ON THE VISCOSITY OF THE CRITICAL MIXTURE OF TERNARY SYSTEM BENZENE-ALCOHOL-WATER.

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Introduction. It is a well-known phenomenon that a liquid shows critical opalescence at its critical state. Two component system also shows this phenomenon and there are numerous investigations(1) on this problem. The author has studied colloid-chemically on the three component system of organic solvents(2). The optical method seems to be superior, but from the standpoint of colloid chemistry, the viscometric method is one of the most usefull methods for studying the liquid of colloidal nature. In this paper the viscosity of three component system is measured at its critical state and some discussions concerning the colloidal properties of critical mixture are described.

Experimental. The three component system benzene-ethanol-water has been studied by the author and reported in a previous paper(2). This system is the most familiar and the materials are easily purified. Recently the viscosity of this system was measured by Pestemer(3), but he paid no attention to the colloidal nature at the critical state. This system shows critical opalescence at a certain temperature and composition, and when the temperature is raised, the intensity of opalescence becomes weak by and by, and at last the opalescence disappears and the total system becomes homogeneous. It must be noticed that this state which shows critical opalescence is very stable and does not change for long time if the temperature is maintained constant. The viscosity has been measured following this stadium at various temperatures. The apparatus used is a modified type of Ostwald viscosimeter, which is shown in Fig. 1.

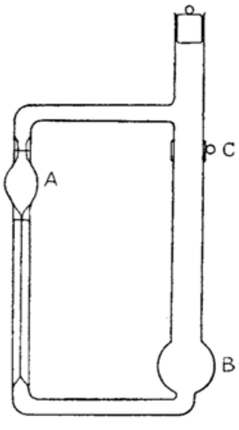

Fig. 1.

Even a slight vaporisation of a component affects the state of the system markedly, so that after pouring the liquid in viscosimeter the inlet tube is

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(1) J. Friedländer, *Z. physik. Chem.*, **38** (1901), 435. V. Rothmund, *Z. physik. Chem.*, **63** (1908), 54. Wo. Ostwald, *Ann. Phys.*, (4), **36** (1911), 848.

(2) N. Sata and O. Kimura, this Bulletin, **10** (1935), 409.

(3) M. Pestemer, *Kolloid-Z.*, **65** (1933), 25.

sealed. The total apparatus is dipped in a thermostat, the temperature of which is changeable. To measure the viscosity the apparatus is rotated in left hand, C being the axis of rotation, so that the liquid in B fills the bulb A. Then it is again rotated reversely and the apparatus is fixed vertical. The transpiration time of liquid between two marks is measured by a stopwatch. On the other hand the density of the liquid is measured by Ostwald pycnometer and the viscosity is calculated. The viscosity was measured on five series of different compositions, of which three systems showed critical opalescence, and the other two did not. The compositions of these five systems are shown in Table 1, and graphically in Fig. 2. The temperature is varied from homogeneous domain to the critical point.

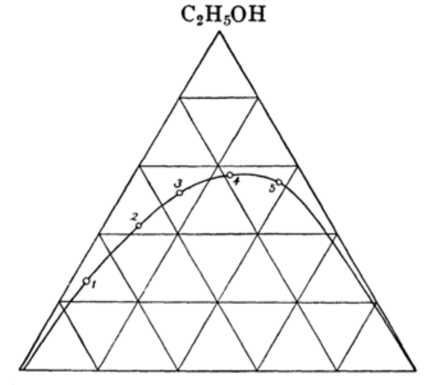

Fig. 2.

Table 1. Compositions of Five Systems in Volume Percent.

System	Ben-zene	Ethanol	Water	Remarks
1	70.3	26.2	3.5	shows opalescence
2	48.3	42.3	9.4	,,
3	33.7	52.2	14.1	,,
4	18.1	57.6	24.3	no opalescence
5	7.2	55.7	37.1	,,

Results and Discussion. The experimental results are shown graphically in Fig. 3. It is seen that the viscosity-temperature curve has a gentle slope in homogeneous region and a steep one in the region which shows opalescence. This sudden increase of viscosity in critical region was pointed out by Friedländer and Rothmund, but the reason of this increase was not discussed. It may be easily supposed that this sudden increase of viscosity is caused by the existence of colloidal particles which are the small droplets of benzene covered with thin film of alcohol, as was reported in the previous paper. Moreover this conception is confirmed by the experimental data that the viscosity-temperature curve of the system which shows no opalescence (i.e. there is no colloidal region) has gentle slope, while that of the system which shows opalescence is very steep in colloidal region. To show this more quantitatively some considerations have been made.

Concerning viscosity-temperature relation, there are numerous formulas theoretical and empirical. Among these Andrade's formula⁽⁴⁾ is an excellent one because it is very simple and contains only two constants and furthermore it is applicable to wide range of temperature and many substances. The formula is as follows:

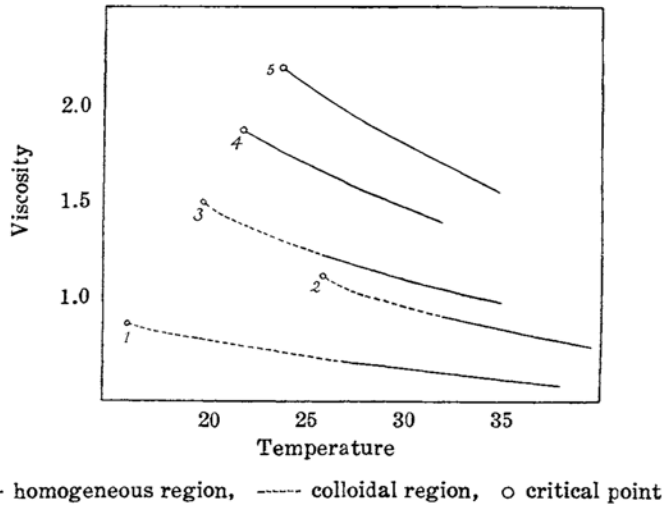

Fig. 3.

$$\eta = Ae^{b/T},$$

where A and b are constants, and T is the absolute temperature.

The formula was applied to the homogeneous region determining the two constants by means of the least square. The formula is highly applicable to the homogeneous region within the deviation of 0.5%. But when it is extrapolated in the colloidal region, the deviation from calculated values is remarkable and the nearer the critical point the greater the deviations. To the system which shows no opalescence it is applicable up to the critical point. This deviation is, as already explained due to colloidal nature (i.e. emulsion) of the system.

For the viscosity-concentration relation of emulsion Hatschek presented following formula:

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(4) C. Andrade, *Nature*, **125** (1930), 309.

$$\eta = \eta_m \frac{1}{1-\sqrt[3]{\phi}},$$

where η is the viscosity of emulsion, η_m that of medium, ϕ the volume of dispersed phase in unit volume of emulsion. This formula was verified experimentally by many investigators, and among those Sibree(5) has carefully measured the viscosity of emulsions and concluded that Hatschek's formula is applicable to many types of emulsion very satisfactorily if not strictly. If this formula can be applied to this case, the concentration of emulsion is cal-

Table 2. System 1.

°C.	t (sec.)	d	$\eta_{obs.}$	$\eta_{calc.}$	$\Delta\eta$	ϕ
38.0	54.3	0.8403	0.5836	0.5836	0.0000	
37.0	55.2	0.8413	0.5940	0.5931	+0.0009	
36.0	55.9	0.8422	0.6021	0.6028	−0.0007	
35.0	56.7	0.8432	0.6115	0.6129	−0.0014	
34.0	57.7	0.8441	0.6229	0.6230	−0.0001	
33.0	58.7	0.8451	0.6345	0.6334	+0.0009	
32.0	59.5	0.8461	0.6438	0.6450	−0.0012	
31.0	60.5	0.8470	0.6554	0.6551	+0.0003	
30.0	61.5	0.8479	0.6670	0.6662	+0.0008	
29.0	62.5	0.8489	0.6786	0.6784	+0.0002	
28.0	63.5	0.8498	0.6902	0.6896	+0.0006	
27.0	64.5	0.8508	0.7002	0.7017	−0.0015	
26.0	65.5	0.8517	0.7135	0.7140	0.0005	0.000005
25.0	67.0	0.8527	0.7307	0.7265	0.0042	0.00004
24.0	68.0	0.8536	0.7414	0.7390	0.0024	0.00002
23.0	69.3	0.8546	0.7574	0.7527	0.0047	0.00005
22.0	70.8	0.8556	0.7747	0.7662	0.0085	0.00009
21.0	72.2	0.8565	0.7909	0.7802	0.0107	0.00011
20.0	73.7	0.8575	0.8083	0.7945	0.0138	0.00014
19.0	75.0	0.8584	0.8234	0.8090	0.0144	0.00014
18.0	76.5	0.8594	0.8409	0.8241	0.0168	0.00017
17.0	78.4	0.8603	0.8626	0.8393	0.0233	0.00023
16.3	79.6	0.8610	0.8765	0.8504	0.0261	0.00026
16.0	critical point					

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(5) J. O. Sibree, *Trans. Faraday Soc.*, **26** (1930), 104; **27** (1931), 161.

Table 3. System 2.

°C.	t (sec.)	d	$\eta_{\text{obs.}}$	$\eta_{\text{calc.}}$	$\Delta\eta$	ϕ
40.0	71.4	0.8398	0.7669	0.7673	−0.0004	
39.0	73.0	0.8408	0.7850	0.7852	−0.0002	
38.0	74.7	0.8418	0.8042	0.8037	+0.0005	
37.0	76.3	0.8428	0.8224	0.8227	−0.0003	
36.0	78.1	0.8439	0.8430	0.8422	+0.0008	
35.0	79.7	0.8449	0.8613	0.8627	−0.0014	
34.0	81.7	0.8459	0.8839	0.8834	+0.0005	
33.0	83.6	0.8469	0.9055	0.9048	+0.0007	
32.0	85.5	0.8479	0.9272	0.9272	+0.0000	
31.0	88.0	0.8489	0.9554	0.9500	+0.0054	0.0000001
30.0	91.4	0.8499	0.9935	0.9734	+0.0201	0.0000087
29.0	93.1	0.8510	1.012	0.9993	+0.013	0.0000022
28.0	95.8	0.8520	1.044	1.023	+0.011	0.0000013
27.0	99.0	0.8530	1.080	1.049	+0.031	0.000026
26.0	103.8	0.8540	1.134	1.076	+0.058	0.00016
25.0	critical point					

Table 4. System 3.

°C.	t (sec.)	d	$\eta_{\text{obs.}}$	$\eta_{\text{calc.}}$	$\Delta\eta$	ϕ
35.0	92.4	0.8451	0.9987	0.9992	−0.001	
34.0	94.4	0.8461	1.022	1.022	0.000	
33.0	96.6	0.8471	1.047	1.046	+0.001	
32.0	98.7	0.8481	1.071	1.071	0.000	
31.0	101.0	0.8491	1.097	1.097	0.000	
30.0	103.2	0.8501	1.122	1.123	−0.001	
29.0	105.7	0.8511	1.151	1.151	0.000	
28.0	108.2	0.8521	1.176	1.178	−0.002	
27.0	110.8	0.8531	1.209	1.207	+0.002	
26.0	113.4	0.8541	1.239	1.236	+0.003	
25.0	116.8	0.8551	1.277	1.267	+0.010	0.0000005
24.0	120.0	0.8560	1.314	1.297	+0.017	0.000002
23.0	123.2	0.8570	1.350	1.331	+0.019	0.000003
22.0	126.7	0.8580	1.390	1.364	+0.026	0.000007
21.0	130.4	0.8589	1.432	1.399	+0.033	0.000013
20.0	136.8	0.8599	1.505	1.435	+0.070	0.000116
19.5	critical point					

Table 5. System 4.

°C.	t (sec.)	d	$\eta_{obs.}$	$\eta_{calc.}$	$\Delta\eta$
32.0	126.7	0.8646	1.401	1.401	0.000
31.0	130.3	0.8655	1.442	1.440	+0.002
30.0	134.0	0.8664	1.485	1.481	+0.004
29.0	137.4	0.8673	1.524	1.526	−0.002
28.0	141.1	0.8682	1.567	1.567	0.000
27.0	145.1	0.8691	1.613	1.613	0.000
26.0	148.9	0.8700	1.657	1.660	−0.003
25.0	153.3	0.8709	1.708	1.709	−0.001
24.0	157.7	0.8718	1.758	1.757	+0.001
23.0	162.2	0.8727	1.811	1.811	0.000
22.0	167.0	0.8736	1.866	1.866	0.000
21.0	critical point				

Table 6. System 5.

°C.	t (sec.)	d	$\eta_{obs.}$	$\eta_{calc.}$	$\Delta\eta$
35.0	136.0	0.8917	1.551	1.555	−0.004
34.0	140.0	0.8926	1.598	1.601	−0.003
33.0	144.4	0.8934	1.650	1.651	−0.001
32.0	149.0	0.8943	1.704	1.700	+0.004
31.0	153.2	0.8952	1.754	1.752	+0.002
30.0	157.6	0.8960	1.806	1.805	+0.001
29.0	162.1	0.8969	1.859	1.865	−0.006
28.0	166.8	0.8977	1.915	1.920	−0.005
27.0	172.4	0.8986	1.981	1.980	+0.001
26.0	177.2	0.8994	2.038	2.043	−0.005
25.0	183.2	0.9003	2.110	2.108	+0.003
24.0	189.3	0.9012	2.182	2.173	+0.009
23.0	critical point				

culated as follows. In the formula η is the viscosity of emulsion which is the observed viscosity in this case, and η_m is the viscosity of medium, which can be calculated from Andrade's formula. Then we obtain

$$\phi=\left(\frac{\eta-\eta_m}{\eta}\right)^3=\left(\frac{\varDelta\eta}{\eta}\right)^3.$$

Thus the values of ϕ were calculated for three systems which showed critical opalescence. These values are illustrated in Table 2, 3, 4, 5, and 6. In the tables the 1st column is the temperature in centigrade, the 2nd the time of transpiration between two marks, the 3rd the density, the 4th the observed viscosity, in centipoise, the 5th the viscosity calculated by using Andrade's formula, the 6th the difference between observed and calculated viscosities, and the 7th the concentration calculated from Hatschek's formula.

It is seen from the tables that the concentration of colloid particles which are supposed to be the droplets of benzene covered with thin film of alcohol is of the order of 0.0001 near the critical point and decreases as the temperature is raised. There may be some relations between the concentration and the intensity of opalescence, which also shows maximum at critical point and decreases as the temperature is raised. The experiment on this line is now in course.

Summary.

(1) The viscosity of the three component system benzene-ethanol-water was measured in the neighbourhood of critical point.

(2) To the homogeneous region Andrade's formula is strictly applicable but not to the colloidal region. This deviation is caused by the existence of colloid particles.

(3) The concentration of colloid particles was calculated by using Hatschek's formula, and it was of the order of 0.0001 near the critical point.

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