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Viscosity of Aqueous NaCl Solutions in the Temperature Range 25–200°C and in the Pressure Range 0.1–30 MPa

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New precise viscosity data are presented for aqueous solutions of NaCl; these data cover the temperature range 25–200°C, the pressure range 0.1–30 MPa, and the concentration range 0–6 $\text{mol}\cdot\text{kg}^{-1}$. The experimental precision is ±0.5%; a comparison of the present results with data available in the literature indicates that the accuracy of the present data is also of the order of ±0.5%. Two empirical correlations that reproduce the data within the precision are also given.

KEY WORDS: aqueous solutions; sodium chloride; viscosity.

1. INTRODUCTION

In a series of papers [1–6] we have reported the viscosity of various aqueous electrolyte solutions over the ranges 20–150°C and 0.1–30 MPa. These data were obtained with a modified oscillating-disk viscometer [2], previously employed for measurements of the viscosity of steam [7]. Because this instrument suffered from several disadvantages when subjected to high temperatures and corrosive environments [2, 8], a new viscometer was built to continue the study of these systems to higher temperatures and pressures. In a recent paper [8] we have described the construction of the new viscometer and reported data for the viscosity of water over the ranges 25–200°C and 0.1–30 MPa. This preliminary work proved that the new instrument was capable of providing viscosity data with a precision of ±0.3% for $20 < t < 150$°C, degrading to ±0.5% for temperatures in excess

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of 150°C. In this paper we present new precise data for the viscosity of aqueous NaCl solutions in the concentration range 0–6 $\mathrm{mol \cdot kg^{-1}}$, the temperature range 25–200°C, and the pressure range 0.1–30 MPa. The reasons for choosing this system for study were twofold; first, because of the existence of a wealth of experimental data for the NaCl system in the literature, it was possible to validate the accuracy of the new results, and, second, the corrosive nature of this system would permit us to judge the behavior of the new instrument under the conditions for which it was designed.

2. EXPERIMENTAL PROCEDURE

2.1. The Viscometer

The viscosity was measured in an oscillating-disk viscometer, which has been described in an earlier publication [8]. Details of the methods of temperature measurement and control and pressure measurement are also included in that paper. The characteristics of the oscillating system are given in Table I.

2.2. Calibration

Due to design limitations [2], absolute measurements of the viscosity of the liquids of interest here are almost impossible in an oscillating-disk viscometer. Hence a relative methods based upon the formulation of Kestin *et al.* [9, 10] was employed. The working equations pertinent to this method have been well documented [2, 8–10]. Calibration of the viscometer involves measurements upon a fluid of known viscosity in order to determine the dependence of the edge-correction factor C on the boundary-layer thickness δ, defined by

$$\delta = (\nu T_0/2\pi)^{1/2} \tag{1}$$

Here ν is the kinematic viscosity of the reference fluid and T_0 is the period

Table I. Characteristics of the Oscillating System

Radius of disk R (mm)	33.972
Thickness of disk d (mm)	3.210
Separation between disk and fixed plates b (mm)	2.249
Moment of inertia I ($\mathrm{g \cdot mm^2}$)	59,093
Period in air at 25°C, T_0 (s)	16.7336
Decrement *in vacuo* at 25°C, Δ_0	3.0×10^{-5}

of oscillation *in vacuo*, which in the present circumstances is identified with that in air [2]. Distilled water was used as the primary calibration fluid. Viscosity data were taken from the critical reevaluation of the viscosity of liquid water by Kestin *et al.* [11]. The calibration was performed over the temperature range 25–150°C, which corresponds to a boundary-layer range of $\delta = 0.73\text{–}1.53$ mm. In order to measure the viscosity of the more viscous NaCl solutions without relying upon an extrapolation of the edge-correction factor outside this range, we decided to emply one of the solutions to calibrate the viscometer between $\delta = 1.5$ and 1.85 mm. The reference viscosity data were taken from the work of Gonçalves and Kestin [12].

Figure 1 contains a plot of the data used to determine the edge-correction factor; the majority of the points shown in this figure correspond to an average of two measurements of C. The calibration data have been correlated in terms of the boundary-layer thickness by the empirical equation

$$C(\delta) = 1 + \sum_{i=1}^{3} c_i \delta^i \tag{2}$$

with a standard deviation of 0.2%. The coefficients c_i are collected in Table II.

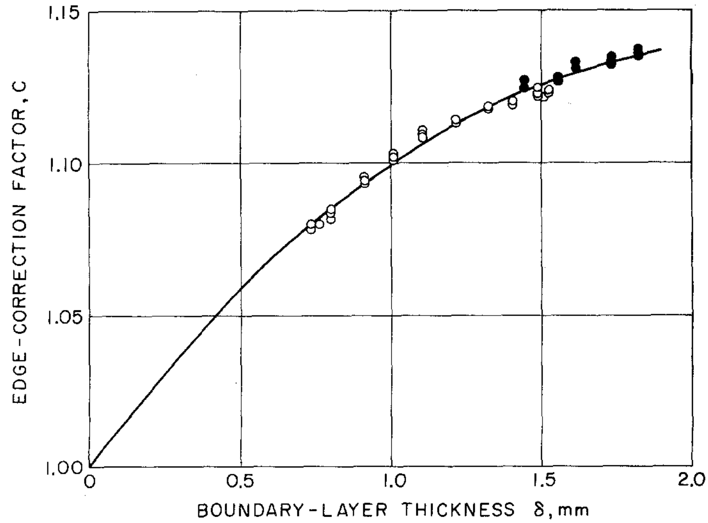

Fig. 1. Calibration curve; ○, H_2O data; ●, NaCl solution (4.4538 mol · kg^{-1}).

Table II. Coefficients for Calibration Correlation

c_1	1.3721×10^{-1}	mm^{-1}
c_2	-4.118×10^{-2}	mm^{-2}
c_3	3.618×10^{-3}	mm^{-3}

After performing a set of measurements on a solution the viscometer was dismantled, cleaned, and realigned. Before introducing the next solution the instrument was filled with water for a calibration check at room temperature and at another temperature in the range $25 < t < 150°\mathrm{C}$. If these check points agreed with the correlation (2) to within ±0.2%, then the cleaning and realignment were considered successful.

2.3. Measurement of the Decrement and Period

Prerequisite to the measurement of the viscosity is the determination of the logarithmic decrement Δ and the period of oscillation T. A method in which the determination of Δ can be reduced to the measurement of time has been described earlier [13]. In that paper it was shown that the major source of error in Δ arose from determining the zero position of the oscillation; this error is systematic and is most significant for the more heavily damped oscillations. Here a new method of computing the decrement from the same experimental readings is outlined that removes this small systematic error.

The angular displacement of a damped harmonic motion $\alpha(t)$ can be described by the relation

$$\alpha(t) = a^{*}\exp\left[-\tfrac{1}{2}\pi\Delta(1 + 4t/T)\right]\sin(2\pi t/T) \tag{3}$$

where zero time is defined by an instant when $\alpha = 0$. As described earlier [13], the determination of the decrement can be reduced to measuring times t_i at which the amplitude attains an arbitrary but fixed nonzero amplitude α_1^{*}. Hence these t_i must satisfy the equation

$$\alpha_1^{*}/\alpha^{*} = exp\left[-\Delta(2\pi t_i/T + \pi/2)\right]\sin(2\pi t_i/T) \tag{4}$$

Experimentally we measure the time intervals τ_i defined by the time taken for the amplitude to attain α_1^{*} after passing through $\alpha = 0$, in addition to the time intervals T_i' between consecutive in-phase attainments of $\alpha = 0$. These time intervals are illustrated diagrammatically in Fig. 2. If there exists a small error $\delta\alpha$ in the physical location of the zero position, then, as shown in Fig. 2, the times T_i' cannot be set equal to T and each τ_i possesses a progressively larger error. To account for these errors, Eq. (4) is expanded

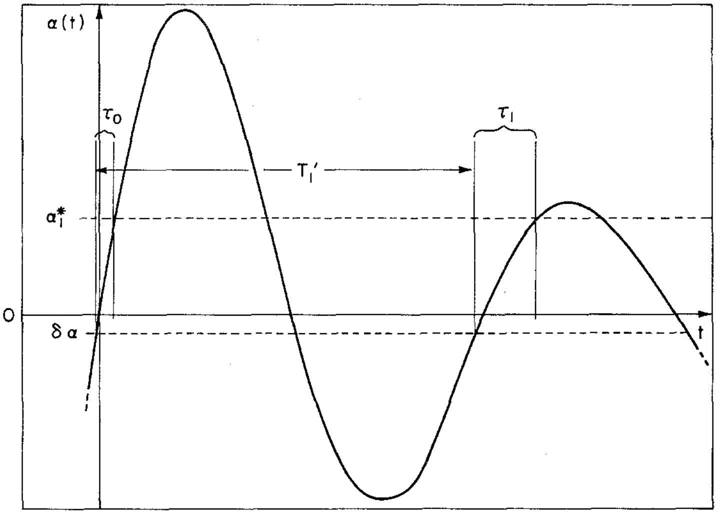

Fig. 2. Effect of zero-position error $\delta\alpha$ on a damped harmonic motion.

about $t = nT$ after setting $\alpha_1^* = \delta\alpha$. Retaining only the linear term gives

$$\delta_t^{(n)} = t - nT = \delta_t^{(0)} \exp(2\pi n \Delta), \qquad n = 0, 1, 2, \ldots \tag{5a}$$

where

$$\delta_t^{(0)} = \frac{\delta\alpha}{\alpha^*} \frac{T}{2\pi} e^{\pi\Delta/2} \tag{5b}$$

and $\delta_t^{(n)}$ represents the error in time caused by assuming that $\delta\alpha = 0$ on the nth pass through this position. Hence the true times t_i and T are given by

$$t_i = \tau_i + \sum_{j=1}^{i} T_j' + \delta_t^{(0)}, \qquad i = 0, 1, \ldots \tag{6a}$$

and

$$T = T_j' + \delta_t^{(0)}\left[1 - \exp(-2\pi\Delta)\right]\exp(2\pi j \Delta), \qquad j = 1, 2, \ldots \tag{6b}$$

For the purpose of computing the decrement, Eq. (4) is written as

$$F_i = \Gamma - \exp(-\pi\Delta/2)\exp(-2\pi t_i \Delta/T)\sin(2\pi t_i/T) \equiv 0 \tag{7}$$

where $\Gamma = \alpha_1^*/\alpha^*$. This equation, in conjunction with Eqs. (6a) and (6b), contains three unknown parameters, namely Δ, Γ, and $\delta_t^{(0)}$; the latter is treated as a disposable parameter. By minimizing the squared deviations F_i^2, these parameters can be computed using a nonlinear regression technique. This method offers one further advantage over the previous calculation scheme in that the presence of an initial transient is readily observable and in most cases its effects can be eliminated.

An initial transient [14] manifests itself as a drifting zero position and thus would be expected to produce nonrandom deviations F_i. To illustrate this, some sample experimental data are reproduced in Table III. When all the measured times are included in the fit to obtain Δ, a seemingly anomalous set of deviations results. If these are due to a transient, then deletion of some of the first measurements should improve the fit. Inspection of Table III reveals this to be the case when τ_0 and T_1' are deleted and a new zero time defined. The last column in Table III lists the deviations between the T_i' measurements and values calculated according to Eq. (6b). This serves as a further consistency check for the values of Δ, Γ, and $\delta_t^{(0)}$.

In the present study another set of time intervals τ_i' corresponding to another fixed amplitude α_2^* were also measured. This permits two estimations of Δ, T and $\delta_t^{(0)}$ to be obtained from a single oscillation. Further, the ratio

$$\Gamma_1/\Gamma_2 = \alpha_1^*/\alpha_2^* \tag{8}$$

which is a geometric constant for the system, can be calculated. In principle, this ratio could be measured independently, or, as in the present

Table III. Sample Data Concerning Oscillations[a]

i	τ_i (s)	T_i' (s)	$100F_i/\Gamma$ (%)	$100F_i/\Gamma$[b] (%)	$\delta T_i'$[b] (ms)
0	0.20229	—	−0.03	—	—
1	0.30047	17.44652	0.08	−0.00	—
2	0.44745	17.44657	−0.01	0.00	0.13
3	0.66916	17.44588	−0.03	0.01	0.11
4	1.01043	17.44496	−0.05	−0.02	−0.04
5	1.56026	17.44301	0.00	0.01	0.34
6	2.59822	17.44155	0.03	0.00	−0.53

$\Delta = 0.062451$, standard deviation $(\Delta) \equiv 0.01\%$, $\Gamma = 0.096242$, $\delta_t^{(0)} = 3.11$ ms, $T = 17.44820$ s

[a] This table is taken from an oscillation in a 4.4538 mol · kg^{-1} solution of NaCl at 40.85°C and 30.6 MPa.

[b] Data in the last two columns apply when τ_0 and T_1' are deleted, as do the values of Δ, Γ, $\delta_t^{(0)}$, and T.

case, a second oscillation performed and another estimation of Γ_1/Γ_2 obtained. The main advantage of the additional measurements lies in the verification of both internal and external consistency relations. That is, the acceptability of a given measurement is determined by the criteria of internal agreement between the calculated Δ, T, and $\delta_t^{(0)}$ and the external agreement between Δ, T, and Γ_1/Γ_2 for oscillations measured in duplicate. The acceptance is defined, *a posteriori*, to be ± 2 standard deviations in the particular quantity.

2.4 Density

The working equations of the oscillating-disk viscometer [9, 10] indicate that in the first approximation

$$\eta \sim \Delta^2/\rho \tag{9}$$

where η and ρ denote the viscosity and density of the fluid, respectively. Hence, any uncertainty in the density is reflected in the viscosity. Density data for water (needed for calibration) were taken from the work of Kell and co-workers [15, 16]. The uncertainty claimed for these data is less than $\pm 0.002\%$. For the aqueous NaCl solutions the density correlation of Rowe and Chou [17] was employed over the ranges $20 < t < 175°\mathrm{C}$ and $0.1 < P < 35$ MPa. The accuracy of this correlation is claimed to be within $\pm 0.15\%$. Above 175°C the correlation of Hilbert [18] was used; the estimated accuracy of these data is $\pm 0.1\%$ over the temperature range of interest. Both of the NaCl correlations employed agreed to within their mutual uncertainties.

3. EXPERIMENTAL RESULTS

The experimental results are summarized in Tables IV–VIII. Each entry in the tables is the average of at least two measurements. Experimental data have been corrected to nominal temperatures by means of the relation

$$\eta(t_{\mathrm{nom}}) = \eta(t) + (\partial\eta/\partial t)_{\mathrm{nom}}(t_{\mathrm{nom}} - t) \tag{10}$$

where the derivative $\partial\eta/\partial t$ has been taken from previous studies of the NaCl system [3, 26]. In the absence of such data, a piecewise Arrhenius fit over a limited range of temperature was employed to estimate $\partial\eta/\partial t$. As these corrections amount to less than 1% of η, any uncertainty introduced by the approximation is insignificant.

Table IV. Viscosity of Aqueous NaCl (1.0661 mol · kg^{-1})

P (MPa)	η (μPa · s)	P (MPa)	η (μPa · s)
(a) $t = 24.0$°C		(b) t = 28.1°C	
0.1	1000.5	0.1	916.4
5.2	999.9	5.4	916.2
10.7	999.5	10.4	916.4
15.6	1000.0	15.5	917.5
20.7	1001.9	20.6	918.7
25.7	1001.2	25.4	920.6
30.7	1002.7	30.3	921.0
0.1	1001.5	0.1	917.6
(c) $t = 34.0$°C		(d) $t = 40.5$°C	
1.1	813.8	0.2	721.3
5.3	814.8	5.2	721.3
10.3	815.8	10.4	724.2
15.4	815.9	15.5	723.6
20.5	817.8	20.9	726.1
25.4	819.4	25.6	728.4
30.3	821.2	30.5	728.6
0.2	815.0	0.3	721.8
(e) $t = 49.3$°C		(f) $t = 65.0$°C	
0.2	622.1	0.3	491.7
5.4	622.5	5.6	493.1
10.5	623.7	10.5	493.4
15.6	625.5	15.6	495.9
20.4	627.4	20.5	497.5
25.5	628.0	25.6	499.7
30.5	628.9	30.2	501.8
0.2	620.3	0.3	491.6
(g) $t = 97.2$°C		(h) $t = 127.0$°C	
0.4	333.6	0.9	252.9
5.3	335.1	5.4	254.1
10.4	335.3	10.4	255.6
15.4	337.5	15.4	256.9
20.6	339.4	20.8	258.0
25.5	340.8	25.7	259.0
30.2	342.2	30.6	261.1
0.5	333.5	0.8	252.7

Table IV. (Continued)

P (MPa)	η (μPa · s)	P (MPa)	η (μPa · s)
(i) $t = 148.5$°C		(j) $t = 173.0$°C	
0.9	213.5	1.7	181.7
5.5	215.1	1.5	182.3
10.3	216.1	7.1	184.2
16.3	217.2	12.1	184.2
20.1	219.4	16.9	185.6
25.6	220.1	22.0	187.6
30.6	221.5	29.6	189.6
0.8	213.3	6.7	183.7
(k) $t = 199.0$°			
2.2	158.3		
2.9	158.5		
7.8	159.5		
12.8	160.6		
12.2	160.9		
18.2	162.8		
23.9	163.6		
30.3	165.1		

Table V. Viscosity of Aqueous NaCl (2.0178 mol · kg^{-1})

P (MPa)	η (μPa · s)	P (MPa)	η (μPa · s)
(a) $t = 24.0$°C		(b) $t = 29.0$°C	
0.8	1094.4	0.5	986.0
5.8	1095.4	5.5	988.5
10.7	1097.7	10.4	989.3
15.7	1098.5	15.6	991.1
21.1	1100.0	20.7	992.0
26.1	1101.5	25.9	994.0
30.8	1103.8	30.8	995.4
0.8	1097.7	0.7	986.2

Table V. (Continued)

P (MPa)	η (μPa · s)	P (MPa)	η (μPa · s)
(c) $t = 34.8$°C		(d) $t = 40.2$°C	
0.6	881.9	0.6	800.5
5.4	883.6	5.4	802.1
10.6	884.7	10.5	802.1
15.6	886.4	15.6	804.8
20.7	888.3	20.7	806.0
25.6	889.5	25.6	808.3
30.6	891.5	30.6	810.1
1.1	882.1	1.1	801.3
(e) $t = 49.8$°C		(f) $t = 66.1$°C	
0.7	682.2	0.5	539.6
5.4	683.7	5.5	540.8
10.7	686.5	10.6	542.5
15.7	687.8	15.8	544.0
20.8	689.2	20.5	545.7
26.0	690.0	25.4	547.6
30.5	692.0	30.6	549.3
1.0	682.7	1.0	539.6
(g) $t = 90.2$°C		(h) $t = 125.7$°C	
0.7	403.6	1.8	288.3
5.5	404.6	7.7	289.8
10.5	406.1	13.5	291.5
15.6	408.0	19.5	294.5
20.6	410.2	26.4	296.7
25.6	411.0	31.2	298.5
30.7	412.9	2.1	289.8
1.2	403.3		
(i) $t = 149.4$°C		(j) $t = 174.0$°C	
3.0	240.7	2.8	205.7
7.9	242.5	8.6	206.8
13.4	243.5	14.8	209.0
19.6	245.2	20.3	210.2
25.7	247.2	26.3	211.4
31.4	248.5	31.2	213.3
2.5	240.8	2.9	206.0
(k) $t = 200.0$°C			
4.0	179.3		
9.5	180.5		
15.5	183.0		
20.3	183.2		
26.4	185.5		
32.1	185.5		

Table VI. Viscosity of Aqueous NaCl (3.5161 mol · kg^{-1})

P (MPa)	η (μPa · s)	P (MPa)	η (μPa · s)
(a) t = 24.2°C		(b) t = 27.9°C	
5.2	1297.5	5.1	1198.1
10.4	1301.5	10.5	1198.8
15.5	1301.4	15.5	1202.7
20.6	1305.8	20.6	1205.2
25.8	1307.0	25.4	1208.8
30.8	1312.0	30.7	1210.8
(c) t = 34.5°C		(d) t = 40.5°C	
5.4	1049.0	5.5	941.4
10.4	1052.2	10.5	943.2
15.6	1054.6	15.4	945.7
20.7	1059.0	20.6	948.0
25.9	1060.7	25.3	950.8
30.7	1063.0	30.4	952.9
(e) t = 50.0°C		(f) t = 65.2°C	
5.2	804.2	0.9	643.5
10.5	806.7	5.4	645.6
15.6	808.5	10.5	648.1
20.5	809.8	15.4	650.0
25.6	812.7	20.7	652.8
30.7	815.3	25.6	654.0
		30.5	656.5
		1.0	643.5
(g) t = 90.0°C		(h) t = 126.0°C	
0.6	478.8	1.9	341.8
5.2	480.8	5.6	344.8
10.5	482.1	10.5	346.5
15.4	484.4	15.4	346.5
20.4	485.8	20.4	348.4
25.7	488.3	25.5	350.2
30.4	489.6	30.4	352.0
0.8	479.2	2.2	343.7
(i) t = 149.2°C		(j) t = 174.7°C	
2.5	288.0	2.7	244.5
5.9	288.8	8.0	245.2
10.5	289.6	13.1	247.1
15.5	290.0	19.3	248.6
20.7	292.7	25.7	250.4
25.5	294.4	31.1	251.9
30.5	296.0	2.5	243.6
2.3	287.3		

Table VI. (Continued)

P (MPa)	η (μPa · s)	P (MPa)	η (μPa · s)
(k) $t = 199.5$°C			
2.7	214.2		
7.8	215.5		
13.2	217.2		
19.7	218.5		
26.0	220.8		
31.6	222.1		

Table VII. Viscosity of Aqueous NaCl (4.4538 mol · kg^{-1})

P (MPa)	η (μPa · s)	P (MPa)	η (μPa · s)
(a) $t = 24.2$°C		(b) $t = 29.2$°C	
0.9	1449.0	0.3	1300.4
5.5	1455.3	5.5	1304.3
10.5	1457.9	10.3	1306.7
15.5	1460.0	15.7	1311.4
20.8	1464.3	20.7	1315.5
25.6	1467.2	25.9	1319.9
31.1	1474.0	31.2	1323.4
0.5	1450.1	0.3	1302.3
(c) $t = 35.8$°C		(d) $t = 40.8$°C	
0.4	1143.4	0.3	1041.2
5.4	1146.6	5.4	1044.0
10.6	1149.6	9.9	1046.8
15.9	1154.0	15.5	1049.7
21.0	1156.9	20.7	1052.9
25.3	1160.3	25.8	1055.7
30.4	1163.4	30.6	1059.8
0.6	1144.4	0.3	1040.9
(e) $t = 50.4$°C		(f) $t = 65.1$°C	
1.1	888.5	0.7	716.1
5.2	889.6	5.5	718.0
10.7	892.9	10.6	721.8
15.4	894.7	15.7	723.3
20.9	897.8	20.8	726.1
25.7	901.1	25.9	728.4
30.8	904.0	30.8	730.5
0.6	886.9	1.0	716.3

Table VII. (Continued)

P (MPa)	η (μPa · s)	P (MPa)	η (μPa · s)
(g) $t = 89.8$°C		(h) $t = 124.8$°C	
0.8	532.8	2.2	386.7
5.4	534.6	8.1	388.9
10.6	537.0	14.4	391.0
15.6	539.3	20.3	392.8
21.0	541.7	26.1	394.7
25.9	545.2	30.8	396.7
31.0	547.3	2.2	385.8
(i) $t = 149.9$°C		(j) $t = 174.2$°C	
2.8	318.2	3.6	273.6
7.6	319.5	9.3	274.0
14.3	321.8	15.0	275.5
20.3	324.1	20.9	277.3
25.7	326.7	25.9	278.7
30.9	327.9	30.8	280.8
2.9	319.2		
(k) $t = 201.5$°C			
3.6	235.4		
9.1	237.1		
16.0	238.4		
20.7	239.8		
25.6	240.7		
31.2	242.2		
31.3	242.6		

Table VIII. Viscosity of Aqueous NaCl (6.0380 mol · kg^{-1})

P (MPa)	η (μPa · s)	P (MPa)	η (μPa · s)
(a) $t = 34.5$°C		(b) $t = 40.0$°C	
4.9	1457.2	3.1	1306.5
10.1	1464.0	5.3	1308.9
15.1	1468.8	10.3	1314.1
20.3	1473.6	15.6	1318.3
25.4	1479.5	20.2	1323.0
30.4	1484.7	25.8	1328.0
2.4	1455.4	30.7	1332.6
		2.9	1306.7

Table VIII. (Continued)

P (MPa)	η (μPa · s)	P (MPa)	η (μPa · s)
(c) $t = 50.5$°C		(d) $t = 66.0$°C	
0.4	1090.0	0.3	868.2
5.3	1095.1	5.4	871.9
9.7	1098.3	10.4	873.9
15.7	1103.5	15.4	876.5
20.8	1108.9	20.7	880.6
25.8	1110.4	25.7	882.7
30.9	1115.5	30.6	887.1
0.7	1092.8	0.9	868.9
(e) $t = 126.0$°C		(f) $t = 151.0$°C	
2.3	455.3	1.9	372.9
5.6	458.5	5.4	375.2
10.5	458.3	10.6	375.5
15.6	461.3	15.8	378.2
20.8	464.6	20.7	380.3
25.7	464.1	25.7	383.1
30.6	467.4	30.6	383.8
1.9	454.9	2.8	374.1
(g) $t = 174.5$°C		(h) $t = 201.5$°C	
4.0	319.2	5.0	278.5
9.6	323.4	10.3	279.0
15.2	324.7	15.4	281.2
20.7	326.2	20.4	282.0
25.6	328.5	25.8	283.5
30.4	329.8	30.6	285.4
4.3	320.6		

4. ANALYSIS AND CORRELATION OF RESULTS

4.1. Effect of Pressure

For each isotherm and concentration the viscosity was measured from near saturation pressure to 30 MPa at approximately 5 MPa intervals. Over this pressure range the viscosity varied by up to 5%. In all cases the pressure dependence could be correlated, within the experimental precision, via the linear relationship

$$\eta(P,t,m) = \eta^0(t,m)\left[1 + \beta(t,m)P\right] \tag{11}$$

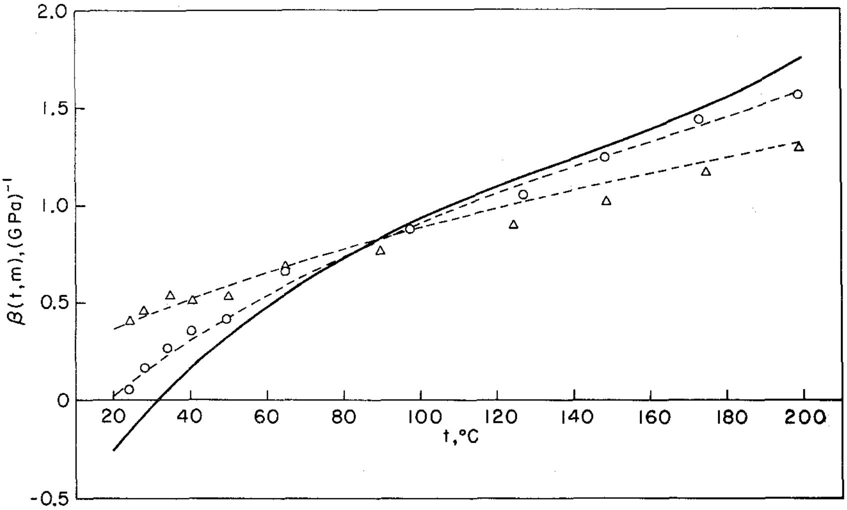

Fig. 3. The pressure coefficient $\beta(m, t)$; ○, 1.0661 mol · kg^{-1}; △, 3.5161 mol · kg^{-1}; - - -, correlation for $\beta(m, t)$; —, correlation for water.

where m represents the molality of the solute and P the pressure. The worst-case standard deviation of such a fit was 0.35% of η^0. Figure 3 illustrates the dependence of β on t and m; not all data are shown in this figure, for the sake of clarity. Inspection of Fig. 3 reveals that for temperatures below about 90°C the relative effect of pressure on the viscosity of the NaCl solutions is greater than that of pure water and above this temperature the reverse is true. In both cases the excess pressure coefficient

$$\beta^E(t,m) = \beta(t,m) - \beta(t,0) \tag{12}$$

increases in magnitude with increasing m. It is interesting to note that for all concentrations studied, there seems to exist a common temperature (~90°C) at which all the $\beta(t,m)$ curves intersect. However, to determine whether or not this reflects the true situation would require an increase in the experimental precision by at least an order of magnitude.

Due to the lack of a general theory of aqueous electrolyte solutions covering wide ranges of temperature, pressure, and concentration, the pressure coefficient data were correlated empirically as a polynomial in t and m,

$$\beta^E(t,m) = \sum_{i=1}^{3} \sum_{j=0}^{3} b_{ij} m^i t^j \tag{13}$$

Table IX. Coefficients b_{ij} for Eq. (13)[a]

j	$i = 1$	$i = 2$	$i = 3$
0	6.26×10^{-1}	-1.64×10^{-1}	1.88×10^{-2}
1	-1.64×10^{-2}	5.24×10^{-3}	-6.36×10^{-4}
2	1.35×10^{-4}	-4.90×10^{-5}	6.11×10^{-6}
3	-3.65×10^{-7}	1.36×10^{-7}	-1.69×10^{-8}

[a] The b_{ij} have units $(\mathrm{GPa})^{-1}(\mathrm{mol}^{-1} \cdot \mathrm{kg})^{i}(^{\circ}\mathrm{C})^{-j}$.

where the coefficients b_{ij} are summarized in Table IX. In order to calculate $\beta^{E}(t,m)$ from the $\beta(t,m)$ data, the correlation for the pressure coefficient of water was taken as [8]

$$\begin{aligned}\beta_w(t) &= \beta(t,0)\\ &= -0.7879 + 2.927 \times 10^{-2}t - 1.584 \times 10^{-4}t^2\\ &\quad + 3.775 \times 10^{-7}t^3 \qquad (14)\end{aligned}$$

Equations (11)–(14) reproduce the pressure dependence of the measured viscosities within an average absolute deviation of 0.13%.

Recently Leyendekkers [19] has applied the Tammann–Tait–Gibson model [20–22] to the calculation of the viscosity of aqueous electrolyte solutions. He hypothesized that the effect of pressure on the viscosity of an electrolyte solution can be related to the viscosity of the *water in solution* η_{wis} by the relation

$$\begin{aligned}\eta(t,P,m)/\eta(t,P_0,m) &= \eta_{\mathrm{wis}}(t,P)/\eta_{\mathrm{wis}}(t,P_0)\\ &= \eta_w(t,P+P_e)/\eta_w(t,P_0+P_e) \qquad (15)\end{aligned}$$

Table X. Comparison of TTG Calculations and Experimental Results at 25°C[a]

m $(\mathrm{mol} \cdot \mathrm{kg}^{-1})$	β_{TTG} $(\mathrm{GPa})^{-1}$	β_{CORR} $(\mathrm{GPa})^{-1}$	Deviation in η at 30 MPa (%)
1.0661	−0.0364	0.103	−0.4
2.0178	0.0864	0.248	−0.5
3.5161	0.206	0.407	−0.6
4.4538	0.279	0.513	−0.7
6.0380	0.391	0.809	−1.2

[a] β_{TTG} and β_{CORR} are the pressure coefficients for Eq. (11) as calculated from the Tammann–Tait–Gibson model and as calculated from the correlation, Eqs. (13) and (14).

where η_w is the viscosity of pure water and P_e is the effective pressure of the ionized solute. Table X shows that at 25°C this type of calculation underestimates the effect of pressure by no more than 1.2% at 30 MPa. The calculations were performed using the P_e data of Leyendekkers and Hunter [22] and the internationally accepted correlation for the viscosity of water [23]. The lack of the necessary P_e data as a function of composition and temperature precluded the testing of Eq. (15) over the full temperature range of measurement.

4.2 Composition and Temperature Dependence

For dilute electrolyte solutions there exist both theoretical evidence and a wealth of experimental data to support the relationship [20, 24, 25]

$$\eta_R = 1 + A\sqrt{I} \tag{16}$$

where $\eta_R = \eta/\eta_w$ is the relative viscosity of the solution and I is the ionic strength defined in terms of the molarity c_i and valence z_i of ions i as

$$I = \frac{1}{2}\sum_i c_i z_i^2 \tag{17}$$

The coefficient A in Eq. (16) arises from long-range interionic interactions and is calculable from the limiting ionic conductances of the constituent ions and the viscosity and dielectric properties of the solvent. This equation is strictly valid at infinite dilution and thus has been found to describe the concentration dependence over the range 0–0.002 $\text{mol}\cdot\text{dm}^{-3}$ [25]. At higher concentrations, as empirical extension of Eq. (16) referred to as the Jones–Dole equation,

$$\eta_R = 1 + A\sqrt{I} + BI \tag{18}$$

has been employed. This equation is capable of describing the concentration dependence to about 0.1 $\text{mol}\cdot\text{dm}^{-3}$ [25]. Although no theoretical means of calculating the coefficient B exists as yet, it has been suggested that it arises from ion–solvent interactions [25]; it has been successfully correlated with other physical properties dependent upon these interactions.

The case of concentrated aqueous electrolyte solutions is less clear, with only a few purely empirical correlations [25] describing the composition and temperature dependence in existence so far. One such empirical equation, employed previously to describe the viscosity of NaCl solutions [26], is known as the Othmer rule,

$$\ln \eta_R(t,m) = A'(m) + B'(m)\ln\left[\eta_w(t)/\eta_w(20°C)\right] \tag{19}$$

Table XI. Othmer-Rule Coefficients

i	A_i ($\mathrm{mol}^{-i} \cdot \mathrm{kg}^{i}$)	B_i ($\mathrm{mol}^{-i} \cdot \mathrm{kg}^{i}$)
1	8.4142×10^{-2}	-3.7797×10^{-2}
2	2.980×10^{-3}	6.205×10^{-3}
3	3.11×10^{-4}	-9.68×10^{-5}

The coefficients $A'(m)$ and $B'(m)$ introduce the concentration dependence and are considered independent of temperature. They have been correlated as

$$A'(m) = \sum_{i=1}^{3} A_i m^i \tag{20a}$$

$$B'(m) = \sum_{i=1}^{3} B_i m^i \tag{20b}$$

The optimum values of A_i and B_i are listed in Table XI. Viscosity data for water were taken from the correlations of Kestin *et al.* [8, 11], which offer a convenient expression for $\ln[\eta_w(t)/\eta_w(20°\mathrm{C})]$. Equations (19) and (20) reproduce the present data within an average absolute deviation of 0.28%,

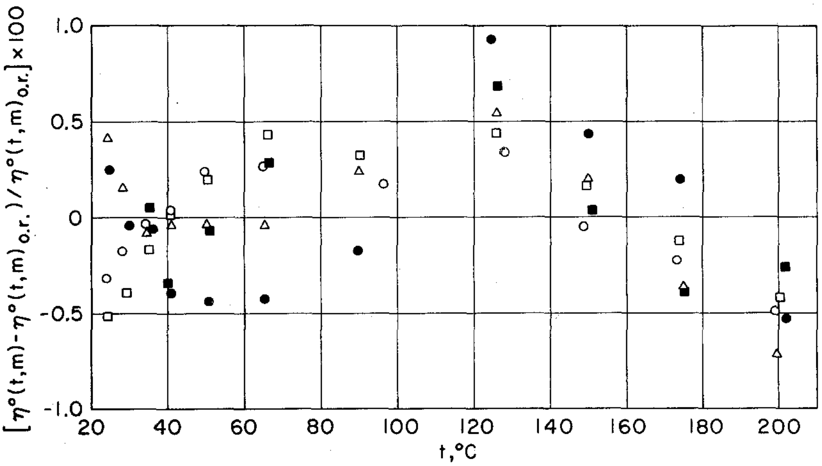

Fig. 4. Deviations between experimental $\eta^0(t, m)$ data and Othmer-rule correlation; ○, 1.0661 mol · kg^{-1}; □, 2.0178, mol · kg^{-1}; △, 3.5161 mol · kg^{-1}; ●, 4.4538 mol · kg^{-1}; ■, 6.0380 mol · kg^{-1}.

with a maximum individual deviation of 0.9%; Fig. 4 contains a plot of all the deviations.

Another empirical correlation sometimes employed stems indirectly from Eq. (18). Because the $A\sqrt{I}$ is generally swamped by the higher terms (e.g., at 25°C $A_{\mathrm{NaCl}} \sim 0.006$ and contributes less than 1% to η_R at saturation) it may be neglected and a simple polynomial in concentration assumed. It is important to note that the minimum concentration employed in this study, ~ 1 mol · kg^{-1}, lies well outside the range used experimentally to determine A. Hence, any value determined from the present set of experimental data has no physical significance. In order to simplify this correlation, the molality concentration scale is employed instead of the temperature- and pressure-dependent molarity. The experimental data could be described by

$$\eta_R = 1 + d_1 m + d_2 m^2 + d_3 m^3 \tag{21a}$$

where

$$d_i = d_{i,0} + d_{i,1} t + d_{i,2} t^2, \qquad i = 1, 2, 3 \tag{21b}$$

with an average absolute deviation of 0.19% and a worst-case deviation of 0.5%. The coefficients $d_{i,j}$ of Eq. (21b) are given in Table XII. Figure 5 depicts the individual deviations of the experimental data from Eq. (21a). No significance is attached to the slightly better fit obtained with this equation in comparison to that obtained with Eq. (19).

The viscosity of a number of concentrated electrolyte solutions and molten salts has been found to obey the Arrhenius–Andrade type [25] relation

$$\eta = A \exp(E_{\mathrm{vis}}/RT) \tag{22}$$

where A and E_{vis} have been considered concentration dependent but temperature independent. A similar type of equation has been developed

Table XII. Coefficients d_{ij} for Eq. (21b)[a]

i	$j = 0$	$j = 1$	$j = 2$
1	6.596×10^{-2}	1.063×10^{-3}	-3.164×10^{-6}
2	6.271×10^{-3}	-1.313×10^{-4}	6.067×10^{-7}
3	1.489×10^{-3}	-1.359×10^{-6}	-3.094×10^{-8}

[a] The d_{ij} have units $(\mathrm{mol}^{-1} \cdot \mathrm{kg})^i (°\mathrm{C})^{-j}$.

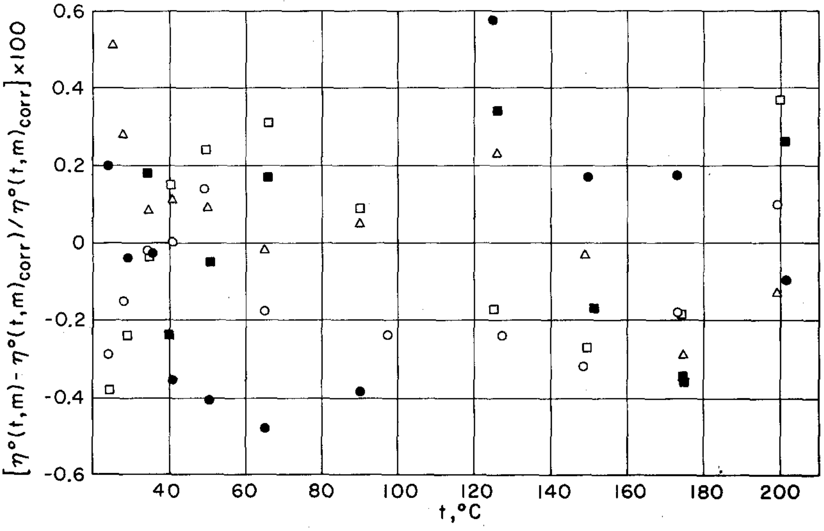

Fig. 5. Deviations between experimental $\eta^0(t, m)$ data and Eq. (21a); ○, 1.0661 mol · kg^{-1}; □, 2.0178 mol · kg^{-1}; △, 3.5161 mol · kg^{-1}; ●, 4.4538 mol · kg^{-1}; ■, 6.0380 mol · kg^{-1}.

by Glasstone *et al.* [27] to describe the temperature dependence of nonassociated liquids with reasonable success. However, Eq. (22) failed to correlate the present data over the complete temperature range 25–200°C. Individual deviations from this equation were as great as 15% in some cases. The failure of the Arrhenius–Andrade equation to describe the experimental data is possibly attributable to the associated nature of the solvent, water, or to the assumption that A is independent of temperature.

5. PRECISION AND ACCURACY

The experimental precision is best judged from the uncertainty in each of the experimental quantities from which the viscosity is determined. Of these, the viscosity is most sensitive to the decrement; the uncertainties in the other quantities, temperature (±0.05°C), pressure (±50 kPa), period (±1 ms), and the period *in vacuo* (±1 ms), have a negligible effect upon the viscosity. The standard deviation in the decrement, when computed from Eq. (7), is typically 0.01% at room temperature, degrading to ~0.2% at 200°C. This degradation arises from refractive effects in the laser-optical system [13], which in turn are caused by transient temperature gradients in the light path. The effect of any uncertainty in Δ is amplified in the viscosity [cf. Eq. (9)]. Overall, the reproducibility of the measurements varied from ±0.1% at 25°C to ±0.5% at 200°C.

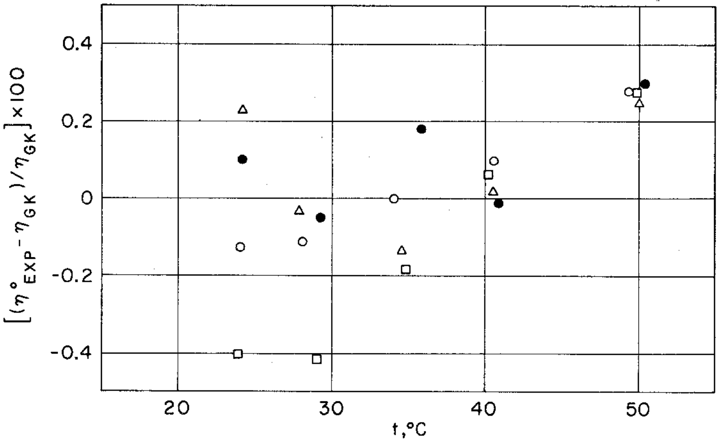

Fig. 6. Deviations between experimental data and correlation of Gonçalves and Kestin [12]; ○, 1.0661 mol · kg^{-1}; □, 2.0178 mol · kg^{-1}; △, 3.5161 mol · kg^{-1}; ●, 4.4538 mol · kg^{-1}.

The experimental accuracy is estimated by comparison with other results, preferably obtained with independent techniques. For this purpose we have chosen to compare our results primarily with two studies; first, the work of Gonçalves and Kestin [12], who obtained data between 25 and 50°C over the concentration range 0–5.5 mol · kg^{-1}, and second, the work of Korosi and Fabuss [26], who studied this sysem for 25–150°C and 0–3.5 mol · kg^{-1}. The former employed viscometers of the Ostwald and Ubbelohde types and is taken as representative of the large body of precise data obtained with such viscometers over limited ranges of temperature. The estimated accuracy of this work was ±0.1%. Korosi and Fabuss employed Cannon-type capillary viscometers and estimated their experimental precision as ±0.2%. To simplify the analysis, the present data were compared directly with the correlations given in these publications. Figures 6 and 7 depict the deviations from the correlations of Kestin and Gonçalves, and Korosi and Fabuss; the average absolute deviations (0.16% and 0.37%, respectively) are within the mutual limits of experimental precision.

Values of the viscosity of concentrated solutions covering the range of temperatures and pressures reported here are extremely scarce. Two such studies, one from this laboratory [3], employing an earlier version of an oscillating-disk viscometer, and another by Pepinov *et al.* [28], who used a modified capillary method, will be used for a comparison. The present data deviate from the previous results from this laboratory with an average deviation of 0.9%, which is within the combined uncertainty limits. However, the correlation of Pepinov *et al.*, with a claimed accuracy of ±1.0%

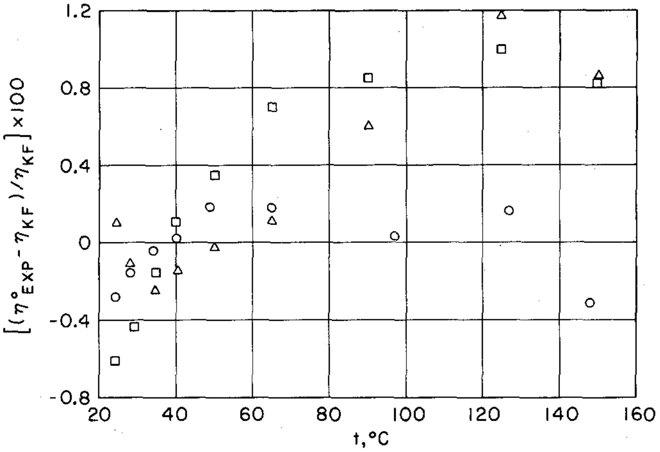

Fig. 7. Deviations between experimental data and correlation of Korosi and Fabuss [26]; ○, 1.0661 mol · kg^{-1}; □, 2.0178 mol · kg^{-1}; △, 3.5161 mol · kg^{-1}.

over the ranges 25–350°C and 0–30 MPa, deviates by as much as 9.0% from the present results, the average discrepancy being 2.3%.

In summary, we can state that the new data exhibit an average precision of better than ±0.5% and an accuracy of comparable magnitude. Two empirical correlations have been proposed to describe the data over 25–200°C, 0–30 MPa, and 0–6 mol · kg^{-1}. The first of these correlations [Eqs. (11), (13), and (19)] reproduces the 750 (t, P, m, η) data points with an average absolute deviation of 0.30% and with a maximum absolute deviation of 1.4%; the corresponding deviations for the second correlation [Eqs. (11), (13) and (21)] are 0.23% and 1.0%. These deviations are considered commensurate with the experimental accuracy.

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