

The Temperature Dependence of the Mobility of Aqueous Fluoride Ion, and the Apparent Molar Volume of Sodium Fluoride

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Abstract

Conductances of aqueous sodium fluoride solutions have been measured at 15°, 25° and 45°C to give the limiting mobility of fluoride ion. Apparent molar volumes have been obtained by means of a continuous dilution dilatometer.

Introduction

The fluoride ion is one of the few monatomic anions which can exist in aqueous solution, and is of particular interest in that it is isoelectronic with both Na⁺ and OH⁻, yet measurements of the physical properties of fluoride solutions are far less complete than those for the other halide ions.

Table 1. Molar conductances of aqueous sodium fluoride

Temp. 15°C		Temp. 25°C		Temp. 45°C	
10 ³ c/ mol dm ⁻³	10 ⁴ Λ/ m ² S mol ⁻¹	10 ³ c/ mol dm ⁻³	10 ⁴ Λ/ m ² S mol ⁻¹	10 ³ c/ mol dm ⁻³	10 ⁴ Λ/ m ² S mol ⁻¹
1.341	80.7 ₉	0.749	103.1	2.136	149.1
2.272	80.0 ₈	1.349	102.3	3.736	147.5
3.735	79.2 ₄	2.949	100.9 ₂	5.652	145.9
5.599	78.4 ₄	4.504	99.9 ₃	8.170	144.3
8.055	77.6 ₀	6.442	98.9 ₅	10.65	143.0
11.07	76.8 ₀	8.443	98.1 ₂	14.56	141.2
15.92	75.6 ₉	10.97	97.2 ₇	37.18	134.5
31.84	73.1 ₄	18.66	95.0 ₉	52.88	131.5
50.23	71.1 ₃	29.69	92.8 ₇	72.01	127.8
72.04	69.3 ₆	44.97	90.5 ₉	113.64	123.6
107.39	67.1 ₆	76.47	87.2 ₅		
		112.61	84.1 ₆		

Experimental

Sodium fluoride stock solutions were prepared, by weight titration of carbonate-free NaOH (prepared by the electrolytic amalgam method) with A.R. hydrofluoric acid, in polythene containers. Their concentrations were calculated from the mass of NaOH solution and the final mass of solution. The NaOH was itself analysed by weight titration against conductimetrically standardized HCl.¹

¹ Stokes, R. H., *J. Phys. Chem.*, 1961, **65**, 1242.

The equivalence point in the NaOH-HF titration, carried out in an argon atmosphere, was determined by a strip of litmus paper which was subsequently removed from the stock solution.

Conductances of appropriately weight-diluted solutions were measured in the cell used by Marsh² in work on NaOH solutions, an oil thermostat and a Leeds & Northrup Jones-Dike conductance bridge being used. Frequency dependence in the range 1–8 kHz was negligible. Corrections were made for the ionization of residual CO₂ in the conductance water. The effects of hydrolysis of fluoride ion and HF₂⁻ formation were examined and found to be negligible provided the stock solution is stoichiometrically neutralized. Results are given in Table 1.

Apparent molar volumes were measured for the stock solutions by a 25-cm³ pycnometer, and for diluted solutions in a continuous dilution dilatometer.^{3,4}

Table 2. Apparent molar volumes and molar conductances for aqueous sodium fluoride at infinite dilution

Temperature/°C	15	25	45
$\phi_v/\text{cm}^3 \text{ mol}^{-1}$	-3.0	-2.3	-1.6
$10^4 \Lambda^\circ/\text{m}^2 \text{ S mol}^{-1}$	83.1	105.4	155.2
$10^4 \lambda^\circ(\text{F}^-)/\text{m}^2 \text{ S mol}^{-1}$	43.3 _s	55.3 ₂	81.5
$\lambda^\circ(\text{F}^-)/\lambda^\circ(\text{Na}^+)$	1.090	1.105	1.106

Limiting values (Table 2) for the molar conductance were obtained by using the Pitts equation,⁵ and for the apparent molar volume by plotting against \sqrt{c} , satisfactory agreement with the theoretical limiting slope being found.

Discussion

Using the known limiting molar conductances of sodium ion we obtain those of fluoride ion given in Table 2. It is noteworthy that the ratio of the mobilities of these two ions changes only 1 % over the temperature range studied, and the small difference between the absolute values suggests that their interactions with the solvent are of similar strength. This is of interest because the accepted model of anion solvation has a proton of the water molecule closest to the anion, while for a cation the oxygen is closest.

Our value (55.3) for $\lambda^\circ(\text{F}^-)$ at 25° confirms those of Walden⁶ (55.4) and Erdey-Gruz *et al.*⁷ (55.3) against those of Kahlweit⁸ (53.8) and Duer *et al.*⁹ (55.7). Though sodium fluoride at higher concentrations shows evidence from activity coefficients of some ion-pairing, this does not appear to be significant at the concentrations (up to 0.1 M) studied here, except in so far as the Pitts equation requires the rather small ion size parameter

$$a = 2.3 \times 10^{-8} \text{ cm}$$

² Marsh, K. N., and Stokes, R. H., *Aust. J. Chem.*, 1964, **17**, 740.

³ Stokes, R. H., Levien, B. J., and Marsh, K. N., *J. Chem. Thermodyn.*, 1970, **2**, 43.

⁴ Stokes, R. H., *Aust. J. Chem.*, 1975, **28**, 2109.

⁵ Pitts, E., *Proc. R. Soc. London, Ser. A*, 1953, **217**, 480; Pitts, E., Tabor, B. E., and Daly, J., *Trans. Faraday Soc.*, 1969, **65**, 849.

⁶ Walden, P., (Ed.) 'Landolt-Bornstein Tabellen' Suppl. Vol. III C, p. 2059 (Julius Springer: Berlin 1936).

⁷ Erdey-Gruz, T., Majthenyi, L., and Kugler, E., *Acta Chim. Acad. Sci. Hung.*, 1963, **37**, 393.

⁸ Kahlweit, M., *Z. Phys. Chem. (N.F.)*, 1959, **21**, 436.

⁹ Duer, W. C., Robinson, R. A., and Bates, R. G., *J. Chem. Soc., Faraday Trans. 1*, 1972, **68**, 716.

The apparent molar volumes (Fig. 1) are negative at low concentrations, and become increasingly so as the temperature is lowered. This behaviour is similar to that found with sodium hydroxide,¹⁰ where the limiting value at 25°C is $\phi_V^\circ = -5.25 \text{ cm}^3 \text{ mol}^{-1}$.

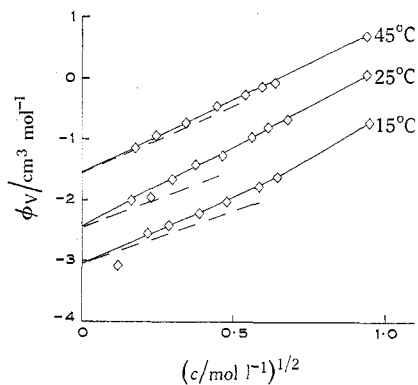


Fig. 1. Apparent molar volumes of sodium fluoride in aqueous solution.

This suggests that the electrostrictive and structural effects of the isoelectronic ions F^- and OH^- on water are fairly similar.

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¹⁰ Hepler, L. G., Stokes, J. M., and Stokes, R. H., *Trans. Faraday Soc.*, 1965, **61**, 505.