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Temperature and Concentration Dependence of Viscosity of Aqueous Electrolytes from 20 to 50 °C. Chlorides of Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Cr^{3+}

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Viscosities of aqueous solutions of the chlorides of potassium, sodium, calcium, magnesium, strontium, barium, cobalt, nickel, chromium, and copper were determined by using a thermostated Ubbelohde flow viscometer in the wide range of concentrations and temperatures at 5 °C intervals from 20 to 50 °C. From the experimental results, the ion–solvent interaction terms (B coefficients) were evaluated in the concentration range of 0.1–5.0 M; the data were also represented by a newly suggested empirical equation of the form $\eta = a_0 \exp(b_0M + c_0M^2)$. The viscosity coefficients estimated from the parameters of this empirical equation were found to be comparable with literature values, but some discrepancies may be due to low-purity chemicals. It was also concluded that the viscosities of these ions in aqueous solutions could be understood in terms of hydration number, charge on the ions, and their ionic radii.

Introduction

Considerable interest has been shown in the study of the viscometric behavior of electrolytes in water. The aim of these studies was to determine the B coefficient of the Jones and Dole equation (*1*) and from it to be able to define the properties of the electrolyte in solution. The relative viscosity of dilute electrolytes has proved to be an effective method for studying ion–solvent interactions, through use of the Jones–Dole equation $\eta/\eta_0 - 1 = AC^{1/2} + BC$, where η/η_0 is the viscosity of the salt solution relative to that of the solvent, water, and C is the molar concentration. The quantities A and B are interaction coefficients whose values depend upon the particular electrolyte, temperature, and solvent under consideration. This empirical equation is valid only at lower concentration. Several other empirical as well as theoretical equations are available in the literature (*2–4*), but unfortunately, they fail to be applicable at high concentrations, except for the Vand equation (*5*) and other related equations (*6*, *7*). Although the Vand equation empirically describes the experimental data at higher concentrations, the theoretical concept on which the Vand equation was developed cannot be valid at these high concentrations. Recently some authors (*8*) have attempted to describe the concentration dependence of viscosity in terms of a new empirical equation shown to be obtainable from the Vogel–Tammann–Fulcher (VTF) equation (*9*). A least-squares fitting of the viscosity data to this isothermal equation has been made, and a surprisingly good fit has been obtained for all the systems under investigation.

A straight line obtained from the plot of ln η versus $(b_0M + C_0M^2)$ of eq 1 (below) verifies the suitability of this equation in describing the concentration dependence to high concentrations at 20–50 °C and also shows that how well the equation represents our data.

Table I. Viscosities (cP) for Aqueous Sodium Chloride

concn, M	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C
0.1	1.001	0.890	0.801	0.724	0.656	0.597	0.546
0.5	1.036	0.921	0.829	0.751	0.682	0.623	0.569
1.0	1.081	0.963	0.869	0.788	0.717	0.655	0.601
1.5	1.133	1.013	0.915	0.830	0.755	0.689	0.633
2.0	1.199	1.072	0.969	0.879	0.800	0.730	0.671
2.5	1.269	1.133	1.025	0.930	0.846	0.773	0.709
3.0	1.352	1.204	1.090	0.991	0.899	0.822	0.753
3.5	1.447	1.292	1.163	1.058	0.960	0.875	0.802
4.0	1.555	1.387	1.249	1.132	1.027	0.935	0.856

Table II. Viscosities (cP) for Aqueous Potassium Chloride

concn, M	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C
0.1	0.994	0.882	0.795	0.719	0.652	0.594	0.544
0.25	0.991	0.882	0.795	0.720	0.655	0.596	0.547
0.5	0.987	0.881	0.794	0.722	0.657	0.600	0.551
0.75	0.983	0.880	0.791	0.725	0.661	0.605	0.556
1.00	0.983	0.881	0.802	0.729	0.665	0.610	0.561
1.25	0.981	0.881	0.802	0.733	0.671	0.615	0.566
1.5	0.982	0.884	0.806	0.737	0.676	0.622	0.572
2.0	0.985	0.890	0.815	0.748	0.686	0.632	0.585
2.5	0.995	0.902	0.827	0.763	0.699	0.645	0.598
3.0	1.005	0.914	0.841	0.774	0.715	0.661	0.615

Table III. Viscosities (cP) for Aqueous Barium Chloride

concn, M	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C
0.1	1.018	0.907	0.815	0.737	0.669	0.609	0.558
0.25	1.053	0.938	0.846	0.766	0.696	0.635	0.581
0.5	1.113	0.995	0.900	0.816	0.743	0.679	0.624
0.75	1.179	1.058	0.958	0.870	0.794	0.726	0.668
1.0	1.255	1.127	1.023	0.932	0.850	0.780	0.716
1.25	1.340	1.207	1.096	1.001	0.923	0.837	0.771
1.5	1.443	1.298	1.181	1.077	0.984	0.901	0.830

Table IV. Viscosities (cP) for Aqueous Strontium Chloride

concn, M	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C
0.1	1.023	0.911	0.816	0.742	0.671	0.611	0.559
0.5	1.134	1.012	0.920	0.830	0.757	0.688	0.629
1.0	1.301	1.165	1.058	0.960	0.874	0.797	0.734
1.5	1.518	1.363	1.237	1.127	1.028	0.937	0.862
2.0	1.814	1.626	1.472	1.340	1.218	1.115	1.027
2.5	2.212	1.979	1.790	1.628	1.483	1.350	1.246
3.0	2.792	2.487	2.246	2.034	1.851	1.677	1.535

Table V. Viscosities (cP) for Aqueous Magnesium Chloride

concn, M	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C
0.1	1.040	0.933	0.832	0.753	0.682	0.618	0.567
0.5	1.209	1.069	1.960	0.868	0.789	0.715	0.654
1.0	1.461	1.295	1.162	1.049	0.949	0.861	0.786
1.5	1.791	1.587	1.419	1.277	1.153	1.043	0.952
2.0	2.221	1.900	1.761	1.573	1.416	1.279	1.163
2.5	2.804	2.462	2.193	1.964	1.759	1.585	1.432
3.0	3.607	3.156	2.794	2.491	2.219	1.994	1.802
3.5	4.700	4.082	3.597	3.189	2.832	2.543	2.281
4.0	6.242	5.439	4.703	4.158	3.671	3.262	2.899
5.0	12.94	10.91	9.374	8.131	7.089	6.218	5.507

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Table VI. Viscosities (cP) for Aqueous Calcium Chloride

concn, M	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C
0.1	1.026	0.912	0.818	0.740	0.672	0.612	0.561
0.5	1.142	1.019	0.918	0.829	0.754	0.688	0.628
1.0	1.318	1.176	1.061	0.966	0.875	0.799	0.734
1.5	1.538	1.375	1.244	1.128	1.028	0.937	0.858
2.0	1.820	1.627	1.473	1.337	1.217	1.111	1.021
2.5	2.185	1.955	1.767	1.604	1.461	1.331	1.219
3.0	2.698	2.331	2.175	1.967	1.786	1.626	1.487
3.5	3.415	3.034	2.733	2.468	2.235	2.031	1.851
4.0	4.492	3.970	3.558	3.195	2.872	2.603	2.362
5.0	8.507	7.373	6.487	5.733	5.078	4.508	4.053

Table VII. Viscosities (cP) for Aqueous Cobalt Chloride

concn, M	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C
0.1	1.040	0.923	0.832	0.749	0.655	0.619	0.567
0.5	1.207	1.068	0.960	0.867	0.784	0.713	0.650
1.0	1.445	1.284	1.154	1.043	0.944	0.855	0.781
1.5	1.762	1.561	1.413	1.270	1.144	1.051	0.946
2.0	2.159	1.910	1.707	1.536	1.383	1.249	1.138
2.5	2.689	2.363	2.111	1.904	1.695	1.526	1.384
3.0	3.399	2.983	2.647	2.362	2.105	1.889	1.708

Table VIII. Viscosities (cP) for Aqueous Copper Chloride

concn, M	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C
0.1	1.034	0.919	0.826	0.746	0.676	0.616	0.563
0.5	1.190	1.057	0.949	0.857	0.776	0.706	0.645
1.0	1.405	1.244	1.117	1.008	0.908	0.823	0.751
1.5	1.655	1.461	1.309	1.176	1.057	0.956	0.867
2.0	1.952	1.712	1.524	1.355	1.223	1.094	0.985
2.5	2.299	2.023	1.791	1.592	1.419	1.273	1.150
3.0	2.721	2.370	2.093	1.855	1.648	1.471	1.323
3.5	3.270	2.826	2.476	2.185	1.930	1.715	1.543
4.0	3.924	3.369	2.929	2.566	2.253	1.994	1.777

Table IX. Viscosities (cP) for Aqueous Chromium Chloride

concn, M	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C
0.1	1.059	0.942	0.847	0.766	0.695	0.635	0.581
0.25	1.184	1.043	0.938	0.845	0.763	0.697	0.637
0.5	1.382	1.223	1.096	0.989	0.893	0.8111	0.739
0.75	1.621	1.431	1.284	1.154	1.044	0.945	0.862
1.0	1.937	1.703	1.523	1.366	1.227	1.112	1.010
1.25	2.296	2.014	1.798	1.611	1.446	1.314	1.888
1.5	2.836	2.485	2.203	1.966	1.754	1.574	1.425
1.75	3.423	2.985	2.642	2.346	2.089	1.868	1.683
2.0	4.639	4.035	3.548	3.138	2.771	2.470	2.207

Table X. Viscosities (cP) for Aqueous Nickel Chloride

concn, M	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C
0.1	1.037	0.919	0.825	0.745	0.677	0.614	0.563
0.5	1.204	1.071	0.962	0.867	0.786	0.717	0.654
1.5	1.776	1.579	1.416	1.274	1.149	1.043	0.947
2.0	2.189	1.928	1.729	1.556	1.398	1.266	1.148
2.5	2.732	2.406	2.145	1.921	1.721	1.555	1.405
3.0	3.491	3.037	2.700	2.398	2.142	1.927	1.734
3.5	4.502	3.909	3.450	3.055	2.707	2.417	2.170
4.0	6.022	5.195	4.527	3.983	3.526	3.130	2.789

Table XI. Interaction Coefficients for Aqueous Sodium Chloride in the Concentration Range 0.1–4.0 M

temp, °C	η range, cP	a_0	b_0	c_0	stand. devn, ln η
20	1.001–1.555	0.994	0.075	0.009	0.153
25	0.890–1.388	0.883	0.078	0.008	0.154
30	0.801–1.249	0.799	0.084	0.007	0.154
35	0.725–1.132	0.718	0.087	0.006	0.155
40	0.656–1.027	0.651	0.091	0.006	0.155
45	0.597–0.935	0.593	0.094	0.005	0.154
50	0.546–0.856	0.541	0.098	0.004	0.155

Table XII. Interaction Coefficient for Aqueous Potassium Chloride in the Concentration Range 0.1–3.0 M

temp, °C	η range, cP	a_0	b_0	c_0	stand. devn, ln η
20	0.994–1.006	0.996	−0.002	0.008	0.0077
25	0.882–0.915	0.883	−0.011	0.007	0.0129
30	0.795–0.841	0.794	0.0	0.006	0.0192
35	0.719–0.774	0.718	0.009	0.005	0.0253
40	0.652–0.715	0.651	0.017	0.004	0.0303
45	0.594–0.661	0.592	0.026	0.003	0.0353
50	0.544–0.615	0.542	0.029	0.004	0.0403

Table XIII. Interaction Coefficients for Aqueous Barium Chloride in the Concentration Range 0.1–1.5 M

temp, °C	η range, cP	a_0	b_0	c_0	stand. devn, ln η
20	1.018–1.444	1.000	0.196	0.032	0.128
25	0.907–1.298	0.888	0.213	0.025	0.132
30	0.815–1.181	0.797	0.229	0.021	0.136
35	0.737–1.077	0.720	0.239	0.019	0.139
40	0.669–0.984	0.653	0.251	0.016	0.143
45	0.609–0.901	0.594	0.260	0.015	0.144
50	0.558–0.830	0.543	0.268	0.009	0.146

Table XIV. Interaction Coefficients for Aqueous Strontium Chloride in the Concentration Range 0.1–3.0 M

temp, °C	η range, cP	a_0	b_0	c_0	stand. devn, ln η
20	1.0237–2.7918	1.0064	0.2101	0.0428	0.3636
25	0.9111–2.4868	0.8944	0.2218	0.0392	0.3639
30	0.8169–2.2464	0.8042	0.2342	0.0354	0.3643
35	0.7423–2.0341	0.7277	0.2399	0.0337	0.3648
40	0.6715–1.8506	0.6594	0.2462	0.0320	0.3657
45	0.6114–1.6770	0.5985	0.2548	0.0290	0.3650
50	0.5599–1.5347	0.5467	0.2647	0.0262	0.3660

Table XV. Interaction Coefficients for Aqueous Calcium Chloride in the Concentration Range 0.1–5.0 M

temp, °C	η range, cP	a_0	b_0	c_0	stand. devn, ln η
20	1.0267–8.5074	1.0294	0.1846	0.0468	0.6670
25	0.9118–7.3731	0.9162	0.1882	0.0451	0.6589
30	0.8189–6.4877	0.8176	0.2071	0.0408	0.6538
35	0.7401–5.7331	0.7376	0.2158	0.0383	0.6471
40	0.6722–5.0781	0.6677	0.2239	0.0358	0.6677
45	0.6123–4.5081	0.6072	0.2305	0.0336	0.6332
50	0.5612–4.0537	0.5551	0.2359	0.0319	0.6277

Table XVI. Interaction Coefficients for Aqueous Magnesium Chloride in the Concentration Range 0.1–5.0 M

temp, °C	η range, cP	a_0	b_0	c_0	stand. devn, ln η
20	1.0403–12.944	1.0319	0.2881	0.0413	0.7944
25	0.9327–10.908	0.9194	0.2941	0.0406	0.7796
30	0.8319–9.3745	0.8213	0.2999	0.0349	0.7643
35	0.7532–8.1315	0.7430	0.3059	0.0349	0.7515
40	0.6817–7.0890	0.6744	0.3168	0.0338	0.7385
45	0.6184–6.2185	0.6109	0.3222	0.0320	0.7284
50	0.5670–5.508	0.5606	0.3319	0.0312	0.7165

Table XVII. Interaction Coefficients for Aqueous Chromium Chloride in the Concentration Range 0.1–2.0 M

temp, °C	η range, cP	a_0	b_0	c_0	stand. devn, ln η
20	1.059–4.639	1.0265	0.5096	0.1144	0.4996
25	0.9421–4.0352	0.9106	0.5028	0.1129	0.4930
30	0.8470–3.548	0.8185	0.5040	0.1069	0.4853
35	0.7669–3.1384	0.7403	0.4991	0.1038	0.4778
40	0.6959–2.7710	0.6707	0.4975	0.0988	0.4697
45	0.6347–2.4702	0.6114	0.4964	0.0933	0.4612
50	0.5815–2.2075	0.5601	0.4889	0.0915	0.4533

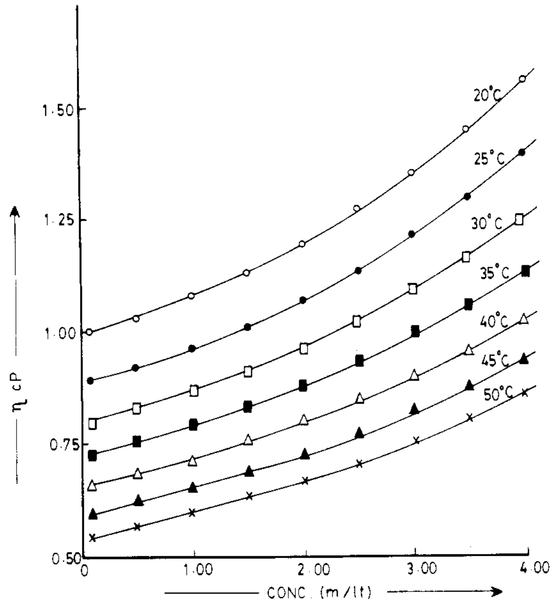

Figure 1. Viscosity (cP)–concentration curves for aqueous sodium chloride.

Table XVIII. Interaction Coefficients for Aqueous Cobalt Chloride in the Concentration Range 0.1–3.0 M

temp, °C	η range, cP	a_0	b_0	c_0	stand. devn, ln η
20	1.040–3.3994	1.0095	0.3368	0.0224	0.4295
25	0.9237–2.9829	0.8949	0.3396	0.0202	0.4253
30	0.8323–2.6476	0.8049	0.3445	0.0171	0.4202
35	0.7498–2.3621	0.7249	0.3489	0.0148	0.4175
40	0.6552–2.1056	0.6381	0.3821	0.0135	0.4188
45	0.6198–1.8896	0.5980	0.3515	0.0122	0.4051
50	0.5676–1.7079	0.5478	0.3432	0.0116	0.4011

Table XIX. Interaction Coefficients for Aqueous Copper chloride in the Concentration Range 0.1–4.0 M

temp, °C	η range, cP	a_0	b_0	c_0	stand. devn, ln η
20	1.0342–3.9249	1.0093	0.3200	0.0045	0.4575
25	0.9195–3.369	0.8972	0.3186	0.0027	0.4456
30	0.8263–2.9293	0.8066	0.3184	0.0006	0.4340
35	0.7459–2.566	0.7298	0.3133	−0.0001	0.4232
40	0.6761–2.2537	0.6613	0.3116	−0.0016	0.4125
45	0.6168–1.9943	0.6039	0.3035	−0.0015	0.4019
50	0.5629–1.7771	0.5523	0.2985	−0.0017	0.3939

Table XX. Interaction Coefficients for Aqueous Nickel Chloride in the Concentration Range 0.1–4.0 M

temp, °C	η range, cP	a_0	b_0	c_0	stand. devn, ln η
20	1.037–6.0223	1.0115	0.3278	0.0287	0.6028
25	0.9196–5.1952	0.8985	0.3289	0.0267	0.5928
30	0.8255–4.527	0.8056	0.3352	0.0235	0.5831
35	0.7456–3.9835	0.7270	0.3371	0.0213	0.5740
40	0.6775–3.5264	0.6607	0.3324	0.0208	0.5648
45	0.6148–3.130	0.6002	0.3357	0.0185	0.5565
50	0.5627–2.7894	0.5492	0.3328	0.0177	0.5478

Experimental Section

A Townson Mercer thermostat, which was provided with an electrically driven stirrer, a heating coil, a constant thermoregulator, and a Beckmann thermometer, was used for the temperature-controlled measurements. The temperature of the bath was kept constant by means of a heating coil, and a constant circulation of water was maintained for a particular reading. The actual temperature of the bath was determined by means of a standard thermometer graduated to 0.1 °C. The time of flow with distilled water was measured five times on five different days, with the five independent fillings of the viscometer giving an average of 113.1 ± 0.2 s at 20 °C. The solutions of each of these electrolytes were prepared from 0.1 M to almost the maximum limit depending upon the solubilities of the electrolytes in water.

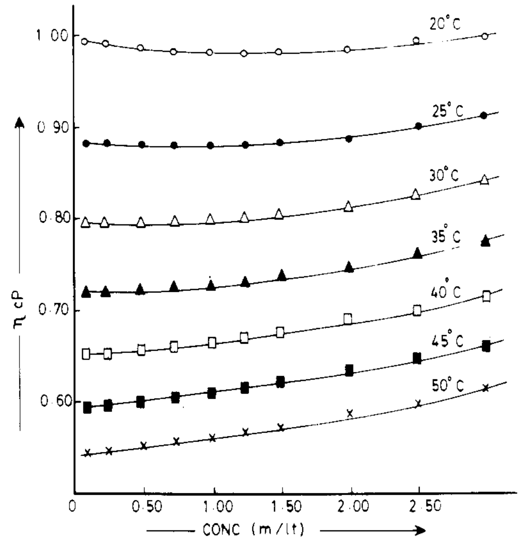

Figure 2. Viscosity (cP)–concentration curves for aqueous potassium chloride.

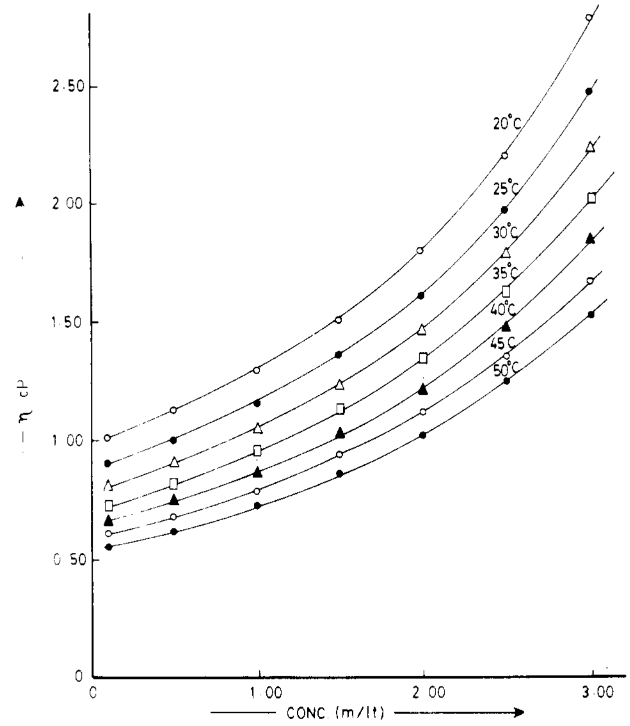

Figure 3. Viscosity (cP)–concentration curves for aqueous strontium chloride.

The densities of the solutions were measured accurately to 0.01% by use of a calibrated pycnometer of about 25 cm^3 capacity. The viscosity measurements were made by using an Ubbelohde viscometer having a fine capillary with flared ends in order to minimize kinetic energy corrections. The times of flow were measured at least three times for each solution and agreed to within ±0.2 s.

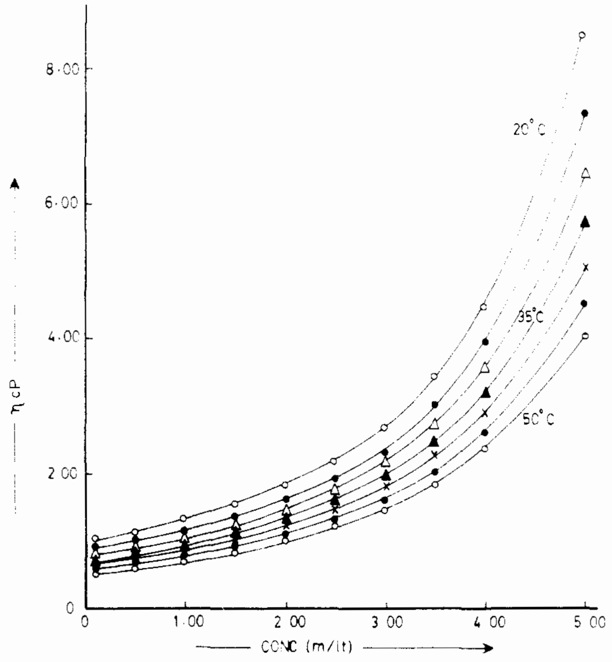

Figure 4. Viscosity (cP)-concentration curves for aqueous calcium chloride.

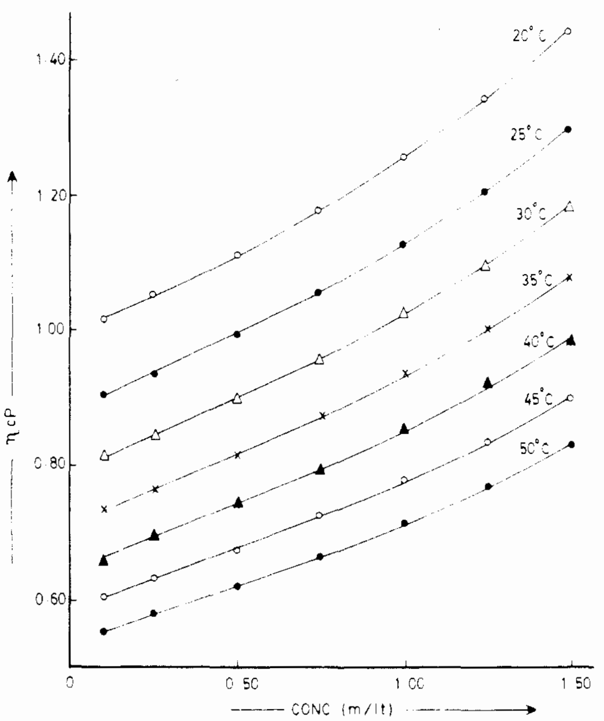

Figure 5. Viscosity (cP)-concentration curves for aqueous barium chloride.

The aqueous solutions of calcium chloride dihydrate, nickel chloride hexahydrate, magnesium chloride hexahydrate, and copper chloride dihydrate were prepared from Merck analytical grade electrolytes. Aqueous barium chloride dihydrate, cobalt chloride hexahydrate, potassium chloride and sodium chloride were prepared from Fluka Garantie electrolytes, whereas aqueous chromium chloride hexahydrate and strontium chloride hexahydrate were prepared from electrolytes obtained from B.D.H. Chemicals Limited. Sodium chloride and potassium chloride were further purified by recrystallization from a hot saturated solution of the electrolyte in pure distilled water and then subjected to prolonged drying in a desiccator. The electrolytes other than potassium chloride and sodium chloride were used without further purification and were believed to contain no impurities in sufficient amounts so as to affect the results measurably.

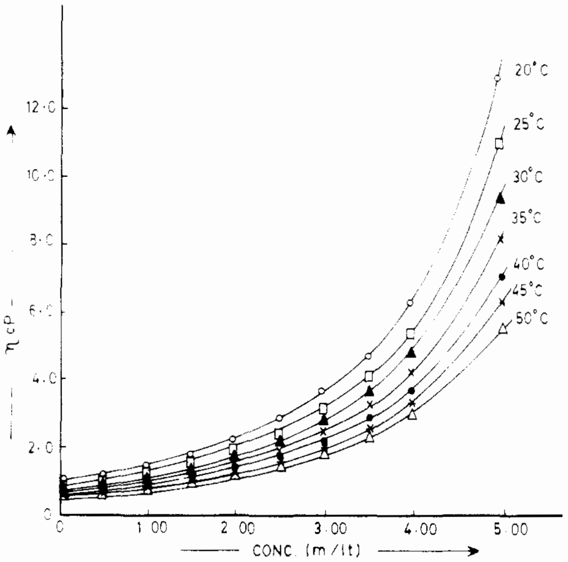

Figure 6. Viscosity (cP)-concentration curves for aqueous magnesium chloride.

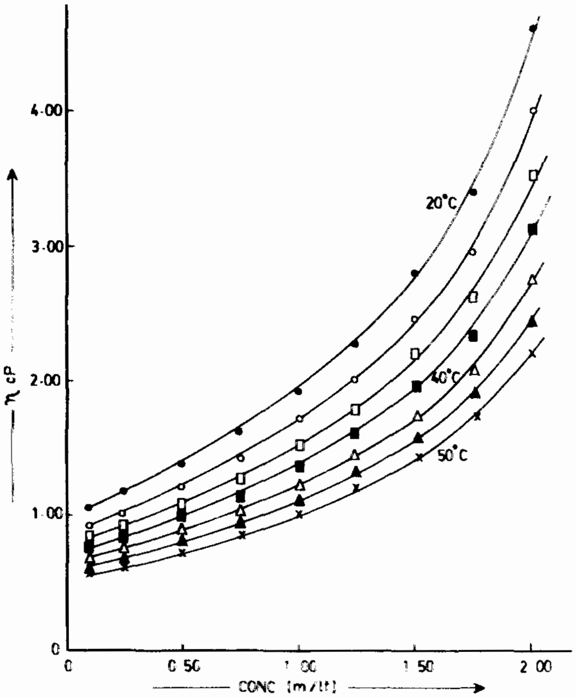

Figure 7. Viscosity (cP)-concentration curves for aqueous chromium chloride.

Results and Discussion

Densities and times of flow were determined for the aqueous systems of NaCl, KCl, $CaCl_2$, $MgCl_2$, $SrCl_2$, $BaCl_2$, $CrCl_3$, $CoCl_2$, $NiCl_2$, and $CuCl_2$ over a wide range of concentration and at various temperatures from 20 to 50 °C at intervals of 5 °C. The densities were calculated through the equation density (d) = mass (m)/volume (v), and the viscosities from $\eta_2 = (t_2/t_1)\rho_2/\rho_1\eta_1$.

An attempt was made to calculate A and B coefficients from the intercepts and the slopes of plots of $(\eta/\eta_0 - 1)/C^{1/2}$ versus

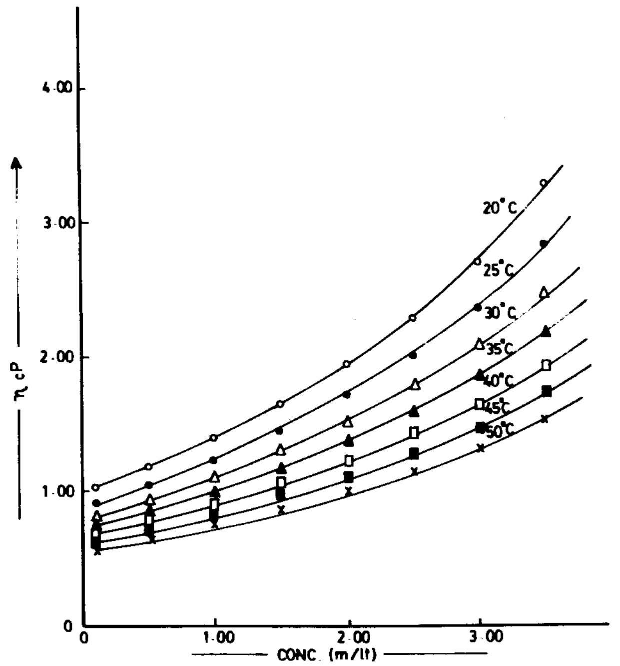

Figure 8. Viscosity (cP)-concentration curves for aqueous copper chloride.

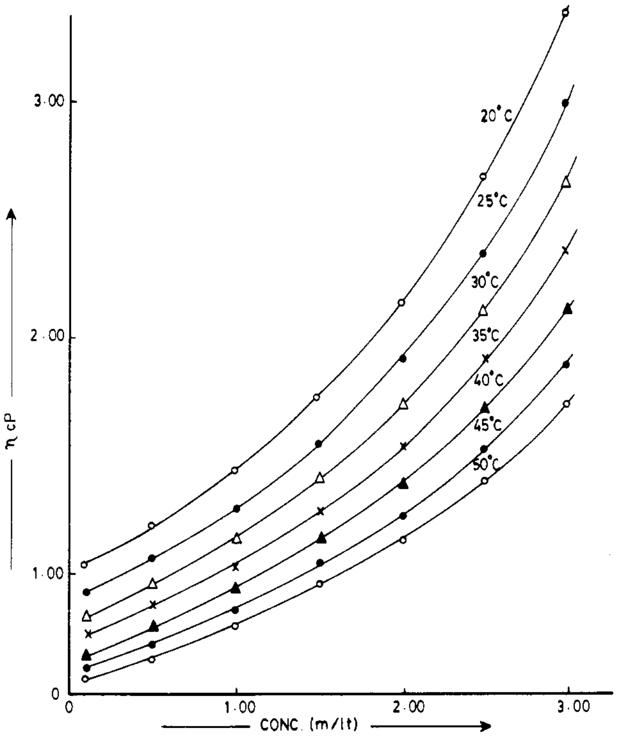

Figure 9. Viscosity (cP)-concentration curves for aqueous cobalt chloride.

$C^{1/2}$ in the Jones and Dole equation (*1*). The systems studied by us deviate from Jones and Dole equation particularly at higher concentration (*10*), and it therefore could not be used to calculate *A* and *B* coefficients. The *A* coefficient represents the contribution from interionic electrostatic forces (*11*). The *B* coefficient measures the order or disorder introduced by the ions into the solvent structure; this constant is a specific and approximately additive property of the ions of a strong electrolyte at a given temperature (*12*). Different interaction

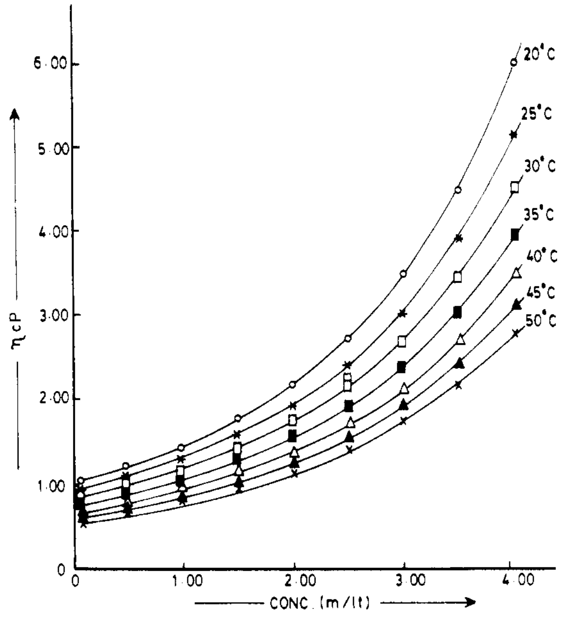

Figure 10. Viscosity (cP)-concentration curves for aqueous nickel chloride.

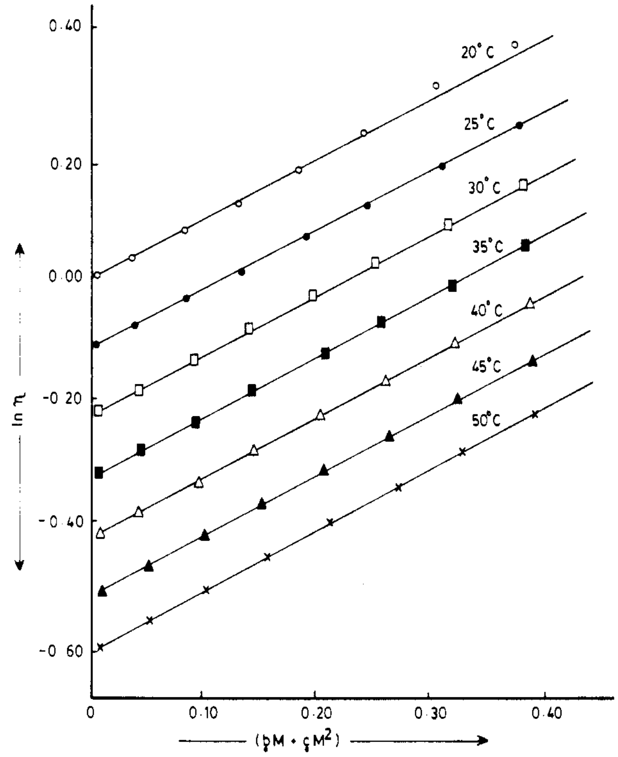

Figure 11. Plots of ln η vs ($b_0M + c_0M^2$) for the NaCl-H_2O system.

coefficients were calculated according to the empirical isothermal equation:

$$\eta = a_0 \exp(b_0M + c_0M^2) \qquad (1)$$

where a_0, b_0, and c_0 are parameters for a particular system and at a particular temperature, where *M* is the concentration (moles per liter).

It is not within the scope of this paper to give a detailed explanation of the data, but brief mention will be made of the relationship between viscosity and concentration, included in Tables I–X and Figures 1–10.

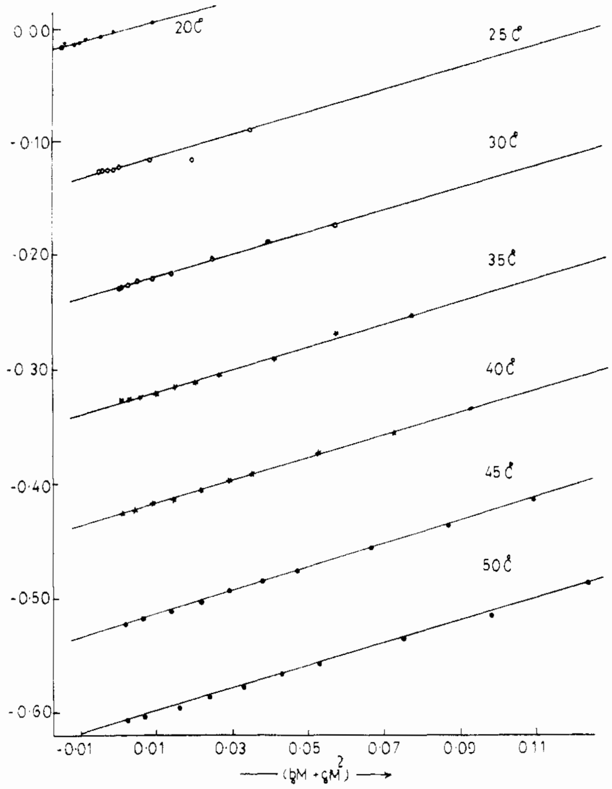

Figure 12. Plots of ln η vs ($b_0M + c_0M^2$) for the KCl–H_2O system.

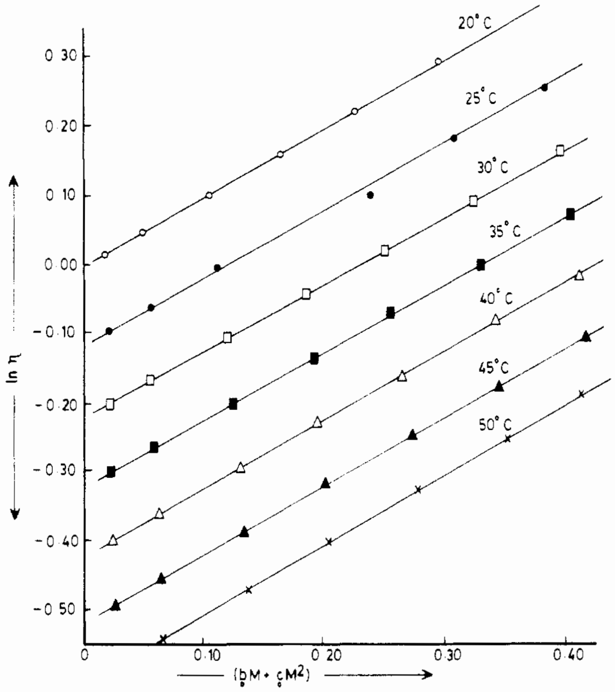

Figure 13. Plots of ln η vs ($b_0M + c_0M^2$) for the BaCl$_2$–H_2O system.

Out of the 10 systems examined, all of them except K$^+$ gave ascending curves, convex to the concentration axis. The viscosity therefore generally increases with the increase in the concentration of the solution; this increase, however, is more at lower temperatures (20 °C) than at high temperatures (50 °C). A comparison of viscosity data of 1 M solution of our electrolytes with a common anion reveals that the highly hydrated cations, e.g., Mg^{2+} and Ca^{2+} (*10*) increase the viscosity of a solution to a larger degree whereas the least hydrated would diminish it. A literature search revealed much data on these systems (*1*, *13*). All of our systems except K$^+$ have positive *B* coefficients at all temperatures from 20 to 50 °C. It might be possible to explain the negative *B* coefficient of potassium chloride as due to the influence of solvation spheres giving negative interaction coefficients, the negative sign being related to structure breaking, and a positive *B* coefficient indicates structure forming of the solvent (*14*).

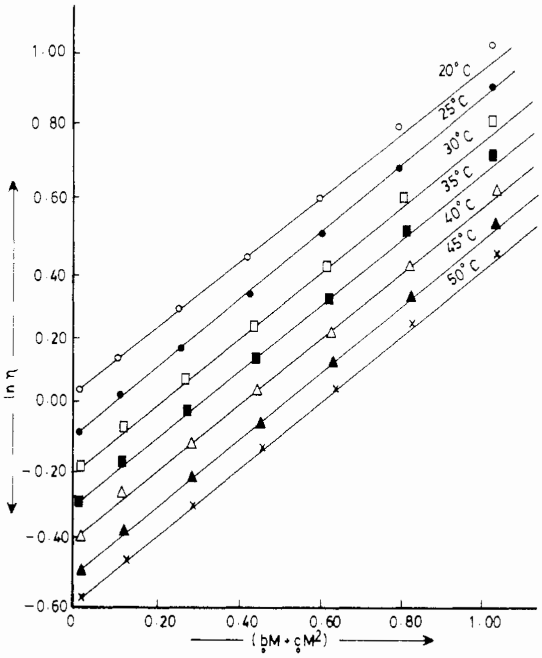

Figure 14. Plots of ln η vs ($b_0M + c_0M^2$) for the SrCl$_2$–H_2O system.

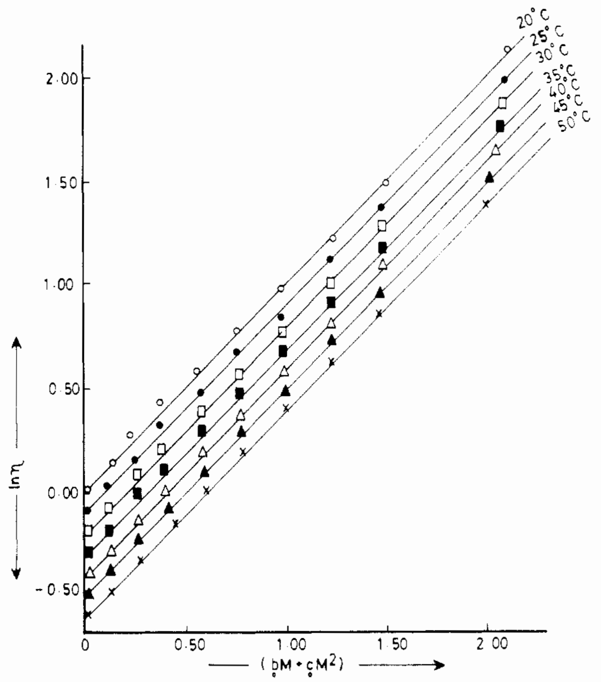

Figure 15. Plots of ln η vs ($b_0M + c_0M^2$) for the CaCl$_2$–H_2O system.

Least-squares values of a_0 and b_0 (*B* coefficient) and c_0 were calculated by use of IBM computer facilities, and it was found to be applicable when a plot of ln η versus ($b_0M + c_0M^2$) yielded straight lines. Plots of ln η versus ($b_0M + c_0M^2$) are given in Figures 11–20. The calculated values of a_0, b_0, and c_0 are given in Tables XI–XX. It may be seen that c_0 has a smaller value than b_0. Therefore, at very low concentrations,

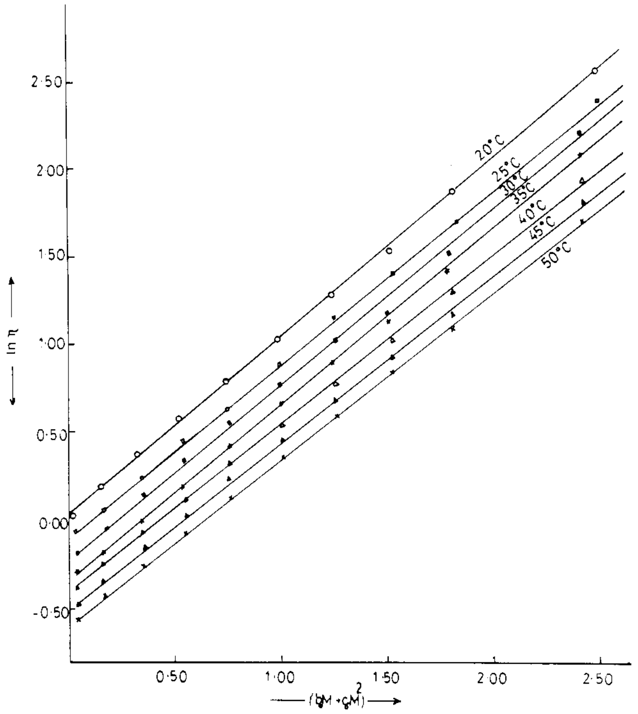

Figure 16. Plots of ln η vs ($b_0M + c_0M^2$) for the MgCl$_2$–H$_2$O system.

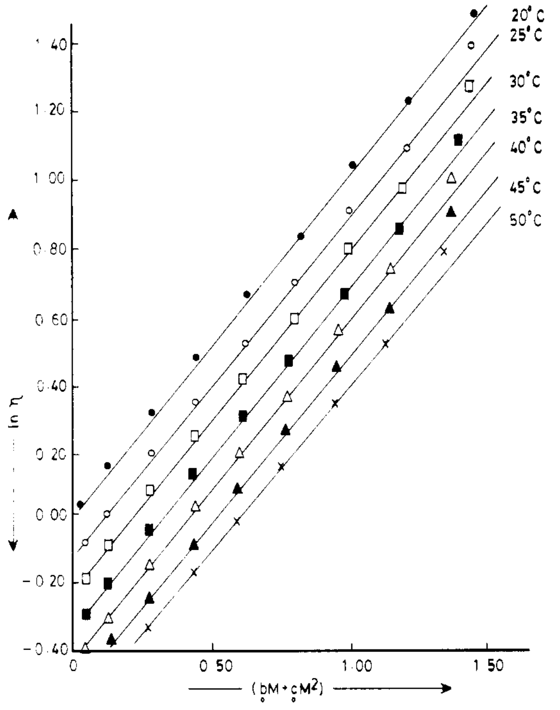

Figure 17. Plots of ln η vs ($b_0M + c_0M^2$) for the CrCl$_3$–H$_2$O system.

the c_0M^2 term may be neglected and eq 1 becomes similar to the Einstein equation (*15*) or the Jones and Dole Equation (*1*) without the ion–ion interaction terms ($\exp(b_0M) \approx 1 + b_0M$ and $M = C$ at lower concentrations). Accordingly, the product of a_0 and b_0 terms must be equivalent to the viscosity B coefficient (*16*). Moreover, neglecting the c_0 term, we can reduce the particular isothermal equation to the Vand equation (*5*), thereby providing a description of the success of the Vand equation at higher concentrations. Furthermore, the reduced form of eq 1 at low concentrations is similar to the Arrhenius isothermal equation (*17*, *18*) and to the equation suggested by Carbonell (*19*).

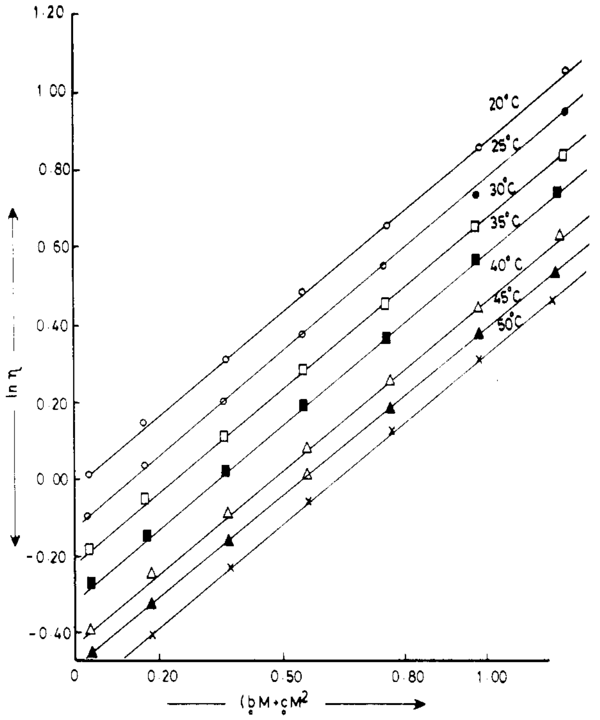

Figure 18. Plots of ln η vs ($b_0M + c_0M^2$) for the CoCl$_2$–H$_2$O system.

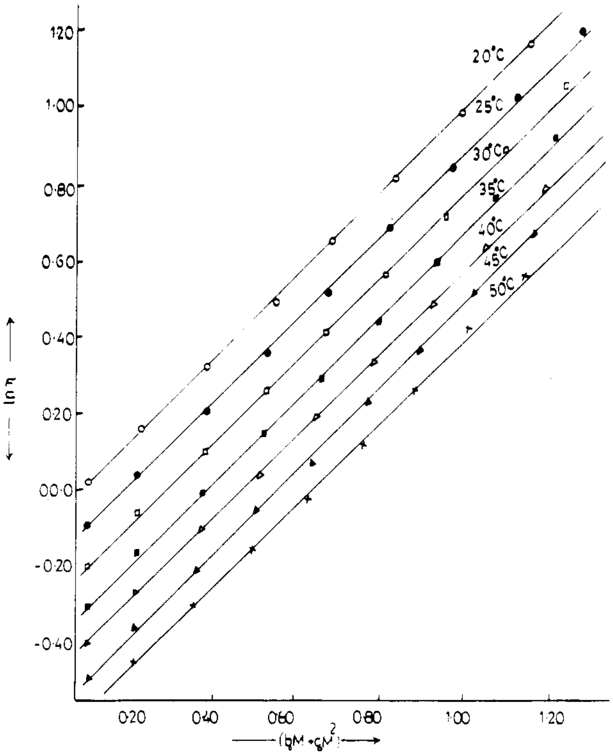

Figure 19. Plots of ln η vs ($b_0M + c_0M^2$) for the CuCl$_2$–H$_2$O system.

The c_0 values, given in Tables XI–XX, decrease from 20 to 50 °C by raising the temperatures, while b_0 and a_0 values increase and decrease, respectively, in this temperature range. The ion–solvent interactions, product of a_0 and b_0 terms, decrease with the rise in temperature and vary much more from electrolyte to electrolyte, and have large temperature coefficients (*7*). The electrolytic ion strongly orders the solvent in the cosphere about the ion. With increasing temperature, the solvent ordering is perturbed by the increase in the thermal energy, and the B coefficient for all the electrolytic ions de-

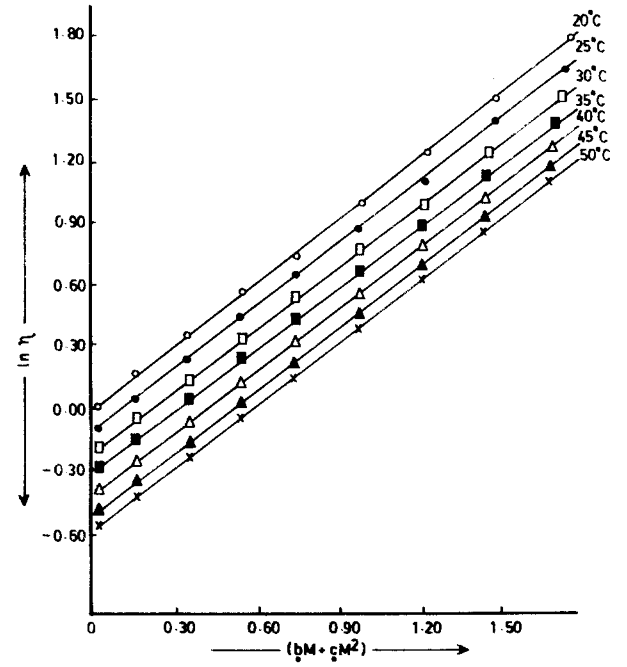

Figure 20. Plots of ln η vs $(b_0M + c_0M^2)$ for the $NiCl_2$–H_2O system.

creases in proportion to the increase in the entropy of hydration (*20*).

Finally, the values for the *B* coefficients estimated from the parameters of this empirical equation were compared with the existing literature data, and it was found that our values are slightly lower than the literature values. The *B* coefficient values at various temperatures for systems such as NaCl, $MgCl_2$ and $NiCl_2$ are given as follows:

system	temp, °C	*B* (lit.)	*B* (exptl)	diff
NaCl	25	0.0793	0.0688	0.0105
$MgCl_2$	25	0.2978	0.2704	0.0274
$NiCl_2$	35	0.2653	0.2451	0.0202

The difference between the two sets of data may be due in part to the uncertainty in temperature, which in our case is about ±0.05 °C, and in measuring flow rates. Our other major source of error springs from the fact that the solutions were prepared directly by weight. For NaCl and KCl this should be satisfactory. However, the other salts were hydrated. Hydrated salts are almost never exactly stoichiometric; they usually have an excess or deficiency of water. In addition, these *B* values were obtained from eq 1 based on data to high concentrations. Literature values are based on lower concentration data only, so they would not give strictly comparable values.

Registry No. NaCl, 7647-14-5; KCl, 7447-40-7; $SrCl_2$, 10476-85-4; $CaCl_2$, 10043-52-4; $BaCl_2$, 10361-37-2; $MgCl_2$, 7786-30-3; $CrCl_3$, 10025-73-7; $CuCl_2$, 7447-39-4; $CoCl_2$, 7646-79-9; $NiCl_2$, 7718-54-9.

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