Presented at the Sixth International CODATA Conference, Santa Flavia (Palermo), Sicily, Italy, May 22-25, 1978.

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Energy and Environment Division

Basic Energy Properties of Electrolytic Solutions Database

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BASIC ENERGY PROPERTIES OF ELECTROLYTIC SOLUTIONS DATABASE

BY

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Division of Geothermal Energy

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Introduction

The research and development of both geothermal energy and of battery systems requires critically evaluated data on the thermodynamic and transport properties of aqueous electrolytes to elevated temperatures and pressures (Ref. 1). In this paper we describe the bibliographic and numerical data compilation and critical evaluation work on aqueous energy data at the Lawrence Berkeley Laboratory. The bibliography contains a listing of world-wide publications mainly covering basic electrolyte properties stored on magnetic tapes for ease of retrieval. This file is managed by the Berkeley Database Management System (BDMS) which indexes information via data elements used as key terms. Tables of data are generated from experimental values contained in the relevant publications; currently, the data tabulation covers the energy properties of aqueous NaCl solutions. The file on critically evaluated data is developed from documented experimental values and/or calculated values.

In this paper, the following definitions apply (Ref. 2, 16):

Bibliography:	An index to formal and informal publications containing information on a selected subject.
Compilation:	Systematic collection and transcription of information on a selected subject with collation and re-organization for optimal presentation to users.
Evaluation:	Critical appraisal of all available information compiled on a selected subject and derivation of consistent best or preferred values with their uncertainties.
Fact Data:	Evaluated information that is non-numerical in character.

While the larger work covers selected basic properties of aqueous electrolytes, this report is limited to data on the viscosity, density,

thermal conductivity, heat capactiy and enthalpy of NaCl solutions. More detailed information on these properties of NaCl solutions is obtained from "Viscosity of Aqueous NaCl Solutions From 0°C to 150°C" (Ref. 3), "Establishment of A Computer Database on Geothermal Properties of Aqueous NaCl, KCl and $CaCl_2$ Solutions" (Ref. 4), "The Volumetric Properties of Aqueous Sodium Chloride Solutions From 0° to 500°C at Pressures up to 2000 Bars Based on A Regression of Available Data in the Literature" (Ref. 5), "Thermal Conductivity of Aqueous NaCl Solutions" (Ref. 6), and "Thermodynamics of Electrolytes. 8. High-Temperature Properties, Including Enthalpy and Heat Capacity, With Application to Sodium Chloride" (Ref. 15).

Aqueous Electrolyte Database

The aqueous electrolyte database (AED) contains over 1000 records covering mainly publications for the time span 1929-1978 on the following major basic properties: viscosity, density, enthalpy, thermal conductivity, solubility, electric conductivity, free energy and activity. While a number of electrolytes are covered, the records largely pertain to NaCl, KCl, and $CaCl_2$. The descriptive cataloguing and indexing procedures used to encode and store the bibliographic records are those of the International Nuclear Information System (INIS) (Ref. 7). Typical bibliographic records in a condensed output format are shown in Figure 1.

The bibliographic citations in Fig. 1 contain information on the documents including author, author affiliation, title of the document, journal or other reference source and descriptors. The descriptors are taken from a thesaurus of controlled vacabulary terms, and together with other selected data elements provide for a number of indexes, e.g., author, author affiliation, subject, journal and descriptor frequency count, which

are machine-generated via our adaptation of BDMS (Ref. 7). An example of these indexes is the author-title-record number index shown in Figure 2. As can be seen, the index sample contains the author name, titles of all publications by the author in the database and record numbers of all citations listed in the database.

In summary, the AED file contains indexed and annotated references to basic properties, mainly covering the time span from 1929 to 1978. Records are added to the file on a continuing basis to include both recent and retrospective data. The BDMS management system provides the basis for data retrieval and a variety of machine-generated indexes to the documents contained in the database.

Numerical Values Databank

This databank contains experimental values for the transport and thermodynamic properties of aqueous electrolytes. The data is internally consistent in terms of parameters; Standard International (SI) units are largely employed. Where necessary, numerical values extracted from the literature are converted, for example, to molal concentration, degrees celsius and ^{12}C atomic weight basis. The file currently contains values for NaCl solutions to elevated temperatures and pressures on viscosity, density, heat capacity, enthalpy and thermal conductivity. A reference to the source of the data is included for each value, using an author short code mnemonic comprised of the last name of the first-named author together with the last two digits of the year of publication. If necessary, a letter is added after the digits when there is more than one publication in the same year for the same author, or for authors of the same name.

Correlation Equation and Smoothed Data

Correlations equations are developed for use in interpolating the experimental values over a wide range of concentrations, temperatures and pressures. They may be based on theoretical or empirical considerations with the basic idea to reproduce the experimental data as closely as possible. Correlation equations are used to generate tables of smoothed values and for machine computation.

Viscosity of NaCl Solutions

A comprehensive search of the published literature for NaCl viscosity data was made covering the time span from 1929 to 1977. All available copies of the original publications were assembled using the following main sources for literature references: The U.S. Department of Energy Technical Information Center's RECON System which includes the following databases: Energy Data Base, Water Resources Abstracts and Engineering Index (COMPENDEX); Chemical Abstracts; the International Critical Tables; and relevant journals and reports. A substantial amount of new data on viscosity was made available by Kestin and co-workers (Ref. 8, 9).

The data selected for correlation from a larger list were the reported experimental values and did not include either smoothed or calculated data. All data were converted where necessary to the ^{12}C scale of atomic weights, to the g/cm^3 basis for density, to centipoise for viscosity, from molar to molal concentrations, and from relative to absolute viscosity values. The needed water viscosity data were taken from the results of the Eighth International Conference on the Properties of Steam (Ref. 10).

The following empirical equation developed from this data was found

convenient for interpolation to 30 MPa and 150°C:

$$\eta = c_1 + c_2 \exp(\alpha_1 T) + c_3 \exp(\alpha_2 m) + c_4 \exp(\alpha_3 T + \alpha_4 m) \qquad (1)$$

where

η = viscosity, cp

T = temperature, °C

m = concentration, molality

$c_1 = 0.0495166$	$\alpha_1 = -0.06653081$
$c_2 = 0.6034658$	$\alpha_2 = 0.1447269$
$c_3 = 0.09703832$	$\alpha_3 = -0.02062455$
$c_4 = 1.025107$	$\alpha_4 = 0.1301095$

Figure 3 compares the experimental viscosity data versus that calculated from Equation (1) for temperatures to 150°C and pressures to 30 MPa, at all concentrations. Data may be interpolated with Equation (1) to a standard deviation of 1.3% over the entire temperature, pressure and concentration range.

Thermal Conductivity of NaCl Solutions

The available experimental data on the thermal conductivity of aqueous NaCl solutions to elevated temperatures and pressures is not large. Recent work published by Yusufova, Pepinov, Nikolaev and Guseinov (Ref. 6), provides additional data to 330°C. Their regression equation reproduces their data to 2% and is of the following form:

$$\frac{\lambda_P}{\lambda_{H_2O}} = 1 - (2.3434 \times 10^{-3} - 7.924 \times 10^{-6}T + 3.924 \times 10^{-8}T)S + (1.06 \times 10^{-5} - 2 \times 10^{-8}T + 1.2 \times 10^{-10}T^2)S^2 \quad (2)$$

where

S = NaCl concentration, % by weight

λ_P = Thermal Conductivity of NaCl Solutions

λ_{H_2O} = Thermal Conductivity of Water

T = Temperature, °C

The equation applies over the range 20°C to 330°C, and at concentrations between 5%w (.9m) and 25%w (5.7m) NaCl.

Additional information on thermal conductivity of NaCl solutions is contained in Reference 6; data on the thermal conductivity of water is contained in Thermophysical Properties of Matter, Vol. VII, Thermal Conductivity (Ref. 17).

Density of NaCl Solutions

Density data have been compiled to temperatures of 770°C and to pressures of 2700 bars (270 MPa) for selected NaCl solutions. Over 1300 data values are currently contained in this AED file.

A series of publications issued as preliminary steam tables containing density and volumetric data for NaCl solutions is provided by the U.S. Geological Survey (Ref. 5, 11, 12). The USGS report Bulletin 1412-C contains extensive tables of smoothed density data covering temperatures to 500°C, pressures to 2000 bars (200 MPa), and concentration of NaCl solutions to 8.0 molal (extrapolated).

A correlation expression was developed for the specific volume of aqueous NaCl solutions to 150°C, pressures to 350 kg/cm^2 (34.3 MPa), and concentrations to 25%w (5.7m). The mathematical expression developed reproduces the data to 0.15% (Ref. 13).

Enthalpy and Heat Capacity of NaCl Solutions

The aqueous electrolyte data banks contain over 850 tabulated enthalpy values for aqueous sodium chloride solutions. Over 500 of these data values represent measured experimental enthalpy changes. The remaining data are smoothed or derived data based on extrapolated standard state enthalpies at infinite dilution. The data has been converted to a common set of units and is available in the form of tables, punched cards or magnetic tape. The extraction of data on the heat capacity of NaCl solutions has begun and is expected to be available in the last quarter of 1978.

Figures 4a and 4b show the extent of the available enthalpy data. As can be seen in figure 4a, the data lies largely in the vapor saturation region below the critical point for water. Saturated vapor pressure curves plotted for several concentrations was calculated using the method and equations suggested by Haas (Ref. 12). The concentration saturation limit shown in figure 4b was calculated using the fitted correlation equation given by Potter et al. (Ref. 14) for NaCl solutions between 0 and 800°C:

$$\text{Wt. percent NaCl} = (26.218 + 0.0072T + 0.000106T^2) \pm 0.05 \text{ weight percent NaCl} \quad (3)$$

Silvester and Pitzer (Ref. 15) fit much of the available thermodynamic data on NaCl solutions to a 13 parameter equation. The computer code that

uses this equation to generate smoothed values for the thermodynamic functions was added to our database. It is expected that the smoothed correlated values for enthalpy and heat capacity of aqueous NaCl solutions based on this equation will be used in the final tabulation of the aqueous electrolyte database for NaCl.

Summary and Conclusions

In summary, a data center containing bibliographic and numerical data has been established to provide evaluated basic energy data on aqueous electrolyte solutions to elevated temperatures and pressures. Evaluated data originate from documented experimental values from which a correlation expression useful in interpolation and machine calculation is developed. Tables of smoothed values are generated from the correlation expression. The data are obtained from various sources including cooperative exchanges with other data centers.

References

1. A Recommended Program in Geothermal Chemistry, R.N. Lyon and G.A. Kolstad, eds., Department of Energy, WASH - 1344, October 1974. Available from National Technical Information Service, Springfield, VA 22161.

2. Pearlstein, S., "The Information Center As A Link Between Basic and Applied Research", CODATA Bulletin 23, May 1977. "Selected Papers Relevant to Energy", 5th International CODATA Conference, Boulder, CO, June 28-July 1, 1976.

3. Ozbek, H., Fair, J.A., Phillips, S.L., "Viscosity of Aqueous Sodium Chloride Solutions From 0-150°C", LBL-5931, Dec. 1977. Available from Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720.

4. Fair, J.A., Phillips, S.L., "Establishment of a Computer Data Base on Geothermal Properties of Aqueous NaCl, KCl and $CaCl_2$ Solutions", CODATA Bulletin 23, May 1977. "Selected Papers Relevant to Energy", 5th International CODATA Conference, Boulder, CO, June 28-July 1, 1976.

5. Potter, R.W. II, Brown, D.L., "The Volumetric Properties of Aqueous Sodium Chloride Solutions From 0° to 500°C at Pressures Up To 2000 Bars Based On A Regression of Available Data In The Literature", U.S. Geological Survey Bulletin 1421-C, 1977. Available from U.S. Government Printing Office, Washington, D.C. 20402. Stock No. 024-001-02946-4.

6. Yusufova,V.D., Pepinov, R.I., Nikolaev, V.A., Guseinov, G.M., "Thermal Conductivity of Aqueous NaCl Solutions", Injenerno Phizicheskii Jhurnal, 29 (4), 600-605 (1975).

7. Trippe, T., White, V., Henderson, F., Phillips, S., "GEODOC - The GRID Document File, Record Structure and Data Element Description", LBL-4432, Nov. 1975. Available from Lawrence Berkeley Laboratory, University of California, Berkeley, Calif. 94720.

8. Kestin, J., Khalifa, H.E., Abe, Y., Grimes, C.F., Sookiazian, H., Wakeham, W.A., "The Effect of Pressure On The Viscosity of Aqueous NaCl Solutions In The Temperature Range 20-150°C", J. Chem. Eng. Data (in press).

9. Goncalves, F.A., Kestin, J., "The Viscosity of NaCl and KCl Solutions In The Range 25-50°C", Ber. Bunsenges. Phys. Chem., 81 (11), 1156-1161 (1977).

10. Hendricks, R.C., McClintok, R.B., Silvestri, G.J., Revised International Representations For The Viscosity of Water And Steam And New Representations For The Surface Tension of Water, Lewis Research Center, NASA, Cleveland, Ohio 44135. NASA TMX-73483, Technical Memorandum (1976).

11. Haas, J.L., Jr., Physical Properties of the Coexisting Phases and Thermochemical Properties of the H_2O Component in Boiling NaCl Solutions, U.S. Geological Survey Bulletin 1421-A (1976). Available from U.S. Government Printing Office, Washington, D.C. 20402. No. 024-001-02904-9.

12. Haas, J.L., Jr., Thermodynamic Properties of the Coexisting Phases and Thermochemical Properties of the NaCl Component in Boiling NaCl Solutions, U.S. Geological Survey Bulletin 1421-B (1976). Available from U.S. Government Printing Office, Washington, D.C. 20402. No. 024-001-03022-5.

13. Rowe, A.M., Jr., Chow, J.C.S., "Pressure-Volume-Temperature-Concentration Relation of Aqueous NaCl Solutions", J. Chem. Eng. Data, 15 (1), 61-67 (1970).

14. Potter, R.W., Babcock, R.S., Brown, D., J. U.S. Geol. Survey, 5 (3), 389 (1977).

15. Silvester, L.F., Pitzer, K.S., "Thermodynamics of Electrolytes. 8. High-Temperature Properties, Including Enthalpy and Heat Capacity, With Application to Sodium Chloride", J. Phys. Chem., 81, 1822 (1977).

16. Lederer, C.M., "Development of a Computer-Based Nuclear Data Compilation - Table of Isotopes", LBL-1261, Lawrence Berkeley Laboratory, University of California, Berkeley, CA (1973).

17. Thermophysical Properties of Matter, Vol. VII, Thermal Conductivity, CINDAS, Purdue University, Lafayette, IN 47906.

Figures

Figure 1. Example printout from aqueous electrolyte database.

Figure 2. Typical printout of author index.

Figure 3. Plot of the measured experimental values for NaCl viscosity compared with those calculated from the correlation as given by Equation 1.

Figure 4. Distribution of available data on the enthalpy of NaCl solutions.

(a) The pressure-temperature surface showing vapor saturation pressures for lines of constant composition (0, and 6.0m).

(b) The temperature concentration surface showing the saturation concentration limit as a function of temperature (solid line).

POTTER 77B

TITLE- A NEW METHOD FOR DETERMINING THE SOLUBILITY OF SALTS IN AQUEOUS SOLUTIONS AT ELEVATED TEMPERATURES.

AUTHOR- POTTER, R.W.;BROWN, D.L. [GEOLOGICAL SURVEY, MENLO PARK, CALIF. (USA)].

BABCOCK, R.S. [WESTERN WASHINGTON STATE COLLEGE, BELLINGHAM, WASH. (USA). DEPT. OF GEOLOGY].

REFERENCE- J. RES. U.S. GEOL. SURV., V. 5 (3), P. 389-395(1977).

DESCRIPTORS- EMPIRICAL EQUATIONS; GRAPHS; TABLES; SOLUBILITY; MEASURING INSTRUMENTS; BOMB SOLUBILITY; POTASSIUM CHLORIDES; SODIUM CHLORIDES; WATER.

1033

VARGAFTIK 75

PHYSICAL CHEMISTRY/AQUEOUS ELECTROLYTE

TITLE- TABLES ON THE THERMOPHYSICAL PROPERTIES OF LIQUIDS AND GASES.

AUTHOR- VARGAFTIK, N.B.

REFERENCE- TABLES ON THE THERMOPHYSICAL PROPERTIES OF LIQUIDS AND GASES. 2ND, HEMISPHERE PUBLISHING CORPORATION, WASHINGTON, D.C., 1975, 758 P.. TRANSLATED BY Y.S. TOVLOUKIAN, CINCAS, PURDUE UNIV., LAFAYETTE, IND..

DESCRIPTORS- EMPIRICAL EQUATIONS; GRAPHS; TABLES; DENSITY; THERMAL CONDUCTIVITY; VISCOSITY; HEAT CAPACITY; SILICATES; BARIUM CHLORIDES; CALCIUM CHLORIDES; HYDROCHLORIC ACID; LITHIUM BROMIDES; LITHIUM CHLORIDES; LITHIUM IODIDES; MAGNESIUM CHLORIDES; MAGNESIUM SULFATES; NITRIC ACID; POTASSIUM BROMIDES; POTASSIUM CARBONATES; POTASSIUM CHLORIDES; POTASSIUM FLUORIDES; POTASSIUM IODIDES; POTASSIUM NITRATES; POTASSIUM SULFATES; SODIUM BROMIDES; SODIUM CARBONATES; SODIUM CHLORIDES; SODIUM IODIDES; SODIUM SULFATES; SULFURIC ACID; WATER.

Fig. 1

C.;
RECORD NUMBER 758
SOLUBILITY AND THERMODYNAMIC FUNCTIONS FOR A 3-2 SALT, SAMARIUM SULFATE, IN WATER AND SULFURIC ACID SOLUTIONS AT TEMPERATURES TO 35. C;
RECORD NUMBER 759

SMAEV, V.N.
DENSITY, VISCOSITY AND ELECTRICAL CONDUCTIVITY OF SEAWATER AT TEMPERATURES UP TO 30 -35. C;
RECORD NUMBER 880

SMITHERMAN, A.
MODELS HAVING THE THERMODYNAMIC PROPERTIES OF AQUEOUS ALKALINE EARTH HALIDES AND SODIUM CHLORIDE-MAGNESIUM CHLORIDE MIXTURES;
RECORD NUMBER 316

SMITH, D.E.
HEATS OF MIXING. II. TEMPERATURE DEPENDENCE OF AQUEOUS ELECTROLYTES WITH A COMMON ION;
RECORD NUMBER 713

SMITH, D.G.
THE MEASUREMENT OF SOLVENT ISOTOPE EFFECT WITH CATION SELECTIVE GLASS ELECTRODES;
RECORD NUMBER 622

SMITH, H.T.
APPARENT MOLAL VOLUMES AND EXPANSIBILITIES OF ELECTROLYTES IN DILUTE AQUEOUS SOLUTION;
RECORD NUMBER 85

SMITH, N.O.
SOLUBILITY AND PARTIAL MOLAR PROPERTIES OF HELIUM IN WATER AND AQUEOUS SODIUM CHLORIDE FROM 25 TO 100 DEG. AND 100 TO 600 ATMOSPHERES;
RECORD NUMBER 89

SMITH, R.P.
THE BOILING POINT ELEVATION. II. SODIUM CHLORIDE 1.05 TO 1.0 M AND 60 TO 100 DEGREES;
RECORD NUMBER 982
THE BOILING POINT ELEVATION. III. SODIUM CHLORIDE 1.0 TO 4.0 M AND 60 TO 100 DEGREES;
RECORD NUMBER 983

SMITH, W.T.
ELECTROMOTIVE FORCE MEASUREMENTS IN AQUEOUS SOLUTIONS AT ELEVATED TEMPERATURES. II. THERMODYNAMIC PROPERTIES OF HYDROCHLORIC ACID;
RECORD NUMBER 108
ELECTROMOTIVE FORCE STUDIES IN AQUEOUS SOLUTIONS AT ELEVATED TEMPERATURES. I. THE STANDARD POTENTIAL OF THE SILVER-SILVER CHLORIDE ELECTRODE;
RECORD NUMBER 109

SMOLYAKOV, B.S.
MAXIMUM EQUIVALENT CONDUCTIVITY OF AQUEOUS SOLUTIONS OF LI+1, NA+1, K+1, RB+1, CS+1, AND

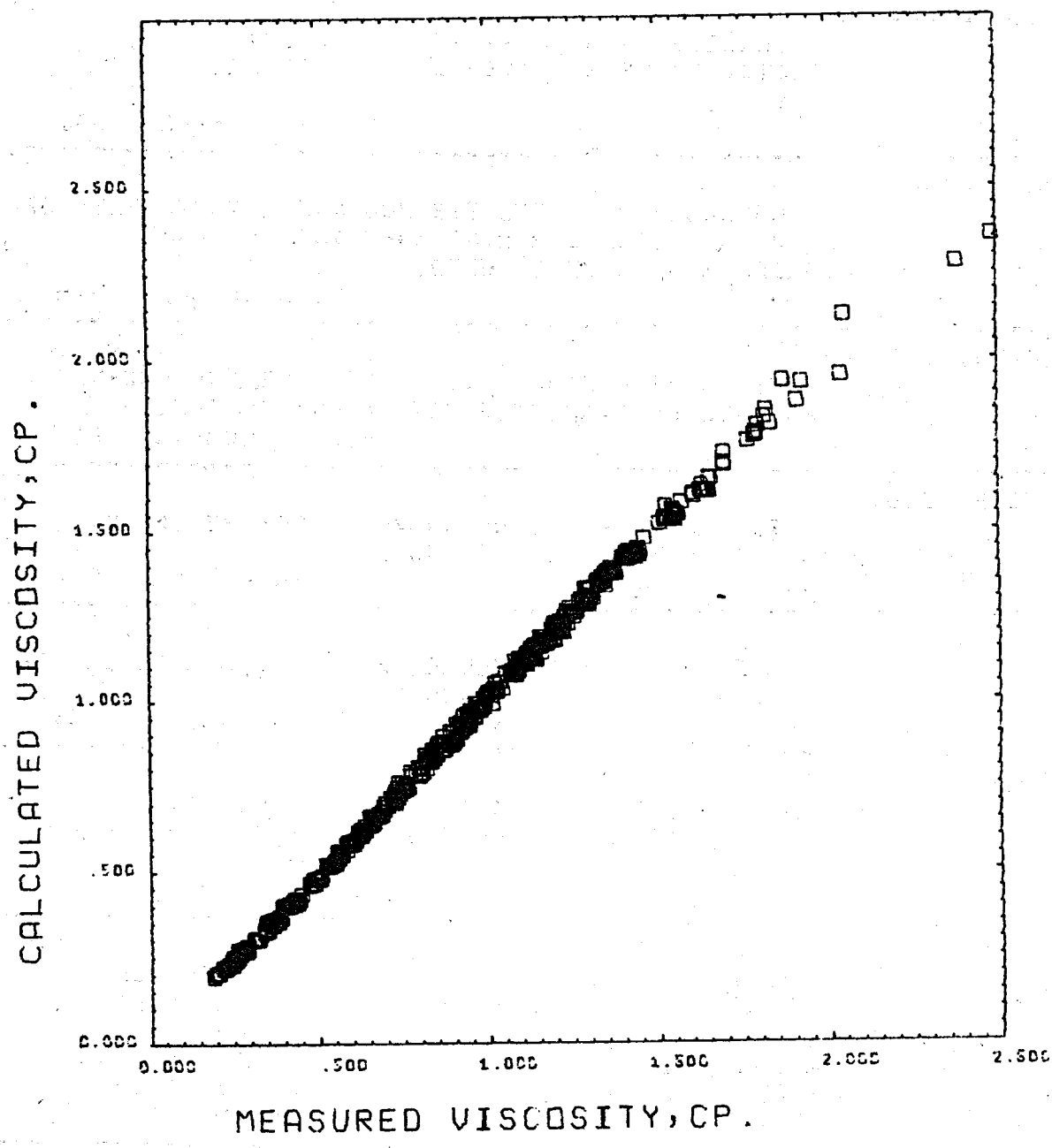
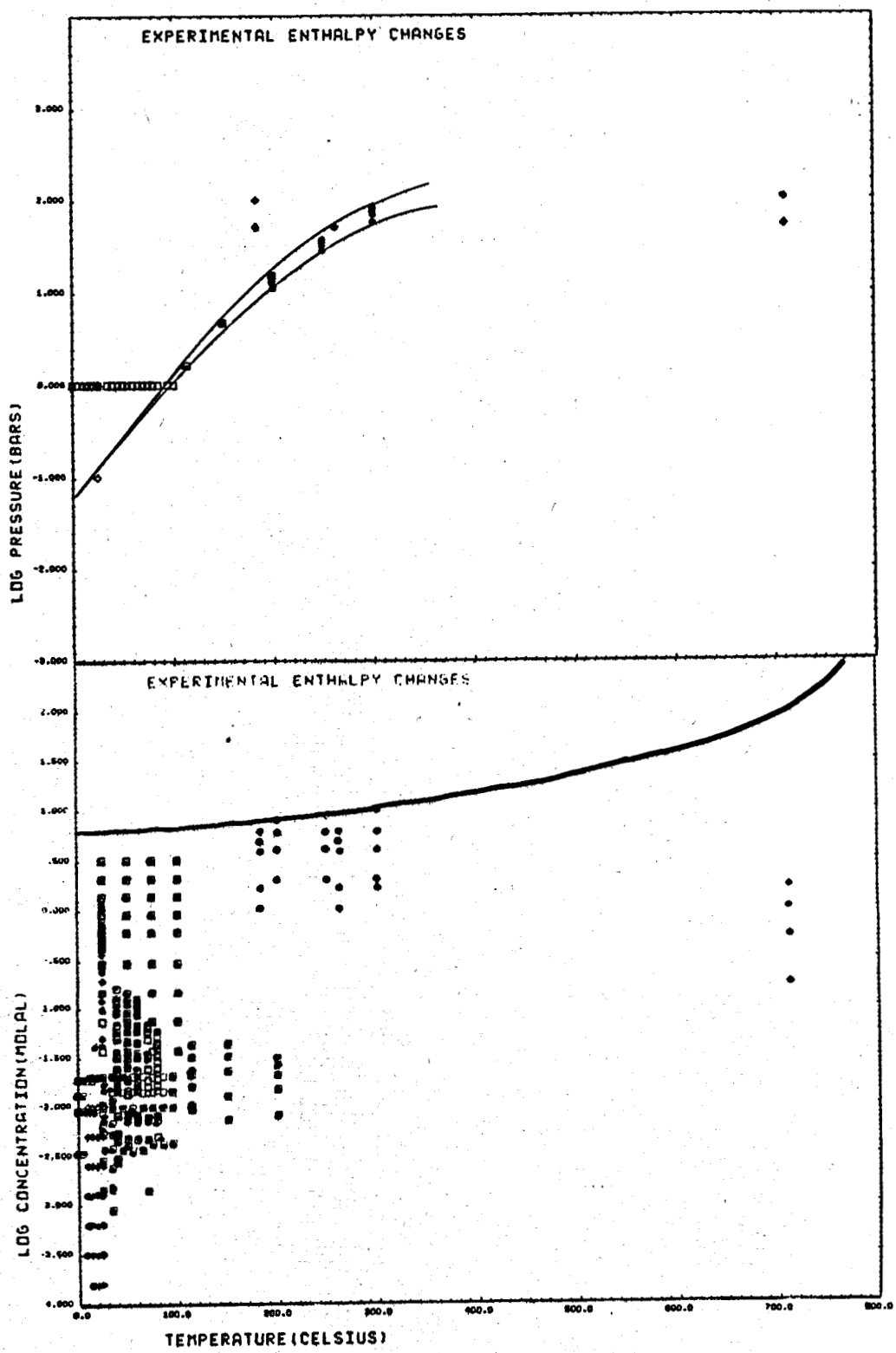

2.500
2.000
1.500
1.000
.500
0.000
CALCULATED VISCOSITY, CP.
0.000
.500
1.000
1.500
2.000
2.500
MEASURED VISCOSITY, CP.

Fig. 3



XBL 788-10126

Fig. 4