Viscosity and Density of H_2O + NaCl + $CaCl_2$ and H_2O + KCl + $CaCl_2$ at 298.15 K

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The viscosity and density of water + sodium chloride + calcium chloride solutions and water + potassium chloride + calcium chloride solutions were measured over the entire concentration range at 298.15 K. The recently extended Jones−Dole equation still functions well for these systems up to a high concentration. It has been empirically found that when a seventh term of molarity was further added to the extended Jones−Dole equation, the viscosity for calcium chloride solutions and the mixed electrolyte solutions with larger ionic strengths could be excellently represented up to their saturated concentrations. In consideration of the large solubility of calcium chloride and furthermore of its large ionic strength and of its large viscosity−concentration coefficient, it could be supposed that the extented Jones−Dole equation in this work should fit many aqueous electrolyte solutions to their rather high concentrations or just to the saturated concentrations. In low concentrations, the calculated viscosity values obtained by simple additivity are close to the experimental values. Above a certain concentration, the calculated viscosities of NaCl + $CaCl_2$ and KCl + $CaCl_2$ mixtures are lower than the experimental values and the difference becomes larger with increasing concentration.

Introduction

The viscosities of H_2O + NaCl + KCl solutions over the entire concentration range have recently been measured, and the results were successfully correlated by us (Zhang and Han, 1996):

$$\eta_r = \eta/\eta^\circ = 1 + Ac^{1/2} + Bc + Dc^2 + Ec^{3.5} \qquad (1)$$

where η_r, η, and η° are the relative viscosity, viscosity of the solution, and viscosity of the solvent, respectively, and c is the concentration in molarity. The A coefficient is a measure of ion−ion interactions and may be calculated from equilibrium theory, as demonstrated by Falkenhagen (1971). The B coefficient, also called the Jones−Dole coefficient, is an empirical constant, qualitatively correlating ion−solvent interactions characteristic for each electrolyte and solvent. Assuming $B_{K^+} = B_{Cl^-}$ the B coefficient can be divided into ionic contributions. A positive B coefficient indicates "structure making", while a negative B coefficient indicates "structure breaking". The D coefficient, which can be related to solute−solute interactions is not well understood. The E is an empirically added coefficient by Zhang and Han (1996). The information about the Jones−Dole equation and its brief extended history may be found in our last paper (Zhang and Han, 1996).

To further examine its reasonableness, generality, and potential extension suitable for higher ion strengths, aqueous solutions of calcium chloride and its mixtures with sodium chloride and potassium chloride have been selected for viscosity measurements. The present work could be considered to be the continuation of our last paper (Zhang and Han, 1996).

Calcium chloride is very soluble and the Ca^{2+} ion has a strong hydrating ability and also $CaCl_2$ has a very large viscosity−concentration coefficient. So $CaCl_2$ should be a good salt for checking and potentially extending the original extended Jones−Dole equation (Zhang and Han, 1996).

There are few precise viscosity values for $CaCl_2$ in the literature (Goncalves and Kestin, 1979; Nowlan et al., 1980; Isono, 1984) and no viscosity measurements for aqueous $CaCl_2$ in the concentrations approaching the saturation. Maybe this could be ascribed to the fact that the precise concentration for an aqueous calcium chloride solution is not easy to achieve owing to its hygroscopic property and the viscosity measurement for it is rather time consuming owing to the large viscosity value for a concentrated solution.

Viscosity values for mixed electrolyte solutions are also lacking. No viscosity values for H_2O + KCl + $CaCl_2$ have been found in the literature. For H_2O + NaCl + $CaCl_2$, only very few experimental viscosity values at moderate concentrations have been found for 1/3, 1/1, and 3/1 (NaCl/$CaCl_2$) (Nowlan et al., 1980).

Experimental Section

Ultrapure NaCl and KCl were dried at 150 °C in vacuum prior to use. Double-distilled deionized water was used. A.R. grade calcium chloride was first dissolved into double-distilled deionized water and then filtered twice. The concentration of an aqueous calcium chloride solution was obtained by determining the Ca^{2+} concentration and Cl^- concentration, respectively. The Ca^{2+} concentration was determined by EDTA titration with a precision of 0.05% and an accuracy of 0.10%. Only from this could the concentration of $CaCl_2$ be achieved with an accuracy of 0.10% and a precision of 0.05%. The Cl^- concentration was determined by the $AgNO_3$ titration, i.e. Mohr's method with an accuracy of 0.10% and a precision of 0.05%. Only from the determination of the Cl^- concentration could the concentration of $CaCl_2$ be obtained with an accuracy of 0.05% and a precision of 0.025%. So by analysis of Ca^{2+} and Cl^- together the accuracy and the precision of the concentration of $CaCl_2$ may be further guaranteed and the

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Table 1. Experimental Density ρ and Viscosity η at 298.15 K for Aqueous $CaCl_2$ and the Viscosity Comparison with Literature Values

m/ mol·kg^{-1}	ρ/ g·cm^{-3}	η/ mPa·s	$[100(\eta - \eta_{cal})/\eta]$/ mPa·s[a]	$[100(\eta - \eta_{cal})/\eta]$/ mPa·s[b]	m/ mol·kg^{-1}	ρ/ g·cm^{-3}	η/ mPa·s	$[100(\eta - \eta_{cal})/\eta]$/ mPa·s[a]	$[100(\eta - \eta_{cal})/\eta]$/ mPa·s[b]
					$CaCl_2$ (I)				
0.0469	1.0014	0.9046	0.29		0.8528	1.0703	1.1386	0.05	0.26
0.0590	1.0025	0.9082	0.34		0.8673	1.0714	1.1431	0.02	0.23
0.0685	1.0033	0.9106	0.34		1.1578	1.0947	1.2430	−0.15	0.14
0.0975	1.0059	0.9186	0.40		1.7100	1.1368	1.4636	−0.04	−0.08
0.1439	1.0101	0.9311	0.47		1.8788	1.1491	1.5409	0.18	−0.10
0.1854	1.0138	0.9425	0.49		1.9790	1.1563	1.5897	0.37	−0.08
0.2046	1.0155	0.9476	0.47		2.0929	1.1645	1.6476	0.64	−0.04
0.2633	1.0206	0.9637	0.49	−0.29	2.1063	1.1654	1.6543	0.94	−0.05
0.2926	1.0232	0.9719	0.48	−0.19	2.5073	1.1932	1.8825	−0.12	0.07
0.3936	1.0320	1.0001	0.46	0.05	2.6380	1.2021	1.9666	−0.33	0.15
0.4007	1.0325	1.0020	0.44	0.05	2.9091	1.2201	2.1566	−0.60	0.26
0.4164	1.0339	1.0063	0.43	0.07	3.4443	1.2540	2.6110	−0.15	0.36
0.5295	1.0435	1.0392	0.37	0.23	3.9093	1.2820	3.1142	1.45	0.29
0.5843	1.0481	1.0554	0.32	0.26	4.7625	1.3297	4.4138		0.01
0.5942	1.0490	1.0583	0.30	0.25	5.3599	1.3604	5.7327		−0.03
0.6043	1.0497	1.0610	0.26	0.25	5.6189	1.3729	6.4365		−0.04
0.6139	1.0506	1.0641	0.28	0.27	6.8525	1.4268	11.2940		
0.7890	1.0651	1.1182	0.12	0.29	7.3330	1.4454	14.0283		
					$CaCl_2$ (II)				
0.0220	0.9991	0.8977	0.21		2.2261	1.1739	1.7186	0.58	−0.01
0.0239	0.9993	0.8982	0.22		2.7870	1.2120	2.0683	−0.51	−0.22
0.0594	1.0025	0.9081	0.32		2.9583	1.2232	2.1939	−0.61	0.28
0.0724	1.0037	0.9117	0.35		3.1438	1.2351	2.3420	−0.56	0.34
0.0816	1.0045	0.9145	0.40		3.2268	1.2403	2.4120	−0.51	0.34
0.1406	1.0097	0.9302	0.44		3.5941	1.2632	2.7611	0.26	0.37
0.1891	1.0141	0.9435	0.33		3.9571	1.2848	3.1731	1.80	0.22
0.1948	1.0146	0.9450	0.49		4.8394	1.3339	4.5635		0.04
0.4869	1.0398	1.0270	0.42	0.20	4.8583	1.3349	4.6003		0.02
0.7154	1.0590	1.0953	0.19	0.31	5.3683	1.3609	5.7538		−0.03
1.1607	1.0949	1.2439	−0.16	0.12	5.7097	1.3772	6.7066		−0.02
1.1891	1.0971	1.2542	−0.17	0.11	5.8689	1.3846	7.2091		0.01
1.3226	1.1075	1.3040	−0.21	0.03	6.1506	1.3973	8.1977		0.11
1.4754	1.1192	1.3638	−0.21	−0.04	6.2514	1.4018	8.5857		
1.5406	1.1241	1.3906	−0.19	−0.06	6.6584	1.4190	10.3407		
1.7575	1.1402	1.4847	0.00	−0.09	7.0766	1.4357	12.5000		
1.7818	1.1421	1.4958	0.04	−0.09	7.3414	1.4458	14.0780		
1.9034	1.1509	1.5530	0.24	−0.07	7.4589	1.4502	14.8392		
1.9407	1.1536	1.5716	0.34	−0.03	7.8783	1.4650	17.8223		
2.2115	1.1728	1.7106	0.63	−0.02					
					$CaCl_2$ (III)				
0.0450	1.0012	0.9042	0.30		1.5227	1.1227	1.3830	−0.21	−0.07
0.0837	1.0046	0.9149	0.38		1.6825	1.1347	1.4510	−0.10	−0.11
0.1317	1.0090	0.9277	0.42		1.7557	1.1400	1.4836	−0.02	−0.12
0.2535	1.0197	0.9609	0.48		2.1167	1.1662	1.6597	0.90	−0.05
0.3488	1.0280	0.9873	0.46	−0.06	2.4106	1.1866	1.8237	0.09	0.03
0.5542	1.0455	1.0459	0.27	0.19	2.5885	1.1987	1.9331	−0.32	0.07
0.5734	1.0472	1.0520	0.31	0.22	2.8391	1.2154	2.1050	−0.57	0.24
0.6696	1.0552	1.0812	0.25	0.31	3.6237	1.2650	2.7913	0.33	0.35
0.7754	1.0639	1.1138	0.13	0.28	3.8589	1.2791	3.0538	1.22	0.30
1.0913	1.0894	1.2189	−0.14	0.14	3.9661	1.2853	3.1825	1.67	0.21
1.4400	1.1165	1.3497	−0.21	−0.02	4.2137	1.2996	3.5150	−0.02	0.23

[a] η_{cal} is calculated by the coefficients in Nowlan et al.'s (1980) paper. The effective concentration region is (0−3.9) mol·kg^{-1}. [b] η_{cal} is calculated by the coefficients in Goncalves and Kestin's work (1979). The effective concentration region is (0.27−5.1) mol·kg^{-1}.

accuracy of 0.05% and the precision of 0.025% may be accepted with a greater reliability. Then solutions were prepared by mass with a precision of 5 × 10^{-5} g. All weighing was corrected to vacuum. For $CaCl_2$ solutions, solutions were made by diluting a stock solution of $CaCl_2$ with its concentration determined as above. For the mixed electrolyte solutions, a ratio of NaCl + $CaCl_2$ or KCl + $CaCl_2$ stock solutions was prepared by mixing NaCl or KCl with double-distilled deionized water and an aqueous $CaCl_2$ solution with a known concentration by mass. Dilution by mass resulted in a series of known concentrations of solutions.

Viscosities were measured with an Ubbelohde type glass capillary tube viscosimeter with a capillary length of 12.2 cm and a capillary diameter of 0.45 mm. The performance for viscosity measurements was as our recent work (Zhang and Han, 1996). The measuring temperature was accurate to (298.15 ± 0.01) K with a stability of ±0.002 K. At 25 °C, the viscosity and density of water are 0.8903 mPa·s and 0.997 07 g·cm^{-3}, respectively (Stokes and Mills, 1965). The viscosity measurement has a precision of 0.025%. The accuracy could reach up to 0.02% in the dilute region and 0.05% in the concentrated region. For $CaCl_2$ solutions in the higher concentrated region the accuracy could be lowered to 0.08% because of the relatively poorer accuracy for $CaCl_2$ concentration and the rather large viscosity values in the concentrated region.

The densities of solutions were measured by an Anton Paar 45 densimeter with a precision of ±5 × 10^{-5} g·cm^{-3} and an accuracy of 0.005%. It was calibrated by double-distilled water and dry air.

Table 2. Density ρ, Viscosity η, and Calculated Viscosity η (Eq 5) at 298.15 K for Aqueous Mixed $CaCl_2$ + NaCl and $CaCl_2$ + KCl at Total Molality m

		mPa·s				mPa·s				mPa·s				mPa·s	
m/mol·kg^{-1}	ρ/g·cm^{-3}	η	η (eq 5)	m/mol·kg^{-1}	ρ/g·cm^{-3}	η	η (eq 5)	m/mol·kg^{-1}	ρ/g·cm^{-3}	η	η (eq 5)	m/mol·kg^{-1}	ρ/g·cm^{-3}	η	η (eq 5)
n_{NaCl}/n_{CaCl_2} = 3.0218															
0.0805	1.0014	0.9016	0.9027	0.8386	1.0399	1.0001	0.9999	2.1492	1.1003	1.2088	1.1777	3.8629	1.1708	1.6016	1.4411
0.1884	1.0070	0.9153	0.9169	1.2958	1.0617	1.0662	1.0600	2.2029	1.1027	1.2187	1.1854	4.0519	1.1779	1.6552	1.4725
0.1959	1.0074	0.9160	0.9178	1.6250	1.0769	1.1178	1.1044	2.4938	1.1152	1.2752	1.2276	4.0913	1.1796	1.6672	1.4792
0.2620	1.0109	0.9241	0.9263	1.6953	1.0801	1.1293	1.1141	2.7129	1.1244	1.3202	1.2601	4.2702	1.1860	1.7206	1.5093
0.4753	1.0218	0.9518	0.9534	1.7648	1.0833	1.1410	1.1237	3.3438	1.1504	1.4648	1.3572	4.7142	1.2028	1.8652	1.5870
0.4912	1.0227	0.9539	0.9554	2.0102	1.0942	1.1835	1.1580	3.5449	1.1583	1.5157	1.3892				
0.7652	1.0362	0.9901	0.9905					3.6734	1.1633	1.5493	1.4100				
n_{NaCl}/n_{CaCl_2} = 1.0001 (I)															
0.0505	1.0005	0.9002	0.9013	0.8437	1.0500	1.0435	1.0415	2.0628	1.1191	1.3210	1.2758	2.8055	1.1576	1.5443	1.4362
0.1247	1.0054	0.9135	0.9148	1.1412	1.0677	1.1033	1.0959	2.2922	1.1312	1.3843	1.3238	3.3025	1.1819	1.7228	1.5525
0.2137	1.0111	0.9290	0.9304	1.2591	1.0767	1.1290	1.1184	2.3136	1.1323	1.3909	1.3283	3.4498	1.1890	1.7811	1.5885
0.3606	1.0204	0.9547	0.9561	1.8499	1.1076	1.2655	1.2325	2.3985	1.1368	1.4160	1.3465	3.6082	1.1968	1.8463	1.6283
0.4630	1.0268	0.9731	0.9749	1.8933	1.1099	1.2766	1.2413	2.6436	1.1494	1.4913	1.3999	3.8786	1.2095	1.9650	1.6979
0.7610	1.0451	1.0280	1.0267					2.6640	1.1504	1.4980	1.4045				
n_{NaCl}/n_{CaCl_2} = 1.0029 (II)															
0.0373	0.9996	0.8980	0.8988	0.5510	1.0323	0.9885	0.9893	1.8152	1.1054	1.2562	1.2252	3.4989	1.1912	1.7999	1.5998
0.0440	1.0002	0.8992	0.9001	0.6233	1.0358	1.0017	1.0020	2.0704	1.1192	1.3221	1.2770	3.5791	1.1950	1.8330	1.6198
0.1157	1.0048	0.9116	0.9131	1.1907	1.0703	1.1129	1.1049	2.3294	1.1329	1.3944	1.3311	3.6924	1.2003	1.8812	1.6485
0.1520	1.0072	0.9179	0.9196	1.4846	1.0872	1.1775	1.1605	2.4070	1.1370	1.4169	1.3478	3.8449	1.2074	1.9483	1.6877
0.2659	1.0145	0.9379	0.9395	1.5343	1.0899	1.1885	1.1700	2.4175	1.1375	1.4200	1.3500	3.9103	1.2105	1.9780	1.7049
0.3694	1.0210	0.9561	0.9576	1.6460	1.0962	1.2150	1.1918	3.0112	1.1676	1.6135	1.4827	4.0365	1.2165	2.0375	1.7386
0.4010	1.0229	0.9618	0.9631					3.2797	1.1807	1.7129	1.5462				
n_{NaCl}/n_{CaCl_2} = 1/2.9994															
0.0145	0.9982	0.8946	0.8950	0.2453	1.0162	0.9460	0.9476	1.3490	1.0950	1.2275	1.2165	3.5427	1.2282	2.2088	2.0132
0.0362	1.0000	0.8997	0.9003	0.4060	1.0282	0.9822	0.9838	1.8159	1.1256	1.3775	1.3502	3.8457	1.2447	2.4193	2.1670
0.0544	1.0014	0.9038	0.9046	0.4845	1.0340	1.0007	1.0017	2.2903	1.1555	1.5567	1.5028	4.0460	1.2554	2.5721	2.2768
0.0783	1.0032	0.9092	0.9101	0.5209	1.0367	1.0093	1.0101	2.6288	1.1760	1.7044	1.6238	4.1158	1.2590	2.6280	2.3165
0.1273	1.0071	0.9201	0.9212	0.6562	1.0466	1.0418	1.0417	2.8655	1.1900	1.8190	1.7153	4.3216	1.2697	2.8039	2.4392
0.1514	1.0089	0.9253	0.9266	0.9876	1.0702	1.1258	1.1223	3.3164	1.2157	2.0668	1.9072	4.4712	1.2775	2.9418	2.5338
n_{KCl}/n_{CaCl_2} = 3.0138 (I)															
0.0043	0.9974	0.8909	0.8912	0.1064	1.0032	0.8979	0.8992	0.5846	1.0298	0.9273	0.9295	3.2759	1.1583	1.1543	1.1183
0.0053	0.9974	0.8910	0.8914	0.1656	1.0066	0.9017	0.9032	0.7406	1.0381	0.9373	0.9393	3.6716	1.1747	1.2000	1.1498
0.0131	0.9979	0.8916	0.8922	0.1793	1.0074	0.9025	0.9040	1.0600	1.0549	0.9584	0.9596	3.9096	1.1845	1.2297	1.1693
0.0397	0.9994	0.8936	0.8945	0.2799	1.0130	0.9083	0.9104	1.1123	1.0576	0.9622	0.9630	4.1326	1.1933	1.2587	1.1877
0.0463	0.9999	0.8941	0.8950	0.2851	1.0133	0.9088	0.9108	1.7861	1.0910	1.0131	1.0082	4.3093	1.2003	1.2822	1.2026
0.0521	1.0002	0.8946	0.8954	0.4813	1.0241	0.9209	0.9230	2.0733	1.1046	1.0366	1.0283				
0.0887	1.0022	0.8971	0.8980					2.2659	1.1136	1.0535	1.0421				
n_{KCl}/n_{CaCl_2} = 3.0155 (II)															
0.0075	0.9976	0.8912	0.8916	0.3673	1.0178	0.9138	0.9159	2.2800	1.1139	1.0534	1.0430	4.0287	1.1886	1.2438	1.1788
0.0560	1.0003	0.8947	0.8957	0.7330	1.0375	0.9363	0.9387	2.9884	1.1454	1.1219	1.0958	4.2295	1.1966	1.2705	1.1956
0.2000	1.0085	0.9036	0.9054	1.3793	1.0707	0.9806	0.9805	3.9055	1.1836	1.2280	1.1686				
n_{KCl}/n_{CaCl_2} = 1.0000 (I)															
0.0130	0.9979	0.8926	0.8933	0.2251	1.0124	0.9206	0.9226	1.0770	1.0666	1.0358	1.0373	3.5053	1.1967	1.5258	1.4399
0.0333	0.9994	0.8956	0.8965	0.2817	1.0162	0.9275	0.9301	1.2289	1.0757	1.0590	1.0587	3.7728	1.2114	1.6024	1.4949
0.0534	1.0007	0.8983	0.8994	0.3029	1.0176	0.9303	0.9329	1.3517	1.0830	1.0779	1.0764	3.9678	1.2206	1.6605	1.5355
0.0809	1.0026	0.9019	0.9033	0.4183	1.0252	0.9450	0.9480	1.5162	1.0926	1.1038	1.1005	4.1343	1.2285	1.7120	1.5712
0.1048	1.0042	0.9052	0.9066	0.6443	1.0397	0.9750	0.9780	2.4113	1.1426	1.2688	1.2418	4.2724	1.2351	1.7568	1.6017
0.1371	1.0064	0.9093	0.9109	0.9416	1.0583	1.0166	1.0184	3.0097	1.1739	1.4015	1.3468				
0.1760	1.0091	0.9142	0.9161					3.3067	1.1888	1.4753	1.4025				
n_{KCl}/n_{CaCl_2} = 0.9996 (II)															
0.0328	0.9994	0.8955	0.8964	0.4151	1.0250	0.9450	0.9476	0.9542	1.0593	1.0192	1.0202	2.0021	1.1206	1.1905	1.1752
0.0510	1.0007	0.8981	0.8991	0.5273	1.0324	0.9596	0.9625	1.0324	1.0640	1.0305	1.0311	2.3770	1.1411	1.2637	1.2362
0.0772	1.0025	0.9016	0.9028	0.5405	1.0332	0.9618	0.9642	1.0489	1.0650	1.0330	1.0334	2.5219	1.1488	1.2938	1.2607
0.1255	1.0058	0.9075	0.9094	0.6981	1.0433	0.9830	0.9853	1.1445	1.0708	1.0466	1.0468	2.7118	1.1589	1.3351	1.2936
0.2093	1.0114	0.9185	0.9206	0.8709	1.0541	1.0072	1.0087	1.4745	1.0905	1.0992	1.0945	2.8382	1.1655	1.3642	1.3161
0.2295	1.0128	0.9210	0.9232					1.8217	1.1105	1.1580	1.1469				
n_{KCl}/n_{CaCl_2} = 1/2.9930 (I)															
0.0071	0.9976	0.8925	0.8928	0.4991	1.0355	0.9925	0.9941	1.8372	1.1285	1.3265	1.3155	3.9322	1.2515	2.2475	2.1116
0.0278	0.9994	0.8972	0.8976	0.7645	1.0551	1.0496	1.0507	1.9389	1.1350	1.3576	1.3443	4.2837	1.2701	2.4850	2.3004
0.0452	1.0007	0.9007	0.9014	1.0255	1.0738	1.1096	1.1093	2.2741	1.1561	1.4675	1.4452	4.5742	1.2848	2.7073	2.4723
0.2042	1.0131	0.9327	0.9339	1.3779	1.0980	1.1973	1.1938	2.3654	1.1618	1.4996	1.4744	4.7571	1.2938	2.8605	2.5887
0.3003	1.0206	0.9521	0.9533	1.6425	1.1158	1.2693	1.2622	2.6535	1.1793	1.6077	1.5712				
0.4389	1.0312	0.9803	0.9817					2.9588	1.1973	1.7350	1.6826				
n_{KCl}/n_{CaCl_2} = 1/2.9860 (II)															
0.0177	0.9985	0.8949	0.8954	0.1587	1.0097	0.9233	0.9247	0.6285	1.0452	1.0203	1.0213	2.6506	1.1793	1.6063	1.5698
0.0491	1.0011	0.9016	0.9022	0.2520	1.0169	0.9419	0.9435	1.2731	1.0909	1.1705	1.1678	4.6633	1.2897	2.7820	2.5276
0.0778	1.0033	0.9073	0.9082	0.2905	1.0198	0.9500	0.9513	1.6893	1.1190	1.2832	1.2746	4.7419	1.2936	2.8501	2.5783
0.1500	1.0089	0.9216	0.9229					1.9623	1.1367	1.3655	1.3509				

Table 3. Experimental, Literature, and Calculated Coefficients in Extended Jones−Dole Equations for NaCl, KCl, $CaCl_2$, and Their Binary Mixtures and the Standard Deviation $\sigma(\eta)$

	experimental						calculated	
mole ratios	B	D	10^4E	10^5F	m_{max}[a]	$10^4\sigma$/mPa·s	A[b]	B[c]
NaCl/KCl[d]								
1:0 (I)	0.0799	0.010 40	7.56		3.7	2.7	0.0061	
1:0 (II)	0.0794	0.011 42	6.19		6.0	2.5		
0:1	−0.0152	0.007 25	0.80		4.8	1.6	0.0051	
NaCl/$CaCl_2$								
0:1 (I)	0.2721	0.047 12	94.1	3.00	7.33	5	0.0157	0.271
	0.2725	0.045 51	104		2.64	6		
	0.2710	0.054 19			0.87	3		
0:1 (II)	0.2722	0.047 15	94.0	3.00	7.87	6		
	0.2726	0.044 32	109		2.96	12		
	0.2715	0.053 90			0.72	1		
0:1 (III)	0.2720	0.047 05	94.0	3.02	4.21	4		
	0.2727	0.044 40	107		2.84	11		
	0.2713	0.052 84			0.78	5		
3:1	0.1276	0.015 14	16.8		4.70	2	0.0081	0.1277
1:1 (I)	0.1765	0.022 15	34.8		3.88	2	0.0104	0.1756
1:1 (II)	0.1764	0.021 64	35.5		4.04	2		
1:3	0.2236	0.033 64	58.4	0.817	4.47	3	0.0129	0.2232
KCl/$CaCl_2$								
3:1 (I)	0.0571	0.009 90	6.09		4.31	5	0.0070	0.0570
3:1 (II)	0.0570	0.009 20	7.09		4.23	2		
1:1 (I)	0.1270	0.017 52	21.3		4.27	4	0.0093	0.1285
1:1 (II)	0.1284	0.017 10	21.9		2.84	2		
1:3 (I)	0.2028	0.027 47	49.5	0.738	4.57[e]	2	0.0122	0.1996
1:3 (II)	0.2007	0.030 09	44.5	0.924	4.66[e]	2		

[a] The maximum concentration for regression. [b] A is calculated by the Falkenhagen theory. [c] B is calculated by eq 3. [d] The parameters for NaCl and KCl are from Zhang and Han (1996). [e] The concentration has been around the saturated.

Results

The densities and viscosities of aqueous $CaCl_2$ solutions are given in Table 1. Three series of $CaCl_2$ solutions, each of which was made with an independent stock solution, were measured. The densities and viscosities of NaCl and KCl solutions are taken from our previous work (Zhang and Han, 1996). The densities and viscosities of aqueous mixtures of NaCl + $CaCl_2$ and KCl + $CaCl_2$ are given in Table 2. The mole ratios of NaCl/$CaCl_2$ or KCl/$CaCl_2$ studied were 3/1, 1/1, and 1/3. For 1/1 NaCl/$CaCl_2$ and all ratios of KCl/$CaCl_2$, two sets of measurements have been made. The maximum experimental concentration for any system in this work was close to saturation.

For the $CaCl_2$ solutions, the maximum concentration eq 1 can satisfactorily fit to is about 3 $mol\cdot kg^{-1}$. (In fact, this is equivalent to 9 $mol\cdot kg^{-1}$ NaCl in terms of ionic strength.) It has been empirically found that when a seventh term in molarity, Fc^7, was added to eq 1 as shown in eq 2.

$$\eta_r = \eta/\eta° = 1 + Ac^{1/2} + Bc + Dc^2 + Ec^{3.5} + Fc^7 \quad (2)$$

The experimental viscosity for aqueous $CaCl_2$ solutions can be ideally represented by eq 2 over all concentrations within the experimental precision and accuracy. Equation 1 or 2 can satisfactorily represent the experimental viscosity data of a mixed NaCl + $CaCl_2$ or a mixed KCl + $CaCl_2$ aqueous solution in different mole ratios within the experimental precision and accuracy over the entire concentration range.

All parameters were obtained by an equal weighting least-squares regression using the theoretical A values. The A values were calculated from the Falkenhagen theory (1971). All the coefficients for eqs 1 and 2 obtained by least-squares regression are listed in Table 3, together with standard deviation $\sigma(\eta)$ and theoretical A values. The Jones−Dole B coefficients calculated by additivity for the mixtures are also given in Table 3. The B coefficient additivity is based on

$$B = x_1B_1 + x_2B_2 \quad (3)$$

where x_i (i = 1, 2) is the mole fraction of one electrolyte in the mixed electrolyte and B_1 and B_2 are the B coefficients of individual electrolytes 1 and 2, respectively.

The simple additivity rule has been used for the comparison of the calculated viscosity values with the experimental values. The simple additivity equation is

$$\Delta\eta_{mix} = \Delta\eta_1 + \Delta\eta_2 \quad (4)$$

$$\eta_{mix} = \eta°(1 + \Delta\eta) \quad (5)$$

where

$$\Delta\eta_1 = A_1c_1^{1/2} + B_1c_1 + D_1c_1^{2} + E_1c_1^{3.5} + F_1c_1^{7} \quad (6-1)$$

$$\Delta\eta_2 = A_2c_2^{1/2} + B_2c_2 + D_2c_2^{2} + E_2c_2^{3.5} + F_2c_2^{7} \quad (6-2)$$

The viscosities of mixed NaCl + $CaCl_2$ and KCl + $CaCl_2$ aqueous solution have been calculated using the parameters obtained for NaCl, KCl, and $CaCl_2$. The calculated values are also listed in Table 2 for comparison with the experimental viscosities.

Our densities for $CaCl_2$ solutions are in agreement with the literature values within 0.01% in the dilute region and 0.02% in the concentrated region (Perron et al., 1981). The maximum concentration of $CaCl_2$ in Perron's work (Perron et al., 1981) is 6.5 $mol\cdot kg^{-1}$. The viscosity comparisons with literature values (Goncalves and Kestin, 1979; Nowlan et al., 1980) for $CaCl_2$ aqueous solutions are also listed in Table 1. The viscosities of the three series of $CaCl_2$ aqueous solutions at the same concentration agree within the precision and accuracy declared. The viscosity comparisons with the literature value (Nowlan et al., 1980) for NaCl + $CaCl_2$ aqueous solutions are listed in Table 4. The viscosities for the two sets of 1/1 NaCl + $CaCl_2$ aqueous solutions coincide within the precision and accuracy declared. The coefficients in eq 2 for the two series of 1/1 NaCl + $CaCl_2$ aqueous solutions are similar and the coefficients for every two sets of the same ratio of KCl +

Table 4. Comparison of Experimental Viscosity η with Calculated Viscosity η_{cal} at 298.15 K for Aqueous Mixed NaCl + $CaCl_2$ at Total Molarity

c/ mol·L^{-1}	η/ mPa·s	$\eta - \eta_{cal}$/ mPa·s	c/ mol·L^{-1}	η/ mPa·s	$\eta - \eta_{cal}$/ mPa·s
		$n_{NaCl}/n_{CaCl_2} = 3^a$			
0.5	0.9532	−0.0025	2.0	1.1910	−0.0076
1.0	1.0203	−0.0058	3.0	1.4317	−0.0033
1.5	1.1017	−0.0044	4.0	1.7499	−0.0168
		$n_{NaCl}/n_{CaCl_2} = 1^a$			
0.5	0.9717	−0.0088	2.0	1.3024	−0.0279
1.0	1.0651	−0.0140	3.0	1.6710	−0.0278
1.5	1.1853	−0.0084			
		$n_{NaCl}/n_{CaCl_2} = 1/3^a$			
0.5	1.0038	−0.0021	2.0	1.4742	−0.0101
1.0	1.1310	−0.0050	3.0	2.0246	−0.0115
1.5	1.2910	−0.0010			

[a] The experimental values are from Nowlan et al. (1980), and the calculated values are obtained from the parameters in this work.

$CaCl_2$ aqueous solutions are also similar, which shows that the method for measuring the viscosity of mixed electrolyte solutions is reliable and accurate and eqs 1 and 2 are reasonable. From Table 3 it can be found that the B coefficient for every mixture is close to that calculated by ion additivity. There are some density values in the literature (Nowlan et al., 1980; Kumar et al., 1982; Oakes et al., 1990) for NaCl + $CaCl_2$ aqueous solutions at 298.15 K. It is not convenient for comparison with ours, and it is also not a serious necessity in this work.

Discussion

Equation 1 not only represents the viscosity of $CaCl_2$ aqueous solutions but also represents the viscosity of NaCl + $CaCl_2$ and KCl + $CaCl_2$ aqueous solutions within the precision and accuracy declared to higher concentrations. If the large solubility and the large viscosity−concentration coefficient for $CaCl_2$ are taken into consideration, it is concluded that eq 1 functions well and it is understandable that eq 1 still could not represent the viscosity of $CaCl_2$ aqueous solutions and some ratios of NaCl/$CaCl_2$ or KCl/$CaCl_2$ aqueous solutions to saturation. Optimizing, it has been found when a term of seventh molarity, Fc^7, was added to eq 1, the obtained eq 2 may represent the viscosity of $CaCl_2$ aqueous solutions to saturation within the experimental precision and accuracy and furthermore may represent the viscosity of NaCl + $CaCl_2$ and KCl + $CaCl_2$ aqueous solutions to saturation within the precision and accuracy declared.

The reasons that eqs 1 and 2 represent the viscosity well are that the A coefficients are the theoretical values, the B coefficients are essentially equal to the B values by ion additivity and the standard deviations for regression are rather good.

From Table 2 it could be found that the calculated viscosities for the mixed electrolyte aqueous solutions by the simple additivity rule are close to the experimental viscosities in dilute concentrations (approximately under 1 mol·kg^{-1}); then, with the concentration increasing, the calculated values become smaller than the experimental values and the difference becomes larger. It may be assumed that, in dilute solutions, enough water could be employed to hydrate all the ions and that, in concentrated solutions, the interactions between ions become stronger and the real concentration of one single electrolyte should be greater due to the presence of another electrolyte that would have a certain quantity of water.

The solubilities of NaCl + $CaCl_2$ or KCl + $CaCl_2$ are smaller than those calculated by the simple additivity rule. This may be a result of a large difference between the hydrating abilities of Ca^{2+} and Na^+ and K^+, the stronger repulsive force between Ca^{2+} and both Na^+ and K^+, and also the greater difference of size and shape between Ca^{2+} and both Na^+ and K^+.

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