[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Cryoscopic Study of Certain Aliphatic Alcohols

BY T. J. WEBB AND C. H. LINDSLEY

An attempt has been made in this investigation to devise a comparatively rapid cryoscopic method suitable for aqueous solutions of nonelectrolytes. The lack of accurate data in this field seems to be a result largely of the difficulty encountered in determining the equilibrium concentration of the solute with an accuracy comparable to that obtainable in the thermal measurement with a multiple-junction thermoelement. The apparatus and technique employed are in most respects similar to those of other investigators in this type of work and hence will not be described in detail here. The chief difference in the present method occurs in the determination of the concentration of the solution in equilibrium with ice. About 1.5 liters of solution, made up accurately by weight to a known concentration, were placed in a bottle in the thermostat. When this solution had been cooled to about 0° and after the usual preliminary readings with both legs of the thermo-element in ice-water baths had been made, the water surrounding one leg was siphoned off and replaced by about 300 cc. of solution. This was in turn replaced by three successive portions of solution. The first two portions served not only to wash the ice and containing vessel free of water, but also to cool them practically to the equilibrium temperature. Hence when the third and fourth portions were delivered, only an amount of ice necessary to bring the solution itself to the equilibrium temperature was melted.

The initial temperature of the solution was measured by means of a five-junction thermoelement and the final equilibrium temperature by means of a fifty-junction thermo-element. From ΔT, the difference between these two temperatures, the amount of ice melting could readily be calculated. It is easily seen that if m_0 be the original concentration of the solution and m_e the equilbirium concentration

$$m_e = m_0 \frac{1}{1 + \frac{\Delta T}{80} + \left(\frac{A}{W} \times \frac{\Delta T}{80}\right)} \cong m_0 \frac{1}{1 + \frac{\Delta T}{80}}$$

approximately, where A and W are the number of grams of solute and water, respectively. The approximation is very good for the dilute solutions studied here.

The validity of this calculation of the equilibrium concentration was demonstrated during every determination, for while there was a marked difference in temperature between the first and second portions of solution when equilibrium had been established, and to a less degree between the second and third portions, the agreement between the equilibrium temperatures for the third and fourth portions was excellent. Occasionally a fifth portion was delivered, but such cases only confirmed the evidence that four were sufficient for the concentration range studied.

The thermo-elements were made of copper (No. 36 enameled wire) and constantan (No. 30 wire). Each length of the latter was annealed at red heat after cutting, then insulated with two coats of Bakelite varnish. The junctions were electrically welded, and the bundles of wires encased in snugly fitting Pyrex tubes. The remaining space in the tubes was filled with paraffin.

The thermo-elements were calibrated by measuring the electromotive force produced when one leg was kept at the temperature of melting ice and the other successively at each of the following temperatures: transition point of sodium sulfate, melting point of acetic acid, melting point of ice, and melting point of mercury. A cubic equation fitted to these data was used to convert the observed e. m. f. to degrees.

White potentiometers and a high-sensitivity d'Arsonval galvanometer were used. The galvanometer scale was placed about 5.5 m. from the mirror. At this distance, with the fifty-junction thermo-element, one microvolt caused a deflection of 28 mm. on the scale. The usual precautions were observed for eliminating errors due to stray and parasitic electromotive forces.

The reliability of the method of determining concentration and the calibration of the thermoelement, in fact the whole procedure, was thoroughly checked by an extended comparison of results with standard results for solutions of sodium chloride,[1] lead nitrate,[2] and mannitol over a range of concentration.

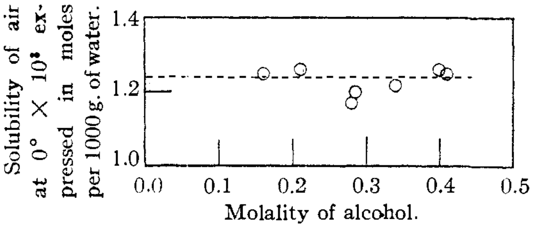

Fig. 1.—Solubility of air in solutions of methanol, ethanol and *n*-butanol.

Materials.—Two fractionating columns were built for the purification of the alcohols. Both were made of Pyrex glass and connected to the flasks holding the liquids to be distilled by ground glass joints. The first column was 45 cm. long, 20 mm. in diameter, with indentations along 35 cm. of its length. The second column was 140 cm. long, 30 mm. in diameter, and filled to a height of 115 cm. with 6–8 mm. lengths of 6-mm. Pyrex tubing. Each column was insulated and wrapped with nichrome wire so that it could be heated to any desired temperature during distillation. In the longer column a valve was made to regulate the reflux–distillate ratio. Thus very efficient fractionation could be obtained. The absolute boiling point of the distillate could not be determined with accuracy, but in every case several fractions were collected, all boiling at nearly the same observed temperature. If these fractions gave the same cryoscopic results, the purity of the material was considered beyond question.

Water.—For the preparation of the solutions and for the ice-water baths water having a specific conductance of 1.25×10^{-6} at 25° was used. The ice was frozen from water having a specific conductance of 3×10^{-6}. The ice was carefully crushed in order to avoid contamination and washed several times.

Methanol.—Merck absolute methanol ("free from acetone") was distilled from magnesium ribbon, then from tartaric acid, and finally fractionated in the smaller column. This, as well as all other alcohols, was kept in a glass-stoppered amber bottle, under bell-jars containing calcium chloride; n^{20}_{D} 1.3284.

Ethanol.—Two samples were prepared. In each case 95% alcohol was twice refluxed with and then distilled from freshly ignited lime. During the first refluxing, a small quantity of sodium hydroxide was added. The alcohol was then refluxed with fresh calcium turnings, distilled, refluxed with tartaric acid, distilled, and finally fractionated; n^{20}_{D} 1.3609.

***n*-Propanol, Iso, Secondary and Tertiary Butanols.**—Eastman Kodak Company best grade was shaken with a fresh saturated solution of sodium bisulfite, decanted, refluxed with 10% sodium hydroxide solution and distilled. The distillate was partially dried with calcium chloride or with sodium sulfate and potassium carbonate, then dried with successive portions of freshly ignited lime, and finally dried with calcium turnings. Ammonia was removed from the dry product by refluxing with tartaric acid, and the alcohol then fractionated in the long column. These fractions were subjected to a very careful refractionation and several portions of each alcohol were collected.

Alcohol	Fractions retained	B. p., °C.	n^{20}_{D}
n-Propanol	4	97.25	1.3855
i-Butanol	2	108.2	Not observed
s-Butanol	4	99.6	1.3970
t-Butanol	4	82.6	Not observed

***i*-Propanol.**—Two samples were prepared. For the first, 98% alcohol (product of the Standard Oil Company) was treated in precisely the same manner as were the last four alcohols. Three fractions were retained. In the second case, C. P. acetone vapor and purified hydrogen were passed over finely divided nickel (supported on kieselguhr and reduced *in situ*). The products were fractionally distilled three times and the middle portion of the third fractionation was then treated with lime, calcium and tartaric acid as described above. Three fractions of the final product were retained. Its index of refraction was 1.3769 and agreed exactly with that of the first sample prepared. In the tabulation of results the samples by the two methods of preparation are designated as I and II, and the individual fractions by Arabic numerals.

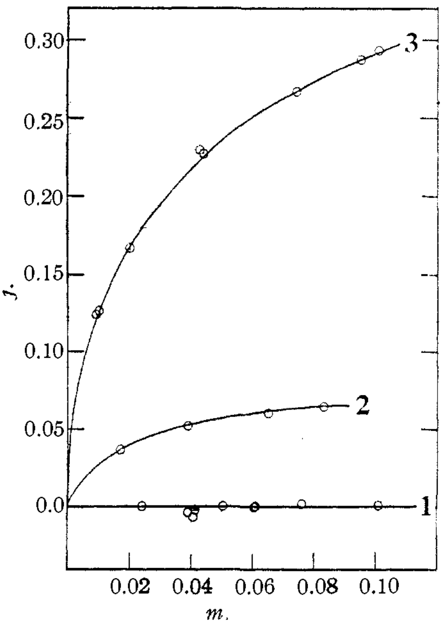

Fig. 2.—Comparison of cryoscopic results by this method with those of other investigators: (1) curve for mannitol; (2) curve for NaCl drawn from results given by Lewis and Randall; (3) curve for $Pb(NO_3)_2$ drawn from results of Randall and Vanselow. Circles represent experimental results of this investigation.

***n*-Butanol.**—A high-grade commercial product was treated with a solution of sodium bisulfite, refluxed with a solution of sodium hydroxide, distilled, and partially

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(1) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 348.

(2) Randall and Vanselow, THIS JOURNAL, **46**, 2418 (1924)

dried with calcium chloride. It was then twice refluxed with freshly ignited lime and distilled. The distillate was fractionated in the smaller column, and four fractions retained (boiling point 117.6°). These fractions are designated as I (1, 2, 3, 4). This method of purification is essentially the same as that used by Harkins and Wampler.[3]

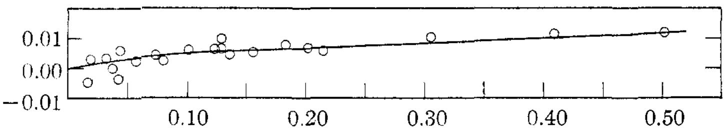

Fig. 3.—Variation of *j* with *m* for methanol.

The cryoscopic results obtained with this sample (some months after purification) differed considerably, though consistently, from those of Harkins and Wampler. The purity of the sample was accordingly questioned. The four fractions were carefully redistilled. Two fractions were retained (II, 1, 2). The cryoscopic results obtained with these samples checked the first results exactly. However, a third sample was purified by the method used for *n*-propanol. This method differs from that in the first purification at several points. The long fractionating column was used for two fractionations of the thoroughly dried material (boiling point, 118°, n^{20}_D 1.3990). The three fractions retained in this final purification are designated as III, 1, 2, 3. The cryoscopic results obtained with this sample agreed exactly with those obtained with the other two samples, and, therefore, the purity of the samples was not further questioned.

i-Pentanol and Benzyl Alcohol.—Mallinckrodt "analytical reagent" grade of *i*-pentanol and Coleman and Bell C. P. grade of benzyl alcohol were treated with small pieces of metallic sodium, and then fractionated in the long column. Only the middle portions were retained.

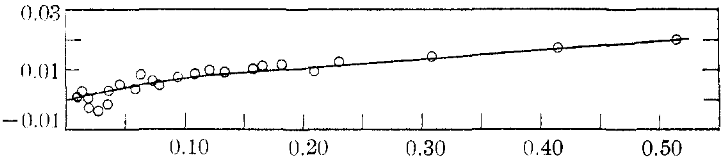

Fig. 4.—Variation of *j* with *m* for ethanol.

Alcohol	Fraction	B. p., °C.	n^{20}_D
i-Pentanol	1	131.6 (754 mm.)	1.4069
	2	131.8 (754 mm.)	1.4068
Benzyl	1	205.1 (754.5 mm.)	1.5405
	2	205.1 (754.5 mm.)	1.5405

Mannitol.—Eastman Kodak Company best grade (melting point 166–166.5°) was used. Four different samples were taken in making up the solutions for the cryoscopic determinations: (1) unpurified material; (2) and (4), each crystallized once from distilled water, centrifuged, and dried in an oven at 90°; (3) crystallized twice from distilled water, centrifuged, and dried.

Lead Nitrate.—This salt was chosen as one of the materials for checking the entire procedure (as well as the calibration of the thermo-element) for several reasons: the salt is easily purified by crystallization; it has a high molecular weight; its molal lowering is high; and, lastly, very precise data are available for comparison. Merck C. P. crystals were used. Two samples were purified by five fractional crystallizations each, the last two being from conductivity water. The crystals were centrifuged and dried in an oven at 125°. Two additional samples were purified by a single crystallization from 0.1 normal nitric acid solution, centrifuged, and dried in the oven. These samples are designated 1, 2, and 3, 4, respectively.

Sodium Chloride.—This material was taken from a sample long used as a standard by the analytical chemists in this Laboratory. It was heated to a dull redness in a covered platinum crucible. The heating was continued for a few minutes after decrepitation had ceased.

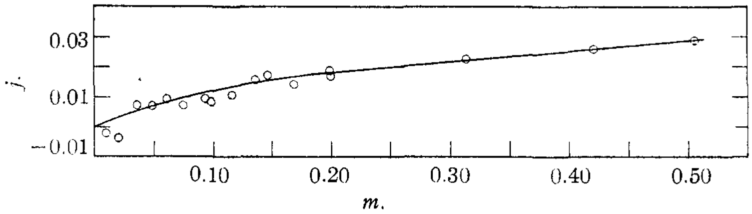

Fig. 5.—Variation of *j* with *m* for isopropanol.

Solubility of Air.—The solubility of air in pure water (used in the reference bath) and in the solutions studied may be markedly different. In pure water it amounts to 1.28×10^{-3} mole per 1000 g. of water at 0°, causing a freezing point depression of 0.0023°. To avoid the difficulty of freeing the solutions and water baths from air and keeping them free, the solubility of air in solutions of methanol, ethanol, and *n*-butanol was measured at room temperature by a method similar to that of Fox.[4] Since even up to high concentrations of alcohol (several molal) all three alcohols were found to affect the solubility of air to approximately the same extent, no distinction in the experimental results has been made. For the same reason it was thought safe to assume that all the alcohols studied would exhibit similar behavior at low concentrations. On the assumption that the change in solubility of air with temperature was the same

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(3) Harkins and Wampler, This Journal, **53**, 850 (1931).

(4) Fox, *Trans. Faraday Soc.*, **5**, 68 (1909).

for dilute alcohol solutions as for water to the desired degree of accuracy, the results shown in Fig. 1 were obtained. From the greatest observed deviation from the solubility in pure water (shown by the dotted line), one sees that the error in the temperature measurement due to different amounts of air dissolved in the solution and in the reference bath is less than one part in 5000. The actual error is probably considerably less than this. This result justifies the assumptions made above. No correction, therefore, was applied to any of the observed temperature lowerings, both solution and reference bath being saturated with air during the procedure.

The various errors involved in precise cryoscopy have been studied exhaustively by Robertson and La Mer.[5] These have all been carefully considered and evaluated in the work here presented. It seems justifiable to the writers to claim an accuracy of one part in a thousand in the concentration; for concentrations under about 0.02 molal the accuracy becomes less and less, while for concentrations greater than about 0.2 molal the accuracy is larger. In the case of the solid compounds used as standards, the accuracy is considerably greater, even at low concentrations. The accuracy in the temperature measurement is about one part in 5000 for large temperature differences; for small differences the uncertainty is ±0.00005°.

Cryoscopic Results.—In the following tables are given the identity of the sample, the molality and the observed freezing point lowering. For the curves, the deviation function j defined in the following way

$$j = 1 - \frac{\vartheta}{n\lambda m} \text{ and } j = 1 - \frac{\vartheta}{\lambda m}$$

for electrolytes and non-electrolytes, respectively, has been plotted against the molality m. Here ϑ is the freezing point depression, λ is the molal freezing point lowering for an ideal solute dissolved in water (1.858°), and n is the number of ions formed from one molecule of an electrolyte.

All the alcohols studied show a deviation from normal behavior, even at low concentrations. This deviation increases with decreasing solubility of the alcohol in water, and is greater for a primary than for the corresponding secondary or tertiary alcohol. In this connection it is particularly interesting to note that the results for t-butanol coincide exactly with those for methyl alcohol over the range of concentration studied. In every case the deviation from ideality indicates association of the alcohol molecules.

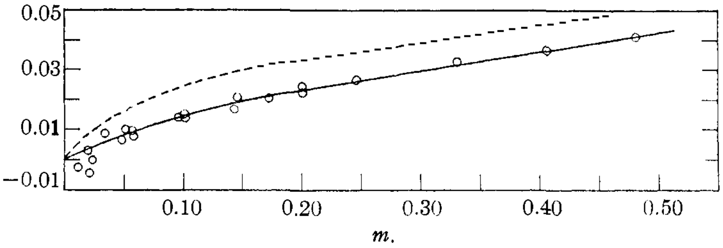

Fig. 6.—Variation of j with m for n-butanol; – – – –, represents curve given by results of Harkins and Wampler.

Sample	m	ϑ	Sample	m	ϑ
	Lead Nitrate			Ethanol	
1	0.009525	0.04651	2	0.00945	0.01757
3	.009778	.04763	2	.01018	.01909
2	.020125	.09315	2	.01420	.02632
1	.04294	.18423	2	.01879	.03493
3	.04380	.18903	1	.01947	.03615
2	.07454	.30466	1	.02729	.05091
4	.09497	.37758	2	.03503	.06522
1	.10046	.39584	1	.03574	.06629
			2	.04684	.08658
	Sodium Chloride		1	.05864	.10854
1	0.01704	0.06094	2	.06360	.11721
1	.03894	.13708	1	.07423	.13708
1	.06506	.22690	2	.07938	.14677
1	.08247	.28640	2	.09517	.17552
			2	.10944	.20172
	Mannitol		2	.12061	.22196
m[a]	0.02389	0.04438	2	.13477	.24821
3	.03893	.07261	2	.15803	.29074
2	.03994	.07455	m[a]	.16668	.30654
1	.04082	.07598	2	.18263	.33535
2	.05027	.09341	m	.2098	.38630
2	.06053	.11262	2	.2307	.42353
1	.06102	.11338	m	.3092	.5666
4	.07620	.14126	m	.4150	.7579
4	.10118	.18780	m	.5160	.9396
	Methanol			*n*-Propanol	
1	0.00906	0.01705	2	0.00919	0.01702
1	.01696	.03166	3	.01468	.02721
1	.01914	.03546	4	.01967	.03618
1	.03191	.05911	3	.03742	.06884
1	.03757	.06981	2	.04542	.08342
1	.04238	.07904	1	.05978	.10977
1	.04351	.08036	4	.07832	.14274
1	.05753	.10663	2	.10090	.18383
1	.07422	.13734	2	.11020	.20131
1	.08006	.14840	2	.13146	.23929
1	.10111	.18689	m[a]	.14850	.26983
1	.12336	.22797	1	.17407	.31684
1	.12771	.23598			
1	.12958	.23837		*i*-Propanol	
1	.13688	.25326	II 2	0.01002	0.01866
1	.15645	.28921	II 2	.02022	.03771
1	.18058	.33311	II 1	.03662	.06752
1	.2021	.37314	II 1	.04900	.09040
1	.2145	.39609	II m[a]	.05123	.09432
1	.3056	.5619	II 3	.07460	.13754
1	.4098	.7527	I 3	.09271	.17057
1	.5039	.9251	II 2	.09708	.17878

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(5) Robertson and La Mer, *J. Phys. Chem.*, **35**, 1953 (1931).

Sample	m	ϑ
II 2	0.11674	0.21457
II 1	.13658	.24979
I 1	.14753	.26937
II 3	.16892	.30930
I 2	.1992	.36350
II 2	.2000	.36534
I m	.3135	.5692
II m	.4222	.7643
I m	.5062	.9133
	n-Butanol	
III 1	0.01066	0.01985
III 1	.02002	.03771
II m[a,b]	.02021	.03745
	.02021	
	.02021	
I 1	.02028	.03786
III 2	.02397	.04453
III 2	.03405	.06273
II 1	.04933	.09106
I 2	.05069	.09325
III 2	.05814	.10712
I 1	.05820	.10712
I 2	.09549	.17501
III 3	.10095	.18475
II 2	.10196	.18678
III 2	.14306	.26137
I 3	.14696	.26753
I 3	.17459	.31781
III 1	.2015	.36539
III 3	.2017	.36621
III m	.2471	.44689
II m	.3306	.5946
III m	.4061	.7266
II m	.4812	.8572
	i-Butanol	
1	0.00984	0.01845
1	.01127	.02124
1	.02089	.03852
1	.02365	.04347
1	.02738	.05060
1	.02769	.05126
1	0.03007	0.05580
1	.03656	.06762
1	.04104	.07572
1	.05077	.09346
1	.05901	.10880
1	.06777	.12434
2	.07808	.14417
1	.10004	.18291
1	.13623	.24862
1	.17574	.31960
	s-Butanol	
3	0.01031	0.01908
3	.02098	.03900
2	.02964	.05468
2	.04085	.07532
3	.06032	.11135
1	.06842	.12577
3	.08049	.14764
2	.10130	.18653
3	.11921	.21859
4	.12609	.23062
2	.15377	.28130
2	.2084	.37997
	t-Butanol[c]	
3	0.02099	0.03902
3	.03957	.07338
3	.05919	.10992
3	.08059	.14911
3	.11037	.20437
3	.14932	.27590
	i-Pentanol[d]	
1	0.02571	0.04710
2	.05014	.09137
1	.09947	.18118
	Benzyl Alcohol[e]	
1	0.02484	0.04535
1	.02955	.05396
2	.05320	.09682
1	.07740	.13979
1	.10067	.18082

[a] In these tables samples designated *m* denote mixtures of the other samples or fractions.

[b] Over five liters of this solution were made up and three independent runs made with it. Hence the weight to be attached to these values is greater than that of the other single determinations.

[c] Only fraction 3 was used in these solutions. The other fractions all had freezing points lower than that of the third. Solutions made with fractions 2 and 4 gave values of *j* somewhat lower and higher, respectively, than those with fraction 3 at corresponding concentrations.

[d,e] These substances were used in order to find out if the cryoscopic behavior is markedly different for solutes near the limit of solubility.

Summary

A fairly rapid method is described for measuring the molal lowering of the freezing point in dilute aqueous solutions of non-electrolytes. The method is checked by obtaining values for the depression in solutions of lead nitrate, sodium chloride and mannitol, and an accuracy of about one part in a thousand is estimated for the cryoscopic results. Data are given for nine aliphatic alcohols and for benzyl alcohol over a range of concentration from 0.01 to 0.5 molal for four primary alcohols, and from 0.01 to 0.2 molal for the others.

PRINCETON, N. J. RECEIVED JANUARY 13, 1934

NOTES

Thermodynamic Dissociation Constant of a Weak Base

BY ELLIOTT J. ROBERTS

The thermodynamic dissociation constant of a weak base may be determined by any one of several galvanic cell arrangements without liquid junctions.[1] The purpose of this paper is to describe a new method which has the same advantages of simplicity of extrapolation which characterize the method used by the writer in the determination of the K_w of water.[2] The essence of the method was the measurement of two electrodes of the second kind directly against each other in a common solution containing ions requisite to the reversibility of both electrodes. In such cells, when monovalent ions alone are involved, the extrapolation to give the E° of the cell is linear with the ionic strength for a considerable range and is generally of slight slope.[2,3]

The above method does not apply to weak bases (except in the case of amphoteric electrolytes),[1c] since the electrode involving the base is of the third kind. However, by inserting an electrode of the first or third kind in place of the silver chloride electrode, the same simple extrapolation should result. Except for alkali and alkali earth metal electrodes, which require dropping electrodes and reference cells, the thallium electrode appears to be the only one of the first kind which

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(1) (a) Harned and Robinson, THIS JOURNAL, **50**, 3157 (1928); (b) Harned and Owen, *ibid.*, **52**, 5091 (1930); (c) Owen, *ibid.*, **56**, 24 (1934).

(2) Roberts, *ibid.*, **52**, 3877 (1930).

(3) Harned and Ehlers, *ibid.*, **54**, 1350 (1932); *ibid.*, **55**, 2379 (1933); Nims, *ibid.*, **55**, 1946 (1933); MacInnes and Belcher, *ibid.*, **55**, 2630 (1933).