Solvent Effect on the Intrinsic Viscosity of Polymers

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It is well known that the intrinsic viscosity, $[\eta]$, of a polymer takes high values in good solvents and low values in poor solvents. If the experimental precautions to be observed in order to obtain reliable data are taken, such difference may be attributed quantitatively to the solvent character which the existing theories of dilute solution viscosity of polymers do not deal with.

Analytical Procedure

In the last report[1], the author derived from his ideal mixture law for viscosity the following form for $[\eta]$, $\mathrm{cm}^3\,\mathrm{g}^{-1}$:

$$[\eta]=\frac{(K_v)_0}{d_2}\left(\frac{\eta_2}{\eta_1}\right),$$
$$(K_v)_0=\left|\frac{(1-z_v)(\eta-\eta_1)}{z_v(\eta_2-\eta)}\right|_{z_v\to 0} \tag{1}$$

in which η_1, η_2 and η denote the viscosities of a solvent, solute of high molecular weight whose density is d_2, and the solution respectively, and z_v is the volume fraction of the solute before mixing.

For an ideal mixture composed of two liquids of low molecular weights, $(K_v)_0=(K_v)_1=K_v$, a constant for all concentrations, and the probable values of K_v relative to benzene of 32 liquids can be computed from K values relative to benzene obtained before[2], by means of the equality:

$$K_v=K\frac{M_1d_2}{M_2d_1} \tag{2}$$

where M_1, M_2, and d_1, d_2 are the molecular weights and densities of components 1 and 2, respectively, benzene being taken as component 1 in this case.

Combining Eq. 1 with Eq. 2, the following assumption is made:

Since $[\eta]$ is an extrapolated value at infinite dilution of a polymer with a given solvent where solvent molecules suffer presumably no change in association, $(K_v)_0$ of polymer/solvent may be inversely proportional to K_v of solvent/benzene, and therefore $[\eta]$ may be inversely proportional to the product

$$\eta_1\times(K_v\text{ of solvent/benzene})$$

so long as $(K_v)_0\times(K_v$ of solvent/benzene) which signifies the solute character term at infinite dilution retains a constant value in different solvents.

In other words, between the intrinsic viscosities of the same polymer in solvent 1 and in solvent 2, there may exist the equation:

$$\frac{[\eta]\text{ in solvent 1}}{[\eta]\text{ in solvent 2}}=\frac{(\eta\times K_v\text{ rel. to benzene) of solvent 2}}{(\eta\times K_v\text{ rel. to benzene) of solvent 1}} \tag{3}$$

Verifications

In order to verify Eq. 3, one quotes from Wales, Marshall and Weissberg's report on the intrinsic viscosities of dextran in water and in formamide at 25°C[3], as one has $K=0.67$ for water and $K=0.34$ for formamide at 25∼40°C[2].

Now, one has for benzene ($M=78.11$) $d=0.87875(20/4)$, $0.86805(30/4)$; for water ($M=18.02$) $d=0.99823$ (20/4), 0.99568 (30/4), $\eta=0.01005$ poise (20°C), 0.00802 poise (30°C); and for formamide ($M=45.04$) $d=1.1349$ (20/4), 1.1266(30/4), $\eta=0.0375$ poise (20°C), 0.0294 poise (30°C)[4,5].

From these values one obtains

$$\frac{(\eta\times K_v\text{ rel. to benzene) of water}}{(\eta\times K_v\text{ rel. to benzene) of formamide}}=1.16(20^\circ\mathrm{C}),\ 1.19(30^\circ\mathrm{C})$$

On the other hand, the inverse ratios of intrinsic viscosity values, $100\,\mathrm{cm}^3\,\mathrm{g}^{-1}$, in formamide to those in water taken from

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[1] T. Ishikawa, This Bulletin, **31**, 791 (1958).

[2] T. Ishikawa and T. Baba, ibid., **11**, 64 (1936); see also T. Ishikawa, ibid., **31**, 524 (1958).

[3] M. Wales, P. A. Marshall and S. G. Weissberg, *J. Polymer Sci.*, **10**, 229 (1953).

[4] "International Critical Tables", III, (1928), pp. 25, 27–30.

[5] F. Henning, "Wärmetechnische Richtwerte", Vdi-Verlag G.m.b.H. (1938), pp. 40–45.

Wales, Marshall and Weissberg's data for dextran of four different molecular weights, M, are:

$$\frac{[\eta] \text{ in formamide}}{[\eta] \text{ in water}}$$

$$=\frac{0.121}{0.097}=1.25 \text{ for } M=11000$$

$$=\frac{0.341}{0.271}=1.26 \text{ for } M=71000$$

$$=\frac{0.446}{0.384}=1.16 \text{ for } M=153000$$

$$=\frac{0.492}{0.421}=1.17 \text{ for } M=185000$$

Comparing these values with the above obtained values, it is seen that the coincidence is satisfactory, especially for dextran of higher molecular weights.

The following is another test applied to the data of the toluene and methyl ethyl ketone (MEK) solutions of one polystyrene sample distributed to several laboratories from the International Union of Pure and Applied Chemistry (IUPAC)[6]. The average values of $[\eta]$, cm^3g^{-1}, assembled by Frank and Mark were 148.3±2.3 for toluene at an average temperature 25.5°C (25°C in eight laboratories, 30°C in one laboratory, and 24.7°C in one laboratory), and 82.9±2.8 for MEK at an average temperature 25.5°C (25°C in seven laboratories, 30°C in one laboratory, and 24.7°C in one laboratory).

For toluene one has $\eta=0.00551$ poise (25°C)[7], and $K=1.24$ (15∼35°C)[2], from which one gets $K_v=1.03$ (25°C) by putting toluene ($M=92.13$) and benzene ($M=78.11$) densities to be 0.86122 (25/4) and 0.87340 (25/4), respectively; for MEK one has $\eta=0.00383$ poise (25°C) but K is unknown because of lack of binary mixtures composed of this liquid as one component in the literature, and, under the author's direction, viscosity measurements on the binary system of benzene (1)-MEK(2) have been carried out by M. Ikeda, lecturer of Nagasaki Prefectural Junior College.

Benzene and MEK used for the present measurements were the guaranteed reagents of Kanto Chemical Co., Inc., the former having test No. 4E033294 and the latter having test No. 3E088722, and both were used without further purification.

Densities and viscosities were measured at 25°C with an automatically regulated thermostat, T-3 type of Shimadzu Seisakusho Ltd., with a Gay-Lussac pycnometer of 25 cm³, and with a Ostwald viscometer with 10 cm³ efflux volume which has given efflux time of 54.70 sec. for water.

To convert density (25/25) to density (25/4) and relative viscosity to absolute viscosity, the author used density of water at 25°C=0.99707[4], and viscosity of water at 25°C=0.008941 poise[8].

TABLE I. BENZENE (1)—METHYL ETHYL KETONE (2), 25°C

z_v	d_4^{25}	η_{obs}	K_v obs.	K_v cacld.	η_{calcd}
0.000	0.8733	0.006158		(1.79)	—
0.125	0.8646	0.005655	2.16	1.86	0.005710
0.250	0.8557	0.005323	1.93	1.94	0.005320
0.375	0.8467	0.004977	2.07	2.03	0.004982
0.500	0.8377	0.004727	2.04	2.13	0.004713
0.625	0.8286	0.004511	2.02	2.23	0.004477
0.750	0.8191	0.004296	2.28	2.35	0.004294
0.875	0.8096	0.004137	2.55	2.48	0.004145
1.000	0.7999	0.004024		(2.63)	—

The experimental results are given in Table I. As seen from the observed K_v values in Table I, this system belongs to the case where the association degree of either of the components decreases with the dilution of the other, and either of the extrapolated values of K_v at $z_v=0$ or $z_v=1$ gives the normal K_v for the mixture. Mixtures of phenol, guaiacol, or benzyl benzoate with benzene or toluene in which the former components suffer molecular dissociation are examples for this case. The formulation of viscosity vs. composition curves of such mixtures can not be generally done, yet a particular case can be solved by a particular means, that is to say, K_v or its reciprocal at each composition to test whether they are in linear relationship with composition or not[9]. For the present case, reciprocal values of K_v against z_v appear to lie nearly on a straight line, $1/K_v=0.56-0.18\,z_v$, hence one has obtained $(K_v)_0=1.79$ and $(K_v)_1=2.63$. Compare the observed and calculated viscosity values in Table I, the deviations being at most less than 1%. It is doubtful, however, that either of components, benzene or MEK, suffers molecular dissociation, so the author refers to the results by making use of Fischler's viscosity data on benzene

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[6] IUPAC, *J. Polymer Sci.*, **17**, 1 (1938).

[7] T. E. Thorpe and J. W. Rodger, *Phil. Trans. Roy. Soc. London. Ser.* **A185**, 397 (1894); J. Batschinski, *Z. physik. Chem.*, **84**, 643 (1913).

[8] "Landolt-Börnstein Tabellen", Eg. I, p. 83.

[9] T. Ishikawa, This Bulletin, **4**, 288 (1929); refer also to 2).

(1)-acetone(2) system⁽10⁾ as found in the literature (see Table II). Since in this system benzene suffers no molecular change throughout the concentration, giving a constant value 2.06±0.05 which is an intermediate value between $(K_v)_0$ and $(K_v)_1$ for MEK/benzene, the same liquid in the benzene(1)-MEK(2) system may also be considered to suffer no molecular change, and therefore $(K_v)_1=2.63$ can be decided as the normal value, K_v, for MEK/benzene, the corresponding association degree of MEK being estimated to be 2.78.

TABLE II. BENZENE(1)—ACETONE(2), 25°C (FISCHLER)

z_v	η	K_v
0.00	0.005758	
0.25	0.004715	2.00
0.50	0.003997	2.08
0.75	0.003507	2.10
1.00	0.003150	
		2.06±0.05

Taking $K_v=2.63$ and $\eta=0.00383$ poise at 25°C for MEK and the above values for toluene, one obtains

$$\frac{(\eta\times K_v \text{ rel. to benzene) of MEK}}{(\eta\times K_v \text{ rel. to benzene) of toluene}}=1.77$$

whereas

$$\frac{[\eta] \text{ in toluene}}{[\eta] \text{ in MEK}}=\frac{148.3}{82.9}=1.79$$

$$\text{for } M=560000\sim590000$$

Also from the similar data on four polystyrene fractions in the previous report⁽11⁾ from IUPAC, the same ratios in respective laboratories are:

$$\frac{[\eta] \text{ in toluene}}{[\eta] \text{ in MEK}}=1.88,\ 1.99 \text{ for } M=860000$$

$$=2.11,\ 2.01 \text{ for } M=655000$$

$$=1.54,\ 1.61 \text{ for } M=234000$$

$$=1.64,\ 1.60 \text{ for } M=\ 82500$$

with an average of 1.80 which is nearly equal to the preceding result. Hence the coincidence is fairly good between the ratios taken from intrinsic viscosity data and from the present theory.

Conclusion

The foregoing verifications lead us to the conclusion that an intrinsic viscosity equation $[\eta]=(K_v)_0(\eta_2/\eta_1)/d_2$ is valid for polymer solutions, and therfore that $[\eta]$ of a polymer in a solvent can be converted to $[\eta]$ of the same polymer in a standard solvent, e. g. benzene, or toluene, or acetone; this procedure will give a reliable value to be further analyzed, if normal K_v values of these solvents relative to the standard solvent are known.

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10) J. Fischler, *Z. Elektrochem.*, **19**, 126 (1913).
11) IUPAC, *J. Polymer Sci.*, **10**, 129 (1953).