ANALYSIS OF TRANSPORT PROPERTIES OF THE ACETONITRILE–WATER SYSTEM USING A SEGMENTED COMPOSITION MODEL

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ABSTRACT

A study has been made of the available information concerning the variation of the viscosities of acetonitrile–water mixtures with composition in the acetonitrile-rich region. The study shows that the viscosity maximum reported at $X(ACN) \simeq 0.9$ is an artifact of an overparameterised curve fitting procedure.

The use of a segmented composition model led to some tentative conclusions about the patterns of molecular aggregation of this system.

INTRODUCTION

Results have been reported of an analysis of excess viscosities of acetonitrile–water mixtures using a model which incorporates the assumption that this system possesses three distinct composition segments [1]. The data employed in that analysis were taken from a tabulation by Moreau and Douhéret [2] which they had generated by interpolation of the primary data of Mato and Hernández [3].

The primary data consists of viscosity values for both of the pure liquids and for eight mixtures at each of five temperatures. A disturbing feature of that data is the sparseness of information for mole fractions of acetonitrile $(X_A) > 0.4$. Bearing in mind that the tabulation of ref. 2 contains an interesting viscosity maximum at $X_A \simeq 0.9$, it was thought to be desirable to look for additional information about the acetonitrile-rich composition region.

A number of viscosity measurements were made in this laboratory at several different temperatures and, while there were no major discrepancies between these values and those of ref. 3, there was no indication of a viscosity maximum at $X_A \simeq 0.9$. Three additional viscosity data sets were found in the literature [4–6]. While the data of ref. 4 differs quite significantly from the other sets, those of refs. 3,5 and 6 form a combined set with

a reasonable level of internal consistency but with no suggestion of a viscosity maximum at $X_A \simeq 0.9$.

There is a further source of information about the transport characteristics of this system in the form of tritiated water and ^{14}C-labelled acetonitrile tracer diffusion coefficients [7].

The original objective of this work was to explore the temperature dependence of the three-segment model parameters for excess viscosity and to determine, and if possible interpret, the model parameters for the excess molar enthalpies and entropies of viscous flow activation.

It soon became apparent that the first priority was to settle the basic question of the shape of the viscosity curve at higher acetonitrile mole fractions. That particular venture was substantially facilitated by the availability of a modification of the original three-segment model, which had been developed in the course of a series of analyses of the excess molar volumes of the acetonitrile–water system [8].

In addition to its utility as a curve-fitting tool, the three-segment model appears to have the merit that its parameters are each related to some aspect of the patterns of molecular aggregation of the system. Consequently, there exists the hope that, from the analyses of a variety of physical properties, one may be able to form a progressively clearer idea of the nature of the dominant structural and energetic features of this particular class of binary liquid mixtures.

The three-segment model was derived for the analysis of excess extensive properties of binary liquid systems. From the standpoint of curve fitting, it does not really matter how the ideal, and hence excess, properties are defined. Nor is the distinction between intensive and extensive properties of any real consequence. Those factors do, however, represent areas of concern when the model parameters are to be contemplated as items of structural information.

EXCESS TRANSPORT PROPERTIES

There does not appear to be an obvious preferred choice of definition for the viscosity of an ideal binary liquid system. As a consequence, different authors may present alternative versions of the excess viscosities of the same system. The approach that has been adopted in this work differs in several respects from that described in ref. 2.

Equation 1 was chosen, for the analyses reported in ref. 1, on the grounds that it has been described as being satisfactory for systems which behave ideally in other, less ambiguous, contexts [9]

$$\ln \eta(\text{ideal}) = (1 - X_A) \ln \eta_W^0 + X_A \ln \eta_A^0 \tag{1}$$

where X_A is the mole fraction of acetonitrile and η_W^0 and η_A^0 are the viscosities of pure water and acetonitrile, respectively.

A more realistic definition might be one that also reflects the sensitivity of the viscosities of liquids to their molar volumes

$$\ln(\eta \overline{V})(\text{ideal}) = (1 - X_A) \ln(\eta_W^0 \overline{V}_W^0) + X_A \ln(\eta_A^0 \overline{V}_A^0) \tag{2}$$

It is noted that the product $\eta \overline{V}$ is a molar property with units of J s mol^{-1}. As such it is presumed to be a more appropriate candidate for analysis by the three-segment model.

Numerous authors have explored the relationship between tracer diffusion coefficients and viscosity. The Stokes–Einstein equation is probably the most familiar and the one most frequently employed as a basis for comparison with others.

$$D_j = \frac{kT}{6\pi r_j \eta} \tag{3}$$

where D_j is the diffusion coefficient of species j moving in a liquid of viscosity η and r_j is the molecular radius of that species.

Before looking at any specific models for viscous flow, it is appropriate to draw attention to a number of empirical relationships.

It was observed by Easteal [7] that

$$D_W^0 \eta_W^0 (1.985) \simeq D_W^A \eta_A^0 (2.006) \tag{4}$$

$$D_A^W \eta_W^0 (1.469) \simeq D_A^0 \eta_A^0 (1.506) \tag{5}$$

where the unit of the products $D\eta$ is 10^{-7} g cm s^{-2}. D_A^W and D_W^A are the respective diffusion coefficients of acetonitrile in pure water and of water in pure acetonitrile.

The differences are comparable in magnitude to the precision of the various measurements.

From those two conditions it follows that

$$\frac{D_W^A}{D_A^0}(1.332) \simeq \frac{D_W^0}{D_A^W}(1.352) \simeq \frac{D_W^0 \eta_W^0}{D_A^0 \eta_A^0}(1.319) \tag{6}$$

Somewhat less exact is the condition that

$$\frac{D_W^0 \eta_W^0}{D_A^0 \eta_A^0} \simeq \left(\frac{\overline{V}_A^0}{\overline{V}_W^0} \right)^{1/3} = (1.430) \tag{7}$$

In the same general context, it is noted that

$$\frac{D_W^0 \eta_W^0}{kT} = 0.150 \left(\frac{N}{\overline{V}_W^0} \right)^{1/3} \simeq \frac{1}{2\pi} \left(\frac{N}{\overline{V}_W^0} \right)^{1/3} \tag{8}$$

$$\frac{D_A^0 \eta_A^0}{kT} = 0.163 \left(\frac{N}{\overline{V}_A^0} \right)^{1/3} \simeq \frac{1}{2\pi} \left(\frac{N}{\overline{V}_A^0} \right)^{1/3} \tag{9}$$

Contrary to the inference that might be drawn from eqns. (4) and (5), the products $D_W \eta$ and $D_A \eta$ show quite significant deviations from being con-

stant across the entire composition range. The ratio D_W/D_A also varies quite markedly with composition.

It is found that the available data is reasonably consistent with the equation

$$\eta \overline{V} = (1 - X_A) \frac{D_W^0 \eta_W^0}{D_W} \overline{V}_W^0 + X_A \frac{D_A^0 \eta_A^0}{D_A} \overline{V}_A^0 \qquad (10)$$

This is a modified version of an empirical relationship proposed by Albright [10]. It differs from the original in so far as it drops the distinction between the partial molar volumes of the components and their pure liquid molar volumes.

It is suggested that the variations in the ratio D_W/D_A, with composition, arise because the molecules of the two components are moving in different time-averaged local environments. It seems appropriate to introduce the concept of effective component viscosities as defined by

$$\eta_W^{X_A} = \frac{D_W^0 \eta_W^0}{D_W^{X_A}} \qquad (11)$$

where $D_W^{X_A}$ is the diffusion coefficient for water in a mixture of composition X_A.

Thus eqn. (10) becomes

$$\eta \overline{V} = (1 + X_A) \eta_W^{X_A} \overline{V}_W + X_A \eta_A^{X_A} \overline{V}_A \qquad (12)$$

It is customary to treat the translational motions of individual molecules in a liquid medium as consisting of a sequence of jumps, which are separated by periods of libration. The jumps are characterised by a distance λ and a frequency ν.

In Eyring and co-workers' treatment, the diffusion coefficient is expressed by [11,12]

$$D_W = (\lambda^2 \nu)_W \qquad (13)$$

The same model defines the viscosity to be

$$\eta = \frac{a_1}{a_2 a_3} \frac{kT}{\lambda^2 \nu} \qquad (14)$$

where a_1 is the distance separating two adjacent molecular layers, $a_2 a_3$ is the area of contact between one molecule and those of the next layer, and k is the Boltzmann constant.

The number of model parameters can be reduced by replacing the ratio $a_1/a_2 a_3$ by a^2/V_m (where $V_m (= \overline{V}/N)$ is the molecular volume), thus

$$\eta = \frac{a^2}{\overline{V}} \frac{NkT}{\lambda^2} \qquad (15)$$

Combining eqns. (8) and (9) with (13) and (15) leads to

$$2\pi a_W^2 \simeq \left(\frac{\overline{V}_W^0}{N} \right)^{2/3} \qquad (16)$$

The most significant aspects of Eyring's work result from the analogy drawn between the jump frequency for viscous flow and a chemical reaction frequency. Using the general approach of absolute reaction rate theory, he produced the following expression for the jump frequency

$$\nu = \left(\frac{RT}{hN}\right) \exp(-G^*/RT) \tag{17}$$

where G^* is the molar free energy of activation for a molecular jump, h is Planck's constant and N is Avogadro's number.

What exactly is embraced by the term free energy of activation is not altogether clear. A hole must be created for the mobile molecular to jump into. At the same time the mobile molecule must detach itself from one group of neighbours in order to join a new group. In the case of a pure liquid both processes involve disruptions to the same pattern of molecular aggregation. Consequently it is not surprising to discover that there is a rough proportionality between enthalpies of activation and heats of vaporization.

To obtain more explicit expressions for the diffusion coefficients, it is necessary to furnish an estimate of the jump distances λ. A reasonable choice, in the case of a pure liquid might be a molecular diameter, i.e.

$$\lambda_W = \left(\overline{V}_W/N\right)^{1/3} \tag{18}$$

This leads to the equations

$$D_W^0 = \left(\frac{\overline{V}_W^0}{N}\right)^{2/3} \frac{RT}{hN} \exp\left(-G_W^{*0}/RT\right) \tag{19}$$

$$\eta_W^0 = \frac{1}{2\pi\overline{V}_W^0} hN \exp\left(G_W^{*0}/RT\right) \tag{20}$$

A more difficult choice is that of an expression for a jump distance of the type λ_W^A; that of a water molecule in a purely organic environment.

It is suggested that, so long as the two molecular species do not differ too greatly in size that, it is reasonable to adopt the assumption that

$$\lambda_W^A = \lambda_W^0 = \left(\overline{V}_W^0/N\right)^{1/3} \tag{21}$$

If such is the case, then from eqns. (6), (7), (13) and (21) we derive

$$\frac{D_W^A}{D_A^0} \simeq \frac{D_A^W}{D_W^0} = \frac{(\lambda^2\nu)_W^A}{(\lambda^2\nu)_A^0} \simeq \left(\frac{\overline{V}_A^0}{\overline{V}_W^0}\right)^{1/3} \simeq \left(\frac{\overline{V}_W^0}{\overline{V}_A^0}\right)^{2/3} \frac{\nu_W^A}{\nu_A^0} \tag{22}$$

Thus

$$\frac{\nu_W^A}{\nu_A^0} = \frac{\nu_W^0}{\nu_A^W} = \frac{\overline{V}_A^0}{\overline{V}_W^0} \tag{23}$$

Combining eqns. (17) and (23) leads to

$$\frac{\overline{V}_A^0}{\overline{V}_W^0} = \exp\left[\left(G_A^{*0} - G_W^{*A}\right)/RT\right] \tag{24}$$

or

$$G_A^{\neq 0} - G_W^{\neq A} = RT \ln\left(\overline{V}_A^0 / \overline{V}_W^0\right) \tag{25}$$

It is appropriate to seek a suitable definition of the ideal molar Gibbs free energy of activation for a mixture of composition X_A.

Given that

$$G^{\neq} = H^{\neq} - TS^{\neq} \tag{26}$$

it seems reasonable to assume that

$$H^{\neq}(\text{ideal}) = (1 - X_A) H_W^{\neq 0} + X_A H_A^{\neq 0} \tag{27}$$

The ideal entropy of a mixture is usually defined as

$$\overline{S} = (1 - X_A)\overline{S}_W^0 + X_A \overline{S}_A^0 - R \ln\left[(1 - X_A)^{(1 - X_A)} X_A^{X_A}\right] \tag{28}$$

It also seems to be reasonable to assume that the mixing term applies to both the equilibrium and activated complex states of the mixtures and, thus

$$\overline{S}^{\neq} \text{ideal} = (1 - X_A)\overline{S}_W^{\neq 0} + X_A \overline{S}_A^{\neq 0} \tag{29}$$

which gives

$$\overline{G}^{\neq} \text{ideal} = (1 - X_A)\overline{G}_W^{\neq 0} + X_A \overline{G}_A^{\neq 0} \tag{30}$$

This is consistent with eqn. (2), if

$$(\eta\overline{V}) \text{ideal} = \frac{hN}{2\pi} \exp(\overline{G}^{\neq} \text{ideal}/RT) \tag{31}$$

If the apparent Gibbs free energy of activation for a mixture of composition X_A is defined by

$$\overline{G}^{\neq} = RT \ln\left(\frac{2\pi\eta\overline{V}}{hN}\right) \tag{32}$$

then the excess quantity is

$$\Delta\overline{G}^{\neq} = RT \Delta \ln(\eta\overline{V}) \tag{33}$$

When viscosity and molar volume values are available over a range of temperatures, it is common practice to plot $\ln(\eta\overline{V})$ against T^{-1} to derive a value for the molar enthalpy of activation.

We may write the equation

$$\ln(\eta\overline{V}) = \ln(hN/2\pi) + \frac{H^{\neq}}{RT} - \frac{S^{\neq}}{R} \tag{34}$$

Some assumptions have to be made in order that plots of $\ln(\eta\overline{V})$ versus T^{-1} can become the source of $H^{\neq}$ and $S^{\neq}$ values:

(a) It is assumed that $H^{\neq}$ and $S^{\neq}$ are both insensitive to temperature changes. If that be the case, the plot should reveal a linear dependence of $\ln(\eta\overline{V})$ upon T^{-1}.

(b) The validity of the values derived for $S^{\neq}$ are directly related to the validity of the term $hN/2\pi$, part of which is inherent in the Eyring model and part in the adoption of eqn. (8).

It is suggested that so many assumptions are involved in the evaluation of $S^{\neq}$ by this approach that the numbers that one arrives at are essentially meaningless.

Some of the problems that might be associated with those assumptions will diminish if interest is restricted to the excess molar quantities $\Delta H^{\neq}$ and $\Delta S^{\neq}$, where

$$\Delta(\ln \eta \overline{V}) = \frac{\Delta H^{\neq}}{RT} - \frac{\Delta S^{\neq}}{R} \tag{35}$$

THE THREE-SEGMENT MODEL

The derivation of the equations which make up the original (five parameter) version of the three-segment model is described in ref. 1. The model incorporates the assumption that the total composition range of the acetonitrile–water system may be treated as consisting of three distinct segments. The equations are derived from the Gibbs–Duhem equation along similar lines to those used to obtain the Margoules equations. It is assumed that both the excess molar quantity $\overline{\Delta Q}$ and its composition derivative $d\Delta\overline{Q}/dX_A$ are single valued at both of the segment junctions $X_A = X_I$ and $X_A = X_{II}$.

The model equations for the three segments are, respectively: For the water rich segment, $0 \leqslant X_A \leqslant X_I$

$$\Delta\overline{Q} = BX_A(1 - X_A) + \Delta\overline{Q}^0_W X_A \left\{ \frac{(1 - X_A) - (1 - X_I)^2}{X_I^2} \right\}$$

$$+ \Delta\overline{Q}^0_A X_A - \tfrac{1}{2} C_W X_A(X_I - X_A)^2 \tag{36}$$

for the central (microheterogeneous) segment, $X_I \leqslant X_A \leqslant X_{II}$

$$\Delta\overline{Q} = BX_A(1 - X_A) + \Delta\overline{Q}^0_W(1 - X_A) + \Delta\overline{Q}^0_A X_A \tag{37}$$

For the acetonitrile rich segment, $X_{II} \leqslant X_A \leqslant 1$

$$\Delta\overline{Q} = BX_A(1 - X_A) + \Delta\overline{Q}^0_W(1 - X_A) + \Delta\overline{Q}^0_A(1 - X_A) \left\{ \frac{X_A - X_{II}^2}{(1 - X_{II})^2} \right\}$$

$$- \tfrac{1}{2} C_A(1 - X_A)(X_A - X_{II})^2 \tag{38}$$

The parameters $\Delta\overline{Q}^0_W$ and $\Delta\overline{Q}^0_A$ appear in the derivation of the model equations as excess molar properties of hypothetical standard states of acetonitrile and water, respectively, for the central composition segment. The

term microheterogeneous has been applied to that segment to express its authors' contention that the molecules of each component tend to self aggregate in some globular or layered fashion [13]. In ref. 8, the excess molar volume parameters $\Delta \overline{V}_W^0$ and $\Delta \overline{V}_A^0$ were determined for this system, for ranges of both temperature and applied pressure, and interpreted as being properties of the component microphases.

B, C_W and C_A are Margoules parameters. B represents the effects upon the property $\overline{Q}$ of interactions between unlike pairs of molecules and thus describes the interface between the two microphases. C_W and C_A are related, in some fashion, to the interactions between the aggregates of the central segment and those of the pure liquids.

It was noted in ref. 8 that the number of model parameters can be reduced from five to three by requiring that $d^2 \Delta \overline{Q}/d X_A^2$ must be single valued at each of the segment junctions. The additional constraints lead to the conditions that

$$\Delta \overline{Q}_W^0 = -\tfrac{1}{2} C_W X_I^3 \tag{39}$$

$$\Delta \overline{Q}_A^0 = -\tfrac{1}{2} C_A (1 - X_{II})^3 \tag{40}$$

In the analyses of excess molar volume data, it was found that there is relatively little difference between the optimal fitted curves derived from the three- and five-parameter models. It was judged that, in that particular context, one should only venture to use the more flexible, and thus error-sensitive, five parameter version when dealing with data with a high point density and a high level of precision.

EXCESS VISCOSITIES AT 25°C

It should be recognised that ref. 3 contains viscosity data for 15, 20, 30, 40 and 50°C but not for 25°C. It was however a simple matter to derive 25°C values by interpolation for each of the eight mixtures studied. The interpolated values all lie close to the fitted curve, derived from the same data, which is given in ref. 2.

The 25°C viscosity data of refs. 3, 5 and 6 were analysed individually and collectively using both the five and three parameter versions of the three-segment model. The segment junctions were fixed at $X_I = 0.25$ and $X_{II} = 0.70$, which had been found to be the optimum combination for the excess molar volume data [8]. Analyses were also performed upon the viscosity curve that is derived from the tracer diffusion coefficient data of ref. 7 using eqn. (12). For what was primarily regarded as a curve fitting exercise, the analyses were carried out on the excess viscosities $\Delta \eta$ as defined by eqn. (1). The results of these analyses are set out in Table 1.

TABLE 1

Results of analyses of excess viscosities of acetonitrile–water mixtures using three-segment models ($X_I = 0.25$, $X_{II} = 0.70$)

Ref.	No. data points	B	$\Delta\eta_W^0$	$\Delta\eta_A^0$	$-\frac{1}{2}C_W X_I^3$	$-\frac{1}{2}C_A(1-X_{II})^3$	σ
Five parameter version							
3	8	0.320	0.121	-0.264	0.653	1.042	0.0081
5	9	-0.715	0.295	0.074	13.3	-0.808	0.0115
6	9	-0.596	0.324	-0.002	0.319	0.009	0.0014
3,5,6		-0.400	0.240	-0.023	0.503	0.149	0.0109
7	(19)[a]	-0.477	0.267	-0.005	0.450	0.023	(0.0037)
Three parameter version							
3		-0.732	0.314	0.034			0.0190
5		-0.639	0.288	0.042			0.0099
6		-0.603	0.324	0.001			0.0013
3,5,6		-0.624	0.302	0.016			0.0131
7		-0.617	0.307	0.019			(0.0063)

Units: centipoise (1 cp = 10^{-2} g cm^{-1} s^{-1}).
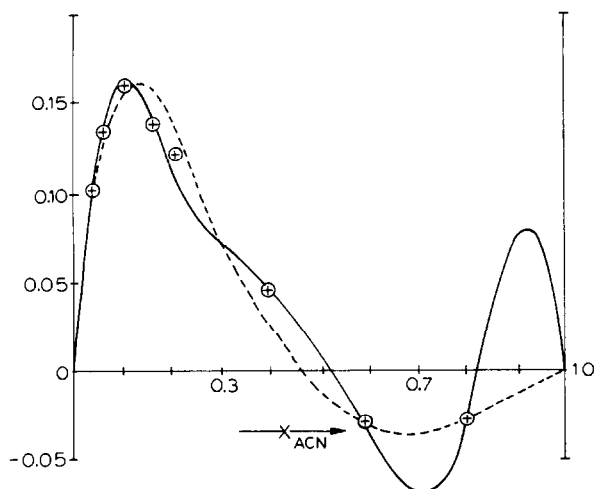[a] The data of ref. 7 are in the form of values of a fitted curve.

Fig. 1. A comparison of the three- and five-parameter fitted curves for the excess viscosities of acetonitrile–water mixtures derived from the data of Mato and Hernández [3]. (————) three-parameter curve, (- - - - - -) five-parameter curve. The data points are represented by crosses.

The fitted curves derived using the five-parameter model for the three individual data sets are all markedly different. The fitted curve for the data of ref. 3 is very similar to that described in ref. 1 for the analysis of the tabulation of ref. 2. Of those three viscosity data sets only that of ref. 6 yields a fitted curve which is similar in form to those obtained from analyses of the combined data.

There is a pleasing consistency among the parameters derived from the various three-parameter analyses. Each of the fitted curves possesses a prominent maximum at $X_A \simeq 0.15$ and a relatively shallow minimum at $X_A \simeq 0.75$. These fitted curves are quite similar in form to those obtained from the five-parameter analyses of the data of ref. 6, of the combined viscosity data and of the excess viscosities that were generated from the diffusion coefficient data of ref. 7.

The difference between the fitted curves derived from the three- and five-parameter analyses of the excess viscosity data obtained from ref. 3 is shown in Fig. 1. It should be pointed out that ref. 7 contains a comparative plot of the Moreau–Douhéret viscosities [2] and viscosities calculated from diffusion coefficients. That plot shows the same general difference of form in the acetonitrile rich segment as is seen in Fig. 1.

Easteal [7] attributed the difference to a failure in Albright's equation [10]. It now seems clear that the peak at $X_A \simeq 0.9$ is spurious and is an artifact of the combination of less than perfect data and an overly flexible fitting function.

The question arises as to whether the differences between the results of the

three- and five-parameter analyses, of the combined excess viscosity data set and of the data derived from diffusion coefficients, are significant. The appropriate answer would appear to be that the distinction drawn in the five-parameter model between the values of $\Delta\eta_W^0$ and $-\frac{1}{2}C_W X_I^3$ is probably significant in a purely curve fitting context, but is not so obviously so that it could be treated as a reliable piece of information about the structural and dynamic characteristics of the system.

It should be pointed out that the diffusion coefficient values, tabulated by Easteal [7], are those of smooth curves fitted to his own primary data. From the accompanying graphs it is evident that the point density of the primary data is high enough so that there is no possibility that the smooth curve contains any significant artifacts of the type identified in the tabulation of ref. 2.

ANALYSES OF $\Delta\ln(\eta\overline{V})$

In view of the doubts expressed about the appropriateness of using the three segment model as an interpretive tool for analysing intensive properties, and the existence of eqn. (33), analyses were carried out upon the quantities $\Delta\ln(\eta\overline{V})$.

The results of those analyses are given in Table 2. The five-parameter results are only given for the data of refs. 6 and 7 and for the combined data of refs. 3, 5 and 6.

Also given in Table 2 are the results of three-parameter analyses carried out on viscosity data obtained at several different temperatures.

Both three- and five-parameter analyses were performed upon the quantities $\Delta\ln(\eta_W\overline{V})$ and $\Delta\ln(\eta_A\overline{V})$ where the quantities η_W and η_A are the effective component viscosities defined by eqn. (11) and derived from the diffusion coefficient data of ref. 7. The results are reported in Table 3.

ACTIVATION PARAMETERS

From Table 2, it is seen that the data of ref. 4 are clearly inconsistent with all of the other sources of information. It is further seen that the three parameters B, $\Delta\ln(\eta\overline{V})_W^0$ and $\Delta\ln(\eta\overline{V})_A^0$ vary in a fairly regular fashion with temperature.

Assuming that all of the appropriate conditions prevail, those three quantities were plotted against T^{-1} to give the components of ΔH^* and ΔS^*.

The same quantities can be derived from the Mato–Hernández data in another way. For each of the eight mixtures and the two pure liquids, one may calculate $\ln(\eta\overline{V})$ at each of the five temperatures. Thus, for each

TABLE 2

Results of analyses of the quantities $\Delta\ln(\eta\bar{V})$ for acetonitrile–water mixtures using the three-segment model ($X_I = 0.25$, $X_{II} = 0.70$)

Three parameter version ($T = 25°C$)

Ref.	B	$\Delta\ln(\eta\bar{V})^0_W$	$\Delta\ln(\eta\bar{V})^0_A$	σ
3	−0.056	0.353	−0.095	0.0219
5	−0.104	0.373	−0.050	0.0143
6	−0.063	0.371	−0.116	0.0116
3,5,6	+0.070	0.345	−0.110	0.0173
7	+0.015	0.358	−0.083	(0.0081)

Five parameter version ($T = 25°C$)

Ref.	B	$\Delta\ln(\eta\bar{V})^0_W$	$\Delta\ln(\eta\bar{V})^0_A$	$-\frac{1}{2}C_W X_I$	$-\frac{1}{2}C_A (1-X_{II})^3$	σ
6	−0.052	0.443	−0.132	0.093	0.016	0.0041
3,5,6	+0.262	0.308	−0.162	0.418	0.019	0.0173
7	+0.205	0.330	−0.143	0.371	0.081	(0.0056)

Three parameter version ($T = 15–50°C$)

Ref.	$T(°C)$	B	$\Delta\ln(\eta\bar{V})^0_W$	$\Delta\ln(\eta\bar{V})^0_A$	σ
3	15	−0.137	0.397	−0.105	0.0231
3	20	−0.106	0.376	−0.101	0.0227
3	30	0.016	0.327	−0.089	0.0203
3	40	0.054	0.295	−0.079	0.0165
3	50	0.086	0.270	−0.078	0.0149
4	20	−0.255	0.422	0.116	0.0204

TABLE 3

Results of analyses of the quantities $\Delta\ln(\eta_W\bar{V})$ and $\Delta\ln(\eta_A\bar{V})$ for acetonitrile–water mixtures using the three-segment model ($X_I = 0.25$, $X_{II} = 0.70$)

	B	$\Delta\ln(\eta\bar{V})^0_W$	$\Delta\ln(\eta\bar{V})^0_A$	$-\frac{1}{2}C_W X_I^3$	$-\frac{1}{2}C_A (1-X_{II})^3$	σ
Three parameter version						
$\Delta\ln(\eta_W\bar{V})$	1.098	0.186	0.032			0.0092
$\Delta\ln(\eta_A\bar{V})$	−0.371	0.209	−0.004			0.0029
Five parameter version						
$\Delta\ln(\eta_W\bar{V})$	1.359	0.118	−0.019	0.414	0.072	0.0043
$\Delta\ln(\eta_A\bar{V})$	−0.406	0.221	0.001	0.162	0.005	0.0024

TABLE 4

Three-segment model parameters for the excess molar enthalpies and entropies of activation for viscous flow of the acetonitrile–water system

	B	$\Delta \bar{Q}^0_W$	$\Delta \bar{Q}^0_A$	σ
From the $\Delta G^{\neq}/RT$ parameters of Table 2				
$\Delta \bar{H}^{\neq}/R$	-623	345	-78	
$\Delta \bar{S}^{\neq}/R$	-2.04	$+0.80$	-0.17	
σ	0.0233	0.0055	0.0027	
From the $\Delta \bar{H}^{\neq}/R$ and $\Delta \bar{S}^{\neq}/R$ curves				
$\Delta \bar{H}^{\neq}/R$	-641	349	-76	31.1
$\Delta \bar{S}^{\neq}/R$	-2.10	$+0.82$	-0.16	0.089

mixture one may obtain the quantities $\Delta H^{\neq}$ and $\Delta S^{\neq}$. The two curves thus generated may then be analysed using the three parameter version of the three-segment model. The results of these analyses are given in Table 4.

DISCUSSION

Curve fitting

For high quality data sets of the excess properties of a binary liquid system, it is customary to fit the data with a continuous function of the form

$$\Delta \bar{Q} = X_A(1 - X_A) \sum_{j=1}^{n} A_j(1 - 2X_A)^{j-1} \tag{41}$$

where the coefficients A_j are determined by least-squares optimisation and the mole fractions X_A might be replaced by volume fractions.

This is equivalent to fitting an $n + 1$ order polynomial to the property $\bar{Q}$. For mixtures of water and polar organic liquids, it is found that the number of terms needs to be at least five to provide a satisfactory replica of the data set. If all that is required of a fitting function is the provision of an algebraic summary of the data and, in the value of the standard deviation $\sigma(\Delta \bar{Q})$, a measure of the quality of the data, there would generally be no need to resort to the use of any other equation.

In this work, however, we have encountered data sets which are too sparse to warrant the use of a fitting function with the flexibility of eqn. (41). It is the sparseness more than the imperfections of the Mato–Hernández data that result in the fitted curve of ref. 2 including features which are demonstrably spurious. The same feature also appears in the fitted curve that is generated by the five parameter version of the three-segment model.

The fitted curves that are generated using the three parameter version of the three-segment model with the excess viscosity data all have the same general form, which happens to be that of the combined data. The three parameter version is to be preferred to more flexible models when the data is restricted to some ten or less points. That may well mean that certain interesting features, at the extremes of the composition range, will be missed but that is a situation which can only be avoided by improving the data base.

STRUCTURAL INFORMATION

The addition of acetonitrile to water, up to $X_A \simeq 0.1$ produces a significant increase in viscosity. This, despite the fact that acetonitrile itself is much less viscous than water. From Tables 1 and 2, it is evident that this increase in viscosity is associated with the variation of the pattern of water self-aggregation. In ref. 8, it was reported that the excess molar volume data for this system is consistent with the idea that, in the presence of acetonitrile, water adopts a more compact than normal mode of grouping to form "microphases". It is also apparent that these microphases represent a lower enthalpy state of water [1].

If the activation parameters are meaningful quantities, we deduce from the results given in Table 4 that microphase water has a higher enthalpy and entropy of activation than does normal water. This is consistent with a situation in which the activated complexes of the two states of water are essentially the same and in which the microphase state is of lower enthalpy and entropy. It is interesting to note that, in a recent review article, Stillinger describes the effect upon the aggregative pattern of the water molecules in the immediate vicinity of an inert solute as leading to decreases in both enthalpy and entropy [14].

From the results given in Table 3, it appears that the formation of microphase water diminishes the mobilities of both components. There is a shoulder in the $\Delta\ln(\eta_w \overline{V})$ curve at $X_A \simeq 0.10$, which is strongly reminiscent of one in the $\Delta\overline{C}_p$ curve of ref. 15. It is the accommodation of this shoulder which is primarily responsible for the decrease in the standard deviation $\sigma(\Delta\ln(\eta_w \overline{V}))$ on going from the three- to the five-parameter model. The parameter C_w is tentatively associated with interactions between microphase and normal water aggregates. Work is currently in progress to see if it is possible to arrive at a clearer concept of the implications of that parameter [16].

From Table 2, it appears that microphase aggregation of acetonitrile results in a net lowering of the free energy of activation for viscous flow. From Table 4 it is seen that there is a modest lowering of both the enthalpies and entropies of activation in the change from normal to microphase acetonitrile. That description seems to be consistent with the earlier findings

that the microphase acetonitrile is both less dense and of higher enthalpy than the normal liquid [1]. The results of the analyses of $\Delta \ln(\eta_W \bar{V})$ and $\Delta \ln(\eta_A \bar{V})$ are ambiguous in so far as information about the acetonitrile microphase is concerned.

Parameters of the type B are associated with the interactions between unlike pairs of molecules. Thus, in some fashion, they contain information about the interface between the two microphases. The results of Table 2 reveal that the B contribution to the excess free energy of activation is relatively small. It should be borne in mind that the maximum contribution $BX_A(1 - X_A)$ is only $0.25B$. The parameter is fairly strongly temperature dependent. $B(\Delta H^{\neq})$ and $B(\Delta S^{\neq})$ are both significantly negative.

It is seen that the respective B parameters for $\Delta \ln(\eta_W \bar{V})$ and $\Delta \ln(\eta_A \bar{V})$ are very different. It appears that the interfacial interactions tend to restrict the mobility of water molecules but there is a modest increase in the acetonitrile mobility.

One may speculate endlessly about the significance of these results, but one keeps coming back to the realization that not only is the three-segment model itself a relatively untried approach to analysis, but one is also working with general models of viscous flow which are of questionable validity.

SUMMARY

The shape of the viscosity versus molar composition curve, for the acetonitrile–water system has been studied and, in so far as its major features are concerned, it has been characterised. It has been demonstrated that the tabulation of ref. 2 contains a spurious peak in the acetonitrile-rich segment. It has also been demonstrated that a simplified version of the three-segment model of ref. 1 is a reasonably safe curve-fitting tool for the primary data of Mato and Hernández.

An effort has been made to formulate a procedure for interpreting the various sets of transport property data that are to be found in the literature.

Results of analyses, using the three-segment model are presented. The dominant viscosity peak is attributed to the formation of aqueous microphases in the presence of acetonitrile. The profound difference between the excess tracer diffusion coefficients of tritiated water and ^{14}C-acetonitrile are associated with the effects of the existence of microphase interfaces on the mobilities of the component molecules.

REFERENCES

1 M.I. Davis, Thermochim. Acta, 63 (1983) 67.
2 C. Moreau and G. Douhéret, Thermochim. Acta, 13 (1975) 297.
3 F. Mato and J.L. Hernández, An. Quim., 65 (1969) 9.
4 A.L. Vierk, Z. Anorg. Chem., 261 (1950) 283.
5 G.P. Cunningham, G.A. Vidulich and R.L. Kay, J. Chem. Eng. Data, 12 (1967) 336.
6 A. D'Aprano and R.M. Fuoss, J. Phys. Chem., 73 (1969) 400.
7 A.J. Easteal, Aust. J. Chem., 33 (1980) 1667.
8 M.I. Davis, Thermochim. Acta., 71 (1983) 59.
9 S. Glasstone, Textbook of Physical Chemistry, 2nd edn., Van Nostrand, New York, 1946.
10 J.G. Albright, J. Phys. Chem., 73 (1969) 1280.
11 H. Eyring, R.E. Powell and R.E. Roseveare, Ind. Eng. Chem., 33 (1941) 430.
12 S. Glasstone, K.J. Laidler and H. Eyring, The Theory of Rate Processes, McGraw-Hill, New York, 1941.
13 Yu.I. Naberukhin and V.A. Rogov, Russ. Chem. Rev., 40 (1971) 207.
14 F.H. Stillinger, Science, 209 (1980) 451.
15 G.C. Benson, P.J. Darcy and Y.P. Handa, Thermochim. Acta, 46 (1981) 295.
16 M.I. Davis, work in progress.