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Viscosity of triglyceride and alcohol solutions: application of the Krone, Doolittle and Macedo–Litovitz equations

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Abstract

The viscosity values of triglyceride and alcohol solutions with newtonian rheological behaviour (triacetin + butanol, tributyrin + butanol, tricaprylin + butanol, tributyrin + ethanol and tributyrin + hexanol) and with molar fraction composition between 0 and 1 are compared with those obtained from application of the equations of Krone, Doolittle and Macedo–Litovitz, in the temperature range 278–313 K.

Keywords: Viscosity; Triglyceride/alcohol solutions; Krone equation; Doolittle equation; Macedo–Litovitz equation

1. Introduction

This work is part of a systematic study on the physicochemical properties of vegetable oils (and their components) in mixtures with organic solvents. The aim is to have enough experimental data to relate these properties with the molecular structure, to establish methods for the estimation of these properties and to calculate design parameters.

Viscosity is a property directly related to momentum transport, so falls entirely within chemical engineering design calculations. In the absence of a systematic and rigorous theory that enables the prediction of the viscosity from molecular-scale models of pure liquids and their mixtures, there are limitations to all model-based theories, although they are suitable for describing physical phenomena.

Theories have been developed for predicting liquid viscosity with reasonably satisfactory results, such as the work of Eyring and coworkers [1], based on the activation energy or on the free volume. The most successful liquid viscosity predictive theories are based on the hypothesis that the structure of the liquids is quasi-crystalline. In such a structure, a molecule vibrates around a position of equilibrium, until it acquires sufficient energy to leave its neighbours' field of attractive forces and there is a free space available for it to occupy.

The probability of a molecule shifting from one position of equilibrium to another depends directly on the probability that the molecule will acquire sufficient energy to leave its neighbours' field of attractive forces and the probability that there is sufficient adjacent empty space to permit the shift from one position of the other. This approach has been used [1,2] without taking account of the role of the free volume in calculating the second probability, and similar expressions have been arrived at which relate viscosity with temperature, though with the drawback that it is not possible to explain the major deviations of the liquids in relation to Arrhenius-type behaviour. The models of McAllister [3], Dizechi and Marschall [4], and Krone [5] represent this approach.

These deficiencies have stimulated the development of expressions for liquid viscosity which are based on the free volume model [6,7]. This model supposes a distribution of space sizes and supposes that the probability of a shift by a molecule from one position of equilibrium to another is determined purely by the probability that an adjacent free volume will be found which is large enough for it to occupy. Each molecule is confined in a cell formed by its neighbours and, for diffusion movements to take place, a space must appear which is large enough to permit a significant displacement of the molecule within the cell. However, the free–volume theories are not successful in seeking to explain the dependence of viscosity on the temperature or pressure of many liquids, particularly at 100 degrees above or below the so-called vitreous transition temperature.

Krone [5] proposed an equation based on a conceptual model of momentum transfer, developed to describe the effects of directional distributions of thermal movements and intermolecular attractions by means of coefficients which can be determined empirically. This proposed model supposes that the momentum transport between adjacent strata of molecules is the result of the interaction between these molecules,

resulting from fluctuations caused by their thermal rotation and vibration and the dense distribution of the adjacent molecules. Each molecule vibrates around a mean position in its neighbours' field of forces and can occasionally interact with molecules in the adjacent stratum, so contributing to the momentum transport, showing that molecule mass must be included in the calculation of the viscosity. These interactions generate a force between the strata, which is damped by their transitory defects, which may be caused by a molecule with sufficient thermal energy to break the attraction with its neighbours. The result is an equation of the form

$$\eta = \beta(T - T_0)\ \exp\left[\frac{E}{RT}\right] \tag{1}$$

where η is the dynamic viscosity, E is the energy required to create a space, T is the absolute temperature, R is the gas constant and β is a parameter defined by the expression

$$\beta = \alpha\delta nkm/hN_A$$

in which α is the fraction of thermal motions that results in an interlayer interaction, δ is the distance between adjacent layers, n is the number of molecules per unit of area, m is the mass of the molecules that act as a unit, N_A is the Avogadro number, h is Planck's constant and T_0 is analogous to the Debye temperature. The product kT_0 represents the average thermal energy that is unavailable for increasing the frequency of interactions with molecules of adjacent layers.

Doolittle [6] proposed an exponential-type equation which relates viscosity to the molar volume

$$\eta = A\ \exp\left(B\ \frac{V_0}{V - V_0}\right) \tag{2}$$

where η is the viscosity, A and B are two characteristic parameters of the liquid, V_0 is the molar volume taken up and represents the volume of the liquid when the temperature is reduced, assuming that there is no change of state and that, as a result of its compact structure, shear movements are not possible between its molecules, and V is the molar volume of the liquid. The difference $V - V_0$ is the so-called "free volume".

Macedo and Litovitz [8] combined the theory of Eyring and coworkers [1] and the free volume theory of Cohen and Turnbull [9] to obtain a hybrid equation expressed as

$$\eta = CT\ \exp\left(\frac{E_v}{RT} + \gamma\ \frac{V_0}{V - V_0}\right) \tag{3}$$

where η is the dynamic viscosity, E_v represents the energy barrier between the positions of equilibrium, R is the gas constant, T is the absolute temperature, V is the molar volume, V_0 is the limit molar volume, γ is a numeric factor of correction of the free volume overlap and C is a parameter given by the expression

$$C = \frac{(R/E_v)^{1/2}(2mk)^{1/2}}{V^{2/3}}$$

in which m is the molecular mass and k is Boltzmann's constant.

2. Discussion

2.1. Krone's equation

To verify the validity of the model proposed by Krone, Eq. (1) was applied to the experimental data on the viscosity of the solutions [10], first determining parameter T_0 according to the criterion of minimizing the sum of errors relative to the square (SE), defined by

$$\mathrm{SE} = \sum\left[\frac{(\eta_e - \eta_c}{\eta_e}\right]^2$$

where η_e is the experimentally observed viscosity and η_c is the calculated viscosity.

In all cases, the value of T_0 that minimizes the sum of the errors relative to the square is zero and the equation is left with two adjustment parameters, i.e. β and E. To make the

Table 1
Values of parameters β^* (mPa s K^{-1}) and E (kJ mol^{-1}) of Eq. (4)

x	Triacetin + butanol		Tributyrin + butanol		Tricaprylin + butanol		Tributyrin + ethanol		Tributyrin + hexanol	
	$\beta^* \times 10^3$	E	$\beta^* \times 10^3$	E	$\beta^* \times 10^3$	E	$\beta^* \times 10^3$	E	$\beta^* \times 10^3$	E
0.0	7.35	21.3	7.35	21.3	7.35	21.3	3.39	14.2	12.60	25.2
0.1	6.99	22.3	7.63	21.5	11.18	23.4	4.77	17.2	11.47	24.5
0.2	7.81	24.8	8.74	22.5	15.70	25.4	6.56	19.8	11.73	24.9
0.3	8.99	26.4	10.06	23.2	20.32	26.9	8.55	21.6	12.36	25.2
0.4	10.59	27.9	11.54	24.0	25.00	28.2	10.58	22.9	13.31	25.4
0.5	12.71	29.3	13.15	24.9	29.54	29.3	12.66	24.1	14.47	25.7
0.6	15.56	31.1	15.07	25.5	34.22	30.2	14.83	25.0	15.89	26.1
0.7	19.37	33.4	17.03	26.1	39.01	31.0	17.09	25.9	17.53	26.5
0.8	24.62	36.4	19.20	26.8	44.30	31.6	19.35	26.8	19.49	26.9
0.9	31.97	40.2	21.73	27.7	49.44	32.6	21.86	27.6	21.75	27.7
1.0	42.68	45.2	24.55	28.7	54.97	33.2	24.55	28.7	24.55	28.7

adjustment to minimize the errors that affect the parameter β, Eq. (1) was modified, taking a reference temperature in the measurement interval of 303 K, such that

$$\ln\left(\frac{\eta}{T}\right) = \ln \beta^* + \frac{E}{R}\left(\frac{1}{T} - \frac{1}{303}\right) \quad (4)$$

This modification does not affect the regression statistics or the value of parameter E. The values obtained for β^* and E are set out on Table 1. The errors that affect these parameters for 95% probability are less than 7% and 8% respectively. The correlation coefficient r^2 is greater than 0.997 in all cases and the absolute average deviation percentage (AAD), defined as

$$\mathrm{AAD} = \left(\frac{100}{N}\right)\sum\left|\frac{(\eta_e - \eta_c)}{\eta_e}\right|$$

where N is the number of data, is less than 3.92%.

The parameters β^* and E increase with the concentration of triglyceride in the solution. This sequence indicates that the parameter β^* depends directly on the mean molecular mass, as defined, and that the molecular interactions also increase with the mean molecular mass, as reflected in the values for E.

The fact that $T_0 = 0$ in the temperature range studied may mean that, at these temperatures, each molecule vibrates within the field of forces of its neighbours without displacing a molecule from an adjacent stratum to the next stratum. Interactions with neighbours will be greater in some directions than in others, with a tendency to form local structures, indicating that these solutions are more solid–liquid than gas–liquid, which is in agreement with Krone's theory [5].

However, it should be noted that, for the same molar fraction x of triglyceride, among the values of the energy parameter E that correspond to tributyrin and ethanol, butanol or hexanol, there are no significant differences. This suggests that, when the triglyceride molecules predominate, the solutions must be structured similarly, irrespective of the alcohol type. However, for solutions of the three triglycerides in butanol, when the molar fraction of triglyceride is greater than that of the butanol, the structure is defined by the molecular characteristics of the triglyceride and more compact ordering is seen in solutions with triacetin, as shown by the values of E.

2.2. Doolittle's equation

Table 2 contains the values for the parameter V_0 which minimize SE, and the values for A and for B, obtained from the correlation of the experimental data using Eq. (2), whose errors for 95% probability are less than 9% and 2% respectively. In all cases, the correlation coefficients are greater than 0.999 and the AAD values are less than 2.13%.

For each system, an analysis of the values for both parameters suggests that A must be related to the type of molecular interaction, given its increasing variation with the molar

Table 2
Values of parameters V_0 (cm^3 mol^{-1}), A (mPa s) and B of Eq. (2)

x	Triacetin + butanol			Tributyrin + butanol			Tricaprylin + butanol			Tributyrin + ethanol			Tributyrin + hexanol		
	V_0	A	B	V_0	A	B	V_0	A	B	V_0	A	B	V_0	A	B
0.0	73.1	0.0118	1.379	73.1	0.0118	1.379	73.1	0.0118	1.379	47.0	0.0685	0.689	104.1	0.0137	1.181
0.1	87.1	0.0497	0.651	91.6	0.0202	1.091	111.3	0.0307	0.912	70.0	0.043	0.481	121.4	0.0351	0.818
0.2	96.9	0.0540	0.591	112.9	0.0492	0.710	148.4	0.0456	0.782	90.8	0.0800	0.536	138.7	0.0595	0.631
0.3	106.1	0.0571	0.577	133.0	0.0862	0.547	186.5	0.0719	0.653	112.4	0.0901	0.518	154.6	0.0781	0.564
0.4	117.9	0.1234	0.383	149.6	0.0685	0.631	222.3	0.0729	0.672	133.9	0.1020	0.499	169.9	0.0893	0.543
0.5	127.1	0.1398	0.374	168.4	0.0806	0.593	260.0	0.0909	0.615	155.3	0.1075	0.499	185.4	0.1020	0.519
0.6	135.4	0.1176	0.432	187.3	0.0980	0.554	295.9	0.0877	0.637	177.9	0.1492	0.438	201.0	0.1176	0.498
0.7	145.4	0.1492	0.396	205.2	0.1010	0.565	332.8	0.0971	0.621	198.5	0.1369	0.475	217.7	0.1562	0.438
0.8	154.1	0.1351	0.432	225.6	0.1408	0.482	369.1	0.1031	0.623	218.1	0.1136	0.544	231.4	0.1369	0.492
0.9	163.9	0.1388	0.424	243.5	0.1388	0.502	405.9	0.1052	0.620	240.5	0.1388	0.503	246.7	0.1388	0.499
1.0	174.2	0.2083	0.378	263.7	0.1785	0.447	446.9	0.1785	0.511	263.7	0.1785	0.447	263.7	0.1785	0.447

fraction of triglyceride, and that B is related to the way in which the molecules are structured: for molar fractions over 0.5, there are no significant differences between the values of A and B when the errors affecting them are considered. This may mean that, when the triglyceride molecules predominate over the alcohol molecules, the alcohol molecules are ordered similarly to the triglyceride molecules.

2.3. Madeco–Litovitz equation

The experimental viscosity data have been correlated according to Eq. (3), modified and linearized as

$$\ln\left(\frac{\eta}{T}\right) = \ln C^* + \frac{E_v}{R}\left(\frac{1}{T} - \frac{1}{303}\right) + \gamma\frac{V_0}{V - V_0} \qquad (5)$$

to minimize the errors that affect the parameter C. This modification does not affect the values of parameters E_v and γ.

To compare this model with the previous model, the regression has been carried out, fixing the value of V_0. By means of iterative calculus, a better regression is obtained when the values of V_0 coincide with the values estimated in Hildebrand's equation [10]. The parameters of Eq. (5) calculated in this way are shown in Table 3.

The errors that affect C^* and E_v for a 95% probability are less than 9% and 11% respectively. The correlation coefficients are greater than 0.999 and the AAD percentages are less than 0.59%.

The parameters C^* and $E_v{}^*$ follow the same variation with composition as for the parameters β^* and E in Eq. (4). This is as expected, because Eq. (5) is transformed into Eq. (4) if γ is made to equal 0. Despite the small values for γ, the inclusion of the free volume term in Eq. (5) helps to improve the quality of the correlation, as is observed in the values of the statistical parameter in the temperature range 283–313 K.

3. Conclusions

Comparing the models (considered as three-parameter models), it can be stated that the Macedo–Litovitz Eq. (5), which combines the activation energy and free volume contributions, offers the best adjustment with experimental data. This fact suggests that both intermolecular forces and the free volume distribution must be considered when studying transport properties such as viscosity. Neglecting one of these factors leads to less satisfactory results.

The successful applications of Eq. (5) to the variety of newtonian solutions presented in this paper and the interpretation of its parameters in terms of molecular properties promise a means for correlating the parameters with the molecular configurations of solutions.

Table 3
Values of parameters C^* (mPa s K^{-1}), E_v (kJ mol^{-1}) and γ of Eq. (5)

x	Triacetin + butanol			Triburyrin + butanol			Tricaprylin + butanol			Tributyrin + ethanol			Tributyrin + hexanol		
	$C^*\times10^3$	E_v	$\gamma\times10^3$	$C^*\times10^3$	E_v	$\gamma\times10^3$	$C^*\times10^3$	E_v	$\gamma\times10^3$	$C^*\times10^3$	E_v	$\gamma\times10^3$	$C^*\times10^3$	E_v	$\gamma\times10^3$
0.0	7.21	20.8	0.9	7.21	20.8	0.9	7.21	20.8	0.9	3.19	13.4	5.1	12.48	24.9	0.4
0.1	6.51	20.4	3.2	7.34	20.5	1.7	10.72	22.2	1.6	4.28	15.3	6.4	11.01	23.3	1.5
0.2	7.11	21.8	3.8	8.15	20.6	3.0	14.86	23.6	1.9	6.04	18.0	4.0	11.03	23.0	2.2
0.3	8.23	23.3	3.4	9.22	20.7	3.6	19.15	24.8	1.9	7.85	19.4	3.7	11.55	22.9	2.5
0.4	9.53	23.9	3.8	10.70	21.7	3.0	23.67	26.0	1.7	9.72	20.6	3.4	12.38	23.0	2.7
0.5	11.51	25.1	3.4	12.21	22.5	2.9	27.96	26.9	1.6	11.68	21.7	3.1	13.40	23.1	2.8
0.6	14.35	27.2	2.6	13.95	22.9	2.9	32.56	27.9	1.4	13.67	22.4	3.0	14.72	23.4	2.7
0.7	18.00	29.3	2.2	15.80	23.5	2.7	37.12	28.6	1.4	15.79	23.3	2.8	16.15	23.6	2.9
0.8	23.28	32.6	1.6	17.71	23.9	2.8	42.37	29.3	1.2	17.99	24.2	2.5	18.06	24.2	2.6
0.9	30.69	36.3	1.0	20.19	24.8	2.5	47.36	30.3	1.1	20.33	24.8	2.4	20.26	24.9	2.4
1.0	41.69	41.5	0.6	22.64	25.4	2.6	52.43	30.5	1.2	22.64	25.4	2.6	22.64	25.4	2.6

Appendix A: nomenclature

A, B, C	constants
C^*	parameter in Eq. (5) (mPa s K^{-1})
E	energy required to create a space (kJ mol^{-1})
E_v	energy barrier between the positions of equilibrium (kJ mol^{-1})
N	number of data
R	gas constant (J mol^{-1} K^{-1})
r^2	regression coefficient
T	temperature (K)
V	molar volume (cm^3 mol^{-1})
V_0	limit molar volume (cm^3 mol^{-1})
x	molar fraction of triglyceride

Greek letters

β^*	parameter in Eq. (4) (mPa s K^{-1})
η	dynamic viscosity (mPa s)
γ	numeric factor of correction of the free volume overlap

Subscripts

c	calculated value
e	experimental data

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