The Viscosity of Ideal Solutions

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The viscosity determination of artificially ideal solutions of glass spheres in a suspending medium with density equal to that of the solids in order to preclude sedimentation, done by Vand[1] and by his followers, Sweeny and Geckler[2], gave a decisive confirmation of Einstein's viscosity equation for infinite dilution

$$\eta_r = 1 + k\phi \text{ with } k = 2.5$$

where η_r is the relative viscosity and ϕ is the volume fraction occupied by N spheres of radius a in a volume V, $\phi = \frac{4}{3}\pi a^3 N/V$

The extention of Einstein's equation to a suspension of finite concentration proposed by Mooney[3],

$$\ln \eta_r = 2.303 \log \eta_r = 2.5\, z_v/(1-\lambda z_v)$$

where λ is a constant, the self-crowding factor, predicted only approximately by Mooney's theory, and z_v is the volume fraction of spheres, fits Vand's data as well as Sweeny and Geckler's data. It is noted here that since $z_v = \phi/(1+\phi)$, z_v becomes ϕ at infinite dilution where Mooney's equation tends to Einstein's equation. For actually ideal solutions, however, Einstein's equation fails and Arrhenius' equation[4] is frequently used:

$$\ln \eta_r = 2.303 \log \eta_r = A z_v$$

where A is a constant determined by the extrapolation of $\ln \eta_r/z_v$ at $z_v = 0$. Its determination, however, is difficult because the limit of precision of viscosity determination is reached. A general viscosity equation for infinite dilution derived later in this paper is

$$\eta_r = 1 + K_v(\eta_2/\eta_1) z_v$$

where η_2/η_1 is the viscosity ratio of the solute 2 to the solvent 1, and K_v is a constant throughout the concentration, determined easily as an arithmetic mean of the values $(1-z_v)(\eta-\eta_1)/z_v(\eta_2-\eta)$ at several finite concentrations, η being the viscosity of the solution at concentration z_v, so that K_v is accurate and trustworthy. The constant $K_v(\eta_2/\eta_1)$ has been found always to have a smaller value than 2.5 for the solute of low viscosity ratio, but its value comes near to 2 or more as the viscosity ratio becomes high.

In a case where the viscosity ratio is high and K_v keep constancy no longer against concentration, Mooney's equation having $(K_v)_0(\eta_2/\eta_1)$ in place of 2.5, namely:

$$\ln \eta_r = 2.303 \log \eta_r = (K_v)_0(\eta_2/\eta_1) z_v/(1-\lambda z_v)$$

where $(K_v)_0$ is the limiting value of K_v at $z_v = 0$, has been proved to be valid for the whole range of concentration.

Derivation of a New Equation at Infinite Dilution.—The hyperbolic form of the present author's fundamental formula for binary mixtures[5] is

$$\frac{(1-z_m)(\eta-\eta_1)}{z_m(\eta_2-\eta)} = \frac{k_2 a_2}{k_1 a_1} = K$$

where z_m is the molar fraction of component 2, a_1 and a_2 are the association degrees of components 1 and 2 respectively, k_1 and k_2 are the characteristic constants of components 1 and 2 respectively and K keeps constancy so long as no change occurs in the molecular association of either or both of components.

Now, between the molar fraction z_m and volume fraction z_v, there is the following relationship:

$$\frac{(1-z_m)M_1}{z_m M_2} = \frac{(1-z_v)d_1}{z_v d_2}$$

in which M_1 and M_2 are the molecular weights of components 1 and 2 respectively, and d_1 and d_2 are the densities of components 1 and 2 respectively, and therefore the similar hyperbolic form with respect to z_v:

$$\frac{(1-z_v)(\eta-\eta_1)}{z_v(\eta_2-\eta)} = K\frac{M_1 d_2}{M_2 d_1} = \text{a constant, say } K_v$$

is valid as well.

At very low concentration where z_v is small enough to be neglected as compared

1) V. Vand, *J. Phys.* and *Colloid Chem.*, **52**, 300 (1948).
2) K. H. Sweeny and R. D. Geckler, *J. Appl. Phys.*, **25**, 1135 (1954).
3) M. Mooney, *J. Colloid Sci.*, **6**, 162 (1951).
4) S. Arrhenius, *Z. Phys. Chem.* **1**, 285 (1887).
5) T. Ishikawa, This Bulletin, **4**, 5 (1929).

to 1, the above formula can be reduced to

$$\frac{\eta-\eta_1}{z_v(\eta_2-\eta)}=K_v$$

from which it follows:

$$\frac{\eta}{\eta_1}=\frac{1+K_v(\eta_2/\eta_1)z_v}{1+K_v z_v}$$

Since K_v has been found to be always less than or very rarely equal to unity in cases where the component having higher viscosity between the two is taken as component 2 (see Table I), the second term of the denominator can be neglected as compared to 1, hence the following general equation results:

$$\frac{\eta}{\eta_1}=\eta_r=1+K_v(\eta_2/\eta_1)z_v$$

In Table I are shown K_v, (η_2/η_1) and $K_v(\eta_2/\eta_1)$ of 18 kinds of ideal mixture quoted from as many viscosity data with respect to z_v as are found in the literature. Each K_v is an arithmetic mean of these at all the concentrations determined. Out of these pairs three cases, the one having the lowest viscosity ratio, benzene-carbon tetrachloride, and the other two having the highest viscosity ratios, toluene-ethyl benzoate and toluene-diphenyl, are exemplified in Tables II, III and IV.

The solutions of naphthalene and of diphenyl in benzene and in toluene have often been used as typical ideal solutions since Kendall and Monroe[6] made the viscosity measurements on these solutions in order to test their own cube-root formula[7], $\eta^{1/3}=(1-z_m)\eta_1^{1/3}+z_m\eta_2^{1/3}$ but they obtained different values 0.0225 and 0.0183 for the solutional viscosity of naphthalene in benzene and in toluene respectively, and 0.0344 and 0.0282 for that of diphenyl in these solvents respectively. The present author[8], by using his own formula described above, obtained concordant values in both solvents, 0.02653 for naphthalene and 0.05413 (revised value 0.05509) for diphenyl. Van der Wyk[9] reported that he had obtained concordant values in both

TABLE I

K_v, (η_2/η_1) AND $K_v(\eta_2/\eta_1)$ VALUES OF IDEAL SOLUTIONS

Component 1	Component 2	t°C	η_1	η_2	η_2/η_1	K_v	$K_v\times(\eta_2/\eta_1)$	Observer
Benzene	Carbon tetrachloride	60	0.00391	0.00582	1.488	0.737	1.097	Thorpe and Rodger[10]
Benzene	Bromobenzene	18.2	0.00654	0.01129	1.726	0.926	1.598	Yajnik et al[11]
Benzene	Ethyl benzoate	25	0.006051	0.01991	3.290	0.430	1.415	Kendall and Monroe[7]
Benzene	Naphthalene	25	0.006048	(0.02653)	4.387	0.347	1.522	Kendall and Monroe[6]
Benzene	Diphenyl	25	0.006051	(0.05509)	9.104	0.172	1.566	Kendall and Monroe[6]
Toluene	Chlorobenzene	20	0.00447	0.00709	1.586	1.063	1.681	Yajnik et al[11]
Toluene	Bromobenzene	25	0.00447	0.00880	1.969	0.877	1.725	Yajnik et al[11]
Toluene	Ethyl benzoate	25	0.005520	0.01990	3.605	0.446	1.609	Kendall and Monroe[7]
Toluene	Naphthalene	25	0.005526	(0.02653)	4.716	0.322	1.519	Kendall and Monroe[6]
Toluene	Diphenyl	25	0.005520	(0.05509)	9.980	0.168	1.677	Kendall and Monroe[6]
Ethyl ether	Benzene	25	0.00230	0.00599	2.604	0.494	1.287	Linebarger[12]
Acetone	Benzene	25	0.00315	0.005758	1.823	0.486	0.886	Fischler[13]
Ethyl alcohol	*iso*-propyl alcohol	25	0.01080	0.02048	1.896	0.595	1.128	Parks and Kelley[14]
Methyl alcohol	Nitrobenzene	25	0.005608	0.018126	3.232	0.303	0.979	Fischler[13]
Cyclohexane	Decaline	25	0.009287	0.02171	2.338	0.539	1.259	MacFarlane and Wright[15]
Ethylene chloride	Ethylene bromide	25	0.007812	0.01613	2.065	0.646	1.334	MacFarlane and Wright[15]
Benzene	Benzyl benzoate	25	0.006044	0.08454	13.99	0.132 ~0.225	1.847	Kendall and Monroe[7]
Toluene	Benzyl benzoate	25	0.005520	0.08450	15.31	0.124 ~0.215	1.898	Kendall and Monroe[7]

6) J. Kendall and K. P. Monroe, *J. Am. Chem. Soc.*, **43**, 115 (1921).
7) J. Kendall and K. P. Monroe, ibid., **39**, 1787 (1917).
8) T. Ishikawa, This Bulletin, **5**, 47 (1930).
9) A. J. A. van der Wyk, *Nature*, **138**, 845 (1936).
10) T. E. Thorpe and M. D. Rodger, *J. Chem. Soc.*, **71**, 360 (1897).
11) N. A. Yajnik, M. D. Bhalla, R. C. Talwar and M. A. Soofi, *Z. phys. Chem.*, **118**, 305 (1925).
12) C. E. Linebarger, *Am. J. Sci.*, [4] **2**, 331 (1896).
13) J. Fischler. *Z. Elektrochem.*, **19**, 126 (1913).
14) G. S. Parks and K. K. Kelley, *J. Phys. Chem.*, **29**, 727 (1925).
15) W. MacFarlane and R. Wright, *J. Chem. Soc.*, **1933**, 114.

TABLE II

BENZENE(1)-CARBON TETRACHLORIDE(2), 60°C

z_v	z_m	η_{obs}	K_v	η_{calc}	S_v	λ
0.000	0.0000	0.003905				
0.208	0.1949	0.00422	0.738	0.00422	1.11	−9.33
0.414	0.3944	0.00456	0.730	0.00456	1.12	−4.66
0.656	0.6377	0.00503	0.743	0.00503	1.10	−2.81
1,000	1.0000	0.005835	0.737		1.11	

N. B. $K_v(\eta_2/\eta_1)=1.097$, $2.303\log(\eta_2/\eta_1)/S_v=0.358$

TABLE III

TOLUENE(1)-ETHYL BENZOATE(2), 25°C

z_v	z_m	η_{obs}	K_v	η_{calc}	S_v	λ
0.0000	0.0000	0.005520				
0.1951	0.1524	0.006845	(0.4187)	0.006924	1.202	−2.35
0.4256	0.3546	0.009076	0.4434	0.009094	1.170	−0.89
0.6964	0.6299	0.01279	0.4448	0.01279	1.207	−0.48
0.7890	0.7349	0.01452	0.4474	0.01451	1.219	−0.40
0.8798	0.8442	0.01655	0.4498	0.01653	1.229	−0.33
1.0000	1.0000	0.01990	0.4464		1.205	

N. B. $K_v(\eta_2/\eta_1)=1.609$, $2.303\log(\eta_2/\eta_1)/S_v=1.064$

TABLE IV

TOLUENE(1)-DIPHENYL(2), 25°C

				η_{calc}				
z_v	z_m	η_{obs}	K_v	Ishikawa $\eta_2=0.05509$	Kendall $\eta_2=0.0282$	van der Wyk $\eta_2=0.0374$ $\eta_{12}=0.0154$	S_v	λ
0.000	0.0000	0.005520						
0.186	0.1398	0.007335	0.166	0.007353	0.007369	0.007334	1.62	−0.52
0.282	0.2197	0.008587	0.168	0.008588	0.008584	0.008547	1.65	−0.25
0.348	0.2761	0.009627	0.169	0.009599	0.009528	0.009552	1.67	−0.14
			0.168				1.65	

N. B. $K_v(\eta_2/\eta_1)=1.677$, $2.303\log(\eta_2/\eta_1)/S_v=1.395$

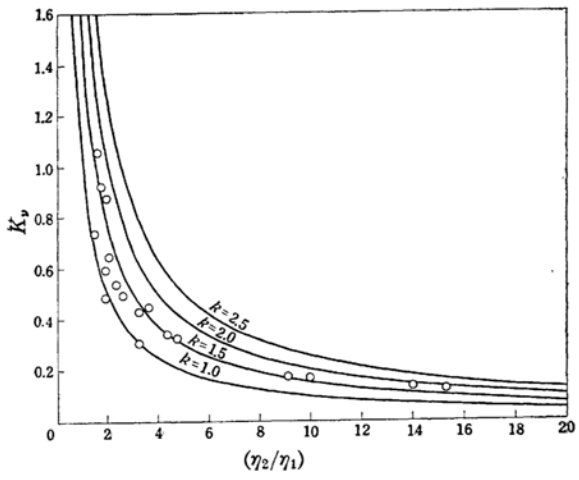

Fig. 1. The relation between K_v and (η_2/η_1) of ideal solutions.

solvents, 0.0219~0.0224 for naphthalene and 0.03740 for diphenyl by the use of his formula

$$\log\eta=(1-z_m)^2\log\eta_1+2z_m(1-z_m)\log\eta_{12}+z_m^2\log\eta_2$$

In Table IV are also shown for reference the calculated viscosity values due to Kendall and Monroe's formula and van der Wyk's formula.

Fig. 1 shows a plot of K_v against (η_2/η_1) for the results given in Table I. Let the product $K_v(\eta_2/\eta_1)$ be denoted by k as the same signature as the above, mixtures or solutions having the same values as k will take positions on a hyperbolic curve $K_v(\eta_2/\eta_1)=k$. In Fig. 1 solid lines represent $k=1.0$, 1.5, 2.0 and 2.5. As seen from the positions of the points, it appears that the higher (η_2/η_1) becomes, the less K_v decreases, and that this tendency undoubtedly signifies the approach of k to 2 or more, yet its limit can not be determined by this method of deduction.

Cases where K_v varies with Concentration. — Kendall and Monroe[7] took the

following four systems: benzene-ethyl benzoate, toluene-ethyl benzoate, benzene-benzyl benzoate, and toluene-benzyl benzoate, as chemically indifferent mixtures having great differences in viscosities and molecular weights of both components, and ascertained the validity of their cube-root formula with good result for the first two mixtures, but with bad result for toluene-benzyl benzoate contrary to their presupposition that this system was regarded to be a normal mixture as judged from the fact of there being no appreciable thermal effect and volume change on mixing.

Since then the data of this system have been used for the verification of ideal viscosity formulas. The present author[16] considered, however, that if component 2 suffers molecular dissociation in solution, K of his formula keeps no more constancy, and that if observed K values lie on a straight line, the extrapolation values at $z_m=0$, and $z_m=1$ can be obtained with ease and accuracy, and he obtained for this mixture 0.250 at $z_m=0$, and 0.390 at $z_m=1$. Lederer[17] proposed an ideal viscosity formula in the form

$$\log\eta=\frac{(1-z_m)\log\eta_1}{1-z_m+z_m/S}+\frac{z_m\log\eta_2/S}{1-z_m+z_m/S}$$

where S is the ratio of association degrees of component 2 to that of component 1. His idea of an association molecule of liquids is a molecule similar to a chemically fast-combined molecule. This is quite different from the present author's idea expressing an associated molecule as a group of single molecules interchangable with singly existing molecules, which is in accord with an idea of a cybotactic group proposed a short time later by Stewart[18]. The value of S obtained by Lederer for this mixture is 1.197[19] which is an arithmetic mean of 1.250, 1.217, 1.190, 1.166 and 1.160 at respective concentrations in their order in Table V. Van der Wyk[9] also treated this mixture with his formula, and obtained, by putting $\eta_{12}=0.0275$, fairly concordant values with experimental data (see columns 9 and 10 in Table V).

As stated above, K for this mixture varies linearly with z_m, so K_v varies with z_v and is found to be expressible by a linear equation with $(K_v)_0=0.124$ and $(K_v)_1=0.215$. Similarly for benzene-benzyl benzoate mixture we get $(K_v)_0=0.132$ and $(K_v)_1=0.225$. These values are tabulated in Table I, and the accuracy of these values can be acknowledged from η calculated from thus obtained K_v in column 6 in Tables V and VI.

If there be among the dissociated molecules the crowding effect postulated by Mooney's theory, the following modified form of his equation having $(K_v)_0(\eta_2/\eta_1)$ in place of 2.5 would be valid for these cases:

$$\ln\eta_r=2.303\log\eta_r=(K_v)_0(\eta_2/\eta_1)z_v/(1-\lambda z_v)$$

A few trials have given satisfactory results to this presumption: $(K_v)_0(\eta_2/\eta_1)=1.898$ and $\lambda=0.300$ for toluene-benzyl benzoate, and $(K_v)_0(\eta_2/\eta_1)=1.847$ and $\lambda=0.296$ for benzene-benzyl benzoate, and the calculated viscosity values by making use of these equations are tabulated in column 7 in Tables V and VI.

A severe test which must be made here is the viscosity data of the system, petroleum-non-plastic asphalt ($\eta_2/\eta_1=10^6$ at 15°C), observed by Saal and Koens and studied by Cragoe[20] for the confirmation of the latter's formula for ideal mixtures:

$$L_m=(1-z)L_1+zL_2$$

where z is the weight fraction of component 2, L with suffixes 1, 2 and m (the mixture) are defined by $\eta=Ae^{\frac{B}{L}}$, and A and B are constants, $A=5\times10^4$ and $B=1000\ln 20$. Cragoe applied his formula with success not only to mixtures of viscosity ratios less than 100, but also to this system, for which other formulas such as those of Arrhenius[4], Bingham ($1/\eta=(1-z_v)/\eta_1+z_v/\eta_2)^{21}$, and Kendall and Monroe[7] failed.

For this mixture the variation of K_v values displays a strongly sagged curve not to be satisfactorily expressed by any simple functional form, so we obtain at first 5.45 as the extrapolation value of the usual form η_{sp} (specific viscosity)$=kz_v$, by assuming a straight line to pass the values at two low concentrations, $z_v=0.224$ and 0.464, and then put this or a near value in the modified Mooney's equation to find λ to have a constant against z_v. By a few trials the following equation has been found to fit the observed values:

$$\ln\eta_r=2.303\log\eta_r=5.40z_v/(1-0.608z_v)$$

16) T. Ishikawa, This Bulletin, **4**, 288 (1929).
17) E. L. Lederer, *Proc. World Petroleum Congress, London*, **2**, F. 526 (1933).
18) G. W. Stewart, *Rev. Mod. Phys.*, **2**, 116 (1930); *Koll. Z.*, **67**, 130 (1934).
19) E. L. Lederer, *Nature*, **139**, 27 (1937).
20) C. S. Cragoe, *Proc. World Petroleum Congress, London*, **2**, F. 529 (1933).
21) E. C. Bingham, *Am. Chem. J.*, **35**, 195 (1906).

TABLE V

TOLUENE(1)-BENZYL BENZOATE(2), 25°C

z_v	z_m	η_{obs}	K_v	$(K_v)_{calc}$	Ishikawa eq. with $(K_v)_{calc}$	Modified Mooney eq. $\lambda=0.300$	Lederer eq. $S=1.197$	Van der Wyk eq. $\eta_{12}=0.0275$	S_v
0.0000	0.0000	0.005520		(0.124)					
0.3558	0.2367	0.01183	0.157	0.156	0.01179	0.01175	0.01154	0.0115	1.686
0.5693	0.4261	0.02015	0.172	0.176	0.02043	0.02031	0.01993	0.0201	1.463
0.7682	0.6502	0.03614	0.191	0.194	0.03642	0.03670	0.03624	0.0364	1.498
0.8694	0.7890	0.05080	0.202	0.203	0.05070	0.05143	0.05104	0.0515	1.526
0.9416	0.9002	0.06660	0.212	0.210	0.06650	0.06660	0.06707	0.0667	1.541
1.0000	1.0000	0.08450		(0.215)					1.507

N. B. $(K_v)_0(\eta_2/\eta_1)=1.898$, $2.303\log(\eta_2/\eta_1)/S_v=1.811$

TABLE VI

BENZENE(1)-BENZYL BENZOATE(2), 25°C

z_v	z_m	η_{obs}	K_v	$(K_v)_{calc}$	Ishikawa eq. with $(K_v)_{calc}$	Modified Mooney eq. $\lambda=0.296$	S_v
0.0000	0.0000	0.006044		(0.132)			
0.3308	0.1886	0.01196	0.165	0.163	0.01190	0.01190	1.416
0.5991	0.4124	0.02301	0.185	0.188	0.02326	0.02319	1.455
0.7484	0.5832	0.03584	0.205	0.202	0.03550	0.03567	1.434
0.8844	0.7827	0.05478	0.214	0.214	0.05477	0.05523	1.506
0.9478	0.8952	0.06883	0.220	0.220	0.06885	0.06884	1.535
1.0000	1.0000	0.08454		(0.225)			1.467

N. B. $(K_v)_0(\eta_2/\eta_1)=1.847$, $2.303\log(\eta_2/\eta_1)/S_v=1.755$

TABLE VII

PETROLEUM(1)-NON-PLASTIC ASPHALT(2), 15°C

z	z_v	η_{obs}	$(\eta_T)_{obs}$	K_v	$(\eta_T)_{calc}$: Modified Mooney eq. $\lambda=0.608$	$(\eta_T)_{calc}$: Lederer eq. $S_v=2.52$	$(\eta_T)_{calc}$: Cragoe eq.	S_v
0.00	0.000	1.31	1.000					
0.25	0.224	5.30	4.046	1.097×10^{-5}	4.055	4.122	4.450	2.56
0.50	0.464	39.6	30.23	5.564×10^{-5}	32.77	33.94	39.54	2.63
0.75	0.724	1850	1412	56.01×10^{-5}	1078	1133	1328	2.36
1.00	1.000	1.26×10^{6}	9.618×10^{5}		9.582×10^{5}	9.670×10^{5}		2.52

N. B. $(K_v)_0(\eta_2/\eta_1)=5.40$, $2.303\log(\eta_2/\eta_1)/S_v=5.47$

the calculated values being tabulated in column 6 in Table VII with reference to Cragoe's results. $(K_v)_0=0.561\times10^{-5}$ obtained by putting $(K_v)_0(\eta_2/\eta_1)=5.40$ may be an acceptable value as supposed from a plot of K_v against concentration. Furthermore, $\lambda=0.608$ is quite coincident with the hydrodynamic interaction constant 0.609 derived by Vand[22].

It is noted that another method of finding the shape factor k and the crowding factor λ is the proposition recommended by Maron et al.[23] that a graph $z_v/\log\eta_T$ *vs* z_v should be linear.

Applicability of Modified Mooney's Equation.—Since Lederer's formula is analogous in form to the author's formula, it can be transformed into the following hyperbolic form with respect to z_v:

$$\frac{(1-z_v)(\log\eta-\log\eta_1)}{z_v(\log\eta_2-\log\eta)} = \text{a constant, say } 1/S_v$$

or

$$\log\eta_T=\frac{\{\log(\eta_2/\eta_1)/S_v\}z_v}{1-(1-1/S_v)z_v}$$

and therefore

$$\ln\eta_T=2.303\log\eta_T=\frac{2.303\{\log(\eta_2/\eta_1)/S_v\}z_v}{1-(1-1/S_v)z_v}$$

This transformed formula, when it is applied to the above taken petroleum-non-plastic asphalt system with constant

22) V. Vand, *J. Phys.* and *Colloid Chem.*, **52**, 277 (1948).
23) S. H. Maron, B. P. Madow and I. M. Krieger, *J. Colloid Sci.*, **6**, 584 (1951).

$S_v=2.52$, is found to be available with accuracy equal to the modified Mooney's equation (see column 7 in Table VII), so that these two equations appear to be identical. If the identity is generally true, the numerical values of the corresponding factors $2.303\log(\eta_2/\eta_1)/S_v$ and $(K_v)_0(\eta_2/\eta_1)$ should coincide with each other, and to such solutions only the applicability of the modified Mooney's equation should be restricted, because its application to solutions of low viscosity ratios (K_v=constant) gives λ negative inconstant values as seen from λ values in Tables II, III and IV.

Examinations of all the data taken in this paper lead us to the conclusions (1) that for solutions of low viscosity ratios (K_v=constant) e.g., benzene-carbon tetrachloride, toluene-ethyl benzoate, and toluene-diphenyl (see N. B. in Tables II, III and IV), $2.303\log(\eta_2/\eta_1)/S_v$ is always less than $(K_v)_0(\eta_2/\eta_1)$, (2) that for solutions of appreciably high viscosity ratios in which slight molecular dissociation occurs e.g., benzene-benzyl benzoate and toluene-benzyl benzoate (see N. B. in Tables V and VI), the constancy of S_v is not favorable and, if we take the mean of such S_v values, $2.303\log(\eta_2/\eta_1)/S_v$ becomes slightly less than $(K_v)_0(\eta_2/\eta_1)$ to make the validity of Ledere's formula inferior to the modified Mooney's equation, and (3) that for solutions of extemely high viscosity ratios where the molecular dissociation follows and consequently geometric crowding action and hydrodynamic interaction occur among the dissociated molecules, e. g., petroleum-non-plastic asphalt (see N. B. in Table VII), these two factors coincide with each other and $(1-1/S_v)$ will tend to λ in consequence.

From what has been discussed above a modified form of Mooney's equation with $(K_v)_0(\eta_2/\eta_1)$ in place of 2.5:

$$\ln\eta_T=2.303\ln\eta_T=(K_v)_0(\eta_2/\eta_1)z_v/(1-\lambda z_v)$$

may be regarded as a viscosity formula for ideal solutions of high viscosity ratios.

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