Viscosity Blending Equations

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ABSTRACT:

In lubricating and specialty oil industries, blending is routinely used to convert a finite number of distillation cuts produced by a refinery into an infinite number of final products matching given specifications regarding viscosity. To find the right component ratio for a blend, empirical or semi-empirical equations linking viscosity of the blend to viscosities of the individual components are used. Perhaps the best known among viscosity blending equations are the double-logarithmic equation of Refutas and the cubic-root equation of Kendall and Monroe. The kinetic theory led the way to a deeper understanding of viscosity blending principles for binary mixtures, culminating in Grunberg-Nissan, Oswal-Desai and Lederer-Roegiers equations. These equations have lifted viscosity blending calculations to a practically useful accuracy level. Ironically, despite being the most accurate one-parameter equation, the viscosity blending equation due to Lederer and Roegiers remained largely unknown to the oil research community until recently.

INTRODUCTION

Viscosity blending is perhaps the most common operation in lubricant manufacture. All blenders rely upon their viscosity-blending calculators, often used as a magic black-box giving the right blend composition [1,2]. Accurate viscosity prediction for binary mixtures of two components with a large difference in viscosity remains a challenging task because viscosity blending curves may show a large degree of non-linearity. Strongly non-linear viscosity blending curves are often observed for binary systems such as base oil / polymeric thickener or viscosity index improver, which are quite common in lubricant formulation practice.

VISCOSITY BLENDING EQUATIONS COMMONLY USED IN THE PETROLEUM INDUSTRY

In the petroleum industry, empirical or proprietary blending equations are common. The best known are the double-logarithmic equation of Refutas and the cubic-root equation of Kendall and Monroe [3-5]. The Refutas equation calculates the viscosity, μ_{12}, of the binary blend from viscosities and weight fractions of the components by introducing the so-called viscosity blending index (ASTM D7152),

$$A_i = 14.534\ln[\ln(\mu_i + 0.8)] + 10.975 \quad (i = 1, 2) \quad (1)$$

where x_i is the weight fraction, μ_i is the kinematic viscosity of the ith component in the blend. Then, the blend viscosity is calculated as,

$$\mu_{12} = \exp\left[\exp\left(\frac{A_{12} - 10.975}{14.534}\right)\right] - 0.8 \quad (2)$$

where A_{12} is the average viscosity blending index,

$$A_{12} = x_1 A_1 + x_2 A_2 \quad (3)$$

Kendall-Monroe equation calculates the blend viscosity as the cubic-root average of the component viscosities,

$$\mu_{12}^{1/3} = x_1 \mu_1^{1/3} + x_2 \mu_2^{1/3} \quad (4)$$

The above equations hardly afford any meaningful theoretical substantiation and have unsatisfactory accuracy.

KINETIC THEORY APPROACH TO VISCOSITY BLENDING CALCULATIONS

At the moment there is no universal theory which would allow exact calculation of the viscosity of a complex mixture from the viscosities of the individual components [6,7]. The majority of the existing theories are limited to the so-called ideal binary mixtures.

A binary mixture is said to be ideal if mixing the components does not produce any change in volume. In other words, for an ideal mixture, the excess volume of mixing is zero. The dynamic viscosity, η_{12}, of an ideal binary mixture consisting of the components with viscosities η_1 and η_2 obeys the Arrhenius equation,

$$\ln\eta_{12} = x_1 \ln\eta_1 + x_2 \ln\eta_2 \quad (5)$$

where x_i (i = 1,2) is the mole fraction the ith component in the mixture.

The Arrhenius equation can be rationalised within the framework of the absolute reaction rate theory [8].

According to this theory, the fluidity (the inverse of viscosity) of a liquid is related to the flow activation energy, $\Delta E \neq$, which is a measure of intermolecular cohesion,

$$\frac{1}{\eta_i} = \frac{v_i}{h} \exp\left(-\frac{\Delta E^{\neq}}{RT}\right) \quad (6)$$

high activation energy corresponding to low fluidity and vice versa. This implies that

$$\ln \eta_i = const + \frac{\Delta E_i^{\neq}}{RT} \quad (i = 1,2) \quad (7)$$

Assuming that the flow activation energy for the mixture follows the additivity principle,

$$\Delta E_{12}^{\neq} = x_1 \Delta E_1^{\neq} + x_2 \Delta E_2^{\neq} \quad (8)$$

one immediately arrives at the Arrhenius equation.

From a practical viewpoint, the Arrhenius equation lacks accuracy and has limited value. Deviations from the Arrhenius equation are normally linked to the fact the interaction energy between two unlike molecules is in general different from the interaction energies of two like molecules. To account for non-ideality of the system, an additional term has been included in the above equation by Grunberg and Nissan [9], following the ideas of the regular solution theory,

$$\ln \eta_{12} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + \varepsilon x_1 x_2 \quad (9)$$

where ε is an empirical interaction parameter.

An amendment to the Grunberg-Nissan equation has been proposed by Oswal and Desai [10], who added two additional terms,

$$\ln \eta_{12} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + \varepsilon x_1 x_2 \quad (10)$$
$$+ K_1 x_1 x_2 (x_1 - x_2) + K_2 x_1 x_2 (x_1 - x_2)^2$$

However, the improvement in accuracy comes at a price of introduction of two additional fitting parameters with rather obscure physical meaning. For that reason, the Oswal-Desai equation will not be considered here.

Another useful blending equation has been proposed independently by Lederer [11] and Roegiers, Sr. [12,13],

$$\ln \eta_{12} = \ln \eta_1 + \frac{\alpha x_2}{x_1 + \alpha x_2} (\ln \eta_2 - \ln \eta_1) \quad (11)$$
$$= \frac{x_1}{x_1 + \alpha x_2} \ln \eta_1 + \frac{\alpha x_2}{x_1 + \alpha x_2} \ln \eta_2$$

where α is an empirical parameter to account for the difference in intermolecular cohesion energies between the component 1 and 2.

Unfortunately, the authors published their original work in difficult-to-access sources, and as a result, the above equation has remained largely unknown to the lubricant research community until recently.

The Lederer-Roegiers equation can be derived the same way as the Arrhenius equation but assuming an asymmetric mixing rule for the flow activation energy,

$$\Delta E_{12}^{\neq} = \frac{(1-\gamma)x_1}{(1-\gamma)x_1 + \gamma x_2} \Delta E_1^{\neq} + \frac{\gamma x_2}{(1-\gamma)x_1 + \gamma x_2} \Delta E_2^{\neq} \quad (12)$$

where $0 < \gamma < 1$. If $\gamma < 0.5$, the contribution of component 1 to the flow activation energy is greater than that of component 2, and vice versa, if $\gamma > 0.5$, the contribution of component 1 to the flow activation energy is less than that of component 2. Indeed, from a hydrodynamic viewpoint, viscosity reflects the momentum flux from one liquid layer to another when two adjacent liquid layers slide against each other. Since the molecules of the components 1 and 2 differ in molecular weight, size and electron density distribution, the energies of pair-wise interactions 1-1, 1-2, and 2-2 are also different. Putting $\alpha = \gamma / (1 - \gamma)$, the Lederer-Roegiers equation is arrived at. For $\gamma = 0.5$, $\alpha = 1$, and the Lederer-Roegiers equation (6) becomes identical to the Arrhenius equation (1).

The presence of highly polar compounds with strong orientational forces such as hydrogen bonding may result in S-shaped viscosity plots. Such behaviour is often observed when blending polymer-thickened oils having a sufficiently large difference in solubility.

Examples are polyalphaolefin / olefin copolymer / fatty ester or polyalphaolefin / fatty ester / polyester systems. In this case, changing the component ratio has a strong effect on the solvent power of the mixture, which, in its turn, has an effect on the random coil configuration of the polymeric thickener. For instance, the mean radius of gyration of a polyester molecule in polyalphaolefin solution is smaller than it is in fatty ester solution. Vice versa, the mean radius of gyration of an olefin copolymer molecule in polyalphaolefin solution is greater than it is in fatty ester solution. Generally speaking, such systems normally reveal non-Newtonian rheology - their viscosity becomes a complex shear-rate-dependent quantity. However, this is outside the subject of the present communication. As long as the mixture behaves nearly like a normal liquid (and not as a gel), the effect of random coil radius change on viscosity can be described by an asymmetric correcting function of the type $x_1(1 - x_1)(2x_1 - 1)^{2k+1}$, as has been done in eq.(10) by Oswal-Desai [10].

It should also be commented that the above blending equations refer to dynamic viscosity, η. The corresponding equations for kinematic viscosity, μ, are obtained using the relationship $\eta = \rho\mu$, where ρ is the density. To link the density of a binary mixture to the densities of its components, the excess volume of mixing should be determined. Luckily, most mineral oils behave as normal fluids, for which the excess volume of mixing is close to zero. Furthermore, since the densities of components in mineral oil blends are usually close to each other, rarely falling outside the range 0.8 to 1.0 g/cm³, the term $\ln\rho_{12} - x_1\ln\rho_1 - x_2\ln\rho_2$ is close to zero. Therefore, in practice, the above-mentioned viscosity-blending equations (5), (9), (10) and (11) can well be applied for calculation of kinematic viscosities. For the same reason, mole fractions are substituted by weight fractions.

APPLICATIONS OF LEDERER-ROEGIERS EQUATION

a. Determination of the intermolecular cohesion parameter

The easiest way to determine the intermolecular cohesion parameter for a given blend is via measuring the blend viscosity for component weight ratio 50:50, in which case

$$\ln \mu_{12} = \ln \mu_1 + \frac{\alpha}{1+\alpha}(\ln \mu_2 - \ln \mu_1) \ (x_1 = x_2 = 0.5) \tag{13}$$

and hence,

$$\alpha = \frac{\ln(\mu_{12} / \mu_1)}{\ln(\mu_2 / \mu_{12})} \tag{14}$$

A more scientific way is to treat α as a fitting parameter and to base its determination on the method of least squares.

b. Calculation of viscosity for a blend of two components with a given intermolecular cohesion parameter.

Once the intermolecular cohesion parameter for a given pair of components has been determined, the entire viscosity blending curve can be calculated. The typical values of intermolecular cohesion parameter for various base oil types are as follows:

Light hydrocarbon / Heavy naphthenic	0.3 - 0.4
Light hydrocarbon / Heavy paraffinic	0.5 - 0.9
Light paraffinic / polyol ester	1.0 - 1.4
Light naphthenic / polyol ester	1.3 - 1.7

c. Determination of the weight ratio of components for getting a certain blend viscosity

The desired component ratio is obtained by rearranging terms in eq.(11),

$$\frac{x_1}{x_2} = \alpha \left[\frac{\ln(\mu_2 / \mu_1)}{\ln(\mu_{12} / \mu_1)} - 1 \right] \tag{15}$$

In order to demonstrate remarkable accuracy of the Lederer-Roegiers equation in describing viscosity of binary blends of various hydrocarbon fractions, viscosity measurements were carried out

Property	Method	Base Oil or Petroleum Distillate					
		Exxol D60	PAO2	NS8	100N	Bright stock	T4000
density at 15ºC (g/cm³)	ASTM D4052	0.782	0.798	0.879	0.869	0.901	0.967
viscosity at 40ºC (cSt)	ASTM D445	1.20	5.10	7.88	22.4	462	4400
refractive index at 20ºC	ASTM D1747	1.433	1.443	1.479	1.480	1.496	1.527
flash point (ºC)	ASTM D93	66	161	144	210	302	237

Table 1: Physical properties of base oils and petroleum distillates used in this study.

for a number of paraffinic, naphthenic and synthetic oils. Some physicochemical properties of oils used in this study are summarised in Table 1. Kinematic viscosity of the individual components and their binary mixtures was measured at 40ºC according to ASTM D445.

From the theoretical viewpoint, the Grunberg-Nissan equation and the Lederer-Roegiers equation are the most substantiated single-parameter viscosity blending equations. In the following, we compare accuracy of those two equations.
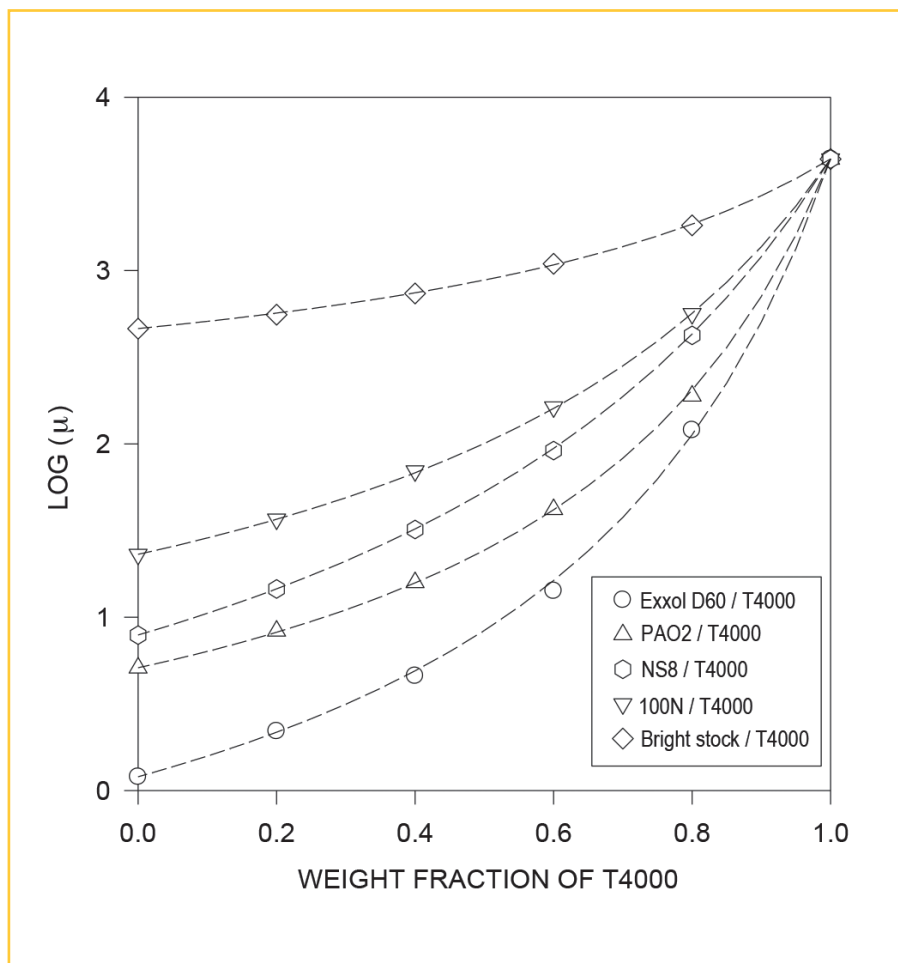

Figure 1: Viscosity curves for binary mixtures of various petroleum products with a heavy naphthenic base oil T4000. Theoretical viscosity-blending curves obtained using the Roegiers equation are shown by broken lines. Values of the best-fit parameter were as follows: α = 0.31 for Exxol D60/T4000; α = 0.30 for PAO2/T4000; α = 0.39 for 100N/T4000; α = 0.40 for Bright Stock/T4000; α = 0.31 for NS8/T4000. The average error 4%, the maximum error 15% in absolute viscosity values.

Figures 1 and 2 show experimental viscosity blending curves for PAO2 and a number of petroleum products - ranging from light solvent distillate to bright stock - with a heavy naphthenic base oil T4000. The system Exxol D60/T4000 resembles the system hexane/Mobiloil bright stock studied in the original work by Roegiers, Sr. [12]. Due to a big difference in component viscosities and molecular size, both the systems show quite significant deviation from the Arrhenius equation. The Lederer-Roegiers equation demonstrate remarkable accuracy in predicting the blend viscosity in this case (Figure 1), whereas the Grunberg-Nissan equation fails to adequately account for such a level of non-linearity (see Figure 2).

CONCLUSION

Of single-parameter viscosity blending equations, the Grunberg-Nissan equation and the Lederer-Roegiers equation are probably the only equations which afford a meaningful theoretical rationalisation and give an accuracy level adequate for practical applications. For mixtures of components with greatly differing viscosities, which show large deviation from ideal behaviour, the Lederer-Roegiers equation give a significantly more accurate blend viscosity prediction than the Grunberg-Nissan equation.

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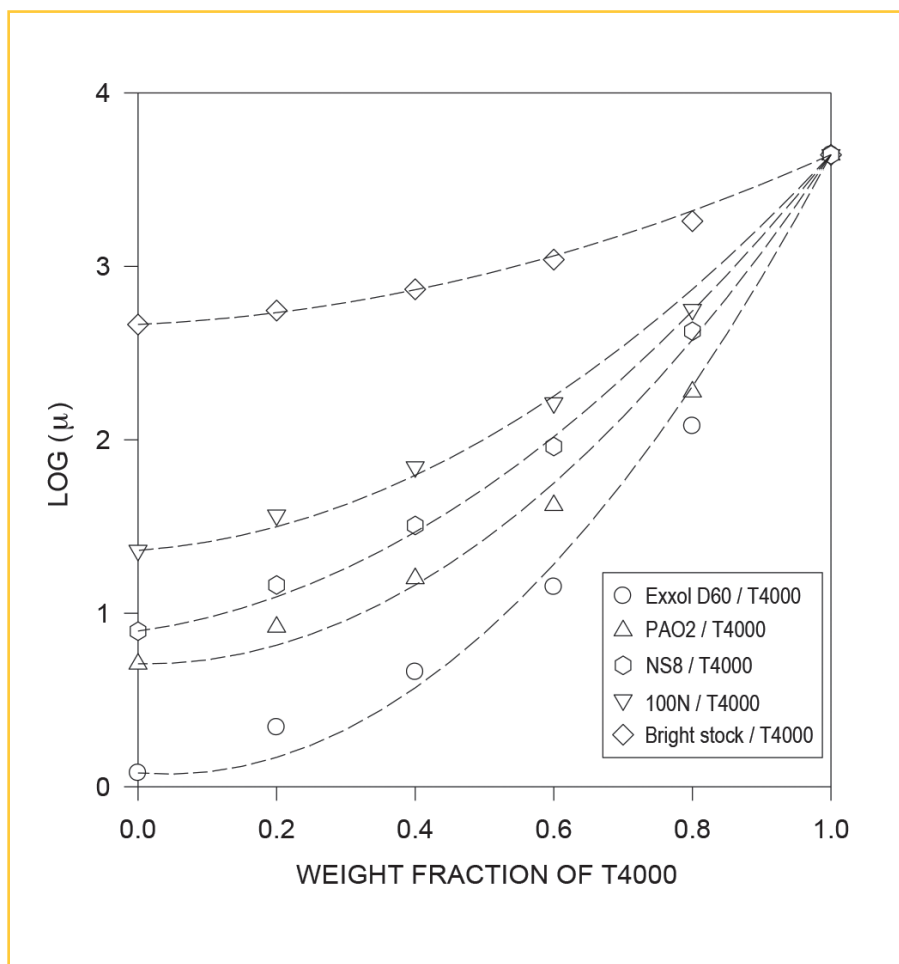
Figure 2: Viscosity curves for binary mixtures of various petroleum products with a heavy naphthenic base oil T4000. Theoretical viscosity-blending curves obtained using the Grunberg-Nissan equation are shown by broken lines. Values of the best-fit parameter were as follows: ε = -3.9 for Exxol D60/T4000; ε = -3.0 for PAO2/T4000; ε = -2.0 for 100N/T4000; ε = -0.8 for Bright Stock/T4000; ε = -2.2 for NS8/T4000. The average error 15%, the maximum error 90% in absolute viscosity values.