

THE RELATIVE VISCOSITIES OF BUTANOL, ETHANOL AND ACETIC ACID

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Introduction

Viscosity data has, greatly, aided scientists in their interpretation of both the structure, and causes of liquid aggregates.

The theories, explaining such complexes, are beyond the scope of this paper. The reader is referred to the articles by Bingham, White, Thomas and Caldwell⁶, Errara⁹, Langmuir¹³, Longinescu¹⁴, and Matthews and Cooke¹⁵. While interpretations vary, there is general agreement that pure liquids can be classified as associated or molecular aggregates; and unassociated, or monomolecular compounds.

Liquid mixtures then are composed as follows:

1. Mixtures of non-associated liquids.
2. Mixtures of associated liquids.
3. Mixtures of associated and non-associated liquids.
4. Chemically reacting liquids.

From the above, it would seem, that mixtures of non-associated liquids should be ideal; and the others should make up the non-ideal. This is not always the case, for association or disassociation often occurs when liquids are mixed.

Of the many works discussing viscosimeters, only a few can be listed. Among the standard authorities are the following: Barr¹, Bingham², Hatcheck¹¹, and Merrington¹⁶.

Investigators have studied the (1) effects of temperature, (2) chemical structure, (3) composition or concentration of solutions, (4) relationship to density of solutions, (5) relationship to surface tension, and (6) vapor pressure of solutions, as they affect the viscosity.

In their report on "The Relative Viscosity of Methanol and Acetic Acid", Froemke and DeLap¹⁰ stressed the "Time" factor in viscosity measurements. Their investiga-

tion seems to indicate that changes of association, disassociation and solvate formation tend to reach an equilibrium after considerable time has elapsed. While these men could find no direct evidence of another possibility, namely esterification, this factor must not be overlooked.³

The report of Froemke and DeLap¹⁰ demands that formulas expressing viscosity must contain a time factor, as well as volume, weight, or molecular factors. While these investigators used the partial mole-viscosity equation to express limiting values, this does not express the viscosity at other times. This would apply to other mathematical formulas such as "The Fluidity Equation" by Bingham⁴, "Logarithmic Equation", by Egner⁸, "Density, Mole Fraction" by Drucker⁷, "The Cube Root of the Viscosity-mole Equation" of Kendall¹², and the equation of Bingham and Brown⁵ introducing an empirical constant.

In order to study the "Time" factor more thoroughly, the authors selected both binary and ternary mixtures of butanol, ethanol and acetic acid, for investigation. Special attention was given to:

- (1) Time through which viscosity changes
- (2) Effects of a third component
- (3) Effect of esterification, if any
- (4) Applications of mathematical equations

Methods of Investigation and Results

This investigation was conducted according to the plan suggested by Froemke and DeLap¹⁰. An Ostwald Viscosimeter was used. The relative viscosities were calculated, by means of the standard formula

$$\frac{\eta_1}{\eta_0} = \frac{d_1 t_1}{d_0 t_0} \quad \text{in which}$$

d_1 is density of unknown liquid
 d_0 is density of known liquid
 t_1 is time of flow of unknown liq.
 t_0 is time of flow of known liq.
 η_1 is the rel. vis. of unknown liq.
 η_0 is the rel. vis. of known liq.

The liquids were carefully fractionated. Only the portions having the proper boiling point and density were used.

Ten bottles were prepared for each "Run". These were sealed to protect contents from moisture. Composition of the mixtures, time of taking the determinations, as well as relative viscosities are given in Table I.

TABLE I

Relative Viscosity Values

Temperature 22° C—Mixtures given in volume %.

Liquids and Mixtures

Time	BuOH	EtOH	HAc	BuOH	EtOH	EtOH	BuOH	HAc	EtOH	HAc
				50%	50%	50%	50%	50%	50% 33 1/3 %	
				HAc	HAc	EtOH	EtOH	EtOH	BuOH	BuOH
				50%	50%	50%	25%	25%	25%	33 1/3 %
							HAc	BuOH	HAc	EtOH
							25%	25%	25%	33 1/3 %
Immed.	1.639	.694	.694	1.070	.818	1.000	1.026	.928	.862	.934
1 day	1.626	.700	.702	1.075*	.813	1.000	1.024	.921	.850	.922
1 week	1.670	.712	.716	1.039	.778	1.000	1.003	.903	.840	.908
2 w.	1.686	.711	.772	1.023	.763	1.000	.998	.891	.819	.874
4 w.	1.695	.705	.759	.975	.717	1.000	.925	.832	.784	.835
6 w.	1.664	.698	.736	.943	.686	1.000	.908	.807	.770	.813
8 w.	1.628	.681	.712	.930	.691*	1.000	.887	.783	.746	.782
16 w.	1.676	.712	.715	.869	.651	1.000	.835	.729	.717	.728

*Reading may be high, but it is within the limits of the probable error of a single determination, and is therefore retained in the table.

Ester formation was noticed in the mixture containing butanol and acetic acid at the end of two weeks. But, in the mixture of ethanol and acetic acid only a slight odor of ethylacetate was first discovered at the end of a four weeks period. In each case a sudden change in the relative viscosity can be noticed. See Table I. Changes in viscosity up to the time of esterification can be attributed to association, dissociation, and possible solvate formation. Then when esterification begins, both ester and water enter into the mixture. This makes the liquid a complex mixture of associated and non-associated liquids.

The mixture of butanol-ethanol was chosen as the reference liquid. The time of flow and density remained most constant, throughout the entire time of the investigation.

The viscosity of this liquid mixture, as calculated from data on butanol, ethanol and acetic acid is given in Table II.

TABLE II
Relative and Absolute Viscosity Values of Butanol-Ethanol
Temperature 22° C

Liquid	Relative Viscosity	Absolute Viscosity	Calculated BuOH-EtOH Viscosity
Butanol	1.661±.006	.0280cp	.0169
Ethanol	.702±.002	.0137	.0167
Acetic Acid	.729±.007	.0120	.0165
		Average	.0167

TABLE III
Observed and Theoretical Relative Viscosity Values

Liquid Mixtures	Initial and final relative viscosities		Calculated Values		
	Experimental		Initial ¹	Ester ²	Graph ³
HAc 50% BuOH 50%	1.070	.869	1.087	.66	.69
HAc 50% EtOH 50%	.818	.651	.711	.56	.53
BuOH 50% EtOH 50%	1.000	1.000	.982		
BuOH 50% EtOH 25% HAc 25%	1.026	.835	1.081	.80	.78
HAc 50% BuOH 25% EtOH 25%	.928	.729	.884	.59	.61
EtOH 50% BuOH 25% HAc 25%	.862	.717	.876	.69	.67
HAc 33½% BuOH 33½% EtOH 33½%	.934	.728	.943	.65	.62

1 Calculated from mole fractions

$$\eta = x_1\eta_1 + x_2\eta_2 + x_3\eta_3$$

where η_1, η_2, η_3 are the relative viscosities
and x_1, x_2, x_3 are the partial mole fractions

2 Calculated assuming esterification had reached its limiting value. Mole fraction formula was used as in No. I.

3 Read from graph (See Fig. I) where $\frac{1}{T^{1/2}}$ approaches zero.

A comparison of calculated and experimental values of viscosity is given in Table III. While the authors are only too willing to admit that not too much significance should be attached to the calculated values, they, nevertheless, present them as a means of comparison. The initial readings were the first, or immediate viscosity reading. The initial calculated value is derived using the mole-viscosity formula.

$$\eta = \eta_1x_1 + \eta_2x_2 \text{ where } x_1, x_2 = \text{mole frac. of components}$$

η = viscosity of mixture
 η_1, η_2 = viscosities of components

The final reading is the last reading, namely after 16 weeks had elapsed. The limiting values were derived by calculating should esterification reach equilibrium.* The mixture would then include alcohol, acid, water and ester. In case of two alcohols, esterification was assumed to follow the mole fractions. The other limiting value of each mixture was found by graphing the relative viscosity against the reciprocal of the square root of the time in weeks and extrapolating to zero value. See Figure 1.

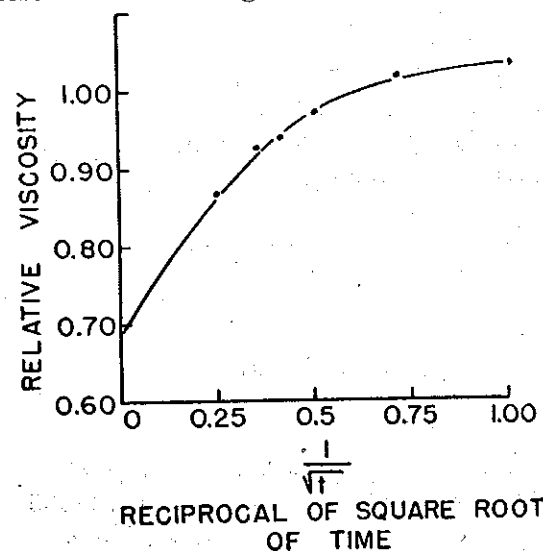


Fig. 1. Variation of Relative Viscosity of a Mixture Containing 50% Acetic Acid and 50% Butanol over a Period from 1 week to 16 weeks.

*From standard ester-equilibrium formula.

During the study of the data, it became evident that no single mathematical formula would suffice. Consequently the authors chose to use these rather simple formulas.

Conclusion

This investigation, clearly, indicates that higher alcohols esterify easier than the lower, or short chained alcohols. Butanol acetic acid mixtures were the first to esterify, ethanol acetic acid mixtures were considerably slower, and Froemke and DeLap¹⁰ failed to find any evidence of esterification even at the end of 16 weeks.

Esterification did not reach a limiting value, as might be expected. This agrees with the observations of Berthelet and Saint Gilles. (See Cohan³)

The first changes of viscosity may well be ascribed to association, dissociation and possible solvate formation. But, certain mixtures of associated liquids may behave like unassociated liquids. This was the case with the butanol-ethanol mixture. This maintained its viscosity throughout the investigation.

Whether or not, the change of viscosity is a typical rate reaction, (bi- or ter-molecular) will be considered in subsequent investigations. The limiting value of the relative viscosity can be approximated from the graph. Viscosity plotted against the reciprocal of the square root of time in weeks.

BIBLIOGRAPHY

1. Barr, G. Monograph on Viscosimetry, Oxford University Press (1931).
2. Bingham, E. C. Fluidity and Plasticity, McGraw, Hill & Co. (1922)
3. Berthelet and Saint-Gilles, (see Cohan, Organic Chemistry, Edward, Arnold & Co. 5th ed. p. 360. (1931)
4. Bingham, E. C. Am. Chem. J. **35**, 195, (1906)
5. Bingham and Brown J Rheol. **3**, 95, (1932)
6. Bingham, White, Thomas and Caldwell, Z. physikal Chem. **83**, 641, (1913)
7. Drucker, C. Z. physical Chem. **92**, 287, (1918)

8. Egner Meddel. Vetenskapsakad. Nobelinst. **3**, 22, (1918)
9. Errara, J. Z. physical Chem., **138**, 332, (1913)
10. Froemke and DeLap, Proc. S. Dak. Acad. of Science, Vol. XXVII (1948)
11. Hatcheck, E. Viscosity of Liquids, G. Bell, London, (1928)
12. Kendall and Monroe, J. A. C. S., **39**, 1787, (1917)
13. Langmuir, I., J. A. C. S. **38**, 2221, (1916)
14. Longinescue, G. G. Molecular Association, Chem. Rev. 381-418, (1929)
15. Mathews and Cooke, J. Phys. Chem. **18**, 559, (1914)
16. Merrington, A. C., Viscosimetry, Longman's Green and Co. (1949)