Viscosity-Temperature Relation for Solutions

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WHILE MANY investigations (*3, 14, 15*) have been made to represent the temperature dependence of the viscosity of single liquids by theoretical or empirical equations, comparatively less attention has been paid to the case of solutions. However, dependence of viscosity on the concentrations and viscosities of individual components has been well investigated (*3, 14*).

Perhaps the best known equation for representing the viscosity-temperature relation is due, to Andrade (*1, 2*) and Guzman (*8*)

$$\eta = Ae^{b/T} \tag{1}$$

where η is the viscosity, T is temperature in ° K, and A and b are constants. Other related references to this equation are given (*15*). This equation is successful for simple liquids but associated liquids, oils, fused salts, and some liquid metals are known to show serious deviations (*15*).

Kampmeyer (*11*) and Girifalco (*5*) have recently modified the Andrade-Guzman equation as follows:

$$\log_{10}\eta = \alpha + \beta/T + \gamma/T^2 \tag{2}$$

where α, β, and γ are constants. Girifalco has attempted a theoretical justification for this equation. We will call it the Kampmeyer-Girifalco equation, or K-G equation. (Note. Our α and γ are different from those of Girifalco.)

In the following the applications of the K-G equation to some liquids are summarized.

Kampmeyer (*11*) has tested it on mercury in the temperature interval 0° to 299° C. The maximum percentage error was 2.83.

Girifalco (*5*) has found it satisfactory for the following liquids: water, methanol, ethyl alcohol, *n*-propyl alcohol, *n*-butyl alcohol, formic acid, acetic acid, butyric acid, sulfuric acid, ethylene glycol, glycerol, ethyl acetate, and aniline. However, he has not given the temperature interval used and the percentage errors obtained.

Moore, Burkardt, and McEwan (*13*) have applied this equation to the system trinitrotoluene-picric acid and to four related substances. It yielded a good fit to the data even well into the supercooled region.

In recent years a number of workers have attempted to apply the Andrade-Guzman relation to mixtures of liquids. Waring and Becher (*16*) considered it satisfactory for a number of mixtures of organic liquids and water. Grunberg (*7*) has applied Equation 1 to the system CCl_4-C_6H_6. Glasstone, Laidler, and Eyring (*6*) have expressed E_{visc} equal to bR of mixtures in terms of the E_{visc} values of the components.

In the present paper, we have investigated the viscosity-temperature relation for ethyl alcohol-water mixtures and aqueous sucrose solutions. Figures 1 and 2 show log η against $1000/T$ for a few concentrations of these solutions. In all cases, the linear relation is not followed. In the case

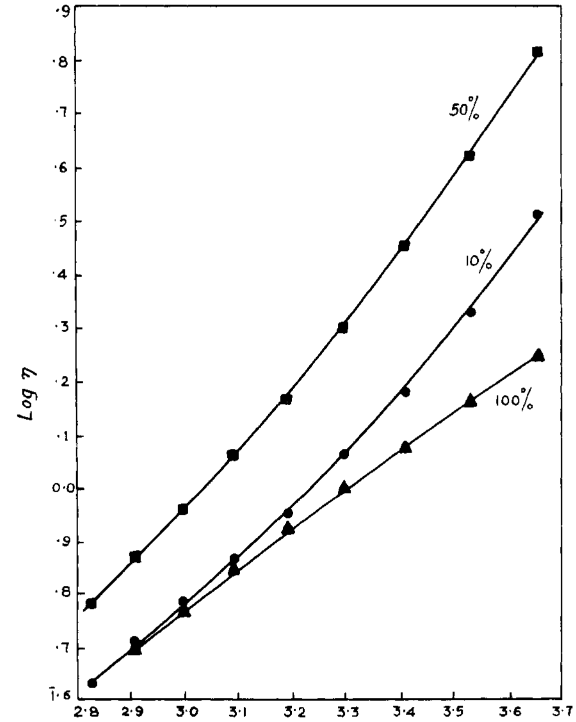

Figure 1. Relation between log η and $1/T$ for mixtures of ethyl alcohol and water

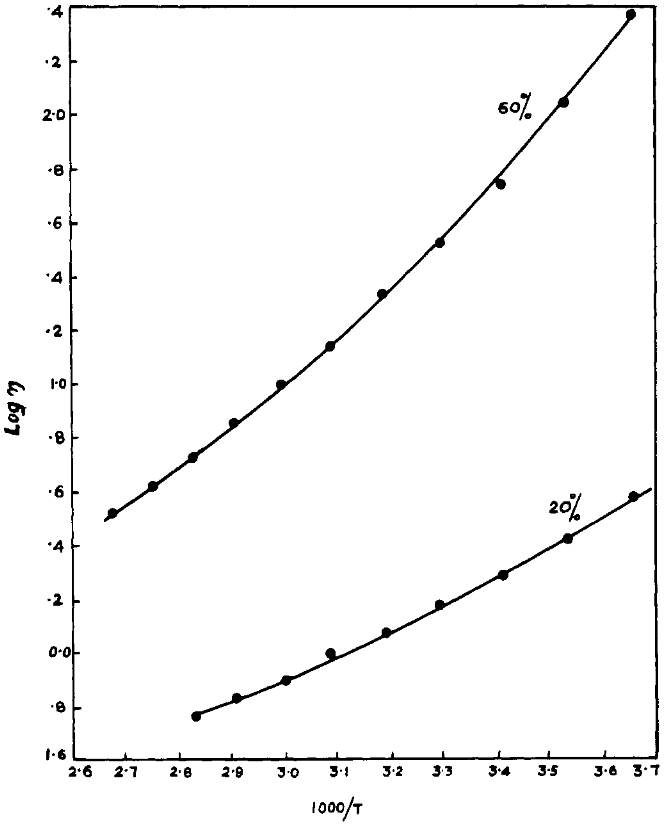

Figure 2. Relation between log η and $1/T$ for sucrose solutions

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of alcohol-water mixtures the curvatures at low concentrations—e.g., 10%, 50%—and those at high concentrations—e.g., 100%—are opposite. All data have been taken from Bingham and Jackson (*4*) as reproduced by Hodgman (*9*).

In view of the nonlinearity of the (log η, $1/T$) plots, the applicability of the Kampmeyer-Girifalco equation was considered. The constants α, β, and γ for various concentrations were derived by the method of least squares and are tabulated in Tables I and II. Only these values which were at 10° C. intervals were used—e.g., 0°, 10°, 20° C. etc. Observed and calculated values of viscosities for a few concentrations have been compared in Tables III and IV. Average per cent errors for the various concentrations are recorded in Table V.

Table I. Values of Constants for Ethyl Alcohol-Water Mixtures

(Viscosity in centipoises, temperature in degrees Kelvin)

Ethyl Alcohol, Wt. %	α	$\beta \times 10^{-3}$	$\gamma \times 10^{-6}$
10	1.70539	−2.1168884	0.49101796
20	1.64562	−2.1479645	0.5174730
30	1.84380	−2.3092525	0.5555916
40	1.42248	−2.023635	0.51063353
50	0.00065	−1.092250	0.359280
60	−1.17603	−0.31050564	0.2287420
70	−1.41487	1.1128734	0.0001159420
80	−1.13657	1.0094524	0.000688754
90	−0.83253	0.89222352	0.0000228949
100	−0.42873	0.73448806	0.0000723301

Table II. Values of the Constants for Sucrose Solutions

(Viscosity in centipoises, temperature in degrees Kelvin)

Sucrose, Wt. %	α	$\beta \times 10^{-3}$	$\gamma \times 10^{-6}$
20	0.05868	−0.93083144	0.29305808
40	0.57748	−1.2673559	0.39072203
60	2.31887	−2.5230944	0.69256612

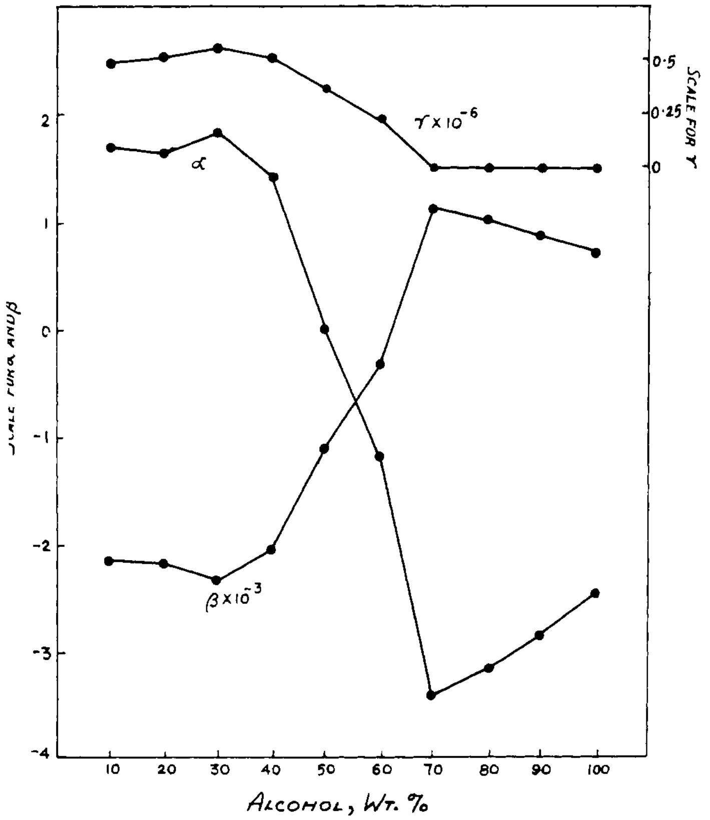

Figure 3. Variations of factors α, β, and γ with concentrations of alcohol in ethyl alcohol–water mixtures

Table III. Observed and Calculated Values of η for Ethyl Alcohol–Water Mixtures

(All viscosities in centipoises)

Wt. %	Temp., ° K.	η, Obsd.	η, Calcd.	% Error
40	273.16	7.14	7.20	+0.84
	283.16	4.39	4.40	+0.22
	293.16	2.91	2.89	−0.69
	303.16	2.02	2.01	−0.50
	313.16	1.482	1.470	−0.81
	323.16	1.132	1.122	−0.88
	333.16	0.893	0.889	−0.45
	343.16	0.727	0.7275	+0.07
	353.16	0.601	0.610	+1.50
80	273.16	3.69	3.629	−1.65
	283.16	2.710	2.686	−0.88
	293.16	2.008	2.029	+1.04
	303.16	1.531	1.562	+2.02
	313.16	1.203	1.223	+1.66
	323.16	0.968	0.9707	+0.20
	333.16	0.789	0.782	−0.88
	343.16	0.650	0.639	−1.83
100	273.16	1.773	1.816	+2.42
	283.16	1.466	1.467	+0.68
	293.16	1.200	1.190	−0.83
	303.16	1.003	0.9844	−1.85
	313.16	0.834	0.823	−1.32
	323.16	0.702	0.6972	−0.68
	333.16	0.592	0.5959	+0.66
	343.16	0.504	0.514	+1.98

Table IV. Observed and Calculated Values of η for Sucrose Solutions

(All viscosities in centipoises)

Wt. %	Temp., ° K.	η, Obsd.	η, Calcd.	% Error
20	273.16	3.804	3.790	−0.37
	283.16	2.652	2.668	+0.60
	293.16	1.960	1.965	+0.25
	303.16	1.504	1.503	−0.07
	313.16	1.193	1.187	−0.50
	323.16	0.970	0.9649	−0.52
	333.16	0.808	0.8035	−0.56
	343.16	0.685	0.6836	−0.20
	353.16	0.590	0.5923	+0.38
60	273.16	238.0	231.2	−2.85
	283.16	109.0	111.6	+2.38
	293.16	56.5	58.8	+4.03
	303.16	33.78	34.02	+2.19
	313.16	21.28	21.03	−1.17
	323.16	14.01	13.90	−0.78
	333.16	9.83	9.66	−1.72
	343.16	7.15	7.04	−1.54
	353.16	5.40	5.33	−1.29
	363.16	4.15	4.19	+0.96
	373.16	3.34	3.39	+1.47

Table V. Average Per Cent Error

Ethyl Alcohol				Sucrose	
Wt. %	Av. % error	Wt. %	Av. % error	Wt. %	Av. % error
10	1.66	60	0.63	20	0.38
20	1.08	70	1.73	40	1.13
30	0.83	80	1.27	60	1.85
40	0.66	90	0.49		
50	0.34	100	1.29		

DISCUSSION

The agreement between the observed and calculated values (Tables III and IV) is satisfactory. The average percentage errors (Table V) are usually less than 1.5%.

The variation of α, β, and γ with concentration (weight percentage) for ethyl alcohol-water mixtures is shown in Figure 3. Although the behavior is not smooth, there are some interesting features. Three parts can be distinguished: 10, 20, 30, and 40%; 50 and 60%; and 70, 80, 90, and 100%. In the first part α, β, and γ are roughly constant. In the second, there are sharp changes in the values of the three constants. In the third, there are small and regular variations in α and β. The sign of β in the third part (positive) is opposite to that in the first part (negative), while the reverse is true for α.

The values of α, β, and γ for ethyl alcohol (100%) used here are different from those determined by Girifalco (*5*). Perhaps he has taken a greater range of temperature. For ethyl alcohol, Jobling and Lawrence (*10*) have found that log η is linear with $1/T$ at constant volume [See also Mitra and Chakravarty (*12*)].

Waring and Becher (*16*) have demonstrated that for a number of organic liquids and organic liquid mixtures a simple relation holds between the constants A and b of Equation 1: Log A is linear with b. For the K-G equation, the corresponding quantities are α and β. Figures 4 and 5 show α *vs.* β for ethyl alcohol-water mixtures and sucrose solutions, respectively. We find that in both cases α is linear with β.

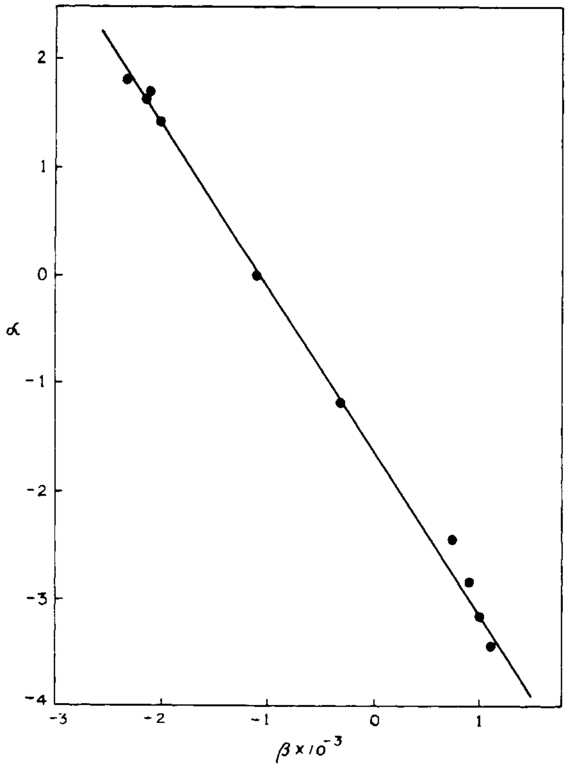

Figure 4. Linear relationship between α and β for ethyl alcohol–water mixtures

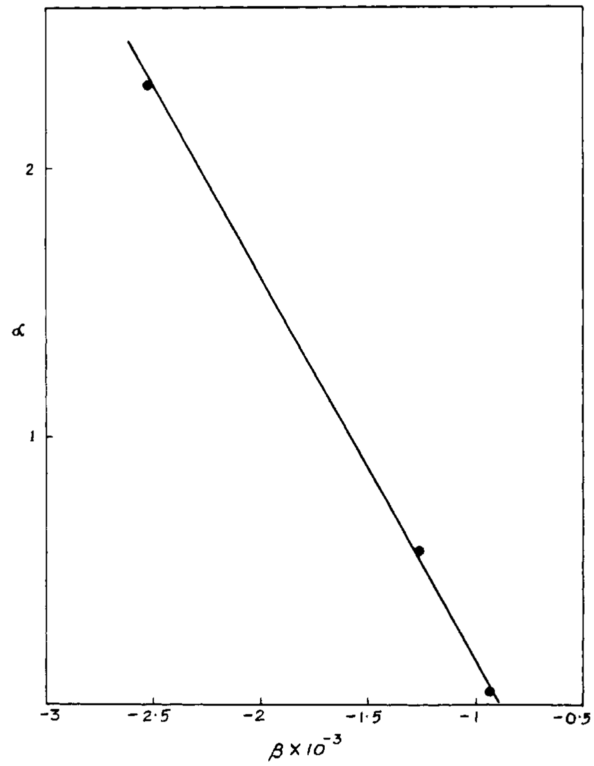

Figure 5. Linear relationship between α and β for sucrose solutions

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