Part III

On the Viscosity of Ternary Mixtures

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A modified form of an equation developed earlier by Katti and Chaudhri for binary systems is proposed for the representation of viscosity in ternary mixtures. Results by this approach are compared with experimental data and with results predicted by use of the more complex equation of Kalidas and Laddha. The present approach is correlated with the experimental data equally as well as is that of Kalidas and Laddha.

ACCURATE analytical viscosity-concentration functions are essential to a solution of fluid flow problems in multicomponent systems. In addition, for purposes of theoretical interpretation, it is desirable that such equations include separately contributions from ideal mixing and terms that arise from interaction between components. The present work is concerned with two such equations. The purpose is to demonstrate that, with modifications proposed here, the regular solution approach of Katti and Chaudhri (2) will yield values that correlate as well with experimental results as do those obtained by the equation of Kalidas and Laddha (1). The latter equation is based upon extension of work by McAllister (3) on binary systems by a three-body approach, and is rather complex in form. For example, in ternary systems, all but one of the 21 terms are of the third degree in component mole fractions. Use of this equation is thus rather time-consuming, and one of equivalent validity but lesser complexity is desirable.

If Katti and Chaudhri's application (2) of the Eyring viscosity model is extended to multicomponent systems with the assumption of binary interaction only, the result may be expressed as

$$\log \nu = \sum_{i=1}^{n} x_i \log \nu_i + \sum_{i=1}^{n} x_i \log M_i - \log \sum_{i=1}^{n} x_i M_i + \delta_{i...n} \quad (1)$$

where

$$\delta_{i...n} = \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j \alpha_{ij} \quad (2)$$

α_{ij} is an interaction parameter, with $\alpha_{ij} = \alpha_{ji}$ and $\alpha_{ii} = \alpha_{jj} = 0$. $\delta_{i...n}$ is a deviation function, representing departure from a noninteracting system.

Two aspects of Equation 1 must now be considered: the use of terms in α_{ij} for representation of the binary interactions, and the supposition that interactions are not higher than binary. The first aspect may be considered using the data of Katti and Chaudhri (2). In a binary system 1-2, Equation 2 becomes simply

$$\delta_{12} = x_1 x_2 \alpha_{12} \quad (3)$$

Thus, if the assumed interaction term is correct, $\delta_{12}/x_1 x_2$ is independent of concentration. All three of their binary systems show, however, a linear variation in $\delta_{12}/x_1 x_2$ when that function is plotted against $x_1 - x_2$. Clearly, a relationship more suitable than Equation 3 will be obtained if one assumes instead that

$$\delta_{12} = x_1 x_2 [\alpha_{12} + \alpha'_{12}(x_1 - x_2)] \quad (4)$$

It follows that, in a multicomponent system, assuming binary interaction only, instead of Equation 2 there results

$$\delta_{i...n} = \sum_{\substack{i=1 \\ i<j}}^{n} x_i x_j [\alpha_{ij} + \alpha'_{ij}(x_i - x_j)] \quad (5)$$

The assumption of an asymmetry term with the constant α_i in Equations 3 and 4 is suggested by the frequent use of such a

Table I. Application of Viscosity Equations to Binary Systems

Systems of Katti and Chaudhri (2)[d]	Constants of Equation 4		Dev. of Exptl. Values from Calcd. Values			
			Av. Dev., %[a]		Max. Dev., %	
	α_{12}	α'_{12}	Lit.[b]	This work[c]	Lit.[b]	This work[c]
Benzyl acetate (1)–aniline (2)	0.0452	−0.0266	0.59	0.08	1.12	0.18
Benzyl acetate (1)–m-Cresol (2)	−0.0774	0.0660	1.21	0.49	1.69	0.78
Benzyl acetate (1)–dioxane (2)	0.1010	0.0272	0.93	0.72	2.00	1.36
Systems of Kalidas and Laddha (1)						
Acetone (1)–methanol (2)	−0.1295	0.1307	0.60	0.33	0.97	0.69
Acetone (1)–ethylene glycol (2)	−0.6080	−0.2022	1.45	1.28	2.76	2.62
Methanol (1)–ethylene glycol (2)	0.2982	−0.0784	1.51	1.38	2.58	2.28

[a] $(\Sigma d^2/n)^{1/2}$ where $d = 100(\nu_{exptl} - \nu_{calcd})/\nu_{exptl}$.
[b] Unweighted data, see text.
[c] Weighted data, see text.
[d] From the work of Katti and Chaudhri, α_{12} for these three systems are 0.044, −0.078, 0.102, repectively (2).

Table II. Application of Viscosity Equations to Ternary System Acetone(1)–Methanol(2)–Ethylene Glycol(3)(1)

Constants of Equations 7, 8

β_{123}, Equation 7	−0.8317
β_{123}, Equation 8	−0.8495
β'_{123}, Equation 8	−0.2227

Av. Dev., %[c]

Lit.	−0.95[a]
This work, Equations 7, 6	−1.06[b]
This work, Equations 8, 6	−0.96[b]

Max. Dev., %

Lit.	−1.81[a]
This work, Equations 7, 6	−2.32[b]
This work, Equations 8, 6	−2.05[b]

[a] Unweighted data (1), see text.
[b] Weighted data, see text.
[c] Defined in Table I.

term in representing the excess molar Gibbs free energy of mixing in nonelectrolyte systems that depart only slightly from regular behavior (4). The physical significance of αRT in the above is, in fact, the excess molar Gibbs free emergy of activation of flow in the mixture (2).

In the first three systems of Table I, results obtained with Equation 3 are compared with those obtained by Equation 4. Included there, also, are the constants of the equations used. Consideration of the asymmetry of the systems results in a significant improvement in agreement between calculated and experimental viscosities. This reflects the fact that the bracketed quantity in Equation 4 shows a variation of up to 85% of the value at $x_1 = x_2$ in these systems. The constants of Equation 4 were obtained by a least-squares treatment of that equation arranged into the linear form

$$\delta_{12}/x_1 x_2 = \alpha_{12} + \alpha'_{12}(x_1 - x_2)$$

For best results in programing these data, statistical weighting is necessary. Presence of the factor $x_1 x_2$ in the term $\delta_{12}/x_1 x_2$ may cause a considerable spread in the data as $|x_1 - x_2|$ approaches unity. There, $x_1 x_2$ becomes comparatively small, with a relatively large uncertainty in the term, $\delta_{12}/x_1 x_2$. This effect has been allowed for by letting the weight of a data point be inversely proportional to the square of the probable error in the product $x_1 x_2$ (5). Thus, the ratio of the weight of a point at $x_1 = x_2 = 0.5$, for example, to that of a point at $x_1 = 9x_2$ is about 12.5. In applying Equation 3 to their data, Katti and

Chaudhri evaluated α_{12} from the data at equimolar concentration, where the data uncertainty is obviously the least. Their results, therefore, reflect an implicit quasi-weighting of the data. Thus, the difference between results by Equations 3 and 4 is essentially due to the effect of the asymmetry term.

The second aspect of Equation 1—that was concerned with the adequacy of assuming binary interactions only—may be conveniently considered with data on the ternary system reported by Kalidas and Laddha (1). Results of treating their three constituent binaries with Equation 4 are summarized in Table I. If the six constants α_{ij} and α'_{ij} are now incorporated into Equations 5 and 1 for the ternary system, the mean deviation of experimental data from results thereby is several per cent. Assumption of totally binary interaction is inadequate, and Equation 5 must be expanded for a ternary system by inclusion of a term for ternary interaction. Let this expanded form be written, for the ternary system 1–2–3, as

$$\delta_{123} = \sum_{\substack{i=1 \\ i<j}}^{i=3} x_i x_j[\alpha_{ij} + \alpha'_{ij}(x_i - x_j)] + x_1 x_2 x_3 \beta \qquad (6)$$

where β might be constant

$$\beta = \beta_{123} \qquad (7)$$

or a concentration dependent function such as, for example,

$$\beta = \beta_{123} + \beta'_{123} (x_1 - x_2) \qquad (8)$$

The form of Equation 8 is suggested by the linearity of a plot of the ternary data with Equation 6 as

$$\left\{ \delta_{123} - \sum_{\substack{i=1 \\ i<j}}^{i=3} x_i x_j[\alpha_{ij} + \alpha'_{ij}(x_i - x_j)] \right\} / x_1 x_2 x_3$$

vs. $x_1 - x_2$.

Comparison of experimental results with those obtained by use of Equations 7 and 6 with those by use of Equations 8 and 6 is made in Table II. Results obtained by Equation 8 are rather less in error than those by Equation 7, but the uncertainty in the experimental measurements makes it difficult to assess the significance of the improvement.

Let us now consider the alternate approach of Kalidas and Laddha (1), noting both the relative complexity of it and

results obtained thereby. For a multicomponent system, that equation may be written as

$$\log \nu = \sum_{i=1}^{n} x_i^{3} \log \nu_i + \sum_{i=1}^{n} x_i^{3} \log M_i - \log \sum_{i=1}^{n} x_i M_i +$$

$$3 \sum_{\substack{i=1 \\ i \neq j}}^{n} \sum_{j=1}^{n} x_i^{2} x_j \log \left(\frac{2M_i + M_j}{3} \right) + \qquad (9)$$

$$\sum_{\substack{i=1 \\ i \neq j \neq k \neq i}}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} x_i x_j x_k \log \left(\frac{M_i + M_j + M_k}{3} \right) + \delta_{1 \dots n}$$

where

$$\delta_{1 \dots n} = 3 \sum_{\substack{i=1 \\ i \neq j}}^{n} \sum_{j=1}^{n} x_i x_j \log \nu_{ij} + \sum_{\substack{i=1 \\ i \neq j \neq k \neq i}}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} x_i x_j x_k \log \nu_{ijk} \quad (10)$$

and ν_{ijk} is the same for given i, j, k regardless of the order of i, j, k. Both ν_{ij} and ν_{ijk} are constants, and are evaluated from experimental data in the appropriate binary and ternary systems, respectively. The relatively greater complexity of Equation 9 compared with Equation 1 is apparent. For a binary system, 1-2, Equation 10 reduces to

$$\delta_{12} = x_1 x_2 \left[\frac{3}{2} (\log \nu_{12} + \log \nu_{21}) + \right.$$

$$\left. \frac{3}{2} (\log \nu_{12} - \log \nu_{21})(x_1 - x_2) \right] \qquad (11)$$

Thus, Equations 4 and 11 show that in binary systems, although not in higher systems, the dependence of δ_{12} on concentration is of the same functional form by both approaches. Both approaches will require weighting of the data.

Results reported by Kalidas and Laddha (1) for the three constituent binaries of the ternary system are shown in Table I. These are unweighted data, and for the best comparison of the results by the regular solution and three-body approaches, the effect of weighting on the latter must be considered. This effect was evaluated and because of a fortuitous distribution of data scattering at large $|x_1 - x_2|$, the result was a decrease in error or no more than 0.1% except in the acetone-methanol system. There the effect was a reduction of the average and maximum deviations, respectively, from 0.60 and 0.97% to 0.33 and 0.69%. Results by the three-body approach are not superior to those by the modified regular solution approach in the binary systems.

The results of Kalidas and Laddha (1) for the ternary system are shown in Table II. They have not been corrected by the present author to include the effect of weighting required by the

presence of the factor $x_1 x_2 x_3$ in Equation 10. The effect of weighting was examined when the data were treated by the regular solution approach. The ternary data are so scattered that weighting reduced the error by only a few hundreths of one per cent. Moreover, as the major binary interaction is between pairs including ethylene glycol, the previously noted correction for weighting the acetone-methanol system has also been omitted. Trial calculations indicated this omission was virtually without effect on the conclusions stated in the present work. Table II shows that results obtained by the two approaches are comparable.

Those experimental points showing poor agreement with one approach are also in poor agreement by the other. It may be assumed that considerable portion of the lack of agreement between experimental and predicted values is due to lack of precision in the data. This conclusion is supported for the binary systems in that plots of deviations from the Arrhenius equation

$$\log \eta = x_1 \log \eta_1 + x_2 \log \eta_2$$

show that the suspect data points also deviate considerably from the smoothed values there.

While the present work does not consider explicitly results in systems higher than ternary, it may be anticipated that, for those systems, higher interaction terms may well be required. Thus, in quaternary systems, for example, a term in $x_1 x_2 x_3 x_4$ might be suitable.

NOMENCLATURE

x_i	=	mole fraction of component i
M_i	=	molecular weight of component i
α_{ij}, α'_{ij}	=	binary constants in equations based upon the regular solution approach
β_{ijk}, β'_{ijk}	=	ternary constants in equations based upon the regular solution approach
δ	=	deviation from noninteraction in a mixture
ν	=	kinematic viscosity of mixture
ν_i	=	kinematic viscosity of pure component i
ν_{ij} (ν_{ijk})	=	binary (ternary) constants in equations based upon the three-body approach
η	=	absolute viscosity of mixture
η_i	=	absolute viscosity of pure component i

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