Thermal Conductivity of Aqueous Sodium Chloride Solutions

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This paper presents new absolute measurements of the thermal conductivity of aqueous sodium chloride solutions with the transient coated-hot-wire technique. The data cover the range 295–365 K at pressures slightly above the vapor pressures and a concentration range of 0–6 mol kg^{-1}. The instrument is able to measure the thermal conductivity with a precision and reproducibility better than ±0.2%, and a comparison of the present results with data available in the literature indicates that the accuracy of the present data is better than ±0.5%. An empirical correlation that reproduces the data within the claimed accuracy is given.

Introduction

The important role played by aqueous solutions of electrolytes in a wide variety of areas from biology to geology is well recognized. Often the availability of reliable thermophysical property data on that kind of systems is of great importance for applications and studies in those areas from both industrial and scientific points of view. Properties of electrolyte solutions, such as the viscosity, diffusion coefficients, or electrical conductivity, have long been the subject of considerable attention and study (*1–3*). However, for the thermal conductivity there is still a lack of sufficiently accurate data to support the development of reliable theoretical or semiempirical equations in order to predict this property.

The available data from 1950 to 1966 on the thermal conductivity of sodium chloride solutions is compiled in the review article of Ozbek and Phillips (*4*). Most of the data (*5–10*) were obtained by steady-state techniques, and consequently their nominal accuracies limited to a modest ±2%. Only recently (*11–13*) was the transient hot-wire technique successfully applied to electrolyte solutions producing data of the same level of accuracy which has become usual for electrically nonconducting liquids (±0.5%). In these recent developments, new instruments were developed from the classical transient hot-wire method in which the bare hot wire is replaced by a coated hot wire to avoid the problems derived from the electrical contact between the hot wire and the conducting liquid (*11–14*).

In the present paper, we present new absolute thermal conductivity measurements of three different compositions of sodium chloride solutions from 295 to 365 K, near the saturation vapor pressure using the transient coated-hot-wire technique. The results are compared with the values of other researchers, and the accuracy of the data is estimated to be ±0.5%. An empirical correlation with an estimated accuracy of ±0.5% is also proposed.

Experimental Procedures

The thermal conductivity measurements were performed in an absolute manner with transient coated-hot-wire equipment described in detail elsewhere (*15*). The Wheatstone bridge circuit used to record the resistance change and therefore the temperature rise of the wires is similar to the one described by Wakeham et al. (*16*), where details of its construction can be found. Only a short description of the method and the appropriate working equations is provided here, as they have been described previously (*11, 12*).

The transient coated-hot-wire method is based on the use of a tantalum wire, anozidized *in situ* with an insulating layer of tantalum pentoxide, simultaneously as a heat source and a temperature sensor, in contact with the test fluid. The temporal evolution of the wire's temperature (ΔT_{id}), after a step voltage is applied, is recorded. According to the ideal mathematical model of an infinite line heat source, the thermal conductivity can be obtained from the slope of the line ΔT_{id} *versus* the logarithm of time according to eq 1, where q is the

$$\Delta T_{id} = \frac{q}{4\pi\lambda} \ln \frac{4kt}{r_i^2 C} \qquad (1)$$

heat dissipation per unit length, λ is the thermal conductivity, t is the time, r_i is the radius of the wire, k is the thermal diffusivity, and C is equal to $\exp(\gamma)$ where γ is Euler's constant.

However, as a real instrument departs from its ideal model, a number of small corrections have to be applied to the observed temperature rise of the wire. For the present mesurements an addition to the usual set of corrections of the transient hot-wire method (*17*) must be used, due to the existence of the extra layer of the wire coating. Thus, from experimental measurements of the temperature of the wire, ΔT_w, the ideal temperature, ΔT_{id}, is obtained from eq 2, where

$$\Delta T_{id} = \Delta T_w + \sum_i \delta T_i \qquad (2)$$

the various corrections δT_i have been summarized elsewhere (*17, 18*). The particular correction for the effect of the

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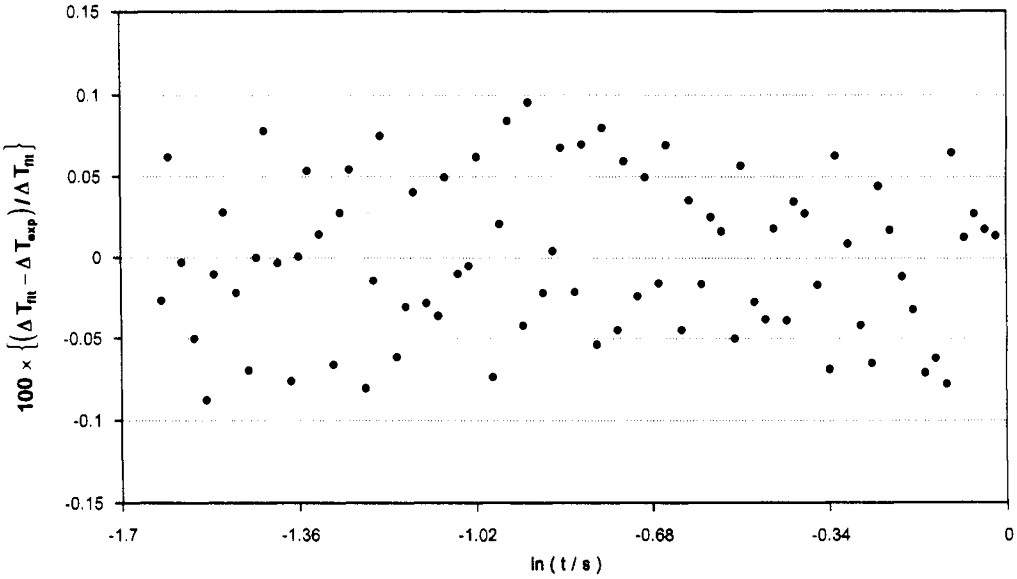

Figure 1. Percentage deviations of the measured temperature rise as a function of the logarithm of time, from the linear fit for a 5.892 mol·kg^{-1} NaCl solution, at 348.943 K and near the saturation line.

Table 1. Thermal Conductivity, λ, of Aqueous NaCl Solutions at Temperatures *T* and Molalities *m*

m = 0.2249 mol·kg^{-1}		*m* = 2.7015 mol·kg^{-1}		*m* = 5.892 mol·kg^{-1}	
T/K	λ/(W·m^{-1}·K^{-1})	*T*/K	λ/(W·m^{-1}·K^{-1})	*T*/K(W·m^{-1}·K^{-1})	λ/(W·m^{-1}·K^{-1})
297.877	0.6056	297.360	0.5858	298.915	0.5756
297.897	0.6041	297.398	0.5891	298.824	0.5752
303.978	0.6145	304.739	0.5966	302.782	0.5821
312.052	0.6234	304.967	0.6007	302.921	0.5820
312.081	0.6234	308.840	0.6069	307.445	0.5887
317.166	0.6286	319.624	0.6223	307.515	0.5854
317.277	0.6289	319.634	0.6195	307.476	0.5866
328.616	0.6398	325.702	0.6277	316.923	0.5963
328.641	0.6420	326.872	0.6276	321.757	0.5996
328.705	0.6422	336.417	0.6381	321.725	0.5981
336.442	0.6471	340.234	0.6427	327.721	0.6061
339.726	0.6508	340.254	0.6413	327.693	0.6038
		340.333	0.6413	338.517	0.6138
		345.598	0.6453	338.421	0.6119
		346.686	0.6454	348.943	0.6202
		346.706	0.6472	348.263	0.6198
		350.680	0.6467	348.292	0.6188
		351.746	0.6488	357.721	0.6221
		351.829	0.6484	357.764	0.6220
		356.293	0.6496	362.112	0.6231
		356.294	0.6520	362.157	0.6259
		356.309	0.6508	363.270	0.6269
		362.800	0.6511		
		362.814	0.6516		

Table 2. Optimum Values of the Coefficients *A*, *B*, and *C* and Their Standard Deviations in Equation 6 for the Concentrations Studied

	m = 0.2249 mol·kg^{-1}	*m* = 2.7015 mol·kg^{-1}	*m* = 5.892 mol·kg^{-1}
A	0.566 16	0.536 17	0.541 95
σ_A	0.0006	0.001	0.001
B	0.001 757	0.002 39	0.001 514
σ_B	0.0001	8.3 × 10^{-5}	8.9 × 10^{-5}
C	−7.4 × 10^{-6}	−1.2 × 10^{-5}	−6.5 × 10^{-6}
σ_C	1.6 × 10^{-6}	7.2 × 10^{-7}	7.6 × 10^{-7}

insulation that must be added in the present work, δT_c, is given by

$$\delta T_c = -\left(\frac{B}{t}\right)\Delta T_{id} + \frac{q}{4\pi\lambda}\left\{\ln\left(\frac{r_0}{r_i}\right)^2\left(1-\frac{\lambda}{\lambda_c}\right) - \frac{\lambda}{2\lambda_w} - \frac{1}{t}\left[C - B\ln\frac{4k}{r_i^2 C}\right]\right\} \quad (3)$$

where

$$B = \frac{1}{2\lambda}\left[r_i^2\left(\frac{\lambda_c}{k_c}-\frac{\lambda_w}{k_w}\right) + r_0^2\left(\frac{\lambda}{k}-\frac{\lambda_c}{k_c}\right)\right] \quad (4)$$

$$C = \frac{r_i^2}{8}\left[\left(\frac{\lambda-\lambda_c}{\lambda_w}\right)\left(\frac{1}{k_w}-\frac{1}{k_c}\right) + \frac{4}{k_c} - \frac{2}{k_w}\right] + \frac{r_0^2}{2}\left(\frac{1}{k}-\frac{1}{k_c}\right) + \frac{r_i^2}{\lambda_c}\left(\frac{\lambda_c}{k_c}-\frac{\lambda_w}{k_w}\right)\ln\frac{r_0}{r_i} + \frac{1}{2\lambda}\left[r_i^2\left(\frac{\lambda_c}{k_c}-\frac{\lambda_w}{k_w}\right) + r_0^2\left(\frac{\lambda}{k}-\frac{\lambda_c}{k_c}\right)\right]\ln\frac{4k}{r_0^2 C} \quad (5)$$

In the above expressions, λ is the thermal conductivity, *k* is the thermal diffusivity, r_i is the wire radius, and r_0 is the insulated wire radius; the subscripts c and w refer to the coating layer and wire, respectively.

If the instrument operates correctly, the corrected measured temperature rise, ΔT_{id}, should thus be a linear function of ln *t* provided that no forms of heat transfer other than conduction

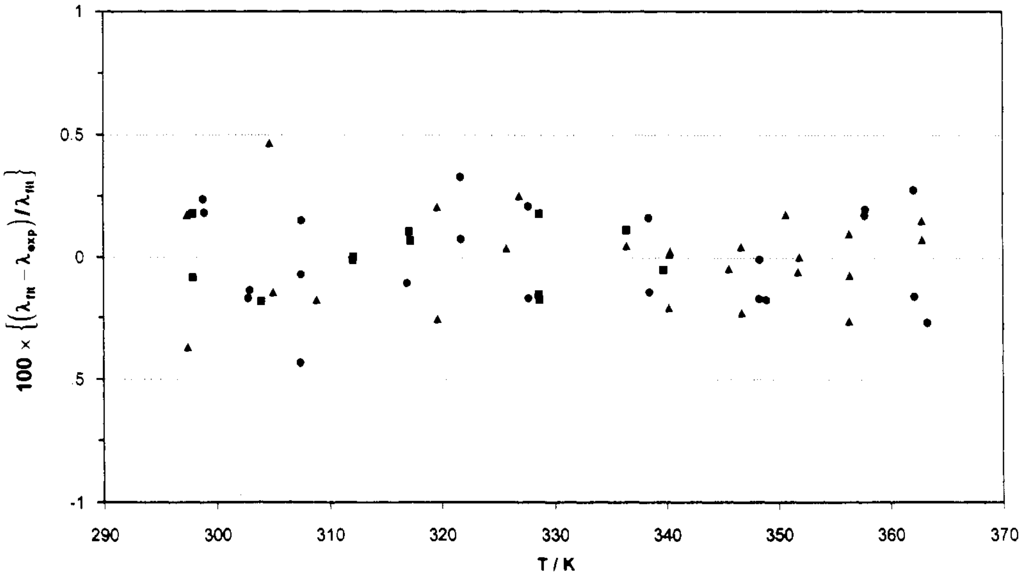

Figure 2. Overall comparison between the present experimental results and eq 6: ■, m = 0.2249 mol·kg^{-1}; ▲, m = 2.7015 mol·kg^{-1}; ●, m = 5.892 mol·kg^{-1}.

are developed in the measurement cells. Figure 1 shows an example of a plot of the deviations of corrected experimental data (ΔT, ln t) from linearity, obtained for a typical run of a 5.892 mol·kg^{-1} NaCl solution, at a reference temperature of 348.263 K, slightly above the saturation pressure. No datum departs from the straight line by more than ±0.1%, and no systematic curvature is found. The same behavior was observed in all of the measurements reported. Results of this kind prove that the instrument operates correctly, and it confirms the absence of significant heat transfer by radiation or convection (*17*, *18*).

Results and Discussion

The thermal conductivity measurements have been carried out for the concentrations 0.2249, 2.7015, and 5.892 mol·kg^{-1} (mol of NaCl/kg of H_2O) in the temperature range 295–365 K at pressures slightly above the vapor pressures.

The sodium chloride solutions were prepared gravimetrically using a precision balance with a total capacity of 1000 g and a resolution of 0.1 g. Sodium chloride was supplied by M&B p.a., and before weighing it was dried at 150 °C for 24 h. The water used in the preparation of the solutions was obtained from a Millipore device with an electrical conductivity of 18 MΩ·cm^{-1}. The estimated uncertainty in the final composition of the solutions is ±0.04%.

The density data for the various compositions, necessary to apply the small corrections in the analysis of the data, were obtained from a correlation proposed by Lo Surdo et al. (*19*), and those for the heat capacity were obtained from a correlation of Smith-Magowan et al. (*20*).

Table 1 contains the experimental results for the thermal conductivity of aqueous sodium chloride solutions 0.2249, 2.7015, and 5.892 mol·kg^{-1}, at a reference temperature T and near their vapor pressures. The accuracy assigned to these measurements is estimated to be the one of ±0.5% according to the assessment procedure described elsewhere (*14*, *15*).

The temperature dependence of the thermal conductivity of the sodium chloride solutions of different compositions has been represented by a second-degree polynomial of the form

$$\lambda(\mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}) = A + B(T/\mathrm{K} - 273.15) + C(T/\mathrm{K} - 273.15)^2 \quad (6)$$

Table 2 contains the values of the coefficients A, B, and C for the three compositions, together with the respective

Table 3. Optimum Values of Coefficients a_{ij} in Equation 7[a]

j	$i = 0$	$i = 1$	$i = 2$
0	0.5621 (0.002)	−0.013 94 (0.003)	0.001 77 (0.00005)
1	0.001 99 (9.8×10^{-5})	0.000 294 (0.0001)	-6.3×10^{-5} (1.9×10^{-5})
2	-8.6×10^{-6} (8.6×10^{-7})	-2.3×10^{-6} (9.7×10^{-7})	4.5×10^{-7} (1.6×10^{-7})

[a] Standard deviations of the coefficients are represented within parentheses.

standard deviations. In Figure 2 the deviations of the present results from the fitting equations are plotted, and it can be seen that they do not exceed ±0.4%.

The simultaneous temperature and composition dependence of the thermal conductivity of NaCl aqueous solutions has been represented by a polynomial in temperature and molality of the form

$$\lambda(T,m)/(\mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}) = \sum_{i=0}^{2}\Big[\sum_{j=0}^{2} a_{ij}(T/\mathrm{K} - 273.15)^j\Big](m/(\mathrm{mol{\cdot}kg^{-1}}))^i \quad (7)$$

where m is the molality of the solution. The coefficients a_{ij}, together with their standard deviations, are given in Table 3. The experimental results (Table 1) are reproduced by eq 7 with a standard deviation of ±0.2%. Figure 3 shows the deviations of the present experimental data from eq 7. It can be seen that no systematic deviation is observed, and most of the data depart no more than ±0.5% from the correlation. Included in the same figure are deviations of the experimental results of other researchers (*5*–*11*, *21*, *22*) from eq 7 as a function of temperature.

Comparison of the present results with those of other researchers is diaplayed in Figure 4, as a function of the molality of the sodium chloride solutions. Most of the previous measurements were made with steady-state methods,namely, the results obtained by Riedel (*5*), Kaputinski (*6*), Vargaftik (*7*), Tufeu (*8*), Chernen'kaya (*9*), and Y. Ganiev (*21*). From Figures 3 and 4, it is observed that there is good agreement of those data with the present results, the maximum deviation not exceeding ±2%, well within the uncertainty limits of their measurements. On the other hand, the data obtained by Korosi and Fabuss (*7*) depart enormously from the present data, up to −25%, and are not shown in the figures. This result is not surprising because these researchers

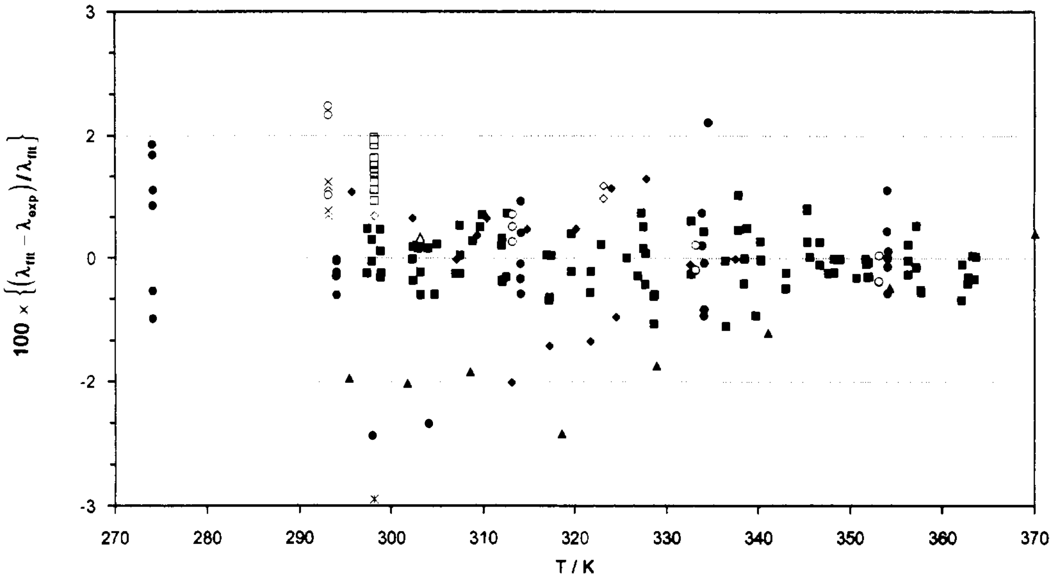

Figure 3. Comparison of the experimental measurements of the thermal conductivity of NaCl, as a function of temperature, with correlation 7 (base line): ■, present work; ◆, ref 22; ▲, ref 21; ●, ref 13; ×, ref 5; ◇, ref 6; *, ref 7; ○, ref 8; □, ref 9; △, ref 10.

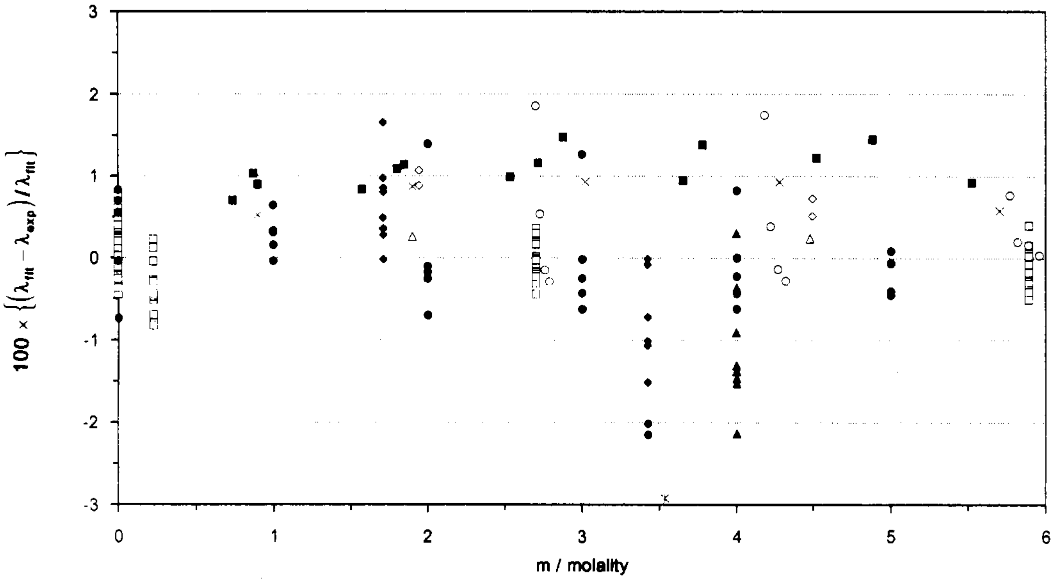

Figure 4. Comparison of the experimental measurements of the thermal conductivity of NaCl, as a function of composition, with correlation 7 (base line); ■, present work; ◆, ref 22; ▲, ref 21; ●, ref 13; ×, ref 5; ◇, ref 6; *, ref 7; ○, ref 8; □, ref 9; △, ref 10.

Table 4. Thermal Conductivity, $\lambda/(\mathrm{W \cdot m^{-1} \cdot K^{-1}})$, Values Obtained from Equation 7 as a Function of Temperature, *T*, and molality, $m/(\mathrm{mol \cdot kg^{-1}})$

T/K	$m = 0$	$m = 1$	$m = 2$	$m = 3$	$m = 4$	$m = 5$	$m = 6$
290	0.5932	0.5844	0.5773	0.5718	0.5680	0.5659	0.5655
300	0.6093	0.6020	0.5955	0.5898	0.5850	0.5809	0.5776
310	0.6238	0.6176	0.6115	0.6056	0.5998	0.5941	0.5885
320	0.6365	0.6310	0.6253	0.6191	0.6125	0.6055	0.5982
330	0.6474	0.6424	0.6367	0.6302	0.6231	0.6152	0.6066
340	0.6567	0.6517	0.6458	0.6391	0.6316	0.6231	0.6138
350	0.6642	0.6589	0.6527	0.6457	0.6379	0.6292	0.6198
360	0.6701	0.6640	0.6573	0.6500	0.6421	0.6336	0.6245
370	0.6742	0.6670	0.6596	0.6520	0.6442	0.6362	0.6279

have used a bare-hot-wire technique which has been shown (*11*, *12*) to be inadequate for measurements in electrically conducting liquids.

The results obtained by Nagashima and collaborators (*13*) with a transient coated-hot-wire technique, using a polyester-coated platinum wire, are in excellent agreement with those of the present work. The maximum deviation amounts to no more than ±0.6% from eq 7, although the experimental range extends to lower temperatures than in the present work by 25 K.

Assael et al. (*22*) measured two sodium chloride solutions from 298 to 340 K using the same technique as employed in this work. Although there is good agreement with our results for the more dilute solution, the deviations of the more concentrated one are slightly larger (±2%) than the estimated mutual uncertainties of the data (±1%).

In Table 4 a list of values obtained from eq 7 is presented in order to help a check of any programming of it.

Conclusions

Thermal conductivity results have been reported for different concentrations of aqueous sodium chloride solutions near the saturation line. The experimental results were obtained with the transient coated-hot-wire technique and have been shown to be consistent with other previous measurements along the vapor pressure curves.

A correlation is proposed which reproduces the present experimental data within an uncertainty of ±0.5%.

Literature Cited

(1) Phillips, S. L.; Igbene, A.; Fair, J. A.; Ozbek, H.; Tavana, M. In *Proceedings of the 8th Symposium on Thermophysical Properties*; Sengers, J. V., Ed.; ASME: New York, 1982; Vol. II, p 345.
(2) Kestin, J.; Shankland, I. R. *Int. J. Thermophys.* **1984**, *5*, 241.
(3) Horne, F. H.; Borey, B. K. *Int. J. Thermophys.* **1986**, *7*, 87.
(4) Ozbek, H.; Phillips, S. L. *J. Chem. Eng. Data* **1980**, *25*, 263.
(5) Riedel, L. *Chem.-Ing.-Tech.* **1951**, *23*, 59 (quoted in ref 4).
(6) Kaputinski, A. F.; Ruzavin, I. I. *Zh. Fiz. Khim.* **1955**, *29*, 2222 (quoted in ref 4).
(7) Vargaftik, N. B.; Os'minin, Yu. P. *Teploenergetika (Moscow)*, **1956**, *3*, 11 (quoted in ref 4).
(8) Tufeu, R.; Le Neindre, B.; Johannin, P. *C. R. Acad. Sci., Ser. B*, **1966**, *262*, 229 (quoted in ref 4).
(9) Chernen'kaya, E. I.; Vernigora, G. A. *Zh. Prikl. Khim. (Leningrad)* **1972**, *45*, 1704 (quoted in ref 4).
(10) Korosi, A.; Fabuss, B. M. Thermophysical Properties of Saline Water. Office of Saline Water Research and Development Progress Report No. 363; Office of Saline Water Research and Development: Washington, DC, 1968 (quoted in ref 4).
(11) Nagaska, Y.; Nagashima, A. *J. Phys. E: Sci. Instrum.* **1981**, *14*, 1435.
(12) Alloush, A.; Gosney, W. B.; Wakeham, W. A. *Int. J. Thermophys.* **1982**, *3*, 225.
(13) Nagasaka, Y.; Okada, H.; Suzuki, J.; Nagashima, A. *Ber. Bunsen-Ges. Phys. Chem.* **1983**, *87*, 859.
(14) Ramires, M. L. V.; Fareleira, J. M. N. A.; Nieto de Castro, C. A.; Dix, M.; Wakeham, W. A. *Int. J. Thermophys.* **1993**, *14*, 1119.
(15) Ramires, M. L. V. Ph.D. Thesis, Universidade de Lisboa, Lisbon, 1992.
(16) Wakeham, W. A.; Zalaf, M. *Fluid Phase Equilib.* **1987**, *36*, 183.
(17) Nieto de Castro, C. A.; Li, S. F. Y.; Nagashima, A.; Trengrove, R. D.; Wakeham, W. A. *J. Chem. Ref. Data* **1986**, *15*, 1073.
(18) Assael, M. J.; Nieto de Castro, C. A.; Roder, H. M.; Wakeham, W. A. In *Transient Methods for Thermal Conductivity in Measurements of the Transport Properties of Fluids – Experimental Thermodynamics*; Wakeham, W. A., Nagashima, A., Sengers, J. V., Eds.; Blackwell Scientific Publications: London, 1991; Vol. 3, Chapter 7.
(19) Lo Surdo, A.; Alzola, E. M.; Millero, F. J. *J. Chem. Thermodyn.* **1982**, *14*, 649.
(20) Smith-Magowan, D.; Wood, R. H. *J. Chem. Thermodyn.* **1981**, *13*, 1047.
(21) Ganiev, Y. A.; Musoyan, M. O.; Rastorguyev, Y. L.; Grigoryev, B. A. In *Proceedings of the 11th International Conference on the Properties of Water and Steam*; Pichal, M., Snifer, O., Eds.; Hemisphere Publishing Corp.: New York, 1989.
(22) Assael, M. J.; Charitidou, E.; Stassis, J. Ch.; Wakeham, W. A. *Ber. Bunsen-Ges. Phys. Chem.* **1989**, *8*, 887.

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