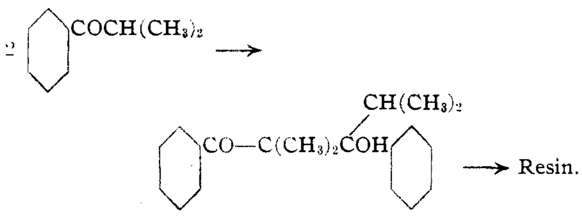
For isobutyrophenone



For benzophenone and α-trichloroacetophenone similar condensations cannot take place.

Summary

Aromatic ketones were found to condense with themselves in the presence of hydrogen fluoride. Those containing two or three hydrogen atoms on the carbon atom adjacent to the carbonyl group (propiophenone and acetophenone) gave benzoic acid and a resin as the products. At a lower temperature dypnone was formed from acetophenone and 1,3-diphenyl-2-methylpentene-2-one-1 from propiophenone. A similar treatment with dypnone gave benzoic acid and a resin. α-Methylstyrene and 3-phenylpentene-2 were obtained, respectively, from the resins from acetophenone and propiophenone. Isobutyrophenone gave a resin but no benzoic acid, and benzophenone and α-trichloroacetophenone gave no reaction.

It is postulated that the condensation proceeds to form first a tertiary alcohol. Only ketones with one or more alpha hydrogen atoms can do this. This tertiary alcohol can polymerize. It can also dehydrate to form an unsaturated ketone, if there are two or three alpha hydrogen atoms in the original ketone. This unsaturated ketone can either polymerize or react with hydrogen fluoride to form benzoyl fluoride and a substituted styrene polymer.

STATE COLLEGE, PA.

RECEIVED APRIL 1, 1943

[CONTRIBUTION FROM SHAWINIGAN CHEMICALS LIMITED]

The Viscosity Function. IV. Non-ideal Systems

BY ERNEST P. IRANY

Measurements and interpretations of the viscosity of liquid mixtures have been and are being published in great scope and variety. While the reliability of the measurements cannot in general be questioned, the conclusions drawn from them are mostly based on postulates which are misleading.

Recognition of ideality or non-ideality[1,2] in a given system and the correct location of maximum and minimum deviations depend entirely on the use of significant and additive quantities. A survey of the literature shows viscosity and concentration expressed in units of various definitions, the choice and combination being more a matter of precedent or preference than of reasoned principle. In consequence, a large number of published statements on association and compound formation are uncertain if not definitely wrong. It is the purpose of this paper to emphasize the need of critical revision of the whole field based on a uniform and reliable method of evaluation.

As claimed in the preceding papers of this series[1] the existence of unique and generally valid solutions of the viscosity function of liquids has been established. These solutions have been expressed in the form of functional scales of viscosity which in the following are applied to a selection of typical non-ideal mixtures. The viscosity measurements are taken from the literature; where required they are supplemented by the author's own data.

In all methods of graphical analysis of viscosity-composition diagrams the investigator tacitly assumes from the start, a certain law of ideality. If, for example, he has decided on weight units for composition and on absolute viscosity units for viscosity, he bases all his observations on the understanding that the straight line connecting the pure components in his diagram represents that sequence of conditions which should obtain if the mixture were ideal. Any divergence from this straight line may then be credited with significance. Each combination of units thus defines its own regime of ideal additivity, but obviously only one can be true.

The errors incurred become most serious where the actual divergence from ideality is small and

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[1] Irany, THIS JOURNAL, **60**, 2106 (1938); **63**, 2611 (1941).

[2] Parks and Huffman, "Free Energies of Some Organic Compounds," Chemical Catalog Co., New York, N. Y., 1932, p. 127.

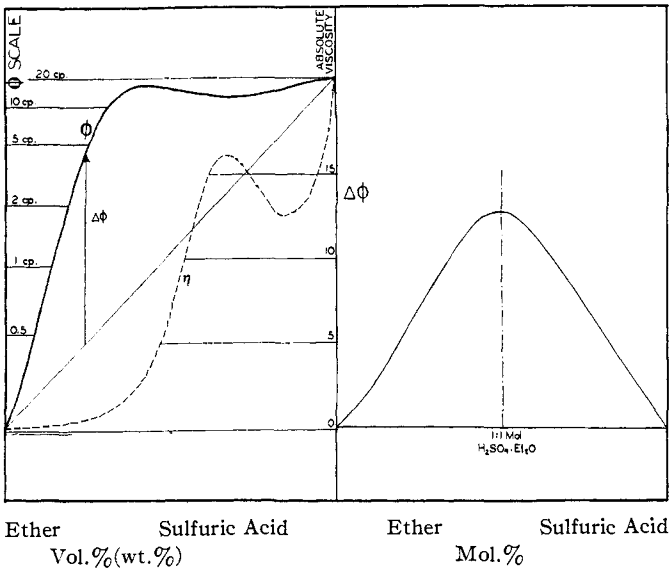

Fig. 1.—System sulfuric acid–ethyl ether: A, ϕ scale–volume diagram (Curve ϕ); Curve η (dotted), absolute viscosity–weight per cent.; B, ϕ scale deviations from straight chord plotted against molar composition.

where the viscosities of the pure components are far apart. A typical example of this kind is the system sulfuric acid–ethyl ether.[3] The plot of absolute viscosity against weight per cent. composition (curve η, Fig. 1) yields a quite incomprehensible sinuous curve with a sharp maximum between two minima, the former near the composition $3H_2SO_4 \cdot 2Et_2O$. The logarithm of viscosity[4] shifts this maximum toward equimolar proportions but does not remove the minima; fluidity (reciprocal viscosity[5]) would indicate a compound near $H_2SO_4 \cdot 2Et_2O$.

None of these functions suggests a simple interaction, nor can concordant conclusions be drawn from them. This author has proposed an empirically derived viscosity function, the ϕ scale[1] which represents the additive law of viscosity in liquid mixtures. It has been shown by an extensive survey that the use of volume abscissas is mandatory.[6]

Figure 1 shows the system sulfuric acid–ethyl ether plotted in ϕ scale against volume concentration. Comparison with the (dotted) absolute viscosity–weight per cent. curve makes it apparent that the ϕ scale so alters the shape of the curve that the deviations from the straight chord remain positive. Plotted against molar composition these deviations rise steadily and symmetrically toward a sharp maximum for the compound $H_2SO_4 \cdot Et_2O$. Hence, the various extrema encountered in diagrams based on inadequate coördinates, which have led to much interpretation, are fictitious and due only to distortion of the true curve.

The system sulfuric acid–water[7] yields very similar curves and the analogy between water and ether in these mixtures has been variously assumed. However, water gives a different compound, $H_2SO_4 \cdot 2H_2O$.

Figure 2 shows the system dioxane–formamide[8] in a ϕ scale–volume diagram as well as in absolute viscosity–weight units.[9] The single maximum deviations not only appear at the same compositions independent of temperature but the three curves shown appear correlated throughout their course. They indicate the existence of an association compound or aggregate of the composition 1 dioxane·2 formamide,[9] as against 1 dioxane·5 formamide reported by the authors of the measurements. There is not, as claimed, a simple correspondence with the system dioxane–water for which Geddes[10] reported an analogous com-

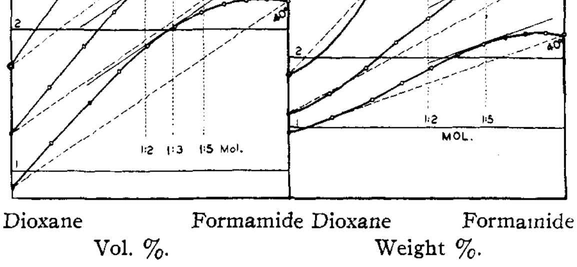

Fig. 2.—System dioxane–formamide: liquid viscosity of dioxane (m. p. 10°) at 5°, 1.755 cp. (by extrapolation of θ line of pure dioxane, Fig. 3B).

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[3] Pound, *J. Chem. Soc.*, **99**, 698 (1911).

[4] "Second Report on Viscosity and Plasticity," Nordemann Publishing Co., Inc., New York, N. Y., 1938.

[5] Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., Inc., New York, N. Y., 1922.

[6] The volumes are those of the components as added to the mixture, irrespective of expansion or contraction of the latter.

[7] Rhodes and Barbour, *Ind. Eng. Chem.*, **15**, 850 (1923).

[8] Parks, LeBaron and Molloy, THIS JOURNAL, **63**, 3331 (1941).

[9] The authors quote and extend earlier work based on the same units.

[10] Geddes, THIS JOURNAL, **55**, 4832 (1933).

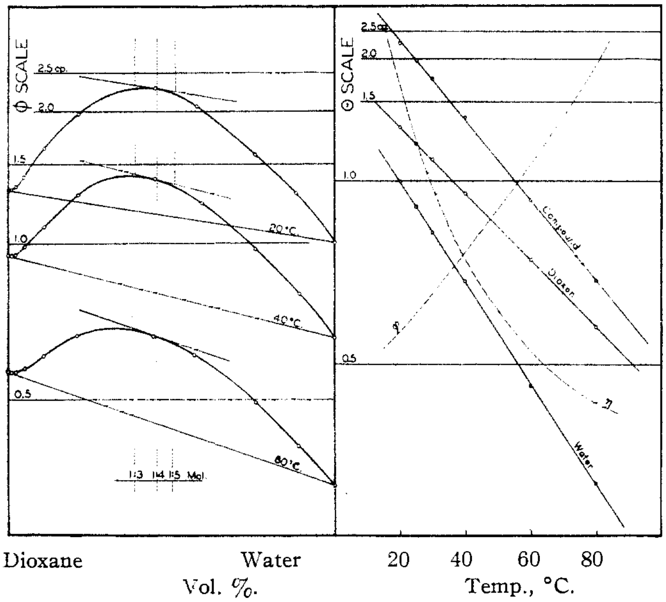

Fig. 3.—System dioxane–water: A, ϕ scale–volume diagram; B, θ scale–temperature diagram of the pure components and the 1:4 molar mixture. Absolute viscosity (η) and fluidity (φ) plotted against θ show that neither is additive in terms of temperature.

pound 1 dioxane·5 water. Employing the ϕ scale, the latter reveals a very sharp and temperature-independent maximum deviation for 1 dioxane·4 water (Fig. 3). The even numbers of 2 and 4 water molecules per dioxane molecule are more in accord with the symmetrical constitution of the latter and, as will be seen below, seem to fit into a rule of broad validity.

In the discussion of their results the quoted authors point out certain inconsistencies which they were unable to remove. The inflected curves appearing in the absolute viscosity–weight diagrams such as shown in Fig. 2, in the words of Geddes, suggest a most "unusual type of behavior." Actually, these inflections are non-existent as shown in ϕ scale. Parks, *et al.*, connect the negative deviations with volume contractions observed in the mixtures. This, of course, is contrary to experience; volume contraction always parallels increased viscosity. In the present case this holds true through the whole range of compositions. Getman,[11] Geddes,[10] Parks, *et al.*,[8] Dunstan and Thole[12] and others in similar cases observed that the magnitude of the absolute viscosity deviations and, hence, the presumable quantity of the addition complex, decreases rapidly and finally vanishes as the temperature is raised. Such a steep decline of the equilibrium constant would indicate an entirely improbable amount of free energy, considering the type of compound and process involved. The ϕ scale shows almost congruent figures at the various temperature levels and very little change in the magnitude of the deviations, indicating a reaction affinity of low order.

Compounds whose state of aggregation remains unaltered through a given temperature range all follow the same viscosity function designated as the θ scale of viscosity.[1] Whether the compound is held together by primary valences or, in part, by secondary forces, makes no difference as long as its identity is preserved. A molecular aggregate obeying this fundamental law may well be considered a compound even if it cannot be isolated. In Fig. 3B the viscosities of water and those of dioxane[13] give perfectly straight lines in the θ scale–temperature diagram and the same holds for the viscosities of the deviation maxima. Accordingly, the complex 1 dioxane·4 water represents a definite hydrate of considerable stability.

That the lower monohydric fatty alcohols form association complexes with water is long known and much work has been done on the viscosities of these mixtures. In most cases the viscosities of the components are not greatly different and the deviations are extremely large both factors favoring correct results. Nevertheless, the maximum deviations have been placed at very different molar proportions. Poiseuille,[14] Graham,[15] Traube[16] and Dunstan and Thole[12], gave 1ROH·3 water as the general composition of the alcohol–water complexes; for ethyl alcohol Varenne and Godefroy[17] listed $1EtOH \cdot 3H_2O$, $1EtOH \cdot 2H_2O$, $1EtOH \cdot 6H_2O$, $3EtOH \cdot 2H_2O$ and $1EtOH \cdot 22H_2O$. Bingham, White, Thomas and Caldwell[18] found the maximum deviation from the fluidity rule at $1EtOH \cdot 4H_2O$.

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(11) Getman, *J. chim. phys.*, **4**, 386 (1906).

(12) Dunstan and Thole, *J. Chem. Soc.*, **95**, 1556 (1909).

(13) Referring to dioxane itself, Geddes[10] concluded from its fluidity–temperature relationship that it becomes more associated with rising temperature while the fluidity–specific volume function indicated the reverse trend. However, both deductions are unreliable because fluidity is merely a crude approximation to the true additive viscosity function θ. This appears clearly in the curved line obtained by plotting fluidity against θ, Fig. 3B.

(14) Poiseuille, *Mem. Inst. Paris*, **9**, 433 (1846).

(15) Graham, *Phil. Trans.*, **151**, 373 (1861).

(16) Traube, *Ber.*, **19**, 871 (1886).

(17) Varenne and Godefroy, *Compt. rend.*, **137**, 993 (1903).

(18) Bingham, White, Thomas and Caldwell, *Z. physik. Chem.*, **83**, 641 (1913).

The ϕ scale–volume diagram, Fig. 4, furnishes in all cases continuous curves with a single sharply located maximum which is independent of temperature and occurs at the following molar compositions

Methyl alcohol[19]	$1MeOH \cdot 2H_2O$*
Ethyl alcohol[19]	$1EtOH \cdot 4H_2O$, $1EtOH \cdot 8H_2O$
n-Propyl alcohol[19]	$1PrOH \cdot 4H_2O$
i-Propyl alcohol (Table I)	$1Me_2CHOH \cdot 6H_2O$
t-Butyl alcohol (Table I)	$1Me_3COH \cdot 8H_2O$
Allyl alcohol[20]	$1C_3H_5OH \cdot 4H_2O$

These molar proportions suggest a graded capacity of the alcohol oxygen to hold pairs of water molecules. Each substitution of one H atom on the carbon carrying the hydroxyl, by methyl or other alkyl, causes the inclusion of one pair of water molecules into the association complex. This distinction between methyl alcohol, primary, secondary and tertiary alcohols seems to satisfy some requirements of symmetry or coördination. It may be noted that no other but even numbers (except unity) of water molecules occur in any of the systems here surveyed.

The monobasic fatty acids, excepting formic acid, also give unmistakable evidence of associating with water. The literature mentions no deviation for formic acid,[16,21,22,23] a monohydrate for acetic acid[16,21,22] and propionic acid.[21] Butyric acid has been reported as forming a dihydrate containing about 70% acid.[21]

The ϕ scale–volume plot of the system water–formic acid (Fig. 5A) shows a slight but appreciable associative deviation. In the case of acetic acid a monohydrate undoubtedly is the main product; however, there is a noticeable irregularity in the ascending part of the curve on the side of water which appears at all temperatures (Fig. 5B). The meaning of this subsidiary deviation becomes clear in the peculiar curve of *n*-butyric acid (data, see Table I). If the ϕ scale deviations are plotted against molar compositions (bottom of figure) a very pronounced superimposed maximum deviation is found for $1PrCOOH \cdot 8H_2O$ and the analogous complex also exists in acetic acid. Separately shown, the respective deviations yield smooth curves and sharply defined maxima.

The polyhydric alcohols and alcohol acids are very highly associated and their viscosities are far above that of water. The usual approximations have been responsible for much futile and erroneous speculation regarding the conditions in these aqueous mixtures. Dunstan[20] investigated the system ethylene glycol–water in absolute viscosity and weight units. He obtained a strongly concave curve from which he deduced that ". . . so far from . . . association taking place, the reverse is indicated" and that the glycol ". . . in consequence of its two hydroxyl groups . . . is broken down by the water into simpler complexes." This observation evidently would mean an abrupt reversal of the trends in the monohydric alcohols whose association complexes are augmented rather than broken down by water.

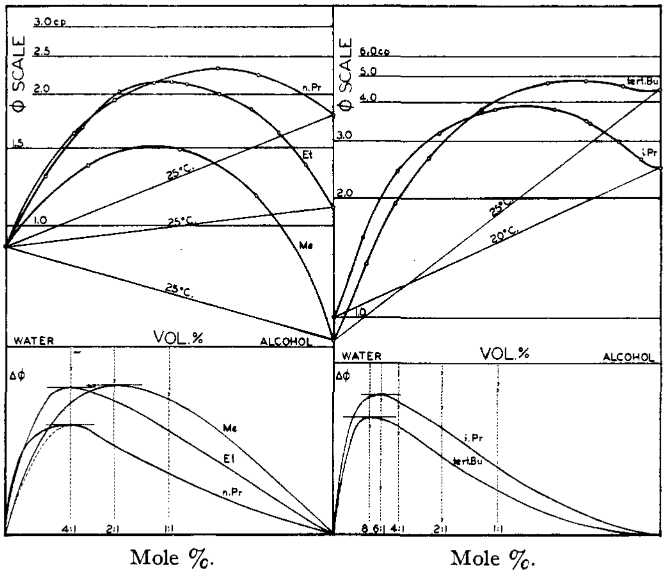

Fig. 4.—Aqueous mixtures of alcohols: (Me, methanol; Et, ethanol; *n*-Pr, *n*-propanol; *i*-Pr, isopropanol; *t*-Bu, tertiary butanol). ϕ scale deviations are plotted against molar compositions at bottom of figures.

Dunstan's viscosity measurements are very inaccurate but the errors are scarcely noticeable in absolute viscosity measure, due to the disproportionate emphasis upon but a few points at high viscosities. The ϕ scale which represents experimental errors as truly as the viscosities themselves, as a rule makes wrong data very conspicuous; by this standard Dunstan's measurements appear entirely useless. According to viscosities determined by this author (see Table I) a smooth curve deviating toward association is obtained

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[19] "International Critical Tables," Vol. V, pp. 22, 23.

[20] Dunstan, *J. Chem. Soc.*, **87**, 11 (1905).

[21] Tsakalatos, *Compt. rend.*, **146**, 1146 (1908).

[22] Dunstan and Mussell, *J. Chem. Soc.*, **97**, 1935 (1910).

[23] Davis and Jones, THIS JOURNAL, **37**, 1194 (1915).

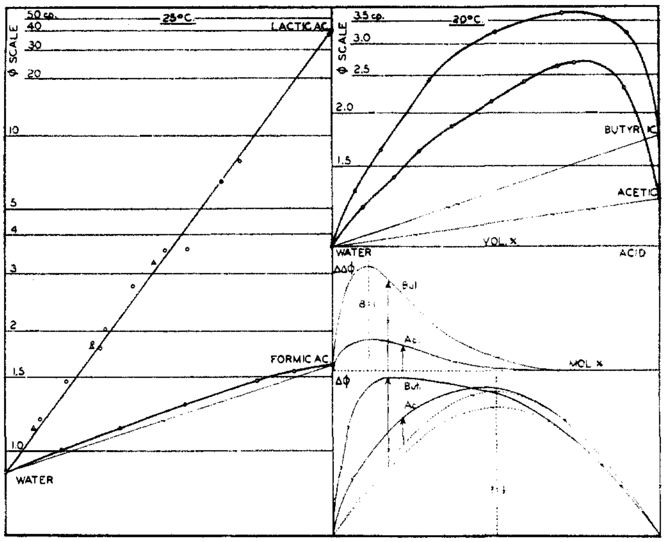

Fig. 5.—Aqueous mixtures of fatty acids: A, no or little compound formation; B, strong deviations indicating hydrates; Δφ, φ scale deviations plotted against mole %; ΔΔφ, subsidiary maxima above dotted (1:1 mole) curves.

which is shown in absolute viscosity as well as φ scale ordinates in Fig. 6. The deviation is much smaller than that in the case of ethyl alcohol which has been included in the figure for comparison. The maximum seems to be at approximately 1 glycol·4 water,[24] *i. e.*, only 2 molecules water per hydroxyl group. Thus both the capacity and the affinity for water addition appear diminished either through a resonance effect (intramolecular association between the two hydroxyl groups) or through steric hindrance. This depolarization becomes almost complete in glycerol whose mixtures with water[25] deviate very little from the base line in the φ scale–volume diagram. However, the system cannot be accepted as ideal since glycerol evolves heat on admixture with water[26] and the total volume contracts.[27] The system water–lactic acid[20,28] also shows no deviation.

TABLE I

VISCOSITY MEASUREMENTS

Isopropyl Alcohol and Water

Alcohol Vol. %	Alcohol Mol. %	Sp. gr. at 20°	Viscosity, cp.
0.0	0.0	0.998_2	1.00_5
9.0	2.3	$.990_1$	1.51
21.9	6.0	$.976_1$	2.42
32.2	10.1	$.961_8$	3.15
49.4	19.0	$.926_1$	3.78
67.4	33.1	$.883_0$	3.75
77.4	44.8	$.857_0$	3.47
78.4	46.2	$.854_9$	3.40
87.0	61.5	$.830_4$	2.96
94.0	78.8	$.810_4$	2.60
100.0	100.0	$.789_6$	2.47

t-Butyl Alcohol and Water

Alcohol Vol. %	Alcohol Mol. %	Sp. gr. at 25°	Viscosity, cp.
0.0	0.0	0.997_1	0.89_5
10.0	2.1	$.985_3$	1.34
19.1	4.3	$.974_3$	1.93
29.3	7.3	$.958_3$	2.64
45.5	14.0	$.923_0$	3.79
65.5	26.6	$.876_5$	4.71
77.2	39.2	$.846_0$	4.80
88.2	58.4	$.817_3$	4.58
100.0	100.0	.781	4.43

Butyric Acid and Water, 20°

0.0	0.0	0.998_2	1.00_5
7.0	1.5	1.005_2	1.31
15.2	3.4	1.007_4	1.64
30.0	7.8	1.006_8	2.41
50.0	16.5	1.001_6	3.24
70.1	31.6	0.995_2	3.71
83.0	49.7	0.986	3.60
90.0	66.4	0.979	3.25
100.0	100.0	0.963	1.78

Ethylene Glycol and Water, 20°

0.0	0.0	0.998_2	1.00_5
11.95	4.5	1.019_7	1.46
28.0	10.4	1.042_4	2.25
38.2	16.2	1.056_2	2.98
48.3	22.5	1.070_4	3.96
67.7	40.4	1.091_6	7.10
79.7	56.9	1.103_4	10.30
100.0	100.0	1.118_2	21.4

Considerable attention has been paid to the mixtures of formamide with the lower aliphatic alcohols and acids, in comparison with the corresponding aqueous systems.[29,30] As shown in the case of dioxane (see above) such comparisons are meaningless if based on arbitrary precepts of additivity. Merry and Turner[29] plotted absolute viscosities against molar composition and found ". . . a well marked order in the viscosity deviations, the greatest being with water, the least with ethyl alcohol . . . for higher alcohols the deviation may change from negative to positive and lead ultimately to a maximum point." They note that ". . . as we proceed up the homologous series, the deviation of the viscosity from the mixture rule becomes more and more pronounced" but they admit that ". . . there is no evidence that will lead us to believe that isoamyl alcohol will form a compound with formamide when the lower and more active alcohols will not."

The φ scale–volume diagram eliminates all these contradictions (Fig. 7A). Water and formamide show a strong negative deviation and give no sign of compound formation. Methyl alcohol and formamide as well as all the higher alcohols form compounds; the deviations gradually diminish in magnitude upon ascending the homologous series. The curves suggest that the formation of the complexes depends on preliminary dissociation of the alcohols.

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(24) De Forcrand, *Compt. rend.*, **132**, 688 (1901), found the heat of solution at a maximum for 1 glycol·2 water and Schwers, *Ann. chim.*, **26**, 234 (1902), for 1 glycol·6 water.

(25) Schöttner, *Sitzber. Akad. Wiss. Wien*, **77**, 682; **79**, 1979 (1878); Sheely, *Ind. Eng. Chem.*, **24**, 1060 (1932).

(26) Kolosovsky, Katz, Gerlach, Ems and Berthelot, *cf.* Lawrie, "Glycerol and the Glycols," The Chemical Catalog Co., New York, N. Y., 1928.

(27) Gerlach and Bosart, *cf.* Lawrie[26].

(28) Reyher, *Z. physik. Chem.*, **2**, 744 (1888).

(29) Merry and Turner, *J. Chem. Soc.*, **105**, 748 (1914).

(30) English and Turner, *ibid.*, **105**, 1656 (1914).

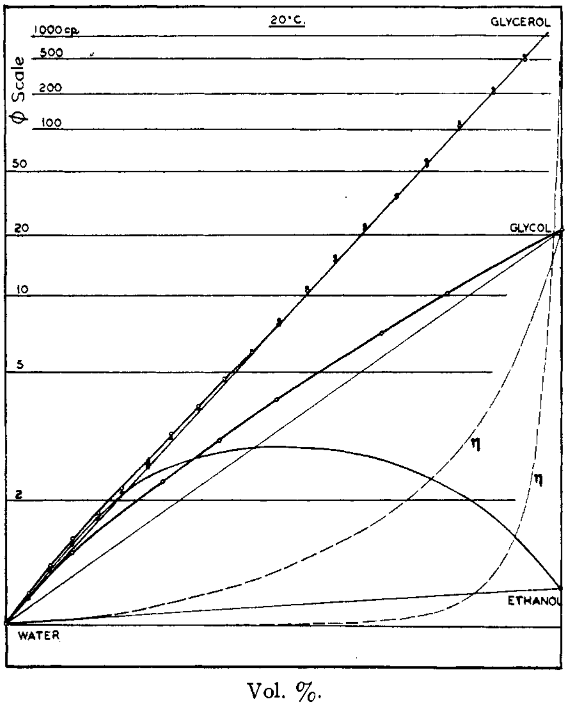

Fig. 6.—Aqueous mixtures of polyhydric alcohols: absolute viscosity–weight per cent. curves (η) proportioned so as to make their end-points coincide with those of ϕ scale base lines; data, for (glycerol) O, Schöttner[25]; ●, Sheely.[25]

Conditions in the mixtures of formamide with the fatty acids have much in common with the analogous aqueous systems. The principal maxima appear at equimolar proportions of the components but there is evidence of the existence of two other types of compounds, one with a higher proportion of acid and the other containing more formamide. A shift from the former toward the latter occurs upon ascending the series of acids. Unlike water, formamide associates with formic acid (Fig. 7B).

Referring in general to stoichiometric proportions indicated by maximum deviations of the viscosity function, these are not necessarily due to the formation of compounds for whose existence ". . . isolation and analysis are the only satisfactory tests."[9] The restrictions imposed upon the free mobility of the molecules which are observable as viscosity may remain more or less diffused among large and varying numbers of molecules or they may affect only pairs or particular assemblies. Hence, a maximum occurring at an exact stoichiometric proportion could be due to some preferred but transitory grouping as well as to the formation of a fixed compound. Negative deviations cannot be understood in the latter sense but some investigators have accepted negative maxima as evidence of compound formation.

Summary

The interpretation of viscosity data in terms of the state of liquids and of the interaction of substances in the liquid phase is based on various arbitrary premises inherent in the customary methods of graphical analysis. The central problem—the correct formulation of the additive function of viscosity in mixtures—is still inaccessible by purely speculative approach. Due to the prevailing confusion in the methods of evaluation, such a large number of recorded observations on association, dissociation, compound formation, etc., are wrong that the whole field is in need of critical revision.

Analysis of viscosity data by means of the functional scales developed in the preceding papers of the series continues to prove its reliability as shown in application to a selection of non-ideal systems. The system sulfuric acid–ether, the aqueous and formamide mixtures of dioxane, the lower alcohols and fatty acids have been discussed as examples. The method not only yields more plausible and concordant results

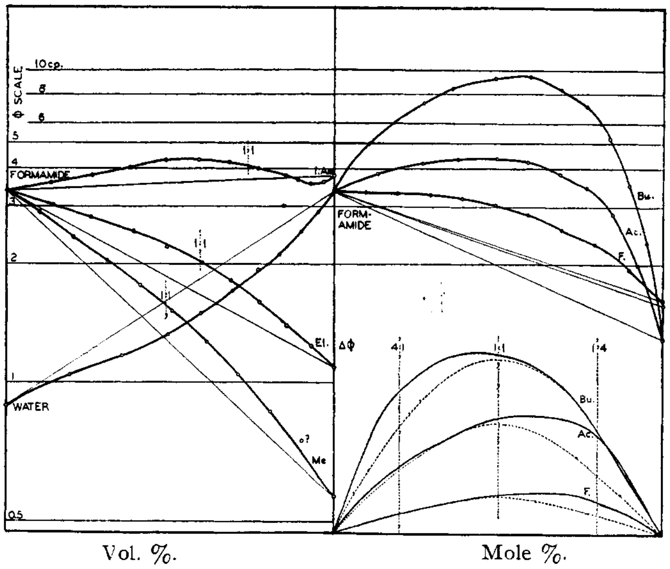

Fig. 7.—Formamide mixtures of A, water, alcohols; B, fatty acids (Me, methanol; Et, ethanol; *i*-Am, isopentanol; F, formic acid; Ac, acetic acid; Bu, *n*-butyric acid); bottom of B, analysis of ϕ scale deviations.

than otherwise are obtainable but it also reveals fine distinctions which, in the commonly adopted practices of evaluation, are entirely lost.

SHAWINIGAN FALLS, QUE. RECEIVED APRIL 9, 1942

[CONTRIBUTION FROM THE WESTERN REGION, BUREAU OF MINES, U. S. DEPARTMENT OF THE INTERIOR]

Heat Content of Manganese Dioxide and Carbonate at High Temperatures[1]

BY G. E. MOORE[2]

In the course of a program of investigation of the thermodynamic properties of manganese compounds being conducted at the Pacific Experiment Station of the Bureau of Mines, some measurements of the heat content of manganese dioxide and manganese carbonate (rhodochrosite) above 25° have been made. These data are required for accurate thermodynamic calculations on the dissociation equilibria of these substances and on certain proposed hydrometallurgical processes involving them. The entropies from low-temperature specific heat data have been reported.[3,4]

Method and Materials

The procedure employed is the so-called "drop" method; the apparatus has been described.[5] The samples were contained in a platinum-rhodium alloy capsule having a snugly fitting but not gas-tight cap.

The manganese dioxide was part of the sample used by Kelley and Moore, prepared by decomposing aqueous manganous nitrate, followed by careful and complete dehydration. Analysis gave substantially 100.0% MnO_2. The density was carefully measured with a pycnometer under carbon tetrachloride and found to be[6] d^{25}_4 5.11_8; this is somewhat higher than the value reported by Krüll[7] (d^{25}_4 4.943) for a similarly prepared material.

The manganese carbonate sample was a portion of the rhodochrosite used by Anderson,[4] who reported the impurities as 2.0% calcium carbonate, 0.1% silicon dioxide and 0.1% ferrous carbonate. The results given below were corrected for 2.0% calcium carbonate using data compiled by Kelley[8]; the correction amounted to about 0.3%.

In each case, the highest temperature of the measurements was that at which dissociation began to occur, as evidenced by a slight loss in weight.

Results

The experimentally determined heat contents above 298.16°K. are given in Table I, in the order in which they were obtained. The results are expressed in defined calories (1 calorie = 4.1833 int. joules) per gram formula weight, computed in accordance with the 1941 International Atomic Weights. It is estimated that the error in these data probably is about 0.5% at the higher temperatures, increasing to about 1.5% below 400°K. Table II is a summary of values at 100° intervals read from smooth curves through the data, together with the calculated entropy increments above 298.16°K. in cal./g. f. w.-deg.

TABLE I

HEAT CONTENTS ABOVE 298.16°K.

$MnCO_3$ (g. f. w. = 114.94)		MnO_2 (g. f. w. = 86.93)	
T, °K.	$H^0_T - H^0_{298.16}$, cal./g. f. w.	T, °K.	$H^0_T - H^0_{298.16}$, cal./g. f. w.
419.3	2592	406.7	1546
476.1	3961	405.6	1530
476.2	3954	501.2	3035
467.4	3715	509.9	3184
471.7	3853	572.8	4236
542.1	5609	573.0	4233
608.8	7330	358.3	847
660.3	8716	341.2	587
594.0	6973	662.0	5757
		663.0	5767
		733.7	6992
		777.9	7762

TABLE II

HEAT CONTENTS AND ENTROPIES ABOVE 298.16°K. AT 100° INTERVALS

	$MnCO_3$		MnO_2	
T, °K.	$H^0_T - H^0_{298.16}$, cal./g. f. w.	$S^0_T - S^0_{298.16}$, cal./g. f. w. deg.	$H^0_T - H^0_{298.16}$, cal./g. f. w.	$S^0_T - S^0_{298.16}$, cal./g. f. w. deg.
400	2160	6.22	1445	4.18
500	4550	11.55	3021	7.69
600	7095	16.19	4687	10.72
700	9800	20.36	6413	13.38
800	..	...	8186	15.75

The data show no irregularities in the range investigated; they may be represented to within about 0.3% by the following equations, derived from the data in Table II. The equations for C_p were obtained by differentiating the corresponding heat-content equations.

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(1) Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Not copyrighted.

(2) Chemist, Western Region, Bureau of Mines.

(3) K. K. Kelley and G. E. Moore, THIS JOURNAL, **65**, 782 (1943).

(4) C. T. Anderson, *ibid.*, **56**, 849 (1934).

(5) J. C. Southard, *ibid.*, **63**, 3142 (1941).

(6) The density measurements were made by Dr. E. H. Huffman of this Station.

(7) F. Krüll, *Z. anorg. allgem. Chem.*, **208**, 135 (1932).

(8) K. K. Kelley, U. S. Bur. Mines, Bull. 371.