Theory of the Cloud-point Method for Determining Theta-conditions

D. R. NAPPER†

A theory of the modified Elias cloud-point method for determining theta-conditions is developed. This takes the form of an explicit relationship between the interaction parameter and the volume fraction of polymer at incipient phase separation. With the aid of this relationship, numerical calculations are performed easily, without resort to electronic computation. The conditions necessary for the unmodified Elias method to yield correct results are also determined.

ELIAS[1,2] has proposed a cloud-point procedure for determining theta-compositions. This method consists of titrating with non-solvent dilute solutions of polymer, at different concentrations, to incipient phase separation. The volume fraction of non-solvent (v_{ns}) thus required when plotted against the polymer concentration (c_2 in g cm^{-3}) at the cloud-point, usually on a log/log basis, can be linearly extrapolated to log $c_2=0$. The corresponding value of v_{ns} was claimed by Elias to be the theta-composition. Morawetz[3] has pointed out that a sound theoretical basis for the method was not established; instead, Elias[2] adopted a pragmatic approach and showed experimentally that the method commonly yielded theta-compositions comparable to those obtained by thermodynamically based techniques.

Subsequently, Cornet and van Ballegooijen[4] modified the Elias procedure. They proposed that v_{ns}, rather than the more usual log v_{ns}, is the correct parameter to plot as ordinate and that the correct abscissa is the logarithm of the volume fraction (not the concentration) of polymer (v_2). In support of these proposals, Cornet and van Ballegooijen presented computer calculations, based upon the Flory–Huggins theory, which established a linear dependence of the interaction parameter χ_1 on log v_2 when $10^{-5} \leqslant v_2 \leqslant 10^{-2}$. Extrapolation of such plots to $v_2=1$ gave $\chi_1=\frac{1}{2}$. This corresponds[5] to the attainment of theta-conditions. As v_{ns} and χ_1 can also be related linearly[4], these calculations provided the first thermodynamic justification for the cloud-point method, albeit in its modified form. An analogous procedure[4] was also devised for determining theta-temperatures.

Cornet and van Ballegooijen[4] were, however, unable to find an explicit mathematical dependence of χ_1 on log v_2 which would constitute the theoretical justification called for by Morawetz. Consequently, they were forced to rely upon electronically calculated relationships obtained by trial-and-error computation from the raw Flory–Huggins equations. Our purpose is to develop an explicit relationship between log v_2 and χ_1 to a point where it is unnecesssary to resort to computer calculations. In addition, as it might perhaps be inferred that the unmodified Elias method is invariably grossly

---

†Queen Elizabeth II Fellow at the University of Sydney.

in error, we will determine the mathematical conditions under which it may give correct results.

THEORY

The following notation is used:

μ	Chemical potential
v	Volume fraction
χ_1	Interaction parameter
x	Polymer lattice site occupation number
subscript 1	denotes the solvent
subscript 2	denotes the polymer
superscript c	denotes the concentrated polymer phase
superscript d	denotes the dilute polymer phase.

We begin by identifying v_2^d with the polymer concentration at incipient phase separation. This is justifiable if an infinitesimally small amount of concentrated polymer phase is formed and if $v_2^d \leqslant 0{\cdot}01$. We will further assume that $x \gg 1$, that $v_2^c \gg v_2^d$ and that the interaction parameter is the same in both the concentrated and the dilute phases. Then at equilibrium between the phases:

$$\mu_1^c = \mu_1^d \tag{1}$$

and

$$\mu_2^c = \mu_2^d \tag{2}$$

Since the net segment interaction is small, we may substitute for all four chemical potentials the well-known expressions derived from the Flory–Huggins theory[5] of concentrated polymer solutions. On rearrangement and minor simplification, we obtain from equality (1)

$$\ln(1 - v_2^c) - \ln(1 - v_2^d) + (v_2^c - v_2^d) + \chi_1\,[(v_2^c)^2 - (v_2^d)^2] = 0 \tag{3}$$

where we have set $\chi_1^c = \chi_1^d = \chi_1$. The assumptions $v_2^c \gg v_2^d$ and $v_2^d \leqslant 0{\cdot}01$ are also invoked to give

$$\ln(1 - v_2^c) + v_2^c + \chi_1\,(v_2^c)^2 = 0 \tag{4}$$

Since $v_2^c < 1$, we may expand the logarithm as a power series, neglecting terms higher than third order

$$(v_2^c)^3/3 - (v_2^c)^2\,(\chi_1 - \tfrac{1}{2}) = 0 \tag{5}$$

The non-trivial solution of this cubic equation is

$$v_2^c = 3\,(\chi_1 - \tfrac{1}{2}) \tag{6}$$

On substituting the Flory–Huggins relationships into equality (2) and simplifying, we find

$$\ln v_2^d = \ln v_2^c + x v_2^c + x\chi_1 v_2^c\,(v_2^c - 2) \tag{7}$$

Equation (6) can now be used to eliminate v_2^c from equation (7) whence

$$\ln v_2^d = \ln\,[3\,(\chi_1 - \tfrac{1}{2})] + 9x\,(\chi_1 - \tfrac{1}{2})\,[\chi_1^2 - (\tfrac{7}{6})\,\chi_1 + \tfrac{1}{3}] \tag{8a}$$

i.e.

$$\log v_2^d = \log\,[3\,(\chi_1 - \tfrac{1}{2})] + 3{\cdot}908x\,(\chi_1 - \tfrac{1}{2})^2\,(\chi_1 - \tfrac{2}{3}) \tag{8b}$$

We have now established an explicit relationship between $\log v_2^d$ and χ_1. The RHS of equation (8b) is seemingly more complex than demanded by a simple linear dependence and it cannot be simplified readily. Hence any linear dependence derived from it can be applicable only over a limited range of χ_1 and cannot be completely general. Fortunately equation (8b) is in a form particularly suited to accurate arithmetic computation: given values of x and v_2^d, the corresponding value of χ_1 is quickly calculated by successsive approximations with the aid of little more than a slide rule.

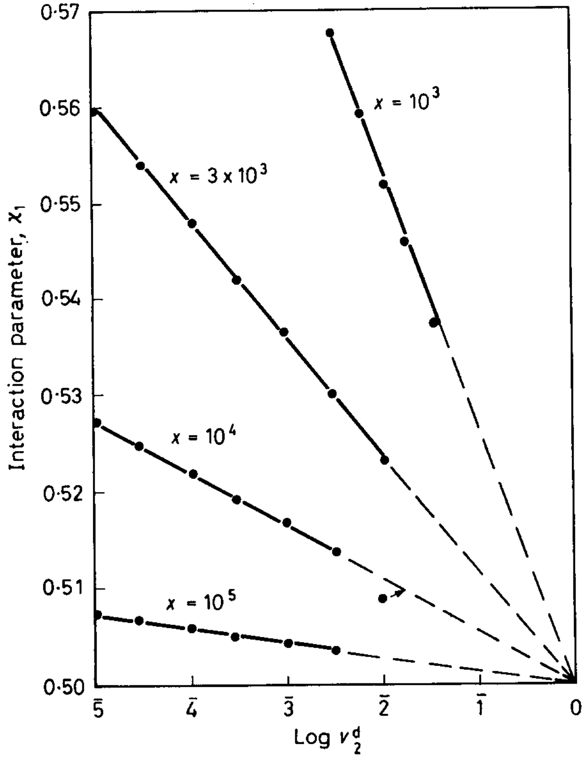

Figure 1—Variation of interaction parameter with polymer volume fraction at incipient phase separation

The results shown in *Figure 1* were generated in this way for $10^3 \leqslant x \leqslant 10^5$ and $10^{-5} \leqslant v_2^d \leqslant 10^{-2}$. The linear relationship between χ_1 and $\log v_2^d$ is immediately obvious in this domain. So, too, is the extrapolation of χ_1 to $\frac{1}{2}$ when $v_2^d = 1$.

The linearity of these plots can be derived less precisely, but without numerical computation, from further algebraic consideration of equation (8a) which takes the form

$$\log v_2^d = \log [3(\chi_1 - \tfrac{1}{2})] + 9x(\chi_1 - \tfrac{1}{2})P/2{\cdot}303$$

where

$$P = \chi_1^2 - (\tfrac{7}{6})\chi_1 + \tfrac{1}{3}$$

On differentiating P with respect to χ_1 we observe that

$$dP/d\chi_1 = 2\chi_1 - \tfrac{7}{6} \sim 0$$

since $0{\cdot}5 < \chi_1 < 0{\cdot}6$. Thus P is approximately constant over the χ_1 range studied, as is $\log [3(\chi_1 - \tfrac{1}{2})]$. The linearity of the plots of χ_1 versus $\log v_2^d$ is accordingly explained. Conversely, non-linearity outside the χ_1 range examined must be expected.

Equation (8b) can thus be regarded as the theoretical basis of the Cornet and van Ballegooijen cloud-point procedure since both v_{ns} and the inverse of the phase separation temperature are linearly related to χ_1. The assumption used in its derivation which is least likely to be valid experimentally is the equality of χ_1 in both the dilute and concentrated phases: this violation is particularly probable in the determination of theta-compositions when the ratio of solvent to non-solvent in the two phases may differ significantly.

Elias[6] has tabulated many theta-compositions, most of which were obtained by his unmodified procedure. Therefore it is relevant to ascertain theoretically whether or not these values are correct. Suppose v_{ns}^M (a constant) is the maximum value of v_{ns} observed for the most dilute solution of a given polymer. For any other polymer concentration the value of v_{ns} will be decreased by an amount δv_{ns}

$$v_{ns} = v_{ns}^M - \delta v_{ns}$$

Hence

$$\ln v_{ns} = \ln v_{ns}^M + \ln [1 - (\delta v_{ns}/v_{ns}^M)]$$

If we assume that $\delta v_{ns}/v_{ns}^M \ll 1$ then

$$\ln v_{ns} = \ln v_{ns}^M - \delta v_{ns}/v_{ns}^M$$

i.e.

$$\log v_{ns} = \log v_{ns}^M + (v_{ns} - v_{ns}^M)/(2{\cdot}303\, v_{ns}^M)$$

This linearity establishes that plots with v_{ns} and $\log v_{ns}$ as ordinates are equivalent if, and only if, $\delta v_{ns}/v_{ns}^M$ is sufficiently small for $\ln [1 - (\delta v_{ns}/v_{ns}^M)]$ to be approximated accurately by $-\delta v_{ns}/v_{ns}^M$. Moreover, the extrapolations to abscissae $c_2 = 1$ and $v_2^d = 1$ are only equivalent if the density of the polymer is not too different from unity. These two conditions must therefore be satisfied before the unmodified Elias method can be expected to yield correct results.

The experimental evidence adduced by Elias[2] to support his unmodified procedure was obtained under precisely these conditions. Conversely, Cornet and van Ballegooijen[4] showed that for polystyrene in cyclohexane at the theta-temperature, when $\delta v_{ns}/v_{ns}^M$ is not small, the unmodified Elias method gave incorrect results. Thus both theory and experiment agree that the data tabulated by Elias[6] are only reliable for those polymers whose densities are close to unity and if the concentration dependence of the volume fraction of non-solvent at the cloud-point is small in comparison with the volume fraction of non-solvent at the theta-composition.

I thank the Queen Elizabeth II Fellowship Committee for support of the completion of this work and Professor A. E. Alexander for the provision of facilities. I am grateful to Professor C. H. Bamford, F.R.S. for bringing reference 4 to my attention.

I.C.I. (Paints Division) Ltd,
Wexham Road, Slough, Bucks.
and *Department of Physical Chemistry,*
University of Sydney,
Sydney, 2006, Australia.

(Received April 1968)

REFERENCES

[1] ELIAS, H.-G. *Makromol. Chem.* 1959, **33**, 140
[2] ELIAS, H.-G. *Makromol. Chem.* 1961, **50**, 1
[3] MORAWETZ, H. *Macromolecules in Solution.* Interscience: New York, 1965
[4] CORNET, C. F. and VAN BALLEGOOIJEN, H. *Polymer, Lond.* 1966, **7**, 293
[5] FLORY, P. J. *Principles of Polymer Chemistry,* Chap XII. Cornell University Press: Ithaca, 1953
[6] ELIAS, H.-G., ADANK, G., DIETSCHY, H., ETTER, O., GRUBER, V. and IBRAHIM, F. W. *Polymer Handbook,* Chap. IV, p 163. Interscience: New York, 1966