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Apparent Molar Volumes of $La(CF_3SO_3)_3(aq)$ and $Gd(CF_3SO_3)_3(aq)$ at 278 K, 298 K, and 318 K at Pressures to 30.0 MPa

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Densities of $La(CF_3SO_3)_3(aq)$ and $Gd(CF_3SO_3)_3(aq)$ have been measured at 278 K, 298 K, and 318 K at pressures of 0.1 MPa, 7.0 MPa, and 30.0 MPa using vibrating-tube densimeters. Apparent molar volumes obtained from the density data have been fitted to the Pitzer equation. The standard partial molar volumes V_ϕ^∞ and the ion-interaction parameters $\beta^{(0)V}$ and $\beta^{(1)V}$ have been determined through least-squares fitting to the experimental results. The standard partial molar volume of the trifluoromethanesulfonate anion $V_\phi^\infty(CF_3SO_3^-,aq)$ was calculated at 298 K and 0.1 MPa from the partial molar volumes of the gadolinium and lanthanum salts and the available values for the standard partial molar volumes of the cations. Excellent agreement is obtained for $V_\phi^\infty(CF_3SO_3^-,aq)$ calculated from the data for the two salts.

Introduction

Aqueous trivalent lanthanide cations are of interest as model systems in long-term studies of the thermodynamic properties of $M^{3+}(aq)$ species. Apparent molar volumes of aqueous lanthanum and gadolinium perchlorates, chlorides, and nitrates at 298.15 K and 0.1 MPa were reported by Spedding et al. (1966, 1974, 1975). Recently, we reported the apparent molar heat capacities and volumes of $LaCl_3(aq)$, $La(ClO_4)_3(aq)$, and $Gd(ClO_4)_3(aq)$ from 328 K to 338 K at 0.1 MPa (Xiao and Tremaine, 1996). Data for the perchlorate salts may be used to obtain the standard partial molar properties for the trivalent cations since $La^{3+}(aq)$ and $Gd^{3+}(aq)$ form only very weak complexes with $ClO_4^-(aq)$ (Chen and Detellier, 1992). However, decomposition of $ClO_4^-(aq)$ at high temperatures may lead to harmful corrosion of the densimeter cells, limiting the temperature range accessible in studies of the perchlorate salts. To avoid the problem of oxidation, Leonard and Swaddle (1975) and Palmer and Drummond (1988) have used triflate (trifluoromethanesulfonate; $CF_3SO_3^-$) as an alternative to perchlorate for high-temperature experiments requiring noncomplexing anions. In this paper we report the apparent molar volumes of $La(CF_3SO_3)_3(aq)$ and $Gd(CF_3SO_3)_3(aq)$ at 278 K, 298 K, and 318 K and at pressures from 0.1 to 30 MPa. Measurements at higher temperatures, currently in progress in our laboratories at ORNL and Memorial University, will be reported in future communications.

Experimental Section

Stock solutions of $La(CF_3SO_3)_3$ and $Gd(CF_3SO_3)_3$ were prepared from the oxides (Aldrich, mass fraction 0.999) and triflic acid (Alfa, mass fraction 0.99) according to the procedure reported by Spedding et al. (1966) and Xiao and Tremaine (1996). The final pH of the stock solutions with $m \approx 1.0$ mol·kg^{-1} was about 2.7. The concentrations of $La^{3+}(aq)$ and $Gd^{3+}(aq)$ were determined by titration with EDTA using xylenol orange as indicator and methenamine to buffer the solution at pH ≈ 6. More dilute solutions were prepared by diluting the stock solution with water by mass.

Densities were measured using a Paar DMA 60 densimeter. A Paar DMA 512 remote cell with a stainless-steel vibrating tube was used for measurements at elevated pressures; a Paar DMA 602 HP remote cell with a glass vibrating tube was used for measurements at 0.1 MPa. The temperature of the vibrating tube assemblies was controlled to ±0.01 K by circulating a thermostated mixture of (ethene glycol + water). A 100Ω platinum RTD (Omega) calibrated against a secondary standard 25Ω RTD (Instrulab) was used to monitor the temperature. The pressure of the densimeters was maintained with a pressure generator (HIP Co.) and was measured with a pressure transducer (Precise Sensors, Inc.). Distilled deionized water and 5.694 mol·kg^{-1} NaCl(aq) solution were used as reference fluids for densimeter calibration. Densities of water were calculated from the equation of state of Hill (1990), while densities of NaCl(aq) were calculated from the equation of state of Archer (1992).

Results and Discussion

The density ρ of a given solution is related to the vibrational period of the solution, τ, and the vibrational period of the reference fluid water, τ_w, as

$$\rho = \rho_w + K(\tau^2 - \tau_w^{\,2}) \qquad (1)$$

where ρ_w is the density of water and K is the calibration constant which is determined from measurements on the two reference fluids.

Apparent molar volumes V_ϕ were calculated from densities according to the usual definition

$$V_\phi = 1000(\rho_w - \rho)/(m\rho\,\rho_w) + M/\rho \qquad (2)$$

where M is molar mass and m is the molality. The results are listed in Table 1.

The instrumental uncertainty in the density determination may be estimated from the standard deviation of the calibration constant K and the standard deviation of the vibrational periods measured for both water and solutions through the following formula:

$$\sigma\rho = \{[(\partial\rho/\partial K)\sigma K]^2 + [(\partial\rho/\partial\tau)\sigma\tau]^2 + [(\partial\rho/\partial\tau_w)\sigma\tau_w]^2\}^{1/2} \qquad (3)$$

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Table 1. Densities and Apparent Molar Volumes of $La(CF_3SO_3)_3(aq)$ and $Gd(CF_3SO_3)_3(aq)$[a]

	$p = 0.1$ MPa		$p = 7.0$ MPa		$p = 30.0$ MPa	
m/mol·kg^{-1}	ρ/g·cm^{-3}	V_ϕ/cm^{-3}·mol^{-1}	ρ/g·cm^{-3}	V_ϕ/cm^{-3}·mol^{-1}	ρ/g·cm^{-3}	V_ϕ/cm^{-3}·mol^{-1}
			$La(CF_3SO_3)_3$, $T = 278.33$ K			
0.058 43	1.023 00	187.59	1.026 33	188.57	1.037 08	192.11
0.083 48	1.032 69	187.85	1.035 99	189.27	1.046 72	192.47
0.123 46	1.047 96	188.29	1.051 23	189.62	1.061 95	192.43
0.196 39	1.075 18	188.88	1.078 37	190.29	1.089 04	192.92
0.298 26	1.111 72	190.15	1.114 88	191.31	1.125 47	193.75
0.469 98	1.170 14	191.41	1.173 20	192.50	1.183 69	194.64
0.693 12	1.240 36	192.88	1.243 28	193.88	1.253 66	195.72
			$Gd(CF_3SO_3)_3$, $T = 278.33$ K			
0.060 02	1.024 77	186.44	1.028 09	187.82	1.038 90	190.75
0.092 89	1.038 04	187.41	1.041 40	188.05	1.052 20	190.77
0.092 89	1.038 06	187.25				
0.118 78	1.048 44	187.26	1.051 74	188.39	1.062 52	191.12
0.252 96	1.100 44	188.31	1.103 66	189.46	1.114 40	191.82
0.380 42	1.147 24	189.40	1.150 48	190.25	1.161 20	192.34
0.533 03	1.200 25	190.53	1.203 62	191.01	1.214 30	192.90
0.723 00	1.262 61	191.00	1.265 62	191.87	1.276 27	193.52
			$La(CF_3SO_3)_3$, $T = 298.04$ K			
0.058 43	1.019 59	195.33	1.022 67	196.46	1.032 68	197.84
0.083 48	1.029 09	195.42	1.032 18	196.32	1.042 21	197.57
0.123 46	1.043 98	196.21	1.047 06	197.02	1.057 08	198.43
0.196 39	1.070 57	196.74	1.073 57	197.79	1.083 61	199.13
0.298 26	1.106 27	197.81	1.109 36	198.35	1.119 42	199.59
0.469 98	1.163 26	198.91	1.166 32	199.44	1.176 44	200.46
0.693 12	1.231 73	200.12	1.234 81	200.53	1.244 97	201.38
			$Gd(CF_3SO_3)_3$, $T = 298.04$ K			
0.060 02	1.021 49	192.20	1.024 51	194.06	1.034 54	195.42
0.060 02	1.021 41	193.29				
0.092 89	1.034 43	194.39	1.037 55	194.64	1.047 61	195.94
0.092 89	1.034 42	194.24				
0.118 78	1.044 62	194.06	1.047 69	195.07	1.057 78	196.12
0.252 96	1.095 39	195.91	1.098 56	196.18	1.108 72	197.24
0.252 96	1.095 38	195.88				
0.380 42	1.141 17	196.76	1.144 40	196.90	1.154 66	197.79
0.380 42	1.141 37	196.21				
0.533 03	1.193 16	197.37	1.196 37	197.60	1.206 70	198.39
0.533 03	1.193 32	197.04				
0.723 00	1.253 76	198.09	1.257 07	198.20	1.267 50	198.86
			$La(CF_3SO_3)_3$, $T = 318.06$ K			
0.058 43	1.012 42	199.97	1.015 46	200.01	1.025 15	201.36
0.083 48	1.021 70	200.35	1.024 79	200.54	1.034 50	201.76
0.123 46	1.036 36	201.22	1.039 49	200.95	1.049 22	202.05
0.196 39	1.062 60	201.41	1.065 59	201.92	1.075 38	202.81
0.196 39	1.062 55	201.56				
0.298 26	1.097 59	202.83	1.100 70	202.92	1.110 58	203.62
0.298 26	1.097 64	202.61				
0.469 98	1.153 51	203.96	1.156 65	204.05	1.166 65	204.59
0.693 12	1.220 71	205.05	1.223 85	205.18	1.234 01	205.54
			$Gd(CF_3SO_3)_3$, $T = 318.06$ K			
0.060 02	1.014 32	196.42	1.017 35	196.53	1.027 07	197.66
0.092 89	1.027 06	198.79	1.030 10	198.87	1.039 86	199.78
0.118 78	1.037 07	198.96	1.040 10	199.22	1.049 90	199.96
0.252 96	1.087 11	200.27	1.090 19	200.46	1.100 15	200.98
0.380 42	1.132 25	200.90	1.135 37	201.04	1.145 48	201.43
0.533 03	1.183 34	201.64	1.186 48	201.80	1.196 74	202.08
0.723 00	1.242 82	202.48	1.246 01	202.60	1.256 44	202.77

[a] The following values for ρ_w were taken from the compilation of Hill (1990) at $p = 0.1$ MPa, 7.0 MPa, and 30.0 MPa: (i) at $T = 278.33$ K, ρ_w/g·cm^{-3} = 0.999 967, 1.003 329, and 1.014 170; (ii) at $T = 298.04$ K, ρ_w/g·cm^{-3} = 0.997 070, 1.000 161, and 1.010 149; (iii) at $T = 318.06$ K, ρ_w/g·cm^{-3} = 0.990 241, 0.993 236, and 1.002 904.

Table 2. V_ϕ^∞ of $Gd(CF_3SO_3)_3(aq)$ and $La(CF_3SO_3)_3(aq)$ from Eq 5

	V_ϕ^∞/(cm^3·mol^{-1})		
p/MPa	$T = 278.33$ K	$T = 298.03$ K	$T = 318.06$ K
		$Gd(CF_3SO_3)_3$	
0.1	183.58	189.57	194.13
7.0	184.54	190.08	194.50
30.0	187.54	191.66	195.66
		$La(CF_3SO_3)_3$	
0.1	184.46	191.45	195.17
7.0	185.56	192.04	195.64
30.0	189.01	194.02	197.09

Table 3. Parameters for the Standard Partial Molar Volumes and Excess Properties $\beta^{(1)V}$ in Eqs 5, 7, and 8[a]

	$T = 278.33$ K	$T = 298.03$ K	$T = 318.06$ K
		$Gd(CF_3SO_3)_3(aq)$	
$\beta^{(1)V}$/kg·mol^{-1}·MPa^{-1}	-2.895×10^{-3}	-2.166×10^{-3}	-4.251×10^{-3}
a_1/cm^3·mol^{-1}	234.84	218.61	214.82
a_2/cm^3·MPa·mol^{-1}	-1.0438×10^{5}	-6.4168×10^{4}	-4.684×10^{4}
a_3/kg·mol^{-1}·MPa^{-1}	-1.629×10^{-3}	-9.240×10^{-4}	-3.790×10^{-4}
a_4/kg·mol^{-1}	3.519	1.930	0.7635
		$La(CF_3SO_3)_3(aq)$	
$\beta^{(1)V}$/kg·mol^{-1}·MPa^{-1}	-3.195×10^{-3}	-2.775×10^{-3}	-3.303×10^{-3}
a_1/cm^3·mol^{-1}	243.22	226.87	221.10
a_2/cm^3·MPa·mol^{-1}	-1.196×10^{5}	-7.814×10^{4}	-5.869×10^{4}
a_3/kg·mol^{-1}·MPa^{-1}	-1.816×10^{-3}	-1.015×10^{-3}	-6.070×10^{-4}
a_4/kg·mol^{-1}	4.201	2.359	1.388

[a] $\beta^{(0)V} = a_3(T) + a_4(T)\kappa_w(T)$. $V^\infty{}_\phi = a_1(T) + a_2(T)\,\kappa_w(T)$.

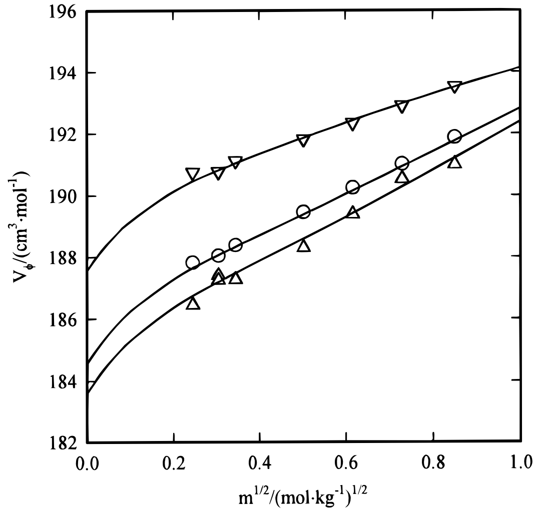

Figure 1. Apparent molar volumes of $Gd(CF_3SO_3)_3(aq)$ at 278 K and at 0.1 MPa (△), 7.0 MPa (○), and 30.0 MPa (▽). The solid lines show values calculated according to eq 5 and parameters in Tables 2 and 3.

where $\sigma\rho$, σK, $\sigma\tau$, and $\sigma\tau_w$ denote the standard deviations associated with ρ, K, τ, and τ_w, respectively. We assume $\sigma\tau \approx \sigma\tau_w$, $\tau \approx \tau_w$, and σK equals the standard deviation associated with the standard deviation of $(\tau^2 - \tau_w^2)$, so that

$$\sigma\rho \approx 4K\tau_w\sigma\tau_w \qquad (4)$$

For a typical run at 298 K and at 0.1 MPa, τ_w in the stainless steel cell is about 1.92 ms with standard deviation $\sigma\tau_w = 3 \times 10^{-6}$ ms and $K = 1.57$ g·cm^{-3}·ms^{-2}. This leads to the value $\sigma\rho \approx 3.6 \times 10^{-5}$ g·cm^{-3}. Combining $\sigma\rho$ with up to 0.1% error in each of the molalities, we estimate that the overall experimental uncertainty in the apparent molar volumes is 0.6 cm^3·mol^{-1} for 0.1 mol·g^{-1} solutions and 0.1 cm^3·mol^{-1} for 0.7 mol·kg^{-1} solutions.

The Pitzer ion-interaction equation for a 3−1 charge-type strong electrolyte was used to represent the concentration dependence of V_ϕ:

$$V_\phi = V_\phi^\infty + 6A_V \ln(1 + bI^{1/2})/b + 6RTm[\beta^{(0)V} + 2\beta^{(1)V}f(I)] \qquad (5)$$

where V_ϕ^∞ is the standard partial molar volume, A_V is the Debye−Huckel limiting slope as defined by Bradley and Pitzer (1979) and evaluated using the dielectric constant of water of Archer and Wang (1990), and $b = 1.2$ kg$^{1/2}$·mol$^{-1/2}$.

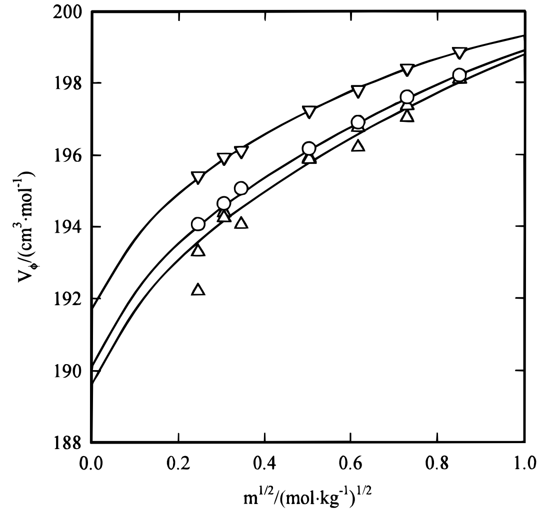

Figure 2. Apparent molar volumes of Gd(CF_3SO_3)$_3$(aq) at 298 K and at 0.1 MPa (△), 7.0 MPa (○), and 30.0 MPa (▽). The solid lines show values calculated according to eq 5 and parameters in Tables 2 and 3.

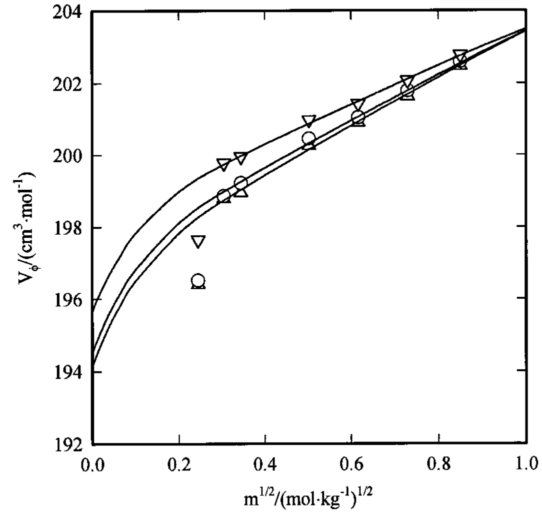

Figure 3. Apparent molar volumes of Gd(CF_3SO_3)$_3$(aq) at 318 K and at 0.1 MPa (△), 7.0 MPa (○), and 30.0 MPa (▽). The solid lines show values calculated according to eq 5 and parameters in Tables 2 and 3.

T is the temperature; $R = 8.314$ J·K^{-1}·mol^{-1}, $\beta^{(0)V}$ and $\beta^{(1)V}$ are two fitting parameters, and the function $f(I)$ is given by

$$f(I) = \{1 - (1 + aI^{1/2}) \exp(-aI^{1/2})\}/(a^2 I) \qquad (6)$$

where $a = 2.0$ kg$^{1/2}$·mol$^{-1/2}$ and I is the ionic strength.

The third virial coefficient usually appearing in eq 5 was neglected since the molalities used for this work are below 1 mol·kg^{-1}. It was assumed that $\beta^{(1)V}$ is independent of pressure and that V_ϕ^∞ and $\beta^{(0)}$ are linear functions of the isothermal compressibility of water, as in the following expressions:

$$V_\phi^\infty = a_1(T) + a_2(T)\kappa_w(T) \qquad (7)$$

$$\beta^{(0)V} = a_3(T) + \alpha_4(T)\kappa_w(T) \qquad (8)$$

where $\kappa_w(T)$ is the isothermal compressibility of water.

Equations 5–8 were fitted to the experimental apparent molar volumes at each temperature by the method of least squares with weights proportional to the solution molality, using isothermal compressibility data from Hill (1990). The standard partial molar volumes V_ϕ^∞ determined from these fits are listed in Table 2, and values for the parameters in eqs 7 and 8 and $\beta^{(1)V}$ from the Pitzer eq 5 are listed in Table 3. The fitted and experimental values of V_ϕ are plotted in Figures 1 to 6. With the exception of data below 0.09 mol·kg^{-1}, the fit lies within the estimated experimental uncertainty.

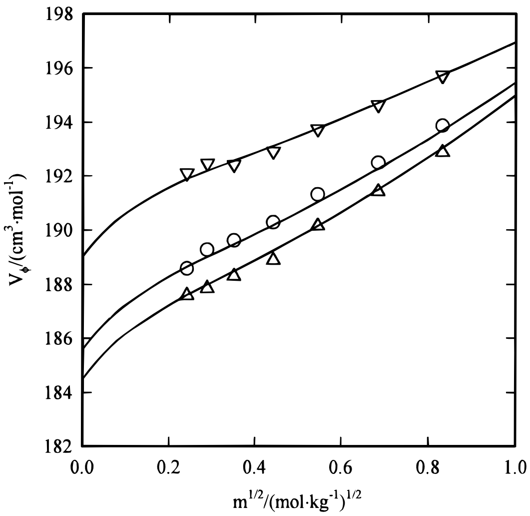

Figure 4. Apparent molar volumes of La(CF_3SO_3)$_3$(aq) at 278 K and at 0.1 MPa (△), 7.0 MPa (○), and 30.0 MPa (▽). The solid lines show values calculated according to eq 5 and parameters in Tables 2 and 3.

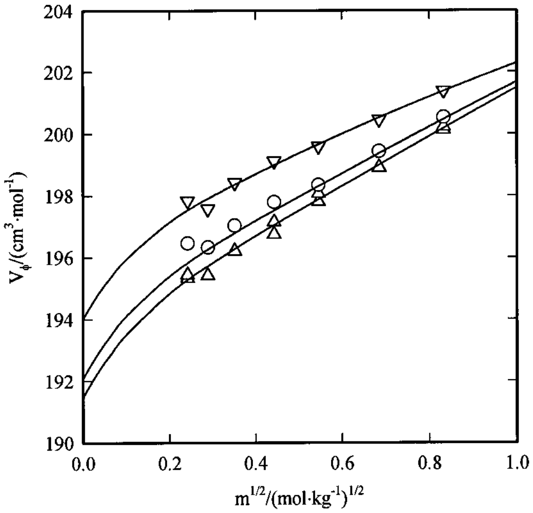

Figure 5. Apparent molar volumes of La(CF_3SO_3)$_3$(aq) at 298 K and at 0.1 MPa (△), 7.0 MPa (○), and 30.0 MPa (▽). The solid lines show values calculated according to eq 5 and parameters in Tables 2 and 3.

Owing to the formation of bubbles on filling the vibrating tube, data at 0.1 MPa are more scattered than those at higher pressures. The pressure dependence of V_ϕ and V_ϕ^∞ for Gd(CF_3SO_3)$_3$(aq) and La(CF_3SO_3)$_3$(aq) decreases with increasing temperature (see Figures 1–6). At 318 K, V_ϕ at 0.1 MPa and V_ϕ at 7.0 MPa differ by only 0.1–0.2 cm^3·mol^{-1}.

The conventional single-ion value for V_ϕ^∞ ($CF_3SO_3^-$,aq) can be calculated using known values for V_ϕ^∞ of Gd^{3+}(aq) or La^{3+}(aq). Taking the values of V_ϕ^∞(Gd^{3+},aq) = −41.21 cm^3·mol^{-1} and V_ϕ^∞(La^{3+},aq) = −38.00 cm^3·mol^{-1} at 298 K and 0.1 MPa obtained from measurements for Gd(ClO_4)$_3$(aq) and La(ClO_4)$_3$(aq) (Xiao and Tremaine, 1996), we obtain V_ϕ^∞($CF_3SO_3^-$,aq) = 76.49 cm^3·mol^{-1} from V_ϕ^∞ of

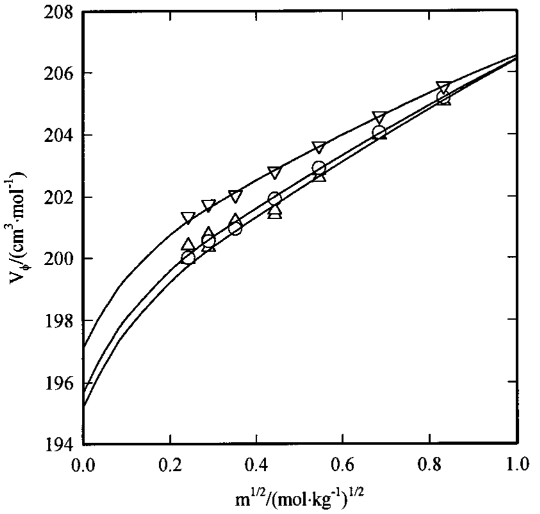

Figure 6. Apparent molar volumes of $La(CF_3SO_3)_3$(aq) at 318 K and at 0.1 MPa (△), 7.0 MPa (○), and 30.0 MPa (▽). The solid lines show values calculated according to eq 5 and parameters in Tables 2 and 3.

$Gd(CF_3SO_3)_3$(aq) and $V_\phi^\infty(CF_3SO_3^-,aq) = 76.92\ cm^3 \cdot mol^{-1}$ from the value for $Gd(CF_3SO_3)_3$(aq). This agreement is excellent.

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