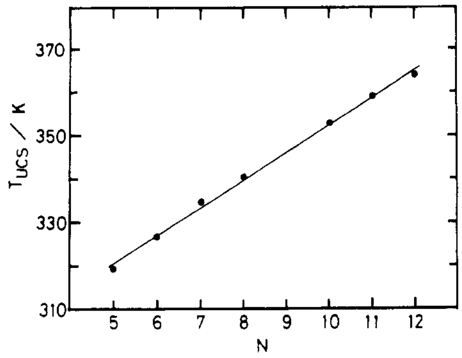

Figure 3. Relationship between the upper critical solution temperature T_{UCS} of ammonia + n-alkane systems and the number N of carbon atoms in the n-alkane.

3 and the deviation of the experimental values of the miscibility temperature from those calculated with eq 3 are shown in Table II. Equation 3 can fit the experimental temperature with a mean deviation of less than 1.1 K. There is a linear relationship between T_{UCS} and the number of carbon atoms, N, in the n-alkane (Figure 3).

$$T_{UCS}/K = 6.4454N + 288.58 \qquad N = 5\text{–}12 \qquad (4)$$

Glossary

A_1, A_2, B, b_1	constants in eqs 2 and 3
N	number of carbon atoms in n-alkane
P	pressure, MPa
T	temperature, K
T_{UCS}	upper critical solution temperature, K
X	mass fraction of ammonia

Subscripts

UCS	upper critical solution point

Registry No. NH_3, 7664-41-7; $H_3C(CH_2)_5CH_3$, 142-82-5; $H_3C(CH_2)_8CH_3$, 124-18-5; $H_3C(CH_2)_9CH_3$, 1120-21-4; $H_3C(CH_2)_{10}CH_3$, 112-40-3.

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Temperature and Concentration Dependence of Viscosity of the $NiCl_2$ + CH_3OH System

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Density and viscosity of the $NiCl_2$ + CH_3OH system were measured as functions of temperature (288.15–323.15 K) and concentration (0.01817–5.3086 m). The temperature dependence of viscosity has been analyzed by using the Vogel–Tammann–Fulcher (VTF) equation. The concentration dependence of viscosity has been described by using a three-parameter isothermal equation.

Introduction

Extensive studies on the properties of aqueous solution has provided sufficient data to enable us to correlate the effects of variation in concentration on the physicochemical properties of aqueous electrolytic solutions. The study of nonaqueous electrolytic solutions to obtain the same type of information, however, has been quite limited.

Earlier we have reported an isothermal equation of the form

$$Y = a \exp(bm + cm^2) \qquad (1)$$

to describe the concentration dependence of Y (viscosity and conductivity) of 1–1, 1–2, and 2–1 valent aqueous electrolytic solutions (*1–3*) over a concentration range. In eq 1, a, b, and c are adjustable parameters and m is the molality.

In the present paper we have made use of eq 1 to describe the viscosity of the $NiCl_2$ + CH_3OH system as function of concentration.

Experimental Section

Materials. Anhydrous nickel chloride (SD, AR grade) was prepared as described elsewhere (*4*) and was kept in a vacuum desiccator over silica gel until used. Methanol (SM, LR grade) was treated with quicklime and was distilled after refluxing for about 4 h. Finally anhydrous methanol was prepared by using a dry magnesium turnings and iodine mixture as described elsewhere (*5*). Only the middle fraction was used in our study. The molecular weights of nickel chloride and methanol used in the present study were 129.62 and 32.04, respectively, having an assay of more than 99.8%. The densities of anhydrous methanol as measured at 298 and 303 K were found to be 0.786 47 and 0.781 70 g cm^{-3}, which are in good agreement with the literature values 0.7864 and 0.7816 g cm^{-3} (*6*) and 0.786 45 and 0.781 81 g cm^{-3} (*7*), respectively.

Preparation of Solutions. Solutions of the nickel chloride–methanol system of different concentration were prepared by weight.

Density Measurements. Densities of all the solutions were measured with a single-stem graduated pycnometer provided with a well-fitted glass stopper to prevent evaporation. The pycnometer was calibrated by using conductivity water. The difference between the duplicate density values of all the solutions were found to be less than 0.01%.

Viscosity Measurements. The viscosities of all the solutions were measured by using a Hoppler BH-2 falling-sphere viscometer. In this viscometer, since the solution is sealed, the condensation of the solvent vapor at low temperatures and the loss of solvent at high temperatures are prevented. The viscometer was calibrated by using conductivity water. The tem-

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Table I. Densities of the $NiCl_2$ + CH_3OH System as Functions of Temperature and Concentration

T/K	ρ/(g cm^{-3})	T/K	ρ (g cm^{-3})
0.01817 m		0.06624 m	
313.50	0.776 05	314.95	0.779 25
312.45	0.776 96	313.90	0.780 43
311.35	0.778 07	312.80	0.781 49
310.20	0.778 99	311.70	0.782 69
309.10	0.780 02	310.60	0.783 84
308.00	0.781 01	309.50	0.784 99
0.11805 m		0.4291 m	
314.45	0.785 93	315.20	0.816 17
313.40	0.786 86	314.50	0.817 33
312.35	0.787 93	313.00	0.818 29
311.25	0.789 12	311.95	0.819 41
310.20	0.790 12	310.85	0.820 47
309.10	0.791 22	309.70	0.821 61
0.8756 m		1.2811 m	
313.80	0.850 48	318.50	0.898 55
312.65	0.851 68	317.20	0.899 83
311.35	0.852 69	315.90	0.900 89
310.15	0.853 85	314.65	0.902 12
308.95	0.854 93	313.35	0.903 29
307.75	0.856 02	312.05	0.904 48
2.1840 m		2.6024 m	
317.25	0.967 56	316.70	1.005 71
315.85	0.968 94	315.30	1.007 24
314.45	0.970 07	313.85	1.008 60
313.00	0.971 40	312.30	1.010 15
311.65	0.972 87	310.75	1.011 93
310.25	0.974 07	309.20	1.013 44
3.3810 m		4.0805 m	
315.85	1.056 15	316.05	1.101 84
314.30	1.057 66	314.45	1.103 34
312.75	1.058 90	312.85	1.105 01
311.20	1.060 35	311.25	1.106 51
309.65	1.061 95	309.65	1.108 09
308.05	1.063 33	307.95	1.109 76
5.3086 m			
315.85	1.173 71		
314.05	1.175 31		
312.35	1.177 09		
310.55	1.178 69		
308.75	1.180 50		
306.85	1.182 29		

Table II. Least-Squares Fitted Values of the Density Equation $\rho = a - b\,(t\ (^\circ C))$ for the $NiCl_2$ + CH_3OH System

m/(mol kg^{-1})	a/(g cm^{-3})	$b \times 10^4$/ (g cm^{-3} °C^{-1})	std dev in ρ, $\sigma \times 10^5$
0.018 17	0.812 43	9.014	6.0
0.066 24	0.823 11	10.486	3.0
0.118 05	0.827 15	9.994	5.0
0.429 1	0.857 75	9.888	3.0
0.875 6	0.887 39	9.066	7.0
1.281 1	0.940 11	9.158	5.0
2.184 0	1.008 59	9.306	9.0
2.602 4	1.050 59	10.304	7.0
3.381 0	1.095 51	9.219	9.0
4.080 5	1.143 86	9.800	4.0
5.308 6	1.214 58	9.580	6.0

perature of the viscometer was maintained by circulating water from the thermostat through the outer jacket of the viscometer. The measured viscosities were reproducible to ±0.1%.

Temperature Control. All the measurements were made in a NBE type ultrathermostat that maintained the temperature to ±0.02 K.

Results and Discussion

The densities (ρ) of the nickel chloride–methanol system, presented in Table I, were found to be a linear function of temperature (Table II) at fixed molality. The dependence of density on molality, m, however, is not linear (Figure 1), similar to that observed for aqueous nickel chloride systems (*2*).

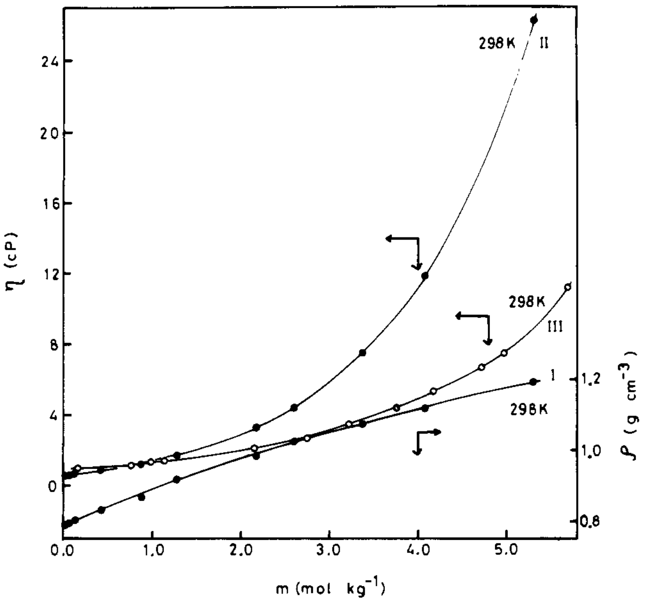

Figure 1. Density isotherm of the (I) $NiCl_2$ + CH_3OH system and viscosity isotherms of the (II) $NiCl_2$ + CH_3OH and (III) $NiCl_2$ + H_2O systems.

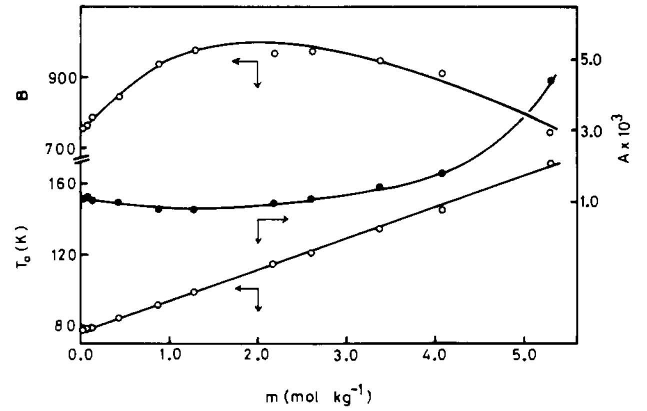

Figure 2. Plots of A, B, and T_0 parameters versus m for the $NiCl_2$ + CH_3OH system.

The measured viscosities (η) are given in Table III. In Figure 1 the viscosity results for $NiCl_2$ + CH_3OH are compared with those for $NiCl_2$ + H_2O at 298.15 K. The variation of viscosity with molality for $NiCl_2$ + CH_3OH is more exponential than that for $NiCl_2$ + H_2O over the experimental range of concentration.

The temperature dependencies of η at different concentrations were fitted by using the least-squares technique to the Vogel–Tammann–Fulcher (VTF) equation of the form

$$\eta = AT^{1/2} \exp[B/(T - T_0)] \qquad (2)$$

where A and B are empirical parameters and T_0 is the ideal glass transition temperature. The computed values of A, B, and T_0 are listed in Table IV. The B parameter has a greater value for the $NiCl_2$ + CH_3OH system compared to $NiCl_2$ + H_2O (*2*), which is characteristic of electrolytic solutions. The concentration dependencies of the parameters A, B, and T_0 are given in Figure 2. The ideal glass transition temperature T_0 (O) of pure methanol obtained from the intercept of the T_0 vs m plot (Figure 2) is 77.0 K, which is in reasonable agreement with the reported glass transition temperature T_g (103 K) (*8*). It has been reported (*9*) that the T_0 usually falls at $0.7T_g$ to $0.8T_g$ for molecular liquids. The concentration at which a

Table III. Viscosities of the $NiCl_2$ + CH_3OH System as Functions of Temperature and Concentration

T/K	η/cP	T/K	η/cP
0.01817 m		0.06624 m	
288.15	0.6472	288.15	0.6910
293.15	0.6029	293.15	0.6404
298.15	0.5607	298.15	0.6129
303.55	0.5216	303.55	0.5556
308.15	0.4899	308.15	0.5227
313.85	0.4582	313.65	0.4915
318.15	0.4359	318.15	0.4635
323.15	0.4121	323.15	0.4390
0.11805 m		0.4291 m	
288.15	0.7275	288.15	1.0103
293.15	0.6756	293.15	0.9314
298.15	0.6295	298.15	0.8552
303.65	0.5786	303.85	0.7756
308.15	0.5459	308.15	0.7271
313.45	0.5069	313.15	0.6665
318.15	0.4802	318.15	0.6281
323.15	0.4529	323.15	0.5882
0.8756 m		1.2811 m	
288.15	1.5217	288.15	2.2304
293.15	1.3684	293.15	1.9843
298.15	1.2321	298.15	1.7554
303.45	1.1191	303.75	1.5531
308.15	1.0186	308.15	1.4136
313.55	0.9148	313.15	1.2666
318.15	0.8534	318.15	1.1570
323.15	0.7875	323.15	1.0560
2.1840 m		2.6024 m	
288.15	4.3442	288.15	6.0186
293.15	3.7597	293.15	5.1283
298.15	3.2746	298.15	4.4423
303.35	2.8386	303.45	3.7923
308.15	2.5242	308.15	3.3490
313.15	2.2089	313.55	2.8936
318.15	2.0051	318.15	2.6058
323.15	1.8062	323.15	2.3259
3.3810 m		4.0805 m	
288.15	10.6027	288.15	17.5837
293.15	8.8761	293.15	14.3634
298.15	7.4782	298.15	11.8473
303.65	6.2569	303.25	9.8877
308.15	5.4345	308.15	8.3651
313.65	4.6391	313.25	7.0786
318.15	4.1263	318.15	6.1609
323.15	3.6377	323.15	5.3658
5.3086 m			
288.15	41.8246		
293.15	32.9394		
298.15	26.2508		
303.25	20.9984		
308.15	17.2695		
313.35	14.2171		
318.15	12.2017		
323.15	10.4500		

Table IV. Least-Squares Fitted Values of the Parameters of Equation 2 for the $NiCl_2$ + CH_3OH System

m/(mol kg^{-1})	$A \times 10^3$	B	T_0/K	std dev in ln η
0.01817	1.0610	754.77	77.5	0.0016
0.06624	1.0930	763.27	78.0	0.0098
0.11805	1.0191	784.60	78.5	0.0031
0.4291	0.9598	843.61	84.0	0.0037
0.8756	0.7641	937.60	91.5	0.0050
1.2811	0.7369	976.40	99.5	0.0040
2.1840	0.9663	966.34	115.0	0.0022
2.6024	1.0442	971.62	121.5	0.0042
3.3810	1.3788	943.29	134.0	0.0030
4.0805	1.8070	909.50	145.0	0.0030
5.3086	4.4007	742.18	171.0	0.0060

Table V. Least-Squares Fitted Values of the Parameters of Equation 1 for the $NiCl_2$ + CH_3OH System

T/K	a	b	$c \times 10^2$	std dev in ln η
288.0	0.6634	0.9284	2.8959	0.036
298.0	0.5791	0.8557	2.6812	0.031
308.0	0.5024	0.8008	2.6139	0.028
323.0	0.4211	0.7162	2.1603	0.022

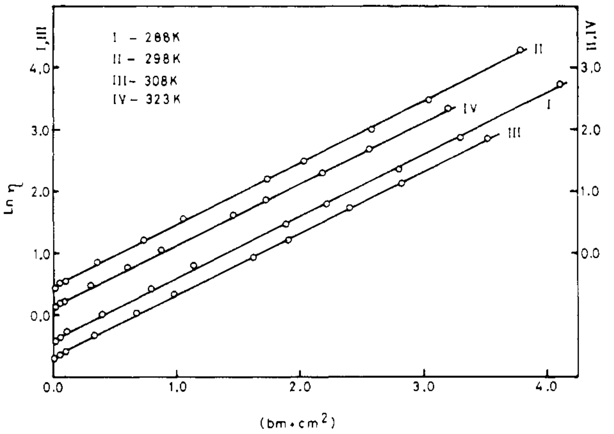

Figure 3. Plots of ln η versus $bm + cm^2$ for the $NiCl_2$ + CH_3OH system.

structural transition commences was found to be at around 2.0 m from the plot of B vs m (Figure 2). This critical concentration is in good agreement with the reported values of $NiCl_2$ + H_2O (*2*, *10*).

In the range of concentration studied, the ion-solvent interaction may be considered to dominate. The viscosity B coefficient, which accounts the ion-solvent interaction, is obtained by multiplying the values of the a and b parameters of eq 1 (*2*). Therefore, viscosity versus concentration data were fitted by using the least-squares technique to eq 1, and a good fit has been obtained over the temperature and concentration range studied (Table V). The success of eq 1 in describing the concentration dependence of viscosity with reasonable accuracy is indicated by the linearity of the plot of ln η vs $bm + cm^2$ (Figure 3). The values of the a parameter (Table V), which is the viscosity of the solution at infinite dilution, are comparable within 4.0–6.0% with the reported viscosity data of methanol (*11*) at the corresponding temperature.

The calculated values of the viscosity B coefficient, 0.6159, 0.4956, 0.4023, and 0.3016 at 288, 298, 308, and 323 K, respectively, for $NiCl_2$ + CH_3OH are found to be about 1.5 times greater than the B values, 0.3255, 0.2653, and 0.2099 at 298, 308, and 323 K, respectively, of the $NiCl_2$ + H_2O system (*2*). The higher B values for $NiCl_2$ + CH_3OH at a given temperature indicate that ion-solvent interactions are greater for the $NiCl_2$ + CH_3OH system than for the $NiCl_2$ + H_2O system.

Registry No. $NiCl_2$, 7718-54-9; CH_3OH, 67-56-1.

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