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## APPENDIX A

### RESULTS OF THE DENSITIES OF SOLUTIONS

Densities of aqueous  $\text{Zn}(\text{ClO}_4)_2$ ,  $\text{ZnSO}_4$ ,  $\text{ZnCl}_2$  and  $\text{CdSO}_4$  were measured at  $25.00 \pm 0.01^\circ\text{C}$  using 10-cm<sup>3</sup> pycnometer. Results of the densities as density curves are shown in Figs. 3.3, 3.4, 3.5 and 3.6.

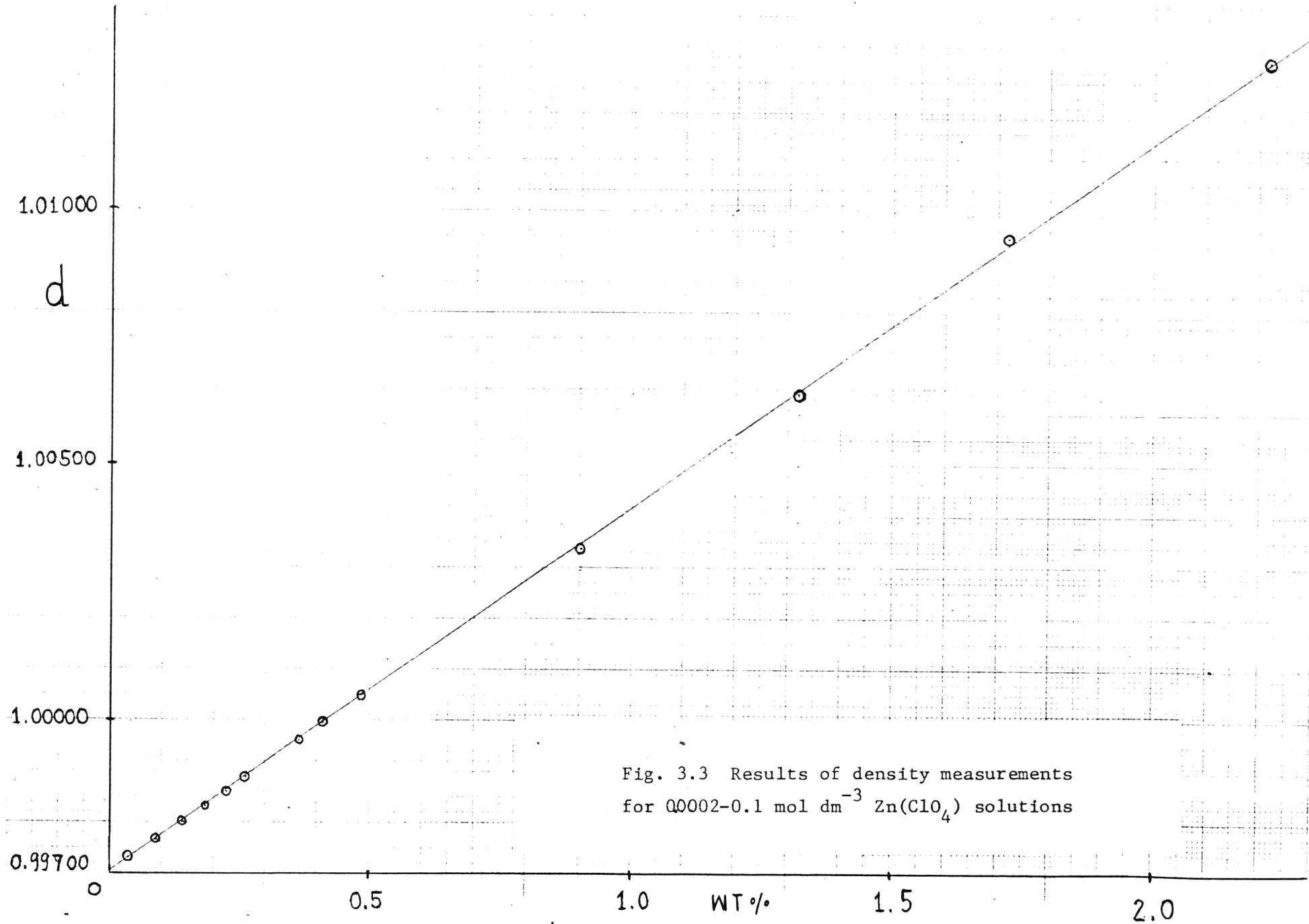


Fig. 3.3 Results of density measurements for 0.0002-0.1 mol dm<sup>-3</sup> Zn(ClO<sub>4</sub>) solutions

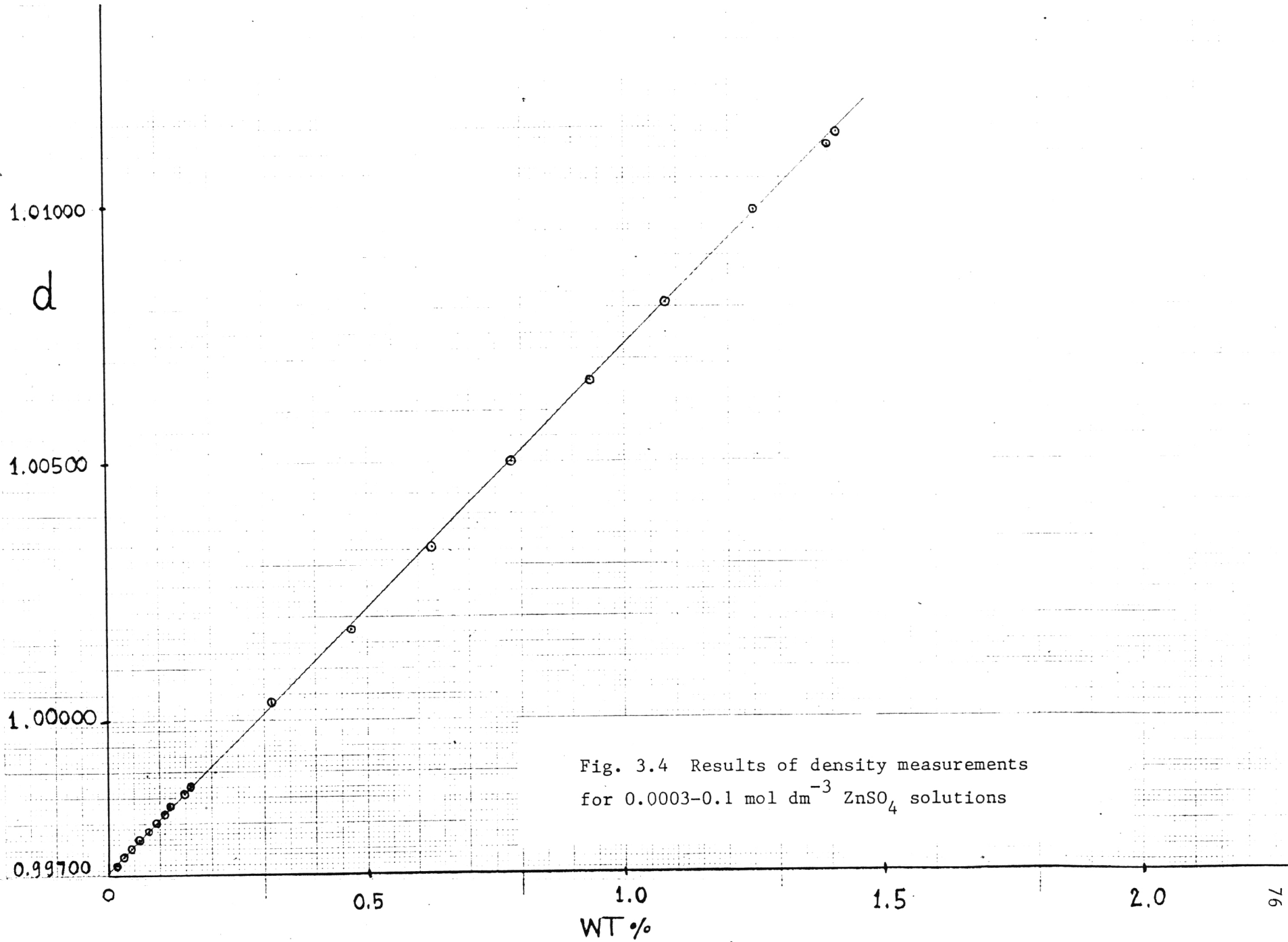


Fig. 3.4 Results of density measurements for 0.0003-0.1 mol dm<sup>-3</sup> ZnSO<sub>4</sub> solutions

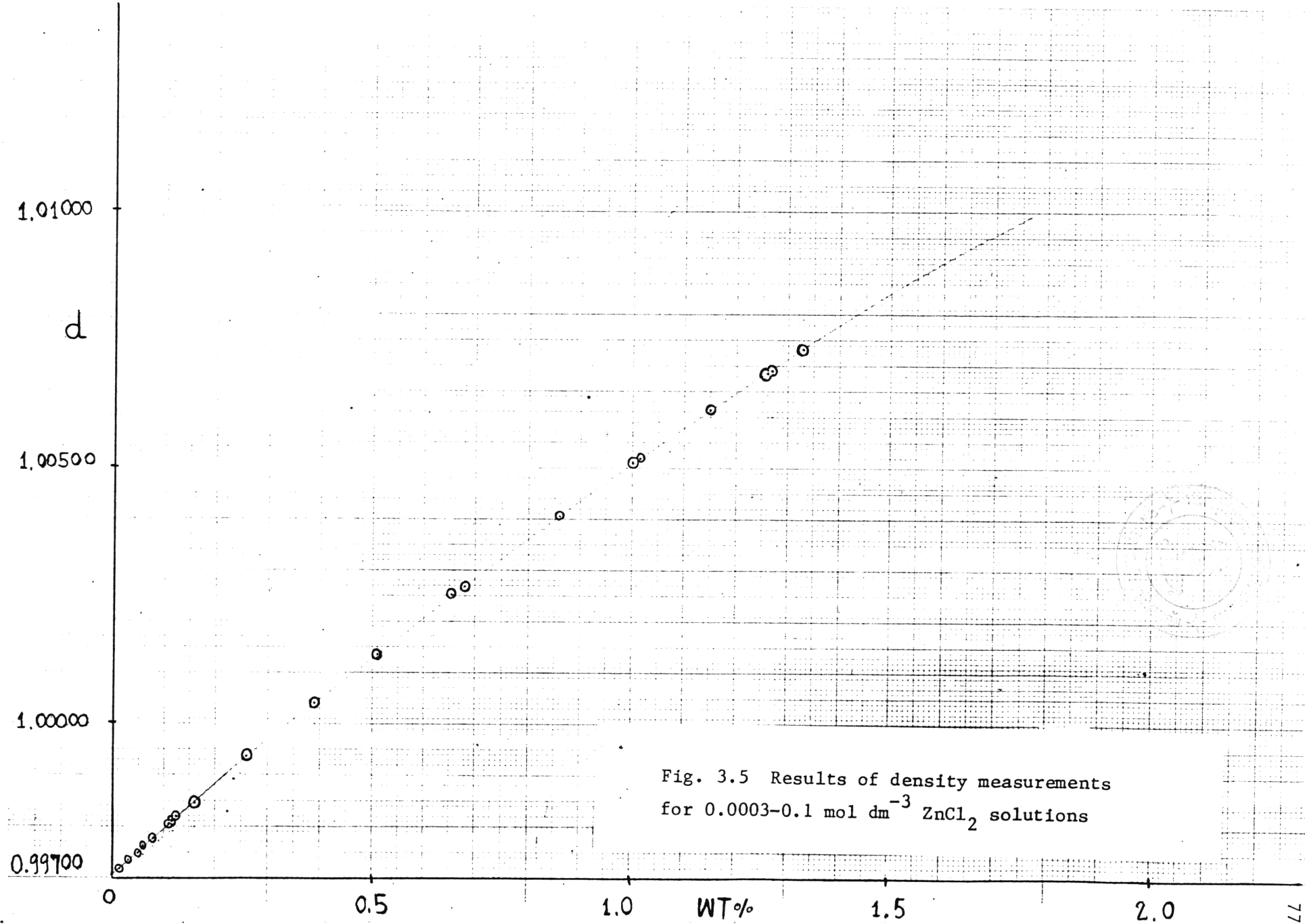


Fig. 3.5 Results of density measurements for 0.0003-0.1 mol dm<sup>-3</sup> ZnCl<sub>2</sub> solutions



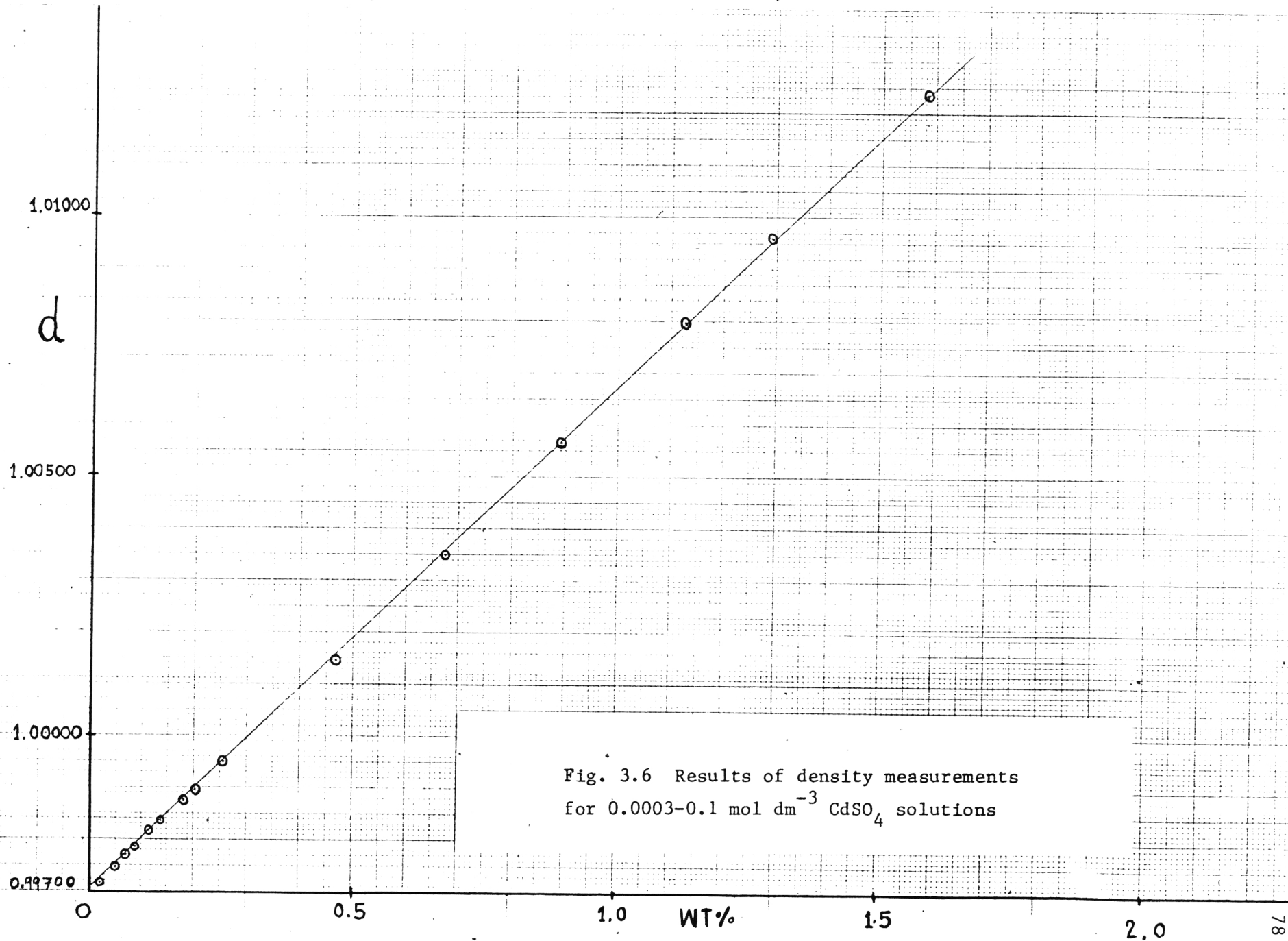


Fig. 3.6 Results of density measurements for 0.0003-0.1 mol dm<sup>-3</sup> CdSO<sub>4</sub> solutions

APPENDIX B

CORRECTIONS TO THE LEE AND WHEATON EQUATIONS

Typing errors in references 5 and 6 have been corrected as follow:

Reference 5 (Part I)

Page 748: equation (5),  $\beta = e^2/DkT$

(T is the absolute temperature used in the original text)

Page 760: equation (76), the denominator of the last term should read  $(1 + q_p^{1/2} \kappa_R + q_p \kappa_R^2/2)$ .

Page 763: equation (99), in the expression of  $H_{2,p,1}(\kappa_R)$ , the last term on the third line should read

$$(1 + q_p^{1/2} \kappa_R) \text{Tr}\{\kappa_R\}/q_p +$$

Page 765: Appendix, in the expression of  $\Delta X_j^{(0,3)}/X$ ,  $\mu_i$  should read  $u_i$ , an ionic strength fraction used in the original text.

Page 766: Appendix, equation. (A2) for  $J_2(\kappa_R)$ , a minus sign was missed out on the third paragraph.

Reference 6 (Part II)

Page 1462: equation (52), in the expression of  $u_{je}^{(0)}$ ,  $\mu_i$  should read  $u_i$ , an ionic strenght fraction.

Page 1463: equation (64), the nominator of the first term of  $u_{je}^{(1)}$  should read  $e_j^2 \kappa_X^2$

Page 1463: equation (66), the denominator of the last term on the first line in the expression of  $Q_p(\kappa_R)$  should read  $(1 + q_p^{1/2} \kappa_R + q_p \kappa_R^2/2)$ .

Page 1468: equation (104), the denominator of the last term in the expression of  $\Delta X_j^{(0,5)}/X$  should have the factor  $(\omega_i + \omega_v)$ .

Page 1473: equation (123), should read

$$\tau = F\zeta e/6\pi\eta$$

Page 1475: equation (136), the first multiple term of the second term on the expression of  $C_{\delta,p}(t)$  should read  $(1 - q_p^2)/2q_p$ .

## APPENDIX C

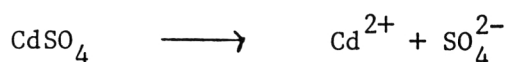
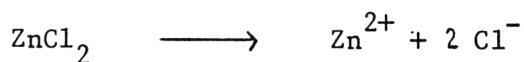
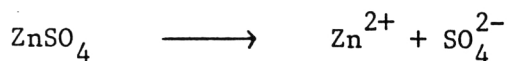
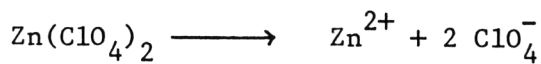
### THE CALCULATION OF THE SHEDLOVSKY EXTRAPOLATION FUNCTION

The Shedlovsky extrapolation function used for the plot of  $\Lambda^{\circ}$  vs. concentration for  $\text{Zn}(\text{ClO}_4)_2$ ,  $\text{ZnSO}_4$ ,  $\text{ZnCl}_2$  and  $\text{CdSO}_4$  solutions is

$$\Lambda^{\circ} = \frac{\Lambda + B_2 M^{1/2}}{1 - B_1 M^{1/2}}$$

where  $\Lambda$  is the observed conductivity from a resistance measurement and  $B_1$ ,  $B_2$  are constants.

Assuming stoichiometric dissociation of these aqueous solutions are



thus at 25°C  $B_1$  and  $B_2$  can be calculated from the equations (24)

$$B_1 = 0.7852 |z_A z_B| \cdot \frac{q}{q^{1/2} + 1} \cdot \left( \frac{I}{M} \right)^{1/2}$$

$$B_2 = 30.32 ( |z_A| + |z_B| ) \cdot \left( \frac{I}{M} \right)^{1/2}$$

wher

$$q = \frac{|z_A z_B| \cdot \lambda_A^{\circ} + \lambda_B^{\circ}}{|z_A| + |z_B| \cdot \lambda_A^{\circ} + |z_A| \lambda_B^{\circ}}$$

for anion A and cation B.

Using  $\lambda_{Zn^{2+}}^{\circ} = 53.0 \text{ cm}^2 \Omega^{-1} \text{ equiv}^{-1}$  (10),  $\lambda_{Cd^{2+}}^{\circ} = 53.5$   
 $\text{cm}^2 \Omega^{-1} \text{ equiv}^{-1}$  (14),  $\lambda_{ClO_4^-}^{\circ} = 67.36 \text{ cm}^2 \Omega^{-1} \text{ equiv}^{-1}$  (29, 30),  
 $\lambda_{Cl^-}^{\circ} = 76.35 \text{ cm}^2 \Omega^{-1} \text{ equiv}^{-1}$  (27, 28) and  $\lambda_{SO_4^{2-}}^{\circ} = 80.02 \text{ cm}^2 \Omega^{-1}$   
 $\text{equiv}^{-1}$  (31) thus

for  $Zn(ClO_4)_2$

$$B_1 = 0.7030239 \quad \text{mol}^{-1/2} \text{ dm}^{3/2}$$

$$B_2 = 1.57547 \times 10^2 \quad \text{dm}^{3/2} \text{ mol}^{-1/2} \text{ cm}^2 \Omega^{-1} \text{ equiv}^{-1}$$

and  $q = 0.4274451$  where  $(I/M)^{1/2} = \sqrt{3}$

for  $ZnCl_2$

$$B_1 = 0.6921399 \quad \text{mol}^{-1/2} \text{ dm}^{3/2}$$

$$B_2 = 1.57547 \times 10^2 \quad \text{dm}^{3/2} \text{ mol}^{-1/2} \text{ cm}^2 \Omega^{-1} \text{ equiv}^{-1}$$

and  $q = 0.4189781$  where  $(I/M)^{1/2} = \sqrt{3}$

for  $ZnSO_4, CdSO_4$

$$B_1 = 1.8398381 \quad \text{mol}^{-1/2} \text{ dm}^{3/2}$$

$$B_2 = 2.4256 \times 10^2 \quad \text{dm}^{3/2} \text{ mol}^{-1/2} \text{ cm}^2 \Omega^{-1} \text{ equiv}^{-1}$$

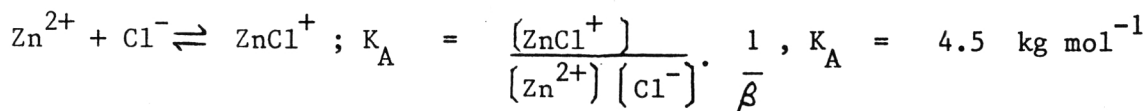
$$q = 0.5 \quad \text{where } (I/M)^{1/2} = 2$$

Substituting  $B_1$  and  $B_2$  in the Shedlovsky equation,  $\Lambda^{\circ}$  can then be calculated for given values of concentration and the corresponding conductivity determined in the experiment.

## APPENDIX D

### THE CALCULATION OF IONIC SPECIES OF ZINC CHLORIDE SOLUTIONS

The effect of incomplete dissociation was studied by Paterson(13) using the method of Reilly and Stokes (15). If only the first complex is considered, then



where  $\beta = \frac{\gamma_{21}^3}{\gamma_{11}^2}$ ;  $\gamma$ 's are activity coefficients in the extended Debye

Hückel form.

From these values, the concentrations of the complexes were calculated at different ionic strengths, I by the following procedure.

Assuming the molality of  $\text{Zn}^{2+}$ ,  $\text{Cl}^{-1}$  and  $\text{ZnCl}^{+}$  are x, y and z respectively.

From the requirements of conservation of mass, electroneutrality and the definition of the ionic strength of the solution, the equation(1) was obtained, i.e.

$$(2K_A\beta)y^2 + (6-2IK_A\beta)y - 4I = 0 \quad (1)$$

This equation was solved for a given value of ionic strength I. The solution of y therefore corresponds to the molality of  $\text{Cl}^{-}$ . The value of x is then calculated from

$$x = \frac{y}{(2 + y K_A\beta)}$$

which is the molality of  $\text{Zn}^{2+}$ . From the above equalities, the concentrations of complexes and the total stoichiometric concentration of  $\text{ZnCl}_2$  can be determined.

APPENDIX E



PROGRAMME (1)

ANALYSIS BY THE LEE AND WHEATON EQUATIONS FOR  $ZnCl_2$  SYSTEM

This programme was assembled according to the conductance equations given in Appendix (H). The numerical input data (e.g.  $D$ ,  $\eta$ ,  $Z_1$ ,  $e_1$ , etc) may be altered depending on the system studies. In the programme, "x(1)" refers to  $R$  and "x(2)" refers to  $\lambda_{ZnCl^+}^\circ$  if  $\lambda_{Zn^{2+}}^\circ$  is fixed at "LAM 1", and vice versa. The list of programme (1) shown below was that used to process aqueous  $ZnCl_2$  data at 25 C, optimising  $\lambda_{Zn^{2+}}^\circ$  and  $R$  at fixed  $\lambda_{ZnCl^+}^\circ$  value.



```

0001      DIMENSION UU(3),ZZ(3),EE(3),WW(3),X(2),ALAM(3),GAMCAL(50),
0002      *TT(3),ALPH(3),QQ(3),ENP(3),CHI(3,2),ZSUMP(3),FINALT(3)
0003      REAL K,LAM1,LAM2,KB,KR,MM(50),LL,NP(3)
0004      COMMON GAMEXP(50),CC(50,3),MM,IPCINT,X,N
0005      READ(1,5)N,IPCINT
0006      5  FORMAT(I1,I2)
0007      DO 10 IA =1,IPCINT
0008      READ(1,15)GAMEXP(IA),CC(IA,3),CC(IA,2),CC(IA,1),MM(IA)
0009      15  FORMAT(F7.3,4E10.5)
0010      10  CONTINUE
0011      R=0.1E-9
0012      X(1)=3.0E-9
0013      DO 31 IY=1,20
0014      Y=0.1
0015      X(2)=52.0
0016      DO 33 IX =1,30
0017      CALL CALCFX
0018      X(2)=X(2)+Y
0019      33  CONTINUE
0020      X(1)=X(1)+R
0021      31  CONTINUE
0022      STOP
0022      END

0001      SUBROUTINE CALCFX
0002      DIMENSION UC(3),ZZ(3),EE(3),WW(3),X(2),GAMCAL(50),
0003      *TT(3),ALPH(3),QQ(3),ENP(3),CHI(3,3),ZSUMP(3),FINALT(3),ALAM(3)
0004      REAL K,LAM1,LAM2,KB,KR,MM(50),LL,NP(3)
0005      COMMON GAMEXP(50),CC(50,3),MM,IPCINT,X,N
0006      TR(X)=EXP(X)*(-.57722-ALOG(X)+X-(X**2)/(2.*2.)+(X**3)/(3.*6.)-X**4
0007      */(4.*24.))
0008      C  ZZ(1),ZZ(2),ZZ(3) ARE VALENCIES OF ION 1,2,3 RESPECTIVELY
0009      C  EE(1),EE(2),EE(3) ARE CHARGES OF ION 1,2,3 RESPECTIVELY
0010      C  D IS DIELECTRIC CONSTANT OF SOLVENT
0011      C  KB IS BOLTZMANN CONSTANT
0012      C  T IS ABSOLUTE TEMPERATURE
0013      C  VIS IS VISCOSITY OF SOLVENT
0014      ZZ(1) =1
0015      ZZ(2) =-1
0016      ZZ(3) =2
0017      EE(1)=4.80325E-10
0018      EE(2) =-4.80325E-10
0019      EE(3)=2.*4.80325E-10
0020      D =78.30
0021      KB=1.380622E-16
0022      T=298.15
0023      VIS=8.903E-3
0024      LAM1=35.
0025      LAM2=76.35
0026      FF=96486.7
0027      BTA=2.307121E-19/(D*KB*T)
0028      TAU=FF*4.80325E-10/(6.*299.7925*3.1415926*VIS)
0029      WW(1)=6.468716E+6*LAM1/ABS(ZZ(1))
0030      WW(2)=6.468716E+6*LAM2/ABS(ZZ(2))
0031      DO 12 IC =1,IPCINT
0032      WW(3)=6.468716E+6*X(2)/ABS(ZZ(3))
0033      C  CALCULATION OF MU1
0034      SUM1=0
0035      DO 30 IA=1,3
0036      30  SUM1=SUM1+6.0222*(4.80325*ABS(ZZ(IA)))**2*CC(IC,IA)
0037      DO 40 IA=1,3
0038      40  UU(IA)=6.0222*(4.80325*ABS(ZZ(IA)))**2*CC(IC,IA)/SUM1
0039      C  CALCULATION OF KAPA
0040      SUM2=0
0041      DO 50 IA=1,3
0042      50  SUM2=SUM2+CC(IC,IA)*ZZ(IA)**2
0043      K=3.556143E+9*SQRT(SUM2)/SQRT(D*T)
0044      C  CALCULATION OF THETA
0045      THETA=0
0046      DO 60 IA=1,3
0047      60  THETA=THETA+UU(IA)*ZZ(IA)**2
0048      C  CALCULATION OF OMEGA
0049      OMEGA=C
0050      DO 70 IA=1,3
0051      70  OMEGA=OMEGA+UU(IA)*ZZ(IA)
0052      C  CALCULATION OF KAPAR
0053      KR=K*X(1)
0054      C  CALCULATION OF WBAR

```

```

0041          WBAR = 0
0042          DO 90 IA=1,3
0043      80    WBAR=WBAR+LU(IA)*WW(IA)
C          CALCULATION OF TCI
0044          DO 90 IA=1,3
0045      90    TT(IA) =UU(IA)*WW(IA)/WBAR
C          CALCULATION OF R
0046          RA=0
0047          DO 100 IA=1,3
0048      100   BA=BA+(1.-TT(IA))*WW(IA)**2
0049          B=BA/2.0
C          CALCULATION OF C
0050          CA=1.0
0051          DO 110 IA=1,3
0052      110   CA=CA*WW(IA)**2
0053          CB=0
0054          DO 120 IA=1,3
0055      120   CB=CB+TT(IA)/WW(IA)**2
0056          C=CA*CB
C          CALCULATION OF ALPHA1, ALPHA2, ALPHA3
0057          ALPH(1)=0
0058          G=SQRT(ABS(B**2-C))
0059          ALPH(2)=SQRT(ABS(B-G))
0060          ALPH(3)=SQRT(B+G)
C          CALCULATION OF ENP(IA)
0061          DO 125 IA =1,3
0062      125   NP(IA)=0
0063          DO 130 IA=1,3
0064          DO 130 IB=1,3
0065      130   NP(IA)=NP(IA)+(TT(IB)*WW(IB)**2)/((WW(IB)**2-(ALPH(IA)**2))**2)
0066          DC126 IA=1,3
0067      126   ENP(IA)=SQRT(ABS(1.0/NP(IA)))
C          CALCULATION OF CHI(IA,IB)
0068          DO 140 IA=1,3
0069          DO 140 IB=1,3
0070      140   CHI(IA,IB)=(ENP(IA)*WW(IB))/(WW(IB)**2-(ALPH(IA)**2))
C          CALCULATION OF QP
0071          DO 145 IA=1,3
0072      145   QQ(IA)=0
0073          DO 150 IA=1,3
0074          DO 150 IB=1,3
0075      150   QQ(IA)=QQ(IA)+(WBAP*TT(IB)*WW(IB))/(WW(IB)**2-(ALPH(IA)**2))
0076          DO 160 JM=1,3
0077          SUMP=0
0078          DO 170 IP=2,3
0079          SQP=SQRT(QQ(IP))
0080          XA=SQP*KR
0081          XB=(1.0+SQP)*KR
0082          XC=(2.0+SQP)*KR
0083          XD=(3.0+SQP)*KR
0084          XE=2.0*KR
0085          XF=3.0*KR
0086          TR1=TR(XA)
0087          TR2=TR(XB)
0088          TR3=TR(XC)
0089          TR4=TR(XD)
0090          TR5=TR(XE)
0091          TR6=TR(XF)
0092          TR7=TR(XF)
0093          C5P=-((1.0(IP)-1.0)-SQP/2.0+SQP*(1.-SQP)*KR/2.0)/SQP-(1.-QQ(IP)**2)**
*TR2/QQ(IP)-CQ(IP)*(1.0+KR*KR**2/2.0)*TR1+(1.0+SQP*KR)*TP5/QQ(IP)**
*(1.0/((1.0+KR)*(1.0+SQP*KR+QQ(IP)*KR**2/2.0)))*(1.0/12.0)
0094          C3P=(-(1.-CQ(IP))*TR5/(2.0*QQ(IP))+(1.-CQ(IP)**2)*
*TR2/(2.0*QQ(IP)*(1.0+SQP*KR+QQ(IP)*KR**2/2.0))+(3.0+SQP)*(1.-QQ(IP))/
*(6.0*SQP)-(8.0*(2.0-QQ(IP))-5.0*SQP-3.0*SQP**3)*KR/24.0)
0095          C1P=((1.0+(1.0+SQP)*KR/2.0)/(1.0+SQP*KR+QQ(IP)*KR**2/2.0))*(1.0/((1.0+SQP
)*(1.0+KR)))*(1.0/3.0)
0096          C2P=-((TR3+.5)/(1.0+SQP*KR+QQ(IP)*KR**2/2.0))*(1.0/((1.0+
*KR)**2))*(1.0/6.0)
0097          C4P=-((4.0/(1.-CQ(IP)))*ALOG(3.0/(2.0+SQP))+(2.0/3.0)*((1.0+SQP)/(2.0+SQP
*)))*(OMEGA**2)*(1.0/((1.0+KR)**2*(1.0+SQP*KR+QQ(IP)*KR**2/2.0)))*
*(1.0/24.0)
0098          C3P=OMEGA*(ALOG(3.0/(2.0+SQP)))/(1.-CQ(IP))*(1.0/((1.0+KR)**2*
*(1.0+SQP*KR+QQ(IP)*KR**2/2.0)))*(1.0/6.0)
0099          C7P=-((3.0+SQP)*TP4/((1.0+KR)**3))*(1.0/(1.0+SQP*KR+QQ(IP)*KR**2/2.0))
** (1.0/18.0)
0100          SUMV=0
0101          DO 171 IV=1,3
C          CALCULATION OF AVP
0102          SUMP11=0
0103          DO 190 I=1,3
0104      190   SUMP11=SUMP11 +UU(I)*((ZZ(I)*WW(I)-ZZ(IV)*WW(IV))/(WW(I)+WW(IV)))
0105          AVP=SUMP11*C1P

```

```

C      CALCULATION OF BVP
0106      BVP1=SUMP11*C4P
0107      SUMP12=0
0108      DO 200 I=1,3
0109      200 SUMP12=SUMP12 +ZZ(I)*ZZ(IV)*(UJ(I))*((ZZ(I)*WW(I)-ZZ(IV)*WW(IV))
          */(WW(I)+WW(IV))))
0110      BVP2=SUMP12*(C2P+C5P)
0111      SUMP13=0
0112      DO 210 I=1,3
0113      210 SUMP13=SUMP13 +((ZZ(I)+Z7(IV))*(UU(I))*((ZZ(I)*WW(I)-ZZ(IV)*WW(IV))
          */(WW(I)+WW(IV))))
0114      BVP3=SUMP13*C3P
C      CALCULATION OF GVP
0115      SGVP1=0
0116      DO 220 I=1,3
0117      SGVP2=0
0118      DO 221 IL=2,3
0119      SQL=SQRT(QC(IL))
0120      XG=(SQL+SQP)*KR
0121      TR8=TR(XG)
0122      C6PL1=((-(SQL+QQ(IP))*(1.-SQL)-(QQ(IP)*(1.-QQ(IL))-(1.-SQL)*(SQP*
          *SQL-1.)/2.)*KR)/(SQP*SQL)-(1.+SQL*KR+QQ(IL)*KR**2/2.)*(1.-QQ(IP)**
          *2)*TR2/QQ(IP)+(1.+SQL*KR+QQ(IL)*KR**2/2.)*(1.+SCP*KR)*TR5/QQ(IP)+
          *(QQ(IL)**2-QQ(IP)**2)*(1.+KR+KR**2/2.)*TR3/(QQ(IL)*QQ(IP))
          *(1.+KR+KR**2/2.)*(QQ(IP)**2*(1.-QQ(IL))+(1.+SQL*KR+QQ(IL)*KR**
          *2/2.-QQ(IL)**2*(1.+SCP*KR))*TR1/(QQ(IL)+QQ(IP)))
0123      C6PL2=(1./((1.+KR)*(1.+S
          *JP*KR+QQ(IP)*KR**2/2.)*(1.+SQL*KR+QQ(IL)*KR**2/2.)))
0124      C6PL=C6PL1*C6PL2
0125      SGVP3=0
0126      DO 230 IA=1,3
0127      230 SGVP3=SGVP3 +TT(IA)*CHI(IL,IA)*ZZ(IA)
0128      SGVP2=SGVP2+SGVP3 *(WW(I)*CHI(IL,IV)-WW(IV)*CHI(IL,I))*C6PL
0129      221 CONTINUE
0130      SGVP1=SGVP1+(UU(I)*ZZ(I)*ZZ(IV)*(SGVP2/(WW(I)+WW(IV))))
0131      220 CONTINUE
0132      GVP=(1./12.)*SGVP1
0133      BVP=3VVP1+BVP2+BVP3+GVP
C      CALCULATION OF CVP
0134      SUMP14=0
0135      DO 240 I=1,3
0136      240 SUMP14=SUMP14 +((ZZ(I)**2*ZZ(IV)**2)*(UU(I))*((ZZ(I)*WW(I)-ZZ(IV)*
          *WW(IV))/(WW(I)+WW(IV))))
0137      CVP=0
0138      BTAK=AVP*(BTA*K)+BVP*((BTA*K)**2)+CVP*((BTA*K)**3)
0139      SUMV=SUMV+(TT(IV)*CHI(IP,IV))*BTAK
0140      171 CONTINUE
0141      SUMP=SUMP+CHI(IP,IV)*SUMV
0142      170 CONTINUE
0143      ZSUMP(JM)=ZZ(JM)*SUMP
C      CALCULATION OF VJ1 AND VJ2
0144      SUMP=0
0145      DO 250 IP=2,3
0146      SUMV=0
0147      DO 251 IV=1,3
0148      SUMP16=0
0149      DO 260 I=1,3
0150      260 SUMP16=SUMP16 +UU(I)*((ZZ(I)-ZZ(IV))/(WW(I)+WW(IV))
          *SUMV+TT(IV)*CHI(IP,IV)*(ZZ(IV)*C8P/2.-WW(JM)*SUMP16*C1P)
0151      251 CONTINUE
0152      250 SUMP=SUMP+CHI(IP,IV)*SUMV
0153      VJ1=-((ZZ(JM)*SUMP)-(1./2.)*(ZZ(JM)*CMEGA*
          *(TR6/((1.+KR)**2)+ALOG(2./3.))-OMEGA**2/6.)*(1.+KR)
0154      VJ2=0
0155      SUMP15=0
0156      DO 270 IV=1,3
0157      270 SUMP15=SUMP15 +((JU(IV))*((ZZ(IV)*WW(IV)-ZZ(JM)*WW(JM))
          */(WW(IV)+WW(J
          *M))))/ZZ(IV)
0158      FINALT(J4)=(ABS(ZZ(JM))*K*TAJ)/(1.+KR)*(1.+VJ1*(BTA*K)+VJ2*
          *((BTA*K)**2)+SUMP15*KR/6.)
0159      160 CONTINUE
0160      ALAM(1)=LAM1
0161      ALAM(3)=X(2)
0162      ALAM(2)=LAM2
0163      GAMCAL(IC)=0
0164      DO 280 IA=1,3
0165      LL=ALAM(IA)*(1.+ZSUMP(IA))-FINALT(IA)
0166      280 GAMCAL(IC)=GAMCAL(IC)+ABS(ZZ(IA))*CC(IC,IA)*LL
0167      GAMCAL(IC)=GAMCAL(IC)/(2.+MM(IC))
0168      12 CONTINUE
0169      SUMSQ=0
0170      DO 13 IA=1,IPCONT
0171      13 SUMSQ=SUMSQ+(GAMCAL(IA)-GAMEXP(IA)**2)
0172      SUMSQ=SUMSQ/IPPOINT
0173      F=SUMSQ*1.0E+3
0174      WRITE(3,18)(X(I),I=1,N),F,LAM1
0175      13
0176      13
0177      RETURN
0178      END

```

## APPENDIX F

### PROGRAMME (2)

#### ANALYSIS BY THE LEE AND WHEATON EQUATIONS FOR $\text{ZnSO}_4$ AND $\text{CdSO}_4$ SYSTEMS

This programme was assembled according to the conductance equations given in Appendix (H). The numerical input data (e.g.  $D$ ,  $\eta$ ,  $Z_i$ ,  $e_i$ , etc) may be altered depending on the system studies. In the programme, "x(1)" refers to  $R$  and "x(2)" refer to  $\lambda_{M^{2+}}^\circ$  ( $M = \text{Zn, Cd}$ ). The list of programme(2) shown below was that used to process aqueous  $\text{ZnSO}_4$  and  $\text{CdSO}_4$  data at  $25^\circ\text{C}$ , optimising  $\lambda_{M^{2+}}^\circ$  and  $R$  value.

```

0001      DIMENSION GG(3), ZZ(3), EE(3), WW(3), XT(2),
      *TT(3), ALPH(3), CC(2), ENP(2), CHI(3,3), ZSLMP(3), FINALT(3),
      *ALAM(3), XM(3), WT(3), GAMCAL(5)
0002      REAL KC, LAM1, LAM2, KB, KH, MM(50), LL, KP(3)
0003      COMMON GAMEXP(50), CC(50,2), MM, IFCINT, X, N
0004      DOUBLE PRECISION ACU(24), CIFXM, DELTA1, XML, CMREF, DIREF, AMEXPT(24),
      *FI, XI(37), XM, DELTA, YY, XX1, ZZ1, SI, GAMMA2, GAMMA1, GAMMA21,
      *GAMA11, ABETA, AAB, BBB, CCC, YYL, XXL, ZZL, AK, O, WT, YXR, XZR, ZZR, XMP
0005      READ(1,5) N, IFCINT
0006      C      FCFMAT(11,12)
      C      XI(J) IS IONIC STRENGTH
0007      READ(1,4) (X(I), I=1,36)
0008      C      FCFMAT(EE5,2)
      C      AMEXPT(K) IS EXPERIMENTAL CONCENTRATION OF SOLUTION IN MOLE PER KG
      C      AT(K) IS EXPERIMENTAL CONCENTRATION OF SOLUTON IN WEIGHT,
0009      CC 1CK=1, IFCINT
0010      READ(1,16) GAMEXP(K), AMEXPT(K), WT(K)
0011      C      FCFMAT(F7.3, E6.4, F7.5)
0012      C      13 CONTINUE
      C      JK IS ASSOCIATION CONSTANT
0013      AK=143.
0014      H=.05E-8
0015      X(1)=4.0E-8
0016      DC 31 IX=1,20
0017      CC 2J=1,36
0018      SI=COSHT(XI(J))
0019      GAMMA2=(-0.5115*4.*SI)/(1.+0.3291*X(1)*SI)
0020      GAMMA22=10.CCC**GAMMA2
0021      XX1=XI(J)/4.
0022      YY1=XI(J)/4.
0023      ZZ1=AK*XX1*YY1*GAMA22**2
      C      XM(J) IS CONCENTRATION IN MOLE PER KG (CORRESPOND TO IONIC STRENGTH)
0024      XM(J)=XX1+ZZ1
0025      C      9 CONTINUE
0026      DC 7 K=1, IFCINT
      C      ACU(K) IS THE ACCURACY OF CONCENTRATION
0027      ACU(K)=0.01/100.*AMEXPT(K)
0028      CC 12J=1,36
0029      L=J+1
0030      IF(AMEXPT(K).LT.XM(J).OR.AMEXPT(K).GT.XM(L)) GO TO 12
0031      CMREF=XM(L)-XM(J)
0032      DIREF=XI(L)-XI(J)
0033      CIFXM=AMEXPT(K)-XM(J)
0034      DELTA1=DIREF*CIFXM/CMREF
0035      FI=XI(J)+DELTA1
0036      GO TO 15
0037      C      12 CONTINUE
0038      C      15 SI=COSHT(FI)
0039      GAMMA2=(-0.5115*4.*SI)/(1.+0.3291*X(1)*SI)
0040      GAMMA22=10.CCC**GAMMA2
      C      YYL, XXL, ZZL ARE CONCENTRATIONS OF IONIC SPECIES IN MOLE PER KG
0041      XXL=FI/4.
0042      YYL=FI/4.
0043      ZZL=AK*XXL*YYL*GAMA22**2
      C      XML IS STOICHIOMETRIC CONCENTRATION OF ELECTROLYTE IN MOLE PER KG
0044      XML=>>XXL+ZZL
0045      IF(XML.LT.AMEXPT(K)) CIFXM=AMEXPT(K)-XML
0046      IF(XML.GT.AMEXPT(K)) CIFXM=XML-AMEXPT(K)
0047      IF(CIFXM.LE.ACUI(K)) GO TO 14
0048      DELTA1=DIREF*CIFXM/CMREF
0049      IF(XML.GT.AMEXPT(K)) FI=FI-DELTA1
0050      IF(XML.LT.AMEXPT(K)) FI=FI+DELTA1
0051      GO TO 15
      C      C IS THE DENSITY OF SOLUTION
0052      C      14 J=.957044+.0102283*WT(K)
0053      XZR=(XXL*G)/(1.+XXL*.1614316)
0054      YZR=(YYL*G)/(1.+YYL*.1614316)
0055      ZZR=(ZZL*G)/(1.+ZZL*.1614316)
0056      XMR=ZZR+XZR
0057      CC(K,1)=XMR
0058      CC(K,2)=YZR
0059      MM(K)=XMR
0060      C      7 CONTINUE
0061      Y=.C2
0062      X(2)=52.C
0063      DC 33 IX=1,30
0064      CALL CALCFX
0065      X(2)=X(2)+Y
0066      C      33 CONTINUE
0067      X(1)=X(1)+R
0068      C      31 CONTINUE
0069      STOP
0070      END

```

```

CCC1      SUBROUTINE CALCFX
CCC2      DIMENSION LL(2),ZZ(2),EE(2),ww(2),X(2),ALPH(2),GAMCAL(50),
          *TT(2),ALPH(2),C(1,2),ENP(2),CHI(2,2),ZSUMP(2),FINALTI(2)
CCC3      REAL KC,LAM1,LAM2,KB,KF,PP(50),LL,NP(2)
CCC4      COMMON GAMEXP(50),CC(50,2),MM,IPCINT,X,N
CCC5      IR(X)=EXP(X)*(-.57722-ALCG(X)+X-(X**2)/(2.*2.)+(X**3)/(3.*6.)-X**4
          */(4.*24.))
C          ZZ(1),ZZ(2),ZZ(2) ARE VALENCIES OF ION 1,2,3 RESPECTIVELY
C          EE(1),EE(2),EE(2) ARE CHARGES OF ION 1,2,3 RESPECTIVELY
C          D IS DIELECTRIC CONSTANT OF SOLVENT
C          KB IS ECLTZMANN CONSTANT
C          T IS ABSOLUTE TEMPERATURE
C          VIS IS VISCOSITY OF SOLVENT
CCC6      ZZ(1)=Z
CCC7      ZZ(2)=-Z
CCC8      EE(1)=2.*4.80325E-10
CCC9      EE(2)=-2.*4.80325E-10
CC10      C = 78.30
CC11      KB=1.260622E-16
CC12      T=298.15
CC13      VIS=8.503E-2
CC14      FF=56486.7
CC15      LAM2=20.32
CC16      YIA=2.207121E-19/(C*KE*T)
CC17      TAU=FF*4.80325E-10/(C.*299.7925*3.1415926*VIS)
CC18      ww(2)=6.46E716E+C*LAM2/AES(ZZ(2))
CC19      DC 12 IC =1,IFCLAI
CC20      ww(1)=6.46E716E+C*X(2)/AES(ZZ(1))
CC21      SUM1=C
CC22      DC 30 IA=1,2
CC23      30 SUM1=SUM1+6.0222*(4.80325*ADS(ZZ(IA)))**2*CC(1C,IA)
CC24      DC 40 IA=1,2
CC25      40 LL(IA)=6.0222*(4.80325*AES(ZZ(IA)))**2*CC(1C,IA)/SUM1
C          CALCULATION OF KAPA
CC26      SUM2=C
CC27      DC 50 IA=1,2
CC28      50 SUM2=SUM2+CC(1C,IA)*ZZ(IA)**2
CC29      KC=3.55E142E+S*SCF1(SUM2)/SQRT(C*T)
C          CALCULATION OF THETA
CC30      THETA=C
CC31      DC 60 IA=1,2
CC32      60 THETA=THETA+LL(IA)*ZZ(IA)**2
C          CALCULATION OF CMEGA
CC33      CMEGA=C
CC34      DC 70 IA=1,2
CC35      70 CMEGA=CMEGA+LL(IA)*ZZ(IA)
C          CALCULATION OF KAPAR
CC36      KR=KC*X(1)
C          CALCULATION OF WBAR
CC37      WBAR=C
CC38      DC 80 IA=1,2
CC39      80 WBAR=WBAR+LL(IA)*ww(IA)
C          CALCULATION OF TEI
CC40      DC 90 IA=1,2
CC41      90 TT(IA) =LL(IA)*ww(IA)/WBAR
CC42      ALPH(1)=C
CC43      ALPH(2)=SQRT(TT(2)*ww(1)**2+TT(1)*ww(2)**2)
C          CALCULATION OF ENP(IA)
CC44      DC 125 IA=1,2
CC45      125 NP(IA)=C
CC46      DC 130 IA=1,2
CC47      DC 130 IB=1,2
CC48      130 NP(IA)=NP(IA)+(TT(1B)*ww(1B)**2)/(ww(1B)**2-(ALPH(IA)**2))**2)
CC49      DC 126 IA=1,2
CC50      126 ENP(IA)=SQRT(AES(1.C/NP(IA)))
C          CALCULATION OF CHI(IA,IB)
CC51      DC 140 IA=1,2
CC52      DC 140 IB=1,2
CC53      140 CHI(IA,IB)=(ENP(IA)*ww(1B))/(ww(1B)**2-(ALPH(IA)**2))
C          CALCULATION OF ZP
CC54      DC 145 IA=1,2
CC55      CC(1A)=C
CC56      DC 150 IA=1,2
CC57      DC 150 IB=1,2
CC58      150 ZQ(IA)=CC(1A)+(WBAR+TT(1B)*ww(1B))/(ww(1B)**2-(ALPH(IA)**2))
CC59      DC 160 JM=1,2
CC60      SUMP=C
CC61      DC 170 IP=2,2
CC62      SCP=SQRT(CC(1P))
CC63      XA=SCF*KR
CC64      XB=(1.C+SCP)*KF
CC65      XC=(2.C+SCP)*KF
CC66      XD=(2.C+SCF)*KF

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CC67      XE=2.0*KR
CC68      XF=3.0*KR
CC69      TR1=TR(XA)
CC70      TR2=TR(XB)
CC71      TR3=TR(XC)
CC72      TR4=TR(XD)
CC73      TR5=TR(XE)
CC74      TR6=TR(XF)
CC75      TR7=TR(XF)
CC76      C5P=-((CC(IP)-1.)-SCP/2.+SCP*(1.-SCP)*KR/2.)/SCP-(1.-CC(IP)**2)*
+TR2/CC(IP)-CC(IP)*(1.+KR+KR**2/2.)*TR1+(1.+SCP*KR)*TR5/CC(IP))*
*(1./((1.+KR)*(1.+SCP*KR+CC(IP)*KR**2/2.)))*(1./12.)
CC77      C3P=(-(1.-CC(IP))*TR5/(2.*CC(IP))+(1.-CC(IP)**2)*
+TR2/(2.*CC(IP)*(1.+SCP*KR+CC(IP)*KR**2/2.))+(3.+SCP)*(1.-CC(IP))/
*(6.*SCP)-(8.*(2.-CC(IP))-5.*SCP-3.*SCP**3)*KR/24.)
CC78      C1P=((1.+(1.+SCP)*KR/2.)/(1.+S)*P*KR+CC(IP)*KR**2/2.)*(1./((1.+SCP
+)*(1.+KR)))*(1./2.)
CC79      C2P=-((TR3+.5)/(1.+SCP*KR+CC(IP)*KR**2/2.))*(1./((1.+
+KR)**2))*(1./6.)
CC80      C4P=-((4./(1.-CC(IP)))*ALOG(3./(2.+SCP)))+(2./3.)*((1.+SCP)/(2.+S)*
+P)*CMEGA**2*(1./((1.+KR)**2*(1.+SCP*KR+CC(IP)*KR**2/2.)))*
*(1./24.)
CC81      C3P=CMEGA*(ALOG(3./(2.+SCP))/(1.-CC(IP)))*(1./((1.+KR)**2*
+*(1.+SCP*KR+CC(IP)*KR**2/2.)))*(1./6.)
CC82      C7P=-((3.+SCP)*TR4/(1.+KR)**3)*(1./((1.+SCP*KR+CC(IP)*KR**2/2.))
+*(1./12.))
CC83      SUMV=C
CC84      CC 1711V=1,2
C          CALCULATION OF AVP
CC85      SUMP11=C
CC86      CC 19C1=1,2
CC87      19C SUMP11=SUMP11 +CC(I)*(ZZ(I)*WW(I)-ZZ(IV)*WW(IV))/(WW(I)+WW(IV))
CC88      AVF=SUMP11*C1P
C          CALCULATION OF BVP
CC89      BVP1=SUMP11*C4P
CC90      SUMP12=C
CC91      CC 20C1=1,2
CC92      20C SUMP12=SUMP12 +ZZ(I)*ZZ(IV)*(UU(I)*(ZZ(I)*WW(I)-ZZ(IV)*WW(IV))
+*(WW(I)+WW(IV))))
CC93      BVP2=SUMP12*(C2P+C5P)
CC94      SUMP12=C
CC95      CC 21C1=1,2
CC96      21C SUMP13=SUMP13 +(ZZ(I)+ZZ(IV))*(UU(I)*(ZZ(I)*WW(I)-ZZ(IV)*WW(IV))
+*(WW(I)+WW(IV))))
CC97      BVP3=SUMP13*C3P
C          CALCULATION OF GVP
CC98      SGVP1=C
CC99      CC 22C1=1,2
C100      SGVP2=C
C101      CC 2211L=2,2
C102      SCL=SQRT(CC(11))
C103      XG=(SCL+SCL)*KR
C104      TR8=TR(XG)
C105      C6PL1=((-(SCL+CC(IP))*(1.-SCL)-(CC(IP)*(1.-CC(IL))-(1.-SCL)*(SCP*
+*SCL-1.)/2.)*KR)/(SCP*SCL)-(1.+SCL*KR+CC(IL)*KR**2/2.)*(1.-CC(IP)**
+*2)*TR2/CC(IP)+(1.+SCL*KR+CC(IL)*KR**2/2.)*(1.+SCP*KR)*TR5/CC(IP)+
+*(CC(IL)**2-CC(IP)**2)*(1.+KR+KR**2/2.)*TR8/(CC(IL)*CC(IP))
+*(1.+KR+KR**2/2.)*(CC(IP)**2*(1.-CC(IL))*(1.+SCL*KR+CC(IL)*KR**
+*2/2.))-CC(IL)**2*(1.+SCP*KR))*TR1/(CC(IL)*CC(IP)))
C106      C6PL2=(1./((1.+KR))*(1.+S
+*2P*KR+CC(IP)*KR**2/2.)*(1.+SCL*KR+CC(IL)*KR**2/2.))
C107      C6PL=C6PL1+C6PL2
C108      SGVP3=C
C109      CC 23C1A=1,2
C110      23C SGVP3=SGVP3 +TT(IA)*CHI(IL,IA)+ZZ(IA)
C111      SGVP2=SGVP2+SGVP3 *(WW(I)*CHI(IL,IV)-WW(IV)*CHI(IL,I))*C6PL
C112      221 CCNTINLE
C113      SGVP1=SGVP1+(UU(I)+ZZ(I)+ZZ(IV))*(SGVP2/(WW(I)+WW(IV)))
C114      22C CCNTINLE
C115      GVP=(1./12.)*SGVP1
C116      BVP=BVP1+BVP2+BVP3+GVP
C          CALCULATION OF CVP
C117      SUMP14=C
C118      CC 24C1=1,2
C119      24C SUMP14=SUMP14 +(ZZ(I)**2*ZZ(IV)**2)*(UU(I)*(ZZ(I)*WW(I)-ZZ(IV)*
+*WW(IV))/(WW(I)+WW(IV))))
C120      CVP=C
C121      BTAK=AVP*(ETA*KQ)+BVP*((ETA*KQ)**2)+CVP*((ETA*KQ)**3)
C122      SUMV=SUMV+(TI(IV)*CHI(IP,IV))*BTAK
C123      171 CCNTINLE
C124      SUMP=SUMP+CHI(IP,IV)*SUMV
C125      17C CCNTINLE

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C126      ZSUMP(JM)=ZZ(JM)*SUMP
C          CALCULATION OF VJ1 AND VJ2
C127      SUMP=C
C128      DC 250 IP=2,2
C129      SUMV=C
C130      DC 251 IV=1,2
C131      SUMP16=C
C132      DC 260 I=1,2
C133      SUMP16=SUMP16 +UU(I)*(ZZ(I)-ZZ(IV))/(WW(I)+WW(IV))
C134      SUMV=SUMV+11(IV)*CHI(IP,IV)*(ZZ(IV)*CBF/2.-WW(JM)*SUMP16*CIP)
C135      251 CONTINUE
C136      250 SUMP=SUMP+(CHI(IP,JM)*SUMV
C137      VJ1=-(ZZ(JM)*SUMP)-(1./2.)*(ZZ(JM)*CMEGA*
          * (TR6/(1.+KR)**2)+ALOG(2./3.))-CMEGA**2/6.)*(1.+KR)
          VJ2=C
C138      SUMP15=C
C139      DC 270 IV=1,2
C140      SUMP15=SUMP15 +(UU(IV)*((ZZ(IV)*WW(IV)-ZZ(JM)*WW(JM))
          */(WW(IV)+WW(JM))))/ZZ(IV)
C141      FINALT(JM)=(ABS(ZZ(JM))*(KC*TAU)/(1.+KR))*(1.+VJ1*(BTA*KC)+VJ2*
          ((BTA*KC)**2)+SUMP15*KR/6.)
C142      160 CONTINUE
C143      ALAM(2)=LAM2
C144      ALAM(1)=X(2)
C145      GAMCAL(1C)=C
C146      DC 280 IA=1,2
C147      LL=ALAM(1A)*11.+ZSUMP(1A))-FINALT(1A)
C148      280 GAMCAL(1C)=GAMCAL(1C)+ABS(ZZ(1A))*CC(1C,1A)*LL
C149      GAMCAL(1C)=GAMCAL(1C)/(2.*MM(1C))
C150      12 CONTINUE
C151      SUMSC=C
C152      DC 13 IA=1,1PCINT
C153      13 SUMSC = SUMSC+((GAMCAL(1A)-GAMEXF(1A))**2)
C154      SUMSC=SUMSC/1PCINT
C155      F =SUMSC*1.0E+2
C156      WRITE(2,18)(X(I),I=1,N),F
C157      18 FORMAT(20X,E12.6,5X,E12.6,5X,E12.6)
C158      RETURN
C159      END
C160

```



APPENDIX G

PROGRAMME FOR CALCULATING THE IONIC SPECIES OF  
ZINC CHLORIDE SOLUTIONS

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0001      DIMENSION XM(37),WT(37)
0002      DOUBLE PRECISION ACU(24),DIFXM,DELTAI,XML,DMREF,DIREF,AMEXPT(24),
      *F1,XI(37),XM,DELTA,YY,XX,ZZ,S1,GAMMA?,GAMMA1,GAMA21,
      *GAMA11,ABETA,AAA,BBB,CCC,YYL,XXL,ZZL,AK,D,WT,YYR,XXR,ZZR,XMR
C
0003      XI(J) IS IONIC STRENGTH
0004      4      READ(1,4) (XI(J),J=1,36)
      FORMAT(6E9.2)
C
0005      AMEXPT(K) IS EXPERIMENTAL CONCENTRATION OF SOLUTION IN MOLE PER KG
0006      6      READ(1,6) (AMEXPT(K),K=1,24)
      FORMAT(6E11.4)
C
0007      WT(K) IS EXPERIMENTAL CONCENTRATION OF SOLUTION IN WEIGHT ,
0008      2      READ(1,2) (WT(K),K=1,24)
      FORMAT(6F7.5)
C
0009      AK IS ASSOCIATION CONSTANT
0010      AK=4.5
0011      DO 8 J=1,36
0012      S1=DSQRT(XI(J))
0013      GAMMA2=(-1.0230*S1/(1.0+1.48095*S1))+0.30*X1(J)
0014      GAMMA1=( 0.5115*S1/(1.0+1.3164*S1))-0.055*X1(J)
0015      GAMA21=10.000**GAMMA2
0016      GAMA11=10.000**GAMMA1
0017      ABETA=(GAMA21**3)/(GAMA11**2)
0018      AAA=2.*AK*ABETA
0019      BBB=6.-(2.*XI(J)*AK*ABETA)
0020      CCC=4.*XI(J)
0021      DELTA=BBB**2+4.*AAA*CCC
0022      YY=(-BBB+DSQRT(DELTA))/(2.*AAA)
0023      XX =YY/(2.*(YY*AK*ABETA))
      ZZ =YY-(2.*XX)
C
0024      XM(J) IS CONCENTRATION IN MOLE PER KG (CORRESPOND TO IONIC STRENGTH)
0025      3      XM(J)=XX+Z
0026      CONTINUE
      DO 7 K=1,24
C
0027      ACU(K) IS THE ACCURACY OF CONCENTRATION
0028      ACU(K)=0.01/100.*AMEXPT(K)
0029      DO 12 J=1,36
0030      L=J+1
0031      IF(AMEXPT(K).LT.XM(J).OR.AMEXPT(K).GT.XM(L)) GO TO 12
0032      DMREF=XM(L)-XM(J)
0033      DIREF=XI(L)-XI(J)
0034      DIFXM=AMEXPT(K) XM(J)
0035      DELTAI=DIREF*DIFXM/DMREF
0036      F1=XI(J)+DELTAI
0037      GO TO 15
0038      1? CONTINUE
0039      15 S1=DSQRT(F1)
0040      GAMMA2=(-1.0230*S1/(1.0+1.48095*S1))+0.30*F1
0041      GAMMA1=( 0.5115*S1/(1.0+1.3164*S1))-0.055*F1
0042      GAMA21=10.000**GAMMA2
0043      GAMA11=10.000**GAMMA1
0044      ABETA=(GAMA21**3)/(GAMA11**2)
0045      AAA=2.*AK*ABETA
0046      BBB=6.-(2.*F1*AK*ABETA)
      CCC=4.*F1
C
0047      YYL,XXL,ZZL ARE CONCENTRATIONS OF IONIC SPECIES IN MOLE PER KG
0048      YYL=(-BBB+DSQRT(BBB**2+(4.*AAA*CCC)))/(2.*AAA)
0049      XXL=YYL/(2.*(YYL*AK*ABETA))
      ZZL=YYL-(2.*XXL)
C
0050      XML IS STOICHIOMETRIC CONCENTRATION OF ZINC CHLORIDE IN MOLE PER KG
0051      XML=XXL+ZZL
0052      IF(XML.LT.AMEXPT(K)) DIFXM=AMEXPT(K) XML
0053      IF(XML.GT.AMEXPT(K)) DIFXM=XML-AMEXPT(K)
0054      IF(DIFXM.LE.ACUC(K)) GO TO 14
0055      DELTAI=DIREF*DIFXM/DMREF
0056      IF(XML.GT.AMEXPT(K)) F1=F1-DELTAI
0057      IF(XML.LT.AMEXPT(K)) F1=F1+DELTAI
      GO TO 15
C
0058      D IS THE DENSITY OF SOLUTION
0059      14 D=.997044+.0022076*WT(K)
0060      YYR=(YYL*D)/(1.+YYL*0.13628)
0061      XXR=(XXL*D)/(1.+XXL*0.13628)
0062      ZZR=(ZZL*D)/(1.+ZZL*0.13628)
0063      XMR=ZZR+XXR
0064      17 WRITE(3,17)YYR,XXR,ZZR,XMR
0065      7      FORMAT(20X,4(5X,D16.8))
0066      CONTINUE
0067      STOP
      END

```

APPENDIX H



THE FINAL CONDUCTANCE EQUATION BY LEE AND WHEATON

A detailed equations used in programme (1) and (2) for calculations in the analysis by the Lee and Wheaton equation are given here. Some corrections have been made as outlined in Appendix (B). These are equations (120) - (137) in the reference 6.

At this stage it is useful to define some new functions; let

$$\xi_{ji} = \frac{u_i(z_i\omega_i - z_j\omega_j)}{(\omega_i + \omega_j)} \quad (120)$$

and let

$$\begin{aligned} \Pi_j^{(1)} &= \sum_{i=1}^s \xi_{ji} & \Pi_j^{(2)} &= z_j \sum_{i=1}^s \xi_{ji} z_i \\ \Pi_j^{(3)} &= \sum_{i=1}^s \xi_{ji} (z_i + z_j) & \Pi_j^{(4)} &= z_j^2 \sum_{i=1}^s \xi_{ji} z_i^2 \\ \Pi_j^{(5)} &= \sum_{i=1}^s \xi_{ji} / z_i & \Pi_j^{(6)} &= \sum_{i=1}^s \frac{u_i(z_i - z_j)}{(\omega_i + \omega_j)} \end{aligned} \quad (121)$$

also let

$$\Omega = \sum_{i=1}^s u_i z_i \quad \text{and} \quad \theta = \sum_{i=1}^s u_i z_i^2 \quad (122)$$

$$\tau = F\zeta e / 6\pi\eta. \quad (123)$$

Assembling and rearranging all of the relaxation and electrophoretic terms we finally obtain

for the New model

$$\lambda_j = \lambda_j^0 \left\{ 1 + z_j \sum_{p=2}^s \chi_j^p \sum_{v=1}^s t_v \chi_v^p [A_v^p(t)(\beta\kappa) + B_v^p(t)(\beta\kappa)^2 + C_v^p(t)(\beta\kappa)^3] \right\} - \frac{|z_j|(\kappa\tau)}{(1+t)} \{1 + V_j^{(1)}(t)(\beta\kappa) + V_j^{(2)}(t)(\beta\kappa)^2 + \Pi_j^{(5)}t/6\} \quad (124)$$

where  $t = \kappa R$  and

$$A_v^p(t) = \Pi_v^{(1)} C_{1,p}(t) \quad C_v^p(t) = \Pi_v^{(4)} C_{7,p}(t) \quad (125)$$

$$B_v^p(t) = \{ \Pi_v^{(1)} C_{4,p}(t) + \Pi_v^{(2)} [C_{2,p}(t) + C_{5,p}(t)] + \Pi_v^{(3)} C_{3,p}(t) + G_v^p(t) \} \quad (126)$$

For the New model;

$$C_{1,p}(t) = \frac{(1 + (1 + q_p^{\frac{1}{2}})t/2)}{3(1 + q_p^{\frac{1}{2}})(1 + t)(1 + q_p^{\frac{1}{2}}t + q_p t^2/2)} \quad (127)$$

$$C_{2,p}(t) = -\frac{(\text{Tr} \{(2 + q_p^{\frac{1}{2}})t\} + \frac{1}{2})}{6(1 + t)^2(1 + q_p^{\frac{1}{2}}t + q_p t^2/2)} \quad (128)$$

$$C_{3,p}(t) = \frac{\Omega \ln(3/(2 + q_p^{\frac{1}{2}}))}{6(1 + t)^2(1 - q_p)(1 + q_p^{\frac{1}{2}}t + q_p t^2/2)} \quad (129)$$

$$C_{4,p}(t) = -\frac{\Omega^2}{24(1 + t)^2(1 + q_p^{\frac{1}{2}}t + q_p t^2/2)} \left\{ \frac{4}{(1 - q_p)} \ln(3/(2 + q_p^{\frac{1}{2}})) + \frac{2(1 + q_p^{\frac{1}{2}})}{3(2 + q_p^{\frac{1}{2}})} \right\} \quad (130)$$

$$C_{5,p}(t) = -\frac{1}{12(1 + t)(1 + q_p^{\frac{1}{2}}t + q_p t^2/2)} \left[ \{(q_p - 1) - q_p^{\frac{1}{2}}/2 + q_p^{\frac{1}{2}}(1 - q_p^{\frac{1}{2}})t/2\}/q_p^{\frac{1}{2}} - (1 - q_p^2) \text{Tr} \{(1 + q_p^{\frac{1}{2}})t\}/q_p - q_p(1 + t + t^2/2) \text{Tr} \{q_p^{\frac{1}{2}}t\} + (1 + q_p^{\frac{1}{2}}t) \text{Tr} \{t\}/q_p \right] \quad (131)$$

$$C_{7,p}(t) = -\frac{(3 + q_p^{\frac{1}{2}}) \text{Tr} \{(3 + q_p^{\frac{1}{2}})t\}}{18(1 + t)^3(1 + q_p^{\frac{1}{2}}t + q_p t^2/2)} \quad (132)$$

$$G_v^p(t) = (1/12) \sum_{i=1}^s \frac{u_i z_i z_v}{(\omega_i + \omega_v)} \sum_{l=2}^s (t_o \chi_o^l z_o) (\omega_i \chi_v^l - \omega_v \chi_i^l) C_{6,p,l}(t) \quad (133)$$

[see below, eqn (1.72)]

$$C_{6,p,l}(t) = \frac{1}{\{(1 + t)(1 + q_p^{\frac{1}{2}}t + q_p t^2/2)(1 + q_l^{\frac{1}{2}}t + q_l t^2/2)\}} \left[ \{-(q_l^{\frac{1}{2}} + q_p)(1 - q_l^{\frac{1}{2}}) - [q_p(1 - q_l) - (1 - q_l^{\frac{1}{2}})(q_p^{\frac{1}{2}}q_l^{\frac{1}{2}} - 1)/2]t\}/q_p^{\frac{1}{2}}q_l^{\frac{1}{2}} - (1 + q_l^{\frac{1}{2}}t + q_l t^2/2)(1 - q_p^2) \times \text{Tr} \{(1 + q_p^{\frac{1}{2}})t\}/q_p + (1 + q_l^{\frac{1}{2}}t + q_l t^2/2)(1 + q_p^{\frac{1}{2}}t) \text{Tr} \{t\}/q_p + (q_l^2 - q_p^2)(1 + t + t^2/2) \text{Tr} \{(q_l^{\frac{1}{2}} + q_p^{\frac{1}{2}})t\}/q_l q_p + (1 + t + t^2/2)\{q_p^2(1 - q_l)(1 + q_l^{\frac{1}{2}}t + q_l t^2/2) - q_l^2(1 + q_p^{\frac{1}{2}}t)\} \text{Tr} \{q_p^{\frac{1}{2}}t\}/q_l q_p \right] \quad (134)$$

$$V_j^{(1)} = -z_j \sum_{p=2}^s \chi_j^p \sum_{v=1}^s t_v \chi_v^p \{z_v C_{8,p}(t)/2 - \omega_j \Pi_v^{(6)} C_{1,p}(t)\} - \frac{1}{2} [z_j \Omega \left\{ \frac{\text{Tr} \{2t\}}{(1 + t)^2} + \ln(2/3) \right\} - \Omega^2/6](1 + t) \quad (135)$$

where

$$C_{8,p}(t) = \left\{ -\frac{(1 - q_p)}{2q_p} \text{Tr} \{t\} + \frac{(1 - q_p^2)}{2q_p} \frac{\text{Tr} \{(1 + q_p^{\frac{1}{2}})t\}}{(1 + q_p^{\frac{1}{2}}t + q_p t^2/2)} + \frac{(3 + q_p^{\frac{1}{2}})(1 - q_p)}{6q_p^{\frac{1}{2}}} \right. \\ \left. [8(2 - q_p) - 5q_p^{\frac{1}{2}} - 3q_p^{\frac{3}{2}}]t/24 \right\} \quad (136)$$

$$V_j^{(2)} = -\frac{z_j^2 \theta \text{Tr} \{3t\}}{2(1 + t)^2} \quad (137)$$

As mentioned in Section 4.2.2, Chapter 4, the programme was written in the way the terms were grouped and combined as outlined above. The  $\lambda_j$  term was expressed in  $(\beta\kappa)$  series as shown in equation (124). The advantage of such expression is to minimise the "rounding off" of the numerical value involved in the calculations. The omitted terms suggested by Wheaton (3) correspond to  $C_v^P(t)$  and  $v_j^{(2)}(t)$  terms in equation (124) given by equations (125), (132) and (137).

## VITA

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