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**COMPOUND FORMATION AND VISCOSITY IN SOLUTIONS
OF THE TYPES ACID : ESTER, ACID : KETONE, AND ACID : ACID.**

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In a recent article¹ the complete specific conductivity-composition curves for a number of systems of the above types have been presented, and their significance with respect to the fundamental relationship between compound formation and ionization in solutions, as postulated in previous papers,^{2,3} critically examined. The point was made clear in the discussion, however, that for a strict comparison of ionization equilibria throughout the different systems a knowledge of other variables was necessary. Among these variables the first in importance is viscosity.

In the present communication the viscosity—composition curves for certain of the above systems are given, not so much with the idea of making immediate and final corrections in the corresponding specific conductivity curves as with the hope of obtaining additional and confirmatory information regarding the relative extent and stability of compound formation between the components in such systems. When progress in other lines has been made, the results here obtained will of course ultimately be of service in making exact corrections upon the conductivity data. The present impossibility of such a procedure, however, is discussed in a later section.

Experimental.

The following systems have been investigated: (a) *acid:ester systems*, trichloro-acetic acid and acetic acid with ethyl acetate and ethyl benzoate; (b) *acid-ketone systems*, trichloro-acetic acid and acetic acid with acetone and acetophenone; (c) *acid:acid systems*, trichloro-acetic acid with acetic acid.⁴

The same careful methods of purification of the substances employed described in earlier articles^{5,3} were followed, and materials of the same high order of purity, as evidenced by suitable physical constants in each case, were obtained throughout. The apparatus used for the determination of viscosities was of the Bingham type.^{6,7} The experimental procedure was essentially as given in previous work,⁸ the only new feature

¹ Kendall and Gross, *THIS JOURNAL*, **43**, 1426 (1921).

² Kendall and Booge, *ibid.*, **39**, 2323 (1917).

³ Kendall and Gross, *ibid.*, **43**, 1416 (1921).

⁴ Other examples of this type (and of its extension into the type: acid-base) have been taken up by previous investigators. The results obtained by them are utilized in the discussion below.

⁵ Kendall and Wright, *THIS JOURNAL*, **42**, 1776 (1920).

⁶ Bingham, *J. Ind. Eng. Chem.*, **6**, 233 (1914).

⁷ Bingham, Schlesinger and Coleman, *THIS JOURNAL*, **38**, 27 (1916).

⁸ Kendall and Monroe, *ibid.*, **39**, 1787 (1917).

presented being the necessity of adopting particular precautions for the protection of the materials employed against water vapor, the hygroscopic character of certain of the substances used (*e. g.*, trichloro-acetic acid⁹) being very pronounced.

TABLE I.
PROPERTIES OF PURE COMPONENTS.

Liquid.	Freezing pt. °C.	Boiling pt. (760 mm.) °C.	Density, 25°/4°.	Viscosity, 25°.	Spec. con- ductivity, (mhos) 25°.
Ethyl acetate	77.1 ± 0.05	0.8948	0.004236	1 × 10 ⁻⁹
Ethyl benzoate ¹⁰	212.9 ± 0.1	1.0458	0.01982	1 × 10 ⁻⁹
Acetone ¹¹	0.7872	0.003065	6 × 10 ⁻⁸
Acetophenone	202.3 ± 0.1	1.0263	0.01681	5.5 × 10 ⁻⁸
Acetic acid ¹²	16.57 ± 0.05	117.8 ± 0.1	1.0499	0.01121	2.4 × 10 ⁻⁸
Trichloro-acetic acid ¹³	59.2	(1.62)	(0.0683)	(3 × 10 ⁻⁹)

The viscosity results obtained for the various systems at 25° are presented in the tables below. Density data are also appended, to enable transformation of the results from molecular percentages to volume percentages to be made if desired. With the Bingham viscometer, very accurate density determinations are not necessary,¹⁴ and the values given are not to be relied upon beyond the third decimal place. The mixtures investigated being essentially non-ideal, linearity in the density-volume composition curve is not to be expected. In some of the systems, considerable heat effects were evident on admixture.

TABLE II.

TRICHLORO-ACETIC ACID : ETHYL ACETATE.

Mol. % acid.	d ₄ ²⁵ .	Viscosity.
0.00	0.8948	0.004236
11.18	0.9972	0.005878
18.40	1.045	0.007309
28.07	1.123	0.01001
38.46	1.202	0.01449

TABLE III.

ACETIC ACID : ETHYL ACETATE.

Mol. % acid.	d ₄ ²⁵ .	Viscosity.
0.00	0.8948	0.004236
10.49	0.9092	0.004590
20.70	0.9211	0.004949
30.37	0.9308	0.005331
39.90	0.9417	0.005762

⁹ Work with this substance was confined to cold, dry days.

¹⁰ The density here obtained is slightly greater than that given by Kendall and Wright (Ref. 5); the viscosity is slightly less, but practically identical with the former value of Kendall and Monroe. The boiling-point recorded in Kendall and Wright's article (p. 778) is in error, the value for a preliminary sample having been accidentally substituted.

¹¹ Jones and Mahin (*Am. Chem. J.*, **41**, 440 (1909)) quote a much higher viscosity for acetone. The result here given, however, is very close to the interpolated value of Thorpe and Rodger (*Phil. Trans.*, **185A**, 397 (1894)) and to the more recent value of Dunstan and Hilditch (*Z. Elektrochem.*, **18**, 186 (1912)).

¹² Dunstan (*Z. physik. Chem.*, **51**, 732 (1905)) gives a higher viscosity value, but the present result is again in good agreement with Thorpe and Rodger's data.

¹³ The values given are extrapolated from measurements at higher temperatures, as described later.

¹⁴ The density enters into the working formula only in a correction factor (approximately 1% of the total), hence approximate values are sufficient. In a few cases the figures given are interpolated results.

TABLES II AND III (Continued).

Mol. % acid.	d_4^{25}	Viscosity.	% acid.	d_4^{25}	Mol. Viscosity.
48.78	1.295	0.02176	49.85	0.9557	0.006289
61.42	1.386	0.03467	59.96	0.9697	0.006890
70.08	1.454	0.04709	69.88	0.9850	0.007668
			80.11	1.0015	0.008590
			87.42	1.0165	0.009430
			100.00	1.0499	0.01121

TABLE IV.

TRICHLORO-ACETIC ACID : ETHYL BENZOATE.

Mol. % acid.	d_4^{25}	Viscosity.
0.00	1.0458	0.01982
8.874	1.0864	0.02324
20.96	1.1466	0.02930
31.25	1.1915	0.03711
39.82	1.2413	0.04610
49.07	1.2922	0.05848
57.95	1.3501	0.07068
67.58	1.4027	0.08374

TABLE V.

ACETIC ACID : ETHYL BENZOATE.

Mol. % acid.	d_4^{25}	Viscosity.
0.00	1.0458	0.01982
10.41	1.046	0.01948
21.29	1.046	0.01874
30.45	1.047	0.01797
38.82	1.047	0.01727
47.50	1.047	0.01651
58.22	1.048	0.01538
68.26	1.048	0.01446
79.56	1.049	0.01322
91.32	1.049	0.01202
100.00	1.050	0.01121

TABLE VI.

TRICHLORO-ACETIC ACID : ACETONE.

Mol. % acid.	d_4^{25}	Viscosity.
0.00	0.7872	0.003065
4.84	0.8541	0.003680
13.16	0.9342	0.004855
25.43	1.073	0.008156
38.26	1.209	0.01433
50.48	1.319	0.02571
59.71	1.400	0.03829
71.75	1.483	0.05808

TABLE VII.

ACETIC ACID : ACETONE.

Mol. % acid.	d_4^{25}	Viscosity.
0.00	0.7872	0.003065
9.96	0.8089	0.003496
20.35	0.8351	0.004046
30.25	0.8568	0.004636
40.49	0.8847	0.005350
49.86	0.9064	0.006098
59.73	0.9333	0.006994
69.68	0.9609	0.008026
80.15	0.9907	0.009213
90.37	1.0255	0.01036
100.00	1.0499	0.01121

TABLE VIII.

TRICHLORO-ACETIC ACID : ACETOPHENONE.

Mol. % acid.	d_4^{25}	Viscosity.
0.00	1.026	0.01681
8.96	1.076	0.02112
14.00	1.103	0.02402
21.21	1.146	0.02931
29.39	1.192	0.03735
40.90	1.268	0.05540
48.76	1.317	0.07349
57.94	1.376	0.09330
68.15	1.442	0.1115

TABLE IX.

ACETIC ACID : ACETOPHENONE.

Mol. % acid.	d_4^{25}	Viscosity.
0.00	1.0263	0.01681
9.98	1.0272	0.017407
21.07	1.0287	0.017536
29.35	1.0300	0.01742
42.53	1.0325	0.01703
48.85	1.0338	0.01668
60.03	1.0365	0.01598
69.98	1.0390	0.01524
80.02	1.0420	0.01420
90.13	1.0453	0.01293
100.00	1.0499	0.01121

TABLE X.

TRICHLORO-ACETIC ACID : ACETIC ACID.

Mol. % CCl_3COOH .	d_4^{25}	Viscosity.
0.00	1.049	0.01121
7.37	1.129	0.01532
17.77	1.223	0.02228
32.09	1.337	0.03362
43.48	1.409	0.04346
52.62	1.457	0.05176
58.53	1.491	0.05859
65.81	1.508	0.06854

Consideration of Results.

The majority of the systems with trichloro-acetic acid as one component are reproduced in diagram form in Fig. 1; those with acetic acid as one component are shown in Fig. 2.

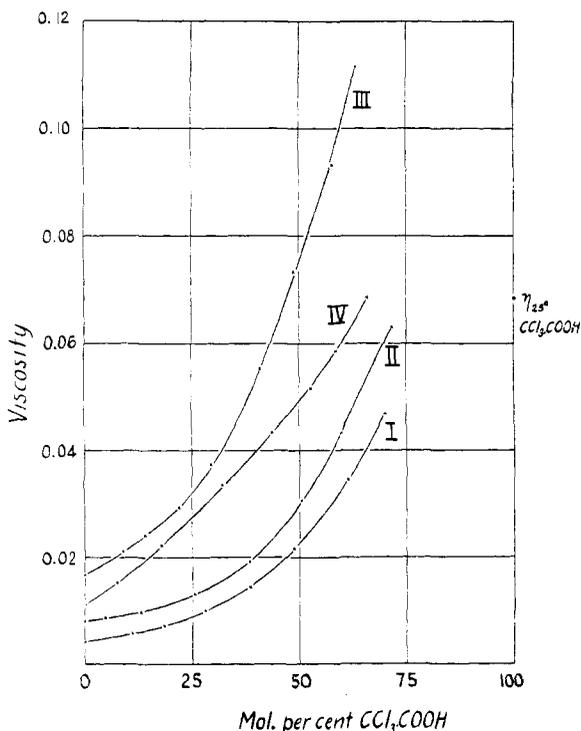


Fig. 1.—Trichloro-acetic acid systems. I. Trichloro-acetic acid:ethyl acetate; II. Trichloro-acetic acid:acetone (subtract 0.005 from viscosity scale); III. Trichloro-acetic acid:acetophenone; IV. Trichloro-acetic acid:acetic acid.

It will be noticed that the trichloro-acetic acid curves are incomplete. This is due to the fact that pure trichloro-acetic acid melts at 59.4° ; consequently solutions containing more than 70 mol. % (approximately) of trichloro-acetic acid begin to solidify at temperatures above 25° . In a few cases slightly supercooled solutions were successfully investigated at this temperature. With any large excess of acid, however, crystallization during the determinations, stopping up the capillary and rendering all measurements impossible, could not be prevented.

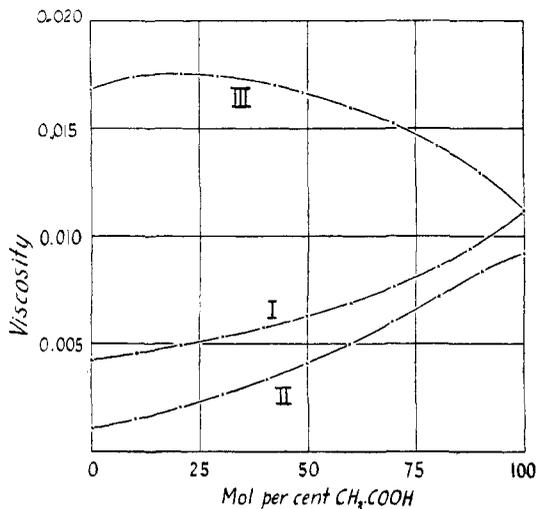


Fig. 2.—Acetic acid systems. I. Acetic acid:ethyl acetate; II. Acetic acid:acetone (add 0.002 to viscosity scale); III. Acetic acid:acetophenone.

An approximate value for the viscosity of pure trichloro-acetic acid at 25° was derived by making measurements with an Ostwald viscometer in a small bath at two temperatures above its melting point and extrapolating the results. At 60° the density and viscosity were 1.595 and 0.0397 respectively, and at 70° they were 1.588 and 0.0315. By linear extrapolation the viscosity at 25° is 0.0683; in view of the uncertainty of the extrapolation¹⁵ and the relatively large experimental errors involved in the Ostwald method of measuring viscosity this figure must be regarded as merely indicative.

The position of the point for pure trichloro-acetic acid on the diagram

¹⁵ Viscosity is not, of course, a linear function of temperature, but the various relationships proposed for normal liquids (Batschinski, *Z. physik. Chem.*, **84**, 643 (1913); Arrhenius, *Meddel. K. Vetenskapsakad. Nobelinst.*, **3**, No. 20 (1918)) will certainly not be applicable to an associated liquid such as trichloro-acetic acid. Linear extrapolation is here adopted as the simplest possible procedure and cannot, in view of the shortness of the temperature interval, involve any extreme error.

(Fig. 1), however, makes it evident that the viscosity curves for all systems examined containing this acid as one component exhibit a very sharp maximum in the neighborhood of 80 to 90 mol. % acid. The existence of such a maximum must be ascribed, in each case, to the extensive formation of complex addition compounds of higher viscosity than the pure components. It was at one time common practice¹⁶ to deduce the formulas for such addition compounds from the position of the maximum on the composition axis. The fallacy of such a procedure has been exposed by Findlay¹⁷ and by Denison,¹⁸ who have employed the more logical method of marking the position of maximum deviation from the normal curve rather than the actual maximum point. Unfortunately, in the case of viscosities, we have not yet succeeded in establishing the ideal curve¹⁹ all that we know with certainty is that it is not linear but considerably sagged. We cannot therefore postulate, from examination of the above curves, what compounds are present in the solutions. We are justified, however, in regarding the curves as confirming the fact, already indicated by freezing-point data, that addition compounds are formed in quantity in all cases.

The curves with acetic acid as one component are of a different nature. Only in one system here studied (acetic acid:acetophenone) is a maximum obtained, and even this is exceedingly flat. While we can legitimately draw, from this, the conclusion (also previously indicated by freezing-point data^{20,21}) that compound formation is in general much less extensive in systems of esters and ketones with acetic acid than in systems of the same substances with trichloro-acetic acid, yet the absence of a maximum must not be taken to signify that compound formation is entirely absent. Thus the curve for the system acetic acid:acetone is not sagged throughout, but shows a point of inflection; while the curve for the system acetic acid:ethyl benzoate is entirely concave (instead of convex) towards the composition axis. Compounds are evidently present in solution in these cases in quantity sufficient to raise the curves considerably above their normal position, but insufficient to produce an actual maximum. Even in the curve for the system acetic acid:ethyl acetate, which is sagged and apparently ideal throughout, compound formation is undoubtedly a factor, for acetic acid is a typical associated liquid and the addition of a substance entirely inert towards it would normally result in a viscosity curve with a minimum point, due to the progressive disassociation of the acetic acid into less viscous simple molecules as its concentration in the

¹⁶ For references see Walden, *Ahrens' Sammlung*, **15**, 397 (1910).

¹⁷ Findlay, *Z. physik. Chem.*, **69**, 217 (1909).

¹⁸ Denison, *Trans. Faraday Soc.*, **8**, 35 (1912).

¹⁹ See Kendall and Monroe, *THIS JOURNAL*, **43**, 115 (1921).

²⁰ Kendall and Booge, *ibid.*, **39**, 1712 (1916).

²¹ Kendall and Gibbons, *ibid.*, **37**, 149 (1915).

solution diminishes.²² Compound formation, in this case, must approximately counterbalance such disassociation. In the other systems, for the same reason, the true extent of compound formation must be greater than that which is apparent from the shape of the curves (particularly in a case such as acetic acid: acetone, where *both* components of the system are highly associated liquids), owing to the obscuring effect of the disassociation factor.

Systems of the Type Acid:Acid and Acid:Base.—The one system of the type acid:acid here examined (trichloro-acetic acid: acetic acid) gives a sharp maximum on the viscosity curve (see Fig. 1), although at 25° this maximum cannot be experimentally realized owing to its proximity to the trichloro-acetic acid side of the diagram. The viscosity results thus confirm the extensive formation of addition compounds between the two acids of widely divergent acidic strengths previously suggested by freezing-point depression measurements.²³ It is of importance to note that the viscosity curve for the system acetic acid:sulfuric acid²⁴ also shows a maximum. In this case the existence of an equimolecular compound (CH₃COOH, H₂SO₄), with melting point -2.5°, has been directly established by examination of the freezing-point curve.²⁵ With acids of similar acidic strength, however, (*e. g.*, formic acid,²⁶ propionic acid) acetic acid gives a typically sagged curve, indicating that compound formation is practically non-existent.

When we consider acetic acid with bases, increasing diversity again involves increasing compound formation and the maximum reappears. Thus acetic acid:formamide²⁷ and acetic acid:water²⁸ both show curves with comparatively flat maxima. With a still stronger base, (acetic acid:aniline²⁹) the maximum becomes very sharp, flattening out only at high temperatures.

Many other examples of the type acid:base, of similar character, have been investigated by previous workers. It will suffice here to mention the curve for the system sulfuric acid:water³⁰ (which gives a very sharp maximum corresponding to the very stable compound H₂SO₄.H₂O) and the recent work of Bramley³¹ on systems of the type phenol:aniline.

²² Kendall and Monroe, *THIS JOURNAL*, **43**, 122 (1921).

²³ Kendall, *ibid.*, **36**, 1722 (1914).

²⁴ Drucker and Kassel, *Z. physik. Chem.*, **76**, 363 (1911).

²⁵ Unpublished work of Kendall and Davis.

²⁶ Herz, *Z. anorg. Chem.*, **104**, 51 (1918).

²⁷ Merry and Turner, *J. Chem. Soc.*, **105**, 758 (1914).

²⁸ Dunstan and Thole, *ibid.*, **95**, 1560 (1909).

²⁹ Faust, *Z. physik. Chem.*, **79**, 106 (1912).

³⁰ Dunstan and Wilson, *J. Chem. Soc.*, **91**, 83 (1907).

³¹ Bramley, *ibid.*, **109**, 10, 434 (1916).

Application of a Viscosity Correction to Conductivity Data.—Walden³² has shown that for a fixed solute (tetra-ethylammonium iodide) in a series of very divergent solvents the product of Λ_{∞} and η is practically a constant; in other words, the mobilities of the ions are inversely proportional to the viscosity of the medium. If Walden's rule could be directly extended to the systems investigated in this paper, we could at once transform the specific conductivities as determined by Kendall and Gross to relative ionic concentrations by multiplying throughout by the viscosity of each particular solution. Considerable doubt has been cast by subsequent workers³³ in this field, however, upon the general validity of Walden's rule, and the conditions here existent are so different from those in the solutions examined by Walden that we are compelled to hesitate in making this step until more definite advances have been made, lest by attempting to compare our results on a false basis we arrive at entirely unjustified conclusions.

Walden worked with a single solute only³⁴ (and that a salt, as recent work indicates,³⁵ of exceptional character) at very low concentrations. In any particular solvent, therefore, the degree of solvation of the ions would not appreciably vary. In the present work, we are dealing with solutions with compositions ranging all the way from pure component A to pure component B, and the average ionic complexity will undoubtedly change very significantly with composition.³⁶ In the case of aqueous solutions of salts at moderate concentrations, Green³⁷ and Washburn³⁸ have established that a fractional power viscosity correction is more accurate than a linear correction, presumably on account of decreasing hydration of the ions with decreasing water concentration.³⁹ Here, with a much more extended concentration range, viscosity variations are so enormous (over 1000% in some systems) that the value of the exponent in any fractional power correction would need to be very accurately

³² Walden, *Z. physik. Chem.*, **55**, 246 (1906).

³³ For example, Fitzgerald has shown that $\Lambda_{\infty}\eta$ is by no means constant for salts in liquid ammonia, sulfur dioxide and water (*J. Phys. Chem.*, **16**, 645 (1912)). For further references see Kraus, *THIS JOURNAL*, **36**, 35 (1914); Ghosh, *J. Chem. Soc.*, **117**, 1390 (1920).

³⁴ In an article which has just appeared (*Z. anorg. Chem.*, **113**, 85 (1920)) Walden has tried to extend his rule to other solutes, partly answering and partly admitting the objections made by other investigators.

³⁵ Ghosh, *J. Chem. Soc.*, **113**, 630 (1918); Walden, *Z. physik. Chem.*, **94**, 295 (1920).

³⁶ See Kendall and Gross, *THIS JOURNAL*, **43**, 1436 (1921).

³⁷ Green, *J. Chem. Soc.*, **93**, 2049 (1908).

³⁸ Washburn, *THIS JOURNAL*, **33**, 1461 (1911).

³⁹ Similarly Johnston (*ibid.*, **31**, 1010 (1909)) found a fractional power relationship to exist between Λ_{∞} and η as temperature is varied. Schlesinger and Coleman, however, in the case of metal formates in formic acid solutions, claim that no viscosity correction at all is to be applied (*ibid.*, **38**, 271 (1916)).

determined to fix the final position of a curve. Since, furthermore, different systems might very conceivably require quite different exponents and would almost certainly give significantly different values for the product $\Lambda_{\infty} \eta$, any rigorous comparison at this stage is obviously altogether impracticable.

As has been shown above, however, the viscosity results in themselves furnish us with considerable additional information on compound formation in the systems studied, confirming very strongly the rule that compound formation is fundamentally dependent upon diversity in character of the constituent groups of the components, and the data here presented will later, it is hoped, be utilized in making exact and dependable corrections upon the conductivity results of Kendall and Gross.

Summary.

The viscosity-composition curves for the following systems at 25° have been determined: (1) trichloro-acetic acid:ethyl acetate, (2) acetic acid:ethyl acetate, (3) trichloro-acetic acid:ethyl benzoate, (4) acetic acid:ethyl benzoate, (5) trichloro-acetic acid:acetone, (6) acetic acid:acetone, (7) trichloro-acetic acid:acetophenone, (8) acetic acid:acetophenone, (9) trichloro-acetic acid:acetic acid.

The results obtained indicate extensive compound formation in solutions of the esters and ketones with a strong acid (trichloro-acetic). The same substances with a weak acid (acetic) give viscosity curves which are much less abnormal, although compound formation is still evident. The curve for the system trichloro-acetic acid:acetic acid exhibits considerable compound formation, and an examination of the results of previous workers on systems of the types acid:acid and acid:base shows that this behavior is general, except when the components are of similar acidic strength. The rules formulated in previous articles relating the extent of compound formation with diversity in character of the components are hereby confirmed.

The results here presented may ultimately be employed to place the specific conductivity data obtained by Kendall and Gross for the same systems upon a strictly comparable basis. The difficulties which prevent this step being made immediately have been briefly discussed.