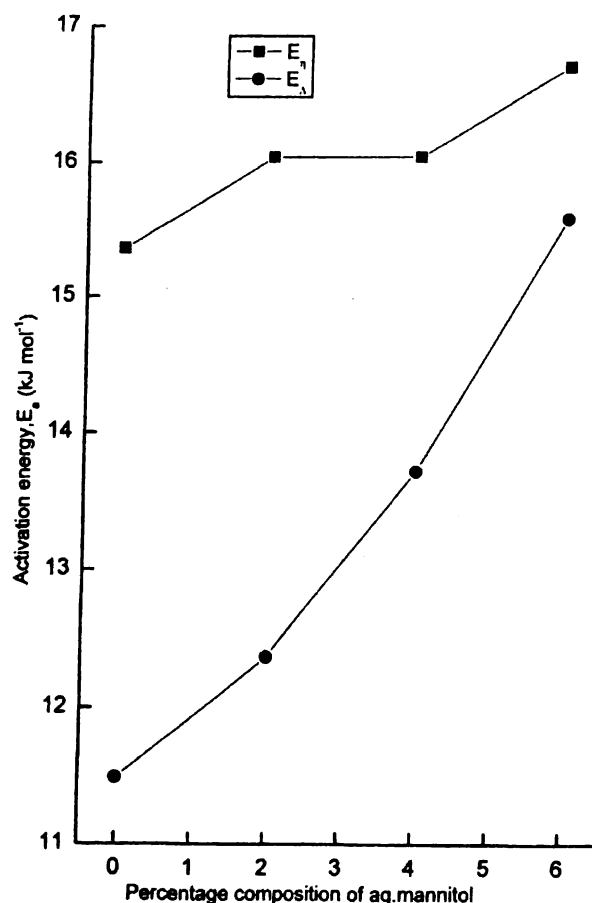
may be due to more solvation of metal ions in water than water-mannitol system and it may also be due to increase in association of nickel sulphate with increase in mannitol composition. The Walden product data $(\Lambda_m^o \eta_0)$ have been recorded in Table 3. The structure making/breaking nature of electrolyte have been determined from temperature coefficient of Walden product i.e. $[d\ (\Lambda_m^o \eta_0)/dT]^{24}$. The negative temperature coefficient of Walden product for nickel sulphate in water suggests an increase in the ion-solvent interactions which indicates that nickel sulphate in water behaves as structure-breaker. The positive temperature-coefficient of Walden product for nickel sulphate in aqueous mannitol suggests that there is decrease in the ion-solvent interactions which indicates that nickel sulphate in aqueous mannitol behaves as structure-maker.

The effect of temperature on conductance is given by equation[25],

$$\Lambda = \Lambda_0\ e^{-E_A/RT} \tag{12}$$

where E_A is the activation energy for conduction and other symbols have their usual significance. The values of E_A for nickel sulphate in water and 2, 4 and 6 wt. % aqueous mannitol were calculated from the slope of the linear plots of $\log \Lambda$ versus $1/T$ and are given in Table 4.

A sample plot of activation energy from viscosity and conductance data versus percentage composition of aqueous mannitol for nickel sulphate (0.06 m) is shown in Fig. 1. The energy of activation for conductance[25], E_A should be less than energy of activation for viscous flow, E_η and it has been found that $E_A < E_\eta$ for nickel sulphate (0.04–0.12 m) in water and 2, 4 and 6 wt. % of aqueous mannitol solutions.

Fig. 1. Plot of activation energy vs percentage composition of aq. mannitol for nickel sulphate (0.06 m).

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