to complex formation, one would expect, however, a positive $\delta V_m^E/dT$ term, whereas the observed V_m^E temperature coefficient is negative and this is a common feature of other complex forming mixtures involving acetonitrile (*10*). (Interpretation of this anomalous behavior has been given in terms of the volume of the complex decreasing with temperature, whose effect more than compensates the decrease in complex formation.) In the case of acetonitrile–sulfolane mixtures one may rather suppose that, owing to the steric hindrance of its globular molecule, only the exposed negative end of sulfolane dipole is involved in complex formation; this implies that the CH_3CN molecules check the proper orientation for interacting; presumalby a parallel alignment of dipoles is needed resulting in the observed increase in the dielectric constant. On complex decomposition, the monomer acetonitrile may accommodate interstitially in the free volumes or cavities of sulfolane, even if weakly structured, and the related volume contraction superimposes to the steric effects in reducing volume on mixing; reasonably this effect would be enhanced by the temperature.

Literature Cited

(1) O. Sciacovelli, L. Jannelli, and A. Della Monica, *Gazz. Chim. Ital.*, **97**, 1012 (1967); A. Sacco and L. Jannelli, *J. Chem. Thermodyn.*, **4**, 191 (1972); L. Jannelli and A. Sacco, *ibid.*, **4**, 715 (1972); L. Jannelli, A. Sacco, and Animesh Kumar Rakshit, *Z. Naturforsch.*, *A.*, **29**, 355 (1974); A. Inglese and L. Jannelli, *Thermochim. Acta*. **23**, 263 (1978); L. Jannelli, A. Azzi, A. Lopez, and R. Jalenti, *ibid.*, **33**, 19 (1979); L. Jannelli, A. Azzi, A. Lopez, and S. Saiello, *J. Chem. Eng. Data*, **25**, 77 (1980).
(2) E. M. Arnett and C. F. Douty, *J. Am. Chem. Soc.*, **86**, 409 (1968).
(3) J. Martinmaa in "The Chemistry of Non-Aqueous Solvents", Vol. IV, J. J. Lagowski, Ed., Academic Press, New York, San Francisco, London, 1976, pp 263, 264, and 343.
(4) J. Martinmaa in "The Chemistry of Non-Aqueous Solvents", Vol. IV, J. J. Lagowski, Ed., Academic Press New York, San Francisco, London, 1976, p 78, V. Gutmann, *Coord. Chem. Rev.* **18**, 225 (1976). J. S. Rowlinson, "Liquids and Liquid Mixtures", Butterworth, London, 1971, p 160 and following.
(5) L. Jannelli, M. Della Monica, and A. Della Monica, *Gazz. Chim. Ital.*, **94**, 552 (1964).
(6) M. Della Monica, L. Jannelli, and U. Lamanna, *J. Phys. Chem.*, **72**, 1068 (1968).
(7) A. C. Brown and D. J. G. Ives, *J. Chem. Soc.*, 1608 (1962).
(8) W. S. Muney and J. F. Coetzee, *J. Phys. Chem.*, **66**, 89 (1962).
(9) A. A. Maryott and E. R. Smyth, *Natl. Bur. Stand* (*U.S.*), *Circ*, **No. 514** (1951).
(10) J. F. Coetzee and W. R. Sharpe, *J. Solution Chem.* **1**, 77 (1972); J. A. Barker, *J. Chem. Phys.*, **20**, 279 (1952); Y. P. Chanda, A. Handa, and D. V. Fenby, *J. Chem. Thermodyn.* **7**, 401 (1975); Y. P. Handa, *ibid.*, **9**, 117 (1977).

Received for review January 15, 1980. Accepted March 25, 1980.

Thermal Conductivity of Aqueous Sodium Chloride Solutions from 20 to 330 °C

Huseyin Ozbek and Sidney L. Phillips*

Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

Selected thermal conductivity data reported in the literature for aqueous sodium chloride solutions are tabulated for geothermal energy applications. Experimental values were converted where necessary to a set of consistent units of degree Celsius, molal concentration and watts per meter Celsius. A selected empirical equation is given to reproduce the data over the temperature range 20–330 °C, concentrations between 0 and 5 *m*, and at saturation pressures. A table of smoothed values is generated by using the correlation which reproduces the experimental data to ±2% up to 80 °C. Between 100 and 150 °C, the percent deviation is +17% to +31% for the one set of available experimental values. Recommendations for additional data needs are given.

An important facet in the development and utilization of geothermal energy is the thermodynamic and transport data for the hot brines which transport heat and the vapors which drive turbines to produce electricity. While geothermal brines contain a large number of dissolved electrolytes and gases, the main constituent is sodium chloride. Consequently, modeling and other studies which require basic data on geothermal brines are generally based on those of aqueous NaCl solutions (*1*, *2*). While data on many basic properties are needed, this report covers a survey of the available data on the thermal conductivity of aqueous NaCl solutions for regions of geothermal interest: temperatures to 350 °C, pressures to 500 bar (50 MPa), and concentrations up to saturation.

The current published literature on the thermal conductivity of sodium chloride solutions to high temperatures is not extensive; this is especially true for work at temperatures exceeding 80 °C. Only one series of measurements are available to 150 °C: these are the data published by Korosi and Fabuss for application to sea water desalination (*3*, *4*). By far, the most extensive data are contained in graphical form in the publication by Yusufova, Pepinov, Nikolaev, and Guseinov with over 50 data points between 100 and 330 °C (*5*). However, accurate values cannot be read from the graphs.

Unless otherwise noted, the data were compiled from the original publications. Numerical values were converted where necessary to units of degree Celsius, molal concentration, and watts per meter degree Celsius. The density data needed to convert molar to molal concentrations were obtained from the paper by Rowe and Chou (*6*). Data on the thermal conductivity of water and the corresponding correlation equation are contained in publications of ref 7 and 8.

Additional information on the theory and instrumentation is obtained from ref 9; theory and correlations are from the publications by Kestin and Whitelaw (*8*), Riedel (*10*), Korosi and Fabuss (*3*, *4*) and Yusufova, Pepinov, Nikolaev, and Guseinov (*5*). Tabulated data for sodium chloride solutions are given in Table I. Of special interest are the survey by Jamieson, Irving, and Tudhope (*11*) and the correlation developed for sea water by Jamieson and Tudhope (*12*).

Scope of Compilation

The time span covered is mainly from 1929 to December 1979; earlier data are found in ref 13. Besides data on the thermal conductivity of aqueous sodium chloride solutions, selected portions of the available literature are included on theory, instrumentation, data estimation methods, other salts (e.g.,

0021-9568/80/1725-0263$01.00/0 © 1980 American Chemical Society

Table I. Experimental Data for Thermal Conductivity of Aqueous NaCl Solutions

temp, °C	concn, *m*	λ, W/(m °C)	ref
20	0.901	0.594	10
20	1.901	0.589	10
20	2.700	0.590	18
20	3.020	0.583	10
20	4.278	0.578	10
20	4.180	0.583	18
20	5.704	0.573	10
20	5.770	0.574	18
25	0.707	0.574	3
25	0.741	0.605	20
25	0.872	0.606	20
25	0.901	0.605	20
25	1.573	0.600	20
25	1.802	0.600	20
25	1.849	0.600	20
25	1.944	0.599	17
25	2.534	0.595	20
25	2.716	0.595	20
25	2.878	0.596	20
25	3.535	0.567	3
25	3.655	0.589	20
25	3.781	0.591	20
25	4.494	0.583	17
25	4.521	0.587	20
25	4.883	0.587	20
25	5.523	0.582	20
20–40	1.061	0.608	19
30	1.901	0.603	14
20–40	1.936	0.604	19
20–40	2.857	0.592	19
20–40	3.434	0.581	19
30	4.278	0.589	14
40	2.730	0.615	18
40	4.220	0.605	18
40	5.820	0.594	18
50	0.707	0.577	3
50	1.944	0.635	17
50	3.535	0.571	3
50	4.494	0.617	17
60	2.760	0.634	18
60	4.270	0.623	18
60	5.890	0.611	18
75	0.707	0.581	3
75	3.535	0.557	3
80	2.790	0.647	18
80	4.320	0.635	18
80	5.960	0.622	18
100	0.707	0.560	3
100	3.535	0.539	3
125	0.707	0.518	3
125	3.535	0.500	3
150	0.707	0.460	3
150	3.535	0.455	3

potassium chloride), and sea water.

Analytical Expressions and Correlations

This section covers selected analytical expressions and empirical correlations which have been used to describe the variation in thermal conductivity for NaCl solutions as a function of concentration and temperature.

On the basis of theoretical considerations, Predvoditelev (*21*) and Vargaftik and Os'minin (*14*) developed the following equation for predicting the thermal conductivity of aqueous solutions:

$$\frac{\lambda}{\lambda_w} = \frac{C_p}{C_{pw}}\left(\frac{\rho}{\rho_w}\right)^{4/3}\left(\frac{M_w}{M}\right)^{1/3} \qquad (1)$$

Vargaftik and Os'minin (*14*) measured the thermal conductivity of various aqueous solutions including NaCl solutions at 30 °C and found that the deviation between the measured and the predicted values by eq 1 was no more than 5%. The only exception was nitric acid solutions, for which the deviation increased as the acid concentration increased to a maximum deviation of 12%.

Riedel developed an equation which has been used to describe the variation in thermal conductivity with temperature and concentration of salt solutions such as NaCl (*10*, *15*) (eq 2), where a_i = experimentally determined coefficient characteristic for each ion (−0.0047 for Cl^-, referred to Na^+ as 0) and C_i = concentration of each electrolyte.

$$\lambda = \lambda_w + \sum_i a_i C_i \qquad (2)$$

Korosi and Fabuss (*3*, *4*) measured the thermal conductivity for 0.7069 *m* NaCl and 3.5345 *m* NaCl, over the temperature range 25–150 °C. The authors obtained 12 data points and developed the following polynomial fits for these two concentrations:

$$0.7069\ m\ \mathrm{NaCl:}\quad \lambda = 0.540 + 0.001567T - 0.00001397T^2$$

$$3.5345\ m\ \mathrm{NaCl:}\quad \lambda = 0.553 + 0.000821T - 0.00000986T^2 \qquad (3)$$

The six values for each concentration were reproduced to better than 1% by eq 3.

Yusufova et al. measured the thermal conductivity of aqueous sodium chloride solutions for temperatures ranging from 20 to 330 °C and concentrations of 5, 10, 15, 20, and 25 wt % NaCl. They developed the following correlation equation which reproduces their experimental data for over 50 values with a reported deviation of 2%:

$$\lambda/\lambda_w = 1.0 - (2.3434 \times 10^{-3} - (7.924 \times 10^{-6})T + (3.924 \times 10^{-8})T^2)S + (1.06 \times 10^{-5} - (2 \times 10^{-8})T + (1.2 \times 10^{-10})T^2)S^2 \qquad (4)$$

where

$$S = \frac{5844.3m}{1000 + 58.443m}$$

However, numerical data are not available for these measurements, and accurate values cannot be obtained from the figures in the publication. For this reason their data are not included in Table I.

Unterberg developed a family of curves which depict changes in the thermal conductivity of NaCl solution with temperatures to 149 °C and for zero to saturation concentrations. Unterberg assumed that the variation of thermal conductivity with temperature followed the same trend for different NaCl concentrations as that for pure water (*16*). In related work, Jamieson and Tudhope fit experimental data on the thermal conductivity of sea water solutions to the equation

$$\ln \lambda = \ln (\lambda_w + X) + \left(2.3 - \frac{G}{T}\right)\left(1 - \frac{T}{T_c + Y}\right)^{0.333} \qquad (5)$$

where T_c = 647 K (critical temperature of distilled water), X = salinity × 0.0002, Y = salinity × 0.003, and G = 343.5 + (salinity × 0.37). Equation 5 fits the experimental data to ±3% for salinities between 0 and 160 g/kg, and temperatures from 0 to 80 °C. For distilled water, the data are fit with an error not greater than 1.3% up to 400 °C (*12*).

In summary, correlations are available which reproduce data on the thermal conductivity of NaCl solutions at vapor saturation pressures and in the temperature and concentration regions of interest for geothermal energy.

Methods for Measuring Thermal Conductivity

The methods commonly used to measure the thermal conductivity of aqueous solutions include the following: coaxial cylinders, flat plate, and continuous line source. The first two are steady-state methods; the third is a transient method.

Chernen'kaya and Vernigora measured the thermal conductivity of NaCl and other solutions at 25 and 50 °C by using a cell comprised of two coaxial thin-walled glass cylinders (*17*). The NaCl solution was placed between the cylinders, and the inner cell was thermostated to 25 or 50 °C for 30 min. The difference in temperature across the NaCl solution was measured by a differential thermocouple. The instrument was calibrated with doubly distilled gas-free water, methyl alcohol, and benzene. Tufeu, LeNeindre and Johannin also used the coaxial cylinder method in their measurements (*18*). The measured values are believed accurate to within about ±5% (*12*). This method was also used by Riedel (*10*).

Yusufova et al. used a flat plate method for measuring the thermal conductivity of NaCl from 25 to 330 °C (*5*). The solution was placed between an upper and a lower circular metal plate; the upper plate was maintained at a high temperature to provide downward heat flow to prevent natural convection. A guard heater was located on the periphery both to ensure linear heat flow and to minimize convection. The main difficulties with this method center on maintaining linear heat flow and eliminating convection around the edges of the heated plates. Kapustinski and Ruzavin used a cell consisting of three silvered copper plates, 1 cm apart and forming two chambers. One chamber was used to hold a standard liquid and the other the NaCl solution. The standard was double-distilled water. The temperature was maintained to 0.001 °C, and the error of measurements was stated to be ±0.1% (*20*).

The non-steady-state method such as the continuous line source method has been widely used. In this case, heat is generated at a constant rate in a long, thin wire which is inserted in a large volume of test liquid. The system is initially at a constant temperature; heat is then applied, and the thermal conductivity of NaCl is determined from the measurements of temperature vs. time at a fixed distance from the wire. Vargaftik and Os'minin (*14*), Chiquillo (*19*), and Korosi and Fabuss (*3*, *4*) used this method in their thermal conductivity measurements. Jamieson and Tudhope used the relative hot-wire method to measure values for sea water solutions in the temperature range 0–125 °C (*12*).

Evaluation and Correlation

The data were converted where necessary to the ^{12}C scale of atomic weights, to units of grams per cubic centimeter for density, to watts per meter Celsius for thermal conductivity, to molal concentrations, and from relative values of thermal conductivity to absolute values for NaCl solutions. The required data and interpolating equation for the thermal conductivity of water were taken from ref 7 and 8.

The correlation given by Yusufova is the only one available which represents a large number of data points in the temperature and pressure range of geothermal interest. As seen, eq 5 is the ratio of the thermal conductivity of NaCl solutions to that of pure water. Yusufova used the following equation for liquid water which was contained in ref 7 and 8.

$$\lambda_w = -0.92247 + 2.8395\left(\frac{T+273.15}{273.15}\right) - 1.8007\left(\frac{T+273.15}{273.15}\right)^2 + 0.52577\left(\frac{T+273.15}{273.15}\right)^3 - 0.07344\left(\frac{T+273.15}{273.15}\right)^4 \quad (6)$$

Equation 6 is valid for temperatures ranging from 0 to 350 °C at saturation pressures.

Equations 4 and 6 were selected in this work to reproduce and interpolate data on the thermal conductivity of NaCl solutions.

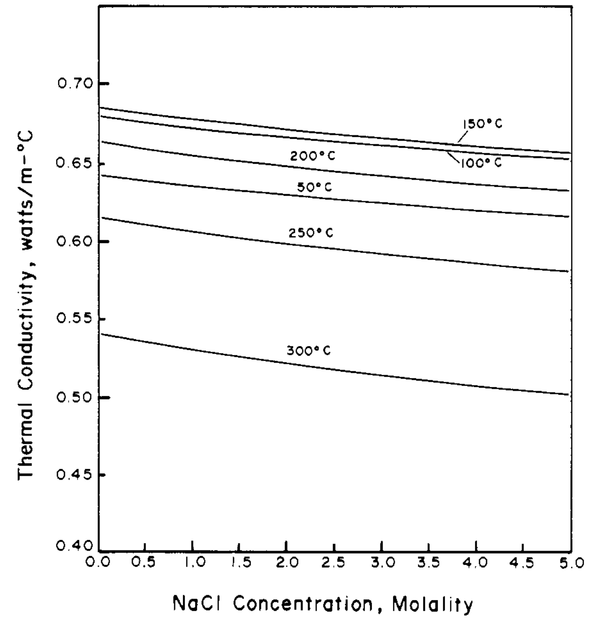

Figure 1. Thermal conductivity of aqueous NaCl solutions as a function of NaCl concentration at temperatures indicated.

Table II. Recommended Values for the Thermal Conductivity of Aqueous NaCl Solutions, Calculated from Equations 4 and 6, W/(m °C) (λ)

temp, °C	concn, *m* 0	1	2	3	4	5
20	0.603	0.596	0.590	0.585	0.580	0.577
30	0.618	0.611	0.605	0.600	0.595	0.592
40	0.632	0.624	0.618	0.613	0.609	0.605
50	0.643	0.636	0.630	0.625	0.621	0.617
60	0.653	0.646	0.640	0.635	0.631	0.627
70	0.662	0.655	0.649	0.644	0.640	0.636
80	0.670	0.663	0.657	0.652	0.647	0.643
90	0.676	0.669	0.663	0.658	0.653	0.649
100	0.681	0.674	0.668	0.662	0.658	0.654
110	0.684	0.677	0.671	0.666	0.661	0.658
120	0.687	0.679	0.673	0.668	0.664	0.660
130	0.688	0.680	0.674	0.669	0.664	0.661
140	0.688	0.680	0.674	0.669	0.664	0.660
150	0.687	0.679	0.673	0.667	0.663	0.659
160	0.684	0.677	0.670	0.665	0.660	0.656
170	0.681	0.673	0.667	0.661	0.656	0.652
180	0.677	0.669	0.662	0.656	0.651	0.647
190	0.671	0.663	0.656	0.650	0.645	0.641
200	0.665	0.656	0.649	0.643	0.638	0.633
210	0.657	0.648	0.641	0.635	0.630	0.625
220	0.648	0.640	0.632	0.626	0.620	0.616
230	0.639	0.630	0.622	0.616	0.610	0.605
240	0.628	0.619	0.611	0.604	0.599	0.594
250	0.616	0.607	0.599	0.592	0.586	0.581
260	0.603	0.594	0.586	0.579	0.573	0.567
270	0.589	0.580	0.571	0.564	0.558	0.553
280	0.574	0.565	0.556	0.549	0.543	0.537
290	0.558	0.548	0.540	0.532	0.526	0.520
300	0.541	0.531	0.522	0.515	0.508	0.503
310	0.523	0.512	0.504	0.496	0.489	0.484
320	0.503	0.493	0.484	0.476	0.470	0.464
330	0.482	0.472	0.463	0.455	0.449	0.443

Figure 1 shows the variation in thermal conductivity for concentrations from 0 to 5 *m* NaCl and temperatures between 50 and 300 °C. As shown, the thermal conductivity decreases almost linearly at each temperature as the concentration increases. Figure 2 is a plot of thermal conductivity vs. temperature with concentration as a parameter. The thermal conductivity increases with increasing temperatures up to a broad maximum near 140 °C and then decreases with concentration, by a maximum of 7% for 5 *m* NaCl as compared

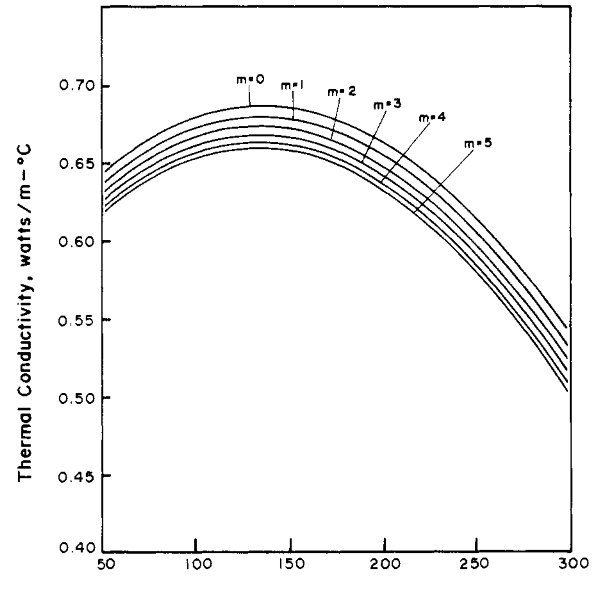

Figure 2. Thermal conductivity of aqueous NaCl solutions as a function of temperature at molalities shown.

with pure water. Table II consists of smoothed values for the thermal conductivity of aqueous NaCl solutions from 20 to 330 °C over the concentration range 0–5 *m*. Table III compares the available experimental data with that calculated from eq 4 and 6.

Summary and Conclusions

The correlation in eq 4 generally reproduces the experimental data to better than ±2% between 20 and 80 °C; an exception is the data of Korosi and Fabuss where the deviation ranges from +5.3 to +13.8%. See Table III. Between 100 and 150 °C, the deviation between the calculated values and the data of Korosi and Fabuss increases to +31.6% at 150 °C. However, we assume their values to be incorrect partly because they are consistently higher than the other values at temperatures below 80 °C and partly because Korosi and Fabuss felt their measurements should be considered tentative (*3*, *4*, *12*). In addition, the values obtained for sea water concentrations to 150 °C are consistently lower than those of Jamieson and Tudhope (*12*).

Recommendations

After a survey of the current experimental values in light of the data requirements, some specific recommendations are appropriate. While data to 80 °C are satisfactory in some respects, there are inadequacies for temperatures to 350 °C and for pressures to 50 MPa. Future work should include the following: (1) development of a theoretical equation to predict the thermal conductivity of NaCl solutions to high temperatures, concentrations, and pressures (The equation would permit estimations of values where data do not exist. Currently, the best available approach is that of Rideal but only for low temperatures and concentrations (*15*).); (2) additional experimental data above 80 °C to augment those of Korosi and Yusufova and to assist in reconciling the difference in their reported values (Data are also needed for mixtures of sodium chloride solutions with potassium chloride and calcium chloride (*24*). Thereby, the effects of these salts would be determined so that geothermal brines could be more closely modeled. Data on KCl and $CaCl_2$ solutions are reported to be available (*22*). Correlation for the thermal conductivity of organic liquids was recently published by Jamieson (*23*).); (3) investigation of the effect of pressure to 50 MPa (All the current data were obtained at saturation vapor pressures.); (4) laboratory measurements of the thermal conductivity of geothermal brines as a function of concentration, temperature, and pressure (The data will provide site-specific information on the variation in thermal conductivity and test the applicability of NaCl solutions for modeling.).

Table III. Comparison of Experimental Data with Those Calculated from Equations 4 and 6

temp, °C	concn, *m*	λ calcd from eq 4 and 6, W/(m °C)	ref	λ_m,[a] W/(m °C)	% dev $(\lambda - \lambda_m)/\lambda \times 100$
30	1.901	0.606	14	0.603	0.5
30	4.278	0.594	14	0.589	0.8
25	1.944	0.598	17	0.599	−0.2
25	4.494	0.586	17	0.583	0.5
50	1.944	0.631	17	0.635	−0.6
50	4.494	0.619	17	0.617	0.3
30	1.061	0.611	19	0.608	0.5
30	1.944	0.605	19	0.604	0.2
30	2.857	0.601	19	0.592	1.5
30	3.434	0.598	19	0.581	2.8
20	0.901	0.597	10	0.594	0.5
20	1.901	0.591	10	0.589	0.3
20	3.020	0.585	10	0.583	0.3
20	4.278	0.579	10	0.578	0.2
20	5.704	0.574	10	0.573	0.2
25	0.741	0.606	20	0.605	0.2
25	0.872	0.605	20	0.606	−0.2
25	0.901	0.605	20	0.605	0.0
25	1.573	0.600	20	0.600	0.0
25	1.802	0.599	20	0.600	−0.2
25	1.849	0.599	20	0.600	−0.2
25	2.534	0.595	20	0.595	0.0
25	2.716	0.594	20	0.595	−0.2
25	2.878	0.593	20	0.596	−0.5
25	3.655	0.590	20	0.589	0.2
25	3.781	0.589	20	0.591	−0.3
25	4.521	0.586	20	0.587	−0.2
25	4.883	0.585	20	0.587	−0.3
25	5.523	0.582	20	0.582	0.0
20	2.700	0.590	18	0.586	0.7
20	4.180	0.583	18	0.580	0.5
20	5.770	0.574	18	0.574	0.0
40	2.730	0.615	18	0.615	0.0
40	4.220	0.605	18	0.608	−0.5
40	5.820	0.594	18	0.602	−1.3
60	2.760	0.634	18	0.637	−0.5
60	4.270	0.623	18	0.630	−1.1
60	5.890	0.611	18	0.624	−2.1
80	2.790	0.647	18	0.653	−0.9
80	4.320	0.635	18	0.646	−1.7
80	5.960	0.622	18	0.640	−2.9
25	0.707	0.606	3	0.574	5.3
25	3.535	0.590	3	0.567	3.9
50	0.707	0.638	3	0.577	9.6
50	3.535	0.623	3	0.571	8.3
75	0.707	0.661	3	0.581	12.1
75	3.535	0.646	3	0.557	13.8
100	0.707	0.676	3	0.560	17.2
100	3.535	0.660	3	0.539	18.3
125	0.707	0.682	3	0.518	24.0
125	3.535	0.666	3	0.500	24.9
150	0.707	0.681	3	0.460	32.5
150	3.535	0.665	3	0.455	31.6

[a] λ_m = measured thermal conductivity.

Glossary

λ	thermal conductivity of aqueous solution, W/(m °C)
λ_w	thermal conductivity of water, W/(m °C)
C_p	heat capacity of aqueous solution, cal/(mol °C)
C_{p_w}	heat capacity of water cal/(mol °C)
ρ	density of aqueous solution, g/cm^3
ρ_w	density of water, g/cm^3
M	molecular weight of NaCl
M_w	molecular weight of water
m	molality

J. Chem. Eng. Data **1980**, *25*, 267–271

T degrees Celsius, °C

Literature Cited

(1) Lyon, R. N., Kolstad, G. A., Eds., "A Recommended Research Program in Geothermal Chemistry", WASH-1344, Department of Energy, Washington, DC, 1974.
(2) Silvester, L. F., Pitzer, K. S., *J. Phys. Chem.*, **81**, 1822 (1977).
(3) Fabuss, B. M., Korosi, A., "Properties of Sea Water and Solutions Containing Sodium Chloride, Potassium Chloride, Sodium Sulphate and Magnesium Sulfate", Office of Saline Water Research and Development Progress Report, **No. 384**, Washington, DC, 1968.
(4) Korosi, A., Fabuss, B. M., "Thermophysical Properties of Saline Water", Office of Saline Water Research and Development Progress Report, No. 363, Washington, DC, 1968.
(5) Yusufova, V. D., Pepinov, R. I., Nikolaev, V. A., Guseinov, G. M., *Inzh.-Fiz. Zh.*, **29**, 600 (1975).
(6) Rowe, A. M., Chou, J. C. S., *J. Chem. Eng. Data*, **15**, 61 (1970).
(7) Haywood, R. W., *J. Eng. Power*, **88**, 63 (1966).
(8) Kestin, J., Whitelaw, J. H., *J. Eng. Power*, **88**, 82 (1966).
(9) Touloukian, Y. S., Liley, P. E., Saxena, S. C., "Thermal Conductivity", Vol. 3, IFI/Plenum Data Corp., New York, 1970.
(10) Riedel, L., *Chem.-Ing.-Tech.*, **23**, 59 (1951).
(11) Jamieson, D. T., Irving, J. B., Tudhope, J. S., "Liquid Thermal Conductivity: a Data Survey to 1973", HMSO, Edinburgh, 1975.
(12) Jamieson, D. T., Tudhope, J. S., *Desalination*, **8**, 393 (1970).
(13) Washburn, E. W., Ed., "International Critical Tables", Vol. V, McGraw-Hill, New York, 1929.
(14) Vargaftik, N. B., Os'minin, Yu. P., *Teploenergetika* (*Moscow*), **3**, 11 (1956).
(15) Chernyshev, A. K., *Tr. GIAP*, **No. 41**, 65 (1976); *Chem. Abstr.*, **91**, 500 (1979).
(16) Unterberg, W., "Thermophysical Properties of Aqueous Sodium Chloride Solutions", Report No. 64-21, May 1964, Department of Engineering, University of California, Los Angeles, Los Angeles, CA.
(17) Chernen'kaya, E. I., Vernigora, G. A., *Zh. Prikl. Khim.* (*Leningrad*), **45**, 1704 (1972).
(18) Tufeu, R., LeNeindre, B., Johannin, P., *C. R. Hebd. Seances Acad. Sci., Ser. B*, **262**, 229 (1966).
(19) Chiquillo, A., "A Measurement of the Relative Thermal Conductivities of Aqueous Salt Solutions by a Non-Steady State Hot-Wire Method", Thesis No. 3955, Eidg. Technische Hochschule, Zurich, Switzerland, 1967.
(20) Kaputinski, A. F., Ruzavin, I. I., *Zh. Fiz. Khim.*, **29**, 2222 (1955).
(21) Predvoditelev, A. S., *Zh. Fiz. Khim.*, **22**, 339 (1948).
(22) Fatullaev, F. G., Kerimov, A. M., *Russ. J. Phys. Chem.* (*Engl. Transl.*), **47**, 913 (1973).
(23) Jamieson, D. T., *J. Chem. Eng. Data*, **24**, 244 (1979).
(24) Verba, O. I., Gruzdev, V. A., Genrikh, V. N., Zakharenko, L. G., Lavrov, V. A., Psakhis, B. I., *Issled. Teplofiz. Svoistv. Zhidk. Rastvorov Splavov*, 40–59 (1977).

Received for review October 15, 1979. Accepted February 19, 1980. Supported by the U. S. Department of Energy, Office of Basic Energy Science, Division of Engineering, Mathematical and Geosciences under Contract W-7405-ENG-48.

Review of Density Estimation of Saturated Liquid Mixtures

Doddipatla Veeranna and Devinder N. Rihani*

Engineers India Ltd., New Delhi 110 001, India

Various correlations with regard to the density model and mixing rules needed for this purpose have been reviewed. It has been found that the modified Rackett equation with the Chueh–Prausnitz mixing rule, which predicts the density within 3%, should be acceptable from an engineering design standpoint. A total of 3600 data points from 88 systems (containing polar and nonpolar constituents) were tested. The data extended well into the critical region for systems with nonpolar components. Whenever polar compounds were present, this was generally in the T_r range of 0.4–0.7 and to that extent the validity of this exercise would be limiting.

1. Introduction

Density is a parameter affecting directly or indirectly every stage of the process design activity. For pure components a large volume of liquid density data has been reported in standard handbooks (*1–4*), etc. However, such is not the case with mixtures where, besides temperature and pressure, composition is also one of the variables. For mixtures the required data are seldom available; it is necessary to reduce and correlate the data for meaningful interpolations. The utility of having a reliable estimation tool can be easily realized if we consider that for an actual system the number of components to be handled may be more than 10—say for the case of a C_8 aromatics separation train this could be close to 20, with some of them being supercritical.

This paper presents the results of a study undertaken to review the estimation procedures for mixtures containing nonpolar and polar components. Attention was given to criteria like (i) accuracy, (ii) range of application, (iii) ease of use, and (iv) availability of input parameters. For use with a computerized thermophysical property package, it would be advantageous to have a method based on common input parameters, i.e., critical properties, acentric factor, etc., which are normally available or can be estimated with a high degree of reliability.

2. Available Correlations

The estimation method may utilize either an equation of state like Redlich–Kwong, BWR, etc., or the corresponding states approach. The latter is preferred because of wider applicability and lesser computational efforts. This paper is also restricted to the corresponding states approach.

2.1 Nonpolar Systems. On the basis of the work of many authors (*5–12*) it was decided to limit this investigation to testing with the following correlations.

(*a*) *Harmens Equation* (*9*). Originally Harmens tabulated $F(T_r)$ as a function of reduced temperature in the range $0.3 \le T_r \le 0.96$. Spencer and Danner (*5*) enhanced its usage by converting it into an analytical form.

(*b*) *Modified Rackett Equation* (*5*). The original equation by Rackett (*13*) has been modified (*14*, *23*) and extended to mixtures. It employs critical temperature, pressure, and an adjustable parameter called the Rackett parameter, Z_{RA}, as shown.

$$V = \frac{RT_c}{P_c} Z_{RA}^{\,1+(1-T_r)^{2/7}} \tag{1}$$

$$V_m = R\left[\sum_{i=1}^{n} \frac{x_i T_{ci}}{P_{ci}}\right] Z_{RAm}^{\,1+(1-T_r)^{2/7}} \tag{2}$$

$$Z_{RAm} = \sum_{i=1}^{n} x_i Z_{RAi} \tag{3}$$

$$T_r = T/T_{cm} \tag{4}$$

T_{cm}, pseudocritical temperature for mixtures, was obtained through one of the mixing rules mentioned later on.

0021-9568/80/1725-0267$01.00/0