

The first column gives the number of moles of acetic acid per liter of solution, the second, the number of moles of potassium acetate per liter of solution, the third, the density, the fourth, the electromotive force corrected to 760 mm. of hydrogen, and the last, the relative activity coefficients of the undissociated acid.

Discussion

A review of data on the activity coefficients of the un-ionized part of weak acids has been given by Randall and Failey.⁶

The methods available for studies of this quantity have been distillation and distribution experiments, and studies on the solubilities of slightly soluble acids. The first two methods lack precision, and the last one obviously is limited to weak acids whose solubility is not large. The method presented in this paper is simple and unambiguous. It can be applied to any weak acid having a slightly soluble mercurous salt. The relative activity coefficients obtained are thermodynamically exact.

The usual method of calculation of the activity of hydrogen ions in a buffer mixture is based on

(6) M. Randall and C. F. Failey, *Chem. Rev.*, **4**, 291 (1927).

the assumption that the undissociated part of the acid has an activity equal to its concentration. From our results it appears that such an assumption is valid if the salt content does not exceed 0.3 molar, at least in the case of acetic acid-potassium acetate buffers.

Further studies of the effects of other acetates upon acetic acid as well as of other weak acid buffer systems are being undertaken in this Laboratory.

Acknowledgment.—We wish to thank Mr. Joseph Norris for his assistance in preparing the chemicals and in measuring many of the cells.

Summary

The standard e. m. f. of the electrode $\text{Hg}/\text{Hg}_2(\text{OAc})_2(s)$, OAc^- is -0.5109 v. at 25° .

A method for determining the activity coefficient of the undissociated part of weak acids has been described. This method can be applied to any weak acid whose mercurous salt is slightly soluble.

Values of the relative activity coefficients of acetic acid molecules in the presence of potassium acetate are presented.

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RECEIVED AUGUST 29, 1938

Volume Changes in the Methyl Alcohol-Toluene System

BY L. S. MASON AND HOMER PAXTON

There has been little systematic study of the changes in volume which attend the formation of a large number of binary systems of organic liquids, and the data which are available seem to permit no satisfactory generalizations. Few investigators consider such changes due to purely physical factors. Possibly relative inter- and intramolecular volumes are significant in some, if not in all, cases, but it is more probable that the seemingly ubiquitous association, dissociation and solvation effects are predominant, particularly when considered in conjunction with the deviations of other physical constants from additivity.

Solutions of methyl alcohol in toluene at 25° show a negative volume change over the entire range of composition, in contrast with solutions of ethyl alcohol and of isopropyl alcohol in toluene and in benzene. Moreover, measurements on this system at two different temperatures have indicated that further measurements over a range

of temperatures might yield interesting information.^{1,2} We have therefore measured the densities of representative solutions of these two substances at -21.1 , 0.0 , 25.0 and 49.7° .

Methyl alcohol and toluene were used without further purification, their densities being 0.78693 and 0.86228 , respectively, in close agreement with the best recent values of 0.78705^3 and 0.78675^4 for methyl alcohol and 0.86106^5 , 0.8625^6 and 0.86233^7 for toluene. The solutions were prepared by weight and precautions taken to reduce the evaporation and distillation effects to a minimum. The

(1) E. R. Washburn and A. Lightbody, *J. Phys. Chem.*, **34**, 2701 (1930).

(2) L. S. Mason and E. R. Washburn, *ibid.*, **40**, 481 (1936).

(3) H. H. Willard and G. F. Smith, *THIS JOURNAL*, **45**, 286 (1923).

(4) K. K. Kelley, *ibid.*, **51**, 180 (1929).

(5) D. Tyrer, *J. Chem. Soc.*, **106**, 2534 (1914); "International Critical Tables," Vol. III, p. 29.

(6) J. F. W. Schulze, *THIS JOURNAL*, **36**, 498 (1914); "International Critical Tables," Vol. VII, p. 77.

(7) J. Timmermans and F. Martin, *J. chim. phys.*, **23**, 755 (1926); "International Critical Tables," Vol. III, p. 27.

TABLE I
 VOLUME CHANGES ACCOMPANYING MUTUAL SOLUTION OF METHYL ALCOHOL AND TOLUENE

Wt. % alc.	Mol. frac. alc.	-21.1°		0.0°		25.0°		49.7°	
		Obsd. dens.	% Vol. change						
0.00	0.000	0.90480		0.88547		0.86228		0.83915	
9.25	.226	.89767	-0.040	.87837	-0.051	.85490	-0.022	.83099	+0.064
21.33	.438	.88876	-.117	.86928	-.115	.84569	-.078	.82171	+.008
30.25	.555	.88216	-.159	.86253	-.142	.83887	-.103	.81480	-.013
40.92	.666	.87398	-.159	.85437	-.149	.83066	-.107	.80658	-.021
50.37	.744	.86717	-.196	.84744	-.175	.82371	-.133	.79966	-.056
59.44	.808	.86021	-.171	.84056	-.161	.81682	-.120	.79284	-.055
69.44	.867	.85276	-.157	.83307	-.145	.80940	-.112	.78545	-.054
74.97	.897	.84855	-.127	.82899	-.132	.80533	-.100	.78149	-.057
89.12	.959	.83804	-.069	.81841	-.066	.79492	-.054	.77120	-.030
100.00	1.000	.82992		.81031		.78693		.76340	

measurements were carried out using pycnometers of the Wade and Merriman type,⁸ weighing 15 g. and holding 25 ml. Measurements at -21.1 and 0.0° were made by immersing the filled pycnometers in a mush of ice, salt and water in one case, and ice and water in the other, in a glass container. For the measurements at 25.0 and 49.7° a thermostat regulating to $\pm 0.03^\circ$ was used.

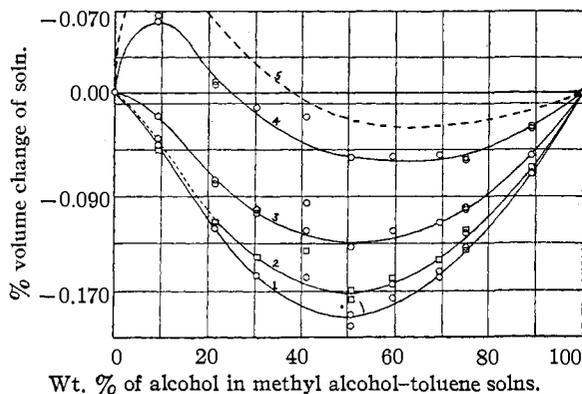


Fig. 1.

The numerical results are collected in Table I and are shown graphically in Fig. 1. Each value of the observed densities of the solutions represents the average of measurements with the two pycnometers. The average deviations of the individual measurements from the means were 0.00002. From these averaged densities the percentage volume changes have been calculated and the results obtained are listed in the Table and are shown graphically in Fig. 1. % volume change represents the percentage departure of the observed volume from what would have been expected had no volume change occurred on mixing.

It can be seen from Fig. 1 that curve 4 for the volume changes at 49.7° shows a relatively large

expansion up to about 25% alcohol; the other concentrations continue to display contractions. The expansion represented by this curve seems to be an advanced stage of the much lesser sways in the other curves. The dotted curve 5 was drawn from values obtained by extrapolating temperature-volume change values up to 60°. Indications are that the system forms a constant boiling mixture at about 61°—a property of the system which needs to be verified later since the data have not been found in the literature. For this reason the extrapolations were made only to 60° since extrapolations beyond the boiling point would be questionable. When the distillation curves of this system have been established some relationships among these various factors might be observed.

It is impossible at the present time to do more than suggest some reasons for the behavior observed. Associated alcohol probably dissociates in non-polar toluene. The fact that the system shows a negative heat of mixing supports this supposition.² Possibly solvation occurs to a sufficient extent to cause a volume contraction at lower temperatures in spite of alcohol dissociation. If so, the heat absorbed by dissociation more than overcomes the heat liberated by solvation so that a negative heat of mixing is observed. At the higher temperatures it would seem reasonable that the alcohol would be more dissociated than at the lower temperatures, and that solvation products might be broken up at the higher temperatures to cause a progressive decrease of the volume contraction, ending finally in a volume expansion for half the concentration range at least near the boiling point. It may be significant that the volume expansion occurs in solutions of low alcohol content where dissociation probably is enhanced by a dilution effect. It will be inter-

(8) J. Wade and R. W. Merriman, *J. Chem. Soc.*, 101, 2429 (1912).

esting to study some related alcohols and hydrocarbons in the same way.

Summary

The relative densities of solutions of methyl alcohol and toluene have been measured over the entire concentration range at -21.1 , 0.0 , 25.0 and 49.7° .

The volume changes attending mutual solution of the two liquids have been calculated from these

densities and the volume changes at a temperature near the boiling point have been estimated by extrapolation.

Suggestions have been offered as to the nature of the association, dissociation and solvation effects which may be responsible for the observed behavior.

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RECEIVED OCTOBER 3, 1938

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Condensation of Tertiary Aliphatic Alcohols with Aromatic Compounds in the Presence of Aluminum Chloride. IV. Tertiary Dimethyl Amyl Carbinols with Phenol

BY R. C. HUSTON AND R. L. GUILÉ¹

Previous papers from this Laboratory^{2,3} have described the condensations of *t*-butyl, *t*-amyl, the *t*-hexyl, and the *t*-heptyl alcohols with phenol in the presence of aluminum chloride. To extend the scope of this investigation the following tertiary dimethyl amyl carbinols, *viz.*: 2-methylheptanol-2,⁴ 2,3-dimethylhexanol-2,⁵ 2,4-dimethylhexanol-2,^{6,7} 2,5-dimethylhexanol-2,⁸ 2-methyl-3-ethylpentanol-2,⁹ 2,3,3-trimethylpentanol-2,¹⁰ 2,3,4-trimethylpentanol-2, and 2,4,4-trimethylpentanol-2,¹¹ were prepared and condensed with phenol. Yields of from 2.1 to 69.5% of a *p*-*t*-alkylphenol were obtained with no isolation of other isomers. The benzoyl esters and α -naphthylurethan derivatives of these phenols excepting 2,3,3-trimethyl-2-*p*-hydroxyphenylpentane were prepared.

The structure of six of these *p*-*t*-alkylphenols was established by synthesis. Thus, in an unpublished paper Huston and Sculati¹² isolated and identified from condensations between benzene and tertiary dimethyl amyl carbinols, 2-methyl-2-phenylheptane, and the 2,3-dimethyl-, 2,4-dimethyl-, and 2,5-dimethyl-2-phenylhexanes. In

a similar fashion Huston and Guile¹ prepared 2,4,4-trimethyl-2-phenylpentane and 2-methyl-3-ethyl-2-phenylpentane. These alkylbenzenes were nitrated, reduced, diazotized, and hydrolyzed to the phenols. The melting points and mixed melting point determinations of the α -naphthylurethans of the phenols thus prepared indicated that they were the same as those prepared in the condensations. The position of the entering group was established through oxidation¹³ of the *p*-nitro-*t*-alkylbenzene by heating a portion with 6 *N* nitric acid in a sealed Carius tube at 103° . In each case the product obtained was *p*-nitrobenzoic acid, which was identified by melting point and mixed melting point.

More evidence in support of the structure of 2,4,4-trimethyl-2-*p*-hydroxyphenylpentane was obtained by synthesizing it by the method of Natelson.¹⁴ This compound was identical with that obtained from the condensation of 2,4,4-trimethylpentanol-2 and phenol under the action of aluminum chloride.

The first four of the above alcohols were prepared by treatment of the Grignard reagent of an amyl halide with acetone. Although the yields in some cases were small by this method, the amyl alcohols could be obtained in sufficient quantities to offset this difficulty. For the preparation of 2,4,4-trimethylpentanol-2 a method outlined by Butlerow¹¹ was used. Syntheses of 2,3,3-trimethylpentanol-2 and 2,3,4-trimethylpentanol-2, the latter not previously reported in

(1) From a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) R. C. Huston and T. Y. Hsieh, *THIS JOURNAL*, **58**, 439 (1936).

(3) R. C. Huston and G. W. Hedrick, *ibid.*, **59**, 2001 (1937).

(4) F. C. Whitmore and F. E. Williams, *ibid.*, **55**, 408 (1933).

(5) L. Clark, *ibid.*, **33**, 529 (1911).

(6) L. Clark, *ibid.*, **30**, 1150 (1908).

(7) P. A. Levene and R. E. Marker, *J. Biol. Chem.*, **91**, 416 (1931).

(8) V. Grignard, *Chem. Zentr.*, **72**, II, 623 (1901).

(9) L. Clark, *THIS JOURNAL*, **39**, 574 (1917).

(10) F. H. Norton and H. B. Hass, *ibid.*, **58**, 2148 (1936).

(11) A. Butlerow, *Ann.*, **189**, 53 (1877).

(12) R. C. Huston and Sculati, *Master's Thesis*, Michigan State College, 1936.

(13) Malherbe, *Ber.*, **52**, 319 (1919).

(14) S. Natelson, *THIS JOURNAL*, **56**, 1583 (1934).