Viscosity Studies of Some First Transition Metal Chlorides Dissolved in Methanol

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Viscosity studies are reported at 20° and 45° C. for $CaCl_2$, $CrCl_3 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 2H_2O$, $CuCl_2 \cdot 2H_2O$, and $ZnCl_2$ (data also at 5° and 25° C. for $ZnCl_2$) dissolved separately in pure methanol. For each salt studied, the ratio, Q (salt molar viscosity at 20° to salt molar viscosity at 45° C.) is independent of the salt concentration. Q is also independent of the degree of hydration for cobalt and nickel chlorides. Q appears to have the same value for all these salts. The new data are used to test the Jones-Talley and the Dawson-Zimmerman equations. Viscosity and conductance data for the first-transition metal chlorides are compared.

JONES AND TALLEY (*13*) found that in aqueous solutions, the solution viscosity (η), the solvent viscosity (η_o) and the salt concentration (C is moles/liter) were related thus:

$$(\eta - \eta_o)/(\eta_o C^{1/2}) = A + BC^{1/2} \qquad (1)$$

Jones and Fornwalt (*12*) showed that this equation fitted data for some salt-methanol soltuions at 25° C. Gurney (*10*) has discussed the significance of the parameters A and B, which are characteristic of the salt. For all solutions studied, A was found to be approximately 1% of B.

Dawson and others (*2*) reported that viscosity data for zinc halide–methanol solutions, collected at temperatures between −50° C. and 20° C., fit the equation:

$$\log_{10}(\eta - \eta_o) = a \log_{10} C + (b + \log_{10}\eta_o) - (d + eT^2 - fT^3)/T \qquad (2)$$

Here T is the absolute temperature; a, b, d, e, and f are 1.39, 5.46, 542.0, 0.013, and "approximately zero," respectively, for $ZnCl_2$ (*2*); $d = E_{\text{vis}}/2.303\,R$ where E_{vis} is the activation energy for viscous flow of the solvent.

Viscosity studies were reported by de Maine and Russell (*6*) for methanol and methanol–carbon tetrachloride solutions containing only $SnCl_2 \cdot 2H_2O$, only $SnCl_4 \cdot 5H_2O$, or $SnCl_2 \cdot 2H_2O$ and $SnCl_4 \cdot 5H_2O$. They found that the ratio, Q (salt molar viscosity at 20° C./salt molar viscosity at 45° C.), was independent of the salt concentration for each salt system and solvent composition studied. Plots of η_{salt}(salt molar viscosity coefficient or $(\eta - \eta_o)/C$) *vs.* the salt concentration were linear for each temperature and solvent composition studied.

The ratio, R (molar conductance at 45° C./molar conductance at 20° C.) for methanol solutions of each of 14 first transition metal chlorides is independent of the salt concentration and of the degree of hydration (*4*). For $ZnCl_2$ the ratio R slowly increased from near 0.830 to near 0.973 as the salt concentration was increased from 0.200M to 1.000M. R values continue to decrease at lower salt concentrations.

Here are reported viscosity studies at 20° and 45° C. for $CaCl_2$, $CrCl_3 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 2H_2O$, $CuCl_2 \cdot 2H_2O$ and $ZnCl_2$ (also data at 5° and 25° C. for $ZnCl_2$) dissolved separately in pure methanol. The new data are used to test the Jones-Talley and Dawson-Zimmerman equations. Viscosity data are compared to conductance data for corresponding systems.

EXPERIMENTAL

The materials used and the concentrations studied are shown in Table I. $CoCl_2 \cdot 2H_2O$ and $NiCl_2 \cdot 2H_2O$ were prepared by the method of Bose and Khundkar (*1*), from the hexahydrates. Chloride contents of all salts were determined by the Fajan adsorption indicator method (*9*). Theoretical and experimental chloride contents checked to within 1%.

Methanol solutions with the desired salt concentrations were made as described in reference (*5*), except that solutions containing dehydrated salts were prepared in a dry nitrogen atmosphere (*3*).

Flow times were measured for all solutions at 20° and 45° C. ($ZnCl_2$ also at 5° and 25° C.) with Ostwald-Fenske viscometers or with the new Free-Flow Electroviscometer (*7*). Densities of the solutions at each temperature were calculated with the assumption that the most concentrated salt-methanol solution mixed with methanol without volume contraction or expansion. Numerous experiments showed that calculated and measured densities agreed to within 0.5% at all temperatures.

A calibration chart (viscosity coefficient *vs.* density times flow-time) was used to compute the viscosity coefficients from data collected with the electroviscometer (*7*). Recently we have used statistical methods to show that viscosity coefficients determined by this method are accurate to within 0.57%.

RESULTS

Plots of the data according to the Jones-Talley equation yielded straight lines with small intercepts and positive slopes (Figure 1). Data for $SnCl_2 \cdot 2H_2O$ and $SnCl_4 \cdot 5H_2O$ in methanol (*6*) are included.

Salt molar viscosities ($\eta_{\text{salt}} = \eta_{\text{sp}}\eta_o/C$) appear to be linearly dependent on the salt concentration at each temperature for each salt studied, (Figures 2 and 3). The ratio Q (η_{salt} at 20°/η_{salt} at 45° C.) appears to be independent of the salt concentration for each of the nine salts studied (Table II). ΔH_Q values (Table II) were calculated from average Q values with the following equation:

$$\log_{10} Q = -\frac{\Delta H_Q}{2.303\,R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

For $ZnCl_2$, ΔH_Q appears to be independent of the temperature range. Average R and ΔH_R (4) values are included together with data for tin chlorides.

The Dawzon-Zimmerman equation (2) would predict that the ratio Q should be independent of the salt concentration. Plots of $\log_{10}\eta_{salt}$ *vs.* $\log_{10}[ZnCl_2]$ are linear with the slope equal to 0.34 at both 25° and 45° C. (Figure 3) only for $ZnCl_2$ concentrations greater that 0.500*M*. We found a value for *a* which is within 3.6% of the value reported by Dawson and others (2).

DISCUSSION

The new data suggest that for methanol solutions the Jones-Talley equation applies approximately over the entire concentration range for each salt studied. Plots for several salts are given in Figure 1. Constant Q values found for all salts (Table II) are' predicted by the Jones-Talley equation since the intercept A is usually small compared to B (Table III). Since ΔH_Q for each salt is, within experimental error, the same (Table II) Q must depend largely on some property of the solvent, and not on the geometry and charge of the ions or ion pairs as suggested by Gurney (*10*). It is difficult to understand why salts with such different molar conductance values (*4, 8*) should have ΔH_Q values so similar (Table II) if Q is in fact dependent in some way on the ion charges (*10*). Moreover the negative A values found for some salts (Table III) are not predicted by the Jones-Talley equation.

While the Dawson-Zimmerman equation also predicts that the ratio, Q should be independent of the salt concentration, the new data for $ZnCl_2$ indicate that at best this equation is applicable for a limited concentration range.

The linear plots from the salt molar viscosity equation (*6*) suggest that the salt molar viscosity coefficients may be of fundamental significance. Moreover, we have found that methanol- $Cd(NO_3)_2 \cdot 6H_2O$, $CeCl_3 \cdot 7H_2O$, or $Cd(C_2H_3O_2)_2 \cdot 2H_2O$ solutions do not obey the Jones-Talley equation but do obey the salt molar viscosity equation.

The increase in viscosity coefficient in passing from the dihydrate to the hexahydrate of nickel (Figure 1) or cobalt chloride can be attributed to the added water in the solution. Our experiments show that addition of 1% (by volume) of water to pure methanol actually increases the viscosity coefficient by 5.5%. Hartley and Raikes (*11*) reported that 0.1% of water increased the viscosity coefficient of pure methanol at 25° C. by 0.4%.

Comparison of Q values with the corresponding R values

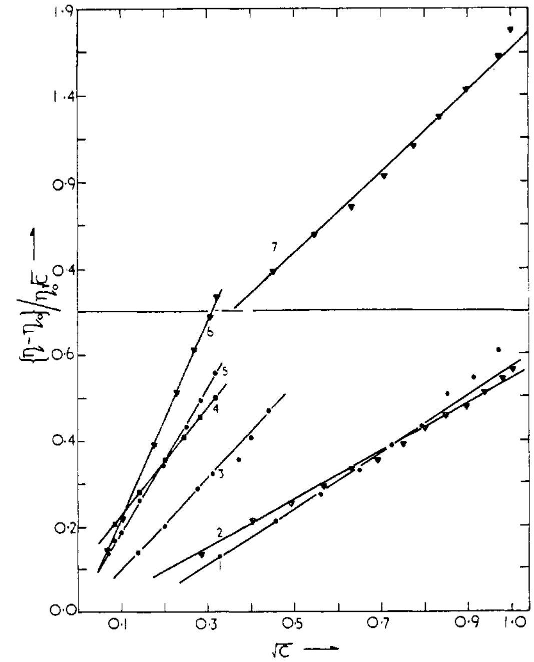

Figure 1. Plots of $(\eta - \eta_o)/\eta_o C^{1/2}$ vs. $C^{1/2}$ for selected salts dissolved in methanol. 1. $ZnCl_2$ 2. $SnCl_2 \cdot 2H_2O$ 3. $CaCl_2 \cdot 2H_2O$ 4. $CoCl_2 \cdot 2H_2O$ 5. $NiCl_2 \cdot 2H_2O$ 6. $NiCl_2 \cdot 6H_2O$; 7. $SnCl_4 \cdot 5H_2O$

Data for tin salts are at 25° C.; for all other salts, at 20° C.

Table I. Viscosity of Salts at 20° and 45° C.

$ZnCl_2$ Solutions Were Measured also at 5° and 25° C.

Salt	Source	Concn. Range, Moles/L.	No. of Samples
$CaCl_2$	[a]	0.00102–0.5107	13
$CrCl_3 \cdot 6H_2O$	[a]	0.000998–0.0998	12
$MnCl_2 \cdot 4H_2O$	[a]	0.001004–0.1521	13
$CoCl_2 \cdot 6H_2O$	[a]	0.000993–0.09927	11
$CoCl_2 \cdot 2H_2O$	[b]	0.000998–0.0998	10
$NiCl_2 \cdot 6H_2O$	[a]	0.001043–0.1043	9
$NiCl_2 \cdot 2H_2O$	[b]	0.001001–0.1001	10
$CuCl_2 \cdot 2H_2O$	[c]	0.00097–0.1940	12
$ZnCl_2$	[a]	0.00010–1.0430	30

[a] Fisher, certified reagent grade. [b] Prepared by Bose and Khundkar Method (*1*). [c] Baker and Adamson, reagent grade.

Table II. Average Q and R Values for Some Salts Dissolved in Pure Methanol

Square-root and Mean-square Deviations are in Parentheses

Salt	Q	R[a]	ΔH_Q Kcal.	ΔH_R Kcal.
$CaCl_2$	1.66 (0.05)	1.186 (0.006)	−3.78 (0.23)	2.54 (0.08)
$CrCl_3 \cdot 6H_2O$	1.58 (0.04)	1.337 (0.009)	−3.41 (0.20)	4.34 (0.08)
$MnCl_2 \cdot 4H_2O$	1.63 (0.02)	1.231 (0.014)	−3.64 (0.11)	3.10 (0.20)
$CoCl_2 \cdot 6H_2O$	1.70 (0.05)	1.191 (0.008)	−3.96 (0.23)	2.60 (0.12)
$CoCl_2 \cdot 2H_2O$	1.68 (0.05)	1.192 (0.010)	−3.87 (0.14)	2.60 (0.12)
$NiCl_2 \cdot 6H_2O$	1.66 (0.05)	1.184 (0.015)	−3.78 (0.23)	2.52 (0.20)
$NiCl_2 \cdot 2H_2O$	1.64 (0.03)	1.193 (0.016)	−3.69 (0.14)	2.62 (0.20)
$CuCl_2 \cdot 2H_2O$	1.58 (0.04)	1.152 (0.008)	−3.41 (0.20)	2.12 (0.16)
$ZnCl_2$	1.60 (0.03)	0.897[b]	−3.55 (0.14)[c]	−1.60[b]
$SnCl_2 \cdot 2H_2O$[d]	1.46 (0.02)[e]	1.434 (0.028)	−3.59 (0.13)	5.40 (0.28)
$SnCl_4 \cdot 5H_2O$[d]	1.49 (0.02)[e]	1.450 (0.010)	−3.78 (0.13)	5.56 (0.16)

[a] R values given in reference (*4*) corrected for temperature-concentration change. [b] Average value for concentrations between 0.200 and 1.000 mole/liter. [c] Data taken at 5° and 25° C. also yield this result. [d] Conductance data (*8*). [e] Temperatures were 25° and 45° C. (*6*).

Table III. *A* (Intercept) and *B* (Slope) Obtained by Solving Jones-Talley Equation

Salt	B	A	Temp., ° C.
$CaCl_2$	1.44	−0.041	20.0
$CrCl_3 \cdot 6H_2O$	2.27	−0.045	20.0
$MnCl_2 \cdot 4H_2O$	1.84	−0.018	20.0
$CoCl_2 \cdot 6H_2O$	2.19	0.000	20.0
$CoCl_2 \cdot 2H_2O$	1.26	0.102	20.0
$NiCl_2 \cdot 6H_2O$	2.26	0.000	20.0
$NiCl_2 \cdot 2H_2O$	1.66	0.028	20.0
$CuCl_2 \cdot 2H_2O$	1.09	−0.011	20.0
$ZnCl_2$	0.650	−0.085	20.0
$SnCl_2 \cdot 2H_2O$[a]	0.557	−0.016	25.0
$SnCl_4 \cdot 5H_2O$[a]	2.20	−0.64	25.0

[a] Data taken from reference 6.

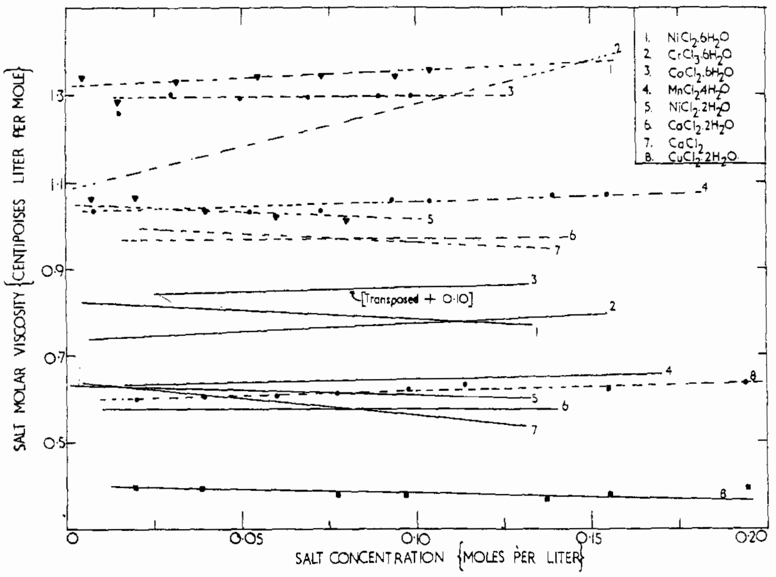

Figure 2. Plot of salt molar viscosity vs. salt concentration of the indicated salt. At least five points define each separate line

---- data collected at 20! C.
—— data collected at 45! C.

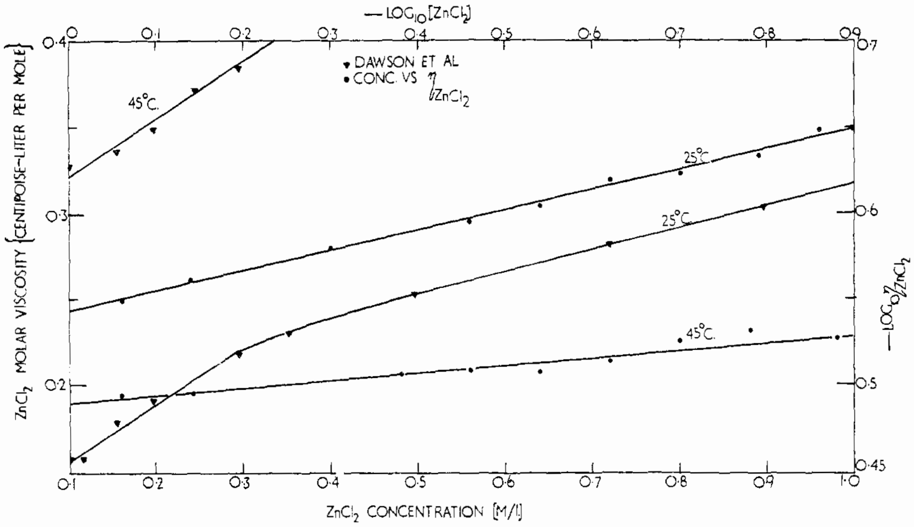

Figure 3. Plots of the data for $ZnCl_2$ solutions using the coordinates shown. η_{ZnCl_2} is the $ZnCl_2$ molar viscosity

reveals no simple correlation (Table II), but it is evident that the variation in *R* values cannot be attributed to variations in viscosity parameters alone.

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