Effect of $NiCl_2·6H_2O$ and $CoCl_2·6H_2O$ on the Viscosity of Aqueous Ethanol Mixtures

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The viscosity of transition metal chlorides ($CoCl_2$ and $NiCl_2$) in aqueous ethanol mixtures (10 % to 50 % (v/v)) was measured in the concentration range ((1.0 to 8.0)·10^{-2}) mol·dm^{-3} at different temperatures ((30 to 50) °C) with an interval of 5 °C. It was found that the viscosities increase with an increase in the concentration of the salts and percent composition of ethanol mixtures. An increase in temperature results in a decrease in the viscosities. Ion−ion and ion−solvent interactions were studied on the basis of the Jones−Dole equation. The values of the *A* and *B* coefficients increase (also irregular), with an increase in the salt percent composition of the ethanol mixtures and temperature. Negative values of the *B* coefficient show that the ion−solvent interaction is small and suggest that cobalt chloride and nickel chloride behave as structure breakers in the aqueous ethanol system. An attempt was also made to determine the energy of activation. It decreases with an increase in the concentration of salt and increases with an increase in percent composition of the ethanol mixtures.

Introduction

It was previously reported[1] that the nature of salts such as LiCl and NaCl in mixed solvent systems such as aqueous butanol can be interpreted in terms of ion−ion and ion−solvent interactions using Jones−Dole equations.[2,8,12] These interactions help to characterize the behavior of the electrolytes used. There are two coefficients of this equation. One of them is the *B* coefficient which, because the ion−solvent interaction decreased with a rise in temperature, led to the conclusion that LiCl and NaCl in an aqueous butanol mixture behave as structure makers, whereas in aqueous media where electrolytes show negative values of the *B* coefficient, they are recognized as structure breakers. Recently, the effect of strong electrolytes (NaOH, HCl, and NaCl) on the viscosity of an edible oil-like sunflower, maize, and canola oils using 1,4-dioxane as solvent was reported.[3−5] The results revealed that these electrolytes behave as structure breakers. The present paper deals with the effect of cobalt chloride ($CoCl_2·6H_2O$) and nickel chloride ($NiCl_2·6H_2O$) on the viscosity of aqueous ethanol mixtures.

Experimental Material

Extra pure $CoCl_2·6H_2O$ and $NiCl_2·6H_2O$ (Merck, 99 % and 98 %, respectively) and ethanol (99.9 % pure, from BDH Analar Grade) were used without purification. The freshly prepared double distilled water conductivity (0.06 μS·cm^{-1}) was used in the preparation of the solvent.

Procedure. Different percentage compositions (v/v) of the water/ethanol system were prepared in double distilled water. These were 10 %, 20 %, 30 %, 40 %, and 50 % aqueous ethanol mixtures. Solutions of cobalt chloride and nickel chloride were prepared within the concentration range (1.0·10^{-2} to 9.0·10^{-2}) mol·dm^{-3}. The viscosity of the solutions was measured with the help of an Ostwald-type viscometer kept in a thermostat bath (type Hack W13) manufactured by Haake Karlshuhes, Germany, for maintaining constant temperature during the experiment. Known volumes of both solvent and solution were placed in the viscometer for 15 min to attain constant temperature. The time of flow between the two marks of the viscometer was recorded with the help of a stop watch with a precision of 0.25 s. The average of three measurements of each solution was recorded to ensure the reproducibility of the observations. The densities of the solvents and solutions were measured with the help of a relative density bottle having a capacity of 10 mL. The measurements were performed at different temperatures ranging from (30 to 50) °C with a difference of (5 ± 0.1) °C.

Results and Discussion

The time of flow for transition metal chlorides ($CoCl_2·6H_2O$ and $NiCl_2·6H_2O$) was measured in 10 %, 20 %, 30 %, 40 %, and 50 % aqueous ethanol at various temperatures ((30 to 50) ± 0.1) °C with a difference of 5 °C. Tables 1 and 2 include the viscosity values in (10 to 50) % aqueous ethanol at the abovementioned temperatures. The results indicate that the viscosity of the metal chlorides in aqueous ethanol increases with increasing concentration while it decreases with a rise in temperature. Similar behavior was also observed in the case of electrolytes of group I of the periodic table in the aqueous ethanol system[1] and strong electrolytes such as HCl, NaCl, and NaOH on the viscosity values of edible oil in 1,4-dioxane.[3−5]

The viscosities of transition metal chlorides in aqueous ethanol were found to follow the Jones−Dole equation[2]

$$\eta_{sp}/\sqrt{C} = A + B\sqrt{C} \qquad (1)$$

where η_{sp} is specific viscosity, i.e., the ratio of difference between the solution viscosity (η) and solvent viscosity (η_o) to the solvent viscosity (($\eta - \eta_o$)/η_o). *A* and *B* are coefficients of viscosity, and $\sqrt{C}$ is the square root of the concentration of salt. The values of the *A* and *B* coefficients of this equation

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Table 1. Viscosity of Cobalt Chloride ($CoCl_2 \cdot 6H_2O$) in Aqueous Ethanol

10^2[salt]	viscosities/m·Pa·s at different temperatures				
mol·dm^{-3}	30 °C	35 °C	40 °C	45 °C	50 °C
10 % Aqueous Ethanol					
η_o	6.791	6.191	5.909	5.763	5.305
1.00	7.281	6.354	6.160	6.025	5.581
2.00	7.456	6.394	6.232	6.078	5.640
4.00	7.806	6.428	6.326	6.161	5.729
6.00	7.820	6.415	6.366	6.219	5.746
8.00	7.920	6.404	6.357	6.183	5.761
20 % Aqueous Ethanol					
η_o	9.735	8.710	7.442	6.476	5.980
1.00	10.143	9.237	8.149	7.191	6.618
2.00	10.204	9.357	8.351	7.402	6.738
4.00	10.277	9.641	8.678	7.732	7.007
6.00	10.379	9.657	8.827	7.929	7.197
8.00	10.476	9.668	8.896	7.944	7.226
30 % Aqueous Ethanol					
η_o	11.864	8.8155	8.614	7.970	6.980
1.00	12.266	9.114	9.157	8.679	7.929
2.00	12.390	9.656	9.224	8.960	8.213
4.00	12.426	9.883	9.285	9.156	8.590
6.00	12.418	9.918	9.335	9.314	8.853
8.00	12.283	10.052	9.420	9.439	8.975
40 % Aqueous Ethanol					
η_o	12.538	11.471	9.262	8.844	7.081
1.00	13.321	12.425	10.173	9.693	8.185
2.00	13.591	12.781	10.373	9.927	8.552
4.00	13.826	13.121	10.656	10.240	9.046
6.00	13.993	13.554	10.821	10.405	9.318
8.00	14.041	13.446	11.025	10.367	9.524
50 % Aqueous Ethanol					
η_o	14.258	12.164	11.397	8.776	8.250
1.00	15.195	13.194	12.485	9.622	9.096
2.00	15.259	13.410	12.796	9.785	9.282
4.00	15.506	13.763	13.931	9.957	9.640
6.00	15.716	14.011	13.534	10.135	9.806
8.00	15.870	14.213	13.427	10.329	9.684

Table 2. Viscosity of Nickel Chloride ($NiCl_2 \cdot 6H_2O$) in Aqueous Ethanol

10^2[salt]	viscosities/m·Pa·s at different temperatures				
mol·dm^{-3}	30 °C	35 °C	40 °C	45 °C	50 °C
10 % Aqueous Ethanol					
η_o	6.791	6.191	5.909	5.763	5.305
1.00	8.678	8.063	7.214	6.921	6.357
2.00	9.364	8.659	7.610	7.181	6.421
4.00	9.802	9.113	7.717	7.177	6.538
6.00	10.210	9.481	7.855	7.303	6.565
8.00	10.564	9.683	7.814	7.132	6.295
20 % Aqueous Ethanol					
η_o	9.735	8.710	7.442	6.476	5.980
1.00	10.971	9.807	8.687	7.828	7.203
2.00	10.960	9.855	8.765	7.912	7.247
4.00	11.059	9.865	8.890	8.044	7.371
6.00	10.927	9.648	8.863	8.211	7.415
8.00	10.533	8.956	8.325	7.886	7.129
30 % Aqueous Ethanol					
η_o	11.864	8.8155	8.614	7.900	6.980
1.00	13.026	10.843	9.776	9.037	7.093
2.00	13.004	11.177	9.807	8.994	8.016
4.00	12.884	11.390	9.791	8.769	7.915
6.00	12.300	11.598	9.394	8.499	7.711
8.00	11.897	11.762	8.930	8.324	7.493
40 % Aqueous Ethanol					
η_o	12.538	11.471	9.262	8.844	7.081
1.00	14.456	12.985	11.008	10.276	8.263
2.00	14.594	12.995	11.095	10.269	8.292
4.00	14.506	12.815	11.291	10.170	8.270
6.00	14.621	12.465	11.031	9.970	8.013
8.00	14.275	11.860	10.833	9.579	7.661
50 % Aqueous Ethanol					
η_o	14.258	12.164	11.397	8.776	8.250
1.00	16.149	14.012	13.384	11.084	9.900
2.00	16.250	14.262	13.620	11.651	9.976
4.00	16.451	14.110	13.586	11.900	10.046
6.00	15.829	13.742	13.406	12.033	9.745
8.00	15.306	13.367	12.718	11.941	9.416

were determined from the intercepts and slopes of linear plots of $\eta_{sp}/\sqrt{C}$ vs $\sqrt{C}$. The representative plots are shown in Figures 1 and 2, and results are tabulated in Tables 3 and 4. The *A* coefficient of the Jones−Dole equation represents ion−ion interactions. It was observed that the value of the *A* coefficient increased with a rise in temperature and also with an increase in ethanol content for both salts. This shows that the ion−ion interaction increased with temperature and percent composition of ethanol with some variations. As the concentration of the organic solvent increases, the dielectric constant of the medium decreases and the ion−ion interaction (*A* coefficient) increased with some exceptions. In mixed solvent system such as aqueous alcohol mixtures, H-bonding to O−H continuously changes the structure of water because of both their cluster forming and cluster disturbing character.[6−8] The order of H-bonding becomes stronger, and proton accepting ability increases from methanol to butanol in the following order: But-OH > Pr−OH > Et−OH > Me−OH. In water/alcohol mixtures, each water molecule can form hydrogen bonds with an alcohol molecule because of the reduced proton concentration and reduced dielectric constant. It is certain from the exothermic contribution of mixing that strong bonds between water and alcohol are formed. Water forms strong coordinating bonds with the transition metal ion and can also form strong hydrogen bonds with negative ions such as fluoride, bromide, and hydroxide. The mixing solute and solvent results in two types of interactions, ion−ion and ion−solvent. This may be due to the interpenetration effect (cation−cation and cation−anion) which brings ions together and is responsible for the increase in ion−ion interactions.[9,10] Similarly, the values of the *B* coefficient were obtained from the slope of linear plots of $\eta_{sp}/\sqrt{C}$ vs $\sqrt{C}$ (Figures 1 and 2). The values of the *B* coefficient are summarized in Tables 3 and 4. These values are influenced by the variation in temperature and composition of the solvent. These coefficients describe the ion−solvent interaction. In both the cobalt chloride and nickel chloride systems, the values are negative and the variation is irregular. The negative values of the *B* coefficient in aqueous ethanol show the structure breaking effect.[11,12] The variation of the *B* values with a change in the percent composition of the solvent represents ion−solvent interaction. The smaller the ion, the stronger the electrostatic interaction and hence the greater the size of the solvent ion. Negative values of the *B* coefficient

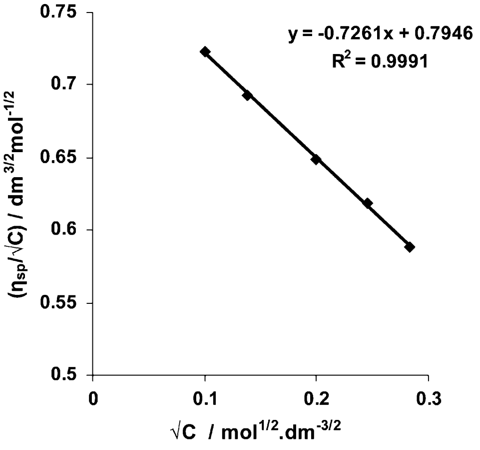

Figure 1. Plot of $\eta_{sp}/\sqrt{C}$ vs $\sqrt{C}$ for $CoCl_2 \cdot 6H_2O$ in 10 % aqueous ethanol at 30 °C.

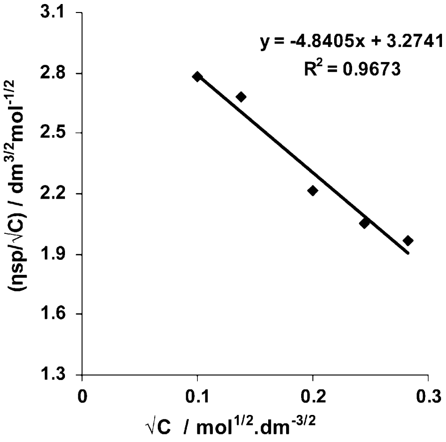

Figure 2. Plot of $\eta_{sp}/\sqrt{C}$ vs $\sqrt{C}$ for $NiCl_2\cdot 6H_2O$ in 10 % aqueous ethanol at 30 °C.

Table 3. Values of Parameters *A* and *B* of the Jones−Dole Equation at Different Compositions of $CoCl_2\cdot 6H_2O$ in Aqueous Ethanol at Various Temperatures

temp	*A* and *B* coefficient of the Jones−Dole equation in different aqueous ethanol solvents				
°C	10 %	20 %	30 %	40 %	50 %
	A Coefficient/$mol^{-1/2}\cdot dm^{3/2}$				
30	0.7946	0.4721	0.4684	0.7425	0.7286
35	0.3446	0.7088	0.8318	0.9733	0.9413
40	0.5089	1.0742	0.7557	1.1154	1.1107
45	0.5453	1.2450	1.1733	1.1364	1.1017
50	0.6269	1.1754	1.5258	1.7396	1.2088
	B Coefficient/$mol^{-1}\cdot dm^{3}$				
30	−0.7261	−0.8044	−1.1721	−1.1159	−1.2719
35	−0.7880	−1.0775	−1.2116	−1.2841	−1.3005
40	−0.8194	−1.3146	−1.6338	−1.6812	−1.5834
45	−0.9961	−1.4641	−1.7755	−1.7907	−1.8549
50	−1.1564	−1.5323	−1.8148	−1.8263	−1.9642

Table 4. Values of Parameters *A* and *B* of the Jones−Dole Equation at Different Compositions of $NiCl_2\cdot 6H_2O$ in Aqueous Ethanol at Various Temperatures

temp	*A* and *B* coefficient of the Jones−Dole equation in different aqueous ethanol solvents				
°C	10 %	20 %	30 %	40 %	50 %
	A Coefficient/$mol^{-1/2}\cdot dm^{3/2}$				
30	3.2839	1.6924	1.4699	1.9913	1.8583
35	3.6008	1.8348	2.8091	1.8974	2.1408
40	2.8314	2.2461	1.959	2.4703	2.4169
45	2.6237	2.6296	2.0116	2.2179	3.3614
50	2.5576	2.6139	2.1996	2.3274	2.7061
	B Coefficient/$mol^{-1}\cdot dm^{3}$				
30	−4.8716	−4.9856	−5.2616	−5.4819	−5.6718
35	−5.8148	−5.9799	−6.1071	−6.3639	−6.4843
40	−6.0821	−6.3201	−6.4815	−6.7993	−7.0887
45	−6.4070	−6.6181	−6.7978	−6.9813	−7.5205
50	−6.7292	−6.9129	−7.1816	−7.3075	−7.9676

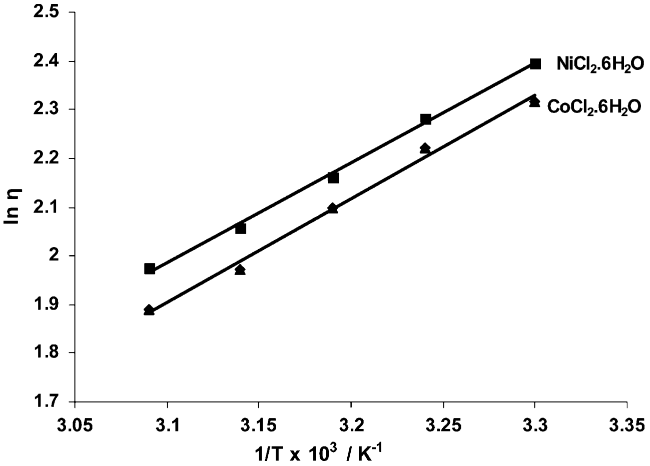

Figure 3. Plot of ln η vs 1/*T* for $CoCl_2\cdot 6H_2O$ and $NiCl_2\cdot 6H_2O$ in 20 % aqueous ethanol at 30 °C.

Table 5. Energy of Activation for Cobalt Chloride ($CoCl_2\cdot 6H_2O$) in (10 to 50) % Aqueous Ethanol

[salt]·10²	activation energy E_η/kJ·mol⁻¹ in aqueous ethanol solvent				
mol·dm⁻³	10 %	20 %	30 %	40 %	50 %
1.00	9.4613	17.6273	14.9801	17.6880	21.4201
2.00	9.8820	16.9763	20.5680	18.7638	20.8756
4.00	10.7500	15.6718	13.2284	17.4602	20.3219
6.00	10.5537	20.8215	13.01307	17.1576	20.1863
8.00	10.9137	14.9785	11.2488	16.5606	20.8165

Table 6. Energy of Activation for Nickel Chloride ($NiCl_2\cdot 6H_2O$) in (10 to 50) % Aqueous Ethanol

[salt]·10²	activation energy E_η/kJ·mol⁻¹ in aqueous ethanol solvent				
mol·dm⁻³	10 %	20 %	30 %	40 %	50 %
1.00	12.3845	17.0727	22.3147	21.5731	19.3383
2.00	15.0142	16.7302	18.9808	21.7560	18.7763
4.00	16.7352	16.2463	19.7366	21.5864	18.4587
6.00	18.2600	15.0034	19.8272	22.7504	17.5866
8.00	21.3985	14.5835	20.1980	23.2916	17.3039

suggest that the solute behaves as a structure breaker in aqueous ethanol. This arises from a breaking of the regular arrangements of solvent molecules due to the dipole interaction with the solute. At higher temperature, the surrounding sheath of the solvent molecules around the ion is broken and ion−solvent interaction weakens. Under such circumstances, ions may get a chance to interact with each other. The irregularities in the values of the *B* coefficients may be because of the degree of hydrolysis in different percent compositions of the solvent. The solute of higher molecular weight indicates that ion−solvent interaction is not strong, and the smaller the ions, the larger the ion−solvent interactions will be.[13,14] The viscosity of a liquid generally decreases with a rise in temperature. This has been explained in terms of the Hole theory of liquids. Intermolecular distances are relatively larger in liquids than in solids. A liquid molecule therefore needs some activation energy to move into a hole. As the activation energy becomes increasingly available with an increase in temperature, a liquid flows more frequently at high temperature. The coefficient of viscosity thus falls appreciably with a rise in temperature. Arrhenius[15] recognized that this typical dependence predicts an exponential increase of the rate or rate constant with temperature. This empirical relation[15] can be conveniently written as

$$\log \eta = \log A + E_\eta/2.303RT \qquad (2)$$

where *A* is called the pre-exponential factor constant for a given liquid; E_η is the energy of activation; *R* is the gas constant; and *T* is absolute temperature. The slope of a linear plot of log η vs 1/*T* determines the value of the energy of activation for the aqueous ethanol for transition metal salts. The values of the activation energy as a function of salt concentration and solvent composition are tabulated in Tables 5 and 6. The representative plots of energy of activation are shown in Figure 3 at $1.0\cdot 10^{-2}$ mol·dm⁻³ (in 20 % aqueous ethanol) of $CoCl_2$ and $NiCl_2$. These results show that the energy of activation is influenced by the concentration of salt and percent composition of solvent. These results also show a decrease in energy of activation with an increase in the concentration of salts. It is also noted that there is an irregular increase or decrease in the energy of activation at different solvent compositions. The increase in activation energy may be due to the fact that at higher solvent composition there is a mobility of ions. It will make it difficult to produce vacant sites in the solvent matrix. This results in a higher energy of activation. The results also show that the activation energy of $NiCl_2$ is higher than that of $CoCl_2$ at a fixed percentage composition of the aqueous ethanol mixture. This reveals that the larger ion produces less vacant sites and increases the viscosity and energy of activation. The values of the activation energy are in agreement with the values of the activation energy of sodium oxalate and sodium tartarate[16] and LiCl and NaCl.[1]

Conclusion

The viscosity data were evaluated in terms of the Jones−Dole coefficients *A* and *B* representing ion−ion and ion−solvent interactions, and it was concluded that cobalt chloride and nickel chloride behave as structure breakers in aqueous ethanol solvents.

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