Acta Chemica Scandinavica, 1993: 47: 338–343
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ACTA
CHEMICA SCANDINAVICA
ISSN 0904-213X

Density of Aqueous Perchloric Acid Solutions in the Molality Range 0–4.4 mol kg^{-1} at 293.15, 298.15, 303.15 and 308.15 K

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Partanen, J. I. and Juusola, P. M., 1993. Density of Aqueous Perchloric Acid Solutions in the Molality Range 0–4.4 mol kg^{-1} at 293.15, 298.15, 303.15 and 308.15 K. – Acta Chem. Scand. 47: 338–343.

Densities of perchloric acid solutions up to a molality of 4.4 mol kg^{-1} were measured at the temperatures of 293.15, 298.15, 303.15 and 308.15 K by a commercially available oscillating tube-type densitometer. The experimental data of the present study agree well with the density results found in the literature for $HClO_4$ solutions. The measured densities up to a molality of 3.0 mol kg^{-1} at the different temperatures can in most cases be correlated to the concentrations within 0.05 mg cm^{-3} by means of a two-parameter equation of the Masson type. Another equation which contains only one electrolyte-dependent parameter is also presented for densities of perchloric acid solutions. With this equation, almost all measured densities of this study can be predicted within 2 mg cm^{-3} up to a molality of about 3.0 mol kg^{-1}. The results of the present density determinations are also considered theoretically according to the Debye–Hückel theory for electrolyte solutions.

Many papers have been published on the thermodynamics of aqueous perchloric acid solutions at 298.15 K. Isopiestically $HClO_4$ solutions at this temperature have been investigated by Robinson and Baker,[1] Boyd,[2] and Haase *et al.*[3] Electrochemically the solutions of this electrolyte at 298.15 K have been studied by Mussini *et al.*,[4] Torrent *et al.*[5] and Covington and Prue.[6] The two former research groups used in their investigations concentration cells containing a perchlorate ion-responsive membrane electrode, and Covington and Prue made measurements on concentration cells with a liquid junction and also determined transference numbers in dilute $HClO_4$ solutions. In addition, Pearce and Nelson[7] have obtained vapor pressures in $HClO_4$ solutions at this temperature by their air-saturation method.

The paper of Pearce and Nelson[7] also contains the density values of the solutions investigated. The densities of this paper are reported with an accuracy of 0.01 mg cm^{-3}. In the literature there are also two other papers, i.e. those of Markham[8] and Kohner and Gressmann,[9] which contain density results measured in perchloric acid solutions at 298.15 K with this accuracy. Markham[8] also reports some densities determined at 303.15 K. With an accuracy of 0.1 mg cm^{-3}, Haase and Dücker[10] have measured several densities in $HClO_4$ solutions at the following nine temperatures: 273.15, 283.15, 291.15, 293.15, 298.15, 303.15, 313.15, 323.15 and 333.15 K. Also, the values of Haase *et al.*[11] at 298.15 K are reported with this accuracy.

On the other hand, the density values suggested by Clark and Putnam[12] cover a composition range from 0 to 60 wt% $HClO_4$ and a temperature range of 273–333 K, and are given with an accuracy of 1 mg cm^{-3}. These results were used by Söhnel and Novotny when they determined their equation for the density of perchloric acid solutions in their book[13] containing density tables of aqueous solutions of nearly 300 inorganic substances.

In the present study, new experimental density data are presented for perchloric acid solutions up to a molality of 4.4 mol kg^{-1} at 293.15, 298.15, 303.15 and 308.15 K. These data were measured by an oscillating-tube-type densitometer with an accuracy of 0.01 mg cm^{-3}. The results of the new measurements therefore supplement, for example, the quite sparse high-precision density data of this electrolyte at the temperatures other than 298.15 K. The density values obtained here agree well with the results of the precise pycnometric determinations published previously (see below). At each temperature of this study, the new density data up to a molality of about 3.0 mol kg^{-1} can be predicted by means of a two-parameter equation for the apparent molar volume of the solute suggested by Masson.[14] The theoretical equation for this quantity, derived by Redlich and Rosenfeld[15] according to the theory of Debye and Hückel for dilute electrolyte solutions, does not apply satisfactorily to the present density data. From the results of the new density data such a one-parameter equation can be obtained by which the densities of perchloric acid solutions between 293 and 308 K may usually be calculated within 0.002 g cm^{-3} up to a molality of 3.0 mol kg^{-1}.

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Experimental

Perchloric acid solutions were prepared by weighing appropriate amounts of 70–72% perchloric acid (Merck 519) and RO-filtered water (Millipore) with a conductivity less than 1 μS cm^{-1}. The exact molality of the strong $HClO_4$ solution was determined by several density measurements at 293.15 and 298.15 K whose results were analysed by means of the density data reported by Smith and Goehler[16] and Kohner and Gressmann,[9] and in Ref. 17 for strong perchloric acid solutions. The value of this molality was 23.73 mol kg^{-1} (70.45 wt%). This value was also checked by titrating potentiometrically several appropriately diluted samples of the strong solution with a freshly prepared KOH solution (1/10 N DILUT-IT, J. T. Baker 4673).

Densities of the studied $HClO_4$ solutions were measured by an Anton Paar DMA 55 densitometer, and the details of the experimental technique have been described in the previous paper[18] concerning HNO_3 solutions.

Results

The experimental densities of aqueous $HClO_4$ solutions determined in the present study are listed in Table 1. The values of this table can be predicted at each temperature up to a molality of 3.0 mol kg^{-1} by means of an empirical equation presented by Masson[14] for the apparent molar volume of the solute (Φ_V). This quantity can directly be calculated from the density (ρ) and the molality (m_2) or the concentration (c_2) of the solution by eqn. (1), where

$$\Phi_V = (\rho_1 - \rho)/(m_2 \rho \rho_1) + M_2/\rho$$
$$= (\rho_1 - \rho)/(c_2 \rho_1) + M_2/\rho_1 \quad (1)$$

ρ_1 is the density of the solvent (component 1) and M_2 is the molar mass of solute (component 2). At a constant temperature, Masson[14] presented eqn. (2) for Φ_V,

$$\Phi_V = V^{\infty}_{m,2} + S_2(c_2)^{1/2} \quad (2)$$

where $V^{\infty}_{m,2}$ is the partial molar volume of the solute at infinite dilution at the temperature under consideration and S_2 is a constant which also depends on the solute and the temperature. Concentration c_2 can be calculated from molality m_2 by eqn. (3). When the experimental density

$$c_2 = m_2 \rho/(1 + m_2 M_2) \quad (3)$$

data of Table 1 is fitted to eqn. (2), the Φ_V-values must first be calculated by eqn. (1) and the c_2-values by eqn. (3). The regression analysis of eqn. (2) must be performed so that a weight of $(c_{2,i}/c^{\circ})^2$, where $c^{\circ} = 1$ mol dm^{-3}, is used for each experimental point i (Ref. 18).

The results of the fitting of the experimental densities of Table 1 according to eqn. (2) are presented in Table 2. As explained in the previous paragraph, the regression lines of Table 2 have been obtained by weighted regression analysis from the points whose molality is less than 3.0 mol kg^{-1}. The error plots of the straight lines of this table are shown in Fig. 1. In the four graphs of this figure, the error defined by eqn. (4) is presented at the different

$$e(\rho) = \rho(\text{observed}) - \rho(\text{predicted}) \quad (4)$$

temperatures as a function of concentration c_2. ρ(predicted) has been calculated with the parameter values of Table 2 by eqn. (5).

$$\rho(\text{predicted}) = \rho_1 - (\rho_1 V^{\infty}_{m,2} - M_2)c_2 - \rho_1 S_2 c_2^{3/2} \quad (5)$$

In the same way as the density values of the nitric acid solutions,[18] the densities of Table 1 up to a molality of

Table 1. Experimentally determined densities of $HClO_4$ solutions at different temperatures.

m/mol kg^{-1}	ρ(293 K)/g cm^{-3}	ρ(298 K)/g cm^{-3}	ρ(303 K)/g cm^{-3}	ρ(308 K)/g cm^{-3}
0.0000[a]	0.9982041	0.9970449	0.9956473	0.9940319
0.1010	1.00390	1.00264	1.00118	0.99950
0.2057	1.00972	1.00841	1.00689	1.00512
0.4236	1.02171	1.02024	1.01857	1.01673
0.6370	1.03327	1.03166	1.02992	1.02792
0.8724	1.04573	1.04395	1.04200	1.03985
1.1151	1.05834	1.05639	1.05442	1.05220
1.3717	1.07147	1.06940	1.06722	1.06488
1.6313	1.08438	1.08213	1.07986	1.07748
1.8758	1.09632	1.09394	1.09146	1.08878
2.2031	1.11210	1.10958	1.10700	1.10421
2.5110	1.12643	1.12368	1.12101	1.11798
2.7804	1.13880	1.13591	1.13305	1.13018
3.1246	1.15426	1.15128	1.14823	1.14521
3.4313	1.16767	1.16449	1.16146	1.15832
3.8676	1.18646	1.18315	1.18005	1.17663
4.3538	1.20670	1.20319	1.19981	1.19631

[a] Given by Kell.[19]

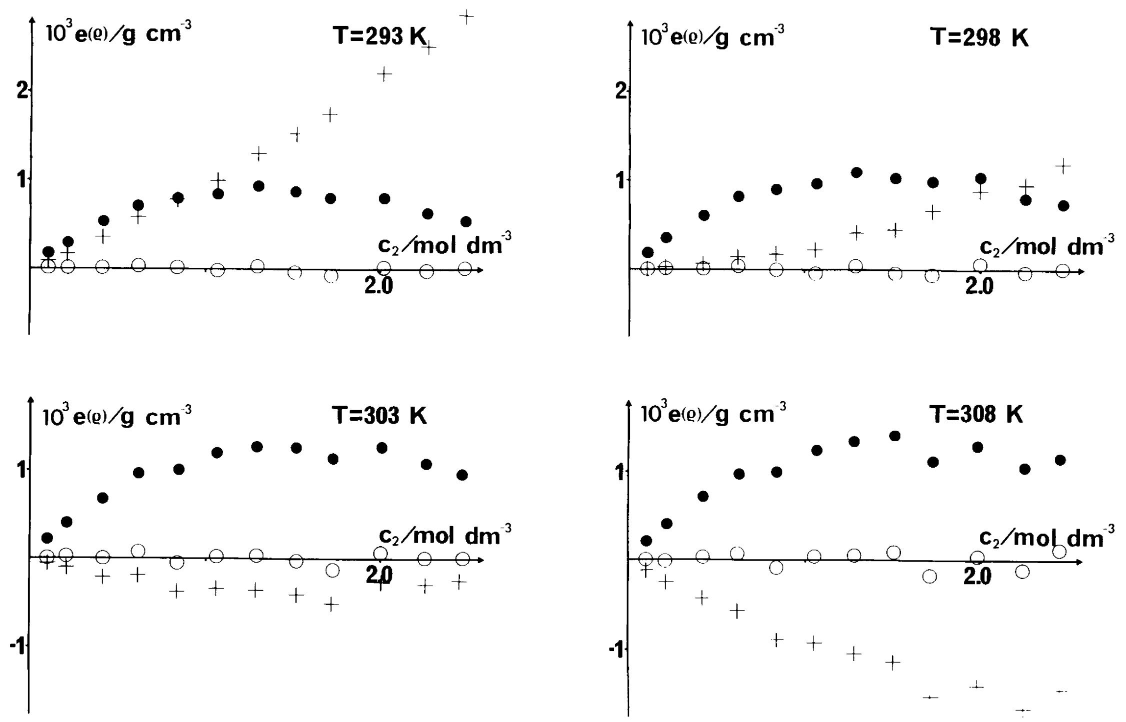

Fig. 1. Difference between the observed and predicted density of perchloric acid solutions as a function of the concentration at different temperatures. The observed values of Table 1 have been used and the predicted values have been calculated by eqn. (5) with the parameter values of Table 2 (○), by the equation of Söhnel and Novotny [eqn. (7)] (●) and by eqn. (6) (+).

3.0 mol kg^{-1} can also be predicted quite accurately for practical purposes by eqn. (6), which contains only

$$\rho = \rho_1(1 + m_2M_2)/(1 + m_2\rho_1\bar{\Phi}_V) \qquad (6)$$

one parameter that is dependent on the electrolyte. The value of $\bar{\Phi}_V$ was determined so that it is the mean value of all 48 Φ_V-values which were calculated from the experimental densities of Table 1 and whose molality is less than 3.0 mol kg^{-1}. The value of 44.767 cm^3 mol^{-1} for $\bar{\Phi}_V$ was thus obtained. The predictive ability of this simple equation is compared to the validity of the equation of Söhnel and Novotny.[13] Their general equation has the form of eqn. (7), where $t°$ is 1 °C and the density ρ_1 is the

$$\rho/(\text{kg m}^{-3}) = \rho_1/(\text{kg m}^{-3}) + A(c_2/c°) + B(c_2/c°)(t/t°) + C(c_2/c°)(t/t°)^2 + D(c_2/c°)^{3/2} + E(c_2/c°)^{3/2}(t/t°) + F(c_2/c°)^{3/2}(t/t°)^2 \qquad (7)$$

density of pure water (as above) and it can be calculated

Table 2. Values of the parameters of the Masson equation [eqn. (2)] in perchloric acid solutions.

T/K	$V^{\infty}_{m,2}$/cm^3 mol^{-1}	$-S_2$/cm^3 (mol dm^{-1})$^{-3/2}$
293.15	44.083	0.2150
298.15	44.890	0.3445
303.15	45.533	0.4298
308.15	46.194	0.5385

according to these workers by eqn. (8). For perchloric

$$\rho_1/(\text{kg m}^{-3}) = 999.65 + 0.20438(t/t°) - 0.061744(t/t°)^{3/2} \qquad (8)$$

acid the coefficients of eqn. (7) are the following: $A = 59.85$, $B = -0.3334$, $C = 0.00319$, $D = 0.05668$, $E = 0.08249$ and $F = -0.0009076$.

The comparison of eqn. (6) and the equation of Söhnel and Novotny was made such that the experimental densities of Table 1 were compared to those calculated by these equations. The results of these tests are presented as error plots in the four graphs of Fig. 1, which also contains the results obtained by the Masson equation, see above.

Discussion

According to Fig. 1, the experimental densities of Table 1 up to a molality of 3.0 mol kg^{-1} can be predicted well by means of eqn. (5), obtained from the Masson equation [eqn. (2)], with the parameter values given in Table 2. The Masson equations of Table 2 can also be tested with the density data available in the literature for perchloric acid solutions. As mentioned above, Haase and Dücker[10] have reported many density values suitable for this comparison at the temperatures of 293.15, 298.15 and 303.15 K. The results of this comparison are presented as error plots in Fig. 2. At 293.15 and 303.15 K the density values of the concentrations below 0.01 mol dm^{-3}, and at

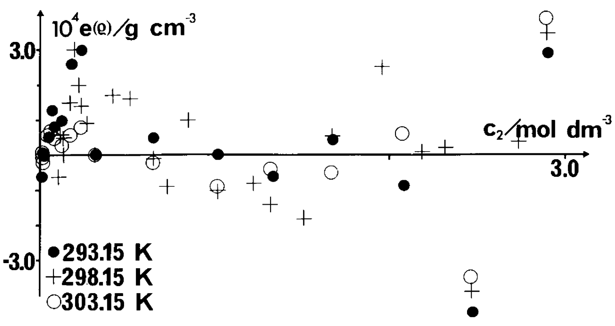

Fig. 2. Difference between the observed and predicted density of perchloric acid solutions as a function of the concentration. The observed values have been measured by Haase and Dücker[10] at the temperatures shown in the figure. The predicted values have been calculated by eqn. (5) with the parameter values of Table 2. An outlier ($T = 298.15$ K, $c_2 = 2.007$ mol dm^{-3}, $e(\rho) = 4.0 \times 10^{-3}$ g cm^{-3}) has been omitted from the figure.

298.15 K those of the concentrations below 0.1 mol dm^{-3}, have been omitted from this figure for the sake of clarity. The largest error obtained by these omitted points is 0.0001 g cm^{-3}. The results of Fig. 2 need only a few comments. The experimental data of Haase and Dücker can very probably be predicted within their precision by means of the Masson equations for 293.15, 298.15 and 303.15 K.

The Masson equation at 298.15 K can also be tested critically by predicting with it the density values reported by Pearce and Nelson,[7] Markham[8] and Kohner and Gressmann[9] for this temperature. The density values published by Hasse *et al.*[11] at 298.15 K are less precise than those of these three sets. Also the earlier density values of Haase's group[11] do not agree very well with the data published slightly later by Haase and Dücker[10] (see above). Therefore, the older density values reported by Haase and his coworkers have been omitted from the present comparison. The results of the comparison of the observed density values of Pearce and Nelson, Markham, and Kohner and Gressmann to the ones predicted by the Masson equation at 298.15 K are shown as error plots in Fig. 3. The experimental density values of the three sets in this figure support this Masson equation well.

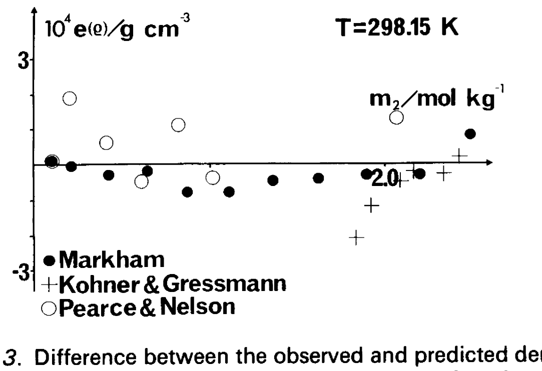

Fig. 3. Difference between the observed and predicted density of perchloric acid solutions at 298.15 K as a function of the molality. The observed values have been measured by Pearce and Nelson,[7] Markham[8] and Kohner and Gressmann.[9] The predicted values have been calculated by eqn. (5) with $V^{\infty}_{m,2} = 44.890$ cm^{3}mol^{-1} and $S_2 = -0.3445$ cm^3 (mol dm^{-1})$^{-3/2}$ (Table 2). To obtain the concentrations from the molalities some iterative calculations were needed.

In a theoretical article, Bigeleisen[20] have presented smoothed values for the apparent molar volume of perchloric acid at 298.15 K at several concentrations from 0.01 to 11.56 mol dm^{-3}. In that study the smoothed values were based on the density data reported in the three sets included in Fig. 3. The recommended values for Φ_V were derived by Bigeleisen from a smoothed curve reproducing the experimental Φ_V-values as reliably as possible. The curve also has the theoretically correct slope at infinite dilution; the recommended value of the Debye–Hückel slope at that time (1943) was 1.86 cm^3 (mol dm^{-1})$^{-3/2}$. The smoothed values of Bigeleisen for Φ_V can be used to test the Masson equation determined above for 298.15 K by calculating first from the Φ_V-values the corresponding density values via eqn. (9), and then

$$\rho = \rho_1 + (M_2 - \rho_1 \Phi_V)\, c_2 \qquad (9)$$

comparing these values to the densities obtained by eqn. (5) with the parameter values given in Table 2. The results of this comparison are presented as an error plot in Fig. 4. According to this figure, the smoothed Φ_V-values presented by Bigeleisen are quite close to those obtained by the Masson equation at 298.15 K, but unfortunately, a clear trend nevertheless appears in the error plot.

Covington and Prue[6] measured pycnometrically densities in dilute $HClO_4$ solutions (i.e. at molalities <0.1 mol kg^{-1}) at 298.15 K, and presented on the basis of these measurements eqn. (10) for the density of the solutions of this kind, where $m^\circ = 1$ mol kg^{-1}. This

$$\rho/\mathrm{g\ cm^{-3}} = \rho_1/\mathrm{g\ cm^{-3}} + 0.0573(m_2/m^\circ) \qquad (10)$$

equation can be used to test the Masson equation at 298.15 K by comparing the predictions of these two equations. The results of this comparison are presented as an error plot in Fig. 4. According to this plot, the predic-

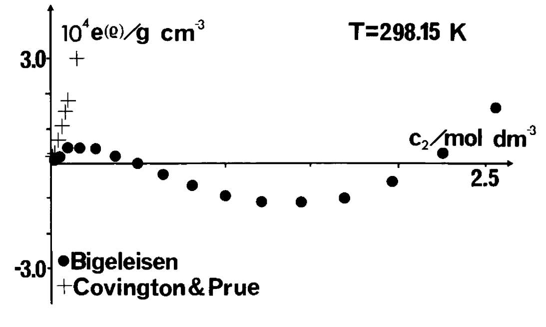

Fig. 4. Difference between the previously recommended densities and those obtained by means of the Masson equation (Table 2) for perchloric acid solutions at 298.15 K as a function of the molality. The literature values have been suggested by Bigeleisen[20] and Covington and Prue[6] (see text).

tions of these two equations differ significantly even at very dilute solutions. Because of the wide experimental evidence presented in Figs. 1–3 it seems to be probable that the Masson equation at 298.15 K gives more reliable density values than either those obtained by the equation of Covington and Prue [eqn. (10)] or those recommended by Bigeleisen.[20] (Fig. 4 also contains the results of the comparison obtained from this set.) For dilute perchloric solutions at 298.15 K an equation of the type suggested by Covington and Prue[6] can also be deduced from the Masson equation determined above. The result is eqn. (11), which predicts the same density value within

$$\rho/\mathrm{g\,cm^{-3}} = \rho_1/\mathrm{g\,cm^{-3}} + 0.0555(m_2/m^\circ) \qquad (11)$$

0.01 mg cm^{-3} as the Masson equation up to a molality of 0.1 mol kg^{-1}.

At 303.15 K there are in the literature two other density values reported by Markham[8] (in addition to those reported by Haase and Dücker, Fig. 2) which can be used to test the Masson equation of this temperature. These values and the corresponding predictions of the Masson equation are the following: [$m_2 = 1.1060$ mol kg^{-1}, $\rho = 1.05385$ g cm^{-3}, ρ(Masson) = 1.05394 g cm^{-3}] and (2.4886, 1.11996, 1.11998). The two density values of Markham accordingly support the new Masson equation well.

Redlich and Rosenfeld[15] have theoretically derived eqn. (12) from the theory of Debye and Hückel for Φ_V in binary solutions of a uni-univalent electrolyte. In

$$\Phi_V = V^{\infty}_{m,2} + k(c_2)^{1/2} \qquad (12)$$

eqn. (12), the slope k is common for all electrolytes of this kind and it can be calculated by a theoretical equation which contains some properties of the solvent (water in this case) and universal constants. When the modern values of these properties and constants are used, it can be calculated, for example, that the value of k at 298.15 K is 1.833 cm^3 (mol $dm^{-1})^{-3/2}$ (Ref. 21). Eqn. (12) is (in the same way as Debye–Hückel theory) most correct in very dilute electrolyte solutions.

As shown in eqns. (2) and (12), the Masson equation has almost the same form as the theoretical equation of Redlich and Rosenfeld. Only the slope in the former equation is dependent on the electrolyte, and in the latter equation it is the same for all uni-univalent electrolytes. Unfortunately, the slope obtained in this study for the Masson equation at 298.15 K [= −0.345 cm^3 (mol $dm^{-1})^{-3/2}$] is far from the theoretical slope [= 1.833 cm^3 (mol $dm^{-1})^{-3/2}$]. However, it should be mentioned that the density determinations of the present study begin at the molality of 0.1 mol dm^{-3}, and so our solutions are perhaps too strong to test the validity of eqn. (12). Also, in more dilute solutions the accuracy of the present density determinations is perhaps not sufficient to test this validity. For example, at a concentration 0.01 mol dm^{-3}, the Masson equation determined above for 298.15 K predicts a value of 44.86 cm^3 mol^{-1} for Φ_V, and the theoretical value for this quantity (calculated by means of a value of 43.90 for $V^{\infty}_{m,2}$ as suggested by Bigeleisen)[20] is 44.09 cm^3 mol^{-1}. The difference between these two Φ_V-values corresponds to such a density difference, which is less than the accuracy of the density determinations presented in this study (i.e. 0.01 mg cm^{-3}). Consequently, according to the measurements of this accuracy in dilute solutions no indisputable choice between these two models can be made.

When the values of the parameters in Table 2 and the appropriate constants are inserted into eqn. (5), the following parameter values are obtained in the general equation (13) for the densities of perchloric acid solutions

$$\rho/\mathrm{g\,cm^{-3}} = \alpha + \beta(c/c^\circ) - \gamma(c/c^\circ)^{3/2} \qquad (13)$$

at the temperatures used in this study: (T = 293.15 K, α = 0.998204, β = 0.056455, γ = −0.000215), (298.15 K, 0.997045, 0.055701, −0.000343), (303.15 K, 0.995647, 0.055124, −0.000428), (308.15 K, 0.994032, 0.054541, −0.000535). In eqn. (13) c is the concentration of $HClO_4$ and c° is 1 mol dm^{-3}. The densities obtained by this equation can be safely recommended. The densities of perchloric acid solutions up to the concentration of about 2.5 mol dm^{-3} can be very probably calculated within 0.05 mg cm^{-3} by eqn. (13).

For practical purposes, at least in the temperature range 293–308 K and in the molality range 0–3.0 mol kg^{-1}, eqn. (6) is in most cases sufficient. It gives the correct density in these conditions, probably within 0.002 g cm^{-3}. According to Fig. 1, this simple equation predicts the experimental densities at least as well as the more general but also more complicated equation of Söhnel and Novotny[13] [eqn. (7)].

Acknowledgments. Financial support to J. P. from the Academy of Finland is gratefully acknowledged.

References

1. Robinson, R. A. and Baker, O. J. *Trans. R. Soc. N. Z. 76* (1946) 250.
2. Boyd, G. E. *Inorg. Chem. 17* (1978) 1808.
3. Haase, R., Dücker, K. H. and Küppers, H. A. *Ber. Bunsenges. Phys. Chem. 69* (1965) 97.
4. Mussini, T., Galli, R. and Dubini-Paglia, E. *J. Chem. Soc., Faraday Trans. 1, 68* (1972) 1322.
5. Torrent, J., Sanz, F. and Virgili, J. *J. Soln. Chem. 15* (1986) 363.
6. Covington, A. K. and Prue, J. E. *J. Chem. Soc.* (1957) 1567.
7. Pearce, J. N. and Nelson, A. F. *J. Am. Chem. Soc. 55* (1933) 3075.
8. Markham, A. E. *J. Am. Chem. Soc. 63* (1941) 874.
9. Kohner, H. and Gressmann, M. L. *Z. Phys. Chem., Teil A 144* (1929) 137.
10. Haase, R. and Dücler, K. H. *Z. Phys. Chem., Neue Folge 46* (1965) 140.

11. Haase, R., Lehnert, G. and Jansen, H. J. *Z. Phys. Chem., Neue Folge 42* (1964) 32.
12. Clark, L. H. and Putnam, G. L. *J. Am. Chem. Soc. 71* (1949) 3445.
13. Söhnel, O. and Novotny, P. *Densities of Aqueous Solutions of Inorganic Substances*, Elsevier, Amsterdam 1985.
14. Masson, D. O. *Philos. Mag. (7) 8* (1929) 218.
15. Redlich, O. and Rosenfeld, P. *Z. Phys. Chem., Teil A 155* (1931) 65.
16. Smith, G. F. and Goehler, O. E. *Ind. Eng. Chem., Anal. Ed. 3* (1931) 61.
17. *International Critical Tables*, McGraw-Hill, New York 1928, Vol III, p. 55.
18. Partanen, J. I., Juusola, P. M. and Minkkinen, P. O. *Acta Chem. Scand. 46* (1992) 338.
19. Kell, G. S. *J. Chem. Eng. Data 20* (1975) 97.
20. Bigeleisen, J. *J. Phys. Colloid Chem. 51* (1947) 1369.
21. Archer, D. G. and Wang, P. *J. Phys. Chem. Ref. Data 19* (1990) 371.

Received July 27, 1992.