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Density, Viscosity, and Specific Conductivity of Trifluoromethanesulfonic Acid Monohydrate from 309.15 K to 408.15 K

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The temperature-dependent density, viscosity, and specific conductivity of the molten salt trifluoromethanesulfonic acid monohydrate are reported from around the freezing point of 309.15 K up to 408.15 K and interpolated by polynomials. The transport properties additionally are fitted with the Vogel−Fulcher−Tammann equation.

Introduction

Trifluoromethanesulfonic acid (TFMSA), CF_3SO_3H, is often used in chemical and electrochemical experiments. The monohydrate is purely ionic as seen from its ^1H NMR spectrum with one triplet peak for the structure H_3O^+-$CF_3SO_3^-$. Its melting point is at about 35 °C (Conway et al., 1992). We recently reported the dielectric behavior of TFMSA monohydrate (Barthel et al., 1998). In the present paper precise data for its density, viscosity, and specific conductivity are given over a wide temperature range.

Experimental Section

Materials. The preparation of trifluoromethanesulfonic acid monohydrate from equimolar amounts of distilled TFMSA and water is described elsewhere (Conway and Tessier, 1981). The salt is very hygroscopic and requires storage under nitrogen in a glovebox.

Methods. The density measurements were performed by use of a vibrating tube densimeter (Paar, DMA 602 HT, DMA 60) at a temperature constancy of ±0.01 K. The density, ρ, was calculated by the equation

$$\rho = (\tau^2 - B)/A \tag{1}$$

where τ is the oscillation period and A and B are the densimeter constants determined at each temperature from 40 °C to 85 °C by calibration with nitrogen (Weast, 1989−1990) and water (Herrington, 1976; Kell, 1975). Above 85 °C calibration was continued only with nitrogen, and the second constant was linearly extrapolated using the values (B/A) from the lower temperatures because this ratio shows linear temperature dependence, in contrast to A and B. Calibration was carried out before and checked after the measurements. No significant change of A and B could be observed. TFMSA was injected into the densimeter with a 5 mL gastight syringe through a short Teflon tube under nitrogen. The outlet tube ended in a glass vessel connected with an inert gas atmosphere held under atmospheric pressure to protect the salt from moisture and to compensate for the thermal expansion. The viscosity η was measured under an inert gas atmosphere with two Ubbelohde suspended level viscosimeters (types I and II) in connection with an automated device (Schott-Geräte, type AVS/G) for the determination of the efflux times t with an accuracy of 0.01 s. The working equation

$$\eta = \rho K(t - \vartheta) \tag{2}$$

is used, which implies the Hagenbach correction ϑ for the kinetic energy (values of ϑ taken from the operating instructions of Schott-Geräte). The constant K_I for the viscosimeter of type I was directly determined with water at 20 °C and 25 °C (IUPAC, 1980) and that of type II indirectly by the comparison of the efflux times of the molten salt at 50, 55, 60, and 65 °C in both viscosimeters and taking K_I as the reference. The constants are $K_I = (1.002 \pm 0.001) \times 10^{-8}$ m² s⁻² and $K_{II} = (1.025 \pm 0.001) \times 10^{-7}$ m^2 s^{-2}. The precision of temperature is ±0.02 K.

Conductivity measurements were made under an inert gas atmosphere with the standard equipment of our laboratory known to yield data with a precision of ±0.02% (Wachter and Barthel, 1979). A cell was used with a cell constant of 4613.2 m^{-1}, which could be filled with a syringe under nitrogen atmosphere. The temperature was controlled within ±0.001 K.

Results and Discussion

The experimental results are shown in Table 1. Literature data for comparison are not available. Data evolution was made with polynomials known to yield correct temperature dependencies (e.g., Barthel and Neueder, 1992):

$$\rho/\text{kg}\cdot\text{m}^{-3} = a_0 + a_1T + a_2T^2 + a_3T^3 \tag{3}$$

$$\ln(\eta/\text{Pa}\cdot\text{s}) = a_0T^{-2} + a_1T^{-1} + a_2 + a_3T \tag{4}$$

$$\ln(\kappa/\text{S}\cdot\text{m}^{-1}) = a_0T^{-2} + a_1T^{-1} + a_2 + a_3T \tag{5}$$

The coefficients are listed in Table 2 together with the standard deviations, s, of the data fits. Graphical representations of the data and interpolation curves are shown in Figure 1.

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Table 1. Density ρ, Viscosity η, and Specific Conductivity κ of TFMSA Monohydrate

T/K	$\rho/10^3$ kg m^{-3}	$\eta/10^{-3}$ Pa s	κ/S m^{-1}
309.15			0.96281
311.15			1.0238
313.15	1.669 00	38.82	1.0871
318.15	1.663 02	32.65	1.2581
323.15	1.657 07	27.42	1.4475
328.15	1.651 08	23.41	1.6555
333.15	1.645 28	20.12	1.8830
338.15	1.639 47	17.35	2.1307
348.15	1.627 62	13.06	2.6906
358.15	1.616 14	10.21	3.3412
368.15	1.604 63	8.060	4.0868
378.15	1.592 90	6.453	4.9333
388.15	1.581 59	5.240	5.8837
398.15	1.569 86	4.308	6.9413
408.15	1.558 39	3.583	8.1031

Table 2. Coefficients a_i of Eqs 3−5 with Standard Deviation s

	eq 3	eq 4	eq 5
a_0	2.2139×10^3	1.2308×10^6 K^2	-4.5896×10^3 K^2
a_1	-2.6088 K^{-1}	-6.1222×10^3 K	3.8771×10^2 K
a_2	3.8215×10^{-3} K^{-2}	9.5940	2.3000
a_3	-3.3435×10^{-6} K^{-3}	-1.8656×10^{-2} K^{-1}	3.9146×10^{-3} K^{-1}
s	8.2×10^{-2}	5.7×10^{-5}	1.2×10^{-3}

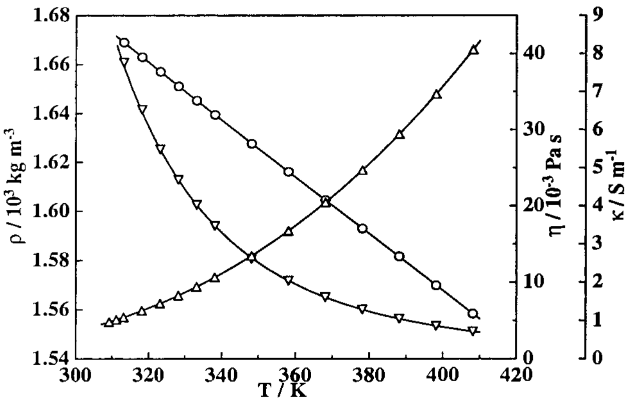

Figure 1. Temperature-dependent density (○), viscosity (▽), and specific conductivity (△) of TFMSA monohydrate. Lines (−) represent the curves obtained from eqs 3−5.

Another current approach to describe the temperature dependence of transport properties, W, of salt melts is the use of the Vogel−Fulcher−Tammann (VFT) equation (Moynihan, 1971):

$$W(T) = A \exp\{-B/[R(T - T_0)]\} \qquad (6)$$

A is taken as temperature-independent, and R is the gas constant. T_0 is the extrapolated glass transition temperature, which should be equal for all transport processes of a given system. The results from the use of eq 6 for fluidity, $\phi = \eta^{-1}$, and conductivity, κ, are shown in Table 3 together with the standard deviations, σ, of the fits. The data are well described with the help of the VFT parameters. Nonetheless, despite the good agreement of T_0 from η and κ curves, the interpretation of T_0 as the glass transition temperature is not unambiguous because the extrapolation must be carried out over a large temperature interval.

Table 3. Coefficients of the Vogel−Fulcher−Tammann eq 6 for the Fluidity, $\phi = \eta^{-1}$, and the Specific Conductivity κ with Standard Deviation, s

	A	B/J mol^{-1}	T_0/K	s
ϕ	98007 Pa^{-1} s^{-1}	16082	78.2	3.1×10^{-1}
κ	1125.7 S m^{-1}	13474	79.7	1.1×10^{-3}

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