

## Viscosity of Liquid-liquid Mixtures

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The viscosity function, suggested by Shukla and Bhatnagar<sup>1</sup>, has been tested for binary liquid systems in cases of components having large differences in their viscosities. The mixtures are composed of chloroform and higher members of alcohols and ketones. The equation appears to satisfy such cases within a maximum deviation of  $\pm 12\%$ .

The viscosity function:

$$(\eta_m)^{\frac{1}{2}} = \frac{d(x_1 R_1 + x_2 R_2 + \dots + x_n R_n)}{M_m} \quad \dots \quad (1)$$

suggested by Shukla and Bhatnagar<sup>1</sup> for calculating the viscosity of liquid-liquid mixtures, was tested by them for binary<sup>1</sup> and ternary<sup>2</sup> systems and for solid-liquid mixtures by Bhatnagar and Mishal<sup>3</sup>. In the cases cited, the viscosities of the components did not differ much. Recently Mishal *et al.*<sup>4</sup> have suggested that for such binary systems, the values for rheochor of solutes should be obtained, not by applying simple mixture law<sup>5</sup>, but by extrapolating rheochor vs. mole fraction ( $R$  vs.  $x$ ) graph to  $x=1$ . The results reported herein are intended to test the validity of the equation of Shukla and Bhatnagar<sup>1</sup> for binary systems in which viscosities of the components differ greatly, namely, chloroform as one of the components and higher members of alcohols and ketones as the other. The measurements correspond to three to four values of  $x$ , the mole fraction, and at three temperatures. The validity of the equation has been tested by using the extrapolated values of ' $R$ ' for the solutes.

## EXPERIMENTAL

Liquids used were B.D.H. (A.R.) reagents and were distilled once. Viscosity determinations at constant temperature were carried out with an Ostwald viscometer. The values of density, measured with the help of a pycnometer, and viscosity were also taken as criteria of purity of the liquids used.

Table I records the observed and extrapolated values of rheochor of solutes; those of viscosities of mixtures, calculated according to Shukla-Bhatnagar's equation, together with observed ones are recorded in Table II.

1. *J. Phys. Chem.*, 1955, 59, 968.

2. *Ibid.*, 1956, 60, 809.

3. *This Journal*, 1962, 38, 63.

4. *J. Vár. Univ. (So. issue)*, 1960, 4, 147; *Z. physical. Chem.*, 1962, 229, 408.

5. Hammick and Andrew, *J. Chem. Soc.*, 1929, 754.

TABLE I

*Rheochors of solutes in chloroform solutions.*

Solute.	At 30°		At 40°		At 50°	
	<i>R</i> (obs.).	<i>R</i> (extrap.).	<i>R</i> (obs.).	<i>R</i> (extrap.).	<i>R</i> (obs.).	<i>R</i> (extrap.).
Isopropanol	108.91	102.30	105.40	100.40	102.64	98.40
Isobutanol	139.70	135.40	134.84	130.00	130.51	127.40
Isopentanol	166.08	163.00	160.27	158.90	155.60	153.00
Cyclohexanol	..	204.80	204.80	198.00	..	182.00
Ethylmethyl- ketone	108.44	109.30	108.33	108.90	107.89	108.40
Methylisobutyl ketone	184.67	185.50	163.21	164.00	161.76	163.50
4-Methyl-2-pentanone	155.59	157.20	154.06	156.00	152.99	155.00

TABLE II

*Calc. and observed viscosities of chloroform solns. containing different solutes.*

$x_1$ .	$d$ .	$M_m$ .	$\eta_m \times 10^3$		% Deviation.
			Calc.	Obs.	
A. System: Isopropanol—CHCl <sub>3</sub> at 50°.					
0.104	1.3642	113.13	5.73	5.68	+0.9
0.310	1.2293	100.90	5.73	5.53	+3.6
0.411	1.1645	94.95	5.77	5.61	+2.8
B. System: Isobutanol—CHCl <sub>3</sub> at 50°.					
0.177	1.3034	111.31	6.50	5.80	+12.0
0.562	1.0367	93.89	7.77	6.93	+12.1
0.774	0.9146	84.35	9.41	9.04	+4.1
C. System: Isopentanol—CHCl <sub>3</sub> at 50°.					
0.145	1.3042	114.80	6.81	5.85	+7.9
0.524	1.0394	102.98	8.54	7.74	+10.3
0.743	0.9209	96.17	10.63	10.19	+4.3
D. System: Ethylmethyl ketone—CHCl <sub>3</sub> at 30°.					
0.182	1.3376	110.71	6.35	6.95	-8.6
0.572	1.0730	92.29	5.69	5.97	-4.6
0.779	0.9403	82.56	5.27	5.25	+0.4
E. System: Methylisobutyl ketone—CHCl <sub>3</sub> at 30°.					
0.131	1.3340	117.55	6.71	7.11	-5.6
0.476	1.0669	112.97	6.25	6.86	-8.9
0.707	0.9340	109.90	6.06	6.31	-4.0
F. System: 4-Methyl-2-pentanone—CHCl <sub>3</sub> at 30°.					
0.140	1.3208	116.61	6.32	7.10	-10.9
0.493	1.0597	109.79	6.16	6.85	-10.0
0.716	0.9351	105.49	6.19	6.34	-2.4

Figs. 1 and 2 represent the data for alcohols and ketones, respectively, at 30° from which by extrapolation the  $R$ -values (Table I) have been obtained. Fig. 3 shows the curves (A, B, C) for cyclohexanol at 30°, 40° and 50° respectively. They deviate from the expected linear relation, but if roughly extrapolated, the values of  $R_m$  at  $x=1$  can be shown as given in parenthesis with the respective graphs.

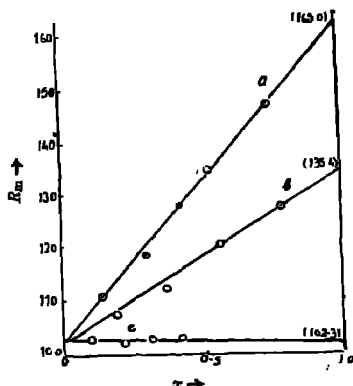


FIG. 1

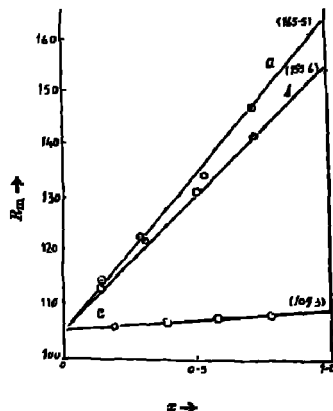


FIG. 2

# DISCUSSION

The present studies with chloroform and higher alcohols indicate clearly that when the viscosity differences between the solute and solvent are large, the mixture law of Ham-mick and Andrews does not apply in its usual form. At constant temperature, the rheochor of mixture increases with the mole fraction,  $x$ , of the solute, as also observed by Mishal and Patil<sup>4</sup>.

The maximum deviation between the observed and extrapolated values in these cases is about 6 units (Table I). The case of cyclohexanol in chloroform is a deviation (Fig. 3) from the mixture law. Thus applicability of mixture law is doubtful in cases where viscosity differences are abnormally large (e.g., in chloroform—cyclohexanol system), but in case of ketones, the law is fairly satisfactory (Table I).

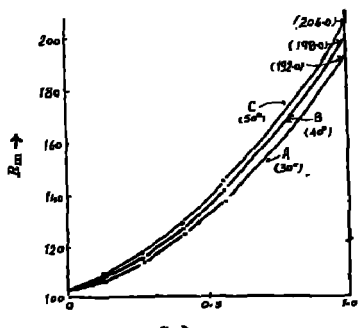


FIG. 3

Now, if the extrapolated values of rheochor of solutes are really representative, it should be proper to use them for testing the applicability of the equation<sup>1</sup>. Table II records the values for viscosities of mixtures as calculated from equation (1). By using the extrapolated values of rheochors of the components, the calculated values of viscosities show considerable deviation from the observed ones. The deviation varies from 12.1% for

chloroform—*isobutanol* system to 10.9% for chloroform—4-methyl-2-pentanone system; these are larger than those reported earlier<sup>1,2</sup> but are practically of the same order as reported by Lima<sup>6</sup> for his equation, utilising 'I', Sauder's viscosity constant.

The values obtained for chloroform—cyclohexanol mixtures vary widely from the observed ones and have therefore not been included in Table II. It may be pointed out here that the equation of Shukla-Bhatnagar for a binary system can also be obtained from Hammick and Andrew's equation<sup>6</sup> by rearranging the terms in equation (1) as shown below

$$R_m = x_1 R_1 + x_2 R_2 = \frac{M_m}{d} (\eta_m)^{\frac{1}{2}} \quad \dots \quad (2)$$

or

$$(\eta_m)^{\frac{1}{2}} = \frac{d(x_1 R_1 + x_2 R_2)}{M_m}$$

This shows that wherever the mixture law is true, the viscosity equation under study is also applicable, otherwise it fails as in the case in cyclohexanol—chloroform system, mentioned above.

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