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Viscosities of Binary Mixtures of Benzyl Acetate with Dioxane, Aniline, and *m*-Cresol

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Accurate measurements of viscosity as a function of composition of binary mixtures of benzyl acetate with dioxane, aniline and *meta*-cresol are reported. The data are interpreted in terms of Eyring's relation for the viscosity of pure liquids. The value of the interaction energy W_{visc} is calculated for each of the three mixtures.

THE STUDIES of Moore and Russel (*3*) and Moore and Styan (*4*) on the dielectric constants, volume and heats of mixing on mixtures of benzyl acetate with dioxane, aniline and *meta*-cresol were extended by our studies on surface tensions, boiling points (*2*), and viscosities. A treatment of viscosities of mixtures based on Eyring's (*6*) theory of viscosities of pure liquids, and assuming a regular solution type model for the activation free energy, represented rather well the dependence of mixture viscosities on composition.

EXPERIMENTAL

The purification of these liquids has already been reported elsewhere (*2*). Viscosities of the pure liquids and mixtures at different concentrations were determined at fixed temperatures. The measurements were carried out in an Ostwald viscometer which for aniline gave a time period of flow of 1479.4 seconds. The thermostat bath was controlled to within ±0.01° C. The densities were measured in a previously calibrated pycnometer and were reproducible to ±0.0001 gram/ml. The viscosities reported here are accurate to within 0.5%. The data for the pure liquids are given in the following table.

	Molecular Weight	Density Gram/Ml. (30° C.)	Boiling Point, ° C.	Viscosity cp.
Benzyl Acetate	150.17	1.0482	214.0	1.3525(40° C.)
Dioxane	88.10	1.0232	106.5	0.6256(40° C.)
Aniline	93.12	1.0151	184.5	3.1457(30° C.)
meta-Cresol	108.13	1.0275	194.4	1.0283(40° C.)

RESULTS AND DISCUSSION

Several empirical or semiempirical relations (*5*) have been used to represent the dependence of viscosity on concentration in binary liquid mixtures. Used frequently among them has been the Arrhenius relation:

$$\ln \eta_s = x_1 \ln \eta_1 + x_2 \ln \eta_2 \tag{1}$$

where η_s, η_1, η_2, are the viscosities of the solution; 1 and 2 the viscosities of pure liquids. This represents well the data for nearly ideal binary mixtures but does not represent data for non ideal solutions. The next order of approximation would appear to be a regular solution model. For this purpose Eyring's (*4*) model for the viscosity of a pure liquid:

$$\eta = \left(\frac{\lambda}{\alpha}\right)^2 \frac{hN}{V} e^{f/RT} \tag{2}$$

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η = is the absolute viscosity
λ = the distance between the adjacent moving layers of the molecules
α = the distance through which the shearing force acts
V = the molar volume
h = the Planck's constant
N = the Avagadro's number
f = the molar free energy of activation of flow
R = the gas constant
T = the absolute temperature

Equation 2 can be written as:

$$\frac{f}{RT} = \ln \frac{\eta V}{hN}\left(\frac{\alpha}{\lambda}\right)^2 \tag{3}$$

If for the mixture one assumes:

$$\frac{f_s}{RT} = x_1 \frac{f_1}{RT} + x_2 \frac{f_2}{RT} \tag{4}$$

and

$$\ln \frac{\alpha_s}{\lambda_s} = x_1 \ln \frac{\alpha_1}{\lambda_1} + x_2 \ln \frac{\alpha_2}{\lambda_2} \tag{5}$$

we then have:

$$\ln \eta_s V_s = x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2 \tag{6}$$

However, for regular solutions f_s would not be a linear function of f_1 and f_2. Instead we would have an additional term W given by the relation:

$$\frac{f_s}{RT} = x_2 \ln \frac{f_1}{RT} = x_2 \ln \frac{f_2}{RT} + x_1 x_2 \frac{W}{RT} \tag{7}$$

and defined as the interaction energy for the activation of flow. Equation 6 then takes the form:

$$\log \eta_s V_s = x_1 \log \eta_1 V_1 + x_2 \log \eta_2 V_2 + x_1 x_2 \frac{W_{\text{visc}}}{RT} \tag{8}$$

Our results on the experimental determination of viscosities and molar volumes at different concentrations for each mixture are shown in Tables I–III. $\Delta \log \eta V$, obtained by:

$$(\Delta \log \eta V)_{\text{exp}} = \log \eta_s V_s - x_1 \log \eta_1 V_1 - x_2 \log \eta_2 V_2 \tag{9}$$

is given in column 4 of each table. W_{visc} calculated at equimolar concentration for each system is presented at the top of the table. Column 5 shows $(\Delta \log \eta V)_{\text{calc}}$ obtained from W_{visc}. The last column shows the calculated viscosity of the mixture as calculated from the viscosities, molar volumes of the pure liquids and W_{visc}.

The agreement between the observed and calculated values of viscosities for all the three mixtures over the whole range of concentration is close and within experimental error.

Table I. Viscosities of Benzyl Acetate (Component 1) and Dioxan (Component 2). Temp., 40° C.

$W_{\text{visc}} = 146$ cal./mole

x_1	η_s	V_s	$(\Delta \log \eta V)_{\text{exp}}$	$(\Delta \log \eta V)_{\text{calc}}$	$\eta_{s\,\text{calc}}$
0.000	0.6256	86.1951	0.000	0.000	0.6256
0.200	0.7250	97.8715	0.0077	0.0163	0.7395
0.300	0.8024	103.8631	0.0210	0.0214	0.8302
0.380	0.8570	108.3284	0.0240	0.0240	0.8569
0.520	0.9581	116.4069	0.0254	0.0255	0.9578
0.645	1.0602	123.5991	0.0258	0.0233	1.0542
0.748	1.1470	129.4787	0.0229	0.0192	1.1369
0.875	1.2333	136.7236	0.0072	0.0112	1.2448
1.000	1.3525	143.9237	0.0000	0.0000	1.3525

Table II. Viscosities of Benzyl Acetate (Component 1) and Aniline (Component 2). Temp., 30° C.

$W_{\text{visc}} = 61$ cal./mole

x_1	η_s	V_s	$(\Delta \log \eta V)_{\text{exp}}$	$(\Delta \log \eta V)_{\text{calc}}$	$\eta_{s\,\text{calc}}$
0.000	3.1457	91.7348	0.000	0.0000	3.1457
0.125	2.9100	98.5560	0.0069	0.0048	2.8932
0.300	2.6000	107.6514	0.0115	0.0092	2.5861
0.435	2.3836	114.6352	0.0127	0.0108	2.3570
0.495	2.2845	117.7107	0.0110	0.0110	2.2844
0.605	2.1235	123.3907	0.0092	0.0105	2.1298
0.750	1.9285	131.0331	0.0060	0.0082	1.9384
0.850	1.8095	136.1135	0.0035	0.0056	1.8183
1.000	1.6524	143.4837	0.0000	0.0000	1.6524

Table III. Viscosities of Benzyl Acetate (Component 1) and *meta*-Cresol (Component 2). Temp., 40° C.

$W_{\text{visc}} = -112$ cal./mole

x_1	η_s	V_s	$(\Delta \log \eta V)_{\text{exp}}$	$(\Delta \log \eta V)_{\text{calc}}$	$\eta_{s\,\text{calc}}$
0.000	6.1800	105.1541	0.0000	0.0000	6.1800
0.115	5.1137	109.6211	−0.0148	−0.0080	5.1943
0.272	3.9172	115.7228	−0.0228	−0.0155	3.9837
0.435	3.0600	122.0481	−0.0196	−0.0192	3.0635
0.620	2.3370	129.1949	−0.0128	−0.0184	2.3082
0.810	1.7646	136.5694	−0.0091	−0.0120	1.7530
1.000	1.3525	143.9237	0.0000	0.0000	1.3525

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