JOURNAL OF APPLIED POLYMER SCIENCE VOL. 19, 2583–2599 (1975)

Viscosimetric Molecular Weights: Some Computer Programs for Experimental Data Elaboration

AMABILE PENATI, GABRIELE PAGANI, GIANCARLO LOCATI, and ENZO BEACCO, *Institute of Industrial Chemistry, Section of Applied Chemistry and Materials, Polytechnic of Milan, Milan, Italy*

Synopsis

New methods have been developed for the computer which allow viscosimetric data elaboration. Two methods evaluate the intrinsic viscosity, the Huggins or the Kraemer constant, the molecular weight, and their confidence limits according the Student's t-distribution starting from the simplest viscosimetric data. The kinetic energy influence is considered. Another method is used when the Huggins constant is known.

INTRODUCTION

The viscosity of dilute solutions is very often used for measuring polymer molecular weights because the experiments are simple and reliable. The graphic elaboration of the experimental data according to Huggins[1] or Kraemer[2] for obtaining the intrinsic viscosity, from which through the Mark-Houwink relationships[3,4] molecular weights are evaluated, is quite tedious and subject to errors. Computer programs have already been prepared for accelerating and improving the treatment of data,[5–8] however, these programs made use of simplified formulas and partially elaborated data.

In this paper, we present programs which evaluate the intrinsic viscosity, the Huggins (or Kraemer) constant, the molecular weight, and their confidence limits according to the Student's t-distribution starting from the simplest viscosimetric data such as the polymer weight, the solvent volume, and the solvent and solution efflux times.

GENERAL RELATIONSHIPS

The specific viscosity η_{sp} and the relative viscosity η_{rel} are so defined[9–11] considering the kinetic energy influence[12,13]:

$$\eta_{sp} = \eta_{rel} - 1 = \frac{\rho\ t}{\rho_s\ t_s} \left[\frac{1 - \dfrac{K}{t^2}}{1 - \dfrac{K}{t^2_s}} \right] - 1 \qquad (1)$$

where ρ_s and ρ are the solvent and solution densities, t_s and t are the efflux

```
      DIMENSION T(1000),X(1000),Y(1000),TITLE(13),ANI(10),VOLSOL(1000),W
     1ESOL(1000),ROSOLU(1000),CC(1000)
   63 READ(5,80)NN
   80 FORMAT(I3)
      DO163 II=1,NN
      READ(5,60) (TITLE(J),J=1,13)
      WRITE(6,59)(TITLE(J),J=1,13)
   60 FORMAT(13A6)
   59 FORMAT(1H1,2X,13A6)
      READ(5,2)(ANI(K),K=1,6),IPERC
    2 FORMAT(6F10.3,I10)
      READ(5,61) AC,AKA
   61 FORMAT(F10.4,E10.3)
   62 READ(5,8)NN,AKK,ROSOLV,ROPOLY
    8 FORMAT(I3,3F15.8)
      IF(NN.LE.1)GOTO163
      READ(5,9)TS,(T(I),I=1,NN)
    9 FORMAT(10F8.3)
      READ(5,99)WEIGHT,(CC(I),I=1,NN)
   99 FORMAT(F10.7,10F7.4)
      SUMCC=0.0
      DO77M=1,NN
      SUMCC=SUMCC+CC(M)
      VOLSOL(M)=SUMCC
      X(M)=WEIGHT*100.0/SUMCC
   77 CONTINUE
      SUMX=0.0
      SUMY=0.0
      SUMXY=0.0
      SUMXQ=0.0
      DO 7 M=1,NN
      IF(AKK.LT.0.0)GOTO444
      VOLPOL=WEIGHT/ROPOLY
      WESOL(M)=VOLSOL(M)*ROSOLV
      ROSOLU(M)=(WEIGHT+WESOL(M))/(VOLPOL+VOLSOL(M))
      Y(M)=ROSOLU(M)*T(M)*(1.0-AKK/T(M)**2)/((ROSOLV*TS*X(M))*(1.0-AKK/T
     1S**2))-1.0/X(M)
  444 IF(AKK.LT.0.0)Y(M)=(T(M)-TS)/(TS*X(M))
      SUMX=SUMX+X(M)
      SUMY=SUMY+Y(M)
      SUMXY=SUMXY+X(M)*Y(M)
      SUMXQ=SUMXQ+X(M)*X(M)
    7 CONTINUE
      WRITE(6,19)
   19 FORMAT(///,1X,' LIST OF MEASURES ',/)
      IF(AKK.LT.0.0)GOTO666
      WRITE(6,667)TS
  667 FORMAT(//,2X,'TS =',F7.2,5X,' WITH DENSITY AND KINETIC-ENERGY CORR
     1ECTIONS ',//)
      IF(AKK.GT.0.0)GOTO777
  666 WRITE(6,668)TS
  668 FORMAT(//,1X,' TS =',F7.2,5X,' WITHOUT CORRECTIONS ',//)
  777 NOBS=NN
      C=NN
      XMED=SUMX/C
      NI=NN-2
      B=(SUMXY-XMED*SUMY)/(SUMXQ-C*XMED**2)
      A=SUMY/C-B*XMED
      PK=B/A**2
      XQ=0.0
      QMIN=0.0
      DO30 M=1,NOBS
      Y1=A+B*X(M)
      QMIN=QMIN+(Y1-Y(M))**2
      XQ=XQ+(X(M)-XMED)**2
      WRITE(6,20)M,T(M),X(M),Y(M),Y1
   20 FORMAT(1X,I2,2X,' TIME(SEC)=',F7.2,2X,' X(G/DL)=',F7.4,2X,' Y=',F7
     1.4,2X,' Y1=',F7.4,/,)
   30 CONTINUE
      SYX=SQRT(QMIN/(C-2.0))
      ALIMB=ANI(NI)*(SYX/SQRT(XQ))
      ALIMA=ANI(NI)*SYX*SQRT(1.0/C+XMED**2/XQ)
      WRITE(6,21)SYX
   21 FORMAT(//,'  STANDARD DEVIATION=',F7.4)
      WRITE(6,39)IPERC
   39 FORMAT(///,'  CONFIDENCE INTERVAL =',I3)
      WRITE(6,5)A,ALIMA
    5 FORMAT(//,'  INTERCEPT(=INTRINSIC VISCOSITY)=',F6.3,3H +-,F6.4,//)
      WRITE(6,69)B,ALIMB
```

Fig. 1 (*continued*)

```
 80*        69 FORMAT(1X,' SLOPE=',E10.4,3H +-,E10.4,/,
 81*           BMAX=B+ALIMB
 82*           BMIN=B-ALIMB
 83*           AMAX=A+ALIMA
 84*           AMIN=A-ALIMA
 85*           PKMAX=BMAX/AMIN**2
 86*           PKMIN=BMIN/AMAX**2
 87*           WRITE(6,233)PK,PKMAX,PKMIN
 88*       233 FORMAT(/,'  HUGGINS CONSTANT=',F7.4,2X,' MAX=',F7.4,2X,' MIN=',F7.
 89*          1 4,)
 90*           IF(AKA.LT.0.0)GOTO73
 91*           AO=A/AKA
 92*           RA=1.0/AC
 93*           AL=ALOG(AO)
 94*           AOA=(A+ALIMA)/AKA
 95*           AOM=(A-ALIMA)/AKA
 96*           ALA=ALOG(AOA)
 97*           ALM=ALOG(AOM)
 98*           ARG=RA*AL
 99*           AM=EXP(ARG)
100*           AMA=EXP(RA*ALA)
101*           AMI=EXP(RA*ALM)
102*           WRITE(6,79)AC,AKA
103*        79 FORMAT(//,1X,' A=',E10.4,4X,' K=',E10.4,///)
104*           WRITE(6,6)AM,AMA,AMI
105*         6 FORMAT(1X,' AVERAGE MOL WEIGHT=',E10.4,2X,' MAX=',E10.4,2X,' MIN='
106*          1,E10.4,/1HO)
107*        73 GOTO 62
108*       163 CONTINUE
109*        26 STOP
110*           END
```

Fig. 1. First computer program using Huggins equation.

```
  1*           DIMENSION T(1000),X(1000),Y(1000),TITLE(13),ANI(10),VOLSOL(1000),W
  2*          1ESOL(1000),ROSOLU(1000),CC(1000)
  3*        63 READ(5,80)MN
  4*        80 FORMAT(I3)
  5*           DO163 II=1,MN
  6*           READ(5,60) (TITLE(J),J=1,13)
  7*           WRITE(6,59)(TITLE(J),J=1,13)
  8*        60 FORMAT(13A6)
  9*        59 FORMAT(1H1,2X,13A6)
 10*           READ(5,2)(ANI(K),K=1,6),IPERC
 11*         2 FORMAT(6F10.3,I10)
 12*           READ(5,61) AC,AKA
 13*        61 FORMAT(F10.4,E10.3)
 14*        62 READ(5,8)NN,AKK,ROSOLV,ROPOLY
 15*         8 FORMAT(I3,3F15.8)
 16*           IF(NN.LE.1)GOTO163
 17*           READ(5,9)TS,(T(I),I=1,NN)
 18*         9 FORMAT(10F8.3)
 19*           READ(5,99)WEIGHT,(CC(I),I=1,NN)
 20*        99 FORMAT(F10.7,10F7.4)
 21*           SUMCC=0.0
 22*           DO77M=1,NN
 23*           SUMCC=SUMCC+CC(M)
 24*           VOLSOL(M)=SUMCC
 25*           X(M)=WEIGHT*100.0/SUMCC
 26*        77 CONTINUE
 27*           SUMX=0.0
 28*           SUMY=0.0
 29*           SUMXY=0.0
 30*           SUMXQ=0.0
 31*           DO 7 M=1,NN
 32*           IF(AKK.LT.0.0)GOTO444
 33*           VOLPOL=WEIGHT/ROPOLY
 34*           WESOL(M)=VOLSOL(M)*ROSOLV
 35*           ROSOLU(M)=(WEIGHT*WESOL(M))/(VOLPOL+VOLSOL(M))
 36*           Y(M)=ALOG(ROSOLU(M)*T(M)*(1.0-AKK/T(M)**2)/(ROSOLV*TS*(1.0-AKK/TS*
 37*          1*2)))/X(M)
 38*       444 IF(AKK.LT.0.0)Y(M)=ALOG(T(M)/TS)/X(M)
 39*           SUMX=SUMX+X(M)
 40*           SUMY=SUMY+Y(M)
 41*           SUMXY=SUMXY+X(M)*Y(M)
 42*           SUMXQ=SUMXQ+X(M)*X(M)
 43*         7 CONTINUE
 44*           WRITE(6,19)
```

Fig. 2 (*continued*)

```
 45*        19 FORMAT(///,1X,' LIST OF MEASURES ',/)
 46*           IF(AKK.LT.0.0)GOTO666
 47*           WRITE(6,667)TS
 48*       667 FORMAT(//,2X,'TS =',F7.2,5X,' WITH DENSITY AND KINETIC-ENERGY CORR
 49*          1ECTIONS ',//)
 50*           IF(AKK.GT.0.0)GOTO777
 51*       666 WRITE(6,668)TS
 52*       668 FORMAT(//,1X,' TS =',F7.2,5X,' WITHOUT CORRECTIONS ',//)
 53*       777 NOBS=NN
 54*           C=NN
 55*           XMED=SUMX/C
 56*           NI=NN-2
 57*           B=(SUMXY-XMED*SUMY)/(SUMXQ-C*XMED**2)
 58*           A=SUMY/C-B*XMED
 59*           QK=B/A**2
 60*           XQ=0.0
 61*           QMIN=0.0
 62*           DO30 M=1,NOBS
 63*           Y1=A+B*X(M)
 64*           QMIN=QMIN+(Y1-Y(M))**2
 65*           XQ=XQ+(X(M)-XMED)**2
 66*           WRITE(6,20)M,T(M),X(M),Y(M),Y1
 67*        20 FORMAT(1X,I2,2X,' TIME(SEC)=',F7.2,2X,' X(G/DL)=',F7.4,2X,' Y=',F7
 68*          1.4,2X,' Y1=',F7.4,/,)
 69*        30 CONTINUE
 70*           SYX=SQRT(QMIN/(C-2.0))
 71*           ALIMB=ANI(NI)*(SYX/SQRT(XQ))
 72*           ALIMA=ANI(NI)*SYX*SQRT(1.0/C+XMED**2/XQ)
 73*           WRITE(6,21)SYX
 74*        21 FORMAT(//,'  STANDARD DEVIATION=',F7.4)
 75*           WRITE(6,39)IPERC
 76*        39 FORMAT(///,'  CONFIDENCE INTERVAL =',I3)
 77*           WRITE(6,5)A,ALIMA
 78*         5 FORMAT(//,'  INTERCEPT(=INTRINSIC VISCOSITY)=',F6.3,3H +-,F6.4,//)
 79*           WRITE(6,69)B,ALIMB
 80*        69 FORMAT(1X,' SLOPE=',E10.4,3H +-,E10.4,/,)
 81*           BMAX=B+ALIMB
 82*           BMIN=B-ALIMB
 83*           AMAX=A+ALIMA
 84*           AMIN=A-ALIMA
 85*           QKMAX=BMAX/AMIN**2
 86*           QKMIN=BMIN/AMAX**2
 87*           WRITE(6,233)QK,QKMAX,QKMIN
 88*       233 FORMAT(//,'  KRAEMER CONSTANT=',F7.4,3X,' MAX=',F7.4,3X,' MIN=',F7
 89*          1.4)
 90*           IF(AKA.LT.0.0)GOTO73
 91*           AO=A/AKA
 92*           RA=1.0/AC
 93*           AL=ALOG(AO)
 94*           AOA=(A+ALIMA)/AKA
 95*           AOM=(A-ALIMA)/AKA
 96*           ALA=ALOG(AOA)
 97*           ALM=ALOG(AOM)
 98*           ARG=RA*AL
 99*           AM=EXP(ARG)
100*           AMA=EXP(RA*ALA)
101*           AMI=EXP(RA*ALM)
102*           WRITE(6,79)AC,AKA
103*        79 FORMAT(//,1X,' A=',E10.4,8X,' K=',E10.4,///)
104*           WRITE(6,6)AM,AMA,AMI
105*         6 FORMAT(1X,' AVERAGE MOL WEIGHT=',E10.4,2X,' MAX=',E10.4,2X,' MIN='
106*          1,E10.4,/1HO)
107*        73 GOTO 62
108*       163 CONTINUE
109*        26 STOP
110*           END
```

Fig. 2. Second computer program using Kraemer equation.

times of the solvent and of the solutions from the capillary viscometer, K is the viscometer constant, which depends on its geometry.

The concentration of diluted solutions is generally very low (<1 g/100 cc) so that the solvent and the solution densities are very close. Supposing that $\rho_s = \rho$, if K/t_s^2 and K/t^2 are both negligible with respect to unity, which can be obtained with suitable viscometers, eq. (1) becomes

$$\eta'_{sp} = \eta'_{rel} - 1 = \frac{t}{t_s} - 1. \tag{2}$$

The equations which correlate η_{sp} and η_{rel} to the concentration c are

$$\eta_{sp} / c = [\eta] + k'c[\eta]^2 \tag{3}$$

$$\ln \eta'_{rel} / c = [\eta] + k''c[\eta]^2 \tag{4}$$

where k' is the Huggins constant,[1] k'' is the Kraemer constart,[2] and $[\eta]$ is the intrinsic viscosity.

```
      C     INTERPOLATION      A0+A(SQUARE+X
            DIMENSION T(1000),C(10),X(1000),Y(1000),Y1(1000),DIF(1000),XR(3)
           1,SQ(3),TITLE(13),R(4),XI(13),CC(100)
         89 READ(5,90)NN
         90 FORMAT(I3)
            DO163II=1,NN
            READ(5,3) (TITLE(J), J=1,13)
          3 FORMAT(13A6)
            WRITE(6,59)(TITLE(J),J=1,13)
         59 FORMAT(1H1,20X,13A6)
         62 READ(5,4)NN,PK,AC,AKA
            IF(NN.LE.1)GOTO163
          4 FORMAT(I3,2F10.4,E10.3)
            READ(5,6)TS,(T(M),M=1,NN)
          6 FORMAT(10F8.3)
            READ(5,61)WEIGHT,(C(M),M=1,NN)
         61 FORMAT(F10.7,10F7.4)
            SUMCC=0.0
            DO77M=1,NN
            SUMCC=SUMCC+CC(M)
            C(M)=WEIGHT*100.0/SUMCC
            X(M)=PK*C(M)
            Y(M)=(T(M)-TS)/(TS*C(M))
         77 CONTINUE
            SUMX=0.0
            SUMXY=0.0
            SUMXQ=0.0
            SUMY=0.0
            DO 51 J=1,NN
            SUMY=SUMY+Y(J)
            SUMX=SUMX+X(J)
            SUMXY=SUMXY+X(J)*Y(J)
         51 SUMXQ=SUMXQ+X(J)*X(J)
            B(1)=1.0
            B(2)=(1.5*SUMX)/SUMXQ
            QN=NN
            B(3)=(QN-2.0*SUMXY)/(2.0*SUMXQ)
            B(4)=-SUMY/(2.0*SUMXQ)
            CALL SEQ3(B,XR,XI,KW,L)
            DO 10 I=1,3
            IF(XI(I).LT.0.0)GOTO10
            IF(XI(I).GT.0.0)GOTO10
            SQ(I)=0.0
            DO 11 J=1,NN
         11 SQ(I)=SQ(I)+(Y(J)-XR(I)-XR(I)*XR(I)*X(J))*(Y(J)-XR(I)-XR(I)
           1*XR(I)*X(J))
            IF(L.EQ.2)QMIN=SQ(I)
            IF(L.EQ.2)RMIN=XR(I)
            IF(L.EQ.2)GOTO40
         10 CONTINUE
            QMIN=SQ(1)
            RMIN=XR(1)
            DO 30 K=2,3
            IF(SQ(K).GT.QMIN)GOTO30
            QMIN=SQ(K)
            RMIN=XR(K)
         30 CONTINUE
         40 QRMIN=RMIN*RMIN
            AO=RMIN/AKA
            AL=ALOG(AO)
            RA=1.0/AC
            ARG=RA*AL
```

Fig. 3 (*continued*)

```
63*            PM=EXP(ARG)
64*            WRITE(6,80)
65*         80 FORMAT(///,1X,' LIST OF MEASURES',/)
66*            WRITE(6,81)TS,PK
67*         81 FORMAT(//,1X,' TS=',F7.2,5X,' HUGGINS CONSTANT=',F10.4,//,)
68*            DO35M=1,NN
69*            Y1(M)=RMIN+QRMIN*X(M)
70*            DIF(M)=Y(M)-Y1(M)
71*            WRITE(6,82)M,T(M),C(M),X(M),Y(M),Y1(M),DIF(M)
72*         35 CONTINUE
73*         82 FORMAT(/,1X,I2,2X,' TIME(SEC)=',F7.2,2X,' C(G/DL)=',F7.4,2X,' X(=P
74*           1K*C)=',F7.4,2X,' Y=',F7.4,2X,' Y1=',F7.4,2X,' DIF=',F7.4)
75*            IF(L.EQ.1)WRITE(6,84)
76*         84 FORMAT(//,1X,' NUMBER OF REAL ROOTS=3 ',)
77*            IF(L.EQ.2)WRITE(6,321)
78*        321 FORMAT(//,1X,' NUMBER OF REAL ROOTS=1 ',)
79*            WRITE(6,83)RMIN,AC,AKA,PM
80*         83 FORMAT(//,1X,' AZERO(=INTERCEPT=INTRINSIC VISCOSITY)=',F7.4,2X,' A
81*           1=',F7.4,2X,' K=',E10.3,2X,' MOL WEIGHT=',E12.4)
82*            GOTO62
83*        163 CONTINUE
84*         99 STOP
85*            END
```

Fig. 3. Third computer program using a known Huggins constant.

```
    POLYISOBUTYLENE A  IN CYCLOHEXANE  T=30C  VISCOM.1

LIST OF MEASURES

TS = 323.50      WITH DENSITY AND KINETIC-ENERGY CORRECTIONS

1   TIME(SEC)= 731.10   X(G/DL)=  .3125   Y= 0.7933   Y1= 0.8084

2   TIME(SEC)= 575.50   X(G/DL)=  .2083   Y= 0.5025   Y1= 0.4916

3   TIME(SEC)= 505.50   X(G/DL)=  .1563   Y= 0.3718   Y1= 0.3332

4   TIME(SEC)= 437.20   X(G/DL)=  .1042   Y= 0.1403   Y1= 0.1748

STANDARD DEVIATION=  .0389

CONFIDENCE INTERVAL = 95

INTERCEPT(=INTRINSIC VISCOSITY)= 3.858 +- .2282

SLOPE=  .3041+01 +-  .1087+01

HUGGINS CONSTANT=  .2043   MAX=  .3133   MIN=  .1171

A=  .6900+00      K=  .2760-03

AVERAGE MOL WEIGHT=  .1018+07   MAX=  .1107+07   MIN=  .9322+06
```

Fig. 4. OUTPUT of the first program according to cards 3–8 of the INPUT of Table II.

```
   POLYISOBUTYLENE A  IN CYCLOHEXANE  T=30C  VISCOM.1

LIST OF MEASURES

TS = 323.50       WITHOUT CORRECTIONS

1   TIME(SEC)= 731.10   X(G/DL)=  .3125   Y= 4.0319   Y1= 4.0468
2   TIME(SEC)= 575.50   X(G/DL)=  .2083   Y= 3.7391   Y1= 3.7265
3   TIME(SEC)= 505.50   X(G/DL)=  .1563   Y= 3.6006   Y1= 3.5663
4   TIME(SEC)= 437.20   X(G/DL)=  .1042   Y= 3.3741   Y1= 3.4061

STANDARD DEVIATION=  .0360

CONFIDENCE INTERVAL = 95

INTERCEPT(=INTRINSIC VISCOSITY)= 3.086 +- .2109

SLOPE=  .3075+01 +-  .1004+01

HUGGINS CONSTANT=  .3229   MAX=  .4935   MIN=  .1905

A=  .6900+00      K=  .2760-03

AVERAGE MOL WEIGHT=  .7368+06   MAX=  .8108+06   MIN=  .6649+06
```

Fig. 5. OUTPUT of the first program according to cards 10–15 of the INPUT of Table II.

Experimentally the viscosimetric measurements are repeated varying the initial concentration with dilution: plotting eqs. (3) and (4), one obtains $[\eta]$ which is correlated to polymer molecular weight M through the Mark-Houwink[3,4] equation

$$[\eta] = KM \tag{5}$$

where K and a are characteristic constants for every polymer–solvent system.

PRINCIPLES OF CALCULATION

First of all, the values of the different concentrations (in g/100 cc) are calculated from the polymer weight and from the solvent volume (cc) added in every test. Considering the additivity of the volumes, the solution densities are calculated from the polymer and solvent densities. According to eq. (1), η_{sp} is calculated from the values of K, t_s, and t for every concentration c. However, it is possible to use the simplified eq. (2), too. At this stage, all the

```
POLYISOBUTYLENE B  IN CYCLOHEXANE  T=30C  VISCOM.2

LIST OF MEASURES

TS = 209.30      WITH DENSITY AND KINETIC-ENERGY CORRECTIONS

1   TIME(SEC)= 563.50   X(G/DL)=  .3212   Y= 6.2817   Y1= 6.3016
2   TIME(SEC)= 429.60   X(G/DL)=  .2141   Y= 5.8420   Y1= 5.8150
3   TIME(SEC)= 361.40   X(G/DL)=  .1606   Y= 5.5975   Y1= 5.5717
4   TIME(SEC)= 302.40   X(G/DL)=  .1071   Y= 5.2957   Y1= 5.3285

STANDARD DEVIATION=  .0378

CONFIDENCE INTERVAL = 90

INTERCEPT(=INTRINSIC VISCOSITY)= 4.842 +- .1505

SLOPE=  .4544+01 +-  .6974+00

HUGGINS CONSTANT=  .1938   MAX=  .2382   MIN=  .1544

A=  .6900+00      K=  .2760-03

AVERAGE MOL WEIGHT=  .1415+07   MAX=  .1480+07   MIN=  .1352+07
```

Fig. 6. OUTPUT of the first program according to cards 17–22 of the INPUT of Table II.

data to be entered into eq. (3) are available. Substituting now $y = \eta_{sp}/c$ and $x = c$, eq. (3) becomes

$$y = a_0 + a_1 x \tag{6}$$

where $a_0 = [\eta]$ and $a_1 = k'[\eta]^2$.

The best values of the constant a_0 and a_1 are obtained by a least-squares method. The confidence intervals (with the coefficient of confidence $1 - \alpha$) for the intercept a_0 and for the slope a_1 are given[14] from

$$a_0 \pm t_{\alpha/2;\,n-2}\, s_{y/x} \sqrt{\frac{1}{n} + \frac{(\bar{x})^2}{\sum_{i=1}^{n} (x_i - \bar{x})^2}} \tag{7}$$

$$a_1 \pm t_{\alpha/2;\,n-2} \frac{s_{y/x}}{\sqrt{\sum_{i=1}^{n} (x_i - \bar{x})^2}} \tag{8}$$

```
   POLYISOBUTYLENE B  IN CYCLOHEXANE  T=30C  VISCOM.2

LIST OF MEASURES

TS = 204.30       WITHOUT CORRECTIONS

1   TIME(SEC)= 563.50   X(G/DL)=  .3212   Y= 5.4738   Y1= 5.4948
2   TIME(SEC)= 424.60   X(G/DL)=  .2141   Y= 5.0357   Y1= 5.0066
3   TIME(SEC)= 361.40   X(G/DL)=  .1606   Y= 4.7881   Y1= 4.7626
4   TIME(SEC)= 302.40   X(G/DL)=  .1071   Y= 4.4848   Y1= 4.5185

STANDARD DEVIATION=  .0392

CONFIDENCE INTERVAL = 90

INTERCEPT(=INTRINSIC VISCOSITY)= 4.030 +- .1559

SLOPE=  .4559+01 +-  .7223+00

HUGGINS CONSTANT=  .2807   MAX=  .3518   MIN=  .2189

A=  .6900+00      K=  .2760-03

AVERAGE MOL WEIGHT=  .1085+07   MAX=  .1146+07   MIN=  .1025+07
```

Fig. 7. OUTPUT of the first program according to cards 24–29 of the INPUT of Table II.

where $t_{\alpha/2;n-2}$ is the Student's t-coefficient with $n-2$ degrees of freedom. The numerical values of the t coefficient are tabulated[15] and reported in Table I as a function of the degrees of freedom $n-2$ (that is, also of the number of tests) and of α; $1-\alpha$ represents the probability that the values of a_0 and of a_1 are included between the limits indicated in eq. (7); $\bar{x}$ is the average value of x_i; $s_{y/x}$ is the standard deviation

$$s_{y/x} = \sqrt{\frac{\sum_{i=1}^{n} (y_i - y_c)^2}{n-2}} \tag{9}$$

where y_c is the calculated value of y.

Then, the calculations of k' $(= a_1/a_0^2)$, M $(= (a_0/K)^{1/a})$, and their maximum and minimum values in the considered confidence intervals are performed.

The FORTRAN IV program of this calculation is reported in Fig 1. Another program, which uses the Kraemer eq. (4), instead of the Huggins eq. (3), is reported in Figure 2. In this case, we make the substitutions $y = \ln \eta_{rel}/c$

```
POLYISOBUTYLENE B  IN CYCLOHEXANE  T=30C  VISCOM.2

LIST OF MEASURES

TS = 204.30      WITHOUT CORRECTIONS

1   TIME(SEC)= 563.50   X(G/DL)=  .3212   Y= 5.4738   Y1= 5.4948
2   TIME(SEC)= 424.60   X(G/DL)=  .2141   Y= 5.0357   Y1= 5.0066
3   TIME(SEC)= 361.40   X(G/DL)=  .1606   Y= 4.7881   Y1= 4.7626
4   TIME(SEC)= 302.40   X(G/DL)=  .1071   Y= 4.4848   Y1= 4.5185

STANDARD DEVIATION=  .0392

CONFIDENCE INTERVAL = 90

INTERCEPT(=INTRINSIC VISCOSITY)= 4.030 +- .1559

SLOPE=  .4559+01 +-  .7223+00

HUGGINS CONSTANT=  .2807   MAX=  .3518   MIN=  .2189
```

Fig. 8. OUTPUT of the first program according to cards 31–36 of the INPUT of Table II.

and $a_1 = k'' [\eta]^2$ in eq. (6). The two programs are very similar, they have the same INPUT, and we can change the program only substituting the cards 36, 37, 38, 59, 85, 86, 87, 88, and 89.

Beyond the approximation of eq. (2), another simplification can be done if we know the value of the Huggins constant. This value must be obtained from careful preliminary calibration tests with polymers of identical polydispersity. Equation (6) can now be written as follows:

$$y = a_0 + k' a_0^2 X \tag{10}$$

Indicating with X the value of $k'x$, we obtain

$$y = a_0 + a_0^2 X \tag{11}$$

where $a_0 = [\eta]$.

TABLE I
Numerical Values of Student's t-Coefficient

$n-2$	$\alpha/2 = 0.2$	0.1	0.03	0.025	0.01
1	1.376	3.078	6.314	12.71	31.82
2	1.061	1.886	2.920	4.303	6.965
3	0.978	1.638	2.353	3.182	4.541
4	0.941	1.533	2.132	2.776	3.747
5	0.920	1.476	2.015	2.571	3.365
6	0.906	1.440	1.943	2.447	3.143

```
   POLYISOBUTYLENE A  IN CYCLOHEXANE  T=30C  VISCOM.1

LIST OF MEASURES

TS = 323.50       WITH DENSITY AND KINETIC-ENERGY CORRECTIONS

1   TIME(SEC)= 731.10   X(G/DL)=  .3125   Y= 2.9294   Y1= 2.9274
2   TIME(SEC)= 575.50   X(G/DL)=  .2083   Y= 3.1760   Y1= 3.1874
3   TIME(SEC)= 505.50   X(G/DL)=  .1563   Y= 3.3321   Y1= 3.3175
4   TIME(SEC)= 437.20   X(G/DL)=  .1042   Y= 3.4423   Y1= 3.4475

STANDARD DEVIATION=  .0137

CONFIDENCE INTERVAL = 95

INTERCEPT(=INTRINSIC VISCOSITY)= 3.708 +- .0803

SLOPE= -.2497+01 +-  .3824+00

KRAEMER CONSTANT= -.1816     MAX= -.1607     MIN= -.2007

A=  .6900+00      K=  .2760-03

AVERAGE MOL WEIGHT=  .9613+06   MAX=  .9917+06   MIN=  .9313+06
```

Fig. 9. OUTPUT of the second program according to cards 3–8 of the INPUT of Table II.

The calculation of a_0 which minimizes the sum of the squares of deviations employs a third-degree equation. In the program of Figure 3, this equation is solved by Cardano formulas using a library subroutine (SEQ 3).

EXAMPLES OF APPLICATION

We report as examples of application the data elaboration of two viscosimetric tests using two different samples of polyisobutylene in cyclohexane at 30°C. The viscometers were chosen in such a way as to evidence the differences of the results obtained according to eqs. (1) and (2). The molecular weights are calculated according to the Krigbaum-Flory relationship[16]:

$$[\eta] = 2.76 \times 10^{-4} M^{0.69} \tag{12}$$

The experimental data are reported in the INPUT cards. Table II reports the INPUT for both the programs of Figures 1 and 2. The INPUT of the program of Figure 3 is reported in Table III.

TABLE II
Example of INPUT for the First and Second Programs

Card number	Card content
1	5
2	1
3	POLYISOBUTYLENE A IN CYCLOHEXANE T=30C VISCOM.1
4	12.710 4.303 3.182 2.776 2.571 2.447 95
5	0.69 2.76 E-04
6	4 12040 0.764 0.918
7	323.5 731.1 575.5 505.5 437.2
8	0.03125 10 5 5 10
9	1
10	POLYISOBUTYLENE A IN CYCLOHEXANE T=30C VISCOM.1
11	12.710 4.303 3.182 2.776 2.571 2.447 95
12	0.69 2.76 E-04
13	4 −1 1 1
14	323.5 731.1 575.5 505.5 437.2
15	0.03125 10 5 5 10
16	1
17	POLYISOBUTYLENE B IN CYCLOHEXANE T=30C VISCOM.2
18	6.314 2.920 2.358 2.132 2.015 1.943 90
19	0.69 2.76 E-04
20	4 4050 0.764 0.918
21	204.3 563.5 424.6 361.4 302.4
22	0.03212 10 5 5 10
23	1
24	POLYISOBUTYLENE B IN CYCLOHEXANE T=30C VISCOM.2
25	6.314 2.920 2.358 2.132 2.015 1.943 90
26	0.69 2.76 E-04
27	4 −1 1 1
28	204.3 563.5 424.6 361.4 302.4
29	0.03212 10 5 5 10
30	1
31	POLYISOBUTYLENE B IN CYCLOHEXANE T=30C VISCOM.2
32	6.314 2.920 2.358 2.132 2.015 1.943 90
33	1 −1
34	4 −1 1 1
35	204.3 563.5 424.6 361.4 302.4
36	0.03212 10 5 5 10
37	1

TABLE III
Example of INPUT for the Third Program

Card number	Card content
1	2
2	POLYISOBUTYLENE A IN CYCLOHEXANE T=30C VISCOM.1
3	4 0.2 0.69 2.76 E-04
4	323.5 731.1 575.5 505.5 437.2
5	0.03125 10 5 5 10
6	1
7	POLYISOBUTYLENE B IN CYCLOHEXANE T=30C VISCOM.2
8	4 0.2 0.69 2.76 E-04
9	204.3 563.5 424.6 361.4 302.4
10	0.03212 10 5 5 10
11	1

```
   POLYISOBUTYLENE A  IN CYCLOHEXANE  T=30C  VISCOM.1

LIST OF MEASURES

TS = 323.50      WITHOUT CORRECTIONS

1   TIME(SEC)= 731.10   X(G/DL)=  .3125   Y= 2.6091   Y1= 2.6158
2   TIME(SEC)= 575.50   X(G/DL)=  .2083   Y= 2.7650   Y1= 2.7622
3   TIME(SEC)= 505.50   X(G/DL)=  .1563   Y= 2.8566   Y1= 2.8355
4   TIME(SEC)= 437.20   X(G/DL)=  .1042   Y= 2.8914   Y1= 2.9087

STANDARD DEVIATION=  .0200

CONFIDENCE INTERVAL = 95

INTERCEPT(=INTRINSIC VISCOSITY)= 3.055 +- .1171

SLOPE= -.1406+01 +-  .5578+00

KRAEMER CONSTANT= -.1506    MAX= -.0983    MIN= -.1951

A=  .6900+00     K=  .2760-03

AVERAGE MOL WEIGHT=  .7262+06   MAX=  .7669+06   MIN=  .6862+06
```

Fig. 10. OUTPUT of the second program according to cards 10–15 of the INPUT of Table II.

```
   POLYISOBUTYLENE B  IN CYCLOHEXANE  T=30C  VISCOM.2

LIST OF MEASURES

TS = 204.30      WITH DENSITY AND KINETIC-ENERGY CORRECTIONS

1   TIME(SEC)= 563.50   X(G/DL)=  .3212   Y= 3.4386   Y1= 3.4291
2   TIME(SEC)= 424.60   X(G/DL)=  .2141   Y= 3.7890   Y1= 3.8068
3   TIME(SEC)= 361.40   X(G/DL)=  .1606   Y= 3.9932   Y1= 3.9956
4   TIME(SEC)= 302.40   X(G/DL)=  .1071   Y= 4.1951   Y1= 4.1844

STANDARD DEVIATION=  .0162

CONFIDENCE INTERVAL = 90
```

Fig. 11 (*continued*)

```
INTERCEPT(=INTRINSIC VISCOSITY)= 4.562 +- .0645

SLOPE= -.3527+01 +-  .2988+00

KRAEMER CONSTANT= -.1695     MAX= -.1596     MIN= -.1787

A=  .6900+00      K=  .2760-03

AVERAGE MOL WEIGHT=  .1298+07   MAX=  .1325+07   MIN=  .1272+07
```

Fig. 11. OUTPUT of the second program according to cards 17–22 of the INPUT of Table II.

```
   POLYISOBUTYLENE B  IN CYCLOHEXANE  T=30C  VISCOM.2

LIST OF MEASURES

TS = 204.30       WITHOUT CORRECTIONS

1   TIME(SEC)= 563.50   X(G/DL)=  .3212   Y= 3.1587   Y1= 3.1613
2   TIME(SEC)= 424.60   X(G/DL)=  .2141   Y= 3.4164   Y1= 3.4156
3   TIME(SEC)= 361.40   X(G/DL)=  .1606   Y= 3.5517   Y1= 3.5427
4   TIME(SEC)= 302.40   X(G/DL)=  .1071   Y= 3.6628   Y1= 3.6699

STANDARD DEVIATION=  .0083

CONFIDENCE INTERVAL = 90

INTERCEPT(=INTRINSIC VISCOSITY)= 3.924 +- .0330

SLOPE= -.2375+01 +-  .1528+00

KRAEMER CONSTANT= -.1542     MAX= -.1468     MIN= -.1614

A=  .6900+00      K=  .2760-03

AVERAGE MOL WEIGHT=  .1044+07   MAX=  .1056+07   MIN=  .1031+07
```

Fig. 12. OUTPUT of the second program according to cards 24–29 of the INPUT of Table II.

```
   POLYISOBUTYLENE B  IN CYCLOHEXANE  T=30C  VISCOM.2

LIST OF MEASURES

TS = 204.30       WITHOUT CORRECTIONS

1   TIME(SEC)= 563.50   X(G/DL)=  .3212   Y= 3.1587   Y1= 3.1613
2   TIME(SEC)= 424.60   X(G/DL)=  .2141   Y= 3.4164   Y1= 3.4156
3   TIME(SEC)= 361.40   X(G/DL)=  .1606   Y= 3.5517   Y1= 3.5427
4   TIME(SEC)= 302.40   X(G/DL)=  .1071   Y= 3.6628   Y1= 3.6699

STANDARD DEVIATION=  .0083

CONFIDENCE INTERVAL = 90

INTERCEPT(=INTRINSIC VISCOSITY)= 3.928 +- .0330

SLOPE= -.2375+01 +-  .152R+00

KRAEMER CONSTANT= -.1582     MAX= -.1868     MIN= -.1614
```

Fig. 13. OUTPUT of the second program according to cards 31–36 of the INPUT of Table II.

```
                POLYISOBUTYLENE A  IN CYCLOHEXANE  T=30C  VISCOM.1

LIST OF MEASURES

TS= 323.50      HUGGINS CONSTANT=     .2000

1   TIME(SEC)= 731.10   C(G/DL)=  .3125   X(=PK*C)=  .3625   Y= 4.0319   Y1= 3.9434,  DIF=  .0885
2   TIME(SEC)= 575.50   C(G/DL)=  .2083   X(=PK*C)=  .0417   Y= 3.7391   Y1= 3.7201   DIF=  .0190
3   TIME(SEC)= 505.50   C(G/DL)=  .1563   X(=PK*C)=  .3312   Y= 3.6906   Y1= 3.6085   DIF= -.0079
4   TIME(SEC)= 437.20   C(G/DL)=  .1042   X(=PK*C)=  .0208   Y= 3.3741   Y1= 3.4968   DIF= -.1227

NUMBER OF REAL ROOTS=3

AZERO(=INTERCEPT=INTRINSIC VISCOSITY)= 3.2734   A=  .6900   K=  .276-03   MOL WEIGHT=  .8026+06
```

Fig. 14. OUTPUT of the third program according to cards 2–5 of the INPUT of Table III.

We report the OUTPUT of the first program, which employs the Huggins equation, in Figures 4–8; the OUTPUT of the second program, which employs the Kraemer equation, in Figures 9–13; the OUTPUT of the third program, in Figures 14 and 15.

```
                    POLYISOBUTYLENE P  IN CYCLOHEXANE  T=30C  VISCOM.2

LIST OF MEASURES

TS= 204.30      HUGGINS CONSTANT=      .2000

1   TIME(SEC)= 563.50   C(G/DL)=  .3212   X(=PK*C)=  .0642   Y= 5.4738   Y1= 5.3851   DIF=  .0887
2   TIME(SEC)= 428.60   C(G/DL)=  .2141   X(=PK*C)=  .0428   Y= 5.0757   Y1= 5.0013   DIF=  .0744
3   TIME(SEC)= 361.40   C(G/DL)=  .1606   X(=PK*C)=  .0321   Y= 4.7881   Y1= 4.8094   DIF= -.0213
4   TIME(SEC)= 302.40   C(G/DL)=  .1071   X(=PK*C)=  .0214   Y= 4.4948   Y1= 4.6275   DIF= -.1327

NUMBER OF REAL ROOTS=3

AZERO(=INTERCEPT=INTRINSIC VISCOSITY)= 4.2337   A=  .6900   K=  .276-03   MOL WEIGHT=  .1165+07
```

Fig. 15. OUTPUT of the third program according to cards 7–10 of the INPUT of Table III.

In cards 4, 11, 18, 25, and 32 of the INPUT of Figure 2, the Student's t-coefficients (already tabulated in Table I) for the desired confidence interval (last number on the right) up to 8 experimental points are reported.

Cards 5, 12, 19, 26, and 33 report the a and K values of eq. (5) for the considered polymer–solvent system: in our case, the data of eq. (12). When the INPUT value for K is negative (especially 33), the program does not calculate the molecular weight.

Cards 6, 13, 20, 27, and 34 report the number of experimental points, the viscometer constant K of eq. (2) (if we write a negative value for K, eq. (3) is employed), therefore the solvent and polymer densities.

Cards 7, 14, 21, 28, and 35 report the solvent and solutions efflux times.

Cards 8, 15, 22, 29, and 36 report first the polymer weight, the initial solvent volume (in cc), and then the solvent volume added at every dilution.

For the same polymer it is possible to place cards of the type 6, 13, etc., after cards of the type 8, 15, etc., obtaining a single list of results.

With regard to the cards reported in the INPUT of Table III, only cards 3 and 8 are different from those of Table II. In these cards, the number of experimental points, the Huggins constant, the a and K values of eq. (12) are reported.

References

1. M. L. Huggins, *J. Amer. Chem. Soc.*, **64**, 2716 (1942).
2. E. O. Kraemer, *Ind. Eng. Chem.*, **30**, 1200 (1938).
3. H. Mark, *Die Feste Körper*, Ed. Akademische Verlag, Lipsia, 1938.
4. R. Houwink *J. Prakt. Chem.* **175**, 15 (1940).
5. P. A. D. De Maine and R. D. Seawright, *Digital Computer Programs for Physical Chemistry*, MacMillan, New York, 1963, p. 394.
6. I. Klein and D. I. Marshall, *Computer Programs for Plastic Engineers*, SPE, Reinhold, New York, 1968, p. 349.
7. M. Pegoraro, A. Penati, J. Barês, and A. Ascheri, *Chim. Ind.* (Milan), **53**, 453 (1971).
8. B. T. Hofeiter, J. O. Ernst, and W. L. Williams, *J. Appl. Polym. Sci.*, **17**, 1449 (1973).
9. Ch'ien Jên-Yüan, *Determination of Molecular Weights of High Polymers*, IPST, Jerusalem, 1963, p. 47.
10. J. B. Kinsinger in *Encyclopedia of Polymer Science and Technology*, Vol. 14, H. F. Mark, N. G. Gaylord, and N. Bikahes, Eds., Interscience, New York, 1971, p. 717.

11. P. J. Flory, *Principles of Polymer Chemistry,* 8th ed., Cornell University Press, Ithaca, N.Y., 1971, p. 309.
12. R. H. Wagner, *Anal. Chem.* **20,** 155 (1948).
13. G. V. Schulz, *Z. Elektrochem.*, **43,** 479 (1937).
14. A. H. Bowker and G. J. Lieberman, *Engineering Statistics,* Prentice Hall, New Jersey, 1959, p. 247.
15. A. H. Bowker and G. J. Lieberman, *ibid.* p. 558.

Received January 10, 1975
Revised January 22, 1975