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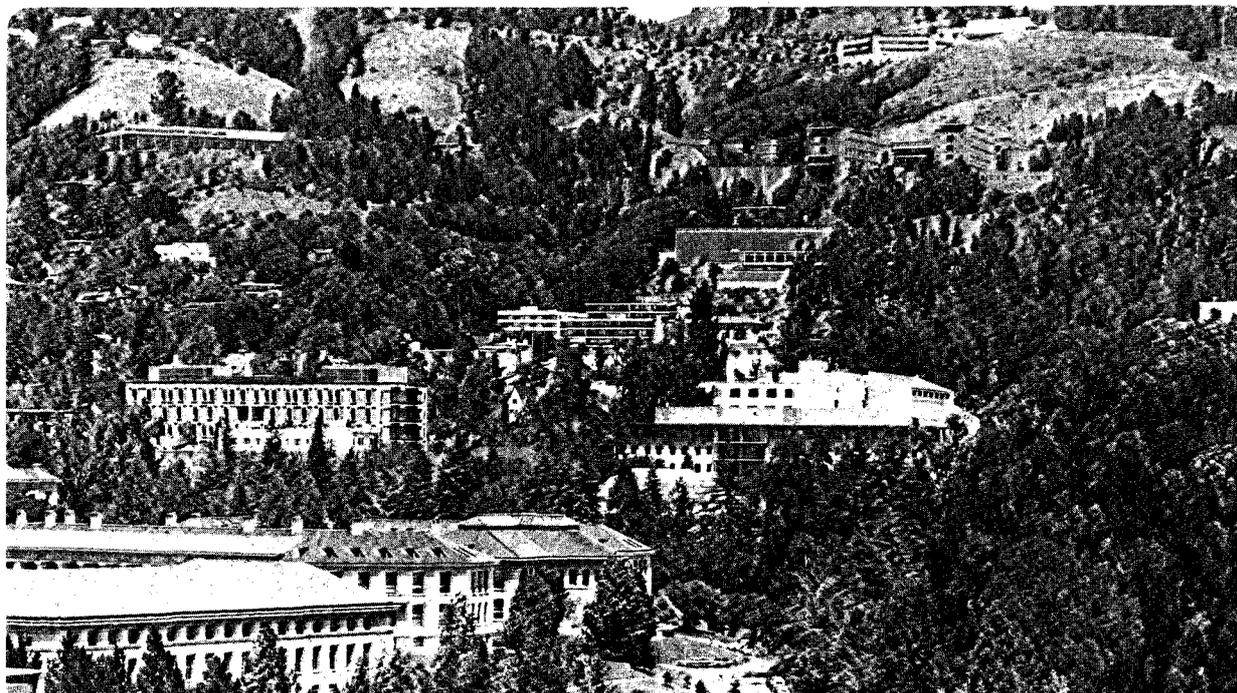
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AQUEOUS SOLUTIONS DATABASE TO HIGH TEMPERATURES
AND PRESSURES. NaCl SOLUTIONS

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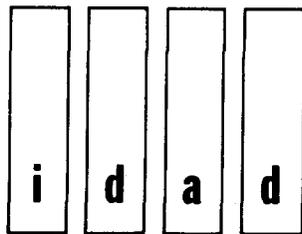
Aqueous Solutions Database to High Temperatures
and Pressures. NaCl Solutions

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ABSTRACT

A survey is made of available experimental data on sodium chloride solutions which are used in geothermal energy exploration and development for electrical power production and direct use. The data are classified as thermodynamic, transport and physical; they are useful in the design and development of a geothermal area from brine production through utilization, to brine disposal. An ideal data system for geothermal energy is described.

I. Introduction

The Lawrence Berkeley Laboratory (LBL) is funded by the U.S. Department of Energy to provide a single, comprehensive database of properties of aqueous solutions involved in basic geothermal energy. The compilation, which includes critical evaluation and correlation, constitutes a single source of recommended values to be used in research and development of both electrical power generation by and direct utilization of geothermal energy. In addition, the result of this work includes identification of areas where data are either lacking or are inadequate, and recommendations for research designed to provide the needed data.

Reliable data are needed on the basic properties of geothermal brines covering a range of conditions up to high temperatures and pressures (Ref.1). However, geothermal brines are site-dependent in the concentration of dissolved substances; the total dissolved solids vary over three orders of magnitude, depending on the site. Concentrations differ also for individual wells within the same geothermal area.

Since data on the basic properties of individual geothermal brines are virtually nonexistent it is common practice to rely on those of sodium chloride solutions in water as a substitute.

The larger LBL project covers energy properties of the following aqueous solutions: (1) Substances which on dissolving in water change the basic properties of the resulting solution. Electrolytes such as NaCl and KCl, and gases, such as CO₂ are examples. (2) Substances which cause scaling, corrosion or erosion when present in brines. Hydrogen sulfide, carbonates and silicates are examples of such substances. (3) Materials which react with the brine and are dissolved by the brine. Examples are rocks in brine reservoirs and steel used in pipes and turbines.

This report is limited to a survey of the experimental data and correlations for NaCl solutions up to 350°C temperatures and 50 MPa pressures. The objectives of the work are mainly to: (1) obtain correlation equations which closely reproduce the available experimental data on the basic properties of aqueous NaCl solutions over a range of temperatures up to 350°C and pressure to 50 MPa; (2) develop tables of smoothed data based on the correlation expressions and to provide reasonable estimates of these properties through extrapolation, where necessary, into the region of geothermal interest; (3) prepare a handbook containing equations, evaluation procedures, tables of smoothed data and also recommendations for future research in areas where the current data is either lacking or inadequate.

The basic properties of NaCl solutions can be organized in several ways; it is convenient here to separate them into a number of categories:

as indicated in Table 1. The table lists these classes of basic energy data for NaCl solutions and the experimental measurement means commonly used to obtain the data.

In this paper it is not possible to cover all the data for each solution of interest. More complete information is obtained from References 2-9, 24.

Data Acquisition Systems for Solutions

Prospective users of aqueous solutions are faced with a formidable assortment of computer databases, theoretical and empirical correlation equations, publications in three major languages, differing units of concentration and basic parameter, extrapolated and interpolated values, values calculated for one property using data for another contained in over 50 journals and reports from over 25 laboratories.

The engineer or scientist needs to consider that for each property the following must be critically evaluated in selecting data or correlations: the purity of the water and NaCl used, the instrumental method employed in the measurement, the calibration procedures used, the number of replicate determinations, the temperature and pressure control, chemical reactions between the NaCl solution and the instrument, and the sampling and data processing procedures used. Each step is important, and the entire data acquisition system must be considered in selecting best values.

Both the discussion which follows and specific examples given will center around the more important geothermal energy properties which have been selected from those listed in A Recommended Research Program in Geothermal Chemistry (Ref. 1), Summaries of Physical Research in the

Table 1. Selected basic energy properties of sodium chloride solutions and commonly used methods of measurement to high temperatures.

| Basic Property | Temperature, °C | Method |
|---------------------------------------|---------------------|---|
| Heat of solution | 0-100 | Calorimeter (glass) |
| | 100-200 | Calorimeter (Ti) |
| | 300 | Calorimeter (Ti-Pd) |
| Heat of dilution | 10-100 | Calorimeter Flow calorimeter |
| | 184-712 (51;100MPa) | Calorimeter (Hastelloy) |
| Heat of solution at infinite dilution | 0-300 | Calorimeter; vapor pressure |
| Heat capacity | 1-85 | Calorimeter (stainless steel) |
| | | Flow calorimeter |
| | | Bomb calorimeter (gold-plated beryllium copper) |
| Vapor pressure | 25-100 | Manometer |
| | 75-700 | Differential manometer (Pt cups) |
| | | Isotensicope |
| | | Bomb (stellite) |
| Viscosity | 25-150 | Cannon glass capillary |
| | | Ostwald and Ubbelohde |
| | | Oscillating disk |
| Thermal conductivity | 25-50 | Coaxial cylinders |
| | 25-150 | Continuous line source |
| | 25-330 | Flat plate |
| Electrical conductivity | 0-800 | Conductance cell (Pt-Ir) |
| | | Four-electrode cell (ceramic, Pt) |
| Density | 0-200 | Sinker |
| | 20-75 | Pycnometer |
| | 25-350 | Hydrostatic weighing |
| | 150-500 | Autoclave, filling temperature |
| Solubility | 0-300 | Sample analysis |
| | 148-425 | Pressure-temperature (Pt vessel) |

Geosciences (Ref. 26), and Preliminary Steam Tables for NaCl Solutions (Ref. 2). The data covered will be confined to that published since the International Critical Tables in 1929.

II. Thermodynamic Properties

The thermodynamic properties covered here are enthalpy, heat capacity and vapor pressure. Despite the need for experimental data to 350°C, 50MPa and saturation concentrations, the majority of thermodynamic data available is still below 100°C and at saturation vapor pressures. See Table 2. The lack of data at higher temperatures is so acute that only a few newly published values are sufficient cause for recalculation of correlation equations. To a large extent, tables of smoothed values are based on calculated and extrapolated data. In the following sections heat of solution, heat of dilution, heat capacity and vapor pressure are discussed as examples of the current status of data on thermodynamic properties of NaCl solutions to high temperatures. This is the experimental data most often used to calculate the total specific enthalpy and entropy of NaCl solutions.

Enthalpy

The total enthalpy of aqueous NaCl solutions changes with temperature. It is calculated from the standard state enthalpy of pure water, the standard state enthalpy of NaCl solutions and the enthalpy differences between the standard state and real solution. The enthalpy of water is obtained from steam tables (Refs. 5,10). The two other terms are obtained from measurements of the heat of solution of NaCl crystals in water, and the enthalpy

change when NaCl solutions are diluted from one concentration to a lower concentration. Table 2 contains selected references to experimental data which have been used in calculating the total enthalpy of NaCl solutions up to high temperatures. Most experimental measurements are below 100°C and only two are at pressures different from saturation vapor pressure. However, there is sufficient data for development of correlation equations.

Bradley and Pitzer fit experimental thermodynamic data to a 30 parameter equation which reproduces the enthalpy and heat capacity data from 0-300°C. They provide tables of heats of solution at infinite dilution, partial molal enthalpy and total enthalpy from 0-300°C. Values of the total relative molal enthalpy agree to within ± 60 J/mole up to 75°C, and 250 J/mole at 100°C for 5 molal NaCl. The large value at 100°C is attributed to incompatibility between the various types of data. More information is in Reference 5. Earlier work includes that of Silvester and Pitzer (Ref.11) and Haas (Ref.2,4). A method for estimating the enthalpy of geothermal brines is given by Grens (Ref.12) and Potter and Haas (Ref.25). Refer to Table 3 and Figure 1.

The effect of added NaCl is to lower the enthalpy of pure water over the temperature range 0°C to 350°C. See Figs. 2a and 2b. For example, at 300°C, a 5m NaCl solution has an enthalpy difference of about 500 KJ/kg compared with pure water at this temperature (Ref.10).

In summary, the experimental data on heat of solution, heat of dilution and heat capacity and vapor pressure are adequate for calculating the total specific enthalpy of NaCl solutions to 300°C. See the equation

Table 2. Selected experimental data of the basic energy properties of NaCl solutions to high temperatures.

| Property | Temperature, °C | Concentration, m | Pressure, MPa | Reference | |
|------------------|------------------|------------------|---------------|-----------------|---------------|
| Heat of solution | 0-95 | 0.0009-0.02 | saturation | Criss 61 | |
| | 10-65 | < 4 | | Abrosimov 77 | |
| | 25 | 0.05-1.3 | saturation | Benson 55,56 | |
| | 114-200 | 0.007-0.04 | saturation | Gardner 69 | |
| | 200-300 | 1.7-10.3 | saturation | Borodenko 75,76 | |
| | <327 | | <100 | Puchkov 78 | |
| | | | | Dimitriev 77 | |
| | 300 | 0.003-0.018 | saturation | Cobble 78 | |
| | Heat of dilution | 10-25 | 0.0002-0.6 | saturation | Gulbransen 34 |
| | | 10-75 | | saturation | Craft 75 |
| 25 | | 0.39-1.2 | saturation | Vaslow 71 | |
| 25 | | | saturation | Wood 69 | |
| 25-100 | | 0.04-5 | saturation | Messikomer 75 | |
| 30 | | 0.1-1 | saturation | Leung 75 | |
| 40-80 | | 0.1-6 | saturation | Ensor 73 | |
| 183-712 | | 0.53-6 | 51; 100 | Kasper 79 | |
| Heat capacity | | 1.5-45 | 0.01-3 | saturation | Perron 75 |
| | 5-85 | 0.04-6 | saturation | Tanner 78 | |
| | 6-48.9 | high dilution | saturation | Arnett 70 | |
| | 10-120 | 0.5 | saturation | Ackermann 58 | |
| | 10-130 | 0.4-1.1 | saturation | Eigen 51 | |
| | 24.15 | 0.01-2 | saturation | Picker 71 | |
| | 25 | 0.01-3 | saturation | Fortier 74 | |
| | 80-200 | 0.35-2 | saturation | Likke 73 | |
| | 50-350 | 0.43-6 | | Puchkov 76 | |
| | 20 | 0.1-2 | 100;200 | Liphard 77 | |
| | Vapor pressure | 25.00 | 0-5.8 | | Pepela 72 |
| | | 20-30 | 2.0-4.0 | | Olynyk 43 |
| | | 25-100 | 1.0-6.1 | | Gibbard 74 |
| 167-265 | | 0.5-1 | | Gardner 69B | |
| 125-270 | | 1-3 | | Gardner 63 | |
| 150-350 | | 1.2-5.6 | | Mashovets 73 | |
| 75-300 | | 4.8-sat. | | Liu 72 | |
| 125-300 | | 0.2-1 | | Liu 70 | |
| 125-300 | | 0.1-3.5 | | Lindsay 68 | |
| 20.3 | | 0.03-0.1 | | Grollman 31 | |
| 75-150 | | 0.1-3.5 | | Fabuss 67C | |
| 350-400 | | 3%-sat. | | Urusova 71C | |
| 250-700 | | saturated | | Sourirajan 62 | |
| 60-101 | | 0.05-1.0 | | Smith 39 | |
| 61-105 | | 1.5-4.0 | | Smith 39B | |
| 15-45 | | 0.1-6.0 | | Robinson 59 | |
| 125-270 | | 1.0-3.0 | | Gardner 63 | |
| 200-400 | | 2-15 | | Urusova 71B | |
| 450-550 | | 3%-sat. | | Urusova 74 | |
| 183-646 | | 0.1-0.5 mole fr. | | Keevil 42 | |

Table 2. (continued)

| Property | Temperature, °C | Concentration, m | Pressure, MPa | Reference |
|-------------------------|-----------------|------------------|--------------------------|------------------|
| Thermal conductivity | 20 | 0.9-5.7 | saturation | Riedel 51 |
| | 20-80 | 2.7-5.9 | saturation | Tufew 66 |
| | 25-150 | 0.7-3.5 | saturation | Korosi 68 |
| | 25 | 0.7-5.5 | saturation | Kapustinski 55 |
| | 25-50 | 1.9-4.5 | saturation | Chernenkaya 72 |
| | 20-40 | 1-3 | saturation | Chiquillo 67 |
| | 30 | 4.2 | saturation | Vargaftik 56 |
| | | | | Prudnikov 70 |
| Viscosity | 0-25 | 0.002-2 | saturation | Jones 37 |
| | 10-40 | 0.1-5.8 | saturation | Lengyel 64 |
| | 12-42 | 0.001-0.5 | saturation | Kaminsky 56 |
| | 18-154 | 0.4-4 | 1-30 | Kestin 77 |
| | 20-80 | 6 | saturation | Postnikov 70 |
| | 23 | 0.3-2.5 | saturation | Gaeta 66 |
| | 25-50 | 0.007-5.8 | saturation | Goncalves 77 |
| | 25 | 0.09-1.2 | saturation | Drucker 46 |
| | 25-150 | 0.1-3.6 | saturation | Korosi 68 |
| | 25 | 0.1-5.6 | saturation | Janz 70 |
| | 25 | 1.0-5.6 | saturation | Ostroff 69 |
| | 25-60 | 1.1-6.1 | saturation | Ezrokhi 52 |
| | 30-55 | 1.0-5.0 | saturation | Suryanarayana 58 |
| | 35 | 0.01-0.07 | saturation | Chacravarti 40 |
| | 20-350 | 1-20%w | < 30 | Pepinov 77 |
| Electrical conductivity | 0-800 | 0.001-0.1 | 1-400 | Quist 68 |
| | 22-375 | 0.2-4 molar | 30 | Ucok 79 |
| | 370-600 | 0.01-0.0005N | | Lukasov 76 |
| Density | 0-25 | 0.002-1.0 | saturation | Jones 37 |
| | 0-55 | 0.01-1 | saturation | Millero 70 |
| | 0.20-100 | 6 | saturation | Cornec 32 |
| | 5 | 0.05-3.5 | saturation | Vaslow 69 |
| | 5-25 | 4 | saturation | Wirth 68 |
| | 40-280 | .001-1.5 | 10 | Gorbachev 74 |
| | 200-680 | 1-6 | 56 -137 | Ikornikova 71 |
| | 150-520 | 1-4 | 25 -175 | Lemlein 61 |
| | 100-440 | 0.1-6 | 1-35 | Khaibullin 66 |
| | 185-414 | 1-2 | 1 -30 | Samoilovich 68 |
| | 385-396 | 0.7-4 | 23 -26 | Copeland 53 |
| | 175-350 | 0.5-3 | | Ellis 63 |
| | 50-200 | 0.1-1 | | Ellis 66 |
| | 25-175 | 0.1-2.5 | saturation | Fabuss 66 |
| | | 73.3-133.9ppm | | Masui 78 |
| | 25-350 | 2-24%w | 0-1000Kg/cm ² | Zaremba 76 |
| | 25-150 | 0.1-3.5 | saturation | Korosi 68 |
| | 20-300 | 0.1-6 | 10 -150 | Polyakov 65 |
| | 0-55 | 0.01-1 | saturation | Millero 70 |

Table 2 (continued)

| <u>Property</u> | <u>Temperature, °C</u> | <u>Concentration, m</u> | <u>Pressure, MPa</u> | <u>Reference</u> |
|----------------------|------------------------|-------------------------|----------------------|------------------|
| | 25 | 0.7-1 | 120 | Millero 72 |
| | 50 | 0.005-1 | | Millero 72B |
| | 20 | 0.1-4 | | Passynski 38 |
| | 25 | 0.002-0.7 | | Kruis 36 |
| Solubility | 148-425 | 29.62-48.42 % | saturation | Potter 77 |
| | 150-350 | | | Schroeder 35 |
| | 285-455 | | | Benrath 37 |
| | 183-646 | | | Keevil 42 |
| | 75-300 | | | Liu 72 |
| Critical temperature | 383-462 | 0.1-1.8 | | Marshall 74 |
| Critical pressure | 374-700 | 0-26.4% | 2 -12 | Sourirajan 62 |

developed by Pitzer et al (Ref. 5). However, additional experimental data are needed to improve the fit of correlation equations above 100°C and data are especially needed on the effect of pressures to 50 MPa.

Heat Capacity

Experimental data on heat capacity are available to 350°C and 0.01-6 molal; however, only one set of data is available at pressures different from vapor saturation. See Table 2. The available data fit the Pitzer et al equation well (Ref. 5).

The data below 100°C showed an error of less than 0.004 J/gm-°C, but the error was as large as 0.01 J/gm-°C at high molalities at temperatures of 45°C and 65°C. Also the error in the fit to experimental data increased with increasing temperature and was ± 0.03 J/mole-°C at 250°C for concentrations below 5 molal; 0.05 J/mole-°C at 275°C, 0.17 J/mole-°C at 300°C; and the error had an average value of 0.56 J/mole-°C at 325°C and 350°C. See Reference 5 for more details.

The empirical correlation equation developed by Otto reproduces experimental values with an error less than $\pm 2\%$ from 5°C to 300°C and less than $\pm 5\%$ between 300°C and 350°C for concentrations between 0 and 6 molal at saturation vapor pressures (Ref. 10).

Figure 3 shows the decrease in heat capacity of NaCl solutions for NaCl concentrations between 0-6 molal. At each concentration, the heat capacity increases with temperature; the magnitude of the increase is less as the concentration increases.

In summary, equations are available for providing tables of smooth values for heat capacity to 350°C and 6 molal. However, data are needed at temperatures above 275°C, especially from 300° - 350°C. Data at high pressures is also needed.

Vapor Pressure

The available vapor pressure data covers the temperature range 25-700°C and concentrations from 0 to saturation (Table 2). The experimental results published by Liu and Lindsay have been widely used. See Refs. 5, 10, 11.

Correlation equations which reproduce vapor pressure data were developed by Haas (Ref. 2,4), MacMullin (Ref. 16) and Korosi and Fabuss (Ref. 15). Vapor pressure estimates may be made as described by Potter and Haas (Ref. 25) and Grens (Ref. 12). Haas gives a table of data covering the temperature range 80-325°C and concentrations from 0 to saturation; the standard error is 0.32% of the observed pressure. The vapor pressure decreases with increasing NaCl concentration, and increases markedly at any particular concentration as the temperature increases. See References 2 and 4 for additional information.

While the data on vapor pressure covers the range of geothermal interest; the correlation should be redone to include the new data published since 1971.

III. Transport Properties

Transport properties cover viscosity, thermal conductivity and electrical conductivity.

A. Viscosity

The currently available experimental data on the viscosity of NaCl solutions is sparse and covers mainly pressures from atmospheric to 30 MPa, concentrations from 0 molal to saturation, and temperatures below 150°C. See Table 2. Above 75°C the available data is that of Korosi and Fabuss, and Kestin. An empirical correlation equation was developed which reproduces the experimental data with an error of less than 1.5% over the temperature range 10 to 150°C (Ref. 7). The equation is convenient for interpolation, and for machine calculations. Additional laboratory measurements on the viscosity of NaCl solutions between 150 to 350°C are needed. Laboratory data are also needed for pressures up to 50 MPa.

The viscosity has been correlated by a number of workers including Ozbek, Fair and Phillips (Ref. 7), Kestin (Ref. 17), and Potter (Ref. 18) as shown in Table 3. The equation developed by Potter permits extrapolation to about 325°C. See Figure 4, taken from Reference 7.

B. Thermal Conductivity

Published experimental data has been available for some time for the thermal conductivity of NaCl solutions up to 150°C and data, in the form of graphs and a correlation equation, to 330°C were published recently (Ref. 6). The correlation equation selected for our data base reproduces most of the published experimental data to better than 3% up to 80°C. The deviation is considerably larger (5-30%) for the data of Korosi and Fabuss (Ref. 19) over the range 25-150°C. Unfortunately, the greatest number of experimental points are not available in tabular form but are

Table 3. Selected correlations for the basic energy properties of NaCl solutions and pure water to high temperatures.

| Property | Temperature, °C | Concentration, m | Pressure, MPa | Accuracy | Reference |
|---------------------------------------|------------------|---------------------|---------------------------------|-------------------------|-------------------------|
| <u>NaCl Solutions</u> | | | | | |
| Thermal conductivity | 20-300 | 0-5 | saturation | ±2% | Ozbek 79 |
| Viscosity | 0-150 0-300 | 0.5-5 0-6 | to 30 saturation | ±1.5% ±1% | Ozbek 77 Potter 78 |
| Electrical conductivity | 0-800 | 0.001-0.1 | to 400 | | Quist 68 |
| Electrical resistivity | 22-375 | 0.2-4 molar | 30 | ±2% | Ucok 79 |
| Solubility | 0-600 | | saturation | | Potter 77 |
| Specific volume | 40-280 0-175 | 0.001-1.5 0-25%w | 10 to 350kg-cm ⁻² | 1.5ppt | Gorbachev 74 Rowe 70 |
| Density | 20-150 80-325 | 0-6 0-30 | to 35 saturation | ±0.002g/cm ³ | Kestin 77 Haas 75 |
| Vapor pressure | 75-325 | 0-saturation | | 0.32% | Haas 75 |
| Heat of solution | 0.01-300 | 0.25-25%w | saturation | <5KJ/mole | Pitzer 79 |
| Heat of solution at infinite dilution | 0-300 | | saturation | | Pitzer 79 |
| Heat of dilution | | | | | Pitzer 79 |
| Heat capacity | 0-300 | 0.25-25%w | saturation | 0.004-0.17 J/mole-°C | Pitzer 79 |
| Total enthalpy | 0-300 | | saturation | | Pitzer 79 |
| Total enthalpy | 0-300 | | saturation | | Pitzer 79 |
| Specific heat capacity | 0-300 | | saturation | | Pitzer 79 |

Water

| Energy Property | Temperature, °C | Pressure, MPa | Reference |
|----------------------|-----------------|-------------------|-----------|
| Thermal conductivity | 0<T<800 | 0.1<P<100 | IAPS 78 |
| Viscosity | 0<T<800 | 0<P<100 | IAPS 76 |
| Specific enthalpy | 0.01<T<374 | 0.0006113<P<22.09 | Keenan 78 |
| Density | | | |
| Specific volume | 0.01<T<374 | 0.0006113<T<22.09 | Keenan 78 |
| Vapor pressure | | | Keenan 78 |
| Heat capacity | | | Keenan 78 |

published as a correlation equation or in graphical form. Based on this equation, which was applied to all the data used in the evaluation, the thermal conductivity of pure water is lowered by dissolved NaCl at all temperatures up to 330⁰C; the change at 140⁰C is about 7% for a 5 molal solution. For any NaCl concentration up to 5 m, the thermal conductivity increases with increasing temperature to a broad maximum at about 140⁰C, then decreases by more than 0.2 watts/m-⁰C as the temperature is further increased to 330⁰C. See Figure 5.

Few experimental data points have been published on the thermal conductivity of NaCl solutions. From 100⁰C to 150⁰C there are only the six measurements reported by Korosi and Fabuss. Data to 330⁰C reported by Yusufova, et al., are not tabulated, but must be calculated from the published correlation equation. No data are available on the effects of elevated pressures on the thermal conductivity of NaCl solutions (Ref. 6).

C. Electrical Conductivity

Experimental data on electrical conductivity are available for NaCl solutions for temperature from 0⁰C to 80⁰C, a pressure range from 0 to 400 MPa and concentrations up to 4 molal. Data were recently correlated as resistivity measurements to 375⁰C. The resistivity decreased with increasing concentration over the range 3-20% w NaCl. With temperature the resistivity decreased to a broad minimum between about 275 and 325⁰C. Beyond about 325⁰C, the resistivity increased to 375⁰C. At 25⁰C, 100⁰C and 300⁰C, the resistivity falls rapidly when the NaCl concentration lies between 3% and 10% w, then more slowly between concentrations of 10% and 26% w. The data were correlated to 2% for NaCl solutions for 3-20% w concentrations over the temperature range 25-375⁰C. See Ref. 20.

IV. Physical Properties

A. Solubility

The solubility of NaCl in water increases continuously with temperature at saturated water vapor pressures to 800°C. Potter et al developed a correlation equation to fit data on the solubility of NaCl solutions from 0°C to 800°C (Ref. 3).

B. Density

The data on density of aqueous NaCl solutions is extensive; over 1300 experimental values have been compiled for temperatures up to 770°C and pressures to 270 MPa. See Table 2.

Correlations equations have been developed by a number of workers, including Kestin (Ref. 17), Rowe and Chou (Ref. 21), Potter and Haas (Ref. 4), Korosi and Fabuss (Ref. 15), and Ozbek, Fair and Phillips (Ref. 22).

The density of NaCl solutions increases with increasing concentration from 0 to 6 molal over the temperature range 0°C to 300°C. There is no significant affect of pressure over this range of temperature up to 20 MPa. Figures 6 and 7 show the change in density with temperature and pressure, respectively.

C. Critical Temperature and Pressure

The critical temperature and pressure of an aqueous electrolyte solution is a function of the concentration of the solution. At a fixed concentration the critical temperature, pressure and density define the critical point. It is at this point that the vapor and liquid phases of the solution have the same density and, in effect, a one-phase fluid system is established for all temperatures and pressures above the critical point. Marshall (Ref. 8) has measured the critical temperature of aqueous NaCl

solutions, as well as for 20 other electrolyte solutions, in the concentration range of 0.1 to 1.8 molality. The electrolytes included both salts and acids. A review of the available data between 0 and 2 molal in concentration is also given by Marshall (Ref. 8). Sourirajan and Kennedy (Ref. 23) reported the critical temperature and pressure for the NaCl-H₂O system for concentrations between 0 and 6.2 molal.

VI. Summary and Conclusions

A review of the current status of data on selected properties of NaCl solutions in the temperature range 0^o to 350^oC and pressures up to 50 MPa shows that only limited data are available for providing tables of smoothed values. Experimental data are needed mainly for pressures different from vapor saturation, and at temperatures above about 150-200^oC for viscosity, thermal conductivity, enthalpy and heat capacity. All properties need to be correlated as new data is made available; this will result in both improved fits of the equations and in better extrapolation procedures.

VII. Recommendations

After reviewing current data in light of the needs of the geothermal energy program, some general observations are appropriate. The "ideal" data obtainable from published literature should include the following:

1. Experimental values in tabular form showing concentration, temperature, pressure and the measurement of the basic property. The data can then be used to develop correlation expressions and for calculations of mean values and deviations from the mean.

2. Measurements on the basic properties of geothermal brines under operating conditions, or from samples which are preserved to the extent possible. These measurements would permit a comparison between NaCl solutions and the various brines.

3. Use of a consistent set of units for the various data. Experimental values are currently published using a variety of units for temperatures, pressure, concentration and property; these must then be converted to a standard form prior to evaluation. The Standard International set of units should be used.

4. A description of any special instrumentation or materials used in obtaining the experimental values. Sodium chloride solutions chemically attack some materials at high temperatures and pressures. This can cause undesirable side reactions and interfere with measurement of the property.

5. Data on the effects of the substances (e.g., KCl, CaCl₂, CO₂) on the properties of NaCl solution. Geothermal brines are complicated solutions which consist of a large number of substances besides NaCl; these are present in amount which may significantly change a property of NaCl solution as the temperature and pressure are changed.

6. Foreign language publications with an English language abstract, and English language headings for both tables of data and for graphs. There is much delay in evaluating data when there is a need for translations.

Acknowledgment

Thanks are given to George A. Morton, Daniel J. Bradley and Susan Lepman of the Lawrence Berkeley Laboratory for their comments.

VIII. References

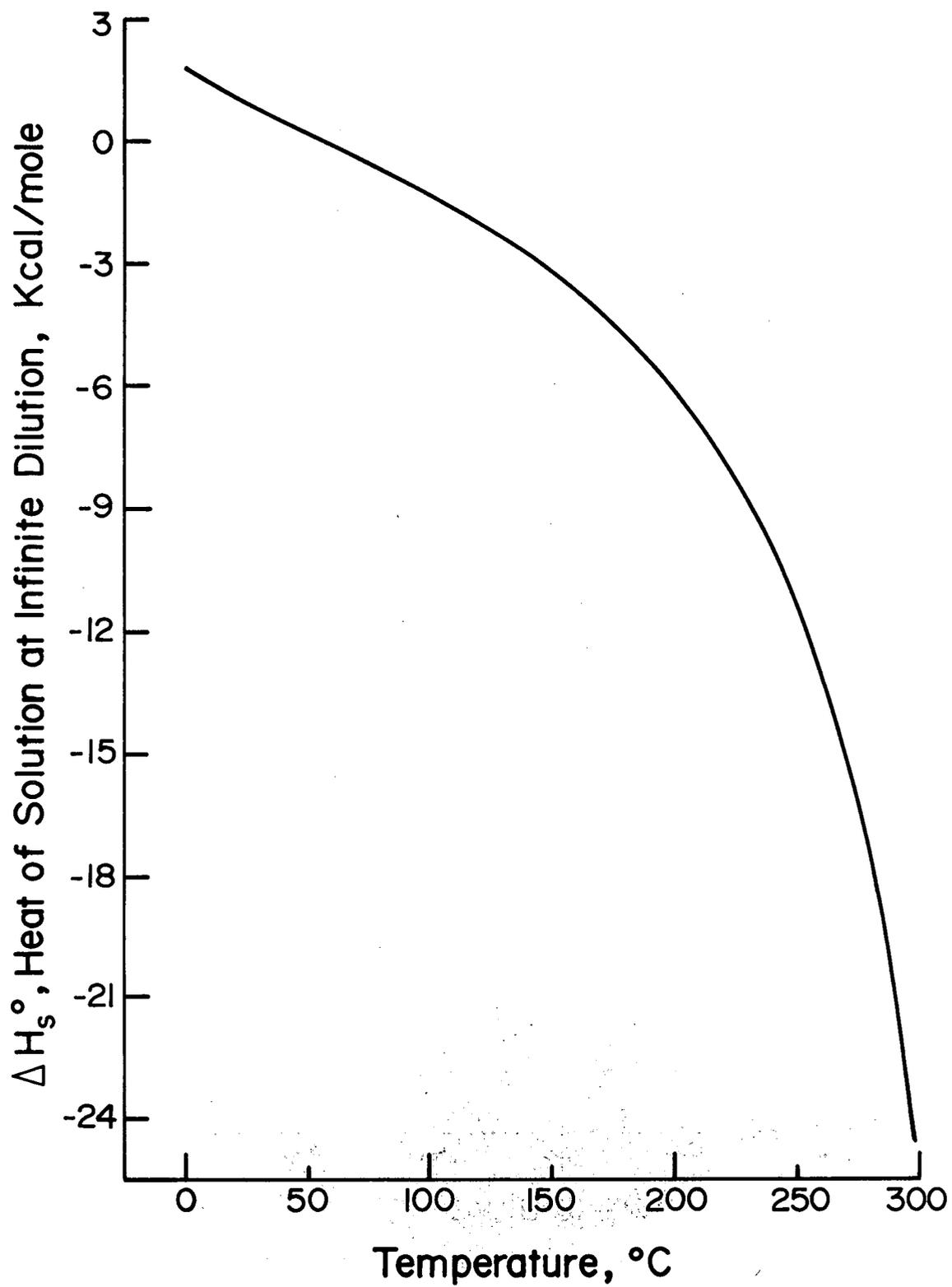
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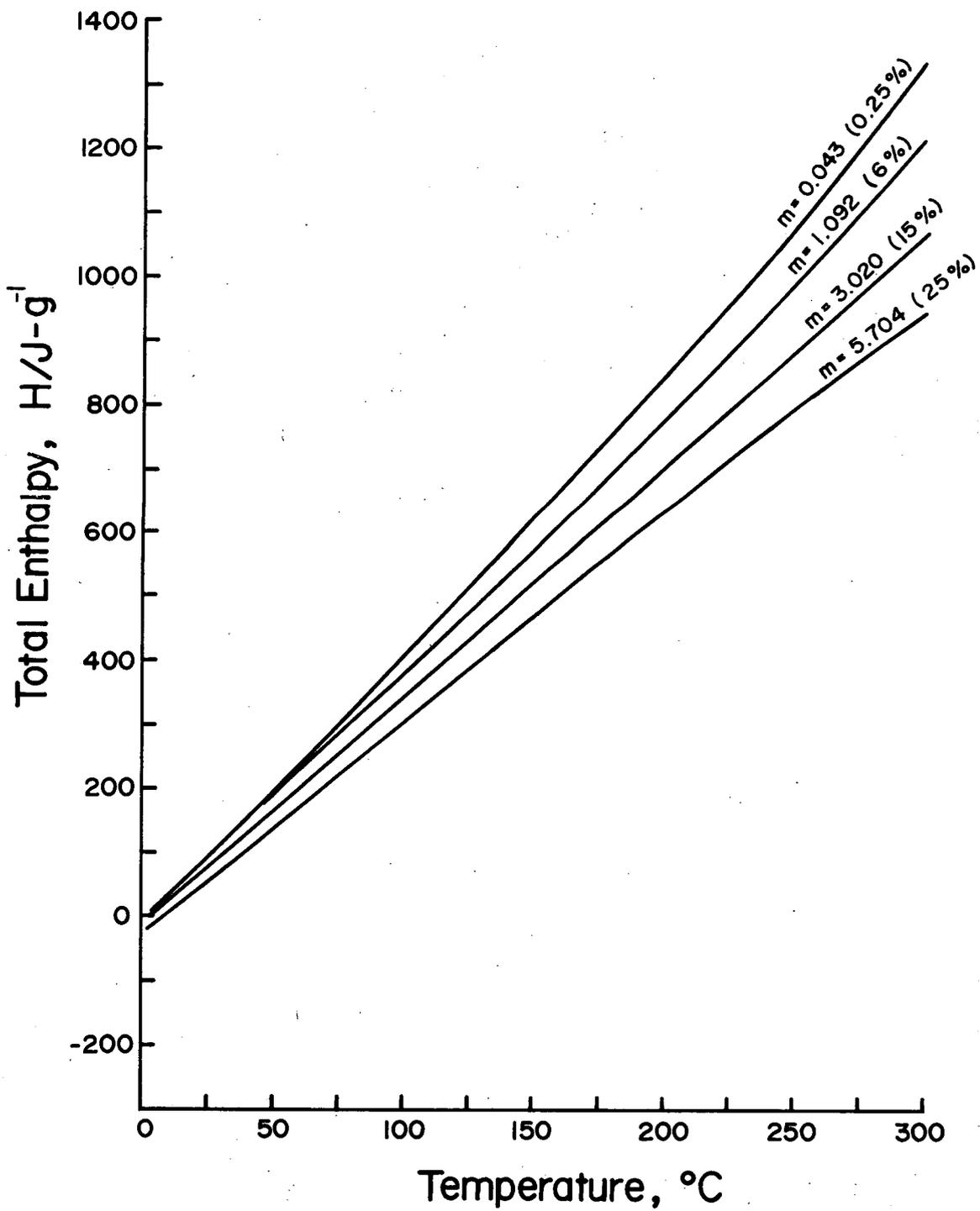
Figures

1. Heat of solution at infinite dilution versus temperature
- 2a. Total specific enthalpy of NaCl solutions versus temperature
- 2b. Total specific enthalpy of NaCl solutions versus molality
3. Specific heat capacity of NaCl solutions versus temperature
4. Viscosity of NaCl solutions from 0 to 150°C
A. 0.5m, B. 1m, C. 2m, D. 3m, E. 4m, F. 5m
5. Thermal conductivity of NaCl solutions from 50 to 300°C
6. Density of NaCl solutions from 0 to 300°C
7. Density of NaCl solutions at 20MPa pressure.



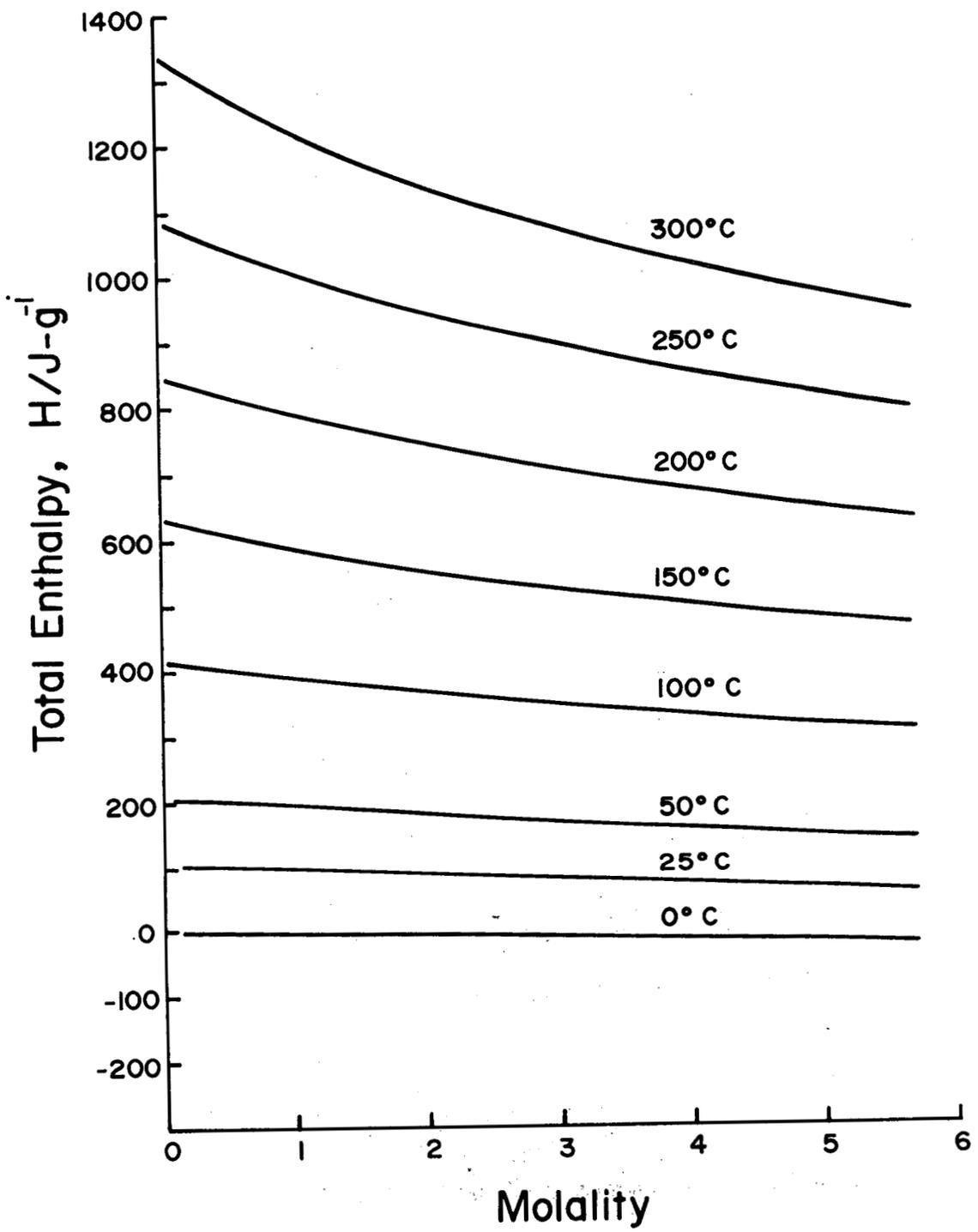
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Figure 1. Heat of solution at infinite dilution versus temperature



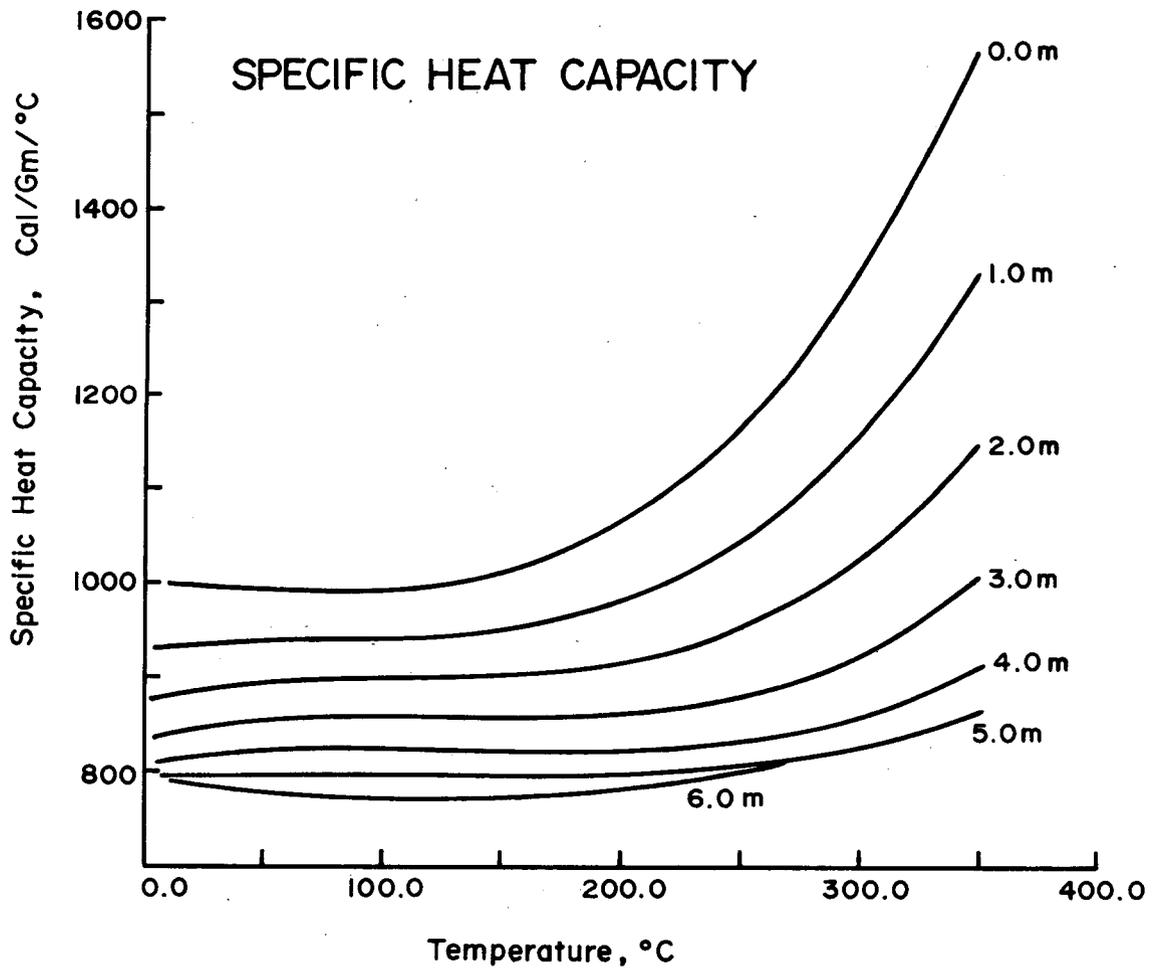
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Figure 2a. Total specific enthalpy of NaCl solutions versus temperature



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Figure 2b. Total specific enthalpy of NaCl solutions versus molality



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Figure 3. Specific heat capacity of NaCl solutions versus temperature

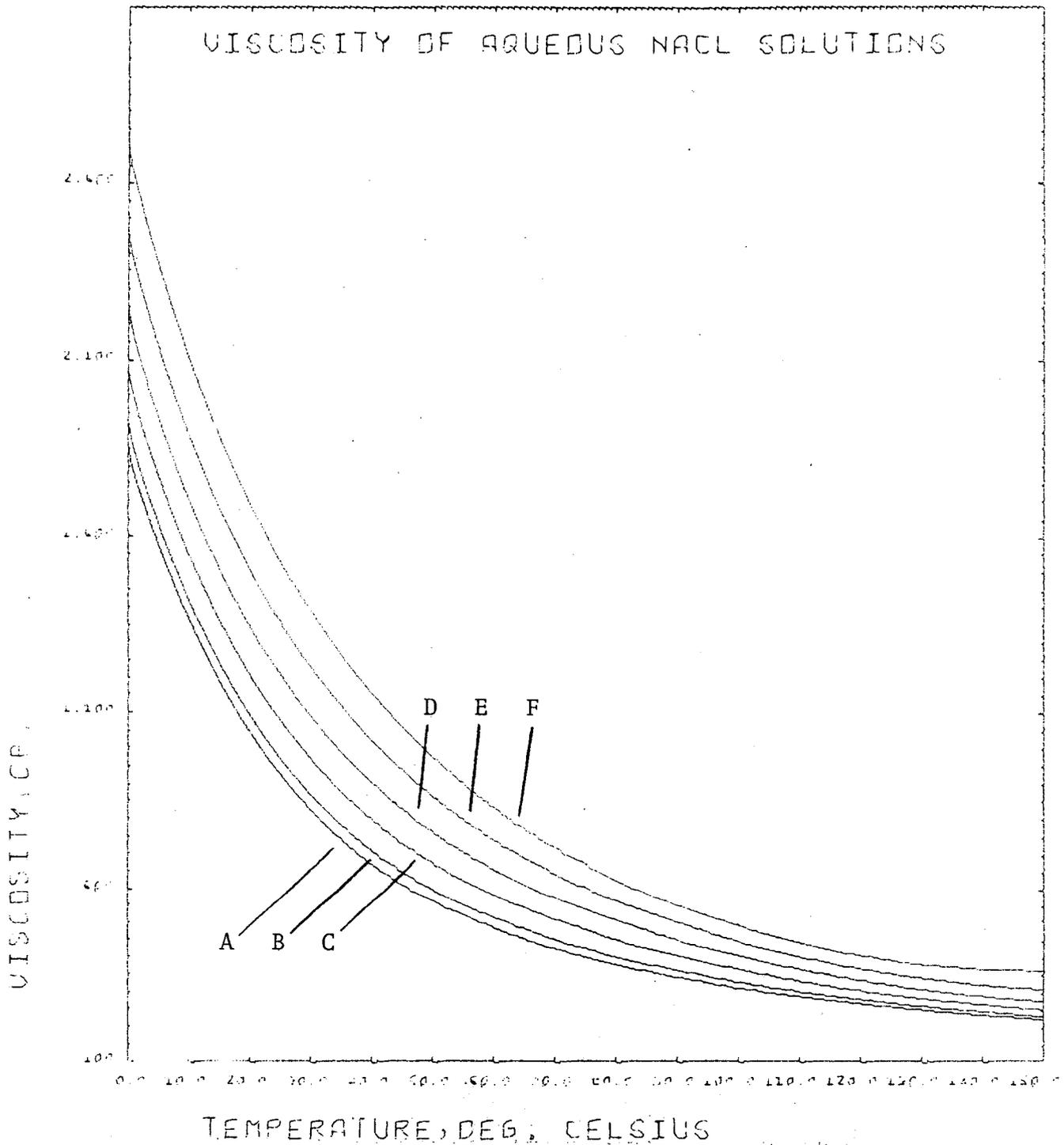


Figure 4. Viscosity of NaCl solutions from 0 to 150°C
 A. 0.5m, B. 1m, C. 2m, D. 3m, E. 4m, F. 5m

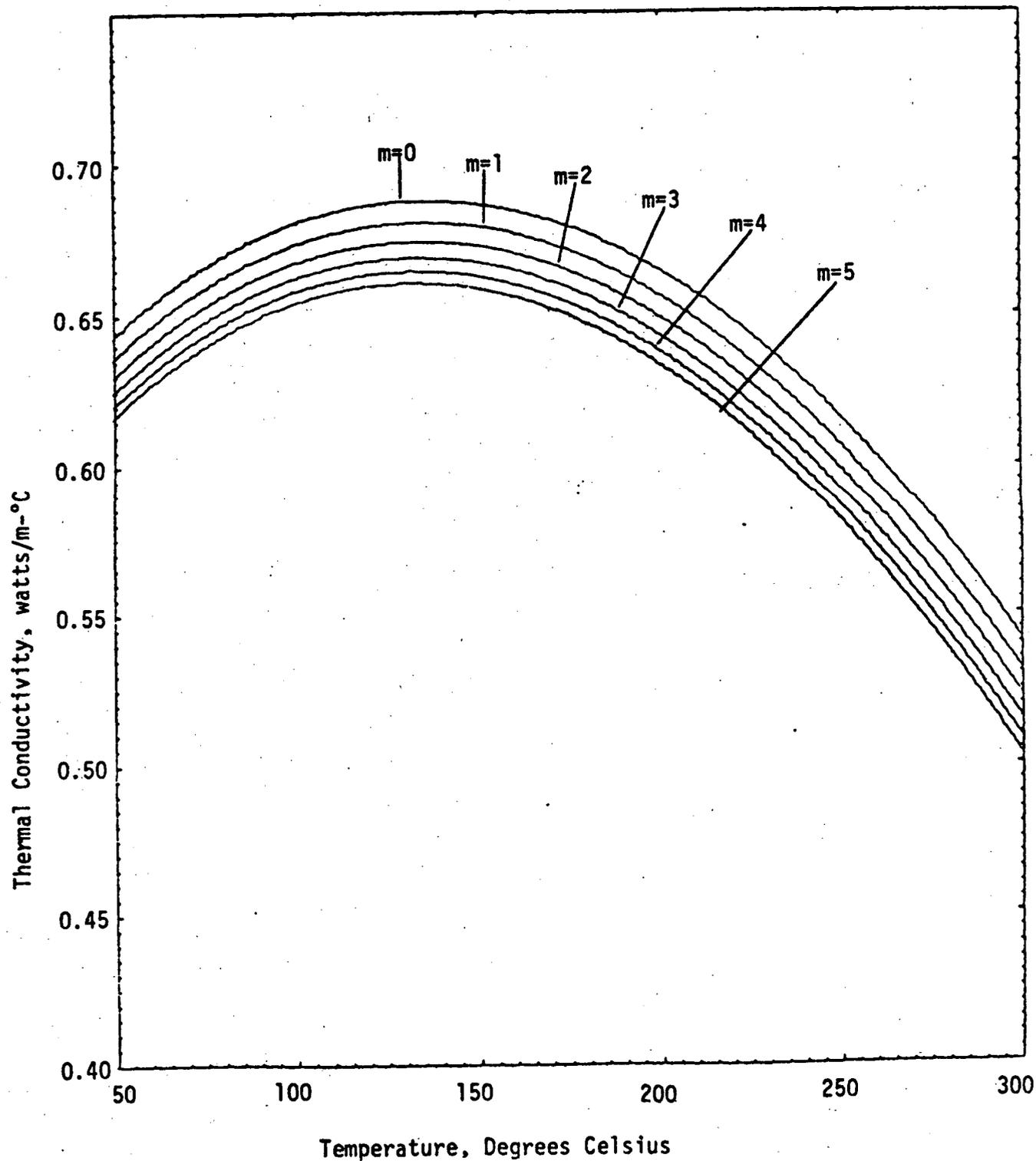


Figure 5. Thermal conductivity of aqueous NaCl solutions as a function of temperature.

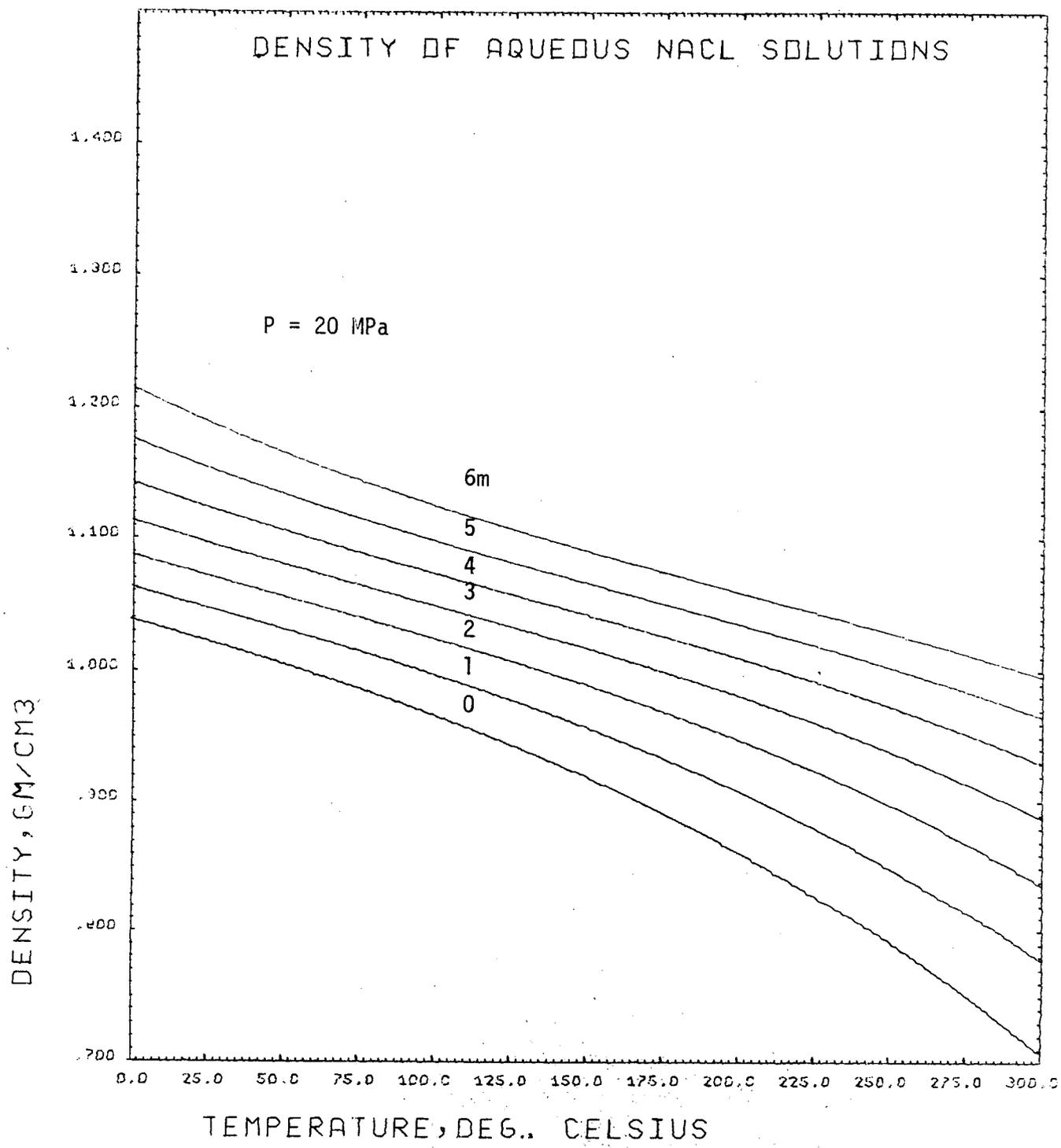


Figure 6. Density of NaCl solutions from 0 to 300°C

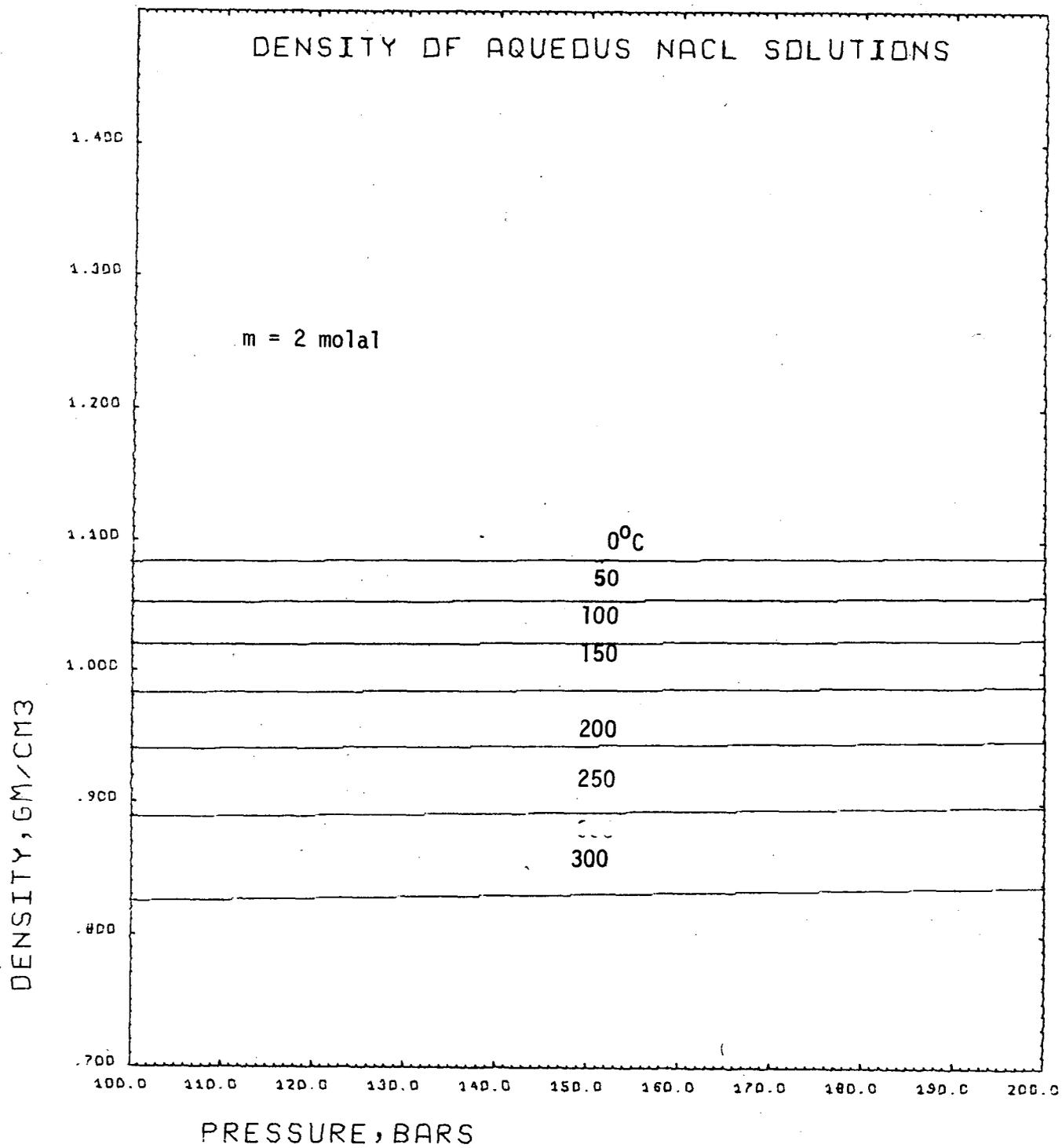


Figure 7. Density of NaCl solutions at 20MPa pressure

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