A STUDY OF THE VISCOSITY OF METHYL MYRISTATE SOLUTIONS IN ORGANIC SOLVENTS

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RESUMEN.—Se estudian las variaciones de la viscosidad con la composición de disoluciones de miristato de metilo en ciclohexano, hexano, tetracloroetileno o tricloroetileno en el intervalo de temperatura de 293 a 313 K. Todas las disoluciones presentan valores negativos de la desviación relativa entre los valores experimentales de viscosidad y los valores teóricos. Existe un valor máximo de desviación relativa que divide al intervalo de concentración en dos zonas, encontrándose en ambas, variaciones lineales de los logaritmos de los valores de viscosidad frente a la fracción volumétrica de miristato de metilo.

SUMMARY.—A study is made of variations in viscosity with the composition of methyl myristate solutions in cyclohexane, n-hexane, tetrachloroethylene or trichloroethylene over a temperature range of 293 - 313 K. All the solutions studied show negative relative deviation values between experimental viscosity values and the theoretical values. There is a maximun relative deviation which divides the concentration interval into two zones, in both there are linear variations to the viscosity value logarithms against the volumetric fraction of methyl myristate.

Palabras clave: viscosity, methyl myristate, solutions, organic solvents

INTRODUCTION

The inadequate development of liquid theory has led to the creation of a number of procedures for predicting the viscosity values of pure liquids and their mixtures, most of which are based on empirical or semi-empirical approximations.

The literature contains a large number of equations which have been put forward to estimate the viscosity value for binary liquid solutions. These equations can be grouped according to different criteria. One of these groups is of the so-called additivity equations, which includes those with the following form: $f(\mu) = x_1 f(\mu_1) + x_2 f(\mu_2)$, where $f(\mu_i)$ is a function of the viscosity of the components and of the solution and x_i is the mole or volumetric fraction or the fraction by weight of the components of the mixture.

Within this group, a set of equations has been proposed (1). The estimation of viscosity values with the application of this type of equation proves to be more satisfactory the more similar the viscosity values of the pure components.

EXPERIMENTAL

Four organic solvents and methylic ester were used, whose purities determined by gas chromatography were as follows: cyclohexane 99.7 %, n-hexane 98.7 %, tetrachloroethylene 99 %, trichloroethylene 99.5 %, methyl myristate 99.3 %.

The solutions were prepared by mass, using a Mettler P1210 single-pan balance with a precision of ± 0.01 g. Mole fractions x were accurate to 0.001. Mesurements were made in a thermostated Hetofrig bath, controlled to ± 0.1 K.

The Newtonian rheological behavior of the solutions was measured with a rotation viscosimeter with accuracy of 99 %. The dynamic viscosity was measured with a Haake Model B/BH Höppler falling-ball viscosimeter accurate to ± 0.01 mPa.s. Experimental viscosity values for pure components (except methyl myristate, prepared by syntesis) has been compared with bibliografy data (2, 3). The results offers no significant deviations.

DISCUSSION

In attempting to establish the degree of applicability of these equations to the solutions considered, the relative deviation was obtained between the experimental viscosity values and the theoretical values estimated on the basis of the viscosities of the pure components, with the solutions treated as being ideal (4). These relative deviation values, calculated from the experimental results (5) are contained in table I, where the values below 0.05 are not considered significant, this being the limit established by the experimental errors.

The relative deviation values of all the solutions studied were negative, showing that there are molecular interactions which reduce the viscosity value, since the average degree of structuring of the molecules in the solution is less than that of the pure components (6).

The relative deviation values above the limits established by the error indicate that the additivity equation is not satisfactorily confirmed throughout the concentration range when the viscosity function is linear. It is seen that all the solutions have a maximum relative deviation at different concentrations: 0.2 - 0.3 in solutions with cyclohexane, 0.4 - 0.4 in solutions with n-hexane, 0.3 in solutions with tetrachloroethylene, and 0.2 in those with trichloroethylene.

Because there is a maximun relative deviation value for all the solutions which divides the concentration ran-

TABLE I

Relative deviations (%) of viscosity values

	Methyl myristate + cyclohexane					Methyl myristate + n-hexane				
x_2	293K	298K	303K	308K	313K	293K	298K	303K	308K	313K
0.1	**-0.09**	**-0.08**	**-0.06**	-0.05	-0.05	**-0.35**	**-0.34**	**-0.28**	**-0.27**	**-0.25**
0.2	**-0.13**	**-0.12**	**-0.09**	**-0.08**	**-0.07**	**-0.50**	**-0.46**	**-0.40**	**-0.36**	**-0.32**
0.3	**-0.14**	**-0.14**	**-0.11**	**-0.09**	**-0.08**	**-0.57**	**-0.53**	**-0.45**	**-0.41**	**-0.36**
0.4	**-0.09**	**-0.10**	**-0.07**	**-0.06**	-0.04	**-0.58**	**-0.54**	**-0.46**	**-0.42**	**-0.36**
0.5	**-0.09**	**-0.09**	**-0.07**	**-0.06**	-0.04	**-0.54**	**-0.52**	**-0.45**	**-0.41**	**-0.36**
0.6	**-0.07**	**-0.08**	**-0.06**	-0.05	-0.04	**-0.45**	**-0.43**	**-0.38**	**-0.37**	**-0.33**
0.7	-0.04	-0.05	-0.04	-0.04	-0.04	**-0.32**	**-0.30**	**-0.27**	**-0.27**	**-0.25**
0.8	-0.02	-0.03	-0.02	-0.02	-0.02	**-0.21**	**-0.19**	**-0.18**	**-0.18**	**-0.17**
0.9	-0.01	-0.01	-0.01	-0.01	-0.01	**-0.09**	**-0.09**	**-0.08**	**-0.09**	**-0.08**
	Methyl myristate + tetrachloroetilene					Methyl myristate + trichloroethylene				
x_2	293K	298K	303K	308K	313K	293K	298K	303K	308K	313K
0.1	**-0.10**	**-0.09**	**-0.06**	-0.05	-0.04	**-0.26**	**-0.23**	**-0.20**	**-0.18**	**-0.16**
0.2	**-0.10**	**-0.09**	**-0.06**	**-0.06**	-0.04	**-0.28**	**-0.26**	**-0.21**	**-0.19**	**-0.17**
0.3	**-0.11**	**-0.10**	**-0.08**	**-0.06**	-0.05	**-0.21**	**-0.18**	**-0.16**	**-0.14**	**-0.11**
0.4	**-0.09**	**-0.09**	**-0.07**	-0.05	-0.03	**-0.16**	**-0.15**	**-0.12**	**-0.11**	**-0.09**
0.5	**-0.08**	**-0.07**	**-0.06**	-0.05	-0.02	**-0.11**	**-0.11**	**-0.08**	**-0.08**	**-0.06**
0.6	-0.04	-0.05	-0.04	-0.04	-0.02	**-0.07**	**-0.08**	**-0.06**	-0.05	-0.03
0.7	-0.04	-0.04	-0.03	-0.03	-0.02	-0.05	-0.05	-0.04	-0.03	-0.02
0.8	-0.02	-0.03	-0.01	-0.02	-0.01	-0.03	-0.03	-0.02	-0.02	-0.01
0.9	-0.01	-0.02	-0.01	-0.01	-0.00	-0.01	-0.01	-0.01	-0.01	-0.01

Relative deviations greater than experimental errors are indicated in bold.

TABLE II

Values of parameters of equations [1], [2], [3] and viscosity of pure components

Solutions	Parameters	293 K	298 K	303 K	308 K	313 K
Methyl myristate + cychlohexane	μ_1	0.608	0.549	0.546	0.500	0.485
	μ_2	4.639	4.086	3.597	3.267	2.914
	μ_4	2.821	2.241	1.965	1.634	1.412
	μ_5	0.999	0.934	0.893	0.834	0.772
	μ_6	3.308	2.734	2.343	2.013	1.726
Methyl myristate + n-hexane	μ_1	0.146	0.141	0.145	0.141	0.148
	μ_2	4.501	4.022	3.560	3.179	2.835
	μ_4	0.657	0.566	0.515	0.448	0.419
	μ_5	0.371	0.350	0.332	0.313	0.293
	μ_6	1.173	1.003	0.875	0.769	0.679
Methyl myristate + tetrachloroethylene	μ_1	0.590	0.581	0.543	0.523	0.552
	μ_2	4.611	4.054	3.633	3.265	2.919
	μ_4	2.723	2.354	1.971	1.706	1.611
	μ_5	0.958	0.911	0.875	0.850	0.817
	μ_6	3.406	2.904	2.501	2.171	1.895
Methyl myristate + trichloroethylene	μ_1	0.325	0.309	0.320	0.303	0.305
	μ_2	4.680	4.148	3.646	3.299	2.955
	μ_4	1.519	1.282	1.167	1.000	0.901
	μ_5	0.580	0.572	0.551	0.529	0.508
	μ_6	1.685	1.444	1.286	1.140	0.997

TABLE II (continuación)

Solutions	Parameters	293 K	298 K	303 K	308 K	313 K
		Viscosity of pure components (mPa.s)				
Methyl myristate		4.66	4.16	3.66	3.30	2.96
Cyclohexane		1.07	0.99	0.93	0.86	0.81
n-Hexane		0.32	0.31	0.29	0.28	0.27
Tetrachloroethylene		1.08	1.02	0.97	0.92	0.88
Trichloroethylene		0.73	0.69	0.66	0.63	0.60

ge into two zones, the equation established by Arrhenius (7) is verified:

$$\ln\mu_m = [1 - t_2] \ln \mu_1 + t_2 \ln \mu_2 \qquad [1]$$

where t_2 is the volumetric fraction of methyl myristate in the solution calculated using the expression $t_2 = x_2 V_2/V_s$, where x_2 and V_2 are the mole fraction and molar volume of the methyl myristate and V_s the molar volume of the solution.

This relation is fulfilled by solutions of methyl myristate in cyclohexane, n-hexane, tetrachloroethylene or trichloroethylene for mole fractions respectively of at least 0.5, 0.6, 0.5 and 0.4.

The results indicate that, in all the solutions, the value of parameter μ_2 estimated with equation [1] above coincides with the experimental value for the viscosity of the methyl myristate, within the limits of error estimated at 4 %. However, the values for parameter μ_1 and the solvent viscosity values do not coincide.

The difference in the behaviour of the different solutions and the discrepancy of the values for the parameter μ_1 may be interpreted in teh light of the fact that the viscosity of a solution involves three types of molecular friction:

* Between two methyl myristate molecules.
* Between two molecules of solvent.
* Between a molecule of methyl myristate and a molecule of solvent.

For the methyl myristate mole fractions considered, it can be accepted that the solvent molecule level is not sufficient in each case to simultaneously cover all the direct friction zones between methyl myristate molecules. For these solutions, with an excess of friction between molecules of methyl myristate, equation [1] can be stated as follows:

$$\ln \mu m = [2\ t_2 - 1] \ln \mu_3 + (1-t_2) \ln \mu_4 \qquad [2]$$

where the first addend represents the contribution to the solution viscosity from the direct friction between molecules of methyl myristate, while the second shows the friction between a molecule of solvent and a molecule of methyl myristate.

Equation [2] coincides with equation [1], given that $\mu_4 = 1_1\ \mu_2$, since the value of μ_3 coincides exactly with that of μ_2.

For mole fractions of methyl myristate not more than 0.3, 0.5, 0.3 and 0.2 with cyclohexane, n-hexane, tetrachloroethylene, and trichloroethylene respectively, where there is excess friction between solvent molecules, equation [1] can be stated as follows:

$$\ln \mu_m = [1-2\ t_2] \ln \mu_5 + t_2 \ln \mu_6 \qquad [3]$$

where the first addend represents the contribution to the solution viscosity of the direct friction between molecules of solvent, while the second shows the contribution

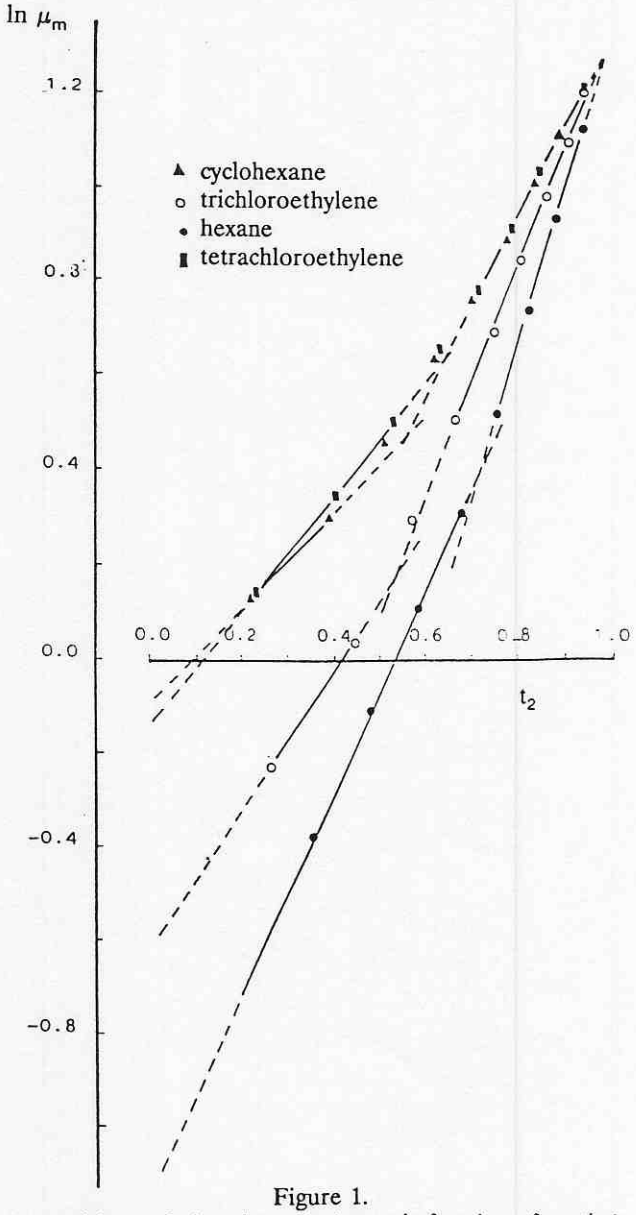

Figure 1.
Logarithms of viscosity vs. volumetric fraction of methyl myristate, at 303 K.

from the friction between a molecule of solvent and a molecule of methyl myristate. This is the interpretation used to explain the behaviour of solutions of oleic acid in n-hexane or cyclohexane (8).

The values of parameters μ_1, μ_2, μ_4, μ_5 and μ_6 are set out on table II. In figure 1 are represented the logarithms, at 303 K, for the viscosity values of the solutions as against the volumetric fraction of the methyl ester.

The diferences between the values for the parameter μ_5 and the viscosity values of the solvents are due to adjustment errors, given the limited number of data in this area of the range. The values for parameter μ_6 cannot be compared with those for parameter μ_4 because of the limited precision with which the former are calculated and the manner in which the latter are defined.

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