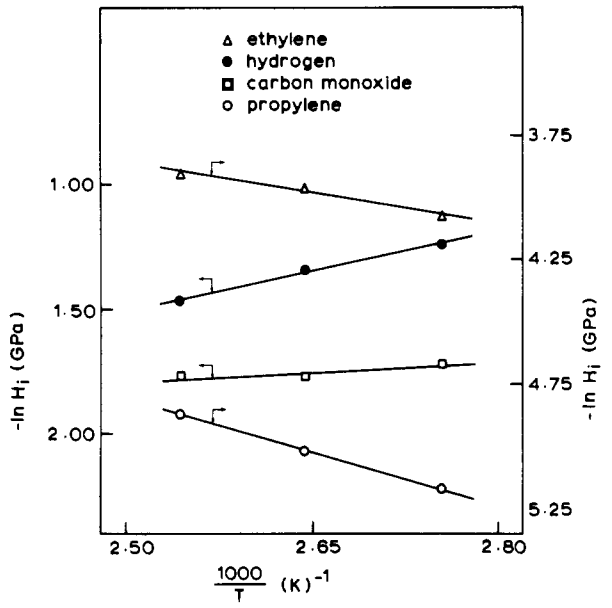

Figure 2. Henry's constants as a function of temperature.

h without showing any crystallization at all. This supercooling of PPh_3 was also observed by using differential scanning calorimetry.

Acknowledgment

We gratefully acknowledge our indebtedness to Professor Dr. J. J. F. Scholten for his stimulating discussions.

Glossary

c_{i0}	equilibrium concentration of component i in the liquid phase at the lower pressure p_0, mol m^{-3}
c_{i1}	equilibrium concentration of component i in the liquid phase at the higher pressure p_1, mol m^{-3}
D_i	diffusion coefficient of component i in liquid PPh_3, m^2 s^{-1}
f_i	fugacity of component i in the gas phase, Pa
H_i	Henry's constant of component i in liquid PPh_3, Pa
L	twice the height of the liquid-phase column in the Cailletet tube, m
T	absolute temperature, K
t	time elapsed since the pressure was suddenly raised from p_0 to p_1, s
V_i	liquid molar volume of solute i at its normal boiling point, cm^3 mol^{-1}
x_i	mole fraction of component i in the liquid phase
γ_i	activity coefficient of component i in the liquid phase; γ_i approaches unity when x_i approaches zero
ϕ	time-averaged mole flux of component i, mol m^{-2} s^{-1}

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Volumetric Properties of Molten Hydrated Salts. 5. $Fe(NO_3)_3 \cdot 8.75H_2O + MNO_3$ System

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A manometric method is used to measure the densities of molten $Fe(NO_3)_3 \cdot 8.75H_2O + MNO_3$ (M = Li, Na, K, NH_4, Ag, and Tl) mixtures from 285 to 365 K. Equations representing the densities and equivalent volumes as a function of temperature are given. Composition dependence of equivalent volumes obeyed the principle of additivity of volumes except for the $LiNO_3$-containing system; small negative deviations in the latter have been explained in terms of the greater electrostriction which the H_2O molecules undergo.

Introduction

Recently an increasing interest in molten hydrated salt systems has developed because of their theoretical (*1-17*) and applied (*18-25*) importance. Molten salt models are generally used to understand the behavior of these systems because their structure is predominantly an ionic distribution perturbed by water molecules. The densities and equivalent volumes of molten mixtures of hydrated nitrates and some monovalent nitrates (*13-16*) have indicated that Li^+ ions strongly compete for water of hydration with divalent hydrated cations. In this paper, the densities of $Fe(NO_3)_3 \cdot 8.75H_2O + MNO_3$ (M = Li, Na, K, NH_4, Ag, and Tl) have been reported to study the effect of different ions on the volumetric properties of trivalent hydrated nitrates.

Experimental Section

The purities and the grades of the chemicals used in this study were as follows: $Fe(NO_3)_3 \cdot 9H_2O$, 98%, LR (SM); $LiNO_3$,

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Table I. Density and Equivalent-Volume Data for $Fe(NO_3)_3 \cdot 8.75H_2O + MNO_3$ Systems

equiv fraction of MNO_3 (X')	temp, K	density, g cm^{-3}	equiv vol, cm^3 equiv^{-1}
0.0000	283.5	1.7115	77.79
	290.2	1.7034	78.16
	304.0	1.6895	78.82
	316.7	1.6769	79.41
	327.7	1.6626	80.09
	340.6	1.6471	80.87
	352.4	1.6328	81.55
	364.2	1.6184	82.28
	$MNO_3 = LiNO_3$		
0.0163	290.2	1.7200	76.81
	294.9	1.7048	77.50
	304.7	1.6939	77.99
	316.2	1.6815	78.57
	327.8	1.6689	79.16
	340.4	1.6528	79.93
	352.1	1.6388	80.61
	363.2	1.6269	81.20
0.0337	286.7	1.7116	76.53
	294.5	1.7046	76.85
	304.4	1.6937	77.34
	316.2	1.6803	77.96
	327.7	1.6659	78.64
	340.7	1.6526	79.27
	351.2	1.6396	79.90
	363.6	1.6259	80.57
0.0671	284.7	1.7179	75.01
	291.2	1.7099	75.36
	304.7	1.6961	75.97
	316.4	1.6825	76.58
	328.5	1.6686	77.22
	340.5	1.6536	77.92
	351.7	1.6412	78.51
	363.4	1.6275	79.17
0.0849	286.2	1.7194	74.27
	290.2	1.7134	74.54
	303.2	1.6910	75.52
	314.4	1.6837	75.85
	326.8	1.6697	76.49
	339.0	1.6545	77.19
	351.7	1.6387	77.98
	363.2	1.6251	78.59
0.1383	284.7	1.7258	72.01
	290.2	1.7188	72.31
	305.0	1.7040	72.94
	317.0	1.6884	73.61
	329.2	1.6732	74.28
	340.1	1.6610	74.82
	352.7	1.6463	75.49
	364.2	1.6318	76.16
0.1574	285.2	1.7287	71.19
	290.2	1.7202	71.54
	302.3	1.6999	72.39
	315.4	1.6844	73.06
	327.2	1.6692	73.73
	339.6	1.6547	74.37
	351.2	1.6414	74.97
	361.6	1.6287	75.56
	$MNO_3 = NaNO_3$		
0.0183	287.2	1.7117	77.28
	294.7	1.7037	77.64
	307.0	1.6910	78.22
	318.2	1.6775	78.85
	329.2	1.6642	79.48
	340.2	1.6511	80.11
	352.2	1.6382	80.74
	363.2	1.6255	81.37
0.0339	286.9	1.7208	76.43
	295.4	1.7100	76.91
	306.4	1.6975	77.48
	317.6	1.6853	78.04
	329.6	1.6704	78.74
	341.0	1.6584	79.31
	352.2	1.6440	80.00
	363.7	1.6320	80.59
0.0530	289.2	1.7272	75.62
	299.2	1.7163	76.10
	312.9	1.7006	76.80
	325.9	1.6853	77.50
	338.8	1.6711	78.15
	351.2	1.6554	78.90
	363.0	1.6399	79.64
0.0747	286.2	1.7255	75.09
	293.5	1.7185	75.39
	304.7	1.7057	75.96
	316.2	1.6930	76.53
	328.2	1.6787	77.18
	240.0	1.6665	77.75
	352.0	1.6535	78.36
	363.4	1.6407	78.97
0.1234	328.2	1.6926	75.16
	339.6	1.6791	75.76
	351.7	1.6643	76.44
	363.0	1.6524	76.99
	$MNO_3 = KNO_3$		
0.0276	286.2	1.7158	77.09
	291.8	1.7109	77.32
	302.4	1.6989	77.86
	313.5	1.6880	78.36
	323.2	1.6764	78.91
	333.2	1.6649	79.45
	343.2	1.6531	80.01
	353.2	1.6416	80.57
	363.2	1.6307	81.12
0.0338	285.7	1.7163	76.95
	295.7	1.7062	77.41
	307.4	1.6936	77.98
	319.9	1.6779	78.71
	331.3	1.6672	79.22
	342.0	1.6548	79.81
	353.2	1.6411	80.48
	364.0	1.6291	81.07
0.0774	286.7	1.7339	75.36
	288.6	1.7320	75.45
	292.2	1.7280	75.62
	305.2	1.7123	76.32
	317.6	1.6991	76.91
	330.0	1.6856	77.53
	342.2	1.6716	78.17
	353.0	1.6588	78.78
	363.2	1.6462	79.38
0.1211	286.2	1.7567	73.59
	288.7	1.7536	73.72
	300.7	1.7405	74.27
	312.4	1.7276	74.83
	323.2	1.7159	75.34
	333.7	1.7034	75.89
	342.9	1.6934	76.34
	353.2	1.6816	76.88
	363.2	1.6696	77.43
0.1825	285.7	1.7760	71.68
	298.2	1.7618	72.26
	310.3	1.7477	72.84
	321.3	1.7349	73.38
	332.2	1.7233	73.88
	342.9	1.7118	74.37
	353.0	1.7004	74.87
	363.2	1.6892	75.37
0.2549	289.9	1.7840	70.06
	301.2	1.7717	70.55
	314.5	1.7586	71.07
	327.3	1.7437	71.68
	339.6	1.7310	72.21
	351.7	1.7175	72.77
	362.9	1.7061	73.26
	$MNO_3 = NH_4NO_3$		
0.0366	282.0	1.7125	76.62
	292.2	1.7008	77.15
	304.6	1.6864	77.81

Table I (*Continued*)

equiv fraction of MNO_3 (X')	temp, K	density, g cm^{-3}	equiv vol, cm^3 equiv^{-1}
	317.0	1.6732	78.42
	329.2	1.6593	79.08
	340.7	1.6460	79.72
	352.2	1.6312	80.44
	363.4	1.6206	80.97
0.0737	284.5	1.7103	75.57
	293.2	1.7015	75.96
	303.8	1.6899	76.48
	316.2	1.6756	77.13
	327.2	1.6617	77.78
	339.8	1.6474	78.45
	351.2	1.6348	79.06
	362.7	1.6227	79.64
0.1262	288.7	1.6886	74.88
	295.2	1.6828	75.14
	304.7	1.6712	75.66
	316.4	1.6598	76.18
	328.2	1.6448	76.88
	340.0	1.6329	77.44
	352.0	1.6202	78.05
	362.9	1.6077	78.65
0.1787	285.4	1.6858	73.35
	291.9	1.6780	73.70
	304.7	1.6645	74.29
	317.7	1.6513	74.89
	329.0	1.6383	75.48
	340.2	1.6273	75.99
	351.4	1.6155	76.54
	362.4	1.6040	77.10
0.2546	284.2	1.6711	71.60
	291.2	1.6648	71.87
	304.7	1.6518	72.44
	316.0	1.6404	72.94
	327.4	1.6282	73.49
	339.7	1.6154	74.07
	351.2	1.6027	74.06
	362.6	1.5920	75.16
0.334	285.7	1.6589	69.56
	292.0	1.6526	69.82
	304.2	1.6407	70.33
	316.7	1.6285	70.85
	328.2	1.6164	71.38
	339.7	1.6046	71.91
	351.2	1.5929	72.43
	362.2	1.5814	72.96
0.4298	291.9	1.6394	67.29
	304.1	1.6270	67.80
	316.2	1.6158	68.27
	328.2	1.6029	68.82
	340.2	1.5902	69.37
	351.6	1.5804	69.80
	363.4	1.5689	70.31
	$MNO_3 = AgNO_3$		
0.0172	285.7	1.7334	77.18
	291.7	1.7264	77.50
	303.9	1.7131	78.10
	316.8	1.6989	78.75
	328.1	1.6845	79.42
	339.7	1.6713	80.05
	351.9	1.6574	80.72
	363.0	1.6446	81.35
0.0351	286.2	1.7550	76.61
	299.7	1.7398	77.28
	313.2	1.7249	77.96
	325.8	1.7110	78.58
	337.9	1.6973	79.22
	349.7	1.6829	79.89
	360.9	1.6701	80.51
0.0550	283.2	1.7845	75.75
	293.2	1.7733	76.24
	305.2	1.7601	76.80
	317.5	1.7462	77.42
	328.4	1.7349	77.92
	340.7	1.7209	78.55
	352.3	1.7066	79.21
	363.5	1.6935	79.82
0.0771	302.4	1.7891	76.02
	315.4	1.7733	76.69
	327.5	1.7595	77.29
	339.2	1.7481	77.79
	351.9	1.7258	78.80
	363.9	1.7150	79.30
	$MNO_3 = TlNO_3$		
0.0172	284.0	1.7529	77.28
	292.7	1.7428	77.72
	303.0	1.7314	78.23
	315.5	1.7163	78.92
	327.5	1.7028	79.55
	338.8	1.6896	80.17
	350.7	1.6747	80.88
	362.2	1.6610	81.55
0.0364	285.7	1.7973	76.78
	293.2	1.7877	77.19
	303.2	1.7777	77.63
	315.4	1.7634	78.26
	327.4	1.7494	78.88
	339.4	1.7337	79.60
	352.1	1.7192	80.27
	364.2	1.7050	80.94
0.0547	286.7	1.8356	76.51
	300.2	1.8207	77.14
	313.5	1.8051	77.81
	326.2	1.7907	78.43
	339.7	1.7696	79.37
	351.4	1.7592	79.84
	363.4	1.7470	80.40
0.0779	286.9	1.8872	76.06
	299.4	1.8782	76.42
	312.2	1.8633	77.04
	323.7	1.8494	77.61
	335.4	1.8347	78.24
	347.5	1.8197	78.88
	359.2	1.8057	79.49
0.1215	303.7	1.9850	75.24
	315.8	1.9701	75.81
	328.1	1.9554	76.38
	339.7	1.9409	76.95
	352.3	1.9234	77.65
	364.1	1.9094	78.22

98%, RPE (Carbo Erba); $NaNO_3$, 99.9%, AnalaR (BDH); KNO_3, 99.9%, AnalaR (BDH); $AgNO_3$, 99.9%, AnalaR (BDH); $TlNO_3$, 99%, Pure (VEB); NH_4NO_3, 99.9%, AnalaR (BDH). A bulk quantity of ferric nitrate nonahydrate was melted in a stoppered flask and filtered through a sintered-glass tube (porosity G-3). The water of hydration, determined volumetrically by redox titration using $K_2Cr_2O_7$ (*26*), was 8.75 ± 0.01 mol/mol of $Fe(NO_3)_3$. The monovalent nitrates were desiccated to constant mass and stored over anhydrous magnesium perchlorate until used. Mixtures were prepared by adding the requisite amounts of the monovalent nitrates to the molten hydrated ferric nitrate and matured by keeping at ~340 K for 6 h; loss of water during this was found to be negligible. The experimental details of the measurements, the densitometer and its calibration, and the precision attained has been described elsewhere (*13*).

Results and Discussion

The experimental densities (ρ) and equivalent volumes (V_e) for the systems investigated are given in Table I. The temperature dependence of ρ and V_e could be expressed by eq 1. Empirical parameters A and B were evaluated by the method of least-squares fitting and recorded in Table II. The

$$\rho,\ V_e = A + B(T - 300) \qquad (1)$$

Table II. Least-Squares Equations of Density and Equivalent-Volume Data for $Fe(NO_3)_3 \cdot 8.75H_2O + MNO_3$ Systems

equiv fraction (X_{MNO_3}')	temp range, K	$\rho = A - B(T-300)$, g cm^{-3}			$V_e = A' + B'(T-300)$, cm^3 equiv^{-1}			expansion coeff, $10^4\alpha$, K^{-1}
		A	10^2B	10^3SE	A'	$10B'$	SE	
				$MNO_3 = LiNO_3$				
0.0163	283-363	1.7023	0.1213	5.35	77.614	0.5737	0.23	7.13
0.0337	283-363	1.6979	0.1128	0.89	77.162	0.5287	0.05	6.64
0.0671	283-363	1.7006	0.1150	0.71	75.775	0.5286	0.05	6.76
0.0849	283-363	1.6996	0.1179	4.00	75.149	0.5488	0.18	6.94
0.1383	283-363	1.7080	0.1178	0.62	72.770	0.5184	0.05	6.90
0.1574	283-363	1.7048	0.1256	3.69	73.657	0.5596	0.15	7.37
				$MNO_3 = NaNO_3$				
0.0183	283-363	1.6978	0.1143	0.58	77.912	0.5424	0.04	6.73
0.0339	283-363	1.7051	0.1156	0.58	77.136	0.5417	0.03	6.78
0.0530	283-363	1.7154	0.1175	0.92	76.134	0.5412	0.06	6.85
0.0747	283-363	1.7107	0.1105	0.46	75.740	0.5047	0.03	6.46
0.1234	283-363	1.7255	0.1171	0.60	73.663	0.5316	0.02	6.79
				$MNO_3 = KNO_3$				
0.0276	283-363	1.7015	0.1116	0.97	77.749	0.5255	0.06	6.56
0.0338	283-363	1.7011	0.1120	1.15	77.638	0.5290	0.06	6.58
0.0774	283-363	1.7190	0.1138	0.58	76.027	0.5193	0.04	6.62
0.1211	283-363	1.7413	0.1121	0.30	74.247	0.4926	0.03	6.44
0.1825	283-363	1.7595	0.1119	0.43	72.3565	0.4745	0.01	6.36
0.2549	283-363	1.7732	0.1071	0.44	70.484	0.4394	0.03	6.04
				$MNO_3 = NH_4NO_3$				
0.0366	283-363	1.6994	0.1187	0.21	77.199	0.5614	0.10	6.96
0.0737	283-363	1.6934	0.1139	0.08	76.321	0.5300	0.04	6.73
0.1262	283-363	1.6768	0.1097	0.07	75.414	0.5097	0.04	6.54
0.1787	283-363	1.6697	0.1058	0.04	74.065	0.4830	0.02	6.34
0.2546	283-363	1.6559	0.1030	0.09	72.264	0.4630	0.05	6.22
0.3344	283-363	1.6446	0.1016	0.08	70.160	0.4462	0.04	6.18
0.4298	283-363	1.6313	0.0996	0.06	67.617	0.4270	0.03	6.11
				$MNO_3 = AgNO_3$				
0.0172	283-363	1.7172	0.1152	0.47	77.917	0.5396	0.04	6.71
0.0351	283-363	1.7396	0.1136	0.80	77.289	0.5230	0.05	6.53
0.0550	283-363	1.7660	0.1127	0.72	76.552	0.5033	0.05	6.38
0.0771	283-363	1.7929	0.1217	0.25	75.824	0.5397	0.01	6.79
				$MNO_3 = TlNO_3$				
0.0172	283-363	1.7346	0.1173	0.51	78.097	0.5449	0.04	6.76
0.0364	283-363	1.7805	0.1175	1.01	77.513	0.5276	0.05	6.60
0.0547	283-363	1.8201	0.1158	1.96	77.165	0.5086	0.08	6.36
0.0779	283-363	1.8760	0.1176	1.88	76.514	0.4959	0.09	6.27
0.1215	283-363	1.9900	0.1261	0.66	75.021	0.4980	0.03	6.34

expansion coefficient (α) of the mixtures, calculated by using eq 2 at 300 K (Table II), was almost constant, indicating the

$$\alpha = -\frac{1}{\rho}\frac{d\rho}{dT} \qquad (2)$$

absence of any significant structural changes on addition of monovalent nitrates.

Isotherms of equivalent volumes (V_e) vs. equivalent fraction (X') (Figure 1) exhibited a decrease in V_e with increasing monovalent nitrate content; this appeared logical as the larger hydrated $Fe(H_2O)_{8.75}^{3+}$ (radius = 3.42 Å, considering all of the water attached to Fe^{3+} ions in the form of the first hydration shell; the effective radius (r) of $Fe(H_2O)_{8.75}^{3+} = r_{Fe^{3+}} + 2r_{H_2O}$) cations are gradually replaced by smaller M^+ (radii for Li^+ = 0.68 Å, Na^+ = 0.97 Å, K^+ = 1.33 Å, NH_4^+ = 1.43 Å, Ag^+ = 1.26 Å, Tl^+ = 1.47 Å) cations. $V_e - X'$ plots (Figure 1) of $LiNO_3$-containing mixtures exhibited small negative deviations, indicating an increase in packing density on addition of $LiNO_3$. Becasue of high surface charge density, Li^+ ions are highly electrostricting and possess a greater hydrophilic tendency; this would probably unbalance the equilibrium between water dipoles and Fe^{3+} ions, resulting in the preferential orientation of water dipoles toward Li^+ ions or decoordination of water molecules from hydrated Fe^{3+} ions, as has been suggested for similar systems (*15*). However, in the $Zn(NO_3)_2 \cdot 6H_2O + LiNO_3$ system (*15*) addition of the latter exhibited positive deviation which was considered to arise because of increased size due to hydration of Li^+ ions. The negative deviations in the present system may suggest that water of hydration in the present system is not wholly attached to Fe^{3+} ions. A part of the water may be loosely attached to anions (*27*) or to the cations in the form of a second hydration envelope (*6*). Addition of Li^+ ions may capture this loosely attached water, resulting in a shrinkage in

Table III. Partial Equivalent-Volume ($\bar{V}_i$) Values of the Components of $Fe(NO_3)_3 \cdot 8.75H_2O + MNO_3$ Systems

MNO_3	temp, K	$\bar{V}_{Fe(NO_3)_3 \cdot 8.75H_2O}$	$\bar{V}_{MNO_3}$
$LiNO_3$	313.2	79.15	39.12 (35.28)[a]
	353.2	81.33	41.09
$NaNO_3$	313.2	79.14	39.87 (40.52)[a]
	353.2	81.39	41.24
KNO_3	313.2	79.28	48.93 (48.24)[a]
	353.2	81.44	49.58
NH_4NO_3	313.2	79.05	54.15 (53.38)[b]
	353.2	81.27	55.04
$AgNO_3$	313.2	79.21	41.05 (40.80)[a]
	353.2	81.33	42.84
$TlNO_3$	313.2	79.37	49.68 (50.41)[a]
	353.2	81.54	50.02

[a] From ref *28*. [b] From ref *14*.

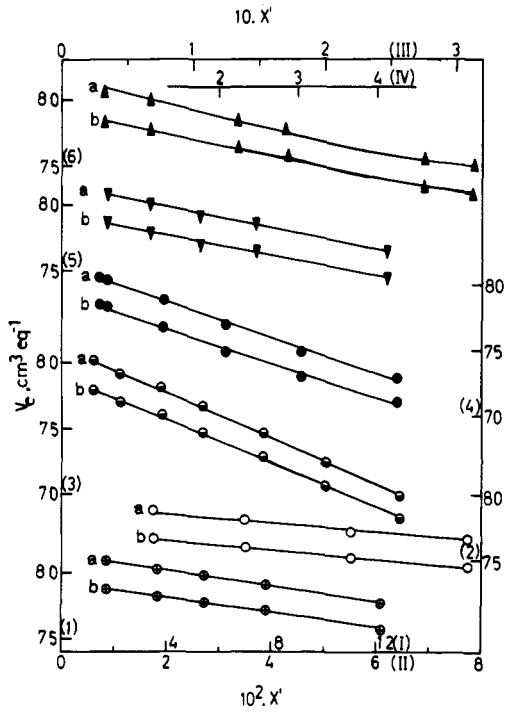

Figure 1. Equivalent volume (V_e) vs. equivalent fraction (X') isotherms of $Fe(NO_3)_3 \cdot 8.75H_2O$ + MNO_3 (M = Li, Na, K, NH_4, Ag, Tl) systems. Temperature: (a) 353.2 and (b) 313.2 K. MNO_3: (▲) $LiNO_3$; (▼) $NaNO_3$; (●) KNO_3; (⊖) NH_4NO_3; (O) $AgNO_3$; (⊕) $TlNO_3$. X axis: (I) $LiNO_3$, $NaNO_3$, and $TlNO_3$; (II) $AgNO_3$; (III) KNO_3; (IV) NH_4NO_3. Y axis: (1) $TlNO_3$; (2) $AgNO_3$; (3) NH_4NO_3; (4) KNO_3; (5) $NaNO_3$; (6) $LiNO_3$.

the volume of the system and an increase in the packing density.

V_e vs. X' isotherms are linear for mixtures containing Na, K, NH_4, Ag, ad Tl nitrates (Figure 1); this indicates that these mixtures are volumetrically ideal, at least to a first approximation, over the composition range employed. Partial equivalent volumes ($\bar{V}_i$) were calculated by least-squares fitting of V_e – X' data into a linear equation (eq 3). $\bar{V}_i$ values of the components would then be E and $E + F$; the values of $\bar{V}_i$ are listed in Table III. The calculated $\bar{V}_{Fe(NO_3)_3 \cdot 8.75H_2O}$ values from different systems exhibit small variations which may be due to the different magnitude of interactions with the monovalent ions. However, these values are in good agreement with the measured volumes of $Fe(NO_3)_2 \cdot 8.75H_2O$ at corresponding temperatures. The partial equivalent volumes of monovalent nitrates are in good agreement with the extrapolated volumes (*14*, *28*) of pure components. The present results further confirm that, while Na^+, K^+, NH_4^+, Ag^+, and Tl^+ ions do not disturb the hydration sheath of the hydrated cations (*15*), Li^+ ions participate in the hydration–dehydration equilibria.

$$V_e = E + FX' \quad (3)$$

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