excess enthalpy respond with a similar sensitivity to the different effects arising when the components are mixed: the excess viscosities are distinctly negative and the excess enthalpies distinctly positive, and the magnitude of both increases with the length of the alkyl chain of the alcohol. At the same time, the excess volumes are smaller, especially for the lower alcohols, than would be expected on the basis of the excess enthalpies and excess viscosities. This, we think, is evidence of the significance of geometrical effects, which affect the excess volumes more than they affect the excess enthalpies and excess viscosities.

Registry No. DEMSA, 2374-61-0; methanol, 67-56-1; ethanol, 64-17-5; 1-propanol, 71-23-8; 2-propanol, 67-63-0; 1-butanol, 71-36-3; 2-methyl-2-propanol, 75-65-0.

Literature Cited

(1) Pikkarainen, L. *J. Chem. Eng. Data* **1987**, *32*, 427.
(2) Pikkarainen, L. *J. Chem. Eng. Data* **1987**, *32*, 429.
(3) Cannon, M. R.; Manning, R. E.; Bell, J. D. *Anal. Chem.* **1960**, *32*, 355.
(4) Raznjevic, K., Ed. *Thermodynamische Tabellen*; VDI Verlag GmbH: Düsseldorf, 1977.
(5) Washburn, E. W., Ed. *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*; McGraw-Hill: New York, 1930.
(6) Stoeckinger, T. M. Ph.D. Dissertation, University of Kentucky, 1968.
(7) Vaughn, J. W.; Sears, P. B. *J. Phys. Chem.* **1958**, *62*, 183.
(8) Joesten, M. D.; Schaad, L. J. *Hydrogen Bonding*; Marcel Dekker: New York, 1974.
(9) Jarva, M.; Saastamoinen, M.; Virtanen, P. O. I. *Finn. Chem. Lett.* **1974**, 169.
(10) Pikkarainen, L. *Finn. Chem. Lett.* **1980**, 33.
(11) Hovius, K.; Zuidema, G.; Engberts, J. B. F. N. *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 633.
(12) Huyskens, P. *J. Mol. Struct.* **1983**, *100*, 403.
(13) Assarsson, P.; Eirich, F. R. *J. Phys. Chem.* **1968**, *72*, 2710.
(14) Westmeier, S. *Z. Phys. Chem. (Leipzig)* **1976**, *257*, 950.
(15) Fort, R. J.; Moore, W. R. *Trans. Faraday Soc.* **1966**, *62*, 1112.
(16) Solimo, H. N.; Riggio, R.; Davolio, F.; Katz, M. *Can. J. Chem.* **1975**, *53*, 1258.
(17) Jannelli, L.; Rakshit, O.; Sacco, A. *Z. Naturforsch. A* **1974**, *29*, 355.

Received for review June 16, 1987. Accepted January 22, 1988.

Heat Capacity of Aqueous $FeCl_2$ from 349 to 597 K

Robert H. Wood,* Dorothy E. White, and William E. Davis

Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716

Peter T. Thompson

Department of Chemistry, Swarthmore College, Swarthmore, Pennsylvania 19081

A differential, flow, heat-capacity calorimeter has been used to measure the heat capacity of $FeCl_2$(aq) at molalities from 0.06 to 3.5 mol kg^{-1} and temperatures from 350 to 600 K at a pressure near 17.9 MPa. The results do not show the large negative values of $C_{p,\phi}$ characteristic of strong electrolytes at high temperatures and low molalities, indicating that $FeCl_2$(aq) like $NiCl_2$(aq) is mainly undissociated at high temperatures and molalities above 0.06 mol kg^{-1}. A sharp maximum in $C_{p,\phi}$ versus temperature may be due to the effects of association equilibria.

Introduction

This work is part of a continuing investigation of the heat capacities of aqueous electrolyte solutions at high temperatures using a flow calorimetric technique (*1-6*). Previous work has shown that alkali-metal halides and alkaline-earth halides have characteristically large, negative apparent molar heat capacities at 600 K and low molalities (*1*, *3-6*) and this has been attributed to large interactions between ions and water, together with the changes in the properties of water as its critical point is approached (*1*, *7-15*). Corresponding effects have been found for enthalpies of solution of salts in water (*7*, *8*). In contrast, the only transition-metal halide for which data are available, $NiCl_2$, does not show these characteristic large negative apparent molar heat capacities at temperatures up to 572 K, and this has been attributed to association of the Ni^{2+} with Cl^- ions.

In this paper we report measurements on another transition-metal halide, $FeCl_2$. Because of experimental difficulties the results are not as accurate as the measurements on the previous systems, but they are the only direct experimental measurements on this system. A knowledge of the thermodynamic properties of aqueous $FeCl_2$ is important in understanding a number of problems in the corrosion of electric power boilers at high temperatures and in the geochemistry of iron-bearing minerals.

Experimental Section

Solutions. The $FeCl_2$ solutions were prepared by dilution of concentrated stock solutions which were prepared separately for each of the two heat capacity runs. In most respects the procedures for the preparation of the stock and run solutions were the same for both sets of data, which were taken about 1.5 years apart. The stock solution was prepared in a 2-L bottle equipped with valves and stainless steel entry ports which allowed storage and transfer to be accomplished under an N_2 atmosphere at all times. Solvent used to prepare all solutions was carefully degassed ion-exchange water containing known amounts of HCl ($\simeq$0.0007 M). Starting material was Baker "analyzed" $FeCl_2{\cdot}4H_2O$ containing 99.9% "Fe" by $KMnO_4$ titration (i.e., total iron) and no listed impurities present at more than 0.005%. The weighed salt was dissolved in known

0021-9568/88/1733-0301$01.50/0

Table I. Apparent Molar Heat Capacity $C_{p,\phi}$ of $FeCl_2$(aq)

m(HCl)/ mmol·kg^{-1}	m($FeCl_2$)/ mol·kg^{-1}	P_s/P_w	c_p/c_p^0	$C_{p,\phi}{}^a$/ J·K^{-1}·mol^{-1}	δ^b	Δ^c	m(HCl)/ mmol·kg^{-1}	m($FeCl_2$)/ mol·kg^{-1}	P_s/P_w	c_p/c_p^0	$C_{p,\phi}{}^a$/ J·K^{-1}·mol^{-1}	δ^b	Δ^c
(A) Second Series													
T/K = 349.00; P/MPa = 17.89; f^d = 1.008													
1.05	0.0678	0.9958	0.9882	−201	18	9	5.09	0.9520	0.9621	0.8719	−100	4	−3
1.05	0.0678	0.9959	0.9883	−198	17	7	5.09	0.9520	0.9621	0.8719	−100	4	−3
1.30	0.1253	0.9931	0.9792	−175	11	−3	8.29	1.6500	0.9456	0.8057	−65	3	−3
1.30	0.1253	0.9930	0.9791	−177	11	−1	8.29	1.6500	0.9455	0.8056	−65	3	−2
1.88	0.2517	0.9871	0.9599	−156	8	−3	11.99	2.4566	0.9331	0.7467	−35	3	−2
1.88	0.2517	0.9870	0.9598	−157	8	−2	11.99	2.4566	0.9333	0.7468	−33	3	−2
3.34	0.5698	0.9741	0.9163	−128	5	−2	30.06	2.5120	0.9323	0.7431	−34	3	−1
3.34	0.5698	0.9743	0.9165	−126	5	−3	30.06	2.5120	0.9325	0.7432	−33	3	−2
14.15	0.5706	0.9737	0.9158	−130	5	1	16.73	3.4908	0.9261	0.6908	−4	2	−2
14.15	0.5706	0.9737	0.9158	−130	5	1	16.73	3.4908	0.9262	0.6909	−4	2	−2
5.09	0.9520	0.9617	0.8715	−102	4	−1							
T/K = 401.47; P/MPa = 18.03; f^d = 1.057													
1.05	0.0678	0.9959	0.9881	−212	19	−1	5.09	0.9520	0.9721	0.8798	−62	4	4
1.05	0.0678	0.9959	0.9881	−215	19	2	5.09	0.9520	0.9721	0.8798	−62	4	4
1.30	0.1253	0.9932	0.9790	−185	12	−1	8.29	1.6500	0.9677	0.8233	−11	2	1
1.30	0.1253	0.9932	0.9790	−183	12	−3	8.29	1.6500	0.9677	0.8234	−11	2	1
1.88	0.2517	0.9877	0.9599	−159	8	11	11.99	2.4566	0.9720	0.7770	33	1	3
1.88	0.2517	0.9881	0.9604	−150	8	3	11.99	2.4566	0.9724	0.7773	33	1	3
1.88	0.2517	0.9880	0.9602	−154	8	6	30.06	2.5120	0.9721	0.7740	34	1	4
3.34	0.5698	0.9789	0.9198	−102	5	7	30.06	2.1520	0.9724	0.7742	35	1	4
3.34	0.5698	0.9788	0.9198	−102	5	7	16.73	3.4908	0.9873	0.7363	75	1	2
14.15	0.5706	0.9786	0.9195	−104	5	9	16.73	3.4908	0.9881	0.7370	76	1	0
14.15	0.5706	0.9785	0.9194	−105	5	9	16.73	3.4908	0.9879	0.7368	76	1	1
T/K = 449.72; P/MPa = 18.03; f^d = 1.030													
1.05	0.0678	0.9962	0.9885	−195	18	−19	5.09	0.9520	0.9935	0.9004	41	2	3
1.05	0.0678	0.9960	0.9883	−204	18	−10	5.09	0.9520	0.9934	0.9003	41	2	4
1.30	0.1253	0.9938	0.9798	−162	12	−6	8.29	1.6500	1.0112	0.8623	112	1	−1
1.30	0.1253	0.9939	0.9799	−157	11	−11	8.29	1.6500	1.0112	0.8623	112	1	−2
1.88	0.2517	0.9906	0.9632	−104	7	0	11.99	2.4566	1.0332	0.8280	151	2	3
1.88	0.2517	0.9907	0.9633	−103	7	−1	11.99	2.4566	1.0332	0.8280	151	2	3
3.34	0.5698	0.9889	0.9301	−21	3	6	30.06	2.5120	1.0327	0.8244	149	2	6
3.34	0.5698	0.9890	0.9301	−20	3	5	30.06	2.5120	1.0330	0.8246	150	2	6
14.15	0.5706	0.9885	0.9297	−23	3	8	16.73	3.4908	1.0515	0.7860	166	2	0
14.15	0.5706	0.9886	0.9297	−23	3	8	16.73	3.4908	1.0509	0.7855	165	2	1
T/K = 498.03; P/MPa = 18.03; f^d = 1.034													
1.05	0.0678	0.9975	0.9898	−111	17	−5	5.09	0.9520	1.0276	0.9324	213	4	2
1.05	0.0678	0.9975	0.9899	−109	17	−8	8.29	1.6500	1.0469	0.8938	221	3	1
1.30	0.1253	0.9974	0.9834	−35	9	−4	8.29	1.6500	1.0463	0.8932	219	3	3
1.30	0.1253	0.9973	0.9833	−39	10	0	8.29	1.6500	1.0467	0.8936	221	3	1
1.88	0.2517	0.9995	0.9720	55	4	7	11.99	2.4566	1.0536	0.8450	199	3	1
1.88	0.2517	0.9997	0.9722	58	4	3	11.99	2.4566	1.0543	0.8456	201	3	0
3.34	0.5698	1.0122	0.9528	171	4	0	11.99	2.4566	1.0536	0.8450	199	3	1
3.34	0.5698	1.0125	0.9530	173	4	−2	30.06	2.5120	1.0522	0.8405	195	2	4
14.15	0.5706	1.0105	0.9510	157	3	15	30.06	2.5120	1.0519	0.8403	194	2	5
14.15	0.5706	1.0109	0.9513	160	3	12	16.73	3.4908	1.0480	0.7834	168	2	5
5.09	0.9520	1.0276	0.9324	213	4	2							
T/K = 549.49; P/MPa = 17.86; f^d = 1.056													
1.04	0.0678	1.0001	0.9925	79	16	33	1.80	0.2324	1.0085	0.9833	263	8	−31
1.04	0.0678	1.0005	0.9929	103	16	9	3.34	0.5692	1.0173	0.9581	238	5	−8
1.28	0.1195	1.0023	0.9891	170	11	10	3.34	0.5692	1.0030	0.9438	104	2	*e*
1.28	0.1195	1.0037	0.9905	230	12	−50	3.34	0.5692	1.0108	0.9517	177	4	52
1.80	0.2324	1.0081	0.9829	253	8	−21							
T/K = 549.70; P/MPa = 17.82; f^d = 1.056													
1.04	0.0678	0.09998	0.9921	49	16	63	3.34	0.5692	1.0151	0.9560	218	5	11
1.04	0.0678	1.0003	0.9927	94	16	18	3.34	0.5692	1.0153	0.9561	219	5	9
1.04	0.0678	1.0007	0.9931	122	17	−11	4.92	0.9134	1.0190	0.9280	193	3	−10
1.28	0.1195	1.0036	0.9905	229	12	−50	4.92	0.9134	1.0190	0.9280	193	3	−10
1.28	0.1195	1.0048	0.9917	280	13	*e*	8.29	1.6486	1.0134	0.8646	137	2	−20
1.28	0.1195	1.0033	0.9901	212	12	−32	8.29	1.6486	1.0134	0.8646	137	2	−20
3.34	0.5692	1.0154	0.9562	220	5	8	12.30	2.5239	1.0008	0.7974	104	0	3
3.34	0.5692	1.0167	0.9575	232	5	−3	12.30	2.5239	1.0004	0.7971	103	0	4
3.34	0.5692	1.0178	0.9586	243	5	−14	30.48	2.5131	0.9985	0.7962	99	1	8
3.34	0.5692	1.0000	0.9409	77	2	*e*	30.48	2.5131	0.9988	0.7964	99	0	8
3.34	0.5692	1.0134	0.9542	202	4	27	16.68	3.4800	0.9844	0.7346	84	1	−2
3.34	0.5692	1.0140	0.9548	207	4	22	16.68	3.4800	0.9845	0.7347	84	1	−2
T/K = 598.57; P/MPa = 17.96; f^d = 1.104													
1.04	0.0678	0.9942	0.9860	−508	32	−2	3.34	0.5692	0.9570	0.8963	−426	13	−26
1.04	0.0678	0.9947	0.9866	−454	31	−56	3.34	0.5692	0.9570	0.8963	−426	13	−26
1.28	0.1195	0.9914	0.9773	−411	21	29	3.34	0.5692	0.9554	0.8946	−446	13	−6
1.28	0.1195	0.9911	0.9771	−424	22	42	3.34	0.5692	0.9558	0.8950	−442	13	−11
1.80	0.2324	0.9827	0.9560	−425	16	10	4.92	0.9134	0.9339	0.8434	−401	12	10
1.80	0.2324	0.9828	0.9560	−422	16	8	4.92	0.9134	0.9328	0.8423	−409	12	19

Table I (Continued)

m(HCl)/ mmol·kg^{-1}	m(FeCl$_2$)/ mol·kg^{-1}	P_s/P_w	$c_p/c_p{}^0$	$C_{p,\phi}{}^a$/ J·K^{-1}·mol^{-1}	δ^b	Δ^c	m(HCl)/ mmol·kg^{-1}	m(FeCl$_2$)/ mol·kg^{-1}	P_s/P_w	$c_p/c_p{}^0$	$C_{p,\phi}{}^a$/ J·K^{-1}·mol^{-1}	δ^b	Δ^c
4.92	0.9134	0.9330	0.8425	−408	12	17	8.29	1.6486	0.8921	0.7510	−347	10	−3
8.29	1.6486	0.8921	0.7510	−347	10	−3	12.30	2.5239	0.8565	0.6706	−283	9	0
(B) First Series													
T/K = 349.23; P/MPa = 17.83; f^f = 1.050													
1.08	0.0622	0.9969	0.9898	−162	27	−32	2.16	0.9408	0.9633	0.8725	−104	11	0
1.08	0.0622	0.9962	0.9891	−210	30	17	2.16	0.9408	0.9628	0.8720	−106	11	2
1.08	0.0622	0.9965	0.9894	−190	29	−3	2.16	0.9408	0.9629	0.8721	−106	11	2
1.15	0.1210	0.9934	0.9797	−183	22	4	2.16	0.9408	0.9629	0.8722	−105	11	2
1.15	0.1210	0.9933	0.9796	−183	22	5	3.05	1.6704	0.9455	0.8023	−69	9	3
1.31	0.2535	0.9871	0.9592	−164	17	5	3.05	1.6704	0.9457	0.8025	−69	9	2
1.31	0.2535	0.9874	0.9595	−158	16	−2	3.05	1.6704	0.9456	0.8024	−69	9	2
1.63	0.5138	0.9766	0.9230	−137	14	3	3.98	2.4231	0.9339	0.7470	−40	8	3
1.63	0.5138	0.9768	0.9232	−135	14	1	3.98	2.4231	0.9341	0.7471	−40	8	3
1.63	0.5138	0.9765	0.9229	−138	14	4	5.25	3.4582	0.9266	0.6903	−9	6	2
1.63	0.5138	0.9776	0.9240	−128	13	−5	5.25	3.4582	0.9265	0.6902	−9	6	2
T/K = 400.32; P/MPa = 17.69; f^f = 1.050													
1.08	0.0622	0.9957	0.9885	−249	33	33	2.16	0.9408	0.9728	0.8815	−60	9	−1
1.08	0.0622	0.9962	0.9891	−212	30	−4	2.16	0.9408	0.9731	0.8818	−58	9	−2
1.15	0.1210	0.9933	0.9796	−188	22	0	2.16	0.9408	0.9730	0.8818	−59	9	−2
1.15	0.1210	0.9939	0.9802	−166	21	−21	2.16	0.9408	0.9731	0.8818	−58	9	−3
1.15	0.1210	0.9938	0.9801	−169	21	−18	3.05	1.6704	0.9690	0.8233	−6	6	−5
1.31	0.2535	0.9885	0.9606	−142	16	−6	3.05	1.6704	0.9688	0.8231	−7	6	−4
1.31	0.2535	0.9885	0.9607	−141	16	−7	3.05	1.6704	0.9689	0.8232	−6	6	−5
1.31	0.2535	0.9885	0.9606	−141	16	−6	3.98	2.4231	0.9737	0.7804	35	3	−3
1.63	0.5138	0.9816	0.9280	−95	11	−8	3.98	2.4231	0.9733	0.7801	34	3	−3
1.63	0.5138	0.9811	0.9274	−100	12	−3	3.98	2.4231	0.9725	0.7795	33	4	−1
1.63	0.5138	0.9809	0.9272	−102	12	−2	5.25	3.4582	0.9869	0.7377	74	1	−1
1.63	0.5138	0.9809	0.9273	−101	12	−2	5.25	3.4582	0.9888	0.7391	77	1	−3
T/K = 448.76; P/MPa = 17.83; f^f = 1.050													
1.08	0.0626	0.9958	0.9886	−246	33	28	2.14	0.9269	0.9936	0.9026	40	3	−2
1.08	0.0626	0.9958	0.9886	−245	33	26	3.05	1.6660	1.0122	0.8623	115	3	−6
1.15	0.1218	0.9936	0.9798	−181	22	10	3.05	1.6660	1.0123	0.8623	115	3	−7
1.15	0.1218	0.9943	0.9805	−154	20	−18	3.05	1.6660	1.0125	0.8625	116	3	−7
1.31	0.2529	0.9914	0.9637	−92	13	−13	3.98	2.4231	1.0330	0.8305	153	4	−2
1.31	0.2529	0.9912	0.9635	−97	13	−9	3.98	2.4231	1.0332	0.8306	153	4	−2
1.69	0.5646	0.9895	0.9309	−19	7	0	3.98	2.4231	1.0333	0.8307	153	4	−2
1.69	0.5646	0.9893	0.9308	−20	7	1	5.25	3.4582	1.0523	0.7890	169	5	−4
2.14	0.9269	0.9932	0.9021	38	3	0							
T/K = 498.61; P/MPa = 17.83; f^f = 1.050													
1.08	0.0626	0.9970	0.9898	−169	29	47	2.14	0.9269	1.0278	0.9352	220	10	−5
1.08	0.0626	0.9977	0.9906	−111	26	−11	2.14	0.9269	1.0277	0.9351	219	10	−4
1.15	0.1218	0.9977	0.9841	−27	13	−13	3.05	1.6660	1.0481	0.8943	226	9	−4
1.15	0.1218	0.9978	0.9842	−23	13	−17	3.05	1.6660	1.0483	0.8945	226	9	−4
1.31	0.2554	1.0002	0.9723	68	4	−1	3.98	2.4230	1.0548	0.8488	205	7	−3
1.31	0.2554	1.0004	0.9726	72	4	−5	3.98	2.4230	1.0553	0.8492	206	7	−4
1.69	0.5646	1.0129	0.9541	179	8	−6	5.25	3.4582	1.0516	0.7884	175	5	−3
1.69	0.5646	1.0130	0.9542	180	8	−7	5.25	3.4582	1.0519	0.7887	176	5	−3
T/K = 549.02; P/MPa = 17.83; f^f = 1.050													
1.08	0.0626	1.0007	0.9937	129	20	e	23.32	0.9442	1.0126	0.9191	153	5	e
1.08	0.0626	1.0004	0.9934	100	19	e	2.14	0.9269	1.0186	0.9264	189	8	e
1.15	0.1218	1.0036	0.9902	224	18	e	2.14	0.9269	1.0193	0.9271	193	8	e
1.15	0.1218	1.0028	0.9893	187	16	e	3.05	1.6660	1.0142	0.8640	138	3	e
1.31	0.2554	1.0089	0.9812	253	15	e	3.05	1.6660	1.0136	0.8635	137	3	e
1.31	0.2554	1.0087	0.9811	250	15	e	3.98	2.4230	1.0042	0.8062	110	1	e
1.69	0.5646	1.0170	0.9582	235	11	e	3.98	2.4230	1.0038	0.8058	109	1	e
1.69	0.5646	1.0168	0.9579	233	11	e	5.25	3.4582	0.9868	0.7376	87	2	e
23.32	0.9442	1.0136	0.9201	159	6	e							
T/K = 596.97; P/MPa = 17.83; f^f = 1.050													
1.08	0.0626	0.9936	0.9863	−579	60	e	23.32	0.9442	0.9458	0.8556	−274	24	e
1.08	0.0626	0.9949	0.9877	−444	52	e	23.32	0.9442	0.9437	0.8536	−289	25	e
1.08	0.0626	0.9955	0.9883	−380	48	e	3.05	1.6660	0.9873	0.8399	63	4	e
1.31	0.2554	0.9810	0.9528	−396	34	e	3.05	1.6660	0.9870	0.8397	62	4	e
1.31	0.2554	0.9814	0.9532	−384	33	e	3.98	2.4230	0.9768	0.7831	59	4	e
1.69	0.5646	0.9574	0.8993	−397	32	e	3.98	2.4230	0.9741	0.7808	51	5	e
1.69	0.5646	0.9569	0.8987	−403	32	e	5.25	3.4582	0.7083	0.5189	−451	36	e
2.14	0.9269	0.9940	0.9029	58	4	e	5.25	3.4582	0.7080	0.5186	−452	36	e
2.14	0.9269	0.9929	0.9018	51	4	e							

[a] The apparent molar heat capacity, $C_{p,\phi}$, was calculated from eq 1 and 2. [b] The estimated error of each $C_{p,\phi}$ value, δ, was calculated assuming absolute errors of ±0.000 15 and relative errors of 1% in $\Delta P/P$. [c] Δ is the value of $C_{p,\phi}$(calculated) − $C_{p,\phi}$(observed). The calculated value is from a cubic spline interpolation of the knots in Table II. [d] The value of the heat loss correction factor, f, was calculated by using the heat capacity of 3.0053 mol·kg^{-1} NaCl as a chemical standard (*3*, *18*). The measured values of $\Delta P/P$ for 3.0053 mol·kg^{-1} NaCl at the experimental pressure were −0.050 78 at 349.00 K, −0.060 86 at 401.47 K, −0.7855 at 449.72 K −0.100 50 at 498.03, −0.147 27 at 549.49, −0.147 69 at 549.70 K, and −0.261 19 at 598.57 K. [e] These data were not included in the least-squares fit (see text). [f] A chemical standard was not used with these runs so the heat loss correction factor, f, was estimated from previous experience with this instrument at these temperatures. For these data, errors were estimated by using a relative error of 5% in $\Delta P/P$ because of the uncertainty of f.

masses of H_2O and known amounts of HCl were added. The resulting concentrated stock solutions were approximately 3.5 and 4.7 *m* in $FeCl_2$, respectively, in the two preparations. Initially the solutions were very dark in color and obviously contained relatively large amounts of ferric ion. Several additions of Baker "analyzed" iron wire, 99.7% pure and 0.22 mm in diameter were made. The weighed wire was allowed to dissolve completely. Tests had indicated that this was an efficient method for reducing Fe^{3+} to Fe^{2+}. The reduction of ferric ion in this manner took several weeks to accomplish, but the final stock solutions were green in color and clear.

A standard assay involving spectrophotometric analysis of ferric thiocyanate complex ion was developed and used to follow the ferric ion concentration in the stock and run solutions. At the end of the reduction period the Fe^{3+} concentration was less than 30 ppm in each case (<0.02% of the total iron in the worst of the two cases). Although the source of the $FeCl_2$ was the same in both cases, the amount of ferric ion present initially in the two preparations was 0.74% of the total iron in the first case and 4.26% in the second case. In each case the amount of iron wire oxidized correlated nicely with the loss of Fe^{3+} ion determined spectrophotometrically according to the reaction $Fe + 2Fe^{3+} = 3Fe^{2+}$.

Chloride ion was determined in the stock solutions by potentiometric titrations with $AgNO_3$ standardized against conductance grade KCl. For the first stock solution iron was determined by potentiometric titration against standard $K_2Cr_2O_7$ which was in turn checked against "Thorn Smith" iron ore and $Fe(NH_4)(SO_4)_2$ standard samples and against analytical grade Fe wire. For the second stock solution iron was determined by EDTA titrations using 2% tiron as indicator. Attempts to determine H^+ concentrations directly by pH measurements were only marginally reliable. It was necessary to dilute the stock solution to avoid a poisoning effect (or dramatic activity effect) on the glass electrode by the concentrated stock solution. The necessary extrapolation of the pH results led to uncertainties in the stock H^+ concentration.

"Nominal" concentrations of $FeCl_2$ and HCl based on the known masses of all added chemicals, including Fe^{2+} resulting from the addition of Fe wire, were calculated. For the first stock solution the iron content deduced from the chloride analysis, after allowing for HCl estimated from the pH determinations, was 0.6% higher than that measured directly. The average of the two results agreed exactly (0.01%) with the nominal concentrations.

In the second stock solution case, analyses were complicated by the fact that they were not performed until after the solution had inadvertently been allowed to undergo some air oxidation of Fe^{2+} to Fe^{3+}. This required the addition of known amounts of HCl before performing the analyses. The iron determination agreed with the nominal concentration within 0.56% but the chloride value differed significantly. Since the nominal results agreed with analysis in the first stock solution case nominal values were used in the second case as well to compute all run solution molalities. The correctness of this procedure is supported by the fact that no significant differences between the results of the two heat capacity runs were observed.

All run solutions were prepared by weight dilution under an N_2 atmosphere. Fe^{3+} was monitored before and after the heat capacity determinations and were always found to be at the low levels implied by less than 30 ppm in the stock solution.

Extra HCl was added to some of the run solutions to test for the occurrence of hydrolysis of Fe^{2+} at the higher temperatures.

Heat-Capacity Measurements. The high-temperature flow heat-capacity calorimeter has been described in detail previously (*1*, *16*). The calorimeter was operated at a water flow rate of 2.0 $mL{\cdot}min^{-1}$ and with heater power of 0.31 W resulting in temperature rises of 1.1–1.8 K. The reported temperatures are the average of the initial and final temperatures of the solution. The back pressure regulator was calibrated (±0.25 MPa) by using a Heise CM gauge (0–4000 psi). A minimum of three heat-capacity measurements were made for each concentration. The instrument measures the electrical power necessary to give the same temperature rise when the sample solution and pure water are flowing in the calorimeter. The specific heat capacity of the sample solution at constant pressure, c_p, is then calculated by the equation

$$c_p/c_p{}^0 = [1 - f\{(P_s - P_w)/P_w\}](d_w/d_s) \qquad (1)$$

where c_p is the specific heat capacity of the soltuion, $c_p{}^0$ is the specific heat capacity of pure water at the experimental temperature and pressure, P_s is the electrical power when the sample solution is in the sample cell, P_w is the power when water is in the sample cell, f is a correction factor for heat losses, and d_w and d_s are the densities of water and of the aqueous salt solution at the experimental pressure and the temperature of the sample loop (25 °C). The densities were taken from Karapet'yants et al. (*17*). The first set of measurements were taken before the importance of using a chemical standard was realized. For these runs the calibration factor was estimated as 1.05 ± 0.005 from previous experience with this calorimeter. For the second set of measurements the correction factor, f, was calculated at each temperature by using 3.0 $mol{\cdot}kg^{-1}$ NaCl as a chemical standard (*18*).

The apparent molar heat capacity, $C_{p,\phi}$, can be calculated from the specific heat capacity ratio, $c_p/c_p{}^0$, by using the equation

$$C_{p,\phi} = \left(M_2 + \frac{1}{m}\right)c_p - \left(\frac{1}{m}\right)c_p{}^0 \qquad (2)$$

where M_2 is the molar mass of the solute and m is the molality of the aqueous salt solution.

Boundary Effects. Fortier, Benson, and Picker (*19*) have shown that errors can arise in flow calorimeters because of mixing and volume changes at the boundary between the sample and reference solutions. This effect can be large when the sample and reference fluids are quite different but is normally negligible with aqueous salt solutions (m < 5.0 $mol{\cdot}kg^{-1}$) (*3*,*6*,*18*).

Results

The results of the present measurements of $C_{p,\phi}$ for $FeCl_2$(aq) are given in Table I together with an estimate of the error of the individual measurements. Karapet'yants, Vasilëv, and Sanaev (*17*) have reported specific heats of aqueous $FeCl_2$ at 298.15 K and 0.5 MPa. We calculated $C_{p,\phi}$ using these authors' value for the specific heat of pure water obtained by extrapolating their results to infinite dilution (see Table II). This eliminates problems with small systematic errors in the heat-capacity measurements and yields values in reasonable agreement with the values of Bernaducci, Morss, and Miksetzl (*20*), $C_{p,\phi} = -256 \pm 30$ $J{\cdot}K^{-1}{\cdot}mol^{-1}$ at $m = 0$ and $C_{p,\phi} = 36.6$ $J{\cdot}K^{-1}{\cdot}mol^{-1}$ at 4.43 $mol{\cdot}kg^{-1}$. Table II gives their results corrected to 17.9 MPa, assuming the change in $C_{p,\phi}$ with pressure is the same as that for $MgCl_2$(aq) as given by Gates (*12*). Above 2.25 $mol{\cdot}kg^{-1}$, this involves an extrapolation of the results of Gates. The pressure corrections to the data at 298.15 K are as high as ±60 $J{\cdot}K^{-1}{\cdot}mol^{-1}$. Since we are using experimental data on $MgCl_2$(aq), errors in this correction of ±60 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ or more are certainly possible.

Table II. $C_{p,\phi}$ for $FeCl_2$(aq) at 298.15 K

m/ mol·kg^{-1}	$C_{p,\phi}$/J·K^{-1}·mol^{-1}		Δ^c
	P/MPa = 0.1[a]	P/MPa = 17.9[b]	(P=17.9 MPa)
0.0318	−263	−209	−1
0.245	−238	−170	4
0.439	−208	−142	−5
0.832	−179	−124	0
0.957	−170	−120	1
1.461	−139	−106	−1
1.972	−118	−104	1
2.688	−91	−103	−1
3.910	−55	−111	0

[a] Calculated from the results of Karapet'yants, Vasilëv, and Sanaev (*17*) by using $c_p(H_2O)$ = 0.9979 J·g^{-1}·K^{-1}. [b] The results at 0.1 MPa were corrected to 17.9 MPa assuming the change in $C_{p,\phi}$ with pressure at 298.15 K is the same as that for $MgCl_2$(aq) as given by Gates (*20*). The corrections above 2.25 mol·kg^{-1} are extrapolations of the results of Gates. [c] Δ is the value of $C_{p,\phi}$(calculated) − $C_{p,\phi}$(observed). The calculated value is from a cubic spline interpolation of the knots in Table II.

Table III. $FeCl_2$ Knot Positions and Knot Values for Calculating $C_{p,\phi}$ at P = 17.9 MPa[a]

m/ mol·kg^{-1}	T/K						
	273.15	298.15	400	450	500	550	600
0.0	−291[b]	−240[b]	−300[b]	−357[b]	−370[b]	−376[b]	−2729[b]
0.2500	−169[b]	−165	−148	−104	72	233	−450
1.5000	−133[b]	−106	−22	99	226	122	−357
3.500	−181[b]	−108	74	166	168	82	594[b]
4.000	−183[b]	−111[b]	88[b]	157[b]	157[b]	51[b]	1428[b]

[a] This is a representation of 218 points. The sum of the squares of the residuals is 38011 and the standard error of the fit is 14. The minimum sum of the squares for this set is 14449. [b] These knots are outside the range of the data. The surface should not be used to predict $C_{p,\phi}$ (1) above 3.5 mol·kg^{-1} at any temperature, (2) above 550 K at molalities either above 2.5 mol·kg^{-1} or below 0.06 mol·kg^{-1}, and (3) below 298.15 K at all molalities. The accuracy above 500 K is not known (see text).

As in previous work (*3*, *21*), the present results, together with the literature results at 298.15 K, were fit with a two-dimensional cubic spline surface as a function of temperature and square root of molality. The Debye–Hückel limiting law was used as an end condition for the cubic spline fits vs square root of molality with the limiting law slope being calculated from the dielectric constant equation of Uematsu and Franck (*22*) and the equation of state for water of Haar, Gallagher, and Kell (*23*). The number of knots in both the molality and temperature dimensions was varied and an *F* test was used to determine if the addition of an extra set of knots significantly reduced the variance of the fit. The resulting set of knots that best fit the data in Tables I and II is given is Table III. The knots at 273.15 K are used in lieu of an end condition which specifies the slope at 298.15 K (*3*, *21*). From this set of knots a cubic spline interpolation as a function of $m^{1/2}$ at each temperature, followed by a cubic spline interpolation as a function of temperature at a given molality, suffices to determine the apparent molar heat capacity at any molality and temperature.

The differences between the experimental measurements and the predictions of the cubic spline surface are given in Tables I and II. Up to 500 K the agreement between the cubic spline surface for the two series of measurements and the runs in both series with extra acid is reasonable. At 550 K, the agreement is still reasonable at 1.6 mol·kg^{-1} and above. However, at 0.94 mol·kg^{-1}, adding extra acid reduced $C_{p,\phi}$ by 35 J·K^{-1}·mol^{-1}, so the results below 0.94 are probably too high. At 600 K, the two series are not in agreement and extra acid in the first series lowers $C_{p,\phi}$ by approximately 330 J·K^{-1}·mol^{-1} at 0.92 mol·kg^{-1}. The second series has more acid than the first series and has a reasonable concentration dependence. Unfortunately, the calorimeter suffered irreparable corrosion damage before we could do the extra acid checks and before we could measure the 3.5 mol·kg^{-1} solution. Because there are no experimental data the knots at 3.5 and 4.0 mol·kg^{-1} are undoubtedly incorrect at 600 K. We have excluded the data for the first series of measurements at temperatures above 500 K from the least-squares fit. We do not know whether the second series had sufficient HCl added to suppress hydrolysis so there may be large errors in the results above 500 K. We report these results because no other data are available. The standard error of the fit is 14 J·K^{-1}·mol^{-1}.

Table IV. Apparent Molar Heat Capacity, $C_{p,\phi}$ /(J•K^{-1}•mol^{-1}), for $FeCl_2$ at P = 17.9 MPa

m/ mol·kg^{-1}	T/K						
	298.15	348.15	398.15	448.15	498.15	548.15	598.15
0.0500	−203	−197	−223	−232	−149	77	−620
0.1000	−189	−183	−196	−187	−68	163	−400
0.2500	−165	−160	−149	−107	61	241	−417
0.5000	−142	−135	−107	−34	157	245	−452
0.7500	−127	−116	−80	12	199	215	−415
1.0000	−117	−101	−59	45	218	182	−370
1.5000	−106	−75	−25	94	224	133	−336
2.0000	−103	−54	5	129	214	119	−365
2.5000	−103	−36	31	152	199	115	−287
3.0000	−105	−21	53	164	184	103	
3.5000	−108	−7	71	163	173	76	

Discussion

The shape of the $C_{p,\phi}$ versus temperature is unusual. At the lowest concentration, $C_{p,\phi}$ goes through a very shallow maximum at about 330 K, decreases slightly until about 440 K, and then increases sharply to a maximum at 550 K before decreasing sharply to 600 K. The maximum at around 340 K is characteristic of other electrolyte solutions (*10*, *23*) but the sharp maximum at high temperatures has not been observed before, although $NiCl_2$(aq) could have a maximum above 575 K (*2*). At higher concentrations the maximum for $FeCl_2$(aq) shifts to lower temperatures, and at the highest concentration, 3.5 mol kg^{-1}, the maximum is at 480 K. It is quite possible that this maximum is due to the association equilibria between Cl^- ions and Fe^{2+}. It is well-known that chemical equilibria like this can give maxima in the heat capacities of solutions (*25*). It would be expected that the association constant is greater at higher temperatures, so that the shift in the maximum to higher temperatures at lower molalities is consistent with this explanation.

At the highest temperatures, 600 K, the apparent molar heat capacities are not nearly as negative as those that have been measured for $CaCl_2$ and $MgCl_2$. $NiCl_2$(aq) shows the same behavior and this difference has been attributed to the low dissociation of $NiCl_2$(aq) at high temperatures (*2*). We conclude that $FeCl_2$(aq) is appreciably associated at 600 K and the concentration investigated in this work. Of course, at sufficiently low concentrations $FeCl_2$(aq) will be dissociated and should exhibit large negative values of $C_{p,\phi}$ like $MgCl_2$(aq) (*21*) and $CaCl_2$(aq) (*5*).

Acknowledgment

We thank Jeffrey A. Gates for help with some preliminary fits of the data, Melody A. Cavalucci Armstrong for helping with some of the experiments, and Vivian Parker for helpful discussions.

Registry No. $FeCl_2$, 7758-94-3.

Literature Cited

(1) Smith-Magowan, D.; Wood, R. H. *J. Chem. Thermodyn.* **1981**, *13*, 1047.
(2) Smith-Magowan, D.; Wood, R. H.; Tillett, D. M. *J. Chem. Eng. Data* **1982**, *27*, 335.

(3) Gates, J. A.; Tillett, D. M.; White, D. E.; Wood, R. H. *J. Chem. Thermodyn.* **1987**, *19*, 131.

(4) White, D. E.; Gates, J. A.; Wood, R. H. *J. Chem. Thermodyn.* **1987**, *19*, 493, 1037.

(5) White, D. E.; Doberstein, A. L.; Gates, J. A.; Tillett, D. M.; Wood, R. H. *J. Chem. Thermodyn.* **1987**, *19*, 251.

(6) White, D. E.; Ryan, M. A.; Cavalucci Armstrong, M. A.; Gates, J. A. *J. Chem. Thermodyn.* **1987**, *19*, 1023.

(7) Cobble, J. W.; Murray, R. C., Jr. *Discuss. Faraday Soc.* **1977**, *64*, 144.

(8) Cobble, J. W.; Murray, R. W., Jr.; Sen, U. *Nature* **1981**, *291*, 566.

(9) Helgeson, H. C.; Kirkham, D. H. *Abstracts of Papers*, 174th meeting of American Chemical Society, New Orleans, LA, March 1977.

(10) Helgeson, H. C.; Kirkham, D. H.; Flowers, D. C. *Am. J. Sci.* **1981**, *281*, 1249.

(11) Wood, R. H.; Quint, J. R.; Grolier, J.-P. *J. Phys. Chem.* **1981**, *85*, 3944.

(12) Wood, R. H.; Quint, J. R. *J. Chem. Thermodyn.* **1982**, *14*, 1069.

(13) Wheeler, J. C. *Ber. Bunsen-Ges. Phys. Chem.* **1972**, *76*, 308.

(14) Gates, J. A.; Wood, R. H.; Quint, J. R. *J. Phys. Chem.* **1982**, *86*, 4948.

(15) Chang, R. F.; Morrison, G.; Levelt-Sengers, J. M. H. *J. Phys. Chem.* **1984**, *88*, 3389.

(16) Smith-Magowan, D. Ph.D. Dissertation, University of Delaware, May 1980.

(17) Karapet'yants, M. Kh.; Vasilëv, D. A.; Sanaev, E. S. *Russ. J. Phys. Chem.* **1977**, *51*, 1281.

(18) White, D. E.; Wood, R. H. *J. Solution Chem.* **1982**, *11*, 223.

(19) Fortier, J.-L.; Benson, G. C.; Picker, P. *J. Chem. Thermodyn.* **1976**, *8*, 289.

(20) Bernaducci, E. E.; Morss, L. R.; Miksztal, A. R. *J. Solution Chem.* **1979**, *8*, 717.

(21) Gates, J. A. Ph.D. Dissertation, University of Delaware, Newark, January 1985.

(22) Uematsu, M.; Franck, E. U. *J. Phys. Chem. Ref. Data* **1980**, *9*, 1291.

(23) Haar, L.; Gallagher, J. S.; Kell, G. S. *NBS/NRC Steam Tables*; Hemisphere: Washington, DC, 1984.

(24) Saluja, P. P. S.; Pitzer, K. S.; Phutela, R. C. *Can. J. Chem.* **1986**, *64*, 1328.

(25) Mains, G. J.; Sarson, J. W.; Hepler, L. G. *J. Phys. Chem.* **1984**, *88*, 1257.

Received for review June 23, 1987. Accepted February 16, 1988. We thank the Electric Power Research Institute (contract No. RP1167-4) for their support of this work.

Solubility Relationship in the System $NaNO_3$–NH_4NO_3–Urea–H_2O at 0 °C

Yong K. Kim,* Joseph W. Williard, and Alva W. Frazier

Division of Research, Tennessee Valley Authority, National Fertilizer Development Center, Muscle Shoals, Alabama 35660

The solubilities of the various components were determined in the system $NaNO_3$–NH_4NO_3–urea–H_2O at 0 °C. The maximum nitrogen in solution contained the minimum amount of $NaNO_3$. A solution of 30.3 wt % nitrogen was composed of 38.2% NH_4NO_3, 9.0% $NaNO_3$, 33.0% urea, and 19.8% H_2O. The saturation solubility data were plotted on a water-free basis, and isoconcentration lines (lines of constant nitrogen content) were drawn to exhibit the graph in an easily interpretable form. A compound, $NaNO_3 \cdot 2urea \cdot 2H_2O$, that had not been previously described was found in the system, and all petrographic data were determined.

Previous work in the field of nitrogen solubility has been mainly with two nitrogen-containing compounds. Polosin and Tarasova (*1*) studied the system $NaNO_3$–urea–H_2O; Sokolov (*2*) published solubility data for the system urea–NH_4NO_3–H_2O; and Seidell (*3*) published the solubility relationship for the system NH_4NO_3–$NaNO_3$–H_2O. Several investigators have reported eutectic information for the system $NaNO_3$–NH_4NO_3–urea (*4*–*6*), where the ternary eutectic mixtures have shown the eutectic temperature to be about 35–39 °C. There were no solubility data available for the four-component system $NaNO_3$–NH_4NO_3–urea–H_2O, which is of interest for the utilization of byproduct sodium nitrate as a fluid fertilizer. This solubility study was initiated to determine the nitrogen concentration at all combinations of the three input compounds at 0 °C. This temperature (0 °C) was selected because it is used as a standard by the fertilizer industry to evaluate fluid products which require storage during winter months.

Material and Experimental Procedures

The equilibrium solutions used to determine the solubility in the $NaNO_3$–NH_4NO_3–urea–H_2O system were prepared from reagent chemicals without further purification. Thirty-four mixtures of 100 g each were prepared with urea in the concentration range 6–40%, ammonium nitrate in the range 5–50%, and sodium nitrate in the range 4–43%. These solutions were equilibrated in a cold room thermostated at 0 ± 0.5 °C and shaken periodically. After 24 h those cells that contained no solids were treated with 10% each of the original salt mixtures and equilibration was continued. This procedure of adding 10% of the original salts was repeated until all the solutions were saturated with at least one solid phase. Equilibration was continued for 2 weeks after a solid phase became stable in each solution. Samples of the solid phases then were taken and filtered on a fritted crucible that had been cooled to 0 °C. The solid phases were identified by polarizing light microscopy (PLM). The total and ammoniacal nitrogen in the liquid phase were determined by Association of Official Analytical Chemists (AOAC) methods (*7*), the nitrate and urea nitrogen were determined by high-performance liquid chromatography (HPLC, unpublished TVA method), and sodium was determined by flame emission spectroscopy.

Results and Discussion

Solubility data for the system $NaNO_3$–NH_4NO_3–urea–H_2O at 0 °C are given in Table I. Since total nitrogen and its three forms (ammonia N, nitrate N, and urea N) were measured individually, the difference (ΔN) between the total nitrogen and the sum of the three nitrogen forms can serve as a check of the deviation in the chemical analysis. The highest deviation occurred in experiment 21, with a ΔN of 0.34. All other tests have a ΔN value of about 0.15, indicating that the nitrogen determinations were reliable.

The distribution of nitrogen among the different forms of nitrogen sources was calculated from the individual nitrogen values and is listed in Table I. Also, the composition of the saturated solution was calculated from the individual nitrogen data, and water was measured as the difference between the weight of solution and solutes. Finally, the composition of the solutes in the saturated solution based on a water-free condition was calculated from the solution composition and is given as