

TESTS OF THE FOUR-SEGMENT MODEL FOR BINARY HYDROORGANIC SYSTEMS

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ABSTRACT

Two data sets for the excess molar volumes of 1-propanol–water mixtures at 25°C were taken from the literature and used as a basis for exploring the scope and limitations of the four-segment model for binary hydroorganic systems. The various analyses that this investigation involved also furnished an opportunity to evaluate the potential utility of an automatic densimetry procedure that is described in the literature.

INTRODUCTION

The evolution and derivation of the four-segment model equations for analysing excess molar property data of binary hydroorganic systems has been described in earlier articles [1,2]. The model is based upon the assumption that it is reasonable to treat these binary systems as though they each possess four discrete composition segments, in each of which the molar properties exhibit no greater than cubic dependence upon mole fractional composition. Assuming that both an excess molar property of the system $\Delta\bar{Q}$ and its derivative with respect to the mole fraction of the organic component $d\Delta\bar{Q}/dX_A$ are single valued, at each of the three segment junctions, leads to the set of four equations that are given in the Appendix.

Thus far, reported applications have been restricted to the acetonitrile (ACN)–water and tetrahydrofuran (THF)–water systems [2,3]. From the results of the analyses of a variety of excess molar properties of these two systems, it was evident that the four model equations constitute an effective curve-fitting tool. Furthermore, it appeared that each of the seven parameters of these equations might be identified with some broad aspect of the patterns of molecular aggregation which exist within such binary mixtures, and that their values might prove to be useful in the evaluation or formulation of conceptual structural models.

In the course of a series of analyses of excess molar property data of alkanol–water systems [4], a pair of parallel data sets were found which, it

was felt, could be used as the basis for an investigation of the scope and limitations of the four-segment model.

Reference 5 contains 61 values of the excess molar volumes of 1-propanol (1-PrOH)-water mixtures at 25°C. While the data adequately cover the entire range of compositions, the point density is substantially higher for $X_A < 0.2$ than elsewhere. Each mixture was prepared separately, its mole fraction was determined by weight and its density determined by the vibrating tube technique.

Reference 6 contains 69 density values for the same system and the same temperature. Again, there is adequate coverage of the entire composition range, with higher point density for $X_A < 0.2$. In this case, the mixtures were prepared by either successive addition of small quantities of the alcohol to water ($X_A < 0.2$) or of water to the alcohol ($X_A > 0.2$). The tabulated densities, also determined by the vibrating tube technique, were translated into excess molar volumes.

Figure 3 of ref. 6, reveals a systematic difference between the two sets of data, for $X_A > 0.2$, which is quite large compared to the accuracy that is normally claimed for vibrating tube densimetry.

The object of carrying out the analyses reported in this article, was to check upon certain possible weaknesses of the four-segment model, rather than to carry out a comparative critique of the two data sets. However, the procedure of automated densimetry, as practised in the acquisition of the data of ref. 6, represents such an attractive innovation that it seemed to warrant more than a cursory examination.

ANALYTICAL STRATEGIES

A basic four-segment model analysis of an excess molar property data set involves the use of the four equations of the Appendix in a least-squares optimized fit of the raw data. Preliminary analyses are required to assign values to the three segment-junction compositions, that are near optimal for all data sets that are at hand for the specific system being studied. In the case of the 1-PrOH-water system, it was found that, in common with ACN-water, THF-water and the other alkanol-water systems [2,4], the combination of $X_{II} = 0.333$ and $X_{III} = 0.667$ is appropriate. The optimal value of X_I appears to be 0.083. With the segment junctions fixed, curve fitting is accomplished by a linear least-squares program which also furnishes estimates of the standard deviations for the seven model parameters. In view of the partially discontinuous nature of the analytical model, it was not obvious how these standard deviations might be translated into limits of confidence.

Uncertainties in the parameter values might arise from flaws in either the model or the data. The primary concern here was with possible weaknesses

in the model. It is quite obvious that the model equations are approximations. The question at issue is that of how crude the approximations may be. What was hoped in establishing the model was that the various assumptions which were adopted in its derivation might be shown to be valid to the extent that the various parameter values are sufficiently well defined as to allow for meaningful discussions of their significance.

Tests were devised to check upon the validity of the various assumptions that are embodied in the model. The primary assumption is that within the central (microheterogeneous) segment ($X_{II} < X_A < X_{III}$), the excess molar properties are adequately represented by quadratic functions of X_A , while in the other three segments cubic dependence is to be anticipated. A program (I) was devised to analyze each segment individually, without regard to any kind of continuity at the segment junctions. Such analyses involve the optimization of 13 independent parameters and, thus, require unusually extensive data sets. A subset of these parameters was used to provide estimates of the seven parameters of the full model.

There is, of course, no reason why $\Delta\bar{V}$ should not be single valued at each of the three segment junctions, since there are no phase changes taking place. Consequently, the introduction of that constraint should not have any significant effect upon the form of the optimized fitted curve. A second program (II) was devised, that incorporates the constraints that $\Delta\bar{V}$ shall be single valued at each segment junction. This program involves the determination of ten independent parameters, from a subset of which the seven parameters of the full model were determined. Any significant deterioration in the quality of fit or variation in the values determined for the parameters of the full model would indicate deficiencies in either the quality of the data or the validity of the four-segment model. The study of two data sets of presumed high quality focusses attention upon the caliber of the model.

Discontinuities in $d\Delta\bar{V}/dX_A$ at any one of the three segment junctions would require that the partial molar volumes, $\Delta\bar{V}_w$ and $\Delta\bar{V}_A$, both possess discontinuities. While such a dramatic sensitivity of the physical properties of these single-phase systems to composition seems to be highly unlikely, one should not rule out the possibility of an apparent discontinuity arising from the adoption of equations that assume such simple composition dependence for the individual segments. The adoption of the constraints of being single valued for the derivatives at the segment junctions takes us from the set of equations (II) to the full model set (III). It was again of interest to see if that switch results in significant changes in either the quality of fit or the values of the full-model parameters.

In the analyses of certain marginally adequate data sets, particularly those of low point density, it was noticed that one or two errant data entries are capable of having a profound effect upon the values of the optimized model parameters. As a safeguard against that contingency, moderately smoothed versions (B) of the original data sets were derived by a modified cubic-splines

procedure. Results of the analyses of these data sets were compared with those obtained from the original data (A).

In both of the data sets, the point density is substantially higher for $X_A < 0.2$ than for $X_A > 0.2$. This must, to some degree, bias the curve-fitting procedure in favor of the water-rich segments. It was of interest to see if the elimination of that bias might have a significant effect upon the estimates of the four-segment model parameters. Accordingly, the cubic-splines procedure was adopted to generate interpolated data curves with equally spaced entries at $\Delta X_A = 0.025$.

Thus, with three sets of model equations and three versions of the data, nine different analyses of each of the two data sets were performed.

RESULTS

Quality of fit

The respective qualities of fit for the various analyses may be appraised from the standard deviations, $\sigma(\Delta\bar{V})$. The values obtained are set out in Table 1.

The standard deviations of less than $2 \text{ mm}^3 \text{ mol}^{-1}$, that were obtained for the data of ref. 5, are indicative of a combination of an exceptionally high level of internal consistency of the data and an effective curve-fitting procedure. The somewhat higher standard deviations obtained for the data of ref. 6 reflect that it is also of good quality and more than adequate for both four-segment model analyses and the kind of analysis for which it was originally intended.

There is little of either interest or concern in the variation of the standard deviations among the various analyses of the data of ref. 5. That the introduction of model constraints should lead to increases in $\sigma(\Delta\bar{V})$, for

TABLE 1

Standard deviations, $\sigma(\Delta\bar{V})$, for the 1-PrOH-water system ($\text{mm}^3 \text{ mol}^{-1}$)

	Ref. 5			Ref. 6		
	I	II	III	I	II	III
A	1.32	1.62	1.92	4.48	4.48	5.08
B	1.21	1.60	1.89	4.11	4.16	4.78
C	1.03	1.44	1.90	5.42	5.44	6.25

A, Analyses of the original data sets; B, analyses of the smoothed data sets; C, analyses of the interpolated data sets. I, Segments fitted independently (13 parameters); II, $\Delta\bar{V}$ constrained to be single valued at the segment junctions (10 parameters); III, $d\Delta\bar{V}/dX_A$ constrained to be single valued at the segment junctions (7 parameters).

each of sequences (I), (II) and (III), is only to be expected. That those increases are fairly modest suggests that the model assumptions are reasonable, at least in a curve-fitting context.

The only feature of the analyses of either data set that is worthy of special comment is the rather large deterioration in the quality of fit in going from the original data (A) to the interpolated version (C) for ref. 6. The implication would seem to be that there is a far higher degree of scatter in the data obtained at $X_A > 0.2$ than at $X_A < 0.2$. This does not seem to be the case for the data of ref. 5.

The parameter sets

While the utility of the four-segment model, in any capacity, must depend upon its effectiveness in a curve-fitting role, the contention that its parameter values might serve as clues in elucidating the patterns of molecular aggregation requires that those values are reasonably well defined.

Thus, it seemed to be appropriate to examine the variations among the parameter sets that were derived from the various analyses. These are set out in Table 2.

The three parameters, B , $\Delta\bar{V}_W^0$ and $\Delta\bar{V}_A^0$, completely define the model curve in the composition segment $X_{II} < X_A < X_{III}$. Their components collectively dominate the data profiles of the majority of the excess molar property curves that have been analyzed by the four-segment model. It is noted that there are no substantial differences between the values of those parameters that were obtained using the same set of model equations for the three versions (A, B and C) of either data set. The differences between the values obtained using the set of equations (I) and those using set (II) are comparable in magnitude to the standard deviations that were estimated using the full model (III) on the original data. For both data sets, much larger differences are encountered between the parameters obtained using equations (I) or (II) and those obtained from the fully constrained model equations (III).

The effects upon the parameters of imposing the constraint that $d\Delta\bar{V}/dX_A$ must be single valued at each of the three segment junctions have to be accepted as being indicative of limitations of the model. Fortunately, the parameter values are still sufficiently well defined that one can discriminate between the physical characteristics of many different systems. These results indicate, however, that the standard deviations that are derived from a basic analysis are likely to provide an unduly optimistic impression of the limits of confidence that can be placed upon the parameters and that the four-segment model is not as precise an analytical tool as one might have hoped.

Quite apart from the differences that exist among the parameter values that were derived from the various analyses of each specific data set, there

TABLE 2

Four-segment model parameters for excess molar volumes of 1-PrOH-water mixtures ($\text{cm}^3 \text{mol}^{-1}$)

		Ref. 5				Ref. 6			
		I	II	III	σ	I	II	III	σ
B	A	-1.54	-1.53	-1.65	0.027	-0.93	-0.89	-1.27	0.075
	B	-1.55	-1.53	-1.66		-0.96	-0.88	-1.28	
	C	-1.56	-1.53	-1.67		-1.00	-0.86	-1.30	
$\Delta\bar{V}_w^0$	A	-0.42	-0.42	-0.39	0.006	-0.56	-0.56	-0.47	0.018
	B	-0.42	-0.42	-0.39		-0.55	-0.57	-0.46	
	C	-0.42	-0.42	-0.39		-0.54	-0.57	-0.46	
$\Delta\bar{V}_A^0$	A	-0.11	-0.12	-0.09	0.007	-0.17	-0.18	-0.10	0.017
	B	-0.11	-0.12	-0.09		-0.16	-0.19	-0.09	
	C	-0.11	-0.12	-0.08		-0.15	-0.19	-0.09	
$\Delta\bar{V}_S^0$	A	-0.21	-0.18	-0.21	0.004	-0.16	-0.14	-0.22	0.012
	B	-0.21	-0.19	-0.20		-0.17	-0.14	-0.21	
	C	-0.22	-0.19	-0.20		-0.17	-0.14	-0.20	
D_S	A	-0.10	-0.17	-0.06	0.020	-0.24	-0.32	-0.05	0.058
	B	-0.07	-0.19	-0.08		-0.25	-0.33	-0.07	
	C	-0.09	-0.15	-0.10		-0.26	-0.31	-0.08	
D_w	A	0.56	0.50	0.50	0.011	0.57	0.54	0.55	0.028
	B	0.53	0.47	0.49		0.55	0.51	0.53	
	C	0.54	0.41	0.47		0.53	0.40	0.50	
D_A	A	-0.08	-0.07	-0.07	0.017	0.01	0.07	0.05	0.040
	B	-0.08	-0.07	-0.08		0.00	0.07	0.04	
	C	-0.09	-0.08	-0.09		-0.02	0.06	0.03	

are fairly substantial differences between the results obtained for the two sets.

The average values obtained for B , $\Delta\bar{V}_w^0$ and $\Delta\bar{V}_A^0$ for ref. 5 are -1.58 , -0.41 and $-0.10 \text{ cm}^3 \text{mol}^{-1}$, respectively, while those for ref. 6 are -1.02 , -0.53 , and $-0.14 \text{ cm}^3 \text{mol}^{-1}$. The discrepancies between the two sets of parameters are directly related to the systematic differences that exist between the $\Delta\bar{V}$ values for $X_A > 0.2$. Figure 3 of ref. 5 demonstrates that there are no such large systematic differences between the data of that work and either of two earlier data sets [7,8]. On this basis, it seems reasonable to assume that there is a systematic error in the data of ref. 6. Since such an error is larger than one could attribute to the densimeter, it must occur in the estimates of the mole fractions of the mixtures. Since the level of scatter in the data is not unduly large, this would seem to imply a modest problem in the calibration of the automatic pipettes. A more accurate calibration might have been achieved on the basis of a few density measurements made of

individually prepared mixtures for which the mole fractions had been determined by weight. The errors, such as they are, do not detract from the conclusions drawn from the analyses performed by Hvidt and her co-workers; nor are they of sufficient magnitude to lead to erroneous conclusions from the four-segment model analyses.

The parameters $\Delta\bar{V}_S^0$ and D_S are primarily associated with the secondary segment, $X_I < X_A < X_{II}$. Their respective values, as obtained using the full-model equations (III), are virtually the same for both data sets. The values of $\Delta\bar{V}_S^0$ are not greatly affected by relaxing the model constraints. The D_S values, by contrast, seem to be quite sensitive to the choice of model equations, particularly those obtained from the data of ref. 6. From the studies on numerous excess data sets for hydroorganic systems, it has been found that parameters of this type tend to be the most poorly defined.

There is a fairly high level of consistency among the values obtained for the parameter D_W . This may be attributed, in part, to the substantial similarity between the two data sets in the water-rich composition segment, $0 < X_A < 0.083$, and, in part, to the exceptionally high point densities which tend to protect the analysis from sensitivity to minor aberrations in the data. It is noted that, for both data sets, the values that were obtained from the analyses of the type CII are rather different from the others. This presumably stems from the fact that, in the interpolated data curves, there are only three entries in the water-rich segment which tends to make D_W vulnerable.

There is a high level of consistency among the values of the parameter D_A , as derived from the data of ref. 5. There is only a modest spread among those for ref. 6. The differences between the mean values obtained for the two data sets are presumably related to the systematic differences in their respective $\Delta\bar{V}$ values, in the organic-rich segment.

CONCLUSIONS

By comparing the respective qualities of fit and sets of parameter values, obtained using a variety of analytical strategies for the two sets of excess molar volumes of 1-PrOH-water, it has been possible to acquire a clearer concept of the scope and limitations of the four-segment model than that which is furnished by a conventional error analysis of the basic procedure.

By exploring the effects of relaxing the constraints that are basic components of the four-segment model, it was found that the standard deviations of the model parameters are unduly flattering. More realistic estimates of the limits of confidence that can be placed upon the values of the model parameters are obtained from the spreads that are encountered among the results of the various types of analysis. Such considerations lead one to conclude that the parameter values are well-defined enough to lead to the

identification of similarities and trends among the physical characteristics of families of binary systems [4].

The excess molar volumes of the 1-PrOH–water system provide a fairly exacting test of the four-segment model since they exhibit a pronounced sensitivity to composition in the water-rich region. It is therefore pleasing that the model should have been demonstrated to perform effectively both in terms of the quality of fit and the definition of its parameters, particularly in its application to the analysis of the exceptionally high-quality data of ref. 5.

The data of ref. 6 possess a somewhat higher degree of scatter than those of ref. 5. As a consequence, the parameter values that were derived from its analysis are correspondingly less well defined. Even so, it is apparent that the parameter values that were obtained using the automatic densimetry procedure are more than adequately defined, when it is recognized that any interpretation of bulk properties in terms of molecular scale characteristics can only contend with significant effects.

Of somewhat greater concern are the systematic differences between the two sets of data and the resulting differences in the sets of parameter values that emerge from their respective analyses. It is suspected that these differences arise from a modest calibration problem in the automatic densimetry procedure. If that is indeed the case, the errors thus introduced are not so large as to lead to the possibility of any serious misinterpretation of the data. It is apparent that a more exact calibration could have been achieved on the basis of a relatively small number of density measurements on mixtures that were prepared individually rather than by successive addition of one component to the other.

It would seem that the series of analyses reported here demonstrate that the four-segment model is capable of producing a set of parameter values which are sufficiently well defined to serve as a basis for describing the composition dependence of the physical characteristics of binary hydro-organic mixtures, in a manner which lends itself to the testing of ideas concerning the nature of the patterns of molecular aggregation.

It would further appear that the analyses demonstrate that the technique of automated densimetry, developed by Hvidt and her co-workers, should prove to be a valuable tool. The economy in time and effort need only result in a modest sacrifice in accuracy which is generally too small to be significant in any realistic endeavor to interpret the data. The economy that is gained in the use of the organic materials could prove to be of great importance when their availability is limited.

APPENDIX. THE FOUR-SEGMENT MODEL EQUATIONS

Microheterogeneous segment ($X_{II} < X_A < X_{III}$)

$$\Delta\bar{Q}(\text{micr}) = BX_A(1 - X_A) + \Delta\bar{Q}_W^0(1 - X_A) + \Delta\bar{Q}_A^0 X_A$$

Organic-rich segment ($X_{III} < X_A < 1$)

$$\Delta\bar{Q}(\text{org}) = \Delta\bar{Q}(\text{micr}) - \Delta\bar{Q}_A^0 \left[\frac{(X_A - X_{III})}{(1 - X_{III})} \right]^3 \\ + D_A (1 - X_A) (X_A - X_{III})^2 / (1 - X_{III})^3$$

Secondary segment ($X_I < X_A < X_{II}$)

$$\Delta\bar{Q}(\text{sec}) = \Delta\bar{Q}(\text{micr}) - \Delta\bar{Q}_W^0 \left[\frac{(X_{II} - X_A)}{X_{II}} \right]^3 + \Delta\bar{Q}_S^0 \left[\frac{(X_{II} - X_A)}{X_{II}} \right]^3 \\ + D_S X_A (X_{II} - X_A)^2 / X_{II}^3$$

Water-rich segment ($0 < X_A < X_I$)

$$\Delta\bar{Q}(\text{wat}) = \Delta\bar{Q}(\text{sec}) - \Delta\bar{Q}_S^0 \left[\frac{(X_I - X_A)}{X_I} \right]^3 + D_W X_A (X_I - X_A)^2 / X_I^3$$

(For greater detail see ref. 2.)

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