doned because of the apparent insolubility of OctdMe₃NOctdSO₄ and KOctdSO₄ in formamide. Recourse was made, therefore, to the Me₃PhNO₃-SPh method which previously has been shown to yield essentially the same results as the OctdMe₃-NOctdSO₄ method for N-methylacetamide solutions.[9] The approximate values thus obtained for the limiting ionic equivalent conductances in formamide are summarized in Table II. On the basis of these findings, the potassium ion for potassium chloride in formamide is characterized by a limiting transference number of 0.415 which differs only 2% from the corresponding value of 0.406 which was determined independently by Dawson and Berger[17] using the Hittorf method.

(17) L. R. Dawson and C. Berger, THIS JOURNAL, **79**, 4269 (1957).

TABLE II

LIMITING IONIC EQUIVALENT CONDUCTANCES IN FORMAMIDE AT 25° BASED ON THE TRIMETHYLPHENYLAMMONIUM BENZENESULFONATE APPROXIMATION METHOD

Cation	Λ^+_0	Anion	Λ^-_0
K+	12.5	PhSO₃⁻	10.6
Me₃PhN+	10.5	I⁻	16.8
Na+	10.0	Cl⁻	17.3
Bu₄N+	6.7		

An analysis of the pattern of results reported herein for formamide solutions with comparable data for water, N-methylacetamide and N,N-dimethylformamide solutions reveals no consistent trends of pronounced parallelism.

LEXINGTON, KENTUCKY

Diffusion Measurements in Aqueous Solutions of Different Viscosities

BY AMILCARE BIANCHERIA[1] AND GERSON KEGELES

The diffusion of approximately 0.5% glycolamide or acetamide has been studied by the Gouy method in various aqueous solutions, whose viscosity was adjusted by the addition of small amounts of a third component to be from 2 to 7% above that of water. Deviations from ideal diffusion behavior were studied to assure that no appreciable interaction of flow occurred between the diffusing and non-diffusing solutes. It was found that the relative decrements of the diffusion coefficients of glycolamide and acetamide were never as great as the relative increments of solvent macroscopic viscosity. Moreover, at a constant increment of macroscopic viscosity, the decrement in diffusion coefficient depended markedly on the nature of the third component. All the diffusion data could be correlated accurately, however, with the volume fraction of third component added, an experimental correlation suggested by the theory developed by Wang to explain the obstruction of the self-diffusion of water by dissolved macromolecules.

Introduction

The Stokes–Einstein–Sutherland equation[2–4] relating diffusion to the observed macroscopic viscosity, was derived on the basis that the solvent medium presents a continuum to the diffusing particle. In many cases, the general form of the relation has appeared to be applicable even outside its intended range of validity. The data of Stokes, Dunlop and Hall[5] for the diffusion of iodine in several organic solvents exemplifies this point. However, the data of Lamm and Sjöstedt[6] for the diffusion of water in glycerol, the study of Polson[7] on diffusion versus molecular weight, and the data of Longsworth[8] for the temperature dependence of diffusion indicate that in those cases where the solvent media can no longer be considered a continuum, the diffusion process is not determined simply by the macroscopic viscosity. Similar considerations have been discussed by Schachman and Harrington[9] for the case of sedimentation.

(1) Presented to the faculty of Clark University, 1957, in partial fulfillment of the requirements for the Ph.D. degree.

(2) G. Stokes, *Trans. Cambridge Phil. Soc.*, **9**, 5 (1856).

(3) A. Einstein, *Ann. Physik*, **19**, 371 (1906).

(4) W. Sutherland, *Phil. Mag.*, **9**, 781 (1905).

(5) R. H. Stokes, P. J. Dunlop and J. R. Hall, *Trans. Faraday Soc.*, **49**, 886 (1953).

(6) O. Lamm and G. Sjöstedt, *ibid.*, **34**, 1158 (1938).

(7) A. Polson, *J. Phys. Colloid Chem.*, **54**, 649 (1950).

(8) L. G. Longsworth, *ibid.*, **58**, 770 (1954).

(9) H. K. Schachman and W. F. Harrington, THIS JOURNAL, **74**, 3965 (1952).

This investigation was undertaken to provide precise additional data on diffusion in discontinuous media for the purposes of examining the validity of the general form of the Stokes–Einstein relation and of furnishing a possible basis for future theoretical considerations.

Basically, the investigation entailed the observation of diffusion of glycolamide and acetamide in various aqueous solutions. The viscosities of these solutions were held at approximately 3 or 6% above that of pure water by controlling the concentration of a third component added to increase the viscosity. In general, third components of zero average charge and low dipole moment were selected to avoid effects due to charge interaction. The molecular size of the third component, was varied in the hope that this parameter could be used to correlate the solvent viscosity with its effect on the diffusion of glycolamide or acetamide.

Experimental

Measurements of diffusion coefficients were made by the Gouy interference method.[10–13] The cell employed was of the Tiselius type,[14] but with clamped optical flats for win-

(10) L. G. Longsworth, *ibid.*, **69**, 2510 (1947).

(11) G. Kegeles and L. J. Gosting, *ibid.*, **69**, 2516 (1947).

(12) C. A. Coulson, J. T. Cox, A. G. Ogston and J. St. L. Philpot, *Proc. Roy. Soc. (London)*, **A192**, 382 (1948).

(13) L. G. Gosting, E. M. Hanson, G. Kegeles and M. S. Morris, *Rev. Sci. Instr.*, **20**, 209 (1949).

(14) A. Tiselius, *Trans. Faraday Soc.*, **33**, 524 (1937).

dows. This cell has been described previously,[15] as have certain of the cell-masking arrangements. A convergent-light system was employed, with a 170 cm. EFL achromatic objective of four inch diameter. For viewing the cell during boundary formation, and for photography of Rayleigh diffusion patterns,[16-19] used here only to count fringes, the track is provided with a removable auxiliary cylindrical-lens schlieren system. The schlieren system was used without a cylindrical-lens, and with a pinhole as a diaphragm[20] in order to view lateral *schliere* at the walls of the cell.[21] The technique used for the study of diffusion has been described elsewhere.[13] Also available elsewhere is a complete description of the design and construction of the apparatus employed in this study.[22] The optical lever arm in this apparatus is 314.014 cm.

The solutions used to form the diffusing boundaries were prepared as follows. (1) A stock aqueous solution was prepared which contained a sufficient amount of a dissolved component to raise the viscosity between 2 and 7% above that of water; (2) into a weighed amount of this solution serving as the solvent for the diffusing solute, was added a weighed amount of pure, solid glycolamide (or in two cases, acetamide); (3) this final solution was layered under an aliquot of the two-component solvent stock solution first described. Consequently, there is a small amount of dilution of the non-diffusing solute caused by the addition of the solid diffusing component. Certain effects of this dilution will be discussed below.

The viscosities of the solvents (aqueous solutions) were measured in an Ostwald–Fenske viscometer[23] having a flow time for water of 314.8 to 315.0 seconds. At least three readings were taken for each solvent, and these always agreed to within 0.3 second. The solutions were passed through sintered glass prior to each filling of the viscometer. For the calculation of viscosities the solvent densities were determined with a Reischauer pyknometer. No kinetic energy corrections were made to the relative viscosities.

To prepare the glycolamide employed, ethyl glycolate was first made by treatment of purified glycolic acid with ethanol and sulfuric acid,[24,25] neutralization and vacuum distillation. After redistillation the ethyl glycolate was subjected to ammonolysis.[26] The recovered glycolamide was recrystallized once, and the product had a melting point of 115.8–115.9°, in agreement with literature values.[27,28] Diffusion measurements at 25° of a 0.5% solution in water against water agreed with values from the equation of Dunlop and Gosting to be better than 0.1%.

Three times crystallized acetamide was kindly provided by H. C. Christoffers of these laboratories, who has also supplied the data for the diffusion of this material in pure water. His diffusion coefficients for twice and three times crystallized material agreed to within 0.1%.

Reagent grade methanol was freshly distilled prior to use.

The following materials, used to increase the viscosity of aqueous solvents employed, were not further purified: reagent grade glycerol, raffinose, Armour bovine plasma albumin, and polyvinyl alcohol samples of different molecular weights kindly provided by E. I. du Pont de Nemours and Co.

All solutions were prepared by weight in air-saturated doubly distilled water, and concentrations were computed after taking into account all vacuum corrections. A den-

sity of 1.390 was used for solid glycolamide[29] and 1.159 for solid acetamide.[30]

Treatment of the Data.—Diffusion coefficients were computed as usual for two-component systems,[10,11,13] computation of the path-difference function[11] $f(z_j)$ being made from the count of the fringe number j above the bottom intensity minimum and the corresponding Airy integral expression Z_j for the number of waves path difference, as given by Gosting and Morris.[31] In order to ascertain that the presence of the small amount of diffusing component did not appreciably alter the chemical potential of the added third component, and consequently cause appreciable flow of this component across the diffusing boundary, it was necessary to examine deviations of interference fringe positions from their expected positions for ideal two-component diffusion experiments. The quantity[32-34] $\Omega_j = e^{-z_j^2} - Y_j/C_t$, which expresses the fringe displacement from its expected value for a corresponding one centimeter long pattern, was plotted against the path difference function $f(z_j)$ for each experiment performed. The constant C_t is the value obtained by extrapolation[32] to $Z_j = 0$. When polyvinylpyrrolidone, or raffinose at relatively high concentrations was added to water to form the solvent, the Ω_j values were large, indicating the probability of some interaction of flow between this solute component and the diffusing components of the system. Such systems can no longer be treated strictly as quasi-two-component diffusing systems. Although the calculated diffusion coefficients of glycolamide in some of these systems did fit into the general picture to be presented, these data have not been included below. In the case of bovine plasma albumin as third component, the dilution of the albumin solution by the addition of glycolamide resulted in Gouy patterns which could not be evaluated by the usual interpretation.

Results

In Table I is presented a description of the upper and lower solutions used in each experiment to form the diffusing boundary. Table II contains interpolated data for the average fringe deviations Ω_j from all photographs, at even fractions $f(z_j)$ of the total path difference, for all of the experiments for which diffusion data are presented below.

Systems 1 and 2 are simply glycolamide diffusing in water, and the fringe deviations for these systems are included in Table II in order to indicate the effect of experimental errors in producing fringe deviations, even from a presumably Gaussian distribution of refractive index gradient. When the fringe deviations for other systems in Table II are quite appreciably outside the range for systems 1 and 2, it may be inferred that the diffusion experiments in question have given rise to non-Gaussian

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(19) L. G. Longsworth, *Anal. Chem.*, **23**, 346 (1951).

(20) H. Schardin, "Das Toeplersche Schlierenverfahren," B, Vol. 5, VDI-Verlag, Berlin, 1934.

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(27) R. H. Stokes, *Trans. Faraday Soc.*, **50**, 565 (1954).

(28) P. J. Dunlop and L. J. Gosting, THIS JOURNAL, **75**, 5073 (1953).

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(31) L. J. Gosting and M. S. Morris, THIS JOURNAL, **71**, 1998 (1949).

(32) D. F. Akeley and L. J. Gosting, *ibid.*, **75**, 5685 (1953).

(33) R. L. Baldwin, P. J. Dunlop and L. J. Gosting, *ibid.*, **77**, 5235 (1955).

(34) P. J. Dunlop and L. J. Gosting, *ibid.*, **77**, 5238 (1955).

TABLE I

KEY TO SYSTEMS STUDIED

System no.	Composition of upper aq. soln.	Compn. of lower aq. soln.
1	Water	0.5057 g. glycolamide added to 99.3228 g. of water
2	Water	0.5021 g. glycolamide added to 99.5079 g. of water
3	0.066% polyvinyl alcohol I[a]	0.5034 g. glycolamide added to 99.5550 g. of 0.066% polyvinyl alcohol I soln.
4	0.099% polyvinyl alcohol II[a]	0.5013 g. glycolamide added to 99.4773 g. of 0.099% polyvinyl alcohol II soln.
5	0.080% polyvinyl alcohol III[a]	0.5021 g. glycolamide added to 100.1532 g. of 0.080% polyvinyl alcohol III soln.
6	1.0907% acetamide	0.5019 g. glycolamide added to 99.3684 g. of 1.0907% acetamide soln.
7	0.15 M NaCl, 0.03 M CH₃-COOH, 0.02 M CH₃COONa	0.5013 g. glycolamide added to 100.2649 g. of acetate buffer used as upper soln.
8	1.0688% methanol	0.5031 g. glycolamide added to 99.6668 g. of 1.0688% methanol soln.
9	1.0229% raffinose stock soln. diluted with 0.37 cc. water per 100 g. stock soln.	0.5088 g. glycolamide added to 99.5092 g. of 1.0229% raffinose stock soln.
10	2.96% glycerol	0.5041 g. glycolamide added to 100.5110 g. of 2.96% glycerol soln.
11	0.067% polyvinyl alcohol IV[a]	0.5150 g. acetamide added to 99.6989 g. of 0.067% polyvinyl alcohol IV soln.
12	1.0806% methanol	0.5159 g. acetamide added to 98.9714 g. of 1.0806% methanol soln.

[a] Approximate weight average molecular weights of polyvinyl alcohols determined at 0.3% in water by Archibald method (W. J. Archibald, *J. Phys. Chem.*, **51**, 1204 (1947); S. M. Klainer and G. Kegeles, *ibid.*, **59**, 952 (1955)) as follows: PVA I, 56,100; PVA II, 25,700; PVA III, 30,200; PVA IV, 47,800.

TABLE II

VALUES OF RELATIVE FRINGE DEVIATIONS,
$10^4 \, \Omega_j = 10^4 \, (e^{-z_j^2} - Y_j/C_t)$

System	0	0.1	0.2	0.3	0.4	$f(z_j)$ 0.5	0.6	0.7	0.8	0.9	1.0
1	0	−1	1	1	1	2	3	4	4	5	0
2	0	0	−3	−3	−3	−3	−4	−2	0	2	0
3	0	−1	−5	−5	−5	−4	−2	−1	0	2	0
4	0	−8	−10	−10	−8	−7	−7	−6	−6	−5	0
5	0	−5	−7	−7	−6	−5	−4	−4	−3	0	0
6	0	0	−2	−3	−2	−1	1	2	4	5	0
7	0	0	0	2	2	4	5	5	5	6	0
8	0	−2	−3	−3	−3	−3	−2	−3	−3	−2	0
9	0	−6	−10	−11	−10	−9	−7	−6	−5	−3	0
10	0	0	1	3	4	6	9	10	11	12	0
11	0	−5	−7	−9	−9	−9	−9	−10	−10	−9	0
12	0	0	0	−1	−1	−1	−1	0	2	5	0

distributions of refractive index gradient. Possible reasons for such distributions are now discussed.

As the effect of dilution due to addition of the solid diffusing component, referred to above, is such as to produce a small negative gradient of concentration of the third component, this would be expected to give rise to small negative fringe deviations, even when interpreted in terms of independent ideal diffusion of two solute components.[32] Such deviations are found for many of the systems in Table II. In the case of the raffinose experiment (system 9) an amount of water, calculated from the partial specific volume of glycolamide in water, was added to compensate, in the upper raffinose solution, for the dilution of raffinose by glycolamide in the lower solution. The resulting fringe deviations shown in Table II are much less negative than those originally obtained in another raffinose experiment, not shown, in which no water was added to the upper solution. The amount of water added was still insufficient to reduce the deviations to zero, however. In the case of glycerol only (system 10), among the experiments reported, there appears to be possible evidence of interacting flows.[33,34] Before proceeding to the final results, it is of interest to indicate the unusual distribution of refractive index resulting from the dilution of a

2.6% bovine plasma albumin solution (dissolved in the same acetate–chloride buffer used in system 7) by the addition of solid glycolamide. When this solution was then layered under the original albumin solution, a negative gradient of albumin was produced in the boundary. Because of the relatively high concentration of albumin used, and the small diffusion coefficient of this component, a refractive index gradient curve with a persistent central minimum resulted. The possibility of obtaining such curves has been discussed in detail by Longsworth.[35] The corresponding Gouy pattern has an extra fringe below the normal broad intensity maximum. It is clear that the bottom fringe must stem from regions in the cell having the two maxima of refractive index gradient, while the broad fringe above the bottom comes from three regions in the cell having the refractive index gradient value of the central minimum. The pattern has not been analyzed further, however.[36]

In Table III are shown densities and viscosities of the solvents used, as well as data obtained for the diffusion experiments. All diffusion coefficients listed have been corrected over the short temperature interval to 25.000° with the aid of the relationship $D\eta/T$ = constant, the relative viscosity of water being used for this correction.

In the final column of Table III, the relative decrements of the diffusion coefficient of approximately 0.5% glycolamide or acetamide solutions in the various aqueous solvents of the first column are shown divided by the relative increments of viscosity of these solvents. This column thus represents the fractional part of the macroscopic viscosity increment which is effective in depressing diffusion.

(35) L. G. Longsworth, in "Electrochemistry in Biology and Medicine," T. Shedlovsky, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, Chap. 12.

(36) We are indebted to Dr. Gosting for suggesting dilution as an interpretation for the irregular Gouy pattern, which had been observed prior to the availability of a corresponding schlieren photograph.

TABLE III

VISCOSITY AND DIFFUSION RESULTS

Solvent	Solvent density	Addend vol. fraction, $\phi \times 10^2$	Solvent relative viscosity η/η_0	Diffusion bath temp., °C.	No. fringes, J_m	Zero time corrn., sec.	25.000° diffusion coefficient, $D \times 10^5$, cm./sec.	$\dfrac{D_0/D - 1}{\eta/\eta_0 - 1}$
Diffusing solute, glycolamide; $D_0 = 1.1390(10)^{-5}$ for 0.5% solution vs. water								
0.066% PVA-I	0.9973	0.051	1.064	25.13_2	68.62	44.8	1.1390	0.000
0.099% PVA-II	.9973	.077	1.032	25.13_6	68.33	61.5	1.1379	.031
0.080% PVA-III	.9972	.062	1.031	25.13_7	68.39	58.4	1.1416	− .074
1.0907% acetamide	.9976	1.034	1.030	25.13_6	68.61	60.5	1.1219	.507
Acetate buffer	1.0043	0.605	1.024	25.13_1	67.65	43.6	1.1257	.491
1.0688% methanol	0.9951	1.266	1.028	25.13_6	68.36	62.0	1.1142	.796
Diluted 1.0229% raffinose	1.0024	0.621	1.029	25.13_7	68.69	62.0	1.1254	.417
2.96% glycerol	1.0027	2.41	1.066	25.09_7	67.85	11.9	1.0982	.563
Diffusing solute, acetamide; $D_0 = 1.2457(10)^{-5}$ for 0.5% solution vs. water								
0.067% PVA-IV	0.9972	0.051	1.039	25.13_6	64.38	87.1	1.2402	.113
1.0806% methanol	0.9950_5	1.280	1.029	25.13_5	64.46	126.6	1.2188	.762

It is observed by inspection of this column that a regular trend exists for the dependence of this ratio on the molecular size of the third component added to make up the solvent. Moreover, in no case is the full effect of the macroscopic viscosity increment felt by the diffusion process. In the case of one sample of polyvinyl alcohol (PVA-III) as solvent addend, a 3.2% increase of macroscopic viscosity above that of water was actually accompanied by an observed *increase* of 0.3% in the diffusion coefficient of glycolamide, and in the case of another sample of polyvinyl alcohol (PVA-I) as solvent addend, a 6.4% increase in viscosity above that of water resulted in no change at all in the observed diffusion coefficient of glycolamide.

It should be pointed out that with the present apparatus, diffusion coefficients can be measured to somewhat better than 0.1%, so that these observed effects are clearly far beyond experimental error. The danger of applying Stokes' law for the frictional coefficient of the diffusing particle in terms of the macroscopic viscosity of the discontinuous solvent is clear. This is not to be regarded as a breakdown of Stokes' law, but rather as a re-emphasis that its use must be restricted to describe the type of system for which it was originally derived: the slow motion of a large sphere in a continuous medium. It might be further emphasized that in the case of a solution of a long-chain molecule such as polyvinyl alcohol, the mechanisms for absorption of energy by viscous flow of the solution and for retardation of the passage of a diffusing particle are quite different. In capillary flow, the long-chain molecule exerts a great influence on macroscopic viscosity by virtue of its many possible motions and distortions in a superposed shear gradient. In diffusion, the practically stationary long-chain molecule merely serves as an obstruction around which the diffusing particle must flow, according to the theory of Wang.[37]

The obstruction theory of Wang was therefore employed as a possible means by which to correlate the data shown in Table III. While this theory was developed for the self-diffusion of water in the

(37) J. H. Wang, THIS JOURNAL, **76**, 4755 (1954).

presence of large protein molecules whose Brownian motion was negligible, it was felt that it might nevertheless serve as a useful guide to the situation for small obstructing molecules. According to Wang's theory, the self-diffusion coefficient D is related to the volume fraction ϕ, in the case of unhydrated obstructing particles by the equation

$$D = D_0(1 - \alpha\phi) \qquad (1)$$

where D_0 is the self-diffusion coefficient in the absence of the obstructing particles. When the obstructing particles are spheres, the theoretical value of α is 1.5. In Fig. 1, the relative diffusion coeffi-
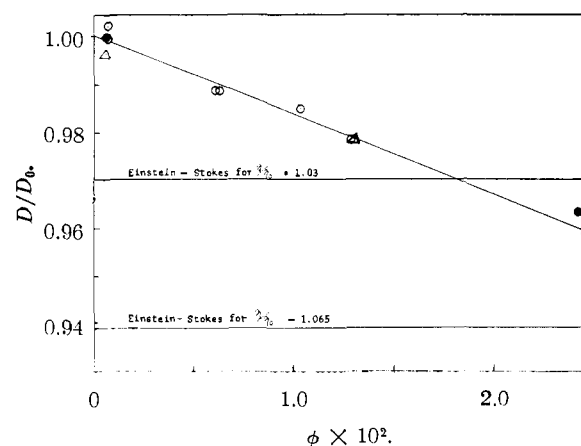

Fig. 1.—Relative diffusion coefficient *versus* volume fraction of addend: ●, glycolamide diffusing, $\eta/\eta_0 \sim 1.065$; O, glycolamide diffusing, $\eta/\eta_0 \sim 1.03$; △, acetamide diffusing, $\eta/\eta_0 \sim 1.03$.

cients D/D_0 for the various experiments shown in Table III have been plotted against the volume fraction, ϕ, of the viscosity-increasing components in the aqueous solvents. The values of ϕ have been computed from apparent specific volumes derived from the density data in Table III. Included in this graph are the types of plots expected at two different constant values of relative viscosity, assuming Stokes' law behavior. At constant rela-

tive viscosity, the diffusion coefficient would be independent of the volume fraction of added third component, if Stokes' law were applicable. Instead, the data show a linear regression with volume fraction of addend to within ± 0.16%. The slope of this line, following the form of equation 1, is 1.66, compared to Wang's value of 1.5 for large unhydrated spheres. This suggests the possibility that an obstruction-effect theory may be devised to account for experiments in which the presence of small molecules slows the diffusion of other small molecules. It is further suggested that the hydrodynamic portion of the concentration dependence of diffusion, which has been treated as a question of

solution viscosity,[38,39] may possibly be reinterpreted as a self-obstruction of diffusion by the small diffusing molecules.[40]

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(39) C. L. Sandquist and P. A. Lyons, THIS JOURNAL, **76**, 4641 (1954).

(40) A similar suggestion has been made by R. H. Stokes, *Austral J. Science*, **19**, 35 (1957).

WORCESTER, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SAINT LOUIS UNIVERSITY]

Etherates of Lithium Borohydride. I. The System Lithium Borohydride–Dimethyl Ether[1]

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RECEIVED APRIL 27, 1957

Pressure–composition isotherms for the system lithium borohydride–dimethyl ether at 20.0, 0.0, −45.2, −63.5 and −78.6° show that the three solid dimethyl etherates, $LiBH_4 \cdot 2(CH_3)_2O$ (I), $LiBH_4 \cdot (CH_3)_2O$ (II) and $(LiBH_4)_2 \cdot (CH_3)_2O$ (III), exist. Values for the heats, free energies and entropies of dissociation of these compounds per mole of dimethyl ether evolved at 25° are ΔH_d = (I) 10.42, (II) 11.13 and (III) 12.25 kcal.; ΔF_d = (I) −0.145, (II) 1.66 and (III) 2.21 kcal.; and ΔS_d = (I) 35.4, (II) 31.7 and (III) 33.7 e.u. The heats and free energies of formation and absolute entropies of the etherates at 25° are ΔH_f^0 = (I) −157.1, (II) −102.4 and (III) −149.3 kcal./mole; ΔF_f^0 = (I) −87.1, (II) −60.0 and (III) −91.0 kcal./mole; and S^0 = (I) 77.4, (II) 49.1 and (III) 66.3 e.u.

Introduction

In recent years, lithium borohydride has come into widespread use because of its unique properties as a reducing agent for both organic[3] and inorganic[3,4] compounds. The reactivity of lithium borohydride places serious restrictions on the media which may be used to facilitate its reactions and useful solvents have been generally found among the ethers. In some reactions of lithium borohydride, the ether acts not merely as a solvent, but must play a more direct role in the chemical process. A striking example[5] is the effect of diethyl ether on the rate of production of diborane in the reaction between copper(I) chloride and lithium borohydride. The reaction rate increases with the amount of diethyl ether until the mole ratio of ether to borohydride is one to one; more than this amount of diethyl ether is not reflected by a further increase in the rate of production of diborane. This fact has been interpreted to indicate that the reacting species may be the one to one adduct of lithium borohydride and diethyl ether rather than

(1) Presented at the 132nd meeting of the American Chemical Society, New York, N. Y., September, 1957.

(2) Taken in part from a thesis presented by T. L. Kolski to the Graduate School of Saint Louis University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1957.

(3) N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956.

(4) (a) G. W. Schaeffer, J. S. Roscoe and A. C. Stewart, THIS JOURNAL, **78**, 729 (1956); (b) A. C. Stewart and G. W. Schaeffer, *J. Inorg. Nuc. Chem.*, **3**, 194 (1956); (c) E. Wiberg, *Angew. Chem.*, **65**, 16 (1953).

(5) R. H. Toeniskoetter, M.S. thesis, Saint Louis University, February, 1956.

lithium borohydride itself. Such a diethyl etherate of lithium borohydride has been described by Schlesinger and his co-workers,[6] who found that it is formed when diethyl ether and lithium borohydride are brought together at 0°.

The present paper describes an investigation of the binary system lithium borohydride–dimethyl ether and subsequent papers will describe similar investigations of systems of lithium borohydride with diethyl ether and with tetrahydrofuran. It is hoped that the information obtained in these studies will prove helpful in extending the usefulness of lithium borohydride–ether systems and in elucidating the role of the ether in reactions of lithium borohydride.

Results and Discussion

Pressure–composition isotherms for the system lithium borohydride–dimethyl ether at 20.0, 0.0, −45.2, −63.5 and −78.6° clearly show the existence of three solid dimethyl etherates of lithium borohydride: an hemi-(dimethyl etherate), $(LiBH_4)_2 \cdot (CH_3)_2O$; a dimethyl etherate, $LiBH_4 \cdot (CH_3)_2O$; and a bis-(dimethyl etherate), $LiBH_4 \cdot 2(CH_3)_2O$. Experimentally determined pressures at various mole fractions of lithium borohydride (n_2) are given in Table I and plots of these data are shown in Fig. 1.

In each of these phase diagrams, the uppermost plateau indicates the constant vapor pressure of a saturated solution in equilibrium with the solid

(6) H. I. Schlesinger, H. C. Brown, H. R. Hoekstra and L. R. Rapp, THIS JOURNAL, **75**, 199 (1953).