

A VISCOSITY FORMULA FOR BINARY MIXTURES, THE ASSOCIATION DEGREES OF CONSTITUENTS BEING TAKEN INTO CONSIDERATION. VIII.

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If the writer's viscosity formula for chemically indifferent mixtures is assumed rigorously valid, it may be also applicable to a binary mixtures, each component of which is composed of a homogeneous mixture of two or more chemically indifferent liquids. A typical case of such mixture is a binary mixture of lubricating oils. The problem to make up a mixture having a desired viscosity from lubricating oils light and heavy is of technical importance, but few attempts have been done to find a satisfactory formula by which the viscosity of a blended lubricant may be calculated from the viscosities of its components.

Quite recently Epperson and Dunlap⁽¹⁾ studied the viscosities at 210°F. of lubricating oils prepared from the fractions of Midcontinent and Pennsylvania oils, together with the cryoscopic study of their molecular weights, and came to the conclusion that Kendall and Monroe's cube-root formula is in close agreement with observed values but gives a few per cent divergence.

The present paper is the results of the test of the writer's formula by use of Epperson and Dunlap's data. In the following table $\eta_{calc.}$ denotes the calculated values from the writer's formula, η_k those from Kendall and Monroe's formula, and m the ratios of logarithms of measured viscosities to those calculated from Kendall's logarithmic formula for reference to the preceding study on the stability coefficient.

Table 1.
Shell oil 4 (symbol D)—Shell oil 1 (symbol A).

$z_m - A$	η	$\frac{k_2 a_2}{k_1 a_1}$	$\eta_{calc.}$	$\frac{\eta - \eta_{calc.}}{\eta} \times 100$	η_k	$\frac{\eta - \eta_k}{\eta} \times 100$	m
0.000	0.3391		—		—		
0.168	0.2704	1.60	0.2706	-0.07	0.2682	-0.81	0.950
0.347	0.2134	1.39	0.2100	+1.59	0.2044	-4.22	0.909
0.614	0.1340	1.68	0.1369	-2.12	0.1293	-3.51	0.919
0.773	0.1010	1.59	0.1010	± 0.00	0.0915	-9.44	0.932
0.921	0.0707	1.69	0.0714	-0.98	0.0688	-2.13	0.974
1.000	0.0571		—		—		
		1.59					

(1) E. R. Epperson & H. L. Dunlap, *Ind. Eng. Chem.* **24**(1932), 1369.

Table 2.

Shell oil 3 (symbol C)—Shell oil 1 (symbol A).

z_m -A	η	$\frac{k_2 a_2}{k_1 a_1}$	$\eta_{calc.}$	$\frac{\eta - \eta_{calc.}}{\eta} \times 100$	η_k	$\frac{\eta - \eta_k}{\eta} \times 100$	m
0.000	0.1655		—		—		
0.216	0.1416	1.03	0.1404	+0.85	0.1355	-4.31	0.964
0.415	0.1168	1.18	0.1182	-1.18	0.1113	-4.71	0.958
0.579	0.1003	1.10	0.1005	-0.02	0.0936	-6.70	0.952
0.727	0.0853	1.07	0.0849	+0.47	0.0794	-6.92	0.957
1.000	0.0571		—		—		
		1.09					

Table 3.

Shell oil 4 (symbol D)—Shell oil 2 (symbol B).

z_m -B	η	$\frac{k_2 a_2}{k_1 a_1}$	$\eta_{calc.}$	$\frac{\eta - \eta_{calc.}}{\eta} \times 100$	η_k	$\frac{\eta - \eta_k}{\eta} \times 100$	m
0.000	0.3391		—		—		
0.208	0.2840	1.31	0.2872	-1.11	0.2823	-0.60	0.975
0.376	0.2484	1.21	0.2484	± 0.00	0.2413	-2.86	0.953
0.618	0.1973	1.19	0.1967	+0.30	0.1896	-3.90	0.952
0.690	0.1845	1.15	0.1822	+1.26	0.1755	-4.88	0.952
1.000	0.1239		—		—		
		1.21					

Table 4.

Standard oil 2 (symbol F)—Standard oil 1 (symbol E).

z_m -E	η	$\frac{k_2 a_2}{k_1 a_1}$	$\eta_{calc.}$	$\frac{\eta - \eta_{calc.}}{\eta} \times 100$	η_k	$\frac{\eta - \eta_k}{\eta} \times 100$	m
0.000	0.3659		—		—		
0.227	0.2792	1.44	0.2767	+0.90	0.2726	-2.36	0.933
0.389	0.2235	1.50	0.2235	± 0.00	0.2168	-3.00	0.923
0.573	0.1711	1.50	0.1711	± 0.00	0.1632	-4.62	0.921
0.726	0.1303	1.59	0.1331	-2.10	0.1261	-3.22	0.943
1.000	0.0745		—		—		
		1.50					

Table 5.

Standard oil 2 (symbol F)—Shell oil 1 (symbol A).

$z_m - A$	η	$\frac{k_2 a_2}{k_1 a_1}$	$\left(\frac{k_2 a_2}{k_1 a_1}\right)_{calc.}$	$\eta_{calc.}$	$\frac{\eta - \eta_{calc.}}{\eta} \times 100$
0.000	0.3659		(0.85)	—	
0.195	0.3094	0.92	1.05	0.3034	+1.98
0.368	0.2376	1.22	1.22	0.2376	± 0.00
0.507	0.1860	1.36	1.36	0.1860	± 0.00
0.694	0.1250	1.56	1.55	0.1255	-0.40
0.850	0.0888	1.54	1.71	0.0859	+3.38
1.000	0.0571		(1.86)	—	

Table 6.

Shell oil 4 (symbol D)—Standard oil 1 (symbol E).

$z_m - E$	η	$\frac{k_2 a_2}{k_1 a_1}$	$\left(\frac{k_2 a_2}{k_1 a_1}\right)_{calc.}$	$\eta_{calc.}$	$\frac{\eta - \eta_{calc.}}{\eta} \times 100$
0.000	0.3391		(1.30)	—	
0.210	0.2655	1.45	1.45	0.2655	± 0.00
0.380	0.2097	1.56	1.57	0.2094	+0.14
0.572	0.1544	1.73	1.71	0.1550	-0.39
0.723	0.1210	1.80	1.82	0.1205	+0.42
1.000	0.0745		(2.02)	—	

For the first four pairs the constancy of $\frac{k_2 a_2}{k_1 a_1}$ is quite satisfactory in each case and the calculated viscosity values done from the mean value of them are concordant with the observed values. As to the last two pairs i.e. the mixtures of Shell and Standard oils, the values of $\frac{k_2 a_2}{k_1 a_1}$ vary linearly with concentrations, which suggest that these mixtures are chemically reactive and either of the components may suffer molecular dissociation. As the study on the molecular dissociation has been done in part IV,⁽²⁾ it may be enough here to show that the values $\frac{k_A a_A}{k_F a_F} = 1.86$ and $\frac{k_E a_E}{k_D a_D} = 1.30$ out of the extrapolated values at $z_m = 0$ and $z_m = 1$

(2) This Bulletin, 4 (1929), 288.

of each system suffice the condition :

$$\frac{k_A a_A}{k_D a_D} = \frac{k_A a_A}{k_F a_F} \frac{k_F a_F}{k_E a_E} \frac{k_E a_E}{k_D a_D} .$$

From these and the remaining values we may acknowledge that A (Shell 1) dissociates in F (Standard 2) and D (Shell 4) dissociates in E (Standard 1), the degrees of molecular dissociation of the former at infinite dilution of the latter being 0.54 and 0.36 respectively.

Before this manuscript is sent to press, I found the unfortunate communication given by Dunlap (*Ind. Eng. Chem.* **25** (1933), 592-3) that the above viscosities were values substituted for D. sp. grs. at 60°F. instead of those at 210°F. in the Herschel equation :

$$\frac{\eta}{D} = 0.0022t - \frac{1.8}{t} .$$

As it is highly probable, however, that similar oils have almost equal values of the temperature coefficient of viscosities, no serious error may occur in the calculation of $\frac{k_2 a_2}{k_1 a_1} = \frac{(1-z_m)(\eta-\eta_1)}{z_m(\eta_2-\eta)}$, the constancy of which is the criterion of the validity of the writer's formula for physical mixtures.

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