Styrene—butadiene block copolymers in dilute solution. 1. Assessment of extrapolation methods for intrinsic viscosity and viscosity constant determination

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Both the intrinsic viscosities and the viscosity constants of twelve ABA poly(styrene-b-butadiene) copolymers and of polystyrene and polybutadiene were obtained by the Huggins, the Kraemer, the Martin and the Schulz–Blaschke methods in carbon tetrachloride, toluene, benzene, tetralin, cyclohexane and cyclohexanone as well as in the micellating solvents ethyl acetate and methyl ethyl ketone. The extrapolation procedures were compared. It was concluded that the averaging procedures suggested by Sakai were not necessary for this block copolymer.

INTRODUCTION

The concentration dependence of viscosity of dilute polymer solutions is commonly expressed[1] as a power series in concentration (c).

$$\eta - \eta_s/\eta_s c = \eta_{sp}/c = [\eta] + k_1[\eta]^2 c + k_2[\eta]^3 c^2 + \ldots \quad (1)$$

Here η and η_s are the solution and the solvent viscosities, respectively, whilst η_{sp} is the specific viscosity, $[\eta]$ is the intrinsic viscosity and k_1 and k_2 are dimensionless parameters.

In this paper we are concerned with comparing four common methods of obtaining $[\eta]$ in an attempt to achieve the best values for further hydrodynamic investigations of block copolymers of the ABA type. The procedures selected were those developed by Huggins[2], Kraemer[3], Martin[4] and Schulz–Blaschke[5]. The appropriate relations are shown in equations (2)–(5), respectively:

$$\eta_{sp}/c = [\eta]\ \{1 + k_H[\eta]c\} \quad (2)$$

$$\ln\eta_r/c = [\eta]\ \{1 - k_K[\eta]c\} \quad (3)$$

Here η_r is the relative viscosity,

$$\ln(\eta_{sp}/c) = \ln[\eta] + k_M[\eta]\,c \quad (4)$$

$$\eta_{sp}/c = [\eta]\ \{1 + k_{SB}\eta_{sp}\} \quad (5)$$

Conventional extrapolations based on these four equations give only approximate values of $[\eta]$, some of which are overestimated while others are underestimated. It may be, therefore, that an averaging procedure according to Sakai's[6] suggestion would give a result closer to the true value.

For block copolymers, effects other than concentration dependence may be present. These may include preferential adsorption[7], molecular aggregation, micellation and possibly non-Gaussian distribution of segments. In addition, solvent power is a relative term because of the distinct natures of the different blocks. Thus, monotonic change of viscosity with concentration may no longer be valid[6].

EXPERIMENTAL

Polymers

Samples SO1 and SO2 are commercial materials (Cariflex 1101 and 1102, respectively) containing some diblock and homopolymer contamination, but all the others are pure triblock materials and have narrow molecular weight distributions. All copolymer samples were kindly provided by Shell Chemicals. See *Table 1* for characterization data.

Solvents

All the solvents used in this study were dried overnight with molecular sieve prior to redistillation (x2) from which mid-cuts only were taken.

Measurement of viscosity

The intrinsic viscosities (dl/g) were determined at 25° ± 0.01°C using Ubbelohde suspended-level viscometers. Solvent flow times in the range 120–360 sec were obtained. Thus, no kinetic energy corrections were necessary. 0.3% (w/v) of *N*-phenyl-2-naphthylamine was added to each stock solution as antioxidant. No change was noted in the flow times of either the solvents or the solutions on the addition of this material. Filtered nitrogen under pressure was used to raise the liquid level in the viscometers. When at least

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Table 1 Characterization data

Sample	Styrene (wt %)	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	Microstructure[1] *trans*-1,4	*cis*-1,4	1,2
PH4	33	213	1.08	42	38	20
PH3	33	152	1.09	46	39	15
PH1	32	116	1.09	44	38	18
FC1	27	141	1.08	46	36	18
PA3	28	117	1.06	45	40	15
FB1	26	112	1.10	49	36	15
FA1	26	110	1.08	47	40	13
SO1	27	100	1.48	45	38	17
FA2	26	84	1.08	46	39	15
FB2	27	74	1.07	46	39	15
SO2	26	64	1.44	47	38	15
PA5	28	60	1.05	44	40	16
Polystyrene		100	1.1			
Polybutadiene		100	1.4	51	39	10

[1] By n.m.r.

three consecutive flow times which agreed to within ±0.2 sec were recorded, the average flow time was taken. Shear corrections were not taken into consideration because the intrinsic viscosities obtained were less than 3.00 dl/g[8]. The flow volumes of the viscometers used were greater than 5 ml making drainage errors[9] unimportant.

RESULTS AND DISCUSSION

Intrinsic viscosities

The values of $[\eta]$ obtained by all four extrapolation procedures for the copolymers are shown in *Tables 2–5* and for the homopolymers in *Table 6*. In *Tables 2–5* the materials are arranged in order of decreasing molecular weight and are also grouped in two categories depending on the average styrene content. See *Table 1* for details of styrene content. It is quite clear that in the non-micellating solvents all four extrapolation procedures applied to samples with a fixed styrene content show that the intrinsic viscosity decreases

Table 2 Intrinsic viscosities using Huggins method

Solvent	PH4	PH3	PH1	FC1	PA3	FB1	FA1	SO1	FA2	FB2	SO2	PA5
CCl_4	1.87	1.38	1.16	1.55	1.52	1.36	1.34	0.90	1.13	1.05	0.92	0.88
Toluene	1.65	1.22	1.04	1.35	1.25	1.16	1.15	1.04	0.90	0.92	0.81	0.76
Benzene	1.60	1.20	0.98	1.31	1.24	1.12	1.08	1.00	0.92	0.88	0.78	0.78
Tetralin	1.60	1.20	1.03	1.30	1.22	1.12	1.06	0.90	0.90	0.81	0.79	0.74
Cyclohexane			0.91	1.23	1.12	1.03	0.98	0.91	0.85	0.82	0.75	0.69
Cyclohexanone	1.13	0.85	0.74	0.95	0.93	0.80	0.78	0.75	0.66	0.65	0.59	0.57
Ethyl acetate				0.15		0.16	0.14	0.15	0.15	0.21	0.15	
MEK				0.12		0.13	0.13	0.13	0.16		0.13	

Table 3 Viscosities using Kraemer method

Solvent	PH4	PH3	PH1	FC1	PA3	FB1	FA1	SO1	FA2	FB2	SO2	PA5
CCl_4	1.87	1.38	1.16	1.55	1.52	1.36	1.34	0.92	1.12	1.05	0.92	0.88
Toluene	1.65	1.22	1.04	1.35	1.25	1.16	1.15	1.04	0.90	0.92		0.76
Benzene	1.60	1.20	0.98	1.31	1.24	1.12	1.08	1.00	0.92	0.88	0.78	0.78
Tetralin	1.60	1.20	1.03	1.30	1.22	1.12	1.06	0.79	0.80	0.81	0.79	0.74
Cyclohexane			0.91	1.29	1.12	1.00	0.98	0.91	0.85	0.82	0.75	0.69
Cyclohexanone	1.13	0.85	0.74	0.95	0.93	0.80	0.80	0.75	0.66	0.65	0.59	0.57
Ethyl acetate				0.15		0.16	0.14	0.15	0.15	0.21	0.15	
MEK				0.12		0.13	0.14	0.13	0.16		0.13	

Table 4 Intrinsic viscosities using Martin method

Solvent	PH4	PH3	PH1	FC1	PA3	FB1	FA1	SO1	FA2	FB2	SO2	PA5
CCl_4	1.93	1.40	1.18	1.65	1.55	1.42	1.40	0.97	1.18	1.08	0.97	0.91
Toluene	1.69	1.23	1.05	1.38	1.27	1.18	1.22	1.14	1.00	0.94		0.77
Benzene	1.63	1.22	0.98	1.33	1.26	1.16	1.21	1.06	1.02	0.90	0.86	0.78
Tetralin	1.63	1.22	1.04	1.32	1.25	1.17	1.15	1.08	0.91	0.83	0.85	0.75
Cyclohexane			0.90	1.25	1.13	1.04	1.00	0.96	0.89	0.84	0.78	0.69
Cyclohexanone	1.14	0.87	0.75	0.96	0.93	0.82	0.81	0.78	0.68	0.68	0.60	0.58
Ethyl acetate				0.14		0.15	0.14	0.15	0.18	0.20	0.16	
MEK				0.15		0.13	0.13	0.13	0.15	0.12	0.13	

Table 5 Intrinsic viscosities using Schulz–Blaschke method

Solvent	PH4	PH3	PH1	FC1	PA3	FB1	FA1	SO1	FA2	FB2	SO2	PA5
CCl_4	1.95	1.42	1.19	1.70	1.56	1.42	1.36	0.98	1.19	1.10	0.98	0.98
Toluene	1.70	1.24	1.05	1.42	1.28	1.23	1.24	1.19	1.25	0.95		0.78
Benzene	1.64	1.22	1.00	1.37	1.27	1.19	1.28	1.18	1.10	0.91	0.90	0.79
Tetralin	1.64	1.23	1.04	1.34	1.25	1.19	1.20	1.12	1.00	0.84	0.90	0.75
Cyclohexane			0.92	1.30	1.14	1.06	1.05	1.02	0.92	0.83	0.80	0.69
Cyclohexanone	1.14	0.88	0.76	0.98	0.95	0.85	0.87	0.79	0.70	0.68	0.62	0.58
Ethyl acetate				0.14		0.15	0.15	0.15	0.19	0.21	0.19	
MEK				0.15		0.13	0.13	0.13	0.16	0.12	0.14	

Table 6 Intrinsic viscosities of polystyrene and polybutadiene

Solvent	Huggins	Kraemer	Martin	Schultz–Blaschke
	Polystyrene			
Benzene	1.00	1.00	1.01	1.01
CCl_4	0.81	0.81	0.82	0.82
Toluene	0.79	0.79	0.79	0.80
Tetralin	0.76	0.76	0.78	0.77
Cyclohexanone	0.67	0.67	0.69	0.69
Ethyl acetate	0.42	0.42	0.43	0.43
MEK	0.43	0.43	0.43	0.43
	Polybutadiene			
CCl_4	2.84	2.84	2.96	3.00
Toluene	2.22	2.22	2.29	2.34
Benzene	2.05	2.05	2.10	2.10
Tetralin	2.05	2.05	2.12	2.12
Cyclohexane	2.00	2.00	2.04	2.06
Cyclohexanone	1.34	1.34	1.38	1.30

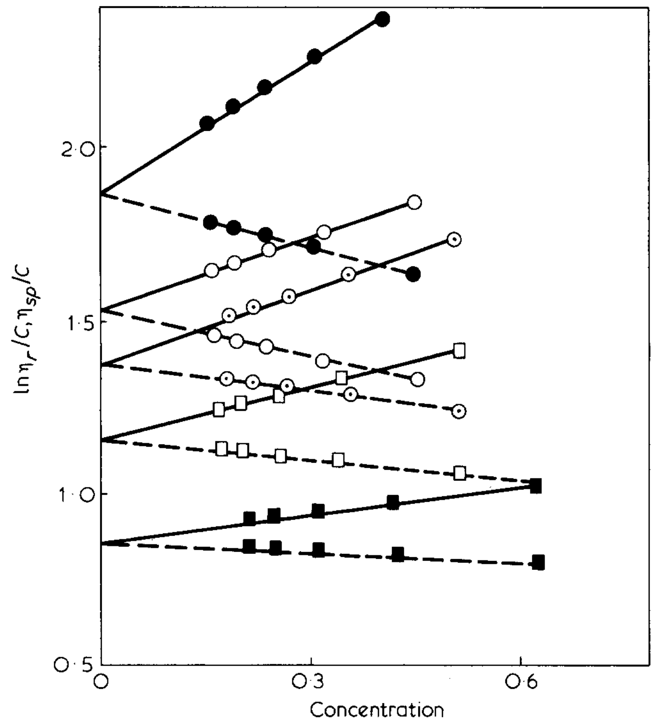

Figure 1 Huggins (———) and Kraemer (– – –) plots of samples PH4 (●), PA3 (○), PH3 (⊙), PH1 (□) and PA5 (■) in carbon tetrachloride

with molecular weight. If samples PH1 and PA3, which have (within experimental error) the same molecular weight, are compared, the PA3 sample which has the higher polybutadiene content also shows higher [η] values in all the non-micellating solvents by all four extrapolation procedures.

From *Table 6* it is clear that of the two equimolecular weight homopolymers it is the polybutadiene which has the higher intrinsic viscosity values.

Tables 2–6 also show the intrinsic viscosity data arranged in order of solvent effect. For the copolymers, irrespective of extrapolation technique, the order was

$$CCl_4 > \text{toluene} > \text{benzene} \simeq \text{tetralin} > \text{cyclohexane} > \text{cyclohexanone}$$

For polystyrene the order was

$$\text{benzene} > CCl_4 > \text{toluene} > \text{tetralin} > \text{cyclohexanone}$$

and for polybutadiene it was the same as for the copolymers, which is not unreasonable as the polybutadiene content is predominant in both groups of copolymer samples.

For the micellating solvents (*Tables 2–6*) it is clear that [η] for the copolymers in ethyl acetate is generally greater than in MEK. The intrinsic viscosities do not follow the regular trend with respect to molecular weight shown in the non-micellating solvents and no systematic variations could be identified. A number of papers exist[10–13] on the influence of block molecular weights on the size of micelles formed by SBS block copolymers. However, it is certainly true to say that all the factors which influence the size and stability of the micelles formed are not fully appreciated. It is, for example, believed[11] that such micellar solutions can undergo changes on ageing. For these reasons it is perhaps not too surprising that the [η] values in MEK and ethyl acetate are not systematic.

Linear plots were obtained using the Huggins, Kraemer and Martin equations when non-micellating solvents were used. *Figure 1* shows Huggins and Kraemer plots for a number of samples in carbon tetrachloride. For samples in MEK and ethyl acetate the Huggins procedure yielded plots showing upward curvature. The Huggins plots for samples FA2 and SO1 in MEK and ethyl acetate are shown in *Figures 2* and *3*, respectively. Such curvature has been reported by Krause[14] for micelles of block copolymers of styrene and methyl methacrylate in acetone. In MEK and ethyl acetate positive slopes were obtained for the Kraemer equation (*Figures 2* and *3*) which confirmed the presence of suspended particles. The Kraemer plots (*Figure 2*) for these micellating solvents sometimes showed upward curvature[15] at concentrations less than 3g/dl. Upward curvature was not observed for samples in the micellating solvents when the Martin equation was used.

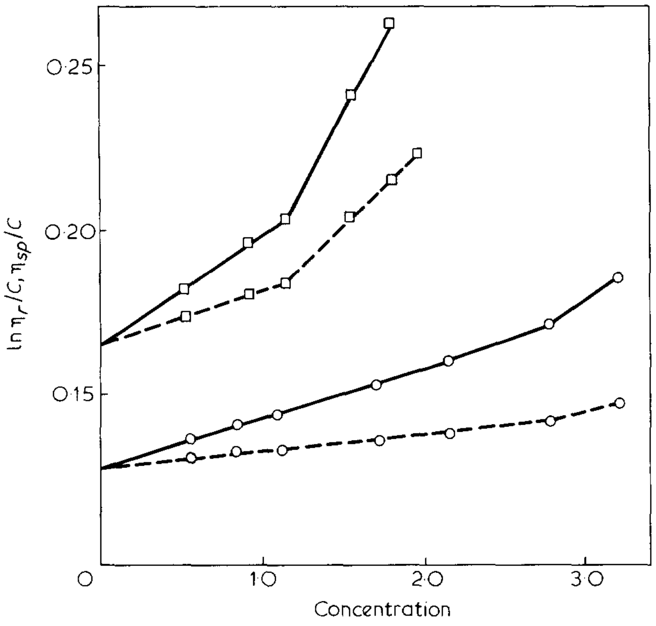

Figure 2 Huggins (———) and Kraemer (— — —) plots of samples FA2 (□) and SO1 (○) in MEK

Comparison of the Huggins and Kraemer [η] data (*Tables 2* and *3*) leads to the conclusion that the homopolymers and the copolymers in all the solvents are within experimental error (±2%) the same. Comparison of the intrinsic viscosities obtained by the Huggins and by the Martin procedures (*Tables 2* and *4*) shows that these values for the copolymers in the good solvents for both blocks were on average about 4% higher using the Martin method. In cyclohexane and cyclohexanone the difference was just on the limits of experimental error. For the micellating solvents the differences were highly variable and no definite comparison could be made For all solvents, the Huggins and Martin procedures yielded, within experimental error, the same intrinsic viscosities for polystyrene, but for polybutadiene the [η] values from the Martin method were on average about 3% higher than those obtained from Huggins plots.

Linear plots were obtained in most cases with the Schulz–Blaschke equation, but downward curvature was observed in a few cases (*Figure 4*) when the concentration exceeded 1.5% (w/v). For the copolymers in cyclohexane and cyclohexanone, the Schulz–Blaschke procedure gave intrinsic viscosity values about 4% greater than those obtained from Huggins plots. For the four solvents which are good for both blocks this difference was, on average, about 7%. Once again for polystyrene in all solvents no significant difference could be detected by these two extrapolation procedures, but for polybutadiene an average difference of about 3% was observed. For polybutadiene in CCl_4 and toluene this difference was about 5.5%.

Sakai[6] concluded that for homopolymers the Schulz–Blaschke relation gives the largest value for [η] and is followed in order by the Martin and the Huggins methods. This is also what has been found for these SBS copolymers. Sakai[6] also suggested that the best value of [η] is obtained from equation (6) for good solvents and from equation (7) for poor solvents.

$$[\eta] \approx \tfrac{1}{2}([\eta]_M + [\eta]_H) \tag{6}$$

$$[\eta] \approx \tfrac{1}{2}([\eta]_{SB} + [\eta]_H) \tag{7}$$

Here $[\eta]_M$, $[\eta]_{SB}$ and $[\eta]_H$ are the intrinsic viscosities obtained by the Martin, the Schulz–Blaschke and the Huggins methods, respectively.

It was decided in any further study of the dilute solution behaviour of these block copolymers that the Huggins and the Kraemer procedures alone would be used to determine the intrinsic viscosities. In other words, the marginal difference between $[\eta]_H$ and $[\eta]_M$ does not seem to demand the use of the Sakai[6] averaging procedure. The same conclusion was drawn for poor solvents.

Slope constants

It was found that there was no trend in any of the four initial slope constants (k_H, k_K, k_M and k_{SB}) with changing molecular weight for either group of copolymers in non-micellating solvents. Thus, for each solvent an average value of each slope constant (± standard deviation) was determined (see *Table 7*). There is no evidence in this Table for any significant dependence of the slope constants on solvent except possibly in cyclohexanone. For both the homopolymers (*Table 8*) all four extrapolation methods result in slope

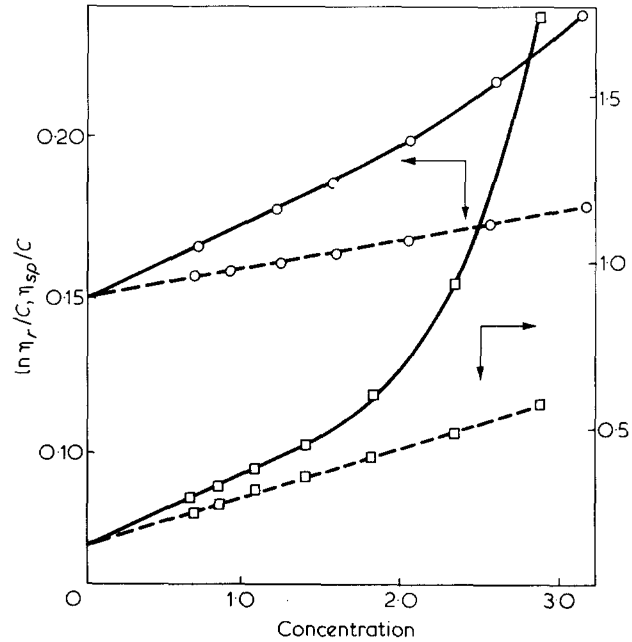

Figure 3 Huggins (———) and Kraemer (— — —) plots for samples FA2 (□) and SO1 (○) in ethyl acetate

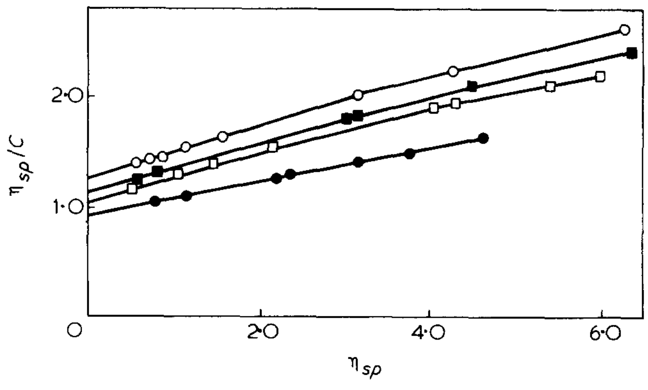

Figure 4 Schulz–Blaschke plots of samples FA1 (○), SO1 (□), FA2 (□) and SO2 (●) in benzene

Table 7 Viscosity slope constants for copolymers

	Polystyrene 33%				Polystyrene 27%			
	k_H	k_K	k_M	k_{SB}	k_H	k_K	k_M	k_{SB}
CCl_4	0.35 ± 0.01	0.16 ± 0.01	0.27 ± 0.02	0.24 ± 0.03	0.36 ± 0.04	0.15 ± 0.02	0.24 ± 0.03	0.22 ± 0.04
Toluene	0.34 ± 0.01	0.16 ± 0.01	0.28 ± 0.04	0.25 ± 0.02	0.39 ± 0.04	0.12 ± 0.05	0.27 ± 0.03	0.22 ± 0.03
Benzene	0.32 ± 0.03	0.17 ± 0.02	0.27 ± 0.06	0.24 ± 0.02	0.39 ± 0.06	0.12 ± 0.04	0.28 ± 0.02	0.21 ± 0.03
Tetralin	0.34 ± 0.04	0.16 ± 0.03	0.27 ± 0.04	0.25 ± 0.02	0.40 ± 0.08	0.13 ± 0.05	0.23 ± 0.03	0.29 ± 0.03
Cyclohexane	0.29 ± 0.03	0.17 ± 0.05	0.23 ± 0.03	0.22 ± 0.01	0.39 ± 0.09	0.14 ± 0.05	0.29 ± 0.05	0.24 ± 0.04
Cyclohexanone	0.38 ± 0.03	0.13 ± 0.02	0.33 ± 0.02	0.30 ± 0.02	0.47 ± 0.06	0.10 ± 0.02	0.34 ± 0.05	0.28 ± 0.02

Table 8 Viscosity slope constants for homopolymers

	Polystyrene				Polybutadiene			
	k_H	k_K	k_M	k_{SB}	k_H	k_K	k_M	k_{SB}
CCl_4	0.31	0.22	0.20	0.20	0.30	0.17	0.21	0.18
Toluene	0.35	0.17	0.31	0.26	0.41	0.10	0.29	0.24
Benzene	0.33	0.24	0.20	0.18	0.38	0.13	0.30	0.25
Tetralin	0.41	0.11	0.28	0.24	0.38	0.16	0.25	0.28
Cyclohexane					0.33	0.16	0.26	0.23
Cyclohexanone	0.50	0.02	0.36	0.37	0.57	0.22	0.43	0.58

Table 9 $k_H + k_K$ for copolymers and homopolymers

	Copolymers			
	Styrene 33%	Styrene 27%	Polystyrene	Polybutadiene
CCl_4	0.51	0.51	0.53	0.47
Toluene	0.50	0.51	0.52	0.51
Benzene	0.49	0.51	0.57	0.51
Tetralin	0.50	0.53	0.52	0.54
Cyclohexane	0.46	0.53		0.49
Cyclohexanone	0.51	0.57	0.52	0.79

constants in cyclohexanone which are distinctly different from those in the other solvents. This is particularly true for polybutadiene for which cyclohexanone is rather a poor solvent.

Comparison of the sets of data for the two groups of copolymers leads to the conclusion that there is no change in the slope constants for this small composition change.

Sakai[6] has reported that the expected trend of the slope constants is $k_H > k_M > k_{SB}$. For the homopolymers and copolymers in this work the order was $k_H > k_M \approx k_{SB}$, except for polybutadiene in cyclohexanone where k_{SB} was, within experimental error, equal to the Huggins constant.

Table 9 shows the $k_H + k_K$ values for both sets of copolymers and for the homopolymers. With the exception of the polybutadiene sample in cyclohexanone, it is clear that most of the $k_H + k_K$ values are, within experimental error, as has been predicted[1], equal to 0.5.

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