

III. Discussion

The temperature dependence of the diffusion coefficient is displayed in Fig. 4, in which the superior semi-logarithmic-reciprocal temperature representation is employed.¹⁴ The activation energies computed from the slopes of these curves decrease from the order of 6000 cal. at 10° to 3000 cal. at 90°. This is the usual range allotted to diffusional and other "physical" processes.¹⁵

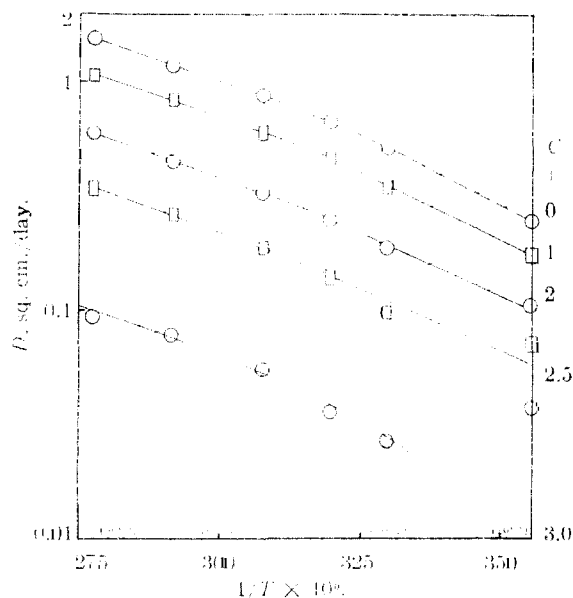


Fig. 4. —Temperature dependence of diffusion coefficient of sucrose.

(14) H. S. Taylor, *J. Chem. Phys.*, **6**, 331 (1938).

(15) S. Glasstone, K. Laidler and H. Eyring, "Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

The parameters usually invoked to explain the temperature and concentration variation of diffusion are the viscosity and the activity. These factors are coupled in the expression^{16,17}

$$D = D_0 \frac{\eta_0}{\eta} \left(1 + \frac{d \ln \gamma}{d \ln c} \right)$$

With the viscosity data of Bingham and White¹⁸ and others^{19,20} the first factor gives computed values of the diffusivity (D) much lower than those observed, and the second activity factor⁵ elevates these values only slightly, to within only a third to a fifth of the actually observed values. This same situation obtains in dilute sucrose solutions but to a less magnified extent.¹¹ Apparently some factor is operating which has a more pronounced effect upon viscosity than upon diffusion.⁵ A (hydrogen bonded)¹⁴ cluster of sucrose molecules might offer tremendous fluid resistance to movement through a medium, and yet lose or exchange its individual members quite freely in diffusion.

IV. Summary

The diffusion coefficients of aqueous sucrose solutions diminish linearly from concentrations above one molar to at least the saturation concentration.

The Stokes-Einstein implication of an inverse diffusivity-viscosity relation is entirely inadequate to explain the results obtained.

Diffusion coefficients of 0.1 *M* potassium chloride exhibit a slight convexity on the usual semi-logarithmic-reciprocal temperature plot.

(16) A. R. Gordon, *J. Chem. Phys.*, **5**, 522 (1937).

(17) P. Van Rysselberghe, *This Journal*, **60**, 2326 (1938).

(18) E. C. Bingham and G. F. White, *Bur. Standards Sci. Paper*, 298 (1917).

(19) *Lappl. Z. deut. Zucker-Ind.*, **82**, 545 (1932).

(20) Taboni, *J. Phys. Chem.*, **33**, 52 (1929).

EASTON, PA.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF SOUTH DAKOTA]

The Solvent Effect of Lithium Nitrate on Zinc Acetate in Acetic Acid

BY ERNEST GRISWOLD, AUGUST ASH AND LEO McREYNOLDS

It has been shown¹ that zinc acetate, which is only slightly soluble in acetic acid, becomes much more soluble when sodium or ammonium acetate is added. Since the acetates are bases in acetic acid,² this phenomenon is analogous, formally at least, to the familiar amphoteric behavior of zinc hydroxide in aqueous solutions of strong alkalis. Evidence that the resemblance is more than a formal one and that specific chemical effects play an important part in the solvent action of the acetates mentioned, is furnished by the fact that ternary addition compounds were isolated containing zinc acetate, sodium or ammonium acetate, and acetic acid.

(1) (a) Davidson and McAllister, *This Journal*, **52**, 519 (1930).

(b) Davidson and Griswold, *ibid.*, **57**, 423 (1935).

(2) Davidson and McAllister, *ibid.*, **52**, 507 (1930).

That salt effects also may be rather large in acetic acid seems probable because of the relatively low dielectric constant of this solvent. Evidence favoring this conclusion has been reported by several investigators.³ Since none of these studies of salt effect involved the use of zinc acetate, however, it seemed of interest to investigate the effect of some neutral salt upon the solubility of this compound in acetic acid, in order that a comparison might be made between the solvent action of the neutral salt and that of the strong bases in this solvent. Lithium nitrate was chosen as a suitable salt for the purpose, and this paper presents the results of a study in which its solvent effect upon zinc acetate was observed.

(3) Seward and Hamblet, *ibid.*, **54**, 554 (1932); Scholl, Hutchison and Chandler, *ibid.*, **55**, 3081 (1933).

Experimental

Materials.—Anhydrous acetic acid was prepared as previously described.⁴ Zinc acetate was prepared according to the method of Davidson and McAllister.^{1a} Analysis of the final product gave 35.63% zinc (calcd., 35.63).

Lithium nitrate was prepared by recrystallizing the hydrate from dilute nitric acid, then carefully heating over a Bunsen flame to remove most of the water of crystallization, and, finally, drying in an oven at 150° for several weeks. Analysis by conversion to the sulfate gave the theoretical percentage of lithium.

Method.—Part of the data reported in this paper were obtained by the synthetic or freezing point method.¹ Solutions containing various fixed proportions of lithium nitrate in acetic acid were used as solvents, and the freezing point curve of zinc acetate in each of these binary solvents was then determined. In this way solubility curves covering the temperature range from 40 to 80°, roughly, were obtained.

The analytical method was used to obtain data at 30°. Again, solutions of lithium nitrate in acetic acid in known proportions were made up in glass tubes, an excess of zinc acetate was added, the tube was sealed off and the mixture tumbled for a period of two weeks or longer in a thermostat maintained at 30.0°. Some of the mixtures, especially those containing the higher concentrations of lithium nitrate, were allowed to approach equilibrium from supersaturation. At the end of the time allowed, filtered samples were weighed and analyzed by titration with standard potassium ferrocyanide solution. Solutions containing the lowest percentages of zinc were analyzed by the pyrophosphate method. Each value reported represents the mean of concordant analyses run on samples obtained from two separate tubes.

To establish the nature of the solid phase, samples of the solid were removed from several of the mixtures chosen at intervals over the entire concentration range of lithium nitrate, and were quickly dried superficially by the use of porous plates. The percentage of zinc was then determined by the method previously mentioned. Results of such analyses made it possible to decide whether the solid phase was simply zinc acetate or an addition compound.

Results

In Table I the results obtained by the synthetic method are presented. The mole percentage of lithium nitrate in the binary solvent is denoted by R, while S represents the mole percentage of zinc acetate in the ternary solution which is in equilibrium with solid phase at the tempera-

TABLE I
SOLUBILITY OF ZINC ACETATE IN LITHIUM NITRATE SOLUTIONS AT VARIOUS TEMPERATURES

R = 1.450%		R = 3.90%		R = 8.00%	
S	T	S	T	S	T
0.1020	37.7	0.317	41.1	0.799	47.7
.1295	48.2	.352	47.7	.902	53.5
.1799	56.9	.448	57.5	.981	57.6
.2352	66.0	.539	65.1	1.150	65.0
.3102	77.5	.650	73.8	1.339	71.5
.3651	83.0	.741	79.1	1.599	77.8
R = 9.60%		R = 11.90%			
0.786	35.6	1.210	39.9		
1.005	46.0	1.386	47.1		
1.063	49.8	1.631	57.7		
1.262	58.1	1.937	69.0		
1.462	67.8	2.230	74.6		
2.067	80.3	2.941	86.0		

(4) Griswold and Olson, THIS JOURNAL, 59, 1894 (1937).

ture T. Examination of the solid phase by the method described above, indicated it to be Zn(C₂H₃O₂)₂ throughout.

Table II shows the results obtained at 30° by the analytical method. R and S have the same meanings as before. Again, the solid phase was found to be zinc acetate throughout the entire concentration range investigated.

TABLE II
SOLUBILITY OF ZINC ACETATE IN LITHIUM NITRATE SOLUTIONS AT 30°

R		S		R		S	
0.000	0.056	2.49	0.159	6.40	0.433		
.663	.055	3.02	.204	7.42	.525		
1.021	.073	3.69	.251	8.46	.574		
1.353	.092	4.38	.309	9.48	.612		
1.694	.129	5.40	.356	10.51	.660		

Graphs, not reproduced here, were prepared from the data in Table I, and values for the solubility of zinc acetate in the various binary solvents at 50 and at 70° were obtained by interpolation. These values were then used to construct two of the isotherms shown in Fig. 1. The third isotherm was plotted directly from the data in Table II.

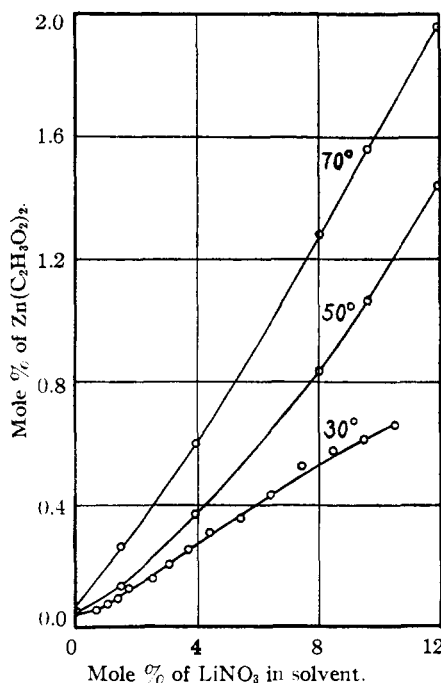


Fig. 1.—Isotherms for the system Zn(C₂H₃O₂)₂-LiNO₃-HC₂H₃O₂.

Discussion

It is apparent that the presence of lithium nitrate results in a distinct increase in the solubility of zinc acetate. The magnitude of the solvent effect of lithium nitrate is, however, very much less than that of either ammonium acetate or sodium acetate. This fact becomes apparent

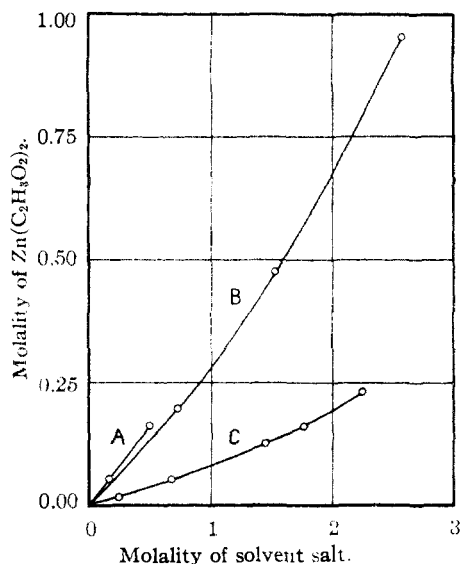


Fig. 2.—Solvent salts: (A) sodium acetate; (B) ammonium acetate; (C) lithium nitrate.

in Fig. 2, where solubility isotherms at 40°, obtained by interpolation from the data of Davidson and his co-workers,¹ may be compared with the corresponding curve from the present work. Thus, for example, in a 1 molal solution of lithium nitrate the solubility of zinc acetate is only about 0.08 molal, whereas its solubility in 1 molal ammonium acetate solution amounts to 0.28 molal. At higher concentrations of solvent salt the difference becomes even more pronounced.

This rather large difference in solvent action lends support to the belief, mentioned above, that specific chemical interaction is involved in the behavior of zinc acetate toward the other acetates. It suggests that the action of lithium nitrate, on the other hand, may perhaps be at-

tributed largely to "salt effect." It does not seem possible at present, however, to subject such a conclusion to a quantitative theoretical test, and the possibility that specific chemical effects may be involved, even here, cannot be excluded.

A brief comment seems called for concerning the solubility of lithium nitrate. Davidson and Geer⁵ report the solubility of lithium nitrate at 30° to be 1.49 moles per 1000 g. of acetic acid. This would correspond to a value of *R* of about 8.2. It will be seen in Table II that three of the binary solutions used had values of *R* higher than 8.2, the highest being 10.51. These more concentrated solutions were prepared hot, the zinc acetate was added to the hot solution, and equilibrium was then approached from above 30°. It is possible that the solutions may have remained supersaturated with respect to lithium nitrate, but it seems more likely that the solubility of lithium nitrate is simply increased by the presence of zinc acetate in the solution. Similar mutual solvent action has been demonstrated in other cases.^{4,5}

Summary

1. The solubility of zinc acetate in solutions of lithium nitrate in acetic acid has been determined over a wide range of temperatures and concentrations, and has been found to increase with increasing concentrations of the latter salt.

2. Comparison with results of previous investigators using other solvent salts has been made. The solvent effect of lithium nitrate is found to be distinctly weaker than those of sodium and ammonium acetates on zinc acetate.

3. It is suggested that the solvent action of lithium nitrate may perhaps be attributed largely to salt effect.

(5) Davidson and Geer, *THIS JOURNAL*, **60**, 1211 (1938).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

Studies in Stereochemistry. V. The Effect of F-Strain on the Relative Base Strengths of Ammonia and Trimethylamine¹

BY HERBERT C. BROWN

In previous articles of this series evidence has been advanced that steric strain is an important factor in the strength of generalized acids and bases.² It has recently been suggested that steric strain is of two kinds, "F-strain" and "B-strain".³ F-strain is that strain which is caused by steric interference of the atoms or groups which are attached to different atoms,

resulting in a force which tends to separate the two atoms. On the other hand, B-strain is that strain which is introduced into a molecule as a result of changes in the normal bond angles of an atom in a molecule, brought about by the steric requirements of bulky groups attached to that atom.

The need for both types of strain may be demonstrated by considering how each affects the strength of a base such as trimethylamine. In this base, the three methyl groups can easily satisfy their steric requirements by a slight spread-

(1) Presented before the Division of Organic Chemistry at the Cleveland meeting of the American Chemical Society, April 6, 1944.

(2) (a) Brown, Schlesinger and Cardon, *THIS JOURNAL*, **64**, 325 (1942); (b) Brown and Adams, *ibid.*, **64**, 2557 (1942).

(3) Brown, Bartholomay and Taylor, *ibid.*, **66**, 435 (1944).