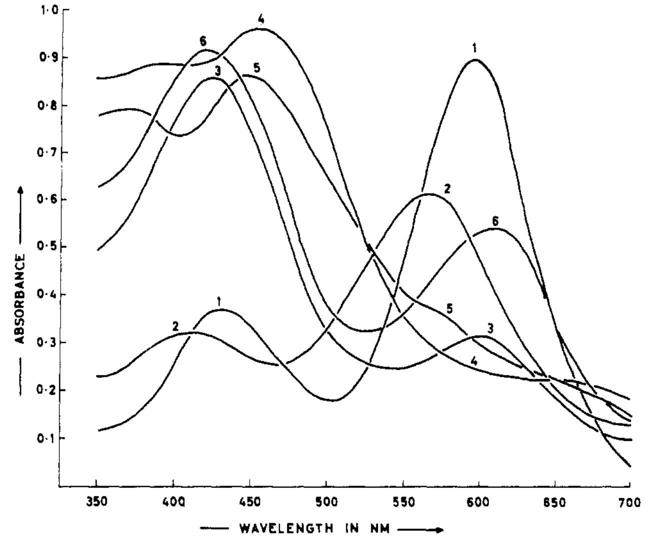

Figure 2. Absorption spectra of diphenylthiocarbazone and substituted diphenylthiocarbazones in 50% (v/v) aqueous dioxan at 25 °C: (1) diphenyl; (2) bis(2,6-dimethylphenyl); (3) bis(2-methyl-5-nitrophenyl); (4) bis(4-methyl-2-nitrophenyl); (5) bis(2-methyl-4-nitrophenyl); (6) bis(4-methyl-3-nitrophenyl).

K_{f_2} values in the case of both the metal chelates. This may be attributed to the fact that the first chelation takes place with partial neutralization of the charge on the central metal ion while the second one completely neutralizes the charge on the central metal ion thereby resulting in the minimum polarity and solvation effect of the metal complex with the medium. Furthermore, due to the octahedral nature of both nickel(II) and zinc(II) complexes, the same steric effect toward ortho substituents is observed. Nickel(II) and zinc(II) complexes of bis(4-methyl-2-nitrophenyl)carbazone possess higher stability in spite of their higher proton displacements constants (K_{pd}). This may be attributed to smaller steric effect of the *o*-nitro group as compared to the *o*-methyl group. One possible explanation would be that the nitro group in the ortho position may orient itself in such a way that it lies out of plane thereby preventing its ability to withdraw electrons by mesomeric effect and thus resulting in increased stability of metal complexes.

Conclusions

In the case of ligands containing sulfur donor atoms (having no steric group), zinc complexes are either almost as stable as or even more stable than the corresponding nickel complexes. However, with ligands containing one oxygen and one nitrogen donor atoms, zinc complexes are either as stable as or even less stable than the corresponding nickel complexes. The ortho-substituted oxygen analogues give significantly weaker complexes with both nickel and zinc, while sulfur-containing ligands give weaker complexes with zinc only. Though the magnitudes of stability orders of zinc and nickel complexes of sulfur and oxygen containing ligands are nearly the same, the proton displacement constants are significantly different. This difference in K_{pd} is due to the higher proton affinity for oxygen than for sulfur in the respective ligands. The higher K_{pd} values make sulfur-donating ligands superior to oxygen analogues because of the formation of complexes at lower pH values.

Registry No. DPTC, 60-10-6; bis(2,6-dimethylphenyl)thiocarbazone, 97234-67-8; bis(2-methyl-5-nitrophenyl)thiocarbazone, 97234-68-9; bis(4-methyl-2-nitrophenyl)thiocarbazone, 97234-69-0; bis(2-methyl-4-nitrophenyl)thiocarbazone, 97234-70-3; bis(4-methyl-3-nitrophenyl)thiocarbazone, 97234-71-4.

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Volumetric Properties of Molten Hydrated Salts. 6. Mixtures of Aluminum Nitrate Decahydrate with Hydrates of Calcium, Cadmium, Zinc, and Magnesium Nitrates

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Densities of the molten binary mixtures of aluminum nitrate decahydrate with hydrates of calcium, cadmium, zinc, and magnesium nitrates were measured at different temperatures and concentrations with a manometric densimeter. Least-squares equations representing densities and molar volumes as a function of temperature are given. The molar volumes of mixtures were additive. Composition variations of α and V_E are explained by considering the complexing nature of the ions.

Introduction

Volumetric behavior of molten hydrated salts has been studied (*1*–*10*) to understand ion–water interactions over the concentration region where solution studies were uncommon. Additivity of volumes is a good approximation to understand the different types of volumetric behavior. The amount of water present in the hydrated salts remains in the form of coordinated and lattice water, perturbed by ionic distribution (*11*, *12*). In continuation of our studies of molten hydrated salts (*3*, *7*–*10*), the results of density measurements of binary molten hydrates of aluminum nitrate with calcium, cadmium, zinc, and magnesium nitrates are reported in this paper.

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Table I. Least-Squares Equations of Density Data for Molten Mixtures of Aluminum Nitrate Decahydrate with the Hydrates of Calcium, Cadmium, Zinc, and Magnesium Nitrates

mole fraction of divalent cation	temp. range, K	data points	$\rho = A - B(T - 300)$, g cm^{-3}						
			A	10^3(error in A)	10^3B	10^5(error in B)	10^2SE	cor coeff	α,[a] 10^4(K^{-1})
			$Al(NO_3)_3 \cdot 10.03H_2O + Ca(NO_3)_2 \cdot 3.99H_2O$						
0.3984	303.2–354.2	7	1.62043	0.10	0.65216	0.32	0.01	0.999	4.03
0.5311	305.2–353.4	7	1.63476	0.09	0.65753	0.31	0.01	0.999	4.02
0.6573	303.2–353.2	7	1.66249	0.30	0.69410	0.96	0.04	0.999	4.17
0.7282	313.2–353.2	6	1.68315	0.07	0.70873	0.21	0.01	0.999	4.21
0.8049	303.2–353.2	6	1.70895	0.46	0.69104	0.41	0.05	0.999	4.04
0.8606	303.2–353.2	6	1.72118	0.15	0.71543	0.48	0.02	0.999	4.16
0.9114	303.2–353.4	7	1.73119	0.19	0.72031	0.62	0.02	0.999	4.16
0.9591	298.7–353.4	8	1.74057	0.31	0.72840	0.98	0.05	0.999	4.19
1.0000	288.2–363.2	10	1.76453	0.26	0.79876	0.79	0.06	0.999	4.53
			$Al(NO_3)_3 \cdot 10.03H_2O + Cd(NO_3)_2 \cdot 4.12H_2O$						
0.1155	313.2–353.2	6	1.62366	0.37	0.65245	1.09	0.03	0.999	4.02
0.2022	318.2–353.2	8	1.66112	0.14	0.67161	0.39	0.01	0.999	4.04
0.3280	308.2–353.2	7	1.72017	0.13	0.71811	0.42	0.01	0.999	4.17
0.4097	308.2–353.2	7	1.76434	0.12	0.75184	0.36	0.01	0.999	4.26
0.5143	303.2–353.2	8	1.83415	0.20	0.76421	0.68	0.03	0.999	4.17
0.7050	303.2–353.2	6	1.97519	0.18	0.88491	0.60	0.02	0.999	4.45
0.7944	308.2–353.2	7	2.06402	0.09	0.93119	0.29	0.01	0.999	4.51
0.8966	303.2–353.2	8	2.17704	0.15	0.98211	0.51	0.01	0.999	4.51
1.0000	313.2–353.2	7	2.29372	0.52	1.06608	0.57	0.05	0.999	4.65
			$Al(NO_3)_3 \cdot 10.03H_2O + Zn(NO_3)_2 \cdot 6.10H_2O$						
0.1518	307.8–353.2	7	1.60740	0.23	0.69429	0.69	0.02	0.999	4.32
0.2879	308.2–353.2	8	1.63298	0.17	0.73595	0.47	0.02	0.999	4.51
0.4008	302.9–353.5	7	1.66051	0.24	0.77467	0.81	0.03	0.999	4.66
0.4836	308.0–343.6	6	1.68863	0.18	0.77784	0.69	0.02	0.999	4.61
0.5343	303.0–353.5	7	1.71626	0.17	0.83677	0.58	0.02	0.999	4.88
0.7246	303.2–353.2	7	1.78949	0.13	0.94349	0.45	0.02	0.999	5.27
0.8902	303.0–353.5	7	1.80546	0.14	1.01267	0.47	0.02	0.999	5.61
0.9418	303.1–353.0	7	1.84245	0.31	1.01267	1.01	0.04	0.999	5.56
1.0000	303.2–353.2	6	2.04230	0.20	1.17405	0.61	0.02	0.999	5.75
			$Al(NO_3)_3 \cdot 10.03H_2O + Mg(NO_3)_2 \cdot 6.02H_2O$						
0.1005	348.2–353.3	7	1.57530	0.26	0.61217	0.66	0.01	0.999	3.89
0.2017	313.2–353.4	9	1.57321	0.15	0.62472	0.42	0.01	0.999	3.97
0.3030	318.2–353.4	7	1.56990	0.19	0.60798	0.53	0.01	0.999	3.87
3.3926	323.2–353.2	5	1.56757	0.59	0.62655	0.55	0.03	0.999	3.99
0.4896	337.5–353.4	5	1.56507	0.37	0.60054	0.30	0.03	0.999	3.84
0.6021	345.2–355.2	4	1.58068	0.44	0.63585	0.86	0.06	0.999	4.02

[a] Expansion coefficient at 300 K.

Experimental Section

Hydrated nitrates of aluminum, calcium, cadmium, zinc, and magnesium were of AnalaR (BDH) grade or equivalent purity. Water content of the salts, determined by volumetric titration using EDTA, was found to be within ±0.01 mol/mol of cation, the water salt mole ratios (R) being 10.03 for aluminum, 3.99 for calcium, 4.12 for cadmium, 6.10 for zinc, and 6.02 for magnesium.

The manometric densimeter (*13*, *14*) enabled direct measurement of the volumes with a precision of 2×10^{-3} cm^3. Calibration of densimeter, dilation correction, thermostat bath, sample preparation, etc., have been described earlier (*14*). Data were recorded both in heating and cooling cycles. Temperature was maintained and known with a precision of ±0.05 K.

Results and Discussion

Least-squares equations representing temperature dependence of density (ρ) and molar volumes (V) of different binary mixtures of $Al(NO_3)_3 \cdot 10.03H_2O$ with $Ca(NO_3)_2 \cdot 3.99H_2O$, $Cd(NO_3)_2 \cdot 4.12H_2O$, $Zn(NO_3)_2 \cdot 6.10H_2O$, and $Mg(NO_3)_2 \cdot 6.02H_2O$, measured over the range of concentration limited by miscibility and at temperatures ranging between 288.2 and 353.2 K, are given in Tables I and II.

Isothermal composition variation of V (Figure 1) exhibited a decrease as hydrates of divalent cations are added to Al(N-

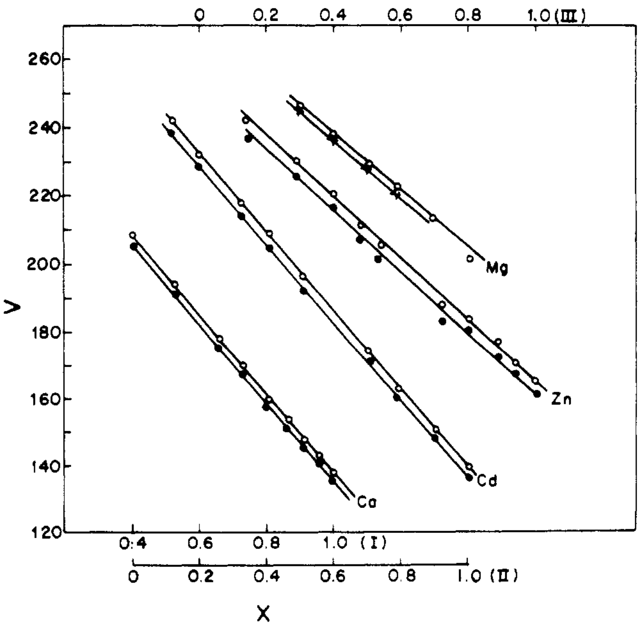

Figure 1. Isotherms of molar volume (V) vs. mole fraction of divalent cation (X) for $Al(NO_3)_3 \cdot 10.03H_2O + M(NO_3)_2 \cdot RH_2O$ systems: ●, 313.2 K; ×, 333.2 K; ○, 353.2 K. Mole fraction axis scale: (I) for Ca, (II) for Cd, (III) for Zn, (IV) for Mg containing mixtures.

Table II. Least-Squares Equations of Molar Volume Data for Molten Mixtures of Aluminum Nitrate Decahydrate with the Hydrates of Calcium, Cadmium, Zinc, and Magnesium Nitrates

mole fraction of divalent cations	temp range, K	$V = A + B(T - 300)$, cm^3 mol^{-1}				SE	cor coeff	10V_E
		A	error in A	10B	10(error in B)			
			$Al(NO_3)_3 \cdot 10.03H_2O + Ca(NO_3)_2 \cdot 3.99H_2O$					
0.3984	303.2–354.2	204.038	0.019	0.8410	0.006	0.027	0.999	0.8410
0.5311	305.2–353.4	189.535	0.014	0.7809	0.004	0.019	0.999	0.7809
0.6573	303.2–353.2	174.437	0.028	0.7459	0.009	0.038	0.999	0.7459
0.7282	313.2–353.2	165.678	0.005	0.7176	0.002	0.005	0.999	0.7176
0.8049	303.2–353.2	156.120	0.039	0.6459	0.001	0.049	0.999	0.6459
0.8606	303.2–353.2	149.100	0.097	0.6381	0.003	0.012	0.999	0.6381
0.9114	303.2–353.4	144.447	0.014	0.6157	0.005	0.020	0.999	0.6157
0.9591	298.7–353.4	139.375	0.021	0.5958	0.007	0.037	0.999	0.5958
1.0000	288.2–363.4	133.840	0.014	0.6177	0.004	0.038	0.999	0.6177
			$Al(NO_3)_3 \cdot 10.03H_2O + Cd(NO_3)_2 \cdot 4.12H_2O$					
0.1155	313.2–353.2	236.055	0.005	0.9743	0.002	0.050	0.999	0.9743
0.2022	318.2–353.2	226.265	0.018	0.9419	0.005	0.014	0.999	0.9419
0.3280	308.2–353.2	212.312	0.015	0.9095	0.005	0.019	0.999	0.9095
0.4097	308.2–353.2	203.066	0.007	0.8898	0.002	0.008	0.999	0.8898
0.5143	303.2–353.2	190.559	0.019	0.8129	0.006	0.030	0.999	0.8129
0.7050	303.2–353.2	168.729	0.018	0.7755	0.006	0.029	0.999	0.7755
0.7944	308.2–353.2	157.805	0.007	0.7322	0.002	0.009	0.999	0.7322
0.8966	303.2–353.2	145.672	0.009	0.6742	0.003	0.015	0.999	0.6742
1.0000	313.2–353.2	134.457	0.026	0.6446	0.008	0.028	0.999	0.6446
			$Al(NO_3)_3 \cdot 10.03H_2O + Zn(NO_3)_2 \cdot 6.10H_2O$					
0.1518	307.8–353.2	235.460	0.044	1.0444	0.013	0.052	0.999	1.0444
0.2879	308.2–353.2	223.780	0.028	1.0417	0.007	0.040	0.999	1.0417
0.4008	302.9–353.5	213.486	0.040	1.0221	0.001	0.060	0.999	1.0221
0.4836	308.0–343.6	205.323	0.022	0.9689	0.008	0.025	0.999	0.9689
0.5343	303.0–353.5	199.242	0.016	0.9984	0.005	0.039	0.999	0.9984
0.7246	303.2–353.2	180.848	0.014	0.9822	0.004	0.020	0.999	0.9822
0.8902	303.0–353.5	170.537	0.018	0.9874	0.006	0.027	0.999	0.9874
0.9418	303.1–353.0	164.568	0.019	0.9433	0.006	0.028	0.999	0.9433
1.0000	303.2–353.2	160.204	0.019	0.9500	0.004	0.013	0.999	0.9500
			$Al(NO_3)_3 \cdot 10.03H_2O + Mg(NO_3)_2 \cdot 6.02H_2O$					
0.1005	348.2–353.3	240.793	0.037	0.9641	0.009	0.025	0.999	0.9641
0.2017	313.2–353.4	232.324	0.022	0.9475	0.006	0.023	0.999	0.9475
0.3030	318.2–353.4	223.972	0.025	0.8918	0.007	0.020	0.999	0.8918
0.3926	323.2–353.2	216.483	0.077	0.8924	0.020	0.049	0.999	0.8924
0.4896	337.5–353.4	208.335	0.018	0.8280	0.004	0.015	0.999	0.8280
0.6021	345.2–355.2	196.531	0.057	0.8238	0.013	0.009	0.999	0.8238

$O_3)_3 \cdot 10.03H_2O$. It has been indicated (*1*) that water of hydration in molten hydrated salts is retained by the cations, resulting in the formation of weak-field cations of type $M(H_2O)_n{}^{m+}$. On addition of hydrated M^{2+} (where M = Ca, Cd, Zn, and Mg) ions to $Al(NO_3)_3 \cdot 10.03H_2O$, the nearest neighbors of NO_3^- ions would be $Al(H_2O)_n{}^{3+}$ and $M(H_2O)_i{}^{2+}$ with different cationic potentials. This would lead to preferential orientation of NO_3^- ions toward the $Al(H_2O)_n{}^{3+}$ because of its higher cationic potential, resulting in the formation of solvent-separated ion pairs and displacement of lattice water (*12*), if any, from the hydration sphere of the Al^{3+} ions. Both the effects could be associated with an increase in ion–ion and ion–water interactions, an increase in packing density, and a decrease in molar volumes, as observed.

The linearity of V–X isotherms indicated that the principle of additivity of volumes may be obeyed by these systems, at least to a first approximation. Partial molar volumes (Table III) were evaluated by graphical extrapolation method and also by least-squares fitting of V–X data into the linear equation $V = E + FX$, the partial molar volumes being E and $E + F$ (*14*). Partial molar volumes of $Al(NO_3)_3 \cdot 10.03H_2O$ ($\bar{V}_1$) for Ca^{2+}-, Cd^{2+}-, and Mg^{2+}-containing mixtures are in good agreement with each other while $\bar{V}_1$'s are about 1% higher for Zn^{2+}-containing mixtures. Comparison of calculated partial molar volumes of hydrated divalent nitrates ($\bar{V}_2$) with those of the molar volumes, at corresponding temperatures, revealed agreement within ±1% for Ca^{2+}-, Cd^{2+}-, and Mg^{2+}-containing mixtures, indicating that the molten mixtures of aluminum nitrate decahydrate with the hydrates of calcium, cadmium, and magnesium are volumetrically additive. The lower partial volumes of $Zn(NO_3)_2 \cdot 6.10H_2O$ (≈4%) as compared with the literature values (*15*) may occur due to increased interactions of NO_3^- ions with the Zn^{2+} ions as evident from IR (*16*) and Raman (*17*, *18*) spectra. However, the linearity of V–X plots is maintained due to a systematic variation in the interactions on addition of $Zn(NO_3)_2 \cdot 6.10H_2O$.

Table III. Partial Molar Volumes of the Components of $Al(NO_3)_3 \cdot 10.03H_2O + M(NO_3)_2 \cdot RH_2O$ Systems

$M(NO_3)_2 \cdot RH_2O$	temp K	V_{1}, cm mol^{-1}	V_{2}, cm mol^{-1}
$Ca(NO_3)_2 \cdot 3.99H_2O$	313.2	252.53	134.59 (135.80)[a]
	353.2	255.79	136.90 (138.30)[a]
$Cd(NO_3)_2 \cdot 4.12H_2O$	313.2	252.61	136.16 (136.71)[a]
	353.2	255.73	138.79 (139.59)[a]
$Zn(NO_3)_2 \cdot 6.10H_2O$	313.2	253.44	157.33 (163.81)[b]
	353.2	257.78	161.07 (167.88)[b]
$Mg(NO_3)_2 \cdot 6.02H_2O$	333.2	252.64	167.06 (166.88)[c]
	353.2	255.57	168.91 (168.20)[c]

[a] Reference *8*. [b] Reference *15*. [c] Reference *19*.

The isothermal composition variation of expansion coefficient ($\alpha = -(1/\rho)(d\rho/dT)$) exhibited an increase and that of molar expansivity ($V_E = dV/dT$) a decrease (Figure 2) when hydrated divalent nitrates were added to $Al(NO_3)_3 \cdot 10.03H_2O$. Sharma et al. (*8*) showed that V_E is related to van der Waals volume (V_0) of the mixture by the equation

$$V_E = \alpha V_0$$

A decrease in V_E resulted from a marked decrease in V_0. The addition of hydrated divalent nitrates decreases the moles of NO_3^- ions, the main space-filling species (*7*–*10*), from 3 to 2 per mole of mixture over the concentration range. Also, the

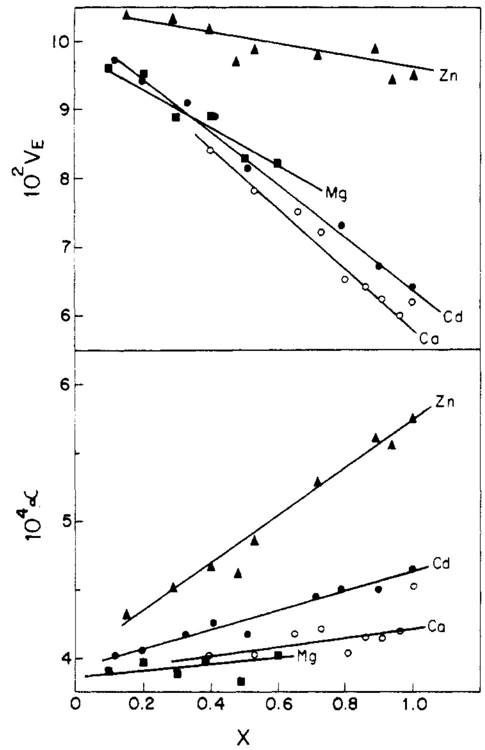

Figure 2. Composition variation of thermal expansion coefficient (α) and molar expansivity (V_E) of $Al(NO_3)_3 \cdot 10.03H_2O + M(NO_3)_2 \cdot RH_2O$ systems at 300 K.

moles of water associated with the cations decrease from 10 to 4/6 per mole of mixture. Both the factors would markedly decrease V_0. It may be noticed that there is a parallelism between the composition variation of V_E and α of Ca^{2+}- and Cd^{2+}-containing mixtures while Zn^{2+}- and Mg^{2+}-containing mixtures exhibited a different trend. This may be attributed to an increased NO_3^--ZN^{2+} interaction (*16-18*). Zinc may undergo ion-pair formation resulting in an increase in V_0 and thereby a flattened curve for V_E and large changes in α.

Registry No. $Al(NO_3)_3$, 13473-90-0; $Ca(NO_3)_2$, 10124-37-5; $Cd(NO_3)_2$, 10325-94-7; $Zn(NO_3)_2$, 7779-88-6; $Mg(NO_3)_2$, 10377-60-3.

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Densities and Apparent Molar Volumes in the Binary System Dimethyl Sulfoxide-Water at 25, 40, 60, and 65 °C

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The densities of binary mixtures of dimethyl sulfoxide and water have been determined at 25, 40, and 60 °C. These data are presented, along with literature values at 45 and 65 °C, and used to calculate the apparent molar volume of each component at all five temperatures at compositions of 0-100 wt % water. The densities show a strong, positive deviation from ideality. Correlations are presented that allow the calculation of densities and apparent molar volumes at each temperature and all compositions.

Introduction

As part of an ongoing research effort designed to investigate the physicochemical properties of a variety of solvent systems, the densities of mixtures of dimethyl sulfoxide (Me_2SO) in water have been measured at 25, 40, and 60 °C across the entire range of composition. The apparent molar volume of each component was calculated by using these data and literature data at 45 and 65 °C (*1*). Both the densities and the apparent molar volumes were fit to equations of the form:

$$P_1 = P_2^0 + AC_1 + BC_1^2 + \ldots + EC_1^6 \qquad (1)$$

The agreement between values calculated by using these equations and the experimental values was approximately equal to the maximum experimental error of ±0.000 10 g/mL in the density measurements.

Experimental Method

Distilled water from the house supply was further purified by using a Millipore "Milli-Q" reagent water system. Ultrapure Me_2SO (Burdick and Jackson) was used without further purification. Water was determined by Karl Fischer titrations that are considered accurate to ±0.01 wt %. Densities were determined with a Mettler/Parr DMA 55 digital density meter calibrated with deaerated water and dry air. Temperatures were held to ±0.05 °C with a water bath.

[†] Operated by Martin Marietta Energy Systems, Inc., for the U.S. Department of Energy.

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