Density and Viscosity Studies of Aqueous Solutions of Cesium Trifluoroacetate at Different Temperatures

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Densities and viscosities of aqueous solutions of cesium trifluoroacetate have been measured at $T =$ (298.15, 303.15, 308.15, and 313.15) K and at atmospheric pressure. Apparent molar volume (ϕ_v), partial molar volume (ϕ^o_v), and the ion–ion interaction parameter (S_v) have been calculated from experimental values of densities. The calculated values for ϕ^o_v are ($105.522 \cdot 10^{-6}$, $109.2591 \cdot 10^{-6}$, $113.028 \cdot 10^{-6}$, and $115.487 \cdot 10^{-6}$) $m^3 \cdot mol^{-1}$, and those of S_v are ($-24.383 \cdot 10^{-6}$, $-33.229 \cdot 10^{-6}$, $-42.194 \cdot 10^{-6}$, and $-49.046 \cdot 10^{-6}$) $m^3 \cdot mol^{-3/2} \cdot kg^{-1/2}$ at $T =$ (298.15, 303.15, 308.15, and 313.15) K, respectively. The viscosity data have been analyzed with the Jones−Dole equation. At $T =$ (298.15, 303.15, 308.15, and 313.15) K, the calculated values for the Jones−Dole coefficient (B) are (0.1534, 0.1612, 0.1725, and 0.1829) $kg \cdot mol^{-1}$, and those of intercept (A) are (−0.0223, −0.01691, −0.01360, and −0.01120) $mol \cdot kg^{-1/2}$, respectively. The molality range has been studied between (0.05671 and 0.5671) $mol \cdot kg^{-1}$. The parameters calculated from experimental values of densities and viscosities indicate strong solute−solvent interactions and water structuring.

Introduction

Salts play an important role in molecular biology applications. Cesium trifluoroacetate is the cesium salt of trifluoroacetic acid. It is highly soluble in water (2 M at 293.15 K). It is used as a medium in density gradient centrifugation for the separation of DNA, RNA, and protein and for plasmid isolation,[1–3] isolation of mRNA prior to the construction of full-length cDNA libraries,[4] and extraction of total RNA from *Pinus radiata*.[5] Water plays a central role in the thermodynamics and structure of biological macromolecules, proteins, DNA, and RNA. Aqueous solutions of cesium triflouroacetate are of considerable interest from biological and chemical points of view.

Solute–solvent interaction has great importance in biological chemistry, physical chemistry, surface chemistry, environmental chemistry, and geochemistry. To understand the processes occurring in living cells, the nature of ion hydration is prerequisite information. Density and viscosity studies of aqueous solutions of salts are useful in understanding the nature of solute–solvent and ion−solvent interactions. Density and viscosity data of aqueous solutions of salts are also required for molecular biology applications.

Densities and conductivities of cesium trifluoroacetate in trifluoroacetic acid have been reported earlier.[6] From the literature survey, it is revealed that there are no reports on density, viscosity, and other volumetric properties of aqueous solutions of cesium trifluoroacetate. This paper reports density and viscosity studies of aqueous solutions of cesium trifluoroacetate over the molality range of ($5.671 \cdot 10^{-2}$ to $5.671.10^{-1}$) $mol \cdot kg^{-1}$ and at $T =$ (298.15, 303.15, 308.15, and 313.15) K.

Experimental Section

Anhydrous cesium trifluoroacetate of purity >99.5 % obtained from Alfa Aesar, USA, was used. Aqueous solutions of cesium trifluoroacetate were prepared by a weight-by-weight method in an airtight, stoppered glass bottle by using triply distilled–deionized water. Masses were recorded on an electronic Dhona balance with a precision of $\pm 1 \cdot 10^{-7}$ kg. The densities of aqueous solutions were measured with the help of a $15 \cdot 10^{-6}$ m^3 double arm pycnometer[7,8] made of Borosil glass. The pycnometer was calibrated with triply distilled–deionized water.

Dynamic viscosities (η) of aqueous solutions were measured using an Ubbelohde suspended-level viscometer[7,8] calibrated with triply distilled water. An electronic digital stopwatch with a precision of ± 0.01 s was used for flow-time measurements. The viscosities were averaged from three readings for each solution. The dynamic viscosity of solutions was calculated using

$$\eta/\eta_0 = (\rho t)/(\rho_0 t_0) \quad (1)$$

where ρ, ρ_0, t, t_0, and η, η_0 are density, flow time, and viscosity of aqueous solutions and water, respectively.

Density and viscosity measurements were made in a transparent glass walled water bath[7,8] having a thermal stability of 0.01 K. The uncertainties in density and viscosity measurements were $\pm 1 \cdot 10^{-7}$ $kg \cdot m^{-3}$ and $0.003 \cdot 10^{-3}$ $m^{-1} \cdot kg \cdot s^{-1}$, respectively.

Results and Discussion

Table 1 lists densities (ρ) of aqueous solutions of cesium trifluoroacetate at $T =$ (298.15, 303.15, 308.15, and 313.15) K and at atmospheric pressure. Variations of densities of aqueous solutions of cesium trifluoroacetate with the square root of molality ($m^{1/2}$) at different temperatures are depicted in Figure 1. Table 1 and Figure 1 show that densities of the aqueous solutions increase with an increase in concentration of cesium trifluoroacetate. At higher temperatures, ρ becomes smaller. From experimental values of densities, apparent molar volumes (ϕ_v) have been calculated by using the following equation.[9,10]

$$\phi_v = (M/\rho) - [1000(\rho - \rho_0)/(m\rho\rho_0)] \quad (2)$$

M is the molar mass of cesium trifluoroacetate, and ρ_0 is the density of water. ϕ_v values are included in Table 1. Figure 2 shows variations of ϕ_v as a function of $m^{1/2}$. The partial molar

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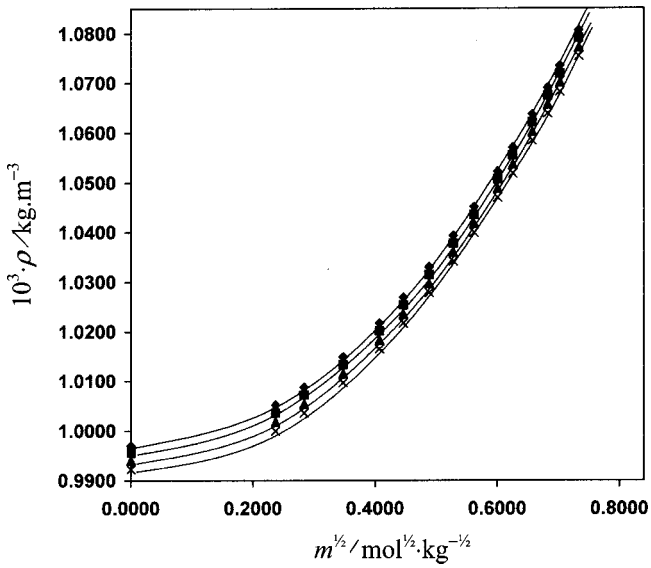

Figure 1. Densities ρ of cesium trifluoroacetate in water as a function of square root of molality $m^{1/2}$ at different temperatures: ♦, $T = 298.15$ K; ■, $T = 303.15$ K; ▲, $T = 308.15$ K; ×, $T = 313.15$ K; —, experimental.

Table 1. Density ρ and Apparent Molar Volume ϕ_v of Cesium Trifluoroacetate in Water from T = (298.15 to 313.15) K

m^a	$10^3 \cdot \rho^b$	$10^6 \cdot \phi_v{}^c$	$10^3 \cdot \rho^b$	$10^6 \cdot \phi_v{}^c$
	$T = 298.15$ K		$T = 303.15$ K	
0.0000	0.9970		0.9956	
0.0567	1.0052	100.367	1.0036	103.829
0.0813	1.0088	99.466	1.0072	101.875
0.1225	1.0149	97.900	1.0133	99.469
0.1687	1.0217	96.962	1.0201	98.079
0.2033	1.0269	95.826	1.0253	96.737
0.2445	1.0330	95.099	1.0314	95.842
0.2866	1.0393	94.182	1.0377	94.802
0.3263	1.0451	93.834	1.0435	94.369
0.3741	1.0522	93.064	1.0506	93.519
0.4066	1.0570	92.631	1.0554	93.042
0.4509	1.0636	91.925	1.0620	92.286
0.4879	1.0690	91.585	1.0674	91.913
0.5185	1.0734	91.418	1.0718	91.722
0.5671	1.0806	90.746	1.0790	91.016
	$T = 308.15$ K		$T = 313.15$ K	
0.0000	0.9940		0.9923	
0.0567	1.0018	107.33	1.0000	109.064
0.0813	1.0054	104.289	1.0036	105.470
0.1225	1.0115	101.039	1.0097	101.790
0.1687	1.0183	99.193	1.0165	99.712
0.2033	1.0235	97.644	1.0217	98.056
0.2445	1.0296	96.579	1.0278	96.905
0.2866	1.0359	95.415	1.0341	95.678
0.3263	1.0417	94.896	1.0399	95.115
0.3741	1.0488	93.965	1.0470	94.143
0.4066	1.0536	93.445	1.0518	93.601
0.4509	1.0602	92.639	1.0584	92.769
0.4879	1.0656	92.232	1.0638	92.548
0.5185	1.0700	92.017	1.0682	92.118
0.5671	1.0772	91.276	1.0754	91.359

[a] $\mathrm{mol \cdot kg^{-1}}$. [b] $\mathrm{kg \cdot m^{-3}}$. [c] $\mathrm{m^3 \cdot mol^{-1}}$.

volume (ϕ^o_v) of cesium trifluoroacetate has been calculated by using the equation[11,12]

$$\phi_v = \phi^o_v + S_v m^{1/2} + B_v m \quad (3)$$

ϕ^o_v, S_v, and B_v have been estimated by the least-squares fitting of the apparent molar volume data in equation 3. The ϕ^o_v, S_v, and B_v values are listed in Table 2. S_v is a measure of ion–ion interactions and depends on charge, salt type, and

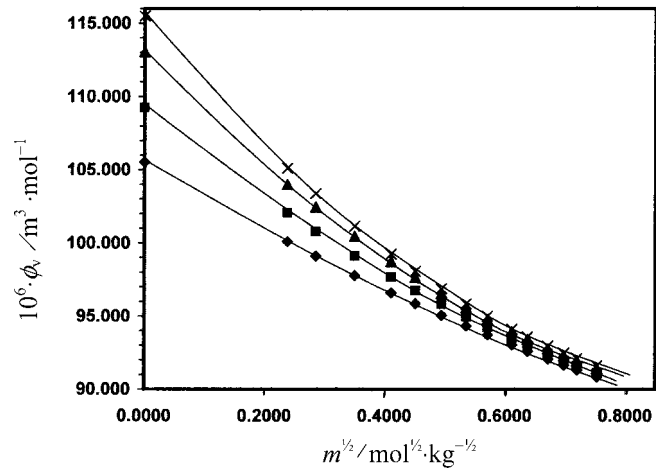

Figure 2. Apparent molar volume ϕ_v of cesium trifluoroacetate in water as a function of square root of molality $m^{1/2}$ at different temperatures: ♦, $T = 298.15$ K; ■, $T = 303.15$ K; ▲, $T = 308.15$ K; ×, $T = 313.15$ K; —, calculated by eq 2.

Table 2. Least-Square Fitted Values of Partial Molar Volume ϕ^o, Ion−Solvent Interaction Parameter S_v, and Constant B_v of Equation 3 and Absolute Average Deviation of Apparent Molar Volume AAD of Cesium Trifluoroacetate in Water from T = (298.15 to 313.15) K

T/K	$10^6 \cdot \phi^o_v{}^a$	$10^6 \cdot S_v{}^b$	$10^6 \cdot B_v{}^b$	$10^6 \cdot$AAD[a]
298.15	105.522 ± 1.914	−24.383 ± 6.607	6.464 ± 5.604	2.537
303.15	109.259 ± 1.905	−33.229 ± 6.579	12.140 ± 5.579	3.169
308.15	113.028 ± 1.901	−42.194 ± 6.565	17.904 ± 5.568	3.809
313.15	115.487 ± 1.965	−49.046 ± 6.785	23.033 ± 5.754	4.142

[a] $\mathrm{m^3 \cdot mol^{-1}}$. [b] $\mathrm{m^3 \cdot mol^{-3/2} \cdot kg^{1/2}}$, ± standard errors.

Table 3. Viscosity η of Cesium Trifluoroacetate in Water from T = (298.15 to 313.15) K

	$10^3 \cdot \eta^b$			
m^a	$T = 298.15$ K	$T = 303.15$ K	$T = 308.15$ K	$T = 313.15$ K
0.0000	0.894	0.800	0.722	0.658
0.0567	0.897	0.805	0.727	0.663
0.0813	0.899	0.808	0.729	0.666
0.1225	0.904	0.812	0.734	0.670
0.1687	0.909	0.817	0.739	0.675
0.2033	0.913	0.821	0.743	0.679
0.2445	0.918	0.826	0.747	0.684
0.2866	0.923	0.830	0.752	0.689
0.3263	0.928	0.836	0.757	0.693
0.3741	0.933	0.841	0.762	0.698
0.4066	0.937	0.845	0.767	0.702
0.4509	0.943	0.850	0.772	0.707
0.4879	0.947	0.855	0.777	0.711
0.5185	0.950	0.858	0.780	0.716
0.5671	0.956	0.864	0.784	0.721

[a] $\mathrm{mol \cdot kg^{-1}}$. [b] $\mathrm{m^{-1} \cdot kg \cdot s^{-1}}$.

nature of the solvent. Table 2 shows that S_v values are negative at all temperatures. The negative values of S_v at all temperatures suggest weak ion–ion interactions in the solutions. The ϕ^o_v value provides information regarding the ion–solvent interactions. The positive values of ϕ^o_v at all temperatures suggest the strong ion–solvent interactions.[13] The trifluoroacetate ion is strongly bound to water by hydration. The ϕ^o_v value decreases, and S_v values increase with a rise of temperature. This is an indication of an increase in ion−solvent interactions and a decrease in ion–ion interactions with temperature.

The viscosities (η) of aqueous solutions are listed in Table 3. Variations of η with $m^{1/2}$ at different temperatures are shown in Figure 3. From Table 3 and Figure 3, it is clear that η increases

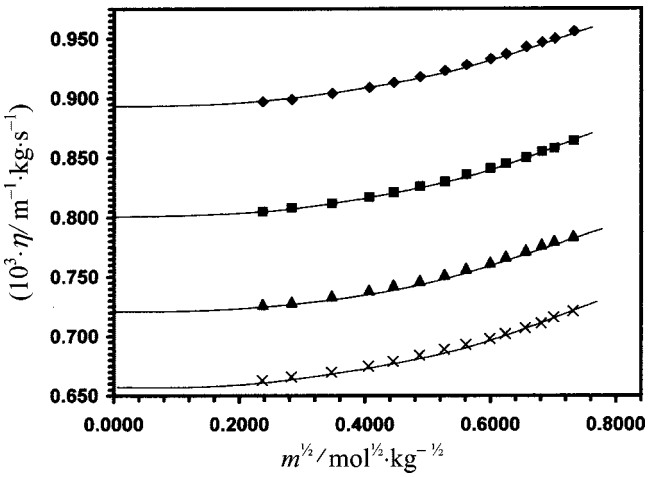

Figure 3. Viscosity η of cesium trifluoroacetate in water as a function of square root of molality $m^{1/2}$ at different temperatures: ♦, $T = 298.15$ K; ■, $T = 303.15$ K; ▲, $T = 308.15$ K; ×, $T = 313.15$ K; —, experimental.

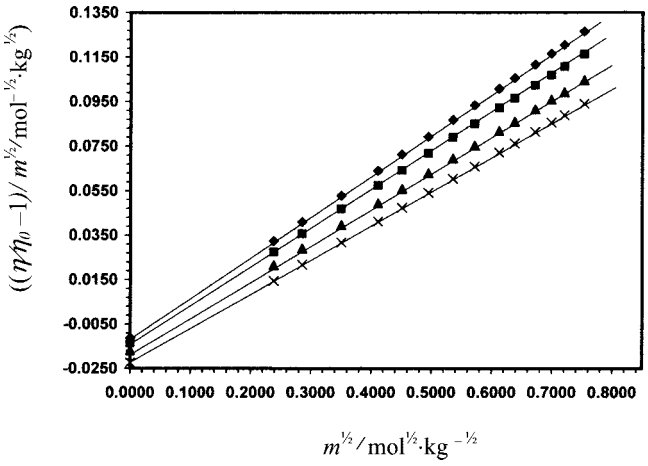

Figure 4. Plots of $(\eta/\eta_0 - 1)/m^{1/2}$ as a function of square root of molality $m^{1/2}$ for aqueous solutions of cesium trifluoroacetate at different temperatures: ♦, $T = 298.15$ K; ■, $T = 303.15$ K; ▲, $T = 308.15$ K; ×, $T = 313.15$ K; —, calculated by eq 4.

with m and decreases with an increase of temperature. The viscosity data have been analyzed using the Jones−Dole equation[14]

$$\eta/\eta_o = 1 + Am^{1/2} + Bm \quad (4)$$

where η and η_o are the viscosities of solute and solvent, respectively. A is a constant independent of concentration. The Jones−Dole coefficient B is related to the interaction between the ions and solvent and is interpreted as a measure of the structure-forming and structure-making capacity of an electrolyte in solutions.[15] Figure 4 shows the variations of $(\eta/\eta_o - 1)/m^{1/2}$ with $m^{1/2}$. The constant A and Jones−Dole coefficient B were calculated by the least-squares method. The values of A and B calculated from eq 4 are listed in Table 4. The values of A and B are negative and positive, respectively. The positive values of B at all temperatures indicate water structuring.[15]

Absolute average deviations (AAD) of apparent molar volume and viscosity have been calculated by using the equation

$$\mathrm{AAD} = |X - \bar{X}|/N \quad (5)$$

where X is apparent molar volume or viscosity and $\bar{X}$ is the average apparent molar volume or average viscosity of aqueous solutions and N is the number of observations. AADs of apparent molar volumes and viscosity are listed in Table 2 and Table 4, respectively.

Table 4. Least-Square Fitted Values of Jones−Dole Coefficient B and Constant A of Equation 4 and Absolute Average Deviation in Viscosity AAD of Cesium Trifluoroacetate in Water from T = (298.15 to 313.15) K

T/K	A^b	B^c	$10^3 \cdot \mathrm{AAD}^a$
298.15	-0.0223 ± 0.0042	0.1534 ± 0.0003	0.0165
303.15	-0.0169 ± 0.0034	0.1612 ± 0.0001	0.0164
308.15	-0.0136 ± 0.0056	0.1725 ± 0.0003	0.0163
313.15	-0.0112 ± 0.0047	0.1829 ± 0.0003	0.0158

[a] $m^{-1} \cdot kg \cdot s^{-1}$. [b] $(mol \cdot kg)^{-1/2}$. [c] $kg \cdot mol^{-1}$.

Conclusions

From density and viscosity studies of aqueous solutions of cesium trifluoroacetate, it is revealed that:

(a) ϕ^o_v values of cesium trifluoroacetate in water are positive and suggest strong ion–solvent interactions. An increase in ϕ^o_v value with temperature is due to an increase in ion−solvent interactions.

(b) Negative values of S_v suggest weak ion–ion interactions. More negative values of S_v at higher temperatures suggest a further decrease in ion–ion interactions.

(c) The values of the Jones−Dole coefficient B are positive. It is indicative of water structuring.

(d) The trifluoroacetate ion is strongly bound to water by hydration.

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