Density of Aqueous Nitric Acid Solutions in the Molality Range 0–3.5 mol kg⁻¹ at 293.15, 298.15, 303.15 and 308.15 K

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Densities of nitric acid solutions up to a molality of 3.5 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 agree well with the sparse density results found in the literature for HNO₃ solutions. The measured densities of this study at the different temperatures can in most cases be correlated to the concentrations within 0.00005 g 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 nitric acid solutions. With this equation, almost all measured densities of this study can be predicted within 0.002 g cm⁻³. The results of the present density determinations are also considered theoretically according to the Debye–Hückel theory for electrolyte solutions.

Recently Söhnel and Novotny[1] presented tables for densities of aqueous solutions of nearly 300 inorganic substances. The densities in these tables are given with an accuracy of 0.001 g cm⁻³. For nitric acid, these workers present two equations (the one for the weight fractions of 0–0.5 and the other for 0.5–1.0) containing both six adjusted parameters and covering temperatures from 273 to 373 K.

Theoretical studies concerning the pressure dependence of electrolyte solutions (as well as many practical applications) require more accurate density values than those which can be obtained from equations of Söhnel and Novotny[1] (see for example Ref. 2). Nowadays, it is not very difficult to measure densities to within 0.00001 g cm⁻³ by using a commercially available oscillating-tube-type densitometer based on the ideas of Kratky et al.[3] For nitric acid solutions, as far as we know, no one has published results measured by a high-precision densitometer of this kind. Although the older literature contains some accurate, pycnometrically determined density values (see below), our present knowledge of the densities of nitric acid solutions is insufficient: in particular, the temperature dependence of the densities is imperfectly known.

In the present study, new experimental data measured with a oscillating-tube-type densitometer are presented for nitric acid solutions up to a molality of 3.5 mol kg⁻¹ at 293.15, 298.15, 303.15 and 308.15 K. The experimental data reported in this paper agree well with the sparse results of the precise pycnometric determinations published previously. At each temperature of this study, the new

density data can accurately be predicted by means of a two-parameter equation for the apparent molar volume of the solute suggested by Masson.[4] The theoretical equation for this quantity, derived by Redlich and Rosenfeld[5] according to the theory of Debye and Hückel for dilute electrolyte solutions, does not apply satisfactorily without any corrections to the present density data. From the results of all our density determinations, a one-parameter equation can be obtained by which the densities of nitric acid solutions between 293 and 308 K may be calculated within 0.002 g cm⁻³ up to a molality of 3.5 mol kg⁻¹.

Experimental

Nitric acid solutions were prepared by weighing appropriate amounts of stock solution and water. The stock solution was made by mixing 65 % nitric acid (p.a., Merck 711) and R.O.-filtered water (Millipore) with a conductivity less than 1 μS cm⁻¹. The molality of the stock solution used in this preparation was 3.3815 mol kg⁻¹, and this value was determined by potentiometric titration with a freshly prepared KOH solution (1/10 N DILUT-IT, J. T. Baker 4673). The exact equivalence points of the five replicate determinations were calculated from the titration results by the method of Kolthoff.[6]

Densities of the HNO₃ solutions were measured by an Anton Paar DMA 55 densitometer which was calibrated at 293.15, 298.15, 303.15 and 308.15 K against air and pure water according to its instruction manual. The temperature of the densitometer was monitored by a MGW Lauda K2 water thermostat. The temperature remained constant within 0.01 K during the experiments at any of the four

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Table 1. Experimentally determined densities of HNO₃ 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]	0.998 2041	0.997 0449	0.995 6473	0.994 0319
0.0901	1.001 24	1.000 05	0.998 60	0.996 96
0.2663	1.007 11	1.005 84	1.004 31	1.002 61
0.4499	1.013 14	1.011 74	1.010 14	1.008 36
0.6268	1.018 89	1.017 38	1.015 70	1.013 87
0.8279	1.025 29	1.023 68	1.022 00	1.020 00
1.0269	1.031 59	1.029 87	1.028 06	1.026 04
1.2206	1.037 62	1.035 78	1.033 89	1.031 76
1.4131	1.043 54	1.041 70	1.039 76	1.037 66
1.6244	1.049 96	1.047 98	1.046 01	1.043 91
1.8244	1.055 97	1.053 86	1.051 78	1.049 51
2.0770	1.063 38	1.061 17	1.058 92	1.056 54
2.2723	1.069 09	1.066 82	1.064 57	1.062 28
2.5212	1.076 26	1.073 89	1.071 61	1.069 15
2.7780	1.083 45	1.080 96	1.078 60	1.076 03
2.9937	1.089 49	1.087 09	1.084 67	1.082 10
3.2460	1.096 33	1.093 54	1.091 03	1.088 28
3.3815	1.099 88	1.097 23	1.094 91	1.092 23

[a]Given by Kell.[7]

temperatures. Air was removed from the solutions and pure water by an ultrasonicator before measurements. Every solution was measured at least twice. Between each sample in a series of measurements, the purity of the oscillating tube was checked by measuring both air and pure water.

Results

The experimental densities of the aqueous HNO₃ solutions determined in the present study are listed in Table 1. The values in this table can be predicted at each temperature by means of an empirical equation presented by Masson[4] for the apparent molar volume of the solute (Φ_V). This quantity can be calculated directly from the density (ϱ) and the molality (m_2) or the concentration (c_2) of the solution by eqn. (1), where ϱ_1 is the density of the solvent (component

$$\Phi_V = (\varrho_1-\varrho)/(m_2\varrho\varrho_1) + M_2/\varrho = (\varrho_1-\varrho)/(c_2\varrho_1) + M_2/\varrho_1 \quad (1)$$

1) and M_2 the molar mass of solute (component 2). At a constant temperature, Masson[4] presented eqn. (2) for

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

Φ_V, where $V^\infty_{m,2}$ is the partial molar volume of the solute at infinite dilution at that temperature and S_2 is a constant which also depends on the solute and the temperature. The concentration c_2 can be calculated from molality m_2 by eqn.

$$c_2 = m_2\varrho/(1 + m_2M_2) \quad (3)$$

(3). When the experimental density data of Table 1 are fitted to eqn. (2), the Φ_V-values must first be calculated from eqn. (1) and the c_2-values from eqn. (3).

In the regression analysis of eqn. (2), it is important to remark that density is the quantity whose precision is probably almost constant at every experimental concentration. This means that the variance of the derived quantity Φ_V depends on the concentration. Therefore, if the regression analysis of eqn. (2) is carried out with equal weights at every experimental point, dilute points are stressed more without any physical reason. In a density error plot (where the errors of the predicted density values are plotted versus the concentration), the errors increase in this case with the concentration. The fitting is performed in a physically more correct way if the square sum S^2, which must be minimised, is written in the form of eqn. (4), where $\hat{\Phi}_V$ is the predicted

$$S^2 = \Sigma w_i (\Phi_{V,i} - \hat{\Phi}_{V,i})^2 \quad (4)$$

value of Φ_V and where the weight w depends on the concentration. By the following reasoning, it can be seen that the weight of point i must in this case be $(c_{2,i}/c°)^2$ where $c°$ is 1 mol dm^{-3}. Let us suppose that the variance of the density determinations is σ^2, i.e. $V(\varrho) = \sigma^2$, and this variance is independent of the concentration. Then we have eqn. (5),

Table 2. Values of the parameters of the Masson equation [eqn. (2)] in nitric acid solutions ($c° = 1$ mol dm^{-3}).

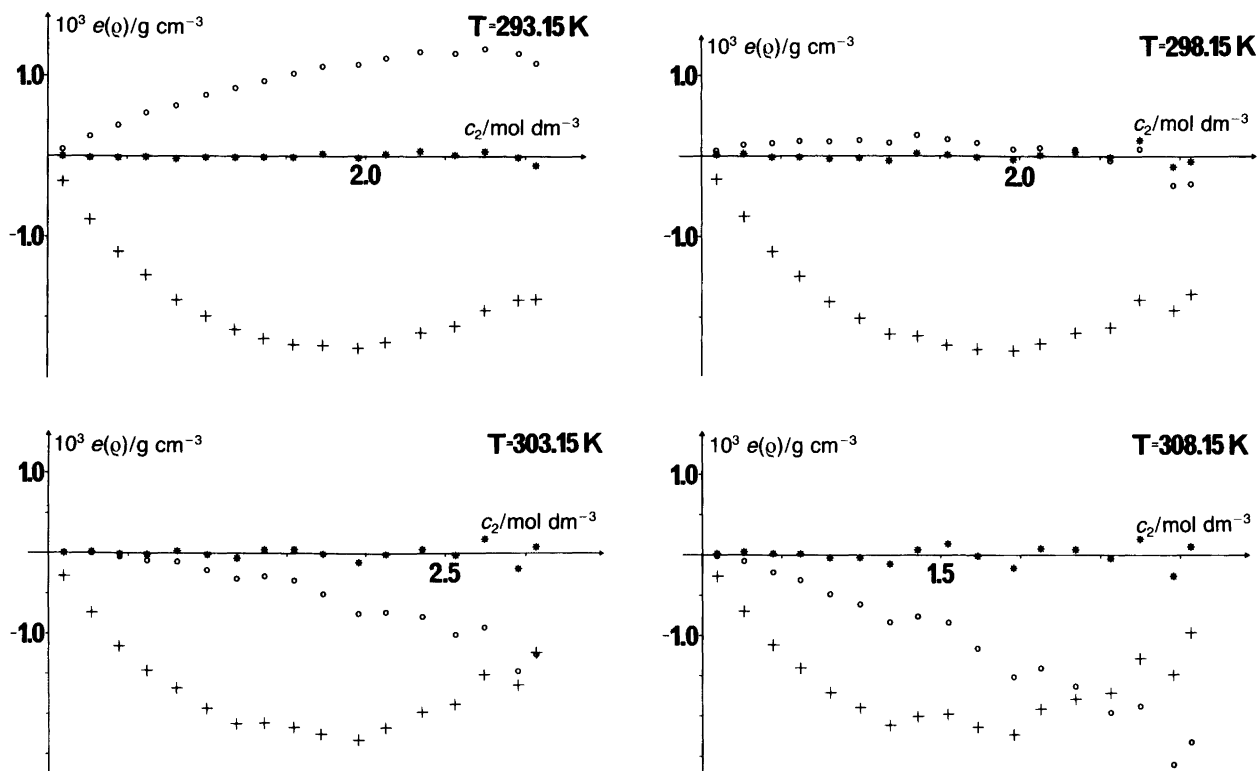| T/K	$V^\infty_{m,2}$/cm³ mol^{-1}	S_2/cm³ (mol dm^{-1})$^{-3/2}$
288.15[a]	27.8	0.925
293.15	28.992	0.5006
298.15	29.625	0.4007
303.15	30.166	0.2751
308.15	30.591	0.2213

[a]Given by Masson.[4]

Fig. 1. Difference between the observed and predicted densities of nitric 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 from the results of this table by eqn. (7) with the parameter values of Table 2 ($\star$), by the equation of Söhnel and Novotny[1] (+) and by eqn. (8) (O).

$$V(w_i^{1/2} \Phi_{V,i}) = V\{(c_{2,i}/c^\circ)[(\varrho_1 - \varrho)/(c_{2,i}\varrho_1)$$

$$+ M_2/\varrho_1]\} = \sigma^2/(c^\circ\varrho_1)^2 \tag{5}$$

and so quantity $w_i^{1/2}\Phi_{V,i}$ has a variance which does not depend on the concentration.
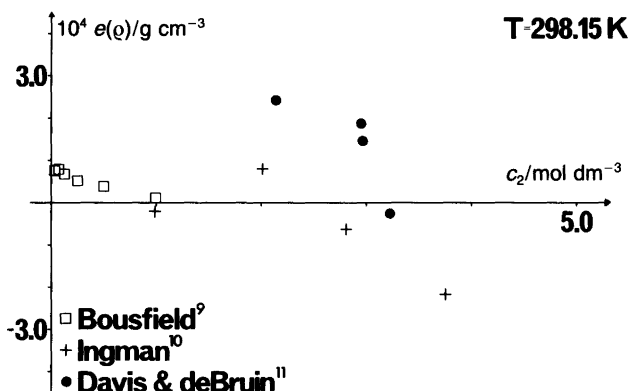

Fig. 2. Difference between the observed and predicted densities of nitric acid solutions as a function of the concentration at 298.15 K. The observed values have been measured by Bousfield,[9] Ingman[10] and Davis and de Bruin.[11] The predicted values have been calculated by eqn. (7) with the parameter values of Table 2.

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. The error plots of the straight lines of this table are shown in Fig. 1. In the four graphs of this figure, the error [eqn. (6)] is presented at the different temperatures as a

$$e(\varrho) = \varrho(\text{observed}) - \varrho(\text{predicted}) \tag{6}$$

function of concentration c_2. $\varrho(\text{predicted})$ has been calculated with the parameter values of Table 2 by eqn. (7).

$$\varrho(\text{predicted}) = \varrho_1 - (\varrho_1 V_{m,2}^\infty - M_2)c_2 - \varrho_1 S_2 c_2^{3/2} \tag{7}$$

During our calculations, we observed that the densities of nitric acid solutions in the concentration and temperature ranges used in this study can be calculated quite accurately for practical purposes by eqn. (8), which

$$\varrho = \varrho_1(1 + m_2 M_2)/(1 + m_2\varrho_1\overline{\Phi_V}) \tag{8}$$

contains only one parameter $(\overline{\Phi_V})$ that depends on the electrolyte. The value of $\overline{\Phi_V}$ was determined so that it is the mean value of all 68 Φ_V-values which were calculated from

Table 3. Comparison of the densities of Ref. 8 for nitric acid solutions with those obtained by means of the Masson equation with the parameter values given in Table 2. $x_w(2)$ is the weight fraction of solute 2.

$x_w(2)$[a]	c_2/mol dm^{-3}	ϱ(ICT)[b]/g cm^{-3}	ϱ(M)[c]/g cm^{-3}
T = 293.15 K:			
0.01	0.1593	1.003 61	1.003 60
0.05	0.8138	1.025 60	1.025 57
0.10	1.6729	1.054 3	1.054 1
0.15	2.5806	1.084 2	1.084 1
0.20	3.5404	1.115 0	1.115 5
T = 303.15 K:			
0.01	0.1588	1.000 9	1.000 9
0.05	0.8111	1.022 2	1.022 2
0.10	1.6664	1.050 3	1.050 0
0.15	2.5691	1.079 4	1.079 3
0.20	3.5230	1.109 4	1.110 0

[a]$x_w(2)$ is the weight fraction of solute 2. [b]International Critical Tables (Ref. 8). [c]This study.

the experimental densities of Table 1. The value of 30.247 cm^3 mol^{-1} for $\overline{\Phi}_V$ was so obtained.

The prediction ability of this simple equation [eqn. (8)] is compared to the validity of the equation of Söhnel and Novotny.[1] The comparison 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 (as mentioned above) the results of the Masson equation.

Table 4. Comparison of the densities calculated by means of the Masson equation at 298.15 K for nitric acid solutions with those calculated by the equation of Stonehill[12] [eqn. (9)] and by the equation of Covington and Prue[13] [eqn. (11)].

c_2/mol dm^{-3}	ϱ(S)[a]/g cm^{-3}	ϱ(CP)[b]/g cm^{-3}	ϱ(M)[c]/g cm^{-3}
0.0100	0.997 36	0.997 38	0.997 38
0.0200	0.997 70	0.997 71	0.997 71
0.0500	0.998 70	0.998 71	0.998 71
0.1000	1.000 36	1.000 38	1.000 38
0.1500	1.002 02	1.002 06	1.002 04
0.2000	1.003 69	1.003 75	1.003 70
0.3000	1.007 01		1.007 02
0.4000	1.010 33		1.010 33
0.5000	1.013 64		1.013 64
0.6000	1.016 95		1.016 95
0.7000	1.020 25		1.020 24
0.8000	1.023 56		1.023 54
0.9000	1.026 86		1.026 83
1.0000	1.030 15		1.030 12

[a]Stonehill. [b]Covington and Prue. [c]This study.

Discussion

According to Fig. 1, the experimental densities of Table 1 can be predicted well by means of eqn. (7), obtained from the Masson equation [eqn. (2)], with the parameter values given in Table 2. In the error plots of this equation, however, the following tendency can be recognised: the errors increase slightly with concentration. This trend appears despite the weighting (see above) and is probably due to the fact that the precision of the density determination somewhat depends on the concentration.

The Masson equations of Table 2 can also be tested, in addition to the experimental densities of Table 1, with the sparse density data available in the literature for nitric acid solutions. Ref. 8 contains the density values given in Table 3 for this comparison. According to this table, the densities of Ref. 8 can be well predicted with the Masson equations determined in this study.

At 298.15 K, experimental density values for HNO₃ solutions have been reported by Bousfield,[9] Ingman[10] and Davies and de Bruin.[11] The Masson equation obtained above for 298.15 K can be tested by predicting the density values of these studies by means of this equation. The results of this test are presented in Fig. 2, where the errors, calculated by eqn. (6) from these sets, are plotted as a function of the concentration. The results of Fig. 2 support well the Masson equation determined above, although the old densities measured by Bousfield[9] in dilute solution appear to be slightly but systematically too high. In the evaluation of the results concerning the densities of Davies and de Bruin,[11] it is important to remark that those densities are only given with an accuracy of 0.0001 g cm^{-3}.

Both Stonehill[12] and Covington and Prue[13] have reported an equation by which the densities of dilute HNO₃ solutions can be calculated at 298.15 K. The equation of Stonehill[12] for the ratio m_2/c_2 ($= r$) has the form of eqn. (9),

$$m_2 c^\circ / (c_2 m^\circ) = r\, c^\circ/m^\circ = 1.002\,98 + 0.029\,855(c_2/c^\circ)$$
$$+ 0.001\,142(c_2/c^\circ)^2 \tag{9}$$

where m° is 1 mol kg^{-1}. By means of this ratio, eqn. (10)

$$\varrho = (1+m_2 M_2)/r \tag{10}$$

can be presented for the density. The equation of Covington and Prue[13] for very dilute HNO₃ solutions (i.e. for molalities less than 0.1 mol kg^{-1}) has the form of eqn. (11).

$$\varrho/\text{g cm}^{-3} = \varrho_1/\text{g cm}^{-3} + 0.0332\,(m_2/m^\circ) \tag{11}$$

The agreement of these two equations with the above-determined Masson equation at 298.15 K can be studied by comparing the densities calculated by these equations. The results of such a comparison are presented in Table 4. According to this table, the equation of Covington and Prue[13] supports the Masson equation excellently up to its

applicability limit. The equation of Stonehill[12] supports the Masson equation even better: in this case the densities agree up to a concentration of 0.8 mol dm^{-3}.

Redlich and Rosenfeld[5] have theoretically derived from the theory of Debye and Hückel eqn. (12) for Φ_V in binary

$$\Phi_V = V_{m,2}^{\infty} + k(c_2)^{1/2} \tag{12}$$

solutions of a uni-univalent electrolyte. In this equation, the slope k is common for all electrolytes of this kind and can be calculated from a theoretical equation depending on the properties of the solvent (water in this case) and the 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 1.83 cm^3 (mol dm^{-1})$^{-3/2}$ (see Ref. 14).

Eqn. (12) is (in the same way as Debye–Hückel theory) most accurate in very dilute electrolyte solutions. The density determinations of the present study begin at a concentration of 0.1 mol dm^{-3}, and so our solutions are perhaps too strong to test the validity of eqn. (12). However, the densities of the Masson equation at 298.15 K agree excellently with the densities predicted by the equation of Covington and Prue[13] (Table 4), which was based on density determinations in dilute HNO$_3$ solutions. On the basis of the Masson equations determined in the present study, therefore, some conclusions can be probably made from the applicability of Debye–Hückel theory to predict the thermodynamic properties of nitric acid solutions. As shown in eqns. (2) and (12), the Masson equation has almost the same form as the theoretical equation of Redlich and Rosenfeld. The only difference is that the slope of the former equation is dependent on the electrolyte, whereas 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 [= 0.401 cm^3(mol dm^{-1})$^{-3/2}$] is far from the theoretical slope [= 1.833 cm^3(mol dm^{-1})$^{-3/2}$].

When the values of the parameters in Table 2 and the appropriate constants are inserted into eqn. (7) the following parameter values are obtained in the general equation

$$\varrho/\text{gcm}^{-3} = \alpha + \beta(c/c^{\circ}) - \gamma(c/c^{\circ})^{3/2} \tag{13}$$

(13) for the densities of nitric acid solutions at the temperatures used in this study: ($T = 293.15$ K, $\alpha = 0.998\,204$, $\beta =$

0.034073, $\gamma = 0.000\,500$), (298.15 K, 0.997045, 0.033475, 0.000400), (303.15 K, 0.995647, 0.032978, 0.000274), (308.15 K, 0.994032, 0.032604, 0.000220). In eqn. (13) c is the concentration of HNO$_3$ and c° is 1 mol dm^{-3}.

The precision of the density determinations presented in Table 1 depends slightly on the concentration (as discussed above), and therefore the theoretical premises of the least-squares method were somewhat violated when the parameters of the Masson equation above were determined. Nevertheless, the results of these calculations can be safely recommended. The densities of nitric acid solutions up to a concentration of about 3 mol dm^{-3} may be calculated within 0.00005 g cm^{-3} by eqn. (13) with the parameter values given in connection with this equation. As explained above, the densities of these equations also agree well with the existing experimental data available in the literature.

For practical purposes (at least in the temperature range 293–308 K and in the molality range 0–3.5 mol kg^{-1}) eqn. (8) is in most cases sufficient. It gives the correct density under these conditions within probably 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.[1]

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