

The structure consists of slightly distorted octahedrally coordinated complexes of two glycine residues and two water molecules about the nickel atoms. These complexes are held to each other by strong oxygen-to-oxygen hydrogen bonds and by both strong and weak nitrogen-to-oxygen hydrogen bonds.

Because of the unfortunate orientation of the

molecule with respect to the axes of the crystal, some of the parameters were not evaluated from projections but were in part calculated from assumed interatomic distances.

The structure of the glycine residues is substantially the same as that found by Corey and Albrecht¹ for glycine.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF LAFAYETTE COLLEGE]

The Diffusivities of Concentrated Sucrose Solutions¹

BY ANDREW VAN HOOK AND HARRY D. RUSSELL²

I. Introduction

Although dilute sucrose solutions are frequently employed as primary standards in diffusion studies, relatively little attention has been paid to the evaluation of this property at higher temperatures and at concentrations of the order of saturation. It is exactly these conditions at which the diffusivity is of much interest and value for the kinetic interpretation of the crystallization of sucrose.³ This paper reports the results of an endeavor to supply this desirable information.

II. Experimental and Results

The Northrup⁴-McBain⁵ porous disk technique was employed. Five different cells were employed, and each value presented in Fig. 1 is the average of at least two determinations in different cells. Solutions were analyzed refractometrically with a Bausch and Lomb dipping instrument, previously calibrated in almost perfect agreement with the values of the "International Sugar Tables."⁶ Weight percentages were computed to molarities, etc., by means of Plato's tables.⁶ Sucrose,⁷ potassium chloride⁷ and hydrochloric acid⁸ were used to calibrate the cells⁹ at temperatures below 35° while mannitol¹⁰ was used at higher temperatures. Excellent agreement was realized with these different standards.

The calibrated cell constant is essentially the ratio of the effective area of all pores to the thickness of the disk; and since the former will vary quadratically with the temperature and the latter changes only linearly, the net change of the cell constant will be a fractional increase of $\alpha \Delta t$, where α is the linear expansion coefficient of the glass of which the disk is constructed. α of Pyrex glass is of the order of 10^{-6} , which with the maximum temperature spread encountered in this work (80°) indicates an insignificant correction to the cell constant. Actually some slight increase in the cell constant is observed at increasing temperatures. Some values determined for some of the cells used in this work are presented in Table I. The values in parentheses were obtained when the cells were not previously well aged at the temperatures designated.

It was intended initially to investigate the diffusivities of supersaturated solutions in par-

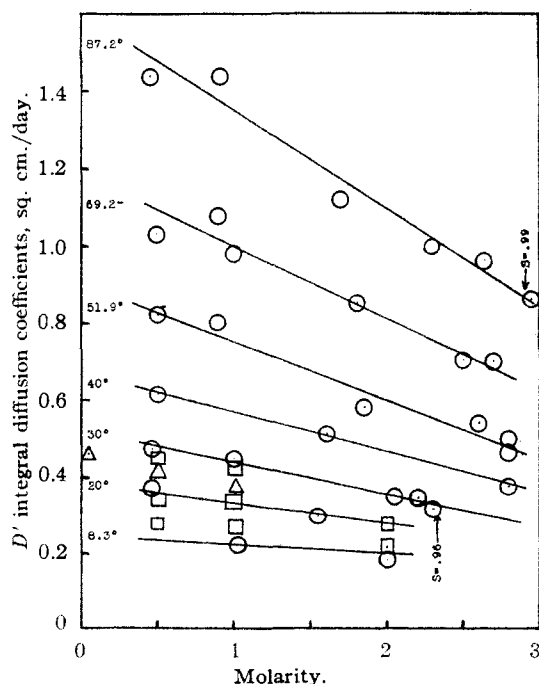


Fig. 1.—Integral diffusivities of sucrose solution: O, this work; □, Ohlm, at 12, 20 and 29°, respectively, "I.C.T."; Δ, McBain,⁵ 25°.

(1) Investigation supported by a grant from the Sugar Research Foundation, Inc.

(2) Present address: University of Wyoming, Laramie, Wyoming; and Tannersville, New York, respectively.

(3) A. Van Hook, *Ind. Eng. Chem.*, **36**, 1042 (1944).

(4) J. H. Northrup and M. L. J. Anson, *Gen. Physiol.*, **12**, 543 (1929).

(5) J. W. McBain and T. H. Liu, *THIS JOURNAL*, **53**, 59 (1931).

(6) International Scale (1936) of Refractive Indices of Sucrose Solutions, C. A. Browne and F. W. Zerban, "Sugar Analysis," 3rd edition, New York, N. Y., 1941.

(7) Landolt-Börnstein, "Tabellen," 1936 (see Fig. 3).

(8) W. A. James and Gordon, *J. Chem. Phys.*, **7**, 963 (1939).

(9) E. J. Cohen and J. T. Edsall, "Proteins," Reinhold, Publ. Corp., New York, N. Y., 1943.

(10) J. D. R. Scheffer and F. E. C. Scheffer, *Von Kon. Ak. Wet. Amst.*, **19**, 148 (1916).

TABLE I
VARIATION OF CELL CONSTANT WITH TEMPERATURE

Temp., °C.	Cells		
	1	2	3
8.3	270 (301)	241	268
30.2	274	(266)	...
40.0	272	245	...
51.9	278	243	...
69.2	...	(272)	...
73.0	...	238	279
88.0	...	245	283
87.2	...	245	...

ticular, but after overcoming the many difficulties of filling the cells with such viscous solutions, only irregular and unreliable results were realized. After such a trial the cell employed would evaluate to its original constant only after being soaked in water. This behavior suggests a crystallization within the pores of the disk, even though this is not observed in the bulk solution. Alternatively, the sintered glass membranes may be able to swell and shrink in accordance with changes in liquids to which they are exposed (J. W. McBain. Communication).

At the higher temperatures investigated in this work a small amount of solvent water condensed on the upper parts of the completely enclosed cell, necessitating a small correction in the volume of the diffusate solution. In a few experiments a regular loss of water was permitted by evaporation and the computations made accordingly were in excellent agreement with the general results.

All solutions were initially adjusted to a pH of 8 by the addition of a minute amount of sodium hydroxide solution. It was computed from the velocity constant of inversion, and independently confirmed (polarimetrically and refractometrically) at the highest temperature and concentration employed, that inversion was not significant during the period of an experiment.

The results obtained are presented in Fig. 1, together with some values from the literature for comparison. Additional values at concentrations below 0.5 M were obtained, and in agreement with reported values they indicate a rather sharp upturning at low concentrations of these seemingly linear curves. They are not discussed in this report since the primary interest was in the values at higher concentrations³ and also since they are not sufficiently comprehensive to contribute, other than in a confirmatory way, to the need for extensive diffusion data in the dilute range.¹¹

The diffusivities represented in Fig. 1, D' , are integral or mean values over a range of concentrations and are to be related to the true differential coefficient, D , by the relation¹²

$$D = D' + C \frac{dD'}{dC}$$

This has been done with the values of Fig. 1 via a

(11) M. A. Lauffer, *THIS JOURNAL*, **66**, 1200 (1944).
(12) H. Neurath, *Chem. Rev.*, **30**, 359 (1942).

least squares method and the computed values are computed as the full lines in Fig. 2, and where the points represent some results of other workers. The curves form a family of straight lines with a common origin at a concentration of approximately 3.26 M. At 90° this is just about a saturated solution, thus coinciding with the questionable suggestion of Mertens,¹³ that the diffusivity of saturated solutions is zero; but at the lower temperatures, where the computations are much more significant, the limiting concentration is much higher than saturation (e. g., at 10°, $D = 0$ at $S = 1.27$, where $S = \% \text{ sucrose in sirup} / \% \text{ sucrose in saturated sirup}$).

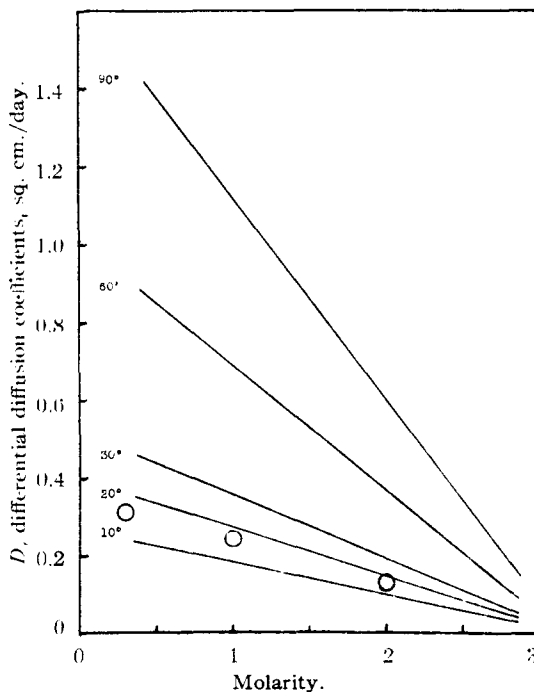


Fig. 2.—Differential diffusivities of sucrose solutions, interpolated from results of Fig. 1: ○, Thovert at 18.5°, Landolt-Börnstein⁷ "Tabellen."

A series of determinations of the diffusivities of 0.1 M potassium chloride were performed at the higher temperatures utilized. The computed results are presented in Fig. 3.

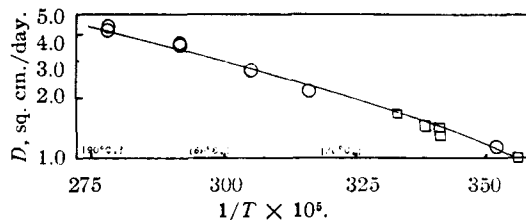


Fig. 3.—Temperature dependence of diffusion of 0.1 N potassium chloride solution: ○, this work; □, Landolt-Börnstein⁷ "Tabellen."

(13) A. Mertens, *IV Cong. Inst. Tech. Chim. Ind. Agr., Bruxelles*, **65-69** (1935).

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.¹⁵ 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

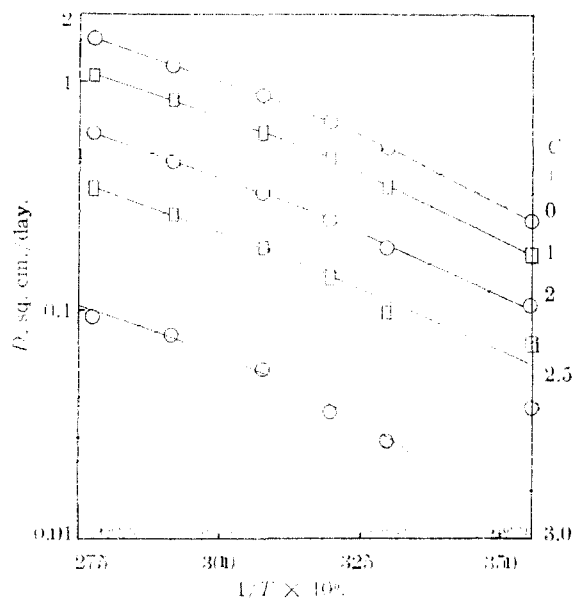


Fig. 4. —Temperature dependence of diffusion coefficient of sucrose.

(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 factor³ 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) Landt, *Z. deut. Zucker-Ind.*, **82**, 345 (1932).

(20) Tamini, *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

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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**, 534 (1932); Scholl, Hutchison and Chandler, *ibid.*, **55**, 3081 (1933).