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

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The viscosity of binary mixtures of partially miscible liquids has been little studied. Chadwell and his coworker(1) made careful determinations of viscosities at 10° and 25°C. of methyl acetate, ethyl acetate and ethyl ether in water, all of which display greater viscosities than the component viscosities—similar phenomena to the water solutions of methyl alcohol, ethyl alcohol, or acetic acid. They believed that the solvation might be the most plausible explanation for these cases, but gave no confirmation of the compound formation, probably with the reason that from these viscosity curves only no tracing could be made up to the points of maxima which roughly determine the composition of the molecular compounds in solution.

Howell(2) studied the system of phenol and water, the viscosity-concentration curves of which are sagged at all the temperatures below the critical solution temperature (66.4°C.), but with somewhat complex nature at 70°C. He noticed that the deviation maximum of the measured viscosities from those calculated from his adopted mixture law (linear in weight fraction) corresponded approximately to a compound of equimolecular proportion of phenol and water, and that from the sagged property of the viscosity curves the hydrate might partially dissociate in the manner: $C_6H_5OH + H_2O \rightleftarrows C_6H_5OH.H_2O \rightleftarrows C_6H_5O' + OH_3^{\cdot}$, but reported in his second communication(3) that the electrical conductivity at this phenol rich solution showed an extremely low value. This fact necessitated another suitable explanation. Thus, he assumed that at phenol rich solutions the other form of the ionic dissociation, $C_6H_5OH+H_2O \rightleftarrows C_6H_5OH_2^{\cdot}+OH'$, might occur and that this ionization might be the least at the equimolecular proportion of phenol and water to form a molecular compound $C_6H_5OH.H_2O$. Before accepting his hypotheses, however, one

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(1) H. M. Chadwell, *J. Am. Chem. Soc.*, **48** (1926), 1912; H. M. Chadwell & B. Asnes, *J. Am. Chem. Soc.*, **52** (1930), 3507.

(2) O. R. Howell, *Trans. Farad. Soc.*, **28** (1932), 912.

(3) O. R. Howell & C. Handford, *Trans. Farad. Soc.*, **29** (1933), 640.

must doubt the adaptability of the mixture law taken by him for calculating the deviation from the observed viscosity values.

The writer⁽⁴⁾ has recently developed the solvation viscosity in the following form:

$$\delta = \eta - \eta_0 = C_0(\eta_1^{\nu_1}\eta_2^{\nu_2})^{\frac{m}{\nu_1+\nu_2}}(1-z_m)^{\nu_1}z_m^{\nu_2}\,,$$

where δ is the solvation viscosity which is the difference of the measured viscosity η from that calculated from his formula for an ideal mixture η_0; η_1 and η_2 the viscosities of components 1 and 2; ν_1 and ν_2 the numbers of molecules of components 1 and 2 taking into chemical reaction to form a molecular compound; z_m the formal molar fraction of component 2; C_0 and m the constants independent of the temperature and concentration so long as the molecular compound exists in the concentration range, m which is termed by the stability coefficient being a numerical measure of the stability of the molecular compound.

The present paper is a study on binary mixtures of partially miscible liquids from the same standpoint of view. The viscosity values of the water solutions of ethyl acetate and of ethyl ether are quoted from Chadwell's data and those of phenol and water are from Howell's observations.

For the first two pairs the quotients $\frac{k_2a_2}{k_1a_1}$ at so near temperatures as 10° and 25°C. are regarded to be quite equal and the following values at 25°C. already obtained⁽⁵⁾ will be used:

For the water (1) and ethyl acetate (2) mixture, $\frac{k_2a_2}{k_1a_1} = \frac{1.64\times 1\ 25}{0.21\times 3.18}$ $= 3.07$; and for the water (1) and ethyl ether (2) mixture, $\frac{k_2a_2}{k_1a_1} = \frac{3.09}{0.21\times 3.18} = 4.63$, the numerator being the mean value of $k_2a_2 = 3.03$ and 3.15 calculated from the two mixtures of ethyl ether and ethyl alcohol and of ethyl ether and propyl alcohol which were discussed in part IV.⁽⁶⁾ For the system of water and phenol the quotient previously obtained at 20°C. may not be applicable to higher temperatures simply considering that the boiling points of these liquids differ much from each other. In fact, as table 1 shows, the quotients $\left(\frac{k_2a_2}{k_1a_1}\right)_z$ at the same concentration have different values at 50°, 60° and 70°C. By trial, the re-

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(4) This Bulletin, **8** (1933), 280.
(5) This Bulletin, **4** (1929), 25.
(6) This Bulletin, **4**(1933), 288.

ciprocals of these quotients at each temperature are found to be linear, from whose relationship the extrapolated values at $z=1$ can be easily estimated provided that the degree of association of water molecules undergo no change at infinite dilution with phenol. In column 7 in table 1 are shown the quotients thus obtained. The values in brackets denote the required quotients $\frac{k_2a_2}{k_1a_1}=\left(\frac{k_2a_2}{k_1a_1}\right)_z\frac{M_2}{M_1}$, M_1 and M_2 being the molecular weights of water and phenol respectively.

Table 1.

$H_2O-C_6H_5OH$ (Howell).

$z-C_6H_5OH$		0.70	0.75	0.80	0.85	0.90	0.95	1.00
$\left(\frac{k_2a_2}{k_1a_2}\right)z$	50°	0.306	0.267	0.239	0.215	0.194	0.178	0.165 (0.86)
	60°	0.337	0.299	0.274	0.249	0.227	0.207	0.194 (1.01)
	70°	0.369	0.331	0.305	0.283	0.263	0.239	0.225 (1.17)

Table 2.

$H_2O-CH_3COOC_2H_5$, 10°C. (Chadwell & Asnes).

$z-CH_3COOC_2H_5$	$z_m-CH_3COOC_2H_5$	η	η_0	δ	$\frac{\delta}{(1-z_m)z_m}$
0.00000	0.00000	0.013105	—		
0.00522	0.00107	0.013230	0.013079	0.000151	(0.141)
0.02613	0.00547	0.014178	0.012972	0.001206	0.222
0.02845	0.00597	0.014242	0.012960	0.001282	0.216
0·03206	0.00673	0.014456	0.012942	0.001514	0.226
0.04804	0.01022	0.015117	0.012859	0.002258	0.223
0.06683	0.01444	0.015968	0.012760	0.003208	0.225
1.00000	1.00000	0.005092	—		
					mean 0.222

25°C. (Chadwell).

$z-CH_3COOC_2H_5$	$z_m-CH_3COOC_2H_5$	η	η_0	δ	$\frac{\delta}{(1-z_m)z_m}$
0.00000	0.00000	0.008949	—		
0.00676	0.00139	0.009095	0.008929	0.000166	0.120
0.00892	0.00184	0.009129	0.008923	0.000206	0.112
0.01815	0.00377	0.009354	0.008895	0.000459	0.122
0.03041	0.00638	0.009652	0.008858	0.000794	0.125
0.03284	0.00690	0.009678	0.008851	0.000827	0.121
0.04809	0.01023	0.010043	0.008804	0.001239	0.122
0.06170	0.01328	0.010357	0.008762	0.001595	0.122
1.00000	1.00000	0.004244	—		
					mean 0.121

Table 3.

$H_2O-(C_2H_5)_2O$, 10°C. (Chadwell & Asnes).

$z-(C_2H_5)_2O$	$z_m-(C_2H_5)_2O$	η	η_0	δ	$\frac{\delta}{(1-z_m)z_m}$
0.00000	0.00000	0.013105	—		
0.01031	0.00253	0.013640	0.012983	0.000657	0.261
0.01408	0.00346	0.013870	0.012939	0.000931	0.270
0.02894	0.00720	0.014747	0.012764	0.001983	0.277
0.05751	0.01462	0.016622	0.012430	0.004192	0.290
1.00000	1.00000	0.002609	—		
					mean 0.275

25°C. (Chadwell).

$z-(C_2H_5)_2O$	$z_m-(C_2H_5)_2O$	η	η_0	δ	$\frac{\delta}{(1-z_m)z_m}$
0.00000	0.00000	0.008949	—		
0.01360	0.00334	0.009366	0.008846	0.000520	0.156
0.02060	0.00509	0.009597	0.008793	0.000804	0.159
0.03089	0.00769	0.009959	0·008716	0.001243	0.163
0.03485	0.00954	0.010099	0.008662	0.001247	0.152
0.05848	0.01488	0.010883	0.008509	0.002437	0.162
1.00000	1.00000	0.002216	—		
					mean 0.158

Table 4.

$H_2O-C_6H_5OH$ (Howell), 50°C.

$z-C_6H_5OH$	$z_m-C_6H_5OH$	η	η_0	δ	$\frac{\delta}{(1-z_m)z_m}$	$\frac{\delta}{(1-z_m)^3z_m}$
0.00	0.0000	0.005500	—			
0.02	0.0039	0.005696	0.005599	0.000097	0.025	
0.04	0.0079	0.005898	0.005700	0.000198	0.025	
0.06	0.0121	0.006110	0.005807	0.000303	0.025	
0.08	0.0164	0.006340	0.005916	0.000424	0.026	
0.10	0.0208	0.006600	0.006027	0.000573	0.028	
				mean	0.026	
0.70	0.3088	0.01775	0.01366	0.00409		0.040
0.75	0.3650	0.01858	0.01523	0.00335		0.036
0.80	0.4339	0.01981	0.01718	0.00263		0.033
0.85	0.5206	0.02164	0.01970	0.00194		0.034
0.90	0.6328	0.02420	0.02306	0.00141		0.036
0.95	0.7843	0.02820	0.02778	0.00042		(0.053)
						mean 0.036
1.00	1.0000	0.03491	—			

60°C.

z—C_6H_5OH	z_m—C_6H_5OH	η	η_0	δ	$\frac{\delta}{(1-z_m)z_m}$	$\frac{\delta}{(1-z_m)^3z_m}$
0.00	0.0000	0.004700	—			
0.02	0.0039	0.004850	0.004784	0.000066	0.017	
0.04	0.0079	0.005000	0.004871	0.000129	0.016	
0.06	0.0121	0.005188	0.004962	0.000226	0.019	
0.08	0.0164	0.005360	0.005055	0.000305	0.019	
0.10	0.0208	0.005568	0.005150	0.000418	0.020	
				mean	0.018	
0.70	0.3088	0.01413	0.01137	0.00276		0.027
0.75	0.3650	0.01485	0.01257	0.00228		0.024
0.80	0.4339	0.01591	0.01405	0.00186		0.024
0.85	0.5206	0.01725	0.01591	0.00134		0.023
0.90	0.6328	0.01910	0.01831	0.00079		0.025
0.95	0.7843	0.02180	0.02155	0.00025		(0.032)
					mean	0.025
1.00	1.0000	0.02614	—			

70°C.

z—C_6H_5OH	z_m--C_6H_5OH	η	η_0	δ	$\frac{\delta}{(1-z_m)z_m}$	$\frac{\delta}{(1-z_m)^3z_m}$
0.00	0.0000	0.004075	—			
0.02	0.0039	—				
0.04	0.0079	—				
0.06	0.0121	—				
0.08	0.0164	—				
0.10	0.0208	0.004771	0.004468	0.000303	0.015	
0.70	0.3088	0.01157	0.00964	0.00183		0.018
0.75	0.3650	0.01215	0.01059	0.00156		0.017
0.80	0.4339	0.01298	0.01174	0.00124		0.020
0.85	0.5206	0.01405	0.01314	0.00091		0.016
0.90	0.6328	0.01547	0.01491	0.00056		0.018
0.95	0.7843	0.01735	0.01720	0.00015		0.019
					mean	0.018
1.00	1.0000	0.02028	—			

As seen from tables 2 and 3, the values $\frac{\delta}{(1-z_m)z_m}$ keep constancy for the studied concentration ranges, and their temperature variations are expressed by the equations:

$$\log\frac{\delta}{(1-z_m)z_m} = 3.513+\frac{2.00}{1+1}\log(\eta_1\eta_2)$$

and

$$\log\frac{\delta}{(1-z_m)z_m} = 3.903+\frac{2.00}{1+1}\log(\eta_1\eta_2)$$

respectively, whence we may postulate that $CH_3COOC_2H_5 . H_2O$ and $(C_2H_5)_2O.H_2O$ exist in solution.

As to the water and phenol mixture, two hydrates exist in solution. The hydrate $C_6H_5OH.3H_2O$ with the stability coefficient $m = 2.00$ at phenol rich solutions is a proof of the extremely low electrical conductivity observed by Howell. The temperature change of the solvation viscosity is completely expressed by the equation:

$$\log\frac{\delta}{(1-z_m)^3 z_m} = 2.680+\frac{2.00}{3+1}\log(\eta_1^3\eta_2)\ .$$

The hydrate $C_6H_5OH.H_2O$ existing at water rich solutions and having

$$\log\frac{\delta}{(1-z_m)z_m} = 1.477+\frac{1.65}{1+1}\log(\eta_1\eta_2)$$

indicates from the magnitude of m that it is undoubtedly subjected to the ionic dissociation, $C_6H_5OH.H_2O \rightleftarrows C_6H_5O' + OH_3^{\cdot}$, the equilibrium being kept by 2/3 part of undissociated molecule and 1/3 part of dissociated into the two ions.

The present and foregoing studies on the stability coefficient m lead to the conclusion (i) that m takes the value 2 if the molecular compound firmly exists without any dissociation such as the molecular compounds $CH_3OH.2H_2O$, $C_2H_5OH.3H_2O$, $CH_3COOC_2H_5 . H_2O$ and $(C_2H_5)_2O.H_2O$—this idea is simply derived from the mathematical consideration of the order of the term, $\eta-\eta_0$, and (ii) that m takes the value less than 2 if the molecular compound suffers ionic dissociation or partial molecular dissociation as are the cases of the monohydrates $CH_3COOH.H_2O$ ($m = 1.68$) and $C_6H_5OH.H_2O$ ($m = 1.65$), or is the case of the dihydrate $C_2H_5OH.2H_2O$ ($m = 1.83$) which is in the equilibrium, $C_2H_5OH.2H_2O \leftrightarrows C_2H_5OH.H_2O + H_2O$.

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