Viscosities of Benzene–Methyl Ethyl Ketone Systems

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Viscosities of benzene–methyl ethyl ketone (2-butanone) mixtures were investigated for the temperature range -32.4° to 26.0° C. Interest in the viscosity behavior of such mixtures was stimulated by the extensive utilization of these solvents by the petroleum industry in solvent dewaxing process.

The thiophene free benzene and methyl ethyl ketone (C.P.) were each fractionated to constant overhead temperature by intermittent withdrawal of distillate. The benzene was fractionated to an overhead temperature of 80.1° C. at 760 mm. of mercury and a refractive index of 1.5011 at 20° C. The methyl ethyl ketone was fractionated to an overhead temperature of 79.6° C. at 760 mm. of mercury and a refractive index of 1.3762 at 25° C.

Blends of the mixtures were made by volumetric methods using calibrated pipettes of 100- and 50-ml. sizes. The pure liquids were stored in a constant temperature bath at 25.0° C. for at least 24 hours before blending. A minimum of 500 ml. of blend was made for each composition in order to minimize errors inherent in measurements of small quantities. Inasmuch as the maximum error in calibration of the 50-ml. pipet was 0.10 ml. and for the 100-ml. pipet 0.16 ml., the maximum error in preparation of the blends is estimated as 0.2%.

The viscosities of the mixtures were determined relative to deionized water, redistilled methanol, and redistilled diethyl ether by the use of the capillary tube flow method. The capillary tube utilized was a No. 50 Fenske viscometer having a capillary length of 78.0 mm. and a radius calculated from efflux time of water at 26° C. of 0.2226 mm. The calculation was based on the equation presented by Cannon and Fenske (*1*)

$$\eta = \frac{\pi \rho g H r^4 t}{8LV} - \frac{mV}{8\pi L t} \qquad (1)$$

The efflux flow times for all conditions observed ranged from 128.3 to 291.6 seconds. At least three readings having a maximum variation of 0.4 second were required for establishing efflux time.

All density and viscosity determinations were made in a controlled temperature bath maintained within a 0.01° C. range by a heater integral with agitator and cooling coils constructed of vertical loops of copper tubing 1/4 inch in diameter placed within the periphery of the bath.

For runs above 0° C., water was used as bath liquid; below 0° C., acetone was used. For control at 25° C., tap water was utilized as the cooling medium, at 9.9° C., ice water was pumped through the cooling coils, and below 9.9° C., acetone was circulated through coils immersed in dry ice–acetone mixtures and then pumped through the cooling coils.

To prevent condensation of water in the Fenske tube when operation below 9.9° C. was required, both ends of the tube were vented to the atmosphere through calcium chloride drying tubes. Before each series of measurements for the composition investigated, the tube was heated in an oven to 110° C., drying tubes were attached, and the Fenske tube was slowly cooled to the run temperature. Precooled solution was rapidly admitted to the tube while one vent was removed and the vent rapidly replaced. Reproducibility of drain time within 0.03% was observed in series of duplication runs.

Densities of the solutions below 0° C. were measured in the following manner. The Weld pycnometer, having a 25-ml. capacity at 20° C., an inner capillary plug and ground joint cap, was immersed in the bath for 30 minutes. Precooled solution was admitted separately to the bottle and to the cap each to overflow condition. The overflow capillary was inserted into the bottle, and the bottle and the cap were attached, all in an inverted position. The pycnometer was placed in the bath in the inverted position. As the solution cooled to the bath temperature, the liquid was drawn from the cap into the bottle leaving a void in the cap. After 30 minutes, the bottle was removed from the bath, and returned rapidly to the upright position, and the cup lifted slightly to allow the excess liquid to drain. The cap was rapidly restored, the pycnometer again inverted and allowed to come to a temperature above the dew point of the air. The pycnometer was weighed, and the weight of the solution was obtained. The volume of solution was determined from a relative measurement with water at room temperature, taking into account the contraction of the pycnometer and air buoyancy correction.

The results are indicated in Table I to III.

The densities of the mixtures in the liquid phase were found

Table I. Viscosities of Methyl Ethyl Ketone–Benzene Mixtures

Composition Fraction Benzene			Temperature					
Volume	Weight	Mole	26.0° C. 78.8° F.	9.9° C. 49.8° F.	-1.7° C. 29.9° F.	-12.2° C. 10.0° F.	-24.7° C. -12.5° F.	-32.4° C. -26.3° F.
0.000	0.000	0.000	0.401	0.471 0.472[a]	0.547 0.550[a]	0.603	0.720	0.801
0.100	0.092	0.098	0.411	0.490	0.563	0.627	0.737	0.825
0.200	0.186	0.198	0.425	0.508	0.587	0.665	0.772	0.864
0.300	0.282	0.298	0.443	0.532	0.611	0.694	0.819	0.909
0.400	0.378	0.398	0.455	0.544	0.647	0.728	0.866	0.974
0.500	0.477	0.498	0.474	0.565	0.688	0.767	0.915	1.043
0.600	0.578	0.599	0.497	0.603	0.711	0.814	0.980	
0.700	0.681	0.699	0.519	0.633	0.751	0.868		
0.800	0.786	0.799	0.546	0.676	0.803			
0.900	0.892	0.899	0.584	0.723	0.864			
1.000	1.000	1.000	0.619 0.595[b]	0.766 0.760[b]				

[a] Literature value (*2*).
[b] Literature value (*3*).

Table II. Fluidities of Methyl Ethyl Ketone–Benzene Mixtures

Composition Fraction Benzene			Temperature					
Volume	Weight	Mole	26.0° C. 78.8° F.	9.9° C. 49.8° F.	-1.7° C. 29.9° F.	-12.2° C. 10.0° F.	-24.7° C. -12.5° F.	-32.4° C. -26.3° F.
0.000	0.000	0.000	2.496	2.123	1.845	1.660	1.389	1.248
0.100	0.092	0.098	2.432	2.042	1.778	1.594	1.357	1.212
0.200	0.186	0.198	2.352	1.970	1.705	1.504	1.296	1.157
0.300	0.282	0.298	2.257	1.879	1.636	1.441	1.221	1.100
0.400	0.378	0.398	2.196	1.838	1.547	1.374	1.154	1.027
0.500	0.477	0.498	2.108	1.771	1.497	1.303	1.093	0.959
0.600	0.578	0.599	2.013	1.657	1.407	1.229	1.021	
0.700	0.681	0.699	1.926	1.579	1.332	1.152		
0.800	0.786	0.799	1.833	1.521	1.246			
0.900	0.892	0.899	1.713	1.384	1.157			
1.000	1.000	1.000	1.615	1.305				

to be essentially linear with composition (Figure 1). There was an observable deviation at -1.7°, 9.9°, and 26° C., indicating a slight contraction on mixing. The average maximum deviation at 50 volume % benzene was 0.12%.

The relationship of viscosities and fluidities with composition of the benzene–methyl ethyl ketone blends are indicated in Figures 2 and 3. The compositions were expressed in volume fraction inasmuch as the fluidities of mixtures of nonpolar liquids are in general additive on this basis (*1*).

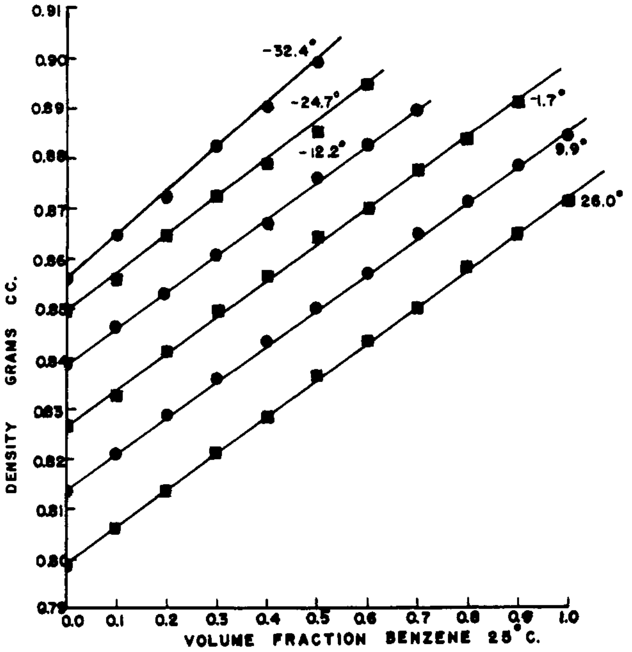

Figure 1. Density *vs.* composition

Temperature range, -32.4° to 26.0° C.

$$\phi = M_1\phi_1 + M_2\phi_2 \qquad (2)$$

However, Table I shows that the mole fraction is equal to the volume fraction and the weight fraction closely approximates the volume fraction (maximum difference, 0.5%). Therefore, the relationship plotted may be considered a function of composition represented by volume fraction or mole fraction and very closely represents the relationship with composition expressed in weight fraction.

Because of the relatively greater increase in the viscosity of benzene with decrease in temperature as compared with that of methyl ethyl ketone, the slopes of the viscosity-composition curves increase with decrease in temperature.

The appearance of a solid phase was observed as follows:

Benzene-Methyl Ethyl Ketone Mixtures

Temperature, °C.	Benzene, %
- 1.7	100
-12.2	80
-24.7	70
-32.4	60

An obvious deviation in anticipated viscosity behavior of methyl ethyl ketone and the mixture containing 10% benzene at -12.2° C. is observable in Figure 2. If the "normal" rate of change of viscosity of methyl ethyl ketone, with temperature following the changes noted at other compositions was maintained, the viscosity of the methyl ethyl ketone would be anticipated to be approximately 0.62 centipoise, the value predicted by the general relationship presented later.

The degree of deviation of the system fluidities from the behavior of an ideal mixture is indicated by Figure 3. The dashed lines indicate ideal behavior (additivity of fluidities), whereas the solid lines indicate the actual system conditions.

Irany (*4*), as a result of an investigation of published viscosity-composition data for binary systems, developed a modified viscosity scale such that, when viscosities of the systems were plotted against composition, straight-line relation-

Table III. Densities of Methyl Ethyl Ketone–Benzene Mixtures

Composition Fraction Benzene			Temperature					
Volume	Weight	Mole	26.0° C. 78.8° F.	9.9° C. 49.8° F.	-1.7° C. 29.9° F.	-12.2° C. 10.0° F.	-24.7° C. -12.5° F.	-32.4° C. -26.3° F.
0.000	0.000	0.000	0.798	0.814	0.827	0.839	0.850	0.856
0.100	0.092	0.098	0.806	0.821	0.833	0.847	0.856	0.865
0.200	0.186	0.198	0.814	0.829	0.842	0.853	0.865	0.873
0.300	0.282	0.298	0.821	0.836	0.850	0.861	0.872	0.883
0.400	0.378	0.398	0.829	0.844	0.857	0.867	0.879	0.890
0.500	0.477	0.498	0.837	0.850	0.864	0.876	0.885	0.899
0.600	0.578	0.599	0.844	0.857	0.870	0.833	0.895	solid
0.700	0.681	0.699	0.850	0.865	0.877	0.889	solid	solid
0.800	0.786	0.799	0.858	0.872	0.884	solid	solid	solid
0.900	0.892	0.899	0.865	0.878	0.891	solid	solid	solid
1.000	1.000	1.000	0.872	0.884	solid	solid	solid	solid

ships resulted. Irany claimed that there might be an error in the accepted concept of viscosity, inasmuch as all systems investigated fitted the new viscosity scales.

However, the deviation from ideality in the evaluation of the viscosities of benzene–methyl ethyl ketone systems was attributed to a molecular interaction of the constituents, and a distorted composition scale was developed to provide a straight-line relationship for the viscosity composition function at 26.0° C. (Figure 4).

When viscosity-composition data for methyl ethyl ketone–benzene mixtures in the liquid phase at the other temperatures were plotted on the distorted composition scale; the data for each temperature fell on a straight line. The only conditions for which deviations from straight line functions were observed were concentrations above 90% methyl ethyl ketone at temperatures of -24.2° and -32.4° C. Significantly, observed viscosities of methyl ethyl ketone at -24.2° and -32.4° C. did not fit the well known temperature-viscosity relationship for pure liquids.

$$\log \eta = \frac{A}{T} + B \qquad (3)$$

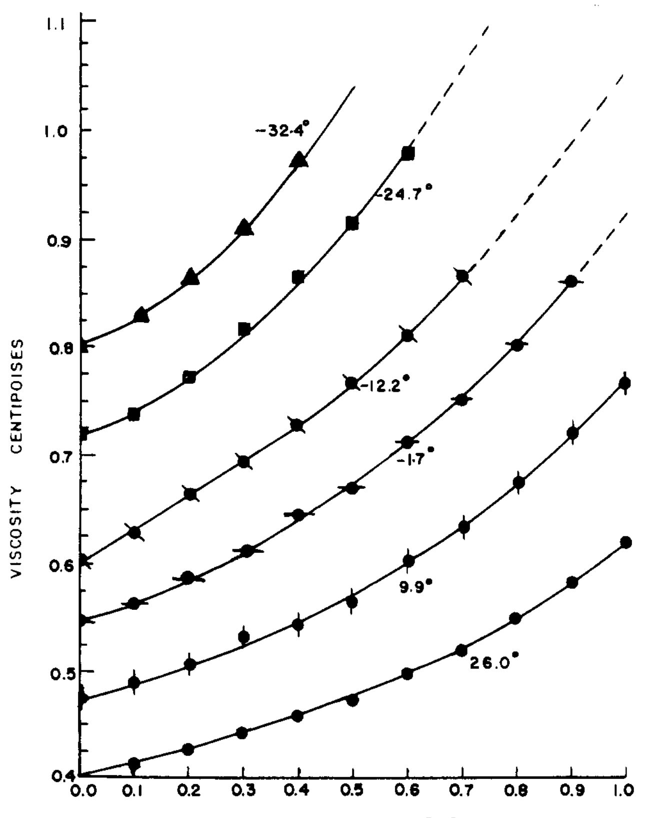

Figure 2. Viscosity *vs.* composition
Temperature range, -32.4° to 26.0° C.

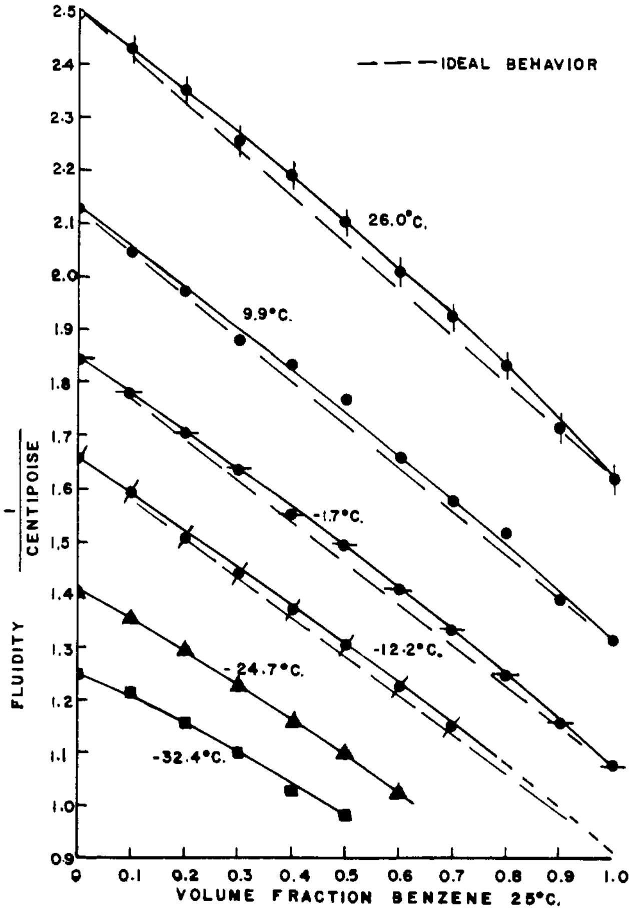

Figure 3. Fluidity *vs.* composition

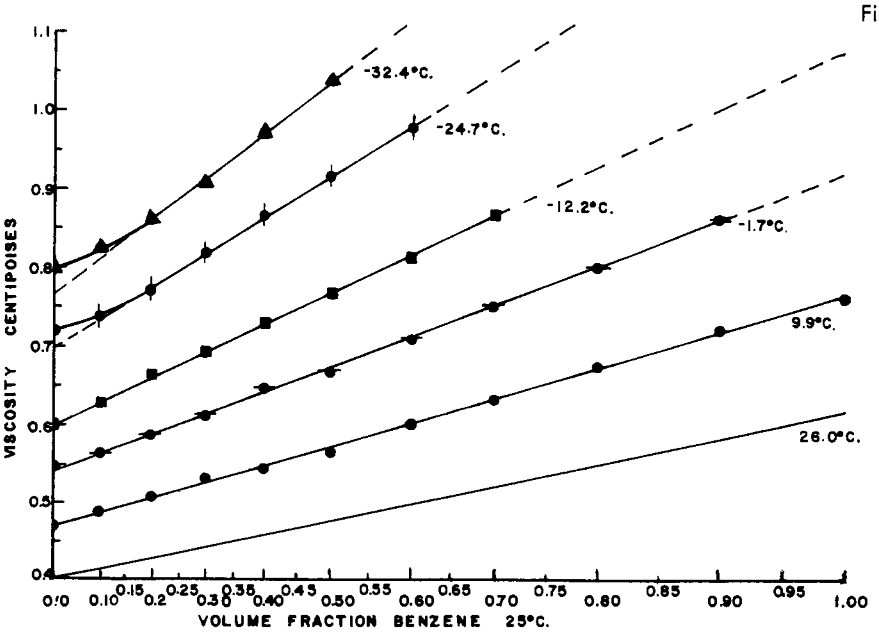

Figure 4. Viscosity *vs.* composition (distorted scale)

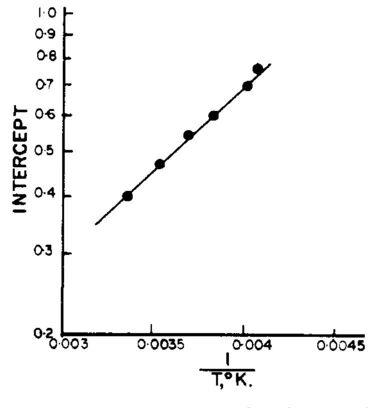

Figure 5. Intercepts of η-distorted composition curves *vs.* 1/T, °K.

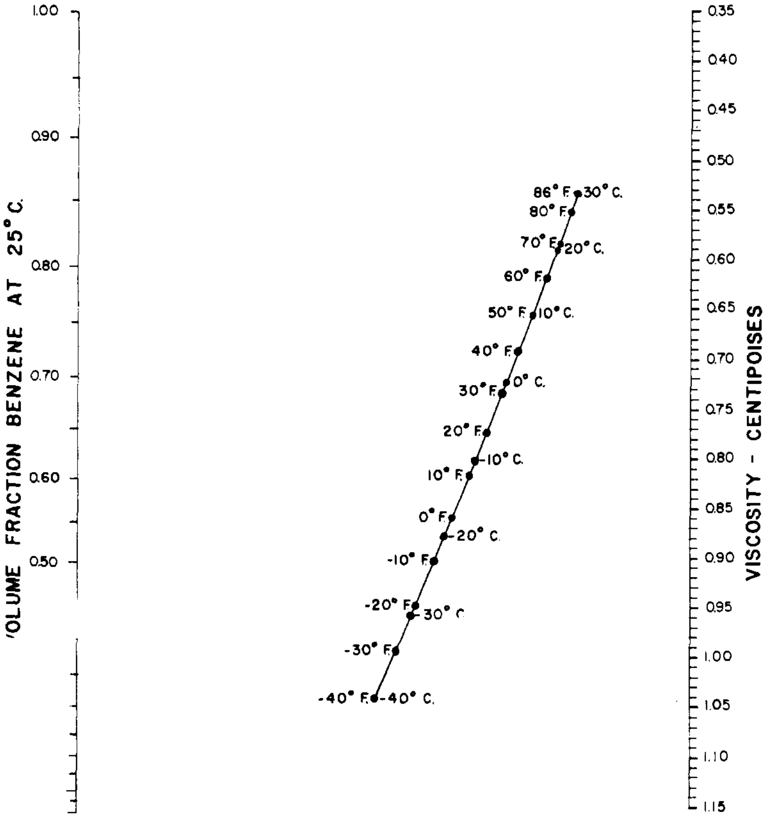

Figure 6. Nomograph of viscosities of benzene–methyl ethyl ketone mixtures

whereas the extrapolated values for the viscosities of the substance at these temperatures, taken from Figure 4, fit the relationship in combination with the viscosities of methyl ethyl ketone observed at the other temperatures investigated (Figure 5).

A nomograph (Figure 6) was constructed on the basis of the distorted composition scale, utilizing an empirical temperature curve. The nomograph is applicable to the estimation of the viscosities of liquid phase methyl ethyl ketone-benzene systems at temperatures ranging from -32.4° to 26.0° C. except for concentrations above 90% methyl ethyl ketone (by volume) at temperatures below -24.7° C.

A mathematical relationship of viscosity of benzene-methyl ethyl ketone mixtures with composition and temperature was needed for estimating the behavior of this system. Inasmuch as straight-line relationships of viscosity with composition for each temperature were attained by utilizing the distorted composition scale, an empirical equation using the scale as a basis was envisaged.

The relationship of the actual and distorted composition is a third power polynomial

$$X_B = 0.0300 + 0.1850\ V_B + 0.8260\ V_B^2 - 0.1000\ V_B^3 \tag{4}$$

where X_B = corrected volume fraction of benzene at 25° C. and V_B = actual volume fraction at 25° C.

Because the viscosity of the system varies linearly with X_B, only the slope and intercept of each constant temperature line had to be determined.

The intercepts (which above -24.2° C., were the viscosities of methyl ethyl ketone) followed Equation 3. The value of the intercept was found to be

$$\text{Intercept} = e^{\left(\frac{848.2}{T} - 3.7516\right)} \tag{5}$$

The slopes of the viscosity-composition curves for the system rose with decrease in temperature. The slopes of the viscosity-distorted composition curves vary with temperature in the following manner:

$$\log \text{slope} = CT + K \tag{6}$$

and had the value

$$\text{slope} = e^{(-0.0216T + 4.914)} \tag{7}$$

Table IV. Comparison of Observed Viscosities with Those Calculated by Equation

Vol. Fract. Benzene	26.0° C.			9.9° C.			-1.7° C.			-12.2° C.			-24.7° C.			-32.4° C.		
	Obsd.	Calcd.	Diff.	Obsd.	Calcd.	Diff.	Obsd.	Calcd.	Diff.	Obsd.	Calcd.	Diff.	Obsd.	Calcd.	Diff.	Obsd.	Calcd.	Diff.
0.000	0.401	0.406	+0.005	0.471	0.471	0.000	0.547	0.546	- 0.001	0.603	0.621	+0.018	0.720	0.733	+0.013	0.801	0.819	+0.018
0.100	0.411	0.413	+0.002	0.490	0.487	- 0.003	0.563	0.557	- 0.006	0.627	0.634	+0.007	0.737	0.750	+0.013	0.825	0.839	+0.014
0.200	0.425	0.422	- 0.003	0.508	0.501	- 0.007	0.586	0.574	- 0.012	0.665	0.655	- 0.010	0.772	0.778	+0.006	0.864	0.872	+0.008
0.300	0.443	0.435	- 0.008	0.532	0.519	- 0.013	0.611	0.597	- 0.014	0.694	0.684	- 0.010	0.819	0.816	- 0.003	0.909	0.917	+0.008
0.400	0.445	0.451	+0.006	0.544	0.542	- 0.002	0.647	0.626	- 0.021	0.728	0.726	- 0.002	0.866	0.864	- 0.002	0.974	0.973	- 0.001
0.500	0.474	0.470	- 0.004	0.565	0.568	+0.003	0.668	0.660	- 0.008	0.767	0.764	- 0.003	0.915	0.920	+0.005	1.043	1.040	- 0.003
0.600	0.497	0.493	- 0.004	0.603	0.600	- 0.003	0.711	0.731	+0.020	0.814	0.814	0.000	0.980	0.984	+0.004			
0.700	0.519	0.518	- 0.001	0.633	0.635	+0.002	0.751	0.747	- 0.004	0.868	0.872	+0.002						
0.800	0.546	0.546	0.000	0.676	0.675	- 0.001	0.803	0.797	- 0.006									
0.900	0.584	0.577	- 0.007	0.723	0.718	- 0.005	0.864	0.853	- 0.011									
1.000	0.619	0.611	- 0.008	0.767	0.765	- 0.002												

Therefore, utilizing a straight-line equation of the form $y = mx + b$, a general equation was evaluated.

The equation for the viscosities of benzene-methyl ethyl ketone mixtures in the liquid phase for temperature in the range -32.4° to 26.0° C. is as follows:

$$\mu = e^{\left(\frac{848.2}{T} - 3.7516\right)} + e^{(-0.0216T + 4.914)}(0.0300 + 0.1850\ V_B + 0.8620\ V_B^2 - 0.1000\ V_B^3) \quad (8)$$

or

$$\mu = e^{\left(\frac{1526.7}{T'} - 3.7516\right)} + e^{(-0.0120T' + 4.914)}(0.0300 + 0.1850\ V_B + 0.8620\ V_B^2 - 0.1000\ V_B^3) \quad (8a)$$

where μ is the viscosity of the mixture.

A comparison of observed viscosities with those calculated by the empirical equation is presented in Table IV. The root mean square deviation of viscosities obtained by Equation 8 from the observed data was 1.20% for the total of 52 points of data.

NOMENCLATURE

m = volume fraction
M = mole fraction
T = absolute temperature, °K.
T' = absolute temperature, °R.
V_B = volume fraction of benzene at 25° C. or mole fraction of benzene
X_B = corrected volume fraction of benzene at 25° C. or corrected mole fraction of benzene
η = viscosity, centipoises

Subscripts

i, w, and m, define system

LITERATURE CITED

(1) Cannon, M. R., Fenske, M. R., *Ind. Eng. Chem., Anal. Ed.* **10**, 299 (1938).
(2) Handbook of Chemistry and Physics, C. D. Hodgman, ed., 36th ed., p. 1700, Chemical Rubber Publ., Cleveland, Ohio.
(3) International Critical Tables, Vol. **V**, p. 12, McGraw-Hill, New York, 1929.
(4) Irany, E. P., *J. Am. Chem. Soc.* **61**, 1734 (1939).

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Viscosity of Nitrogen, Methane, Ethane, and Propane at Elevated Temperature and Pressure

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Numerous determinations of the viscosity of fluids at either elevated temperature or elevated pressure are reported in the literature. However, measurements at both elevated temperature and pressure are scarce and have occasionally been made by techniques that cannot be considered quantitative. In this investigation quantitative measurements were made on the coefficient of viscosity of nitrogen and the three lowest paraffins over a range of conditions significant for theories of dense gases and of practical importance in the petroleum industry. The nitrogen data provide a comparison with what is considered the most reliable information on the viscosity of a compressed gas at elevated temperature.

EXPERIMENTAL

Principle of Viscometer. Rankine (*18*) devised a clever transpiration viscometer for handling small volumes of gases. A pellet of mercury descending in one leg of a closed loop of glass tubing exerts a piston-like action which forces the gas through a capillary comprising the other leg of the loop. The volume rate of gas transpired through the capillary of length, L, and radius, r, is obtained from the time, t, for the descent of the pellet between two marks on the fall tube, the volume, v, between marks being known by previous calibration. The pressure differential across the capillary is approximately the mass of the pellet, m, divided by the mean cross-sectional area, A, of the fall tube. At high pressures the density, ρ, of the gas becomes an appreciable fraction of that of the mercury, ρ_m, and a buoyancy factor for the pellet must be included. The maximum correction was 4.0% for propane and less for the other fluids. Numerical values for the density of these four fluids are available in a recent compilation (*21*). Also, a small experimentally determined term, α, which corrects for the unbalance of surface forces existing between the leading and trailing surfaces of the descending pellet must be subtracted. The instrument is symmetrical and can be inverted for repeated timing in either direction of pellet fall.

The equation for the determination of viscosity by this instrument is given by

$$\eta = \frac{\left[\left(\frac{\rho_m - \rho}{\rho_m}\right) m - \alpha\right] \pi g t}{8 v a \int_0^L dl/r^4} \quad (1)$$

Questions of the importance of the capillary end effects and of the varying velocity of the mercury pellet caused by the compressibility of the fluid have been discussed in detail (*7*).

Description of Viscometer. The Rankine viscometer cannot be used in its most simple form for viscosity measurements at elevated pressure. For sample pressures above several atmospheres, the glass instrument must be installed within a thermostated pressure vessel with a pressure balance maintained be-