

NUMERICAL FITS OF THE PROPERTIES OF LITHIUM-BROMIDE WATER SOLUTIONS

M.R. Patterson, Ph.D.

H. Perez-Blanco, Ph.D.

ASHRAE Member

ABSTRACT

The modeling and design of advanced absorption cycles calls for numerical fits of the working fluids' properties. The numerical fits can be readily implemented in computers. Recently, a worldwide search of available properties of absorption fluids was completed. The present work presents numerical fits of the thermodynamic and transport properties of the lithium bromide water solutions uncovered by the search. The range of existing correlations is extended, and the accuracy of the existing fits improved slightly. A simple test for the thermodynamic consistency of the vapor pressure fit is presented and carried out at one isotherm, with good results.

INTRODUCTION

High efficiency, advanced absorption cycles for heating and cooling are being developed by various institutions (Devault 1987). An essential support activity to these developments has been the computer modeling of absorption cycles. Modeling and design efforts call for the properties of the working fluids. Although charts and tables are useful forms in which the data can be presented, numerical fits are the most convenient for computer modeling.

The need for compiling and assessing the quality of the available property data was recently recognized by the U.S. Department of Energy, and a worldwide search has been completed by Macriss (1986, 1987). Computer routines are needed that accurately summarize the thermodynamic and transport properties of the working fluids of most interest. In this work, the recommended values (Macriss 1986, 1987) for the properties of the most commonly used solution, namely lithium bromide (LiBr) water, are fitted. Previous work on fitting the vapor pressure and the enthalpy of the solution was completed by McNeely (1979) and also by Herold (1987). The correlations of the present work cover a wider range than those completed before. Fits of density, thermal conductivity, viscosity, and surface tension are also presented.

These new computer routines attempt to preserve as much of the original accuracy as possible in fitting the data. Since polynomials are employed for all the properties, the number of coefficients was varied for each property in order to obtain the best possible fit. The criteria used to identify the best possible fit are described in the text, but enough accuracy has been built in to preserve the quality of the original data.

Because these results are being expressed as stand-alone computer routines, features are added that are difficult to apply in hand calculations or in straightforward implementations of formulas for the properties. In particular, for the LiBr water solution, the salt LiBr tends to crystallize at low temperatures and high salt concentrations. In the implementations of computer routines for the properties given below, tests are performed during execution to determine whether the state point is within the crystalline envelope or not. It is probably safe to say that most heat pump cycle designers have access to a digital computer, especially a

*M. R. Patterson is a member of the Computing and Telecommunications Division and H. Perez-Blanco is a research staff member for the Efficiency and Renewables Research Section of the Energy Division of Oak Ridge National Laboratory. Research sponsored by the Office of Buildings and Community Systems, U.S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

microcomputer. The current study makes available reliable computer codes that have been designed for each property and checked for accuracy. These codes are available on an off-the-shelf basis for a limited set of materials and should help standardize the calculation of heat pump performance.

ENTHALPY FIT

The enthalpy of the solution is fitted over the whole range of the data presented by McNeely for lithium bromide concentrations ranging from 0 to 70% and for dew points ranging from 4.4 to 121°C (40 to 250 F). This work is an extension of that done by McNeely, because the range of variables has been expanded and a modest increase has been made in the accuracy of the fit.

McNeely presents tabular values of the enthalpy, h , of a LiBr-water solution for a set of concentrations of 0, 10, 20, 30, 35, 40, 45, 50, 55, 60, 65, and 70% LiBr and for solution temperatures of 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, and 180°C (32 to 356 F). This region is large enough to include some solution conditions where crystallization occurs, and these places were flagged with a special value to exclude them from the fit. For the remaining entries, an extension of the form used by McNeely was applied. The form is given by the formula

$$h(X,T) = \sum_{i=0}^K \sum_{j=0}^2 A_{ij} X^i T^j \quad (1)$$

where the upper limit, K , for McNeely's work was $K = 4$ on the sum for the powers of concentration, X . A study of the data indicates that this form is appropriate and that the temperature dependence is well covered by the quadratic terms in temperature. The form was extended by increasing the upper limit, K , on the concentration terms to a value of 5 rather than 4. The region of temperature-concentration space covered by the fit was increased work from the limits imposed by McNeely:

$$16 (60.8) < T < 165 (329)^{\circ}\text{C (F)} \text{ and} \\ 45 < X < 70\%$$

to the values used in the present work:

$$0 (32) < T < 180 (356)^{\circ}\text{C (F)} \text{ and} \\ 0 < X < 70\%$$

The number of points included from the table by McNeely is 79. The present work included 212 points after removal of the crystallization region.

The fits were made using an available least squares fit routine called LINLSQ (Heath 1980). This version has been modified to return the standard deviation of fit for the enthalpy, the standard deviations for the coefficients A_{ij} , the scaled co-variance matrix, a printout of the input data, calculated fit, and the residual for each point. The standard deviation of the fit is defined as the square root of the quantity of the sum of the squares of the differences between the calculated values and the data points, divided by the number of data points minus the number of coefficients. The standard deviation compared to the mean value of the fitted data is the figure of merit adopted in this work to evaluate the quality of the fit.

Using the above program, the results shown in Table 1 were obtained. Note that the mean value of the enthalpy in this region is 252 kJ/kg, so that the standard deviation is less than 0.5% of the mean enthalpy.

In order to compare the present results with those of McNeely, two more runs were made. The first run was made in a manner analogous to the above with $K = 5$, except that the region of X, T space was restricted to that covered by McNeely. For the second run, the coefficients

obtained by McNeely were programmed to calculate the enthalpy at the 79 points where data are available in the restricted region. As the enthalpy was calculated, the residue was evaluated at each point and the standard deviation of fit was determined. The results are given below:

	Standard Deviation (79 points)
McNeely	0.48
Current Work	0.33

The high quality of McNeely's work is apparent, especially considering that much of his work was done with a hand calculator.

The 18 fitted coefficients corresponding to $K = 5$ are given in Table 2. These coefficients are built into the Fortran function HLIBR(X,T) given in the Appendix and are used for calculating the enthalpy of LiBr water. The value of X in the first argument should be supplied as the concentration of LiBr in the solution in percent. The second argument, T, is the solution temperature in °C. The resultant enthalpy, HLIBR, is calculated in units of kJ/kg.

DEW POINT AND VAPOR PRESSURE

The dew point and solution temperatures are extracted from McNeely's work. The available data for the solution temperature range from 4.4°C (40 F) in steps of 22.2°C (40 F) to 182.2°C (360 F), and the concentration ranges from 0% in steps of 5% to 50% and from 50% in steps of 1% to 70%. Blank entries are made where the salt is crystallized or where the data are not available. These data were entered into the computer and a series of fits were completed in a similar fashion as was done for the enthalpy. The form of the polynomial was more complicated than that used by McNeely because the temperature terms were generated through the quadratic, as had been done for the enthalpy. Terms in the concentration were generated for the quadratic ($K = 2$), cubic ($K = 3$), and higher terms through $K = 5$. The following form was used to calculate the dewpoint temperature:

$$T_{DP}(X,T) = \sum_{i=0}^K \sum_{j=0}^2 B_{ij} X^i T^j \quad (2)$$

A total of 212 points were fitted. The fitting program was run for the values of K presented in Table 3, which also shows the standard deviation for the fit. Since the mean dew point temperature is 53.2°C (127.9 F), the standard deviation for the best case ($K = 5$) is about 0.2% of the mean. The coefficients for the case $K = 5$ are given in Table 4.

The vapor pressure of the water arising from the LiBr water solution can be calculated from the dew-point temperature. The relationship is given by McNeely:

$$\log_{10} P = k_0 + k_1/T + k_2/T^2 \quad (3)$$

where

- P = partial pressure (psia)
- T = water vapor temperature (*R = F + 459.7)
- $k_0 = 6.21147$
- $k_1 = -2886.373$
- $k_2 = -337269.46$

A function subprogram named PRESS(X,T) that incorporates the dew-point temperatures described above to calculate the vapor pressure has been written. The function is given in the Appendix and takes as input the concentration X in percent LiBr and the temperature T in °C. In turn, it calculates the dew point and converts the dew point to pressure in kPa via the formula given above.

The same restrictions apply to the partial pressure as to the dew point: the point (X,T) in phase space must lie in the region where the solution is noncrystalline and has known properties. Otherwise a value of zero is returned and a warning message is written to the user in one of the following forms:

"Temperature higher than table allows" or
 "Point X,T in freezing region."

TRANSPORT PROPERTIES

Thermal conductivity data for LiBr-H₂O solution are available from the work of Tadashi Uemura (1975) in Japan, translated in ORNL/TR-87/9. These data are given as his Table 4 and span a region of temperature and concentration that avoids crystallization. The regions defined above for dew point were used to delineate the region of crystallization.

Tabular values for the conductivity that were used in the fit include 143 points. The best fit, having the smallest standard deviation, occurred for the value K = 4 rather than for the highest value of K. There was very little difference in the standard deviation values for values of K from 2 through 5, as can be seen from Table 5. The values of the coefficients for the case where K = 4 are given in the function subprogram TCON, included in the appendix.

The mean value of the thermal conductivity is 0.5172 W/m·°C (0.4447 kcal/(h·m·°C)), so the standard deviation of 2.081×10^{-3} W/m·°C (1.789×10^{-3}) for K = 4 is less than .4% of the mean.

The viscosity data made available in the Tadashi Uemura reference are used in the fit developed below for viscosity of lithium bromide-water solutions. These viscosities are given for concentrations from 5 to 60 wt % and for temperatures from 0 to 90°C. These data include about 120 data points outside the crystallization region, sufficient to extract the needed coefficients in the fit. The form of the fit was taken to be

$$\eta_u(X,T) = \sum_{i=0}^K \sum_{j=0}^2 E_{ij} X^i T^j,$$

in which the temperature dependence is carried by three temperature terms for each power of the concentration. The concentration dependence is carried by K+1 terms for any given value of the temperature.

The fits obtained as a function of K yielded the standard deviations in Table 6. The smallest standard deviation occurs for the case of K = 5. In fact, the fit improves dramatically from the K = 2 case through the case for K = 5. The mean of the 119 data points is 1.970 c.p., yielding a value of 5.84% for the standard deviation of σ_{η_u} in the best case, K = 5. The 18 coefficients for this best case are given in the function VISCOS(X,T) in Appendix E.

Again using the data quoted by Uemura, a similar form was assumed for the specific mass:

$$m = \sum_{i=0}^K \sum_{j=0}^2 F_{ij} X^i T^j$$

Fits to this form were carried out for the available data, yielding the results given in Table 7. Note that the minimum scatter, $\sigma_m = 1.02 \times 10^{-3}$, occurs for the case K = 4. The 15 coefficients (4+1)*3 are built into the function SPMASS(X,T) in Appendix F. The mean value of the specific mass is 1.339 kg/l so that the percentage variation in one standard deviation is $\sigma_{m_u}/\langle m \rangle$, $100 = 0.08\%$ representing one of the best fits in this series.

The surface tension data given by Uemura, 216 points from his Table 3, were fit with a straightforward form that recognizes the more complicated dependence of the surface tension on concentration than on temperature.

$$\sigma_{st} = \sum_{i=0}^K \sum_{j=0}^2 G_{ij} X^i T^j$$

The standard deviation of the function from the input tabular values of surface tension for various values of K are summarized in Table 8. Although the scatter is the same for cases

K = 4 and K = 5, the case K = 4 was chosen to represent the surface tension by Occum's razor, i.e., that case requires fewer coefficients to represent the data than does the K = 5 case. These coefficients are given in Appendix G, which contains the function STEN(X,T). The mean value of σ_{st} is 77.69 dyn/cm, making the percentage equivalent to one standard deviation be $0.259/77.69 \cdot 100 = 0.33\%$.

CHECK OF THE VAPOR PRESSURE FIT

The vapor pressure fit was done by fitting dew-point data and then calculating the vapor pressure from the dew point. The ratio of the standard deviation to the mean value of the data was employed as the criteria defining the overall quality of the fit. An additional check of the thermodynamic consistency and accuracy of the pressure fit is done here.

The check is based on the rigorous relationship among the activity coefficient of the water in solution and the heat of vaporization of the water as a function of temperature given by Reid (1960). This relationship is derived by Reid, so it will not be presented here. The derivation rests on the equality of the chemical potentials in the vapor and liquid phases as salt is added to the water. The derivation is valid only for the case of a nonvolatile absorbent. A salient point of the relationship is that the heat of vaporization of only the water is required, as opposed to the heat of vaporization from the solution. This feature greatly simplifies the check. The following equality was used

$$(\ln a) (T_b) = - \int_{T_o}^{T_b} (\Delta H/RT^2) dT \quad (4)$$

where:

- a - water activity,
- T_b - solution boiling point,
- T_o - dew point,
- ΔH - heat of vaporization of water,
- R - universal gas constant.

The vapor pressure and the activity at a constant solution temperature of 60°C (140 F) are shown vs. the salt concentration in Figure 1. As the salt concentration increases, the activity decreases. The natural logarithm of the activity is shown in Figure 2, calculated by the relationship presented above and also from the values of Figure 1. There is close agreement over the whole range of concentration. Table 9 shows the values of the natural log of the water activity calculated by both methods.

CONCLUSION

Seven computer routines have been described in this report. Each routine calculates a different property of the LiBr-water solution. The seven properties are enthalpy, dew point, vapor pressure, thermal conductivity, density, viscosity, and surface tension. Vapor pressure and enthalpy have been fit in the past by such investigators as McNeely (1979) and Moran (1987). Our contributions are, first, to extend the range of the input variables to cover all of the known data for noncrystalline regions and, second, to obtain more accurate fits to the available data than those that were available previously. A check of the thermodynamic consistency of the vapor pressure fit was completed, and the results were found satisfactory.

Our fits to the data were effected on a microcomputer using locally available least squares routines. Scatter in the residuals is quoted in the body of the report, and it is less than 0.5% of the mean value of the property, in the case of enthalpy, dew-point temperature, thermal conductivity, density, and surface tension. Direct comparisons of the vapor pressure are not readily available, but its accuracy should correspond to the exponential of the dew point. Listings of the routines are presented in the Appendix.

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APPENDIX A

ENTHALPY OF LiBr-H₂O SOLUTION

The routine HLIBR(X,T) is a double precision function subprogram that takes as its two double precision arguments X, the percent LiBr in the solution, and T, the temperature in °C of the solution. The function then returns the solution enthalpy in kJ/kg. There are two error messages. The first is triggered if the temperature sent in is higher than is allowed in the table and generally means that this enthalpy has not yet been measured. The second error message is invoked if the point (X,T) is within the crystallization region for this salt solution.

The standard deviation of the calculated values produced by HLIBR is about 1.01 kJ/kg as compared to the input values that have been measured for this solution. Since the mean value the enthalpy over the range of interest is about 252 kJ/kg, the accuracy of the routine is about 0.4% on the average and should be adequate for most design calculations.

```
DOUBLE PRECISION FUNCTION HLIBR(X,T)
C      4/27/87-2/18/88
C      THIS FUNCTION HLIBR YIELDS THE ENTHALPY (kJ/kg) OF A LITHIUM BROMIDE
C      -WATER SOLUTION AT X=PERCENT LIBR CONCENTRATION
C      AND T=TEMPERATURE (DEG C)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DOUBLE PRECISION A(18),X,T,XN(7),TN(7),XUNKN(4),TUNKN(4)
      DATA KUP/6/,A/
1     1.134125D+00,-4.800450D-01,-2.161438D-03, 2.336235D-04,
2     -1.188679D-05, 2.291532D-07, 4.124891D+00,-7.643903D-02,
3     2.589577D-03,-9.500522D-05, 1.708026D-06,-1.102363D-08,
4     5.743693D-04, 5.870921D-05,-7.375319D-06, 3.277592D-07,
5     -6.062304D-09, 3.901897D-11/,
8     XN/57.5,62.5,62.5,67.5,67.5,100.0,100.0/,
9     TN/ 0.0,10.0,40.0,50.0,90.0,100.0,180.0/,
A     XUNKN/ 0.0, 37.5, 51.5, 60.5/,
B     TUNKN/126.7,137.8,160.0,182.2/
      HLIBR=0.0D0
C      CALCULATE FREEZING CONCENTRATION XSTAR AT TEMP T
      DO 100 N=2,7
      IF(T.GT.TN(N))GO TO 100
```

```

IF (XN(N).EQ.XN(N-1))THEN
  XSTAR=XN(N)
ELSE
  XSTAR=XN(N-1)+(T-TN(N-1))/(TN(N)-TN(N-1))*(XN(N)-XN(N-1))
ENDIF
IF (X.GE.XSTAR)GO TO 110
GO TO 130
100 CONTINUE
WRITE(*,('' TEMPERATURE HIGHER THAN TABLE ALLOWS,T='',
1      F10.2)')T
GO TO 130
C POINT X,T IN FREEZING REGION
110 WRITE(*,('' POINT X,T IN FREEZING REGION, X,T='',2F10.2)
1      )')X,T
GO TO 999

130 DO 140 N=2,4
IF(T.GT.TUNKN(N))GO TO 140
IF (XUNKN(N).EQ.XUNKN(N-1))THEN
  XSTAR=XUNKN(N)
ELSE
1      XSTAR=XUNKN(N-1)+(T-TUNKN(N-1))/(TUNKN(N)-TUNKN(N-1))*
      (XUNKN(N)-XUNKN(N-1))
ENDIF
IF (X.LE.XSTAR)GO TO 150
GO TO 120
140 CONTINUE
C POINT X,T IN UNKNOWN REGION
150 WRITE(*,('' POINT X,T IN UNKNOWN REGION, X,T='',2F10.2)
1      )')X,T
GO TO 999
C
120 XK=1.0D0
DO 220 K=1,KUP j^@^@^@^@^@ 1 IF(K.GT.1)XK=X*XK
HLIBR=HLIBR + XK * ( A(K) + T* (A(K+KUP)+T*A(K+2*KUP)) )
220 CONTINUE
999 RETURN
END
C
C
C

```

APPENDIX B

DEW-POINT TEMPERATURE FOR LiBr-H₂O SOLUTION

The function for dewpoint temperature of the LiBr-H₂O is also a double precision function having two arguments that are each double precision: X, the LiBr concentration in percent, and T, the temperature in °C. The value that is returned to the calling program is a double precision number. The accuracy of the fit is reflected in the standard deviation of the fit, which is about 0.269 °C, which amounts to about 0.2% of the mean value of 127.9 °C.

If the temperature is higher than any given in McNeely's table, a message is generated saying "temperature higher than table allows, T = ____." If the temperature and concentration are in a region that crystallization occurs, the error message is "point X,T in freezing region, X,T = ____." A zero value of the dew-point temperature is returned in either of these cases.

```

DOUBLE PRECISION FUNCTION TDEW(X,T)
C DATA SOURCE P420 OF MCNEELY, THERMO PROP OF AQ. SOLN OF LIBR
C PH-79-3 NO 3
C ADAPTED FROM HLIBR(X,T) 4/27/87-4/30/87 ON 5/15/87-5/19/87
C THIS FUNCTION TDEW YIELDS THE DEWPOINT (DEG C) OF A LITHIUM BROMIDE

```


WATER VAPOR PRESSURE FOR LiBr-H₂O SOLUTION

The function PRESS(X,T) is a double precision routine that calculates the pressure of water vapor (psia) arising from a LiBr-H₂O solution. The two arguments required are X, the concentration of LiBr in percent, and T, the temperature in F. The values of the partial pressure in psia are determined from the fit to the dew-point temperatures described in Appendix B. First the dew-point temperature is calculated and then that value is used in McNeely's relationship (Table 8, Equation 1):

$$\log_{10} P = K_0 + k_1 / T' + k_2 / T'^2$$

where the values of k_0 , etc., are given below in the function.

The same upper limits for temperature and lower limits for (X,T) are used as in the dew-point routine.

```

DOUBLE PRECISION FUNCTION PRESS(X,T)
C      ADAPTED FROM HLIBR(X,T) 4/27/87-4/30/87 ON 5/15/87-5/19/87
C      THIS FUNCTION PRESS YIELDS THE PRESSURE(Pa) OF A LITHIUM BROMIDE
C      -WATER SOLUTION AT X=PERCENT LIBR CONCENTRATION
C      AND T=TEMPERATURE (DEG C, Horacio says is DEG F)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DOUBLE PRECISION A(18),X,T,XN(7),TN(7),XUNKN(4),TUNKN(4)
DATA KUP/6/,A/
1  -1.313448D-01, 1.820914D-01, -5.177356D-02, 2.827426D-03,
2  -6.380541D-05, 4.340498D-07, 9.967944D-01, 1.778069D-03,
3  -2.215597D-04, 5.913618D-06, -7.308556D-08, 2.788472D-10,
4  1.978788D-05, -1.779481D-05, 2.002427D-06, -7.667546D-08,
5  1.201525D-09, -6.641716D-12/,
8  XN/57.5,62.5,62.5,67.5,67.5,100.0,100.0/,
9  TN/ 0.0,10.0,40.0,50.0,90.0,100.0,180.0/,
A  XUNKN/ 0.0, 37.5, 51.5, 60.5/,
B  TUNKN/126.7,137.8,160.0,182.2/
PRESS=0.0D0
TDEW=0.0D0
C      PH CALCULATE FREEZING CONCENTRATION XSTAR AT TEMP T
DO 100 N=2,7
IF(T.GT.TN(N))GO TO 100
IF (XN(N).EQ.XN(N-1))THEN
XSTAR=XN(N)
ELSE
XSTAR=XN(N-1)+(T-TN(N-1))/(TN(N)-TN(N-1))*(XN(N)-XN(N-1))
ENDIF
IF (X.GE.XSTAR)GO TO 110
GO TO 120
100 CONTINUE
C      WRITE(*,(' TEMPERATURE HIGHER THAN TABLE ALLOWS,T=' ,
C      1 F10.2)')T
GO TO 130
C      POINT X,T IN FREEZING REGION
110 WRITE(*,(' POINT X,T IN FREEZING REGION, X,T=' ,2F10.2)
1 )X,T
GO TO 999
130 DO 140 N=2,4
IF(T.GT.TUNKN(N))GO TO 140
IF (XUNKN(N).EQ.XUNKN(N-1))THEN
XSTAR=XUNKN(N)
ELSE
XSTAR=XUNKN(N-1)+(T-TUNKN(N-1))/(TUNKN(N)-TUNKN(N-1))*
1 (XUNKN(N)-XUNKN(N-1))
ENDIF
IF (X.LE.XSTAR)GO TO 150

```

```

GO TO 120
140 CONTINUE
C POINT X,T IN UNKNOWN REGION
150 WRITE(*,'(' POINT X,T IN UNKNOWN REGION, X,T=' ',2F10.2)
1 )')X,T
GO TO 999
j^@^@^@^@^@ ic CONTINUE WITH CALCULATION, X & T IN SOLUTION REGION
120 XK=1.00D0
TF=9.0/5.0*T+32.0
DO 220 K=1,KUP
IF(K.GT.1)XK=X*XK
TDEW=TDEW + XK * ( A(K) + TF* (A(K+KUP)+TF*A(K+2*KUP)) )
220 CONTINUE
TR=TDEW+459.7
PRESS=10.0D0**((6.21147D0-2886.373D0/TR-337269.46D0/TR)**2)
1 *6.894757E3
999 RETURN
END
C
C

```

APPENDIX D

THERMAL CONDUCTIVITY OF LiBr-H₂O SOLUTION

The thermal conductivity routine is a double precision function having two arguments: X, the concentration in percent of LiBr, and T, the temperature of the solution in °C. The limits for temperature and concentration were taken to be the same as those for dew point. The tabular values given by Uemura have a mean value of 0.4447 kcal/(h·m·°C) were fit with a standard deviation of 0.0018 kcal/(h·m·°C), within 0.4%. The coefficients are given in the routine below.

```

C
DOUBLE PRECISION FUNCTION TCON(X,T)
C ADAPTED FROM TDEW(X,T) 6/23/87
C THIS FUNCTION YIELDS THE THERMAL CONDUCTIVITY (KCAL/M.HR.DEG C)
C OF A LITHIUM BROMIDE
C -WATER SOLUTION AT X=PERCENT LIBR CONCENTRATION
C AND T=TEMPERATURE (DEG C)
C SOURCE: UEMURA, P 16, TABLE 4
C IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DOUBLE PRECISION A(15),X,T,XN(7),TN(7),XUNKN(4),TUNKN(4)
DATA KUP/5/,A/
1 4.815196D-1, -2.217277D-3, -1.994141D-5, 3.727255D-7,
2 -2.489886D-9, 1.858174D-3, 9.614755D-6, -1.139291D-6,
3 2.107608D-8, -1.330532D-10, -7.923126D-6, -1.869392D-7,
4 1.408951D-8, -2.740806D-10, 1.810818D-12/,
5 XN/57.5,62.5,62.5,67.5,67.5,100.0,100.0/,
6 TN/ 0.0,10.0,40.0,50.0,90.0,100.0,180.0/,
7 XUNKN/ 0.0, 37.5, 51.5, 60.5/,
8 TUNKN/260.0,280.0,320.0,360.0/
TCON=0.0D0
C CALCULATE FREEZING CONCENTRATION XSTAR AT TEMP T
DO 100 N=2,7
IF(T.GT.TN(N))GO TO 100
IF (XN(N).EQ.XN(N-1))THEN
XSTAR=XN(N)
ELSE
XSTAR=XN(N-1)+(T-TN(N-1))/(TN(N)-TN(N-1))*(XN(N)-XN(N-1))
ENDIF
IF (X.GE.XSTAR)GO TO 110
GO TO 120
100 CONTINUE

```

```

1 WRITE(*,(' TEMPERATURE HIGHER THAN TABLE ALLOWS,T-',
          F10.2)')T
GO TO 130
C POINT X,T IN FREEZING REGION
110 WRITE(*,(' POINT X,T IN FREEZING REGION, X,T-',2F10.2)
1 )')X,T
GO TO 999
130 DO 140 N=2,4
IF(T.GT.TUNKN(N))GO TO 140
IF (XUNKN(N).EQ.XUNKN(N-1))THEN
XSTAR=XUNKN(N)
ELSE
XSTAR=XUNKN(N-1)+(T-TUNKN(N-1))/(TUNKN(N)-TUNKN(N-1))*
1 (XUNKN(N)-XUNKN(N-1))
ENDIF
IF (X.LE.XSTAR)GO TO 150
GO TO 120
140 CONTINUE
C POINT X,T IN UNKNOWN REGION
150 WRITE(*,(' POINT X,T IN UNKNOWN REGION, X,T-',2F10.2)
1 )')X,T

GO TO 999 j^@^@^@^@^@ 1
C CONTINUE WITH CALCULATION, X & T IN SOLUTION REGION
120 XK=1.00D0
DO 220 K=1,KUP
IF(K.GT.1)XK=X*XK
TCON=TCON + XK * ( A(K) + T* (A(K+KUP)+T*A(K+2*KUP)) )
220 CONTINUE
999 RETURN
END
C
C
C

```

APPENDIX E

VISCOSITY OF LiBr H₂O SOLUTION

The function VISCOS(X,T) is a double precision routine to calculate the viscosity in cP (centipoises) given X, the weight percent of LiBr, and T, the temperature in °C. The best fit to the data has a standard error of 5.8% of the mean value of 1.97 cP in the region $5 < X < 60$ wt % and $0 < T < 90$ °C. The number of data points used in the fit was 119, all taken from the Japanese reference Uemura. The function is given below.

```

DOUBLE PRECISION FUNCTION VISCOS(X,T)
C SOURCE: UEMURA, P.15, TABLE 2
C THIS FUNCTION YIELDS THE VISCOSITY (cP) OF A LITHIUM BROMIDE
C -WATER SOLUTION AT X-PERCENT LIBR CONCENTRATION
C AND T-TEMPERATURE (DEG C)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
DOUBLE PRECISION A(18),X,T,XN(7),TN(7),XUNKN(4),TUNKN(4)
DATA KUP/6/,A/
1 1.488747D+0, 1.143975D-1, -1.278729D-2, 6.999985D-4,
2 -1.638074D-5, 1.456348D-7, -4.164814D-2, 9.636832D-4,
3 -5.981025D-5, -1.282435D-7, 5.703002D-8, -9.842266D-10,
4 3.404030D-4, -2.794515D-5, 2.580301D-6, -9.737750D-8,
5 1.585609D-9, -7.922925D-12/,
5 XN/57.5,62.5,62.5,67.5,67.5,100.0,100.0/,
6 TN/ 0.0,10.0,40.0,50.0,90.0,100.0,180.0/
7 XUNKN/ 0.0, 37.5, 51.5, 60.5/,
8 TUNKN/126.7,137.8,160.0,182.2/
VISCOS=0.0D0

```

```

C      CALCULATE FREEZING CONCENTRATION XSTAR AT TEMP T
DO 100 N=2,7
IF(T.GT.TN(N))GO TO 100
IF (XN(N).EQ.XN(N-1))THEN
XSTAR=XN(N)
ELSE
XSTAR=XN(N-1)+(T-TN(N-1))/(TN(N)-TN(N-1))*(XN(N)-XN(N-1))
ENDIF
IF (X.GE.XSTAR)GO TO 110
GO TO 120

100    CONTINUE
C      WRITE(*,'('' TEMPERATURE HIGHER THAN TABLE ALLOWS,T-'',
C      1      F10.2)')T
      GO TO 130
C      POINT X,T IN FREEZING REGION
110    WRITE(*,'('' POINT X,T IN FREEZING REGION, X,T-'',2F10.2)
1      )')X,T
      GO TO 999
130    DO 140 N=2,4
IF(T.GT.TUNKN(N))GO TO 140
IF (XUNKN(N).EQ.XUNKN(N-1))THEN
XSTAR=XUNKN(N)
ELSE
XSTAR=XUNKN(N-1)+(T-TUNKN(N-1))/(TUNKN(N)-TUNKN(N-1))*
1      (XUNKN(N)-XUNKN(N-1))
ENDIF
IF (X.LE.XSTAR)GO TO 150
GO TO 120
140    CONTINUE
C      POINT X,T IN UNKNOWN REGION
150    WRITE(*,'('' POINT X,T IN UNKNOWN REGION, X,T-'',2F10.2)
1      )')X,T
      GO TO 999
C      CONTINUE WITH CALCULATION, X & T IN SOLUTION REGION
120    XK=1.0000
DO 220 K=1,KUP
IF(K.GT.1)XK=X*KX
VISCOS=VISCOS + XK * ( A(K) + T* (A(K+KUP)+T*A(K+2*KUP)) )
220    CONTINUE
999    RETURN
END

```

APPENDIX F

THE SPECIFIC MASS FOR LiBr-H₂O SOLUTIONS

The specific mass can be calculated from the routine SPMASS(X,T) in kg/L given the input of the concentration X in wt. % and the temperature T in °C. This routine was derived by fitting the data given by Uemura in the region 10 < X < 60 wt % and 0 < T < 100 °C. The specific mass has a mean value of 1.34 in that region, and the standard error on the fit is small, about 0.001 cP or less than 0.1%. This is another case where the standard error is less for K = 4 than for K = 5, so the coefficients for the former are used in the following routine:

```

DOUBLE PRECISION FUNCTION SPMASS(X,T)
C      THIS FUNCTION YIELDS THE SPECIFIC MASS (KG/L) OF A LITHIUM BROMIDE
C      -WATER SOLUTION AT X-PERCENT LIBR CONCENTRATION
C      AND T-TEMPERATURE (DEG C)
C      CALCULATED FROM UEMURA, P.15, TABLE 1
C      IMPLICIT DOUBLE PRECISION (A-H,O-Z)

```

```

DOUBLE PRECISION A(15),X,T,XN(7),TN(7),XUNKN(4),TUNKN(4)
DATA KUP/5/,A/
1 9.939006D-1, 1.046888D-2, -1.667939D-4, 5.332835D-6,
2 -3.440005D-8, -5.631094D-4, 1.633541D-5, -1.110273D-6,
3 2.882292D-8, -2.523579D-10, 1.392527D-6, -2.801009D-7,
4 1.734979D-8, -4.232988D-10, 3.503024D-12/
5 XN/57.5,62.5,62.5,67.5,67.5,100.0,100.0/,
6 TN/ 0.0,10.0,40.0,50.0,90.0,100.0,180.0/,
7 XUNKN/ 0.0, 37.5, 51.5, 60.5/,
8 TUNKN/126.7,137.8,160.0,182.2/
SPMASS=0.0DO

C CALCULATE FREEZING CONCENTRATION XSTAR AT TEMP T
DO 100 N=2,7
IF(T.GT.TN(N))GO TO 100
IF (XN(N).EQ.XN(N-1))THEN
XSTAR=XN(N)
ELSE
XSTAR=XN(N-1)+(T-TN(N-1))/(TN(N)-TN(N-1))*(XN(N)-XN(N-1))
ENDIF
IF (X.GE.XSTAR)GO TO 110
GO TO 120
100 CONTINUE
WRITE(*,'('' TEMPERATURE HIGHER THAN TABLE ALLOWS,T='',
1 F10.2)')T
GO TO 130
C POINT X,T IN FREEZING REGION
110 WRITE(*,'('' POINT X,T IN FREEZING REGION, X,T='',2F10.2)
1 )')X,T
GO TO 999
130 DO 140 N=2,4
IF(T.GT.TUNKN(N))GO TO 140
IF (XUNKN(N).EQ.XUNKN(N-1))THEN
XSTAR=XUNKN(N)
ELSE
XSTAR=XUNKN(N-1)+(T-TUNKN(N-1))/(TUNKN(N)-TUNKN(N-1))*
1 (XUNKN(N)-XUNKN(N-1)) j^@^@^@^@^@ 1 ENDIF
IF (X.LE.XSTAR)GO TO 150
GO TO 120
140 CONTINUE
C POINT X,T IN UNKNOWN REGION
150 WRITE(*,'('' POINT X,T IN UNKNOWN REGION, X,T='',2F10.2)
1 )')X,T
GO TO 999

C CONTINUE WITH CALCULATION, X & T IN SOLUTION REGION:
120 XK=1.00DO
DO 220 K=1,KUP
IF(K.GT.1)XK=X*XK
SPMASS = SPMASS + XK * ( A(K) + T* (A(K+KUP)+T*A(K+2*KUP)) )
220 CONTINUE
999 RETURN
END

```

APPENDIX G

SURFACE TENSION FOR THE LiBr-H₂O SOLUTIONS

Another of the functions presented by Uemura has been fit to yield the surface tension in dyne/cm as a function of X (wt %) and T (°C). The name of this function is STEN(X,T), and it

was fit over the region $5 < X < 60$ wt % and $0 < T < 60^\circ\text{C}$. The standard error was 0.26 dyne/cm or 0.3% of the mean value in the region of 77.7 dyne/cm for the 15-term fit with $K = 4$, smaller error than the eighteen term fit with $K = 5$. In the routine given below, the 15-term fit is used.

```

DOUBLE PRECISION FUNCTION STEN(X,T)
C      SOURCE: UEMURA, P.16, TABLE 3 , VERSION 12/4/87
C      THIS FUNCTION YIELDS THE SURFACE TENSION (DYNE/CM)
C      OF A LITHIUM BROMIDE
C      -WATER SOLUTION AT X=PERCENT LIBR CONCENTRATION
C      AND T=TEMPERATURE (DEG C)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      DOUBLE PRECISION A(15),X,T,XN(7),TN(7),XUNKN(4),TUNKN(4)
      DATA KUP/5/,A/
1      7.626234D+1, 4.583900D-1, -1.463071D-2, 3.834735D-4,
2      -2.733854D-6, -1.507474D-1, -9.057263D-3, 4.459087D-4,
3      -9.542318D-6, 6.610416D-8, -1.107075D-5, 7.238986D-5,
4      -3.822731D-6, 8.077592D-8, -5.681625D-10/,
5      XN/ 57.5,62.5,62.5,67.5,67.5,100.0,100.0/,
6      TN/ 0.0,10.0,40.0,50.0,90.0,100.0,180.0/,
7      XUNKN/ 0.0, 37.5, 51.5, 60.5/,
8      TUNKN/ 126.7, 137.8, 160.0, 182.2/
      STEN=0.0D0
C      CALCULATE FREEZING CONCENTRATION XSTAR AT TEMP T
      DO 100 N=2,7
      IF(T.GT.TN(N))GO TO 100
      IF (XN(N).EQ.XN(N-1))THEN
        XSTAR=XN(N)
      ELSE
        XSTAR=XN(N-1)+(T-TN(N-1))/(TN(N)-TN(N-1))*(XN(N)-XN(N-1))
      ENDIF
      IF (X.GE.XSTAR)GO TO 110
      GO TO 120
100     CONTINUE
      WRITE(*,('' TEMPERATURE HIGHER THAN TABLE ALLOWS,T='',
1      F10.2)')T
      GO TO 130
C      POINT X,T IN FREEZING REGION
110     WRITE(*,('' POINT X,T IN FREEZING REGION, X,T='',2F10.2)
1      )')X,T
      GO TO 999
130     DO 140 N=2,4
      IF(T.GT.TUNKN(N))GO TO 140
      IF (XUNKN(N).EQ.XUNKN(N-1))THEN
        XSTAR=XUNKN(N)
      ELSE
        XSTAR=XUNKN(N-1)+(T-TUNKN(N-1))/(TUNKN(N)-TUNKN(N-1))*
1      (XUNKN(N)-XUNKN(N-1))
      ENDIF
      IF (X.LE.XSTAR)GO TO 150
      GO TO 120
140     CONTINUE
C      POINT X,T IN UNKNOWN REGION
150     WRITE(*,('' POINT X,T IN UNKNOWN REGION, X,T='',2F10.2)
1      )')X,T
      GO TO 999
C      CONTINUE WITH CALCULATION, X & T IN SOLUTION REGION
120     XK=1.00D0
      DO 220 K=1,KUP
      IF(K.GT.1)XK=X*XK
      STEN = STEN + XK * ( A(K) + T* (A(K+KUP)+T*A(K+2*KUP)) )
220     CONTINUE
999     RETURN
      END

```

TABLE 1
Results for the Fit of the Enthalpy Data

Upper limit for exponent of concentration K	Standard Deviation of enthalpy sigma kJ/kg	Btu/lb
3	2.38	1.02
4	1.42	0.61
5	1.01	0.43

TABLE 2
Values of the Coefficients for the Enthalpy Fit

A ₀₀ 1.134125E0	A ₁₀ -4.800450E-1	A ₂₀ -2.161438E-3	A ₃₀ 2.336235E-4	A ₄₀ -1.188679E-5	A ₅₀ 2.291532E-7
A ₀₁ 4.124891E0	A ₁₁ -7.643903E-2	A ₂₁ 2.589577E-3	A ₃₁ -9.500522E-5	A ₄₁ 1.708026E-6	A ₅₁ -1.102363E-8
A ₀₂ 5.743693E-4	A ₁₂ 5.870921E-5	A ₂₂ -7.375319E-6	A ₃₂ 3.277592E-7	A ₄₂ -6.062304E-9	A ₅₂ 3.901897E-11

TABLE 3
Dew-point Standard Deviations

K	Standard deviation C	(° F)
2	0.92	(1.66)
3	0.69	(1.25)
4	0.36	(0.65)
5	0.15	(0.27)

TABLE 4
Dew-point Coefficients

B ₀₀ -1.313448E-1	B ₁₀ 1.820914E-1	B ₂₀ -5.177356E-2	B ₃₀ 2.827426E-3	B ₄₀ -6.380541E-5	B ₅₀ 4.340498E-7
B ₀₁ 9.967944E-1	B ₁₁ 1.778069E-3	B ₂₁ -2.215597E-4	B ₃₁ 5.913618E-6	B ₄₁ -7.308556E-8	B ₅₁ 2.788472E-10
B ₀₂ 1.978788E-5	B ₁₂ -1.779481E-5	B ₂₂ 2.002427E-6	B ₃₂ -7.667546E-8	B ₄₂ 1.201525E-9	B ₅₂ -6.641716E-12

TABLE 5
Standard Deviation of Thermal Conductivity Fit

K Upper limit for exponent of concentration	Standard Deviation	
	W/(m·K)	kcal/(h·m·°C)
2	2.121 * 10 ⁻³	1.824 * 10 ⁻³
3	2.094 * 10 ⁻³	1.800 * 10 ⁻³
4	2.081 * 10 ⁻³	1.789 * 10 ⁻³
5	2.109 * 10 ⁻³	1.813 * 10 ⁻³

TABLE 6
Standard Deviations for Viscosity

K Upper limit for exponent of concentration	Standard deviation of viscosity (c.p.)
2	0.561
3	0.265
4	0.135
5	0.115

TABLE 7
Specific Mass Standard Deviations

K	Standard deviation (kg/dm ³)
2	2.17*10 ⁻³
3	1.74*10 ⁻³
4	1.02*10 ⁻³
5	1.04*10 ⁻³

TABLE 8
Standard Deviation for Surface Tension

K	Standard deviation (dyn/cm)
2	0.271
3	0.270
4	0.259
5	0.259

TABLE 9
Log of Activity

Salt Concentration %	ln a from fit	ln a from Eqn 4
5	-0.016	-0.016
10	-0.053	-0.053
15	-0.098	-0.098
20	-0.149	-0.149
25	-0.211	-0.212
30	-0.298	-0.299
35	-0.427	-0.428
40	-0.616	-0.617
45	-0.883	-0.885
50	-1.241	-1.241
55	-1.696	-1.696
60	-2.237	-2.234
65	-2.826	-2.820



Figure 1. Plot of ln a versus salt concentration for NaCl. The solid line is the fit to the data and the dashed line is the prediction from Eqn 4.

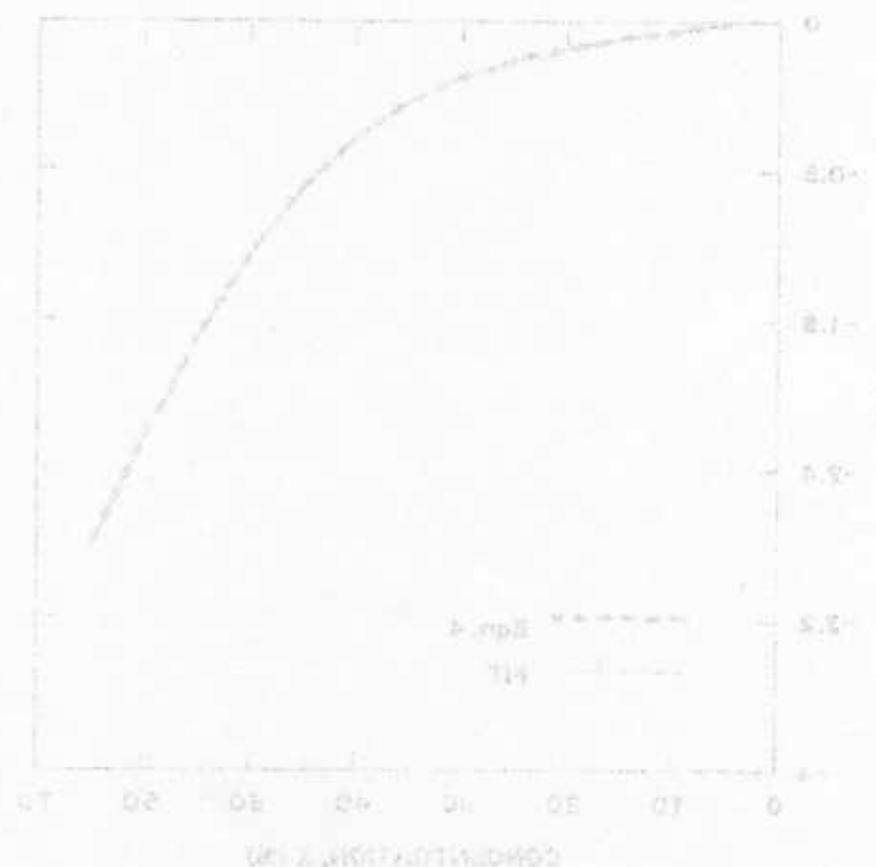


Figure 2. Plot of ln a versus salt concentration for NaCl. The solid line is the fit to the data and the dashed line is the prediction from Eqn 4.

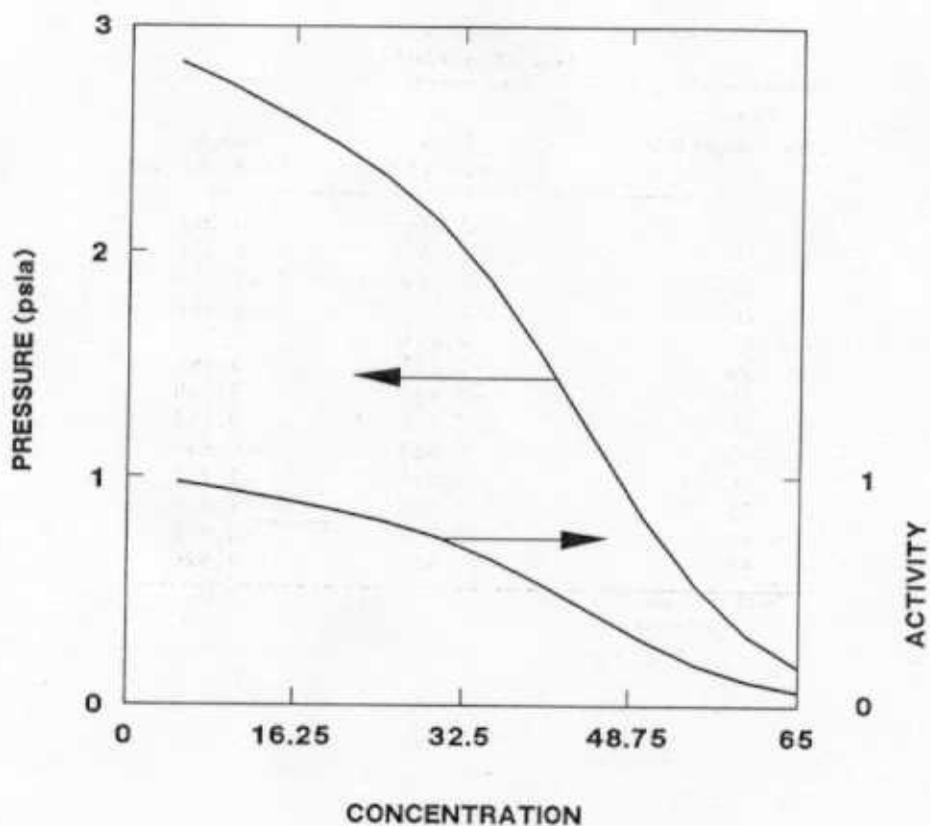


Figure 1 Pressure and activity of water in lithium-bromide solution at 60°C

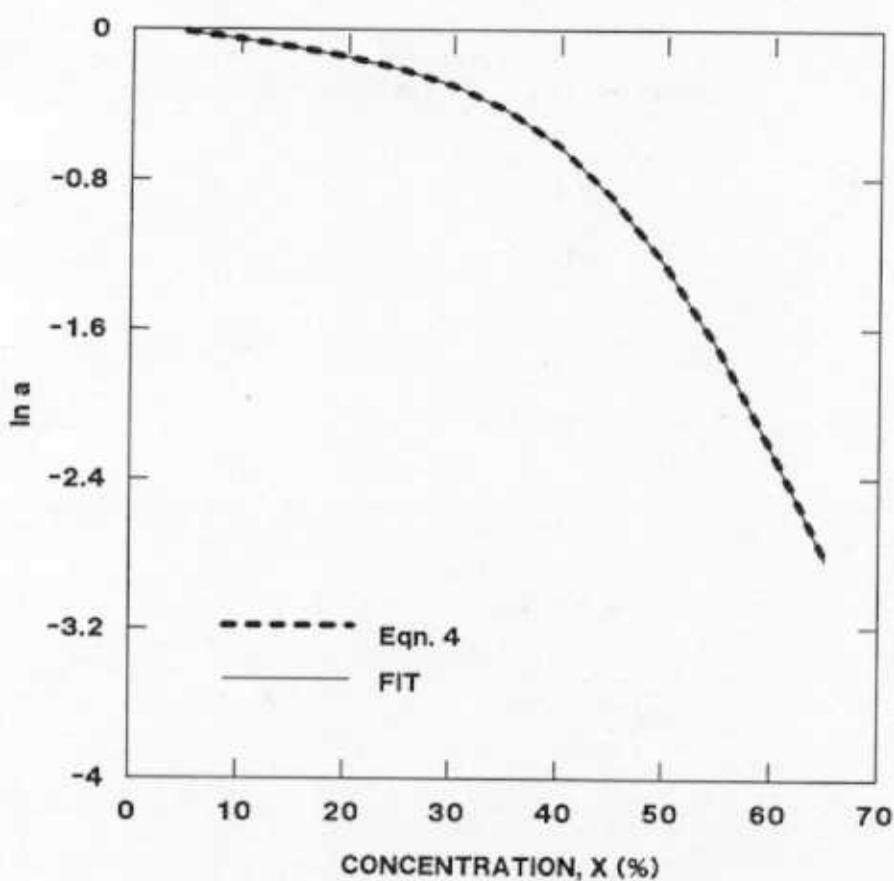


Figure 2 Natural log of activity; from present fit---from Equation 4

DISCUSSION

R.A. Macouss, IGT, Chicago, IL: Was there significant variability in the number of distinct experimental points used in the figures from one property to another?

M.R. Patterson: Yes, some fits used several hundred points, but for other fits only 30 points were available. More measurements are needed, especially for the transport properties.