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

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In the earlier communication of the study on this subject[1] the writer has shown that the viscosity of binary mixtures showing a maximum against the concentration, such as systems CH_3COOH–H_2O, CH_3OH–H_2O, and C_2H_5OH–H_2O, can be explained with quite satisfaction by postulating the difference (δ) of measured viscosity (η) from that calculated from his viscosity formula for chemically indifferent mixtures (η_0) or "the solva-

(1) This Bulletin **4** (1929), 25.

tion viscosity" to be proportionate to the encounter probability of ν_1 and ν_2 molecules of the components to form a molecular compound. Thus,

$$\eta = \eta_0 + \delta ,$$

$$\eta_0 = \eta_1 + (\eta_2 - \eta_1) \frac{k_2 a_2 z_m}{k_1 a_1 (1 - z_m) + k_2 a_2 z_m} ,$$

$$\delta = C(1 - z_m)^{\nu_1} z_m^{\nu_2} ,$$

where η, a, k with suffixes 1 and 2 signify the viscosity coefficients, the association degrees and field constants of components 1 and 2 respectively; z_m a formal molar fraction of component 2; and C a proportional constant.

According to this theory the criterion for determining the composition of a molecular compound is not the position of the maximum often shifting with temperature which has given annoyance to many earlier investigators, but the keeping constancy of the proportional constant C which strictly holds good for viscosity isotherms so long as the molecular compound exists in the mixture.

Dependence of the Field Constant k on Temperature.

Before entering into further study on the proportional constant C, it is necessary to test the dependence of the field constant on temperature. Since association degrees of liquids are functions of temperature, the mixtures which are to be taken for test of the proposition are those which must be composed of two non-associated and chemically indifferent liquids. The following case studied by Meyer and Mylius[2] is very favorable for this purpose.

The fact that is readily understood from Table 1 is that the field constant of any liquid is independent of temperature or otherwise it has the same temperature variation, and that the factor in $\frac{k_2 a_2}{k_1 a_1}$ which changes with temperature is the ratio of the association degree of component 2 to that of component 1. So that, for such pairs as are composed of liquids having the same temperature coefficient of the association degrees, the term $\frac{k_2 a_2}{k_1 a_1}$ is of course independent of temperature and the above equation which originally holds true for viscosity isotherms is also valid for any temperature.

(2) J. Meyer & B. Mylius, *Z. physik. Chem.* **95** (1920), 349.

Table 1.

C_6H_6–C_6H_5Br, Meyer & Mylius.

z—C_6H_5Br		0°C.	10°C.	20°C.	30°C.	40°C.	50°C.	60°C.	70°C.
0.00000	η	0.00912	0.00758	0.00652	0.00564	0.00503	0.00443	0.00392	0.00358
0.24746	η	0.00976	0.00827	0.00703	0.00616	0.00546	0.00487	0.00438	0.00398
	$\left(\frac{k_2 a_2}{k_1 a_1}\right)_z$	0.37	0.46	0.38	0.43	0.39	0.44	0.50	0.39
0.50238	η	0.01115	0.00926	0.00788	0.00685	0.00603	0.00567	0.00500	0.00448
	$\left(\frac{k_2 a_2}{k_1 a_1}\right)_z$	0.49	0.47	0.41	0.41	0.37	0.52	0.48	0.44
0.74746	η	0.01257	0.01059	0.00915	0.00803	0.00709	0.00636	0.00579	0.00524
	$\left(\frac{k_2 a_2}{k_1 a_1}\right)_z$	0.45	0.45	0.44	0.46	0.43	0.42	0.45	0.44
1.00000	η	0.01515	0.01282	0.01117	0.00979	0.00872	0.00794	0.00719	0.00652
Mean	$\left(\frac{k_2 a_2}{k_1 a_1}\right)_z$	**0.44**	**0.46**	**0.41**	**0.43**	**0.40**	**0.46**	**0.48**	**0.42**

Table 2.

CH_3OH–C_2H_5OH, Bingham, White, Thomas, & Cadwell.

z—C_2H_5OH	25°C.		35°C.		45°C.		55°C.	
	η	$\left(\frac{k_2 a_2}{k_1 a_1}\right)_z$	η	$\left(\frac{k_2 a_2}{k_1 a_1}\right)_z$	η	$\left(\frac{k_2 a_2}{k_1 a_1}\right)_z$	η	$\left(\frac{k_2 a_2}{k_1 a_1}\right)_z$
0.0000	0.00548		0.00476		0.00420		0.00371	
0.2616	0.00639	0.55	0.00552	0.59	0.00481	0.60	0.00423	0.66
0.4960	0.00737	0.53	0.00635	0.58	0.00548	0.60	0.00476	0.63
0.7385	0.00880	0.54	0.00746	0.56	0.00636	0.59	0.00546	0.62
1.0000	0.01099		0.00917		0.00766		0.00645	
	Mean	**0.54**		**0.58**		**0.60**		**0.63**

Table 3.

H_2O-CH_3OH, Traube.[3] $\eta_0 = \eta_1 + (\eta_2 - \eta_1)\dfrac{0.96\,z_m}{(1-z_m)+0.96\,z_m}$.

z–CH_3OH		0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.80	1.00
z_m–CH_3OH		0.0000	0.0588	0.1233	0.1943	0.2727	0.3601	0.4576	0.6925	1.0000
20°C.	η	0.01035	0.01338	0.01639	0.01829	0.01881	0.01816	0.01629	0.01142	0.00607
	η_0	—	0.01011	0.00984	0.00955	0.00922	0.00885	0.00844	0.00742	—
	δ		0.00327	0.00655	0.00874	0.00959	0.00931	0.00785	0.00400	
	$\dfrac{\delta}{(1-z_m)^2 z_m}$		0.063	0.069	0.069	0.067	0.063	0.058	0.063	
					Mean	**0.065**				
30°C.	η	0.00819	0.01056	0.01240	0.01378	0.01417	0.01378	0.01273	0.00933	0.00541
	η_0	—	0.00803	0.00786	0.00767	0.00745	0.00722	0.00695	0.00629	—
	δ		0.00253	0.00454	0.00611	0.00672	0.00656	0.00578	0.00304	
	$\dfrac{\delta}{(1-z_m)^2 z_m}$		0.049	0.048	0.048	0.047	0.045	0.043	0.046	
					Mean	**0.047**				
40°C.	η	0.00668	0.00823	0.00960	0.01064	0.01091	0.01073	0.01004	0.00769	0.00463
	η_0	—	0.00656	0.00644	0.00629	0.00614	0.00596	0.00576	0.00528	—
	δ		0.00167	0.00316	0.00435	0.00477	0.00477	0.00428	0.00241	
	$\dfrac{\delta}{(1-z_m)^2 z_m}$		0.032	0.033	0.035	0.033	0.032	0.032	(0.037)	
					Mean	**0.033**				
50°C.	η	0.00566	0.00688	0.00788	0.00867	0.00884	0.00875	0.00817	0.00650	0.00406
	η_0	—	0.00557	0.00547	0.00536	0.00524	0.00510	0.00494	0.00457	—
	δ		0.00131	0.00241	0.00331	0.00360	0.00365	0.00323	0.00193	
	$\dfrac{\delta}{(1-z_m)^2 z_m}$		0.025	0.025	0.026	0.025	0.025	0.024	(0.030)	
					Mean	**0.025**				
60°C.	η	0.00495	0.00565	0.00645	0.00699	0.00717	0.00730	0.00685	0.00569	0.00361
	η_0	—	0.00487	0.00479	0.00470	0.00460	0.00448	0.00435	0.00403	—
	δ		0.00078	0.00166	0.00229	0.00257	0.00282	0.00250	0.00166	
	$\dfrac{\delta}{(1-z_m)^2 z_m}$		(0.015)	0.018	0.018	0.017	0.019	0.019	(0.025)	
					Mean	**0.018**				

(3) J. Traube, *Ber.* **19** (1886), 871.

Table 4.

$H_2O-C_2H_5OH$, International Critical Tables, V, 22.

$$\eta_0 = \eta_1 + (\eta_2 - \eta_1)\frac{0.70\,z_m}{(1-z_m)+0.70\,z_m}\,.$$

	$z-C_2H_5OH$	0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00
	$z_m-C_2H_5OH$	0.0000	0.0417	0.0891	0.1435	0.2068	0.2811	0.3698	0.4773	0.6101	0.7787	1.0000
0°C.	η	0.01794	0.03215	0.05275	0.06900	0.07150	0.06625	0.05715	0.04720	0.03648	0.02694	0.01776
	η_0	—	0.01793	0.01793	0.01792	0.01791	0.01790	0.01789	0.01787	0.01785	0.01781	—
	δ		0.01422	0.03482	0.05108	0.05359	0.04835	0.03926	0.02933	0.01863	0.00913	
	$\frac{\delta}{(1-z_m)^3 z_m}$		(0.388)	0.518	0.565	0.519	0.463	0.424	0.430	0.515	(1.08)	
					Mean	**0.491**						
	$\frac{\delta}{(1-z_m)^2 z_m}$							(0.267)	0.220	0.201	0.239	
									Mean	**0.232**		
10°C.	η	0.01310	0.02162	0.03235	0.04095	0.04355	0.04174	0.03787	0.03268	0.02663	0.02048	0.01480
	η_0	—	0.01315	0.01321	0.01328	0.01336	0.01346	0.01359	0.01376	0.01399	0.01431	—
	δ		0.00847	0.01914	0.02767	0.03019	0.02828	0.02428	0.01892	0.01264	0.00617	
	$\frac{\delta}{(1-z_m)^3 z_m}$		(0.231)	0.284	0.307	0.292	0.271	0.262	0.278	(0.350)	(0.731)	
					Mean	**0.282**						
	$\frac{\delta}{(1-z_m)^2 z_m}$							(0.165)	0.145	0.136	0.161	
									Mean	**0.147**		
20°C.	η	0.01009	0.01548	0.02168	0.02670	0.02867	0.02832	0.02642	0.02369	0.01998	0.01601	0.01221
	η_0	—	0.01015	0.01023	0.01031	0.01042	0.01055	0.01071	0.01092	0.01120	0.01160	—
	δ		0.00533	0.01145	0.01639	0.01825	0.01777	0.01571	0.01277	0.00878	0.00441	
	$\frac{\delta}{(1-z_m)^3 z_m}$		(0.145)	0.170	0.182	0.177	0.170	0.170	(0.187)	(0.243)	(0.522)	
					Mean	**0.174**						
	$\frac{\delta}{(1-z_m)^2 z_m}$							0.107	0.098	0.095	0.116	
									Mean	**0.104**		
30°C.	η	0.00800	0.01153	0.01539	0.01849	0.01991	0.02001	0.01906	0.01744	0.01519	0.01270	0.00997
	η_0	—	0.00806	0.00813	0.00821	0.00830	0.00842	0.00857	0.00877	0.00903	0.00940	—
	δ		0.00347	0.00726	0.01028	0.01161	0.01159	0.01049	0.00867	0.00616	0.00330	
	$\frac{\delta}{(1-z_m)^3 z_m}$		(0.095)	0.108	0.114	0.113	0.111	0.113	(0.127)	(0.170)	(0.391)	
					Mean	**0.112**						
	$\frac{\delta}{(1-z_m)^2 z_m}$							0.071	0.066	0.066	(0.086)	
									Mean	**0.068**		

Table 4.—(*Concluded*)

z—C_2H_5OH	0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00
z_m—C_2H_5OH	0.0000	0.0417	0.0891	0.1435	0.2068	0.2811	0.3698	0.4773	0.6101	0.7787	1.0000
40°C. η	0.00654	0.00896	0.01144	0.01353	0.01455	0.01475	0.01426	0.01328	0.01181	0.01022	0.00824
η_0	—	0.00659	0.00665	0.00672	0.00680	0.00691	0.00704	0.00720	0.00743	0.00775	—
δ		0.00237	0.00479	0.00681	0.00775	0.00784	0.00722	0.00608	0.00438	0.00247	
$\frac{\delta}{(1-z_m)^3 z_m}$		(0.065)	0.071	0.075	0.075	0.075	(0.078)	(0.089)	(0.121)	(0.293)	
				Mean	**0.074**						
$\frac{\delta}{(1-z_m)^2 z_m}$						(0.054)	0.049	0.047	0.047	(0.065)	
							Mean	**0.048**			
50°C. η	0.00549	0.00725	0.00896	0.01038	0.01116	0.01136	0.01109	0.01044	0.00950	0.00835	0.00695
η_0	—	0.00553	0.00558	0.00565	0.00572	0.00580	0.00592	0.00606	0.00625	0.00653	—
δ		0.00172	0.00338	0.00473	0.00544	0.00556	0.00517	0.00438	0.00325	0.00182	
$\frac{\delta}{(1-z_m)^3 z_m}$		(0.047)	0.050	0.052	0.053	0.053	(0.056)	(0.064)	(0.090)	(0.216)	
				Mean	**0.052**						
$\frac{\delta}{(1-z_m)^2 z_m}$						(0.038)	0.035	0.034	0.035	(0.048)	
							Mean	**0.035**			
60°C. η	0.00470	0.00602	0.00728	0.00826	0.00887	0.00904	0.00887	0.00841	0.00778	0.00695	0.00590
η_0	—	0.00474	0.00478	0.00483	0.00489	0.00496	0.00505	0.00517	0.00533	0.00555	—
δ		0.00128	0.00250	0.00343	0.00398	0.00408	0.00382	0.00324	0.00245	0.00140	
$\frac{\delta}{(1-z_m)^3 z_m}$		(0.035)	0.037	0.038	0.039	0.039	(0.041)	(0.047)	(0.068)	(0.166)	
				Mean	**0.038**						
$\frac{\delta}{(1-z_m)^2 z_m}$						(0.028)	0.026	0.025	0.026	(0.039)	
							Mean	**0.026**			
70°C. η	0.00407	0.00509	0.00606	0.00677	0.00724	0.00739	0.00727	0.00696	0.00648	0.00549	0.00506
η_0	—	0.00410	0.00413	0.00417	0.00422	0.00428	0.00436	0.00446	0.00459	0.00477	—
δ		0.00099	0.00193	0.00260	0.00302	0.00311	0.00291	0.00250	0.00189	0.00072	
$\frac{\delta}{(1-z_m)^3 z_m}$		(0.027)	0.029	0.029	0.029	0.030	(0.031)	(0.037)	(0.052)	(0.085)	
				Mean	**0.029**						
$\frac{\delta}{(1-z_m)^2 z_m}$						(0.021)	0.020	0.019	0.020	0.019	
							Mean	**0.020**			

Table 5.

H_2O-CH_3COOH, International Critical Tables, V, 20.

$$\eta_0 = \eta_1 + (\eta_2 - \eta_1)\frac{1.29\,z_m}{(1-z_m)+1.29\,z_m}\ .$$

$z-CH_3COOH$	0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00
z_m-CH_3COOH	0.0000	0.0323	0.0698	0.1140	0.1677	0.2417	0.3104	0.4120	0.4737	0.7300	1.0000
15°C. η	0.01145	0.01360	0.01630	0.01910	0.02160	0.02475	0.02765	0.03020	0.03105	0.02680	0.01350
15°C. η_0	—	0.01153	0.01163	0.01174	0.01187	0.01205	0.01220	0.01242	0.01255	0.01304	—
15°C. δ		0.00207	0.00467	0.00736	0.00973	0.01270	0.01545	0.01778	0.01850	0.01376	
15°C. $\frac{\delta}{(1-z_m)z_m}$		(0.066)	0.072	0.073	0.070	0.069	0.072	0.073	0.074	0.070	
					Mean	**0.072**					
20°C. η	0.01009	0.01210	0.01415	0.01635	0.01870	0.02135	0.02390	0.02640	0.02695	0.02310	0.01265
20°C. η_0	—	0.01020	0.01032	0.01045	0.01062	0.01084	0.01103	0.01131	0.01147	0.01208	—
20°C. δ		0.00190	0.00383	0.00590	0.00808	0.01051	0.01287	0.01509	0.01548	0.01102	
20°C. $\frac{\delta}{(1-z_m)z_m}$		0.061	0.059	0.058	0.058	0.057	0.060	0.062	0.062	(0.056)	
					Mean	**0.060**					
25°C. η	0.00895	0.01065	0.01250	0.01450	0.01655	0.01870	0.02085	0.02290	0.02365	0.02050	0.01155
25°C. η_0	—	0.00906	0.00918	0.00932	0.00949	0.00971	0.00991	0.01019	0.01035	0.01097	—
25°C. δ		0.00159	0.00332	0.00518	0.00706	0.00899	0.01094	0.01271	0.01330	0.00953	
25°C. $\frac{\delta}{(1-z_m)z_m}$		0.051	0.051	0.051	0.051	0.049	0.051	0.053	0.053	0.048	
					Mean	**0.051**					
30°C. η	0.00800	0.00955	0.01110	0.01290	0.01475	0.01660	0.01850	0.02040	0.02095	0.01840	0.01065
30°C. η_0	—	0.00811	0.00823	0.00838	0.00855	0.00877	0.00897	0.00926	0.00942	0.01006	—
30°C. δ		0.00144	0.00287	0.00452	0.00620	0.00783	0.00953	0.01114	0.01153	0.00834	
30°C. $\frac{\delta}{(1-z_m)z_m}$		0.046	0.044	0.045	0.044	0.043	0.045	0.046	0.046	0.042	
					Mean	**0.045**					
35°C. η	0.00721	0.00855	0.01000	0.01150	0.01315	0.01480	0.01650	0.01815	0.01855	0.01655	0.00990
35°C. η_0	—	0.00732	0.00745	0.00759	0.00776	0.00799	0.00820	0.01849	0.00866	0.00930	—
35°C. δ		0.00123	0.00255	0.00391	0.00539	0.00681	0.00830	0.00966	0.00989	0.00725	
35°C. $\frac{\delta}{(1-z_m)z_m}$		0.039	0.039	0.039	0.039	0.037	0.039	0.040	0.040	0.037	
					Mean	**0.039**					

Table 5.—(*Continued*)

z—CH_3COOH		0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00
z_m—CH_3COOH		0.0000	0.0323	0.0698	0.1140	0.1677	0.2417	0.3104	0.4120	0.4737	0.7300	1.0000
40°C.	η	0.00654	0.00780	0.00905	0.01040	0.01180	0.01325	0.01470	0.01620	0.01660	0.01490	0.00925
	η_0	—	0.00665	0.00678	0.00692	0.00709	0.00733	0.00753	0.00782	0.00799	0.00864	—
	δ		0.00115	0.00227	0.00348	0.00471	0.00592	0.00717	0.00838	0.00861	0.00626	
	$\frac{\delta}{(1-z_m)z_m}$		(0.037)	0.035	0.035	0.034	0.032	0.034	0.035	0.035	0.032	
						Mean	**0.034**					
45°C.	η	0.00597	0.00710	0.00820	0.00940	0.01060	0.01185	0.01320	0.01445	0.01485	0.01345	0.00865
	η_0	—	0.00608	0.00620	0.00635	0.00652	0.00674	0.00694	0.00723	0.00739	0.00803	—
	δ		0.00102	0.00200	0.00305	0.00408	0.00511	0.00626	0.00722	0.00746	0.00542	
	$\frac{\delta}{(1-z_m)z_m}$		(0.033)	0.031	0.030	0.029	0.028	0.029	0.030	0.030	0.028	
						Mean	**0.029**					
50°C.	η	0.00549	0.00650	0.00745	0.00855	0.00965	0.01080	0.01190	0.01305	0.01340	0.01225	0.00810
	η_0	—	0.00650	0.00572	0.00586	0.00603	0.00625	0.00645	0.00673	0.00689	0.00752	—
	δ		0.00090	0.00173	0.00269	0.00362	0.00455	0.00545	0.00632	0.00651	0.00478	
	$\frac{\delta}{(1-z_m)z_m}$		(0.029)	0.027	0.027	0.026	0.025	0.026	0.026	0.026	0.024	
						Mean	**0.026**					
55°C.	η	0.00507	0.00600	0.00680	0.00775	0.00880	0.00985	0.01080	0.01195	0.01215	0.01125	0.00760
	η_0	—	0.00517	0.00529	0.00543	0.00559	0.00581	0.00600	0.00627	0.00643	0.00704	—
	δ		0.00083	0.00151	0.00232	0.00321	0.00404	0.00480	0.00568	0.00572	0.00421	
	$\frac{\delta}{(1-z_m)z_m}$		(0.027)	0.023	0.023	0.023	0.022	0.022	0.023	0.023	0.021	
						Mean	**0.023**					
60°C.	η	0.00470	0.00550	0.00625	0.00710	0.00800	0.00900	0.00995	0.01090	0.01105	0.01030	0.00700
	η_0	—	0.00479	0.00490	0.00503	0.00517	0.00537	0.00555	0.00579	0.00594	0.00649	—
	δ		0.00071	0.00135	0.00207	0.00283	0.00363	0.00440	0.00511	0.00511	0.00381	
	$\frac{\delta}{(1-z_m)z_m}$		(0.023)	0.021	0.021	0.020	0.020	0.021	0.021	0.021	0.019	
						Mean	**0.020**					
65°C.	η	0.00437	0.00505	0.00575	0.00655	0.00735	0.00820	0.00900	—	0.01010	—	0.00675
	η_0	—	0.00447	0.00458	0.00471	0.00486	0.00506	0.00524		0.00565		—
	δ		0.00058	0.00117	0.00184	0.00249	0.00314	0.00376		0.00445		
	$\frac{\delta}{(1-z_m)z_m}$		(0.019)	0.018	0.018	0.018	0.017	0.018		0.018		
						Mean	**0.018**					

Table 5.—(*Concluded*)

		0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00
z–CH_3COOH		0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00
z_m–CH_3COOH		0.0000	0.0323	0.0698	0.1140	0.1677	0.2417	0.3104	0.4120	0.4737	0.7300	1.0000
75°C.	η	0.00381	0.00440	0.00495	0.00560	0.00630	0.00700	0.00765	—	0.00855	—	0.00605
	η_0	—	0.00390	0.00401	0.00413	0.00427	0.00446	0.00463		0.00501		—
	δ		0.00050	0.00094	0.00147	0.00203	0.00254	0.00302		0.00354		
	$\frac{\delta}{(1-z_m)z_m}$		0.016	0.015	0.015	0.015	0.014	0.014		0.014		
						Mean	**0.015**					
85°C.	η	0.00336	0.00385	0.00435	0.00490	0.00545	0.00605	0.00660	—	0.00740	—	0.00545
	η_0	—	0.00345	0.00354	0.00366	0.00379	0.00397	0.00413		0.00448		—
	δ		0.00040	0.00081	0.00124	0.00166	0.00208	0.00247		0.00292		
	$\frac{\delta}{(1-z_m)z_m}$		0.013	0.013	0.012	0.012	0.011	0.012		0.012		
						Mean	**0.012**					
95°C.	η	0.00299	0.00340	0.00385	0.00430	0.00475	0.00530	0.00575	—	0.00640	—	0.00490
	η_0	—	0.00307	0.00316	0.00326	0.00338	0.00355	0.00369		0.00402		—
	δ		0.00033	0.00069	0.00104	0.00137	0.00175	0.00206		0.00238		
	$\frac{\delta}{(1-z_m)z_m}$		0.011	0.011	0.010	0.010	0.010	0.010		0.010		
						Mean	**0.010**					

Table 6.

Molecular compound $CH_3OH \cdot 2H_2O$. $\log C_{calc.} = 2.964 + \frac{2.00}{2+1} \log (\eta_1^2 \eta_2)$.

Temp. C.	η_1	η_2	$C_{obs.}$	$C_{calc.}$	η_m
20	0.01035	0.00607	0.065	0.069	6.3
30	0.00819	0.00541	0.047	0.047	4.3
40	0.00668	0.00463	0.033	0.032	3.0
50	0.00566	0.00406	0.025	0.024	2.2
60	0.00495	0.00361	0.018	0.018	1.7

Table 7.

Molecular compound $C_2H_5OH \cdot 3H_2O$. $\log C_{calc.} = 3.191 + \frac{2.00}{3+1} \log(\eta_1^3 \eta_2)$.

Temp. C.	η_1	η_2	$C_{obs.}$	$C_{calc.}$	η_m
0	0.01794	0.01776	0.491	0.498	773
10	0.01310	0.01480	0.282	0.283	439
20	0.01009	0.01221	0.174	0.174	270
30	0.00800	0.00997	0.112	0.111	172
40	0.00654	0.00824	0.074	0.074	115
50	0.00549	0.00695	0.052	0.053	82
60	0.00470	0.00590	0.038	0.038	59
70	0.00407	0.00506	0.029	0.029	45

Table 8.

Molecular compound $C_2H_5OH \cdot 2H_2O$. $\log C_{calc.} = 2.612 + \frac{1.83}{2+1} \log(\eta_1^2 \eta_2)$.

Temp. C.	η_1	η_2	$C_{obs.}$	$C_{calc.}$	η_m
0	0.01794	0.01776	0.232	0.265	108
10	0.01310	0.01480	0.147	0.145	59
20	0.01009	0.01221	0.104	0.102	42
30	0.00800	0.00997	0.068	0.068	28
40	0.00654	0.00824	0.048	0.048	20
50	0.00549	0.00695	0.035	0.035	14
60	0.00470	0.00590	0.026	0.026	11
70	0.00407	0.00506	0.020	0.020	8.2

Table 9.

Molecular compound $CH_3COOH \cdot H_2O$. $\log C_{calc.} = 2.065 + \frac{1.68}{1+1} \log(\eta_1\eta_2)$.

Temp. C.	η_1	η_2	$C_{obs.}$	$C_{calc.}$	η_m
15	0.01145	0.01350	0.072	0.073	8.5
20	0.01009	0.01265	0.060	0.062	7.2
25	0.00895	0.01155	0.051	0.052	6.0
30	0.00800	0.01065	0.045	0.044	5.1
35	0.00721	0.00990	0.039	0.038	4.4
40	0.00654	0.00925	0.034	0.033	3.8
45	0.00597	0.00865	0.029	0.029	3.4
50	0.00549	0.00810	0.026	0.026	3.0
55	0.00507	0.00760	0.023	0.023	2.7
60	0.00470	0.00700	0.020	0.020	2.3
65	0.00437	0.00675	0.018	0.018	2.1
75	0.00381	0.00605	0.015	0.015	1.7
85	0.00336	0.00545	0.012	0.012	1.4
95	0.00299	0.00490	0.010	0.010	1.2

As to the temperature variation of association degrees Ramsay and Shields(4) calculated those of the abnormal liquids-water, methyl alcohol, ethyl alcohol and acetic acid from the deviation of their surface tension equation. Apart from the justification of their calculation for the absolute values of association degrees, we acknowledge from their results that the decreasing rates of molecular association of these liquids with rising temperature are nearly equal, temperature coefficients being $-0.0030 \sim -0.0035$.

A further test for methyl and ethyl alcohols with the viscosity data observed by Bingham, White, Thomas and Cadwell(5) affirms the fact.

Moreover as already studied, the solvation viscosities of systems CH_3COOH-H_2O, CH_3OH-H_2O and C_2H_5OH-H_2O have high values in comparison with η_0 at moderate concentrations, it is quite sufficient to regard that in the calculation of η_0 of each system $\frac{k_2a_2}{k_1a_1}$ is independent of temperature. In the above calculation, therefore, $\frac{k_2a_2}{k_1a_1}$ in each system has been put to be the same value as obtained in the previous paper.

(4) W. Ramsay & J. Shields, *Z. physik. Chem.* **12** (1893), 468; W. Ramsay, *Z. physik. Chem.* **15** (1894), 113.

(5) E. C. Bingham, G. F. White, A. Thomas, J. L. Cadwell, *Z. physik. Chem.* **83** (1913), 652.

The Viscosity Coefficient of a Molecular Compound and its Stability Coefficient.

As the theory demands, the proportional constant C in each system has proved to keep constancy for isothermal mixtures. The next study is its temperature variation.

Since the proportional constant C must involve in it the term which corresponds to the viscosity of a molecular compound, it is expected that there may exist some relationship between C and the viscosities of components η_1 and η_2, and if any, the component viscosities may probably take part in the form $\eta_1^{\nu_1}\eta_2^{\nu_2}$ as considered from the composition term $(1-z_m)^{\nu_1}z_m^{\nu_2}$. Then we may put C in the following form:

$$C = C_0(\eta_1^{\nu_1}\eta_2^{\nu_2})^{\frac{m}{\nu_1+\nu_2}},$$

where C_0 and m are constants independent of temperature.

The test of the postulation with the molecular compounds in the above three pairs is extremely good. The results of the calculation are tabulated in Tables 6, 7, 8 and 9.

Transform the expression into

$$\frac{C}{C_0} = (\eta_1^{\nu_1}\eta_2^{\nu_2})^{\frac{m}{\nu_1+\nu_2}}.$$

The left-hand side of the equation is no other than the viscosity coefficient of a molecular compound and let it be denoted by η_m, then

$$\eta_m = (\eta_1^{\nu_1}\eta_2^{\nu_2})^{\frac{m}{\nu_1+\nu_2}},$$

or taking logarithms of both sides

$$\log \eta_m = m\left\{\frac{\nu_1}{\nu_1+\nu_2}\log \eta_1 + \frac{\nu_2}{\nu_1+\nu_2}\log \eta_2\right\} \quad \ldots\ldots\ldots\ldots \quad (1)$$

Kendall[6] showed, with eighty four mixtures of presumably non-associated and chemically indifferent liquids, that the deviation from the straight line is generally least when the composition in the Arrhenius

(6) J. Kendall, Medd. K. Vetenskapsakad. *Nobelinst.* **2**, No. 25 (1913), 1.

logarithmic formula is expressed as molar fraction, i.e. in the same concentration as above

$$\log \eta = \frac{\nu_1}{\nu_1 + \nu_2} \log \eta_1 + \frac{\nu_2}{\nu_1 + \nu_2} \log \eta_2 \quad \ldots\ldots\ldots\ldots\ldots \quad (2)$$

The average divergence of this formula from the observed viscosity values is estimated by him to be $\pm 2.3\%$ or $m = 1 \pm 0.02$.

Comparing (1) with (2) it is understood that the greater the difference of m from unity the more stable the molecular compound may be in the mixture. The m is called hereafter "the stability coefficient" of a molecular compound. In the following table are summarized the stability coefficients of the molecular compounds above studied.

Molecular compound	m
$CH_3OH \cdot 2H_2O$	2.00
$C_2H_5OH \cdot 3H_2O$	2.00
$C_2H_5OH \cdot 2H_2O$	1.83
$CH_3COOH \cdot H_2O$	1.68

Among the four hydrates the hydrates $C_2H_5OH \cdot 3H_2O$ has η_m of the greatest value which suggests the possibility of crystallization of this hydrate at lower temperatures. In fact, Tammann and Pillsbury[7] reported to yield transparent crystals of a hydrate by cooling the mixtures of 34–43 wt. % (20–30 mol %) alcohol which they attributed to a tetrahydrate, simply considering the admixing composition, but observed no separation of crystalline hydrates of methyl alcohol and acetic acid. The writer also observed transparent crystals of cubic system by cooling the mixtures of molar ratios of from 1 C_2H_5OH : 1 H_2O to 1 C_2H_5OH : 4 H_2O with solid carbon dioxide and alcohol freezer. From the writer's viewpoint of the present study, however, this hydrate of ethyl alcohol is undoubtedly a trihydrate.

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(7) G. Tammann & M. E. Pillsbury, *Z. anorg. allg. Chem.* **172** (1928), 243.