

Estimation of Dilute Solution Viscosity Parameters of Rubber Seed Oil Alkyds

F. E. OKIEMEN,* A. I. AIGBODION

Rubber Research Institute of Nigeria, P.M.B 1049, Benin City, Nigeria

Received 20 November 1996; accepted 31 May 1997

ABSTRACT: Viscosity measurements were carried out in methyl ethyl ketone (MEK) and dimethyl formamide (DMF) for rubber seed oil alkyds having oil content of 20 (I), 30 (II), 35 (III), 40 (IV), 50 (V), and 60% (VI). Viscosity molecular weights, intrinsic viscosities, and viscosity parameters K and α , characteristic for both polymers and solvents, were determined. Generally, solubility properties were found to depend on molecular weight and polarity of the alkyds and solvent. Intrinsic viscosities of the alkyds were larger in DMF than in MEK, suggesting DMF to be a better solvent than MEK for rubber seed oil alkyds. Molecular weights determined for the alkyds range from 441 for sample III to 1323 for sample V. The viscosity molecular weights are in reasonable agreement with the values determined for samples II–V in MEK and samples I–IV in DMF. The values of Huggin's constant for these alkyds were also determined. Data reported also suggest that rubber seed oil alkyds tend to tolerate relatively basic solvent, such as DMF. Fractionation of the alkyds was considered to be in respect of molecular weight and polarity of the alkyds, and results show that low-molecular-weight species constitute greater proportion of the alkyds. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1987–1992, 1997

Key words: rubber seed oil; alkyds; viscosity; solubility parameters; fractionation; molecular weight

INTRODUCTION

In the coating industry, alkyd resins are sold and utilized as solutions in a suitable solvent, thereby requiring knowledge of their solution properties. Consequently, several tests are performed on commercial alkyds to determine their solution properties for the purposes of effective handling, design of processing and storage equipment, and establishing processing conditions.^{1,2}

Generally, methods of characterizing alkyds,

like other polymers, include viscosity measurements, osmometry, and gel permeation chromatography. Most often, expensive and sophisticated equipment are required; and, sometimes, long times are required for completion of experiment. In developing countries, such as Nigeria, the inability of industrialists to acquire such expensive equipment and the lack of trained analysts to operate them have been identified as obstacles in polymer characterization.³

However, in the coating industry, comparative values of molecular weight, rather than absolute values, are required. Therefore, viscosity study is widely used in characterizing alkyd in the industry, as the method is not only suitable for the comparative studies needed, but the operation is

* Present address: Department of Chemistry, University of Benin, Benin City, Nigeria.

Correspondence to: A. I. Aigbodion.

Journal of Applied Polymer Science, Vol. 67, 1987–1992 (1998)

© 1998 John Wiley & Sons, Inc.

CCC 0021-8995/98/121987-06

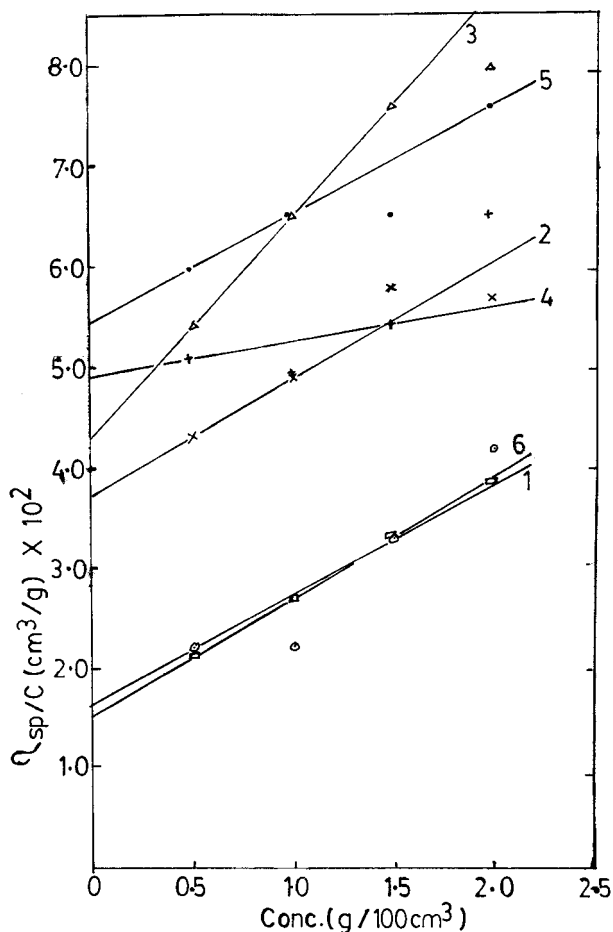


Figure 1 Plots of η_{sp}/C against concentration for unfractionated alkyds in solution of MEK.

also convenient to perform for routine analysis. In addition, simple and cheap equipment is needed.

Dilute solution properties such as K , α , viscosity molecular weight, and Huggin's constant k have been determined for many polymers of commercial value. There is no such information about these constants for rubber seed oil alkyds, which have been found suitable for use in surface coating.⁴⁻⁶ The objective of this study is to carry out viscosity studies on some rubber seed oil alkyds with the view to determining some solution parameters that are characteristic for any polymer, solvent, and temperature. This is the first attempt, to our knowledge, that these parameters are reported on for rubber seed oil alkyds. It is hoped that information obtained from this study will be useful to potential users of these alkyds and will also stimulate interest in further research on this subject.

MATERIALS AND EXPERIMENT

Materials

Rubber seed oil used in the preparation of alkyds was obtained by mechanical screw press. Phthalic anhydride and glycerol of laboratory-grade from BDH were used in the preparation of alkyds without further purification. Methyl ethyl ketone (MEK) and dimethyl formamide (DMF) were of analytical grade and obtained from BDH and used in viscosity measurements. Microanalytical reagent (MAR) camphor from BDH was used in the Rast method.

Preparation of Alkyd Resins

Six different alkyds having oil content of 20 (I), 30 (II), 35 (III), 40 (IV), 50 (V), and 60% (VI) were prepared as described in earlier studies.^{5,7}

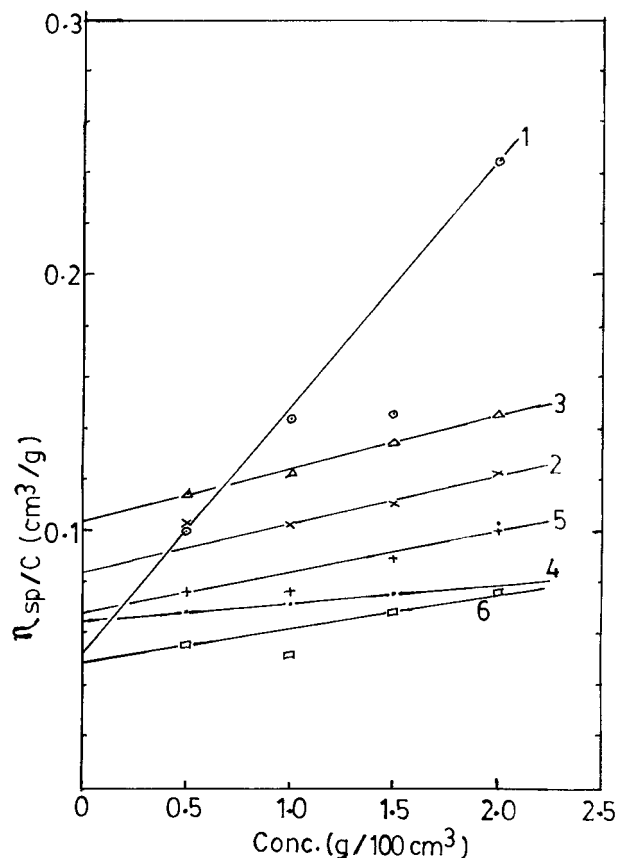


Figure 2 Plots of η_{sp}/C against concentration for unfractionated alkyds in solution of DMF.

Table I Percent Yield (by Weight) of Fractions of the Alkyds and Their Molecular Weight Determined by the Rast Method

Alkyd Sample	Fraction Number	Percent Yield (by Wt) of Fraction	Mol Wt (Rast Method)
I	IF ₁	7.50	661.67
	IF ₂	75.05	360.91
		17.45 loss	
II	IIF ₁	20.25	992.50
	IIF ₂	45.78	661.67
	IIF ₃	27.25	567.14
		6.72 loss	
III	IIIF ₁	4.78	1191.00
	IIIF ₂	6.85	926.33
	IIIF ₃	62.25	496.25
	IIIF ₄	24.53	496.25
		1.61 loss	
IV	IVF ₁	3.40	1111.60
	IVF ₂	61.35	661.67
	IVF ₃	16.55	330.83
	IVF ₄	13.50	283.57
		5.10 loss	
V	VF ₁	40.56	3705.33
	VF ₂	35.53	992.50
	VF ₃	5.58	496.25
	VF ₄	10.03	330.83
		9.36 loss	
VI	VIF ₁	10.00	794.00
	VIF ₂	77.50	330.83
		12.50 loss	

Fractionation of Alkyds

The alkyds were fractionated by fractional precipitation through the addition of *n*-heptane as non-

solvent to the solution of the alkyds (5% w/v) in toluene.⁸⁻¹⁰

Viscosity Measurements

Viscosity measurements were carried out with solutions of the alkyds and their fractions in MEK and DMF using a Ubbelohde 50 viscometer. Three additional dilutions were made in the viscometer, allowing efflux times to be measured at concentrations of 2.5, 2.0, 1.5, and 0.5 g/100 cm³. Viscosity measurements were carried out at temperature of 30 ± 0.5°C.

The intrinsic viscosities were calculated by extrapolation to zero concentration. The plots of η_{sp}/C versus C , where C is the concentration and η_{sp} is the specific viscosity; and $\eta_{sp} = t/t_0 - 1$, where t_0 and t are the efflux times of pure solvent and alkyd solution are shown in Figures 1 and 2, respectively.

The values of Huggin's k' were calculated as follows from the Huggin-Kraemer viscosity relationship:

$$\eta_{sp/c} = [\eta] + k'[\eta]^2C \quad (1)$$

Determination of Molecular Weights

Molecular weights of unfractionated alkyds and their fractions were determined using the Rast method.¹¹

RESULTS AND DISCUSSION

Table I shows the weight of fractions of alkyds obtained by fractional precipitation and the mo-

Table II Intrinsic Viscosities $[\eta]$ in MEK and DMF at 30 + 0.5°C for Unfractionated Alkyds Obtained by Graphical Solution and Calculated from the Huggin-Kraemer Equation

Alkyd Sample	$[\eta]$ 30°C (cm ³ g)			
	Graphical Solution		Calculated ^a	
	MEK	DMF	MEK	DMF
I	0.017	0.052	0.013 (0.960)	0.050 (0.919)
II	0.038	0.084	0.039 (0.923)	0.093 (0.903)
III	0.043	0.104	0.047 (0.982)	0.104 (0.997)
IV	0.050	0.066	0.043 (0.850)	0.054 (0.878)
V	0.060	0.068	0.055 (0.917)	0.063 (0.948)
VI	0.016	0.050	0.017 (0.999)	0.044 (0.908)

^a Values in parentheses are the correlation coefficients.

Table III Intrinsic Viscosities $[\eta]$ in MEK and DMF at 30 + 0.5°C for Fractions of the Alkyds

Alkyd Sample	Fraction Number	$[\eta]$ 30°C (cm g)	
		MEK	DMF
I	IF ₁	0.069	0.060
	IF ₂	0.055	0.038
II	IIF ₁	0.052	0.134
	IIF ₂	0.044	0.112
	IIF ₃	0.009	0.080
III	IIIF ₁	0.161	0.275
	IIIF ₂	0.154	0.230
	IIIF ₃	0.044	0.125
	IIIF ₄	0.038	0.120
IV	IVF ₁	0.038	0.078
	IVF ₂	0.045	0.069
	IVF ₃	0.035	0.030
	IVF ₄	0.017	0.015
V	VF ₁	0.060	0.220
	VF ₂	0.057	0.165
	VF ₃	0.054	0.165
	VF ₄	0.042	0.175
VI	VIF ₁	0.100	0.130
	VIF ₂	0.080	0.100

molecular weight of each fraction determined by the Rast method. The data in Table I shows that greater proportion of the alkyds is constituted by low-molecular-weight species since the fractions with the highest molecular weights were first precipitated. Molecular weights obtained in this study are comparable with the ranges 690–1370 and 580–2450 determined for two different alkyds.¹⁰

Intrinsic viscosities of the alkyds and their fractions in MEK and DMF obtained by graphical solution are shown in Tables II and III, respectively. Linear relationship was observed for the plots of η_{sp}/C against C for all the alkyds studied.

It has been suggested⁸ that the size and, consequently, resistance to flow of alkyd solution depends on the quality of the solvent. The more polar the solvent, the larger the apparent size of the molecule. This more extended state of the molecule is indicated by high intrinsic viscosity. It therefore seems from these results that DMF is a better solvent than MEK for rubber seed oil alkyds.

The Mark–Houwink equation

$$[\eta] = KM \quad (2)$$

has been found to apply to a number of polymers including alkyd resins,^{9,12} where K and α are constants characteristic for a given polymer, solvent, and temperature but are independent of the value of M (molecular weight) and its distribution in the system. It is obvious from this relationship that intrinsic viscosity will increase with molecular weight. However, comparing intrinsic viscosities (Table II) and molecular weights (Table IV), there is no regularity in the variation of molecular weight and intrinsic viscosity of the alkyds. But in studying the structure of alkyds, Nagata¹⁰ observed that glycerol forms part of the main alkyd chain and that free carboxyl could only exist at the end of the chains. The number of such free carboxy groups per molecule is independent of its molecular

Table IV Molecular Weights of the Different Alkyds Determined (Rast Method) and Calculated (Viscosity Molecular Weights)

Alkyd Sample	Molecular Weight ^a		
	Determined	Viscosity (Mol Wt)	
		MEK	DMF
I	496.25	7.72 (98.44)	520.25 (4.84)
II	794.00	832.17 (4.81)	634.93 (20.03)
III	441.11	536.65 (21.66)	407.10 (7.71)
IV	992.50	1015.38 (2.31)	678.48 (31.64)
V	1323.33	1283.48 (3.01)	0.042 (99.99)
VI	496.25	0.77 (99.85)	49.83 (89.96)

^a Values in parentheses refer to the percent of difference between the viscosity molecular weight of the alkyds in solutions of MEK and DMF and the molecular weight determined.

Table V Values of the Constants K and α for the Alkyds in Solutions of MEK and DMF

Alkyd Sample	K		α	
	MEK	DMF	MEK	DMF
I	6.04×10^{-2}	4.59×10^{-4}	0.38	0.75
II	1.14×10^{-9}	4.68×10^{-4}	2.58	0.82
III	1.01×10^{-6}	3.45×10^{-4}	1.71	0.95
IV	1.78×10^{-3}	3.41×10^{-5}	0.46	1.13
V	2.33×10^{-2}	8.80×10^{-2}	0.12	0.11
VI	1.82×10^{-2}	1.75×10^{-2}	6.26	0.30

weight. Therefore, presence of carboxyl groups will confer a certain degree of polarity on the alkyd. It thus seem that solution properties of rubber seed oil alkyds could be affected by molecular weight as well as the polarity of the alkyd.

Intrinsic viscosities of the alkyds calculated from Huggin–Kraemer relationship [eq. (1)] are compared with the values obtained from the graphical solution in Table II. There is slight difference between intrinsic viscosities obtained from the two methods. This difference may be attributed to some assumptions made in the derivation of eq. (1). However, the correlation coefficients show that for the solution of the alkyds in MEK there is high correlation between concentration and viscosity for samples VI at 0.1%; I and III at 1%; and II and V at 10% confidence levels. While in DMF, there is high correlation for samples III at 0.1; V at 1; and I, II, and IV at 5% confidence levels (Table II).

In order to obtain the desired quantities, K and α values with the greatest precision, the method of least squares has been proposed after reducing the Mark–Houwink equation to a linear relationship.^{10,13} The values of K and α calculated for the different alkyds using the data in Tables I and III (for molecular weights and their intrinsic viscosities, respectively) are presented in Table V. These results show that values of K are larger in MEK than in DMF for samples I, IV, and VI while they are larger in DMF than in MEK for samples II, III, and V, showing no regularity in the variation of K values; but it is well known that the value of K is an indication of the heterogeneity of the alkyd.¹⁰ In other words, the higher the value of K , the more heterogeneous the alkyd. However, the results of fractionation in Table I do not portray this trend. It seems thus that fractionation of

the alkyds may not only necessarily be on the basis of polarity of the alkyds.

Values of α in MEK range from 0.12 for sample V to 2.58 for sample V to 1.13 for sample IV. Though Flory and Fox¹⁴ have reported that the value of α approaches 0.8 in a good solvent and 0.5 in a poor solvent, but, generally, α lies between 0.6 and 0.8 for dilute polymer solutions. However, extensive studies on various polymer–solvent systems have shown that α value of well over 1.0 is possible for polar polymer in a good solvent.^{15,16} The polar nature of rubber seed oil alkyds (as they are essentially polyesters) maybe responsible for the high α values found in this study.

Table IV compares the viscosity molecular weights of the alkyds calculated from values of K and α (Table V) and intrinsic viscosities (Table II) using eq. (3) with the values determined. The results show that there is reasonable agreement between these molecular weights for samples II–V in MEK and I–IV in DMF. A large discrepancy between these sets of molecular weights for samples I and VI in MEK and V and VI in DMF was observed. This observation could be a result of the values of the constants k and α used in eq. (2), which were obtained by an empirical method (viscosity) instead of an absolute method, such as light scattering.

The values of Huggin's constant k for the alkyds are presented in Table VI. Values of k are larger in MEK than in DMF. However, it is well known¹⁰ that k , which is a constant for a given polymer and solvent, is independent of the molecular weight of the alkyd and decreases as the quality of the solvent improves. It is therefore obvious from Table VI that DMF is a better solvent than MEK for rubber seed oil alkyds. Since DMF is more basic than MEK, it is believed to serve as a better solvent for rubber seed oil alkyds, which are essentially polyester polymers.

Table VI Values of Huggin's Constant k for the Alkyds in Solutions of MEK and DMF

Alkyd Sample	Values of k	
	MEK	DMF
I	82.84	36.00
II	6.57	1.53
III	8.15	1.89
IV	5.03	7.20
V	3.17	3.99
VI	34.60	8.26

CONCLUSION

Dilute solution viscosity measurements have been carried out on some rubber seed oil alkyds. Results obtained show that these alkyds tolerate slightly basic solvents like DMF more than MEK. Viscosity molecular weights of the alkyds compare favorably with the values determined. It is considered that viscosity measurement could be a reliable technique for characterizing rubber seed oil alkyds. It is hoped that this study will provide reference data and stimulate further studies on rubber seed oil alkyds in this regard.

The authors thank Dr. E. K. Okaisabor, Director, RRIN, and Dr. A. B. Fasina for their encouragement and review of the article; the National Agricultural Research Project (NARP) for funding this research; and Mr. A. Aizoba for typing the manuscript.

REFERENCES

1. *Encyclopedea of Polymer Science and Technology*, Vol. 5, Interscience, New York, 1966, p. 222.
2. *Encyclopedea of Industrial Chemical Analysis*, Vol. 5, F. D. Snell and C. L. Hilton, Eds., Interscience, New York, 1967, p. 50.
3. D. S. Oguniyi, *J. Nig. Soc. Chem. Eng.*, **10**, 14–17 (1991).
4. A. I. Aigbodion, *Ind. J. Nat. Rubb. Res.*, **4**, 114–117 (1991).
5. A. I. Aigbodion and F. E. Okieimen, *Eur. Polym. J.*, **32**(9), 1105–1108 (1996).
6. A. I. Aigbodion and F. E. Okieimen, *J. Rubb. Res. Inst. Sri Lanka*, **75**, 31–38 (1995).
7. A. I. Aigbodion, Ph.D. thesis, University of Benin, Benin City, Nigeria, 1995.
8. E. G. Bobalek and M. J. Chiang, *J. Appl. Polym. Sci.*, **8**, 1147–1168 (1964).
9. E. G. Bobalek, E. R. Moore, S. S. Levy, and C. C. Lee, *J. Appl. Polym. Sci.*, **8**, 625–657 (1964).
10. T. Nagata, *J. Appl. Polym. Sci.*, **13**, 2601–2619 (1969).
11. B. S. Furniss, J. Hannaford, V. Rogers, P. W. G. Smith, and A. R. Tatchell, Eds., *Vogel's Textbook of Practical Organic Chemistry*, 4th ed., ELBS and Longman, London, 1978, pp. 232–233.
12. A. Rudin, G. W. Bennett, and J. McLaren, *J. Appl. Polym. Sci.*, **13**, 2371–2381 (1969).
13. A. I. Goldberg, W. P. Hohenstein, and H. Mark, *J. Polym. Sci.*, **2**(5), 503–510 (1957).
14. P. J. Flory and T. G. Fox, *J. Am. Chem. Soc.*, **73**, 1904 (1951).
15. T. Aifrey, A. Bartorics, and H. Mark, *J. Am. Chem. Soc.*, **65**, 2319 (1943).
16. M. Kurata and W. H. Stockmayer, *Adv. Polym. Sci.*, **3**, 196 (1963).