Note on the Ideal Mixture Law for Viscosity

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Four interesting measurements on the viscosity of mixtures of the same crystal forms were seen in the recent literature, three(1) being those of ionic liquids with tests of Macleod's formula (1924), and one(2) that of the sodium and potassium system with test of Drucker-Kassel's formula (1911). According to their results these formulas hold good with at most 2 % and 1 % divergence respectively. Among the known formulas, however, there are two more worthy to be considered: the one is Kendall's formula (1913)(3)

$$\log \eta = (1-z_m)\log \eta_1 + z_m \log \eta_2$$

and the other is Ishikawa's formula (1929)(4)

$$\eta = \eta_1 + (\eta_2 - \eta_1)Kz_m/(1-z_m+Kz_m)$$

where η_1, η_2 and η denote the viscosities of component 1, 2 and mixture respectively, z_m molar fraction of component 2, K the characteristic constant which signifies, according to the latter's theory, the intensity of the molecular attraction field of component 2 relative to that of component 1.

Tests made with these four pairs are illustrated in tables, from Table 1 to Table 4, in which

(1) B. S. Harrap and E. Heymann, *Chem. Rev.*, **48**, 45 (1951).
(2) C. T. Ewing, J. A. Grand and R. R. Miller, *J. Am. Chem. Soc.*, **73**, 1168 (1951).
(3) J. Kendall, *Meddelanden f. K. Velensk, Novelinstituta*, **2**, No. 25, 1 (1913).
(4) T. Ishikawa, This Bulletin, **4**, 5 (1929).

only percentage deviations $100(\eta_{calc}-\eta_{obs})/\eta_{obs}$ are given for comparison of those obtained by the respective observers.

Table 1

$AgBr\,(1)-AgCl\,(2)$, 500°C.[1]

z_m	Deviation, %		
	Macleod	Kendall	Ishikawa (K=1.21)
0.200	+0.5	+0.5	0
0.400	+0.5	0	0
0.599	+1	+0.5	0
0.732	−2	−0.5	−0.5

Table 2

$CdCl_2\,(1)-CdBr_2\,(2)$, 600°C.[1]

z_m	Deviation, %		
	Macleod	Kendall	Ishikawa (K=0.82)
0.252	0	−0.5	−0.5
0.445	+1	+0.5	0
0.725	+0.5	+0.5	0

Table 3

$PbBr_2\,(1)-PbCl_2\,(2)$, 510°C.[1]

z_m	Deviation, %		
	Macleod	Kendall	Ishikawa (K=0.33)
0.247	0	+3.5	−1
0.436	+1	+7.5	+0.5
0.769	−2	+9	+2

Table 4

$Na\,(1)-K\,(2)$.[2]

z_m	°C.	Deviation, %		
		Drucker-Kassel	Kendall	Ishikawa (K=2.54)
0.214	103.7±0.2	−0.9	+6.6	−0.1
	121.5±0.2	−1.1	+6.1	−0.5
	147.0±0.2	−0.9	+6.0	−0.5
	167.4±0.2	−0.7	+5.9	−0.4
	192.8±0.2	−0.1	+6.4	+0.1
0.361	103.7±0.2	−0.5	+8.3	+0.3
	121.5±0.2	−0.4	+8.4	+0.2
	147.0±0.2	−0.6	+7.7	+0.2
	167.4±0.2	−0.2	+7.8	+0.0
	192.8±0.2	−0.2	+7.6	−0.1
0.683	103.7±0.2	+0.1	+6.5	+0.6
	121.5±0.2	−0.2	+6.3	+0.2
	147.0±0.2	−0.5	+5.6	−0.3
	167.4±0.2	−0.2	+5.8	−0.0
	192.8±0.2	−0.1	+5.7	0
Mean		−0.4	+6.7	±0.3

As seen from each table, the Kendall formula holds good for AgCl–AgBr and $CdCl_2$–$CdBr_2$ systems, but fails for $PbCl_2$–$PbBr_2$ and Na–K systems, whereas the Ishikawa formula holds good for all the pairs, although the constancy of K in $PbCl_2$–$PbBr_2$ system is somewhat doubtful, yet its superiority to other formulas may be accepted without hesitation.

For $PbCl_2$–$PbBr_2$ system, there exist two different opinions even in these years: Delgery[5] claimed the existence of a stable compound PbClBr and an unstable peritectic compound $PbBr^2$ $3PbCl_2$, but Calingaert, Lamb and Meyer[6] confirmed the former but denied the latter by thermal and x-ray diffraction analyses. The present viscosity analysis gives the result that K in $PbCl_2(1)$–$PbBr_2(2)$ system takes a quite different value 3.0 (=1/0.33) as compared with K in AgCl(1)–AgBr(2) and $CdCl_2(1)$–$CdBr_2(2)$ systems, taking 0.826 (=1/1.21) and 0.82 respectively.

For Na–K system, a peritectic melting compound Na_2K was confirmed recently by Mckisson and Bromley[7] from the measurement of heat formation. K of this system takes a unique value 2.54 throughout the observed temperature range.

Since K's in mixtures composed of like liquids differ not so much from unity,[8] K's in AgCl–AgBr and $CdCl_2$–$CdBr_2$ systems are regarded as being normal, but those in $PbCl_2$–$PbBr_2$ and Na–K systems as being abnormal. These anomalous values may clearly be explained by the supposition that the tendency of forming a peritectic compound $PbBr_2 3PbCl_2$ or Na_2K necessitates the activation of attraction field intensity of lead bromide or potassium to have nearly three times or two times that of its ordinary intensity respectively. These systems, therefore, belong to a quasi-ideal mixture. In fact, in Na–K system occurs slight volume contraction of the simplest form Δv (cc./g.)$=Cz(1-z)$ (z=weight fraction) on mixing, giving C 0.056, 0.051 and 0.048 at 103.7, 147.0 and 192.8 °C. respectively, which, though little in magnitude, suggests a compound of molecular ratio 2 Na: K, if it forms.

Summary

Tests made with data in the recent literature show (1) that the Ishikawa formula is superior to the formulas of Macleod, Drucker-Kassel and Kendall which are often used as an ideal mixture law for viscosity, and (2) that the

(5) I. Delgery, *Compt. rend.*, **222**, 886 (1946); **223**, 401 (1946); **224**, 274, 915 (1947).
(6) G. Calingaert, F. W. Lamb and F. Meyer, *J. Am. Chem Soc.*, **71**, 3709 (1949).
(7) R. L. Mckisson and L. A. Bromley, *J. Am. Chem. Soc.*, **73**, 314 (1951).
(8) T. Ishikawa and T. Baba, This Bulletin, **11**, 64 (1936).

extraordinary values of K of his formula in $PbCl_2$–$PbBr_2$ and Na–K systems suggest the tendency of forming peritectic compounds of $PbBr_2 3PbCl_2$ and Na_2K respectively.

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