Viscosity of Multicomponent Systems of Normal Fatty Acids: Principle of Congruence

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ABSTRACT

Dynamic viscosity coefficients are reported on n-dodecanoic, n-tetradecanoic, n-hexadecanoic, and n-octadecanoic acids and their binary systems at several temperatures from 70 to 90 C, and on their ternary and quaternary systems at 70 and 90 C. According to experimental data, liquid systems of normal fatty acids obey the "principle of congruence" in the sense that the viscosity of a mixture depends only on its average chain length.

INTRODUCTION

It is well known that the "principle of congruence," as introduced by Brönsted and Koefoed (1), has been widely applied to the excess thermodynamic properties of liquid and low density vapor mixtures and, more recently, to different transport properties. Thus, van Geet and Adamson (2) apply it to diffusion activation energies and tracer diffusion coefficients of binary mixtures of n-alkanes, Coursey and Heric (3) to the excess Gibbs free energy of activation of flow on binary hydrocarbon systems, and Diaz-Peña and Cheda (4) to the excess viscosity of binary n-alkane vapors.

Although several authors have postulated the extension of the principle of congruence to multicomponent mixtures, little experimental work has been carried out. However, among others, Heric and Brewer (5) used it for prediction of the viscosity of the n-hexadecane + n-tetradecane + n-hexane mixture. In connection with this, the application of this principle to the viscosity of multicomponent systems of n-fatty acids will be the aim of the present work.

TABLE I

Viscosity Data on n-Fatty Acids and Their Binary Mixtures[a]

System	x_1	$\bar{n}$	η (cP) 70 C	80 C	90 C
12	1	12	4.415	3.602	2.982
14	1	14	5.984	4.791	3.906
16	1	16	7.682	6.082	4.885
18	1	18	9.583	7.794	6.294
12+14	0.200	13.60	5.619	4.529	3.721
12+14	0.800	12.40	4.679	3.800	3.148
12+16	0.200	15.20	6.990	5.584	4.536
12+16	0.800	12.80	4.989	4.032	3.329
12+18	0.200	16.80	8.537	6.855	5.531
12+18	0.800	13.20	5.377	4.328	3.558
14+16	0.200	15.60	7.255	5.789	4.681
14+16	0.800	14.40	6.308	5.024	4.139
14+18	0.200	17.20	8.924	7.120	5.691
14+18	0.800	14.80	6.713	5.342	4.367
16+18	0.200	17.60	9.360	7.390	5.902
16+18	0.800	16.40	8.060	6.322	5.109

[a] Labeled by the carbon atom number n_i of its components and defined by its average chain length $\bar{n} = x_1n_1+x_2n_2$, x_1 and x_2 being the molar fractions of the first and secondly given components.

EXPERIMENTAL PROCEDURES

Fluka purissimum chemicals were used without further treatment inasmuch as gas liquid chromatographic analysis yielded $> 99.5\%$ molar purities, the impurities being homologous acids. Experimental density and refractive index values compared well with literature data.

Viscosities were determined by means of a coaxial cylinders viscometer, Reomat RM15, provided with measuring system MS-O. Several rotation speeds equivalent to share rates between ca. 30 and 1800 sec^{-1} were used, and the measurement was performed in a silicone oil bath thermostatized within 0.005 C.

Newtonian behavior was exhibited in all cases, and dynamic viscosity coefficients were calculated by lineal regression of experimental data with a standard error of 0.1%.

RESULTS AND DISCUSSION

Dynamic viscosity coefficients η were measured every 5 degrees between 70 and 90 C on lauric, myristic, palmitic, and stearic acids and their eight binary mixtures at four levels of composition. Some of this data is given in Table I, where an acid is identified by its carbon atom number and a mixture by x_1, the molar fraction of the first component, i.e., that being the shortest in chain length. For the sake of

TABLE II

Viscosity Data on Ternary and Quaternary Mixtures[a]

System	x_1	x_2	x_3	$\bar{n}$	η (cP) 70 C	90 C
12+14+16	0.304	0.339	0.357	14.10	6.030	3.937
12+14+16	0.565	0.100	0.335	13.54	5.534	3.659
12+14+18	0.234	0.266	0.500	15.53	7.421	4.761
12+14+18	0.498	0.133	0.369	14.48	6.466	4.192
12+16+18	0.133	0.367	0.500	16.47	8.191	5.228
12+16+18	0.567	0.100	0.333	14.40	6.347	4.143
14+16+18	0.100	0.333	0.567	16.93	8.676	5.509
14+16+18	0.500	0.233	0.267	15.53	7.311	4.692
12+14+16+18	0.145	0.127	0.113	16.39	8.307	5.240
12+14+16+18	0.210	0.183	0.164	15.68	7.554	4.831
12+14+16+18	0.360	0.226	0.161	14.61	6.548	4.255
12+14+16+18	0.560	0.163	0.146	13.69	5.721	3.759

[a] Similarly as in Table I, x_3 and x_4 (implicity given for quaternary systems) being the molar fractions of the third and fourth components, respectively.

TABLE III

Regression Parameters of the Equation $\log \eta = a_0 + a_1\bar{n} + a_2(\bar{n})^2$

Temperature	a_0	a_1	a_2	Standard error[a] as η (cP)
70 C	-0.602802	0.134844	-0.002591	0.070
90 C	-0.510490	0.101571	-0.001628	0.045

[a] Calculated by $[(\text{exp-cal})^2/\text{number of observations}]^{1/2}$.

brevity, data at temperatures of 75 and 85 C and mixture of 0.4 and 0.6 for x_1 have been omitted.

Similarly, experimental results at 70 and 90 C on the four ternary systems at two levels of composition each and on the quaternary system at four levels of composition are given in Table II.

If we defined a mixture by its average chain length $\bar{n} = \Sigma x_i n_i$, where n_i is the chain length (carbon atom number) of the i component and x_i its molar fraction, it could be seen that, at a given temperature, all the experimental η values fall on a line, as given in Figure 1.

That is, the viscosity of such mixtures is determined primarily by their average chain length and, consequently, they follow the principle of congruence. Thus, congruent mixtures, i.e., different in composition but with the same $\bar{n}$, will exhibit the same viscosity, and, in the case of $\bar{n}$ being an integer, the viscosity will be that of the correspondent pure n-fatty acid. Hence, it will be able to predict the viscosity of a mixture if its composition and the viscosity of its components are known.

The lines on which experimental η values fell were fit by regression methods using an expression of the type

$$\log \eta = \sum_{j=0}^{2} a_j(\bar{n})^j$$

and the regression parameters a_j are given in Table III.

Calculated values for η according to Table III are given by full lines in Figure 1, the standard error at 70 C being much higher than at 90 C, probably due to the highest difficulty in measuring at this temperature by the proximity of the melting points of stearic acid and in stearic acid rich mixtures.

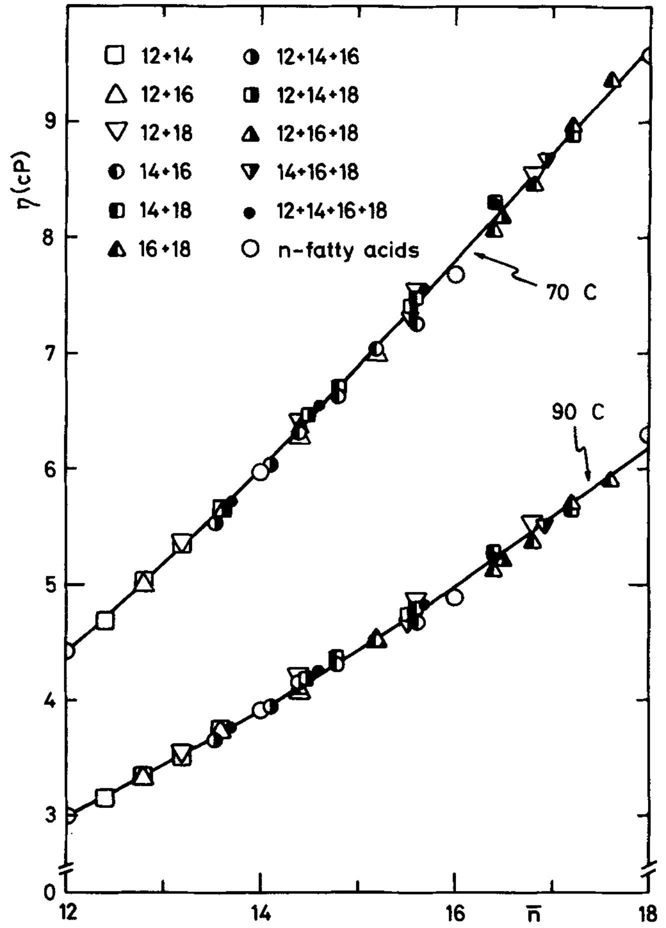

FIG. 1. Dynamic viscosity coefficients of lauric, myristic, palmitic, stearic acids and their binary, ternary, and quaternary mixtures in function of the average chain length.

REFERENCES

1. Brönsted, J.N., and J. Koefoed, Kgl. Danske Videnskab. Selskab. Mat.-Fys. Medd. 22:1 (1946).
2. Geet, A.L. van, and A.W. Adamson, J. Phys. Chem. 68:238 (1964).
3. Coursey, B.M., and E.L. Heric, Mol. Phys. 13:287 (1967).
4. Diaz-Peña, M., and J.A.R. Cheda, An. Quim. 71:262 (1975).
5. Heric, E.L., and J.G. Brewer, J. Chem. Eng. Data 14:55 (1969).

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