In the former case there is extensive ion-pair formation between the $TMPDH^+$ cation and the AHA^- anion, with two types of hydrogen bond involved: N–H–O and O–H–O. While conductivity studies of carboxylate homoconjugate ion-pair formation in benzene show a tenfold increase in the specific conductance over that of ion pairs,[17] and hence a markedly increased dissociation of the homoconjugate, nevertheless the very low value of the specific conductance ($\sim 10^{-11}$ ohm^{-1} cm^{-1} for a 0.0027 *M* solution of TCA in 0.0065 *M* triethylammonium trichloroacetate) means that a very small fraction of the homoconjugate ion pair is undergoing dissociation. This is also evident from molecular-weight studies in benzene. Thus, Bruckenstein and Saito referred to the homoconjugate salt formed by TCA and a tertiary amine as a homoconjugate ion pair —an uncharged ion aggregate.[18] The cation radical of Wurster's Blue may behave quite differently from $TMPDH^+$ as a counterion to the various hydrogen-bonded anionic species which are present in the various solutions. It may be much less capable of forming a hydrogen bond than $TMPDH^+$, since it carries no proton, there is a positive charge on the particle, and there is only one electron rather than a lone pair on a nitrogen atom. The stabilizing effect of the hydrogen bond formed between $TMPDH^+$ and the various anionic species is thus removed. The general pattern of the TMPD–C· redox reaction in benzene is the following: regardless of the number of acid molecules associated with $TMPDH^+$ prior to oxidation, one additional molecule of acid is needed to form the Wurster's Blue. This additional molecule may be needed to stabilize the counteranion to the cation radical because of the disappearance of the hydrogen bond between $TMPDH^+$ and the carboxylate species which existed prior to the oxidation.

It appears, from Table IV, that the chlorinated acetic acids show at least three different orders of acidity in benzene. For dimerization, the order is MCA > DCA > TCA. For simple ion-pair formation with TMPD, the order is TCA > DCA > MCA. The latter sequence is also found for the formation of Wurster's Blue, but the range of values of the equilibrium constants is diminished from three orders of magnitude to one. The values of K_{ox} for the three acids may represent their differing capacities for homoconjugate particle stabilization in the presence of a nonhydrogen-bonding cation.

Acknowledgment. We thank Professor Bruce R. McGarvey for his advice on the esr measurements.

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A Diffusion Study at 25° with a Shearing Diffusiometer. A Comparison with the Gouy and Conductance Methods

C. N. Pepela, B. J. Steel, and P. J. Dunlop*

Contribution from the Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia. *Received February 9, 1970*

Abstract: A new procedure is described for evaluating diffusion coefficients from experimental data obtained with a shearing diffusiometer of Ingelstam design, and diffusion coefficients are reported for aqueous solutions of each of the solutes, sucrose, *n*-butyl alcohol, magnesium sulfate, tetra-*n*-propylammonium bromide, tetra-*n*-butylammonium bromide, thiourea, glycine anhydride, ϵ-caprolactam, and mannitol. Using a Gouy diffusiometer, diffusion data have also been obtained for the systems $MgSO_4$–H_2O, *n*-Pr_4NBr–H_2O, and thiourea–H_2O. Data for the system $MgSO_4$–H_2O are used to compare the shearing diffusiometer with the Gouy and conductance methods.

In 1955 Ingelstam[1] described an optical system which first used a Savart plate[2–5] to shear a plane-polarized wave front of monochromatic light after passage through a cell in which free diffusion was taking place, and then employed an analyzer to permit the sheared light beam to produce a symmetrical system of straight interference fringes. He also indicated a method for obtaining an *approximate* binary diffusion coefficient from the variation with time of the fringe separations. Later Bryngdahl[6,7] developed the method much further and reported diffusion coefficients for dilute solutions of the system sucrose–H_2O. Additional theoretical developments were discussed in a further publication.[8] It should be noted that in 1951 Tsvetkov[9] and in 1957 Tsvetkov and Klenin[10] also described diffusion measurements with a somewhat similar shearing diffusiometer.

The purpose of this paper is to report diffusion data which were obtained for nine aqueous binary systems with a shearing diffusiometer of Ingelstam and Bryngdahl design,[1,6,7] and to compare these results with similar data obtained with a Gouy diffusiometer which has been previously described,[11] and with the data in the

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* Address correspondence to this author

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literature. The systems chosen for study were sucrose–H_2O, *n*-butyl alcohol–H_2O, $MgSO_4$–H_2O, tetra-*n*-propylammonium bromide–H_2O, tetra-*n*-butylammonium bromide–H_2O, thiourea–H_2O, glycine anhydride–H_2O, ε-caprolactam–H_2O, and mannitol–H_2O. The $MgSO_4$–H_2O system was selected so that any data obtained with the shearing and Gouy diffusiometers could be compared with data previously measured with the conductance method of Harned.[12–14] For detailed descriptions of these three methods the reader is referred to the literature;[6,7,11–17] however, several new theoretical and experimental developments for the shearing diffusiometer are included in this study.

Theory

When the diffusion coefficient, D, of a binary system is independent of concentration and the refractive index, n, is a linear function of concentration, the refractive index gradient distribution for *free* diffusion is given by the expression[18–20]

$$(\partial n/\partial x)_{\mathrm{t}} = \frac{\Delta n}{2\sqrt{\pi D t}} \exp(-x^2/4Dt) \qquad (1)$$

where Δn is the difference in the refractive index between the two solutions used to form the initial boundary, t is the time, and the cell coordinate x is measured from the position of the initial boundary and is taken to be positive in the downward direction. Since each fringe generated by the shearing optical system corresponds to a position in the diffusion cell where $(\Delta n/\Delta x)_{\Delta x = b_1}$ is constant, eq 1 may be used to derive an expression to calculate the diffusion coefficient from the variation with time of the fringe positions: $b_1 = (b/G)$, where b is the shear[6] produced by the Savart plate and G is an optical magnification factor.

As a first step in using eq 1 to derive an expression for evaluating D, it is necessary to relate the quantity $\Delta n/\Delta x)$ to the corresponding value of $(\partial n/\partial x)_{\mathrm{t}}$ by using Taylor series to give[1,6]

$$\left(\frac{\Delta n}{\Delta x}\right)_{\Delta x = b_1} = \left[n\left(x + \frac{b_1}{2}\right) - n\left(x - \frac{b_1}{2}\right)\right]\Big/ b_1 = \left(\frac{\partial n}{\partial x}\right)_{\mathrm{t}}\left[1 + \frac{1}{2^2 \cdot 3!}\left(\frac{b_1}{\sigma}\right)^2 \frac{(x^2 - \sigma^2)}{\sigma^2} + \frac{1}{2^4 \cdot 5!}\left(\frac{b_1}{\sigma}\right)^4 \frac{(x^4 - 6x^2\sigma^2 + 3\sigma^4)}{\sigma^4} + \ldots\right] \qquad (2)$$

where $\sigma = \sqrt{2Dt}$ is the standard deviation of the refractive index distribution. For the Gaussian distribution described by eq 1

$$(2\sigma)^2 = (2x_i)^2 = 8Dt_i \qquad (3)$$

where $(2x_i)$ and t_i are the fringe separation and the corresponding time, respectively, for the points of inflexion. Equations 1 and 2 may then be combined to yield

$$\frac{(2x)^2}{8Dt} - 2 \ln(1 + \xi_1 + \xi_2 + \ldots) = 1 + \ln(t_{\mathrm{m}}/t) \qquad (4)$$

where

$$\xi_1 = \frac{1}{24}\left(\frac{b_1^2}{2Dt}\right)\left[\frac{(2x)^2}{8Dt} - 1\right] \qquad (4a)$$

$$\xi_2 = \frac{1}{1920}\left(\frac{b_1^2}{2Dt}\right)^2\left[\frac{(2x)^4}{(8Dt)^2} - \frac{6(2x)^2}{8Dt} + 3\right] \qquad (4b)$$

$$t_{\mathrm{m}} = t_i(1 + \xi_2 + \ldots)^{-2} \qquad (4c)$$

an equation which is a modification of one first suggested by Bryngdahl and Ljunggren.[8] The value of ξ_2 and all higher terms in the logarithmic series on the left-hand side of eq 4 may be neglected when computing a value for D. Then, after using the approximation $\ln(1 + \xi_1) = \xi_1$, eq 4 becomes

$$(2x)^2 = \frac{3A^2t^2}{(3At - b_1^2)}[1 + \ln(B/t)] - \frac{b_1^2At}{(3At - b_1^2)} \qquad (5)$$

where $A = 8D$ and $B = t_{\mathrm{m}}$. When it is assumed that $\xi_2 = 0$ and $\ln(1 + \xi_1) = \xi_1$, the time, $t_{\max}$,[21] at which each fringe pair reaches a maximum separation, $(2x)_{\max}$, is given by

$$t_{\max} \cong t_i \exp(-b_1^2/24Dt_{\max}) \qquad (6)$$

The two constants A and B may be computed quite easily by a standard *nonlinear* least-squares procedure.[22] In addition it is necessary to introduce a zero-time correction, Δt, to all experimental times to allow for the fact that the initial boundary is not perfectly sharp.[23] This correction is computed at the same time as A and B (see Appendix). Thus the nonlinear least-squares procedure generates values of D, t_{m}, and Δt[24] which best reproduce corresponding experimental values of $2x$ and t; the value of $(2x)_{\max}$ is also calculated. Data for nine aqueous binary systems are reported in the following sections.

Experimental Section

The optical system used for all experiments was essentially identical with that used by Bryngdahl.[5] All elements were mounted on a 10-m lathe bed which has been previously described[11] for use with a Gouy diffusiometer. The source slit, the water bath, the cell holder, the camera, and plate holder of the Gouy diffusiometer were also used for the shearing optical system. The other lenses, the two polarizers, and the Savart plate were mounted on lathe riders which incorporated all the adjustments necessary to position them accurately with respect to the optical axis. A stop was attached next to each rider so that the latter could be removed from the lathe bed and then returned to exactly the same position. In this way it was possible to change from the Gouy to the shearing diffusiometer in approximately 10 min. The optical elements were aligned with the aid of a 1-sec transit and a telescope with a gauss eyepiece attachment.[25] The camera magnification factor, M,

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(21) $t_{\max}$, the time for maximum fringe separation, is not equal to t_{m} (eq 4c) or t_i (eq 3); however, when ξ_2 is neglected, $t_{\mathrm{m}} = t_i$.

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(24) When ξ_2 is considered, it turns out that the values of D, t_{m}, and Δt differ negligibly from the corresponding values obtained when ξ_2 is neglected. Also when both ξ_1 and ξ_2 are omitted, essentially the correct value of D is obtained. This is possible because the form of the equations permits the zero-time correction to perform the same function as the b_1 correction. However in this case the zero-time correction, Δt, is no longer a measure of the "sharpness" of the initial boundary.

(25) Telescope (No. M524) and filar eyepiece micrometer (No. M-202G) obtained from Gaertner Scientific Corp., Chicago, Ill.

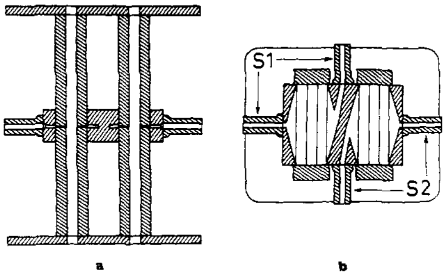

Figure 1. Modified "Tiselius-type" center section of a diffusion cell which uses horizontal slits in the cell walls to form initial boundaries at the optic axis: (a) side view, (b) plan view.

was determined by focusing the camera on a glass scale situated at a plane a distance $a/3$ from the front wall of the cell and in a direction away from the camera. M was approximately 1.22 in all experiments. The scale used had a thickness almost identical with the front wall of the cell and hence it was placed in the cell holder with the scale lines facing toward the light source.[26,27] According to Svensson[28,29] optical aberrations due to Wiener skewness[30] are removed by focusing on this plane.

The cell used for the initial exploratory experiments was the standard Tiselius type which was normally used with the Gouy diffusiometer. However, it soon became apparent that with such a cell and the Kahn–Polson siphoning technique[31] it was impossible to form initial boundaries which were suitable for observation with the shearing diffusiometer. Presumably this was due firstly to the very small density differences between the bottom, B, and top, T, solutions used in each experiment, and secondly to the fact that with the shearing optical system it is desirable to photograph the interference fringes almost immediately after the siphoning is terminated. Accordingly a new center section for the cell was planned which, while essentially retaining the original Tiselius design, also incorporated the boundary-forming technique of Ogston and coworkers;[32,33] *i.e.*, the cell was constructed with two horizontal slits 0.05 mm in width in each arm of the cell. Thus the cell could be operated in much the same way as before, but now the boundary was formed by drawing out liquid through the slits situated on one arm of the cell at the level of the optical axis. Figure 1 shows two sections through the center section of the cell, which had a dimension parallel to the optical axis of 3.103_0 cm. In use one pair of slits was sealed off and the other pair attached to a siphon. It was found that a Nupro bellows valve[34] attached to the cell holder was most satisfactory for accurate control of the siphoning rate, and that identical results were obtained using only one slit to form the boundary. With aqueous solutions a siphoning rate of approximately 2 cm^3/min was usually employed. The cell was unsatisfactory for use with organic solvents for two main reasons, firstly because of the necessity to grease its sliding surfaces when it is assembled (all lubricants were found to be quite unsatisfactory for organic solvents), and secondly because the rubber tubing leading from the slits to the control tap of the siphon was porous to such solvents. Another cell is being constructed with the top, the bottom, and the center sections fused together and which incorporates one slit from pair S1 and one slit from pair S2 (see Figure 1).

The cell was filled in exactly the same way as for an experiment with the Gouy diffusiometer,[11,16] and after thermostating for approximately 1.5 hr, it was opened and siphoning commenced. Normally 30 cm^3 of liquid was removed from the cell before siphoning was terminated. Each diffusion experiment was designed to last approximately 1500 sec, after which period two further experiments were usually performed with the same solutions by resharpening the boundary. The optical system, which employed monochromatic light of wavelength 5460.7 Å, was adjusted to give a maximum separation of 2–3 mm for the *second* outermost pair of fringes when two polarizers were in the "crossed position."[6]

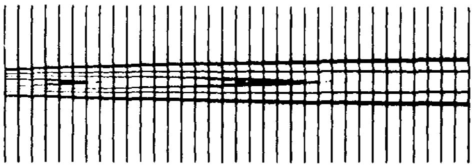

Figure 2. Part of a photographic record taken with the shearing diffusiometer when an 0.18% aqueous solution of tetra-*n*-butylammonium bromide diffused into water at 25°. Exposures were taken every 20 sec with parallel polaroids.

Photographs of the interference fringes were taken every 10 or 20 sec by means of a robot camera controlled by a quartz crystal oscillating at 10 kcps. A relay mechanism was used to activate an electric motor which advanced the photographic plate holder after each exposure had been made. Photographs were originally taken on 4-in. × 5-in. plates which were wide enough to contain 75 exposures. Super Ortho Press and 0.800 Kodak glass plates were used at first, then Kodak Type IIG and OaG, and finally Kodak Royal-X-Pan. Exposures from 1 to 2 sec were normally employed. The distances ($2x$) between the symmetrical interference fringes (see Figure 2) were measured with a Gaertner toolmakers' microscope fitted with a projection screen and a photoelectric indicator attachment.[35,36] The screws of the microscope were accurate to 1 μ.

Materials. The sucrose used in all experiments was a British Drug Houses (BDH) microanalytical reagent which was stored over P_2O_5 and used without further purification. The *n*-butyl alcohol was a BDH laboratory reagent which was purified by distillation in 1-m column enclosed in a vacuum jacket, packed with stainless steel spirals, and fitted with a dividing head. The impurities in the final sample were estimated by gas-phase chromatography to be less than 0.3%. The density of the sample (dried over anhydrous $CaSO_4$) was measured in a 30-cm^3 pycnometer and found to be 0.80577 g cm^{-3}, a value which compares favorably with 0.80568 g cm^{-3} found by Gosting and Fujita[37] and 0.80570 g cm^{-3} found by Jones and Christian.[38] The $MgSO_4$ was an Ajax Chemicals Univar product which was recrystallized twice from distilled water and dried in a vacuum oven at 100°. Analysis for sulfate by precipitation with Analar barium chloride indicated that the composition of the recrystallized product was $MgSO_4 \cdot 1.20H_2O$. The tetra-*n*-propyl- and the tetra-*n*-butylammonium bromides were both white-label Eastman Kodak products which were recrystallized twice from BDH Analar acetone, dried in a vacuum oven at 70°, and then stored in the presence of P_2O_5. The thiourea,[39] the glycine anhydride,[39] and the ϵ-caprolactam[40] samples have been described previously. The mannitol was a BDH microanalytical reagent and was used without further purification.

All solutions were made up by weight using air-saturated doubly distilled water as solvent. Concentrations, C, in mol dm^{-3} were calculated from the weight percentages *in vacuo*, the corresponding molecular weights,[39] and the density data available in the literature.[39-45]

Results

The experimental data obtained with the shearing diffusiometer are summarized in Tables I–VI. Column 1 in each table gives the experiment number, while columns 2 and 3 give values for the mean concentrations, $\bar{C}$, and the differences in concentration, ΔC, between the two solutions used in each experiment.

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Table I.[a,b] Diffusion Coefficients for the System Sucrose–H_2O at 25°

Expt	$\bar{C}$	ΔC	$(2x)_{max}$, cm	t_m, sec	Δt, sec	$D \times 10^5$, cm^2 sec^{-1}	Av dev, μ
671	0.00262	0.00525	0.2299	841.7	9.1	0.524_6	3.2
671*			0.1353	291.9	10.4	0.524_4	2.1
672			0.2292	839.7	9.2	0.522_9	2.8
672*			0.1350	291.7	9.6	0.522_2	1.7
673			0.2298	840.6	8.5	0.525_1	2.5
673*			0.1353	291.2	8.2	0.525_6	2.6
674			0.2295	837.5	8.7	0.525_4	2.7
674*			0.1352	290.5	9.7	0.525_6	1.4
732	0.0291	0.00470	0.2021	663.9	10.2	0.514_1	2.8
733			0.2024	662.8	10.6	0.516_5	2.3
734			0.2027	661.1	10.1	0.519_2	2.8
121	0.0584	0.00472	0.2037	687.8	1.0	0.506_8	5.2
122			0.2048	691.9	3.8	0.508_9	5.5
311	0.0883	0.00482	0.2031	693.4	9.9	0.499_7	3.4
131	0.1184	0.00483	0.2097	752.2	8.4	0.490_7	2.9
132			0.2072	733.5	10.0	0.491_5	5.8
141	0.2062	0.00315	0.1347	328.8	12.8	0.463_6	3.4
142			0.1347	327.8	12.9	0.464_5	3.7
321	0.3343	0.00388	0.1708	562.0	11.2	0.435_8	4.4
322			0.1720	566.5	21.9	0.438_7	4.9
323			0.1720	563.5	11.1	0.433_2	4.8
191	0.4633	0.00377	0.1653	577.4	20.9	0.397_3	4.6
192			0.1676	584.7	16.8	0.403_6	3.3
201	0.4633	0.00362	0.1634	550.4	15.2	0.407_6	3.0
202			0.1625	550.1	15.7	0.404_2	2.9
203			0.1644	551.8	7.8	0.411_3	2.9

[a] All points are not included in Figure 3. [b] An asterisk indicates results obtained from the *third* outermost pair of fringes.

Table II. Diffusion Coefficients for the System *n*-Butyl Alcohol–H_2O at 25°

Expt	$\bar{C}$	ΔC	$(2x)_{max}$, cm	t_m, sec	Δt, sec	$D \times 10^5$, cm^2 sec^{-1}	Av dev, μ
361	0.00223	0.00446	0.2742	647.9	5.5	0.974_9	4.7
362			0.2754	652.3	6.9	0.976_8	4.6
363			0.2758	654.6	6.5	0.975_6	4.9
341	0.4112	0.00411	0.2480	611.5	5.1	0.845_1	3.2
342			0.2480	612.1	6.3	0.844_1	3.6
343			0.2488	613.2	3.5	0.847_9	5.0
351	0.3984	0.00368	0.2541	646.8	10.0	0.838_7	3.0
352			0.2544	646.2	10.5	0.841_0	3.6
353			0.2537	640.8	11.1	0.843_8	4.6

Columns 4, 5, 6, and 7 list corresponding values of the maximum separation, $(2x)_{max}$, between a particular pair of interference fringes, and the characteristic time, t_m, defined by eq 4c, the zero-time correction, Δt, and the differential diffusion coefficient, respectively. These four values were calculated from the experimental data by means of eq 5 using a nonlinear least-squares method (see Appendix) and a CDC 6400 computer. The average deviations between experimental and calculated values of $2x$ are listed in column 8 of each table. The value of b_1 used in eq 5 was 0.0374 cm.

Further diffusion data for the systems $MgSO_4$–H_2O, n-Pr_4NBr–H_2O, and thiourea–H_2O are listed in Table VII. The results were obtained with a Gouy diffusiometer. Complete details for measuring binary diffusion coefficients by this method have been given on many previous occasions.[11,15,16] Three diffusion cells 5A, 2A, and 2B with *a* dimensions of 2.5053, 2.5043, and 2.5018 cm, respectively, were used for the measurements which are believed to be accurate to ±0.2%.

Table III. Diffusion Coefficients for the System $MgSO_4$–H_2O at 25°

Expt	$\bar{C}$	ΔC	$(2x)_{max}$, cm	t_m, sec	Δt, sec	$D \times 10^5$, cm^2 sec^{-1}	Av dev, μ
231	0.00847	0.00942	0.2025	502.5	7.5	0.685_1	3.8
232			0.2021	502.0	11.9	0.683_4	5.2
233			0.2015	503.0	46.3	0.677_5	3.9
401	0.01658	0.01001	0.2311	683.4	2.7	0.656_3	2.9
402			0.2318	688.1	7.0	0.655_1	2.2
403			0.2314	688.1	7.8	0.653_7	2.4
281	0.02103	0.00926	0.1979	516.5	11.0	0.636_5	2.1
261	0.02875	0.00900	0.1859	465.3	8.2	0.624_0	2.7
262			0.1868	465.3	12.6	0.629_8	3.2
263			0.1866	459.9	7.9	0.635_2	4.6
431	0.04498	0.00919	0.2013	554.4	11.2	0.611_0	2.8
434			0.2018	556.1	10.7	0.611_6	3.6
435			0.2021	551.8	8.8	0.618_8	2.7
631	0.05744	0.00913	0.1980	546.5	6.9	0.599_2	4.5
632			0.1980	544.2	6.5	0.602_2	4.7
633			0.1970	550.5	11.4	0.589_5	3.9
621	0.1160	0.00948	0.1988	582.3	6.7	0.566_3	3.4
622			0.1987	586.3	7.4	0.562_1	4.0
623			0.1986	593.0	10.0	0.555_1	5.4
441	0.1705	0.00716	0.1760	478.6	8.3	0.540_9	3.1
442			0.1764	480.8	8.0	0.541_1	3.8
443			0.1760	476.4	8.3	0.543_0	4.0
381	0.3056	0.00994	0.2096	740.7	8.3	0.498_0	2.4
382			0.2102	744.2	7.9	0.498_7	2.6
383			0.2101	735.4	8.2	0.503_8	2.4

Table IV. Diffusion Coefficients for the System Tetra-*n*-propylammonium Bromide–H_2O at 25°

Expt	$\bar{C}$	ΔC	$(2x)_{max}$, cm	t_m, sec	Δt, sec	$D \times 10^5$, cm^2 sec^{-1}	Av dev, μ
161	0.00324	0.00648	0.2248	462.3	3.2	0.917_8	4.9
162			0.2253	459.1	1.0	0.928_5	3.8
163			0.2244	458.2	23.6	0.923_4	4.8
151	0.00396	0.00792	0.2709	675.0	10.4	0.913_4	5.4
152			0.2712	674.6	8.4	0.915_9	4.0
171	0.00900	0.00647	0.2450	473.8	9.4	0.893_3	3.1
172			0.2233	469.7	9.4	0.891_4	4.1
531	0.03982	0.00667	0.2330	546.2	8.4	0.830_6	3.4
533			0.2335	551.8	10.1	0.826_0	2.6
642	0.03987	0.00656	0.2318	542.7	5.2	0.827_7	6.3
643			0.2312	531.9	2.7	0.840_1	4.5
182	0.03988	0.00824	0.2865	827.3	4.2	0.833_0	3.4

Table V. Diffusion Coefficients for the System n-$(Bu)_4NBr$–H_2O at 25°

Expt	$\bar{C}$	ΔC	$(2x)_{max}$, cm	t_m, sec	Δt, sec	$D \times 10^5$, cm^2 sec^{-1}	Av dev, μ
561	0.00263	0.00526	0.2330	567.6	0.4	0.799_2	4.2
562			0.2352	578.5	−1.3	0.798_8	3.5
563			0.2335	569.5	−0.8	0.800_0	4.3
651	0.00278	0.00557	0.2475	644.4	12.1	0.794_7	2.6
652			0.2477	643.2	4.3	0.797_0	3.8
653			0.2480	638.8	10.6	0.804_5	2.5
551	0.00282	0.00563	0.2506	659.4	2.8	0.795_8	3.8
552			0.2532	670.6	−2.2	0.799_0	3.6
553			0.2520	659.0	8.0	0.805_3	3.6
591	0.00990	0.00538	0.2376	615.7	7.5	0.766_1	3.2
592			0.2394	629.2	7.8	0.760_9	2.8
593			0.2379	622.6	10.1	0.759_4	2.6
572	0.04630	0.00575	0.2442	711.5	14.0	0.689_1	3.4
573			0.2460	729.2	9.4	0.693_8	3.2
581	0.09982	0.00466	0.2068	575.2	17.3	0.621_4	3.2
582			0.2088	584.2	11.9	0.623_6	2.8
583			0.2083	577.4	13.2	0.627_9	3.3
661	0.2400	0.00470	0.2117	712.0	14.8	0.526_1	2.8
662			0.2111	704.0	12.8	0.528_8	2.6
663			0.2114	706.3	11.1	0.528_7	2.4

Table VI.[a] Diffusion Coefficients for the Systems Thiourea–H_2O, Glycine Anhydride–H_2O, ϵ-Caprolactam–H_2O, and Mannitol–H_2O at 25°

Expt	$\bar{C}$	ΔC	$(2x)_{max}$, cm	t_m, sec	Δt, sec	$D \times 10^5$, cm² sec⁻¹	Av dev, μ
			Thiourea–H_2O ($D^0 \times 10^5 = 1.326$)[b]				
681	0.00910	0.01820	0.3342	705.5	6.3	1.324	2.8
682			0.3311	688.9	6.4	1.330	2.4
683			0.3342	698.9	6.5	1.336	2.9
			Glycine Anhydride–H_2O ($D^0 \times 10^5 = 0.991$)[b]				
693	0 00843	0.01646	0.2847	689.5	9.8	0.983_1	3.4
693*			0.1671	236.0	8.5	0.988_4	3.0
694			0.2858	688.3	8.5	0.991_7	3.6
694*			0.1676	237.2	8.3	0.990_3	1.6
695			0.2860	690.8	7.6	0.989_5	3.1
695*			0.1679	237.2	−2.6	0.991_2	2.2
			ϵ-Caprolactam–H_2O ($D^0 \times 10^5 = 0.885$)[b]				
701	0.00859	0.01718	0.2722	701.7	0.4	0.882_1	3.2
701*			0.1598	242.6	−0.7	0.879_4	2.5
702			0.2732	705.2	8.6	0.884_9	3.5
702*			0.1599	243.6	10.0	0.878_0	1.6
703			0.2737	704.3	7.8	0.889_0	3.0
703*			0.1604	242.8	8.8	0.885_7	2.4
			Mannitol–H_2O ($D^0 \times 10^5 = 0.666$)[b]				
721	0.00931	0.01862	0.2514	793.5	4.4	0.665_4	2.1
721*			0.1785	400.8	3.4	0.664_5	2.4
723			0.2524	796.2	15.0	0.668_8	3.3
723*			0.1793	404.6	17.7	0.664_3	1.7
751	0.00548	0.01096	0.2636	869.3	7.3	0.665_7	2.9
752			0.2634	866.1	7.3	0.667_3	2.5
753			0.2636	864.4	7.6	0.669_4	2.8
754			0.2634	868.0	8.3	0.665_7	3.0

[a] An asterisk on an experimental number indicates that the third outermost pair of fringes was used. [b] Obtained by extrapolating data obtained with the Gouy diffusiometer to infinite dilution.

Table VII. Diffusion Data Obtained with the Gouy Diffusiometer for the Systems $MgSO_4$–H_2O, *n*-Pr_4NBr, and Thiourea–H_2O at 25°

$\bar{C}$	ΔC	J^a	$(\Delta n/\Delta C) \times 10^3$,[b] dm³ mol⁻¹	$D \times 10^5$, cm² sec⁻¹
		$MgSO_4$–H_2O (Cell 5A)		
0.09230	0.05065	55.76	23.99_6	0.574_9
0.14912	0.06390	69.19	23.60_1[c]	0.545_3
0.21102	0.07737	80.29	22.61_9	0.522_1
0.44224	0.06995	68.27	21.27_3	0.464_3
		n-Pr_4NBr (Cell 2A)		
0.01409	0.02818	51.15	39.58_0	0.875_4
0.01730	0.03460	62.51	39.39_4	0.867_1
0.01872	0.02684	48.51	39.41_0	0.869_0
0.02496	0.02205	39.89	39.44_7	0.852_5
0.02496	0.03599	65.18	39.49_0	0.853_0
0.02496	0.04993	90.48	39.51_4	0.850_9
0.06084	0.03868	70.32	39.64_2	0.802_8
0.09680	0.03493	63.84	39.88_8	0.764_9
0.22493	0.04558	84.65	40.49_6	0.674_9
0.37275	0.03974	74.97	41.13_6	0.605_2
0.90242	0.02018	38.59	41.69_8[c]	0.490_2
1.27809	0.02329	47.37	44.35_0	0.454_0
		Thiourea–H_2O[d] (Cell 2B)		
0.03319	0.06638	62.04	20.39_9	1.320
0.05180	0.10360	96.80	20.39_4	1.315
0.25174	0.06211	58.00	20.38_3	1.276

[a] *J* is the total number of fringes in each Gouy experiment (see ref 20). [b] $(\Delta n/\Delta C)$ is the differential refractive increment (see ref 20). [c] These values appear to be in error. Since the corresponding diffusion coefficient is in agreement with the other values reported for this system, it is believed that these errors are probably due to incorrectly recorded weights. [d] These three experiments were performed by Mr. Claudio Pua.

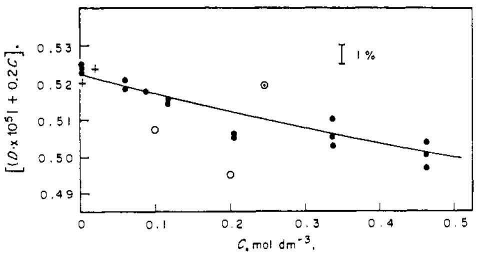

Figure 3. Concentration dependence of the diffusion coefficient of the system sucrose–H_2O at 25°. The solid line reproduces (within ±0.1%) the data obtained with the Gouy,[16,41,46] the Rayleigh,[27,47,48] the Jamin,[49] and the Mach-Zehnder[50] diffusiometers: ⊙, Henrion[51] with the diaphragm cell; ○, Irani and Adamson[52] with a diaphragm cell; +, Bryngdahl with the shearing diffusiometer; ●, this work (see Table I).

Discussion

Sucrose–H_2O. The diffusion data in Table I were the first obtained with the present shearing optical system. Some of the experimental points deviate by more than the estimated (≈ ±0.3%) possibly because insufficient liquid may have been withdrawn when forming the initial boundary or because the tops of the two sides of the diffusion cell were not sufficiently protected from the air which was circulated in the room by means of a large air conditioner (the center section of the cell was not isolated from the top and bottom sections). Later, better results were obtained when two small glass caps were placed over the tops of the two sides of the cell. In Figure 3 the results obtained in this study are compared with the data in the literature.[6,16,41,46–52] The results for the Gouy, the Rayleigh, the Jamin, the Mach-Zehnder, and the shearing diffusiometers agree quite well.

***n*-Butyl Alcohol–H_2O.** Gosting and Fujita[37] have developed a theory which indicates that, if the diffusion coefficient and/or the differential refractive increment[37] are concentration dependent, the reduced height–area ratio,[37] $\mathfrak{D}_A$, which is measured with the Gouy diffusiometer, is a linear function of the *square* of the *difference* in concentration between the two solutions used in a *free diffusion* experiment, provided the mean value of these two concentrations is held constant. Their theory indicates that, with these conditions, the differential diffusion coefficient may be obtained by extrapolating $\mathfrak{D}_A$ *vs.* $(\Delta C)^2$ to $\Delta C = 0$. Thus one would expect that, if experiments could be performed with extremely small values of ΔC, then differential coefficients could be measured directly. Gosting and Fujita studied the system *n*-butyl alcohol–H_2O with $\bar{C} = 0.4$ and varied ΔC to obtain D ($\bar{C} = 0.4$) $= 0.844_2 \times 10^{-5}$ cm² sec⁻¹. Accordingly two experiments were performed with the shearing optical system with $\bar{C} = 0.4$ (see Table II). The data are compared with the data of Fujita and Gosting in Figure 4. The agreement with their extrapolated value is quite satisfactory. Also in-

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(47) J. M. Creeth, *ibid.*, **77**, 6428 (1955).

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(52) R. R. Irani and A. W. Adamson, *J. Phys. Chem.*, **62**, 1517 (1958).

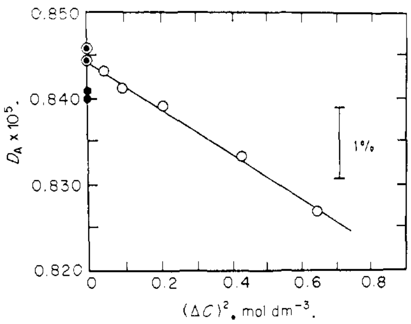

Figure 4. Graph of the reduced height-area ratio, $\mathfrak{D}_A$, *vs.* $(\Delta C)^2$ for five diffusion experiments with the binary system *n*-butyl alcohol-H_2O at 25°. The data were obtained with the Gouy diffusiometer by Fujita and Gosting,[37] and each experiment was performed with the same mean concentration $\bar{C}$ = 0.4. The *six* points which lie at $(\Delta C)^2 \cong 0$ were obtained at the same mean concentration by the shearing interference method used in this study (see Table II).

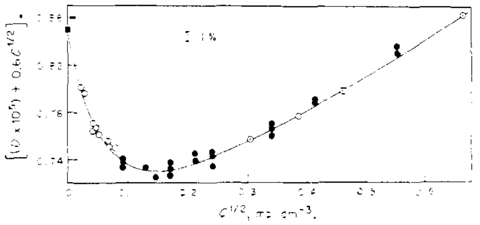

Figure 5. Concentration dependence of the diffusion coefficient of the system $MgSO_4$–H_2O at 25°. The solid line is drawn through the three sets of data: O, Harned and Hudson with the conductance method;[14] ●, this work (see Table III) with the shearing diffusiometer; ⊙, this work (see Table VII) with the Gouy diffusiometer; ■, Nernst limiting value (see eq 7).

cluded in Table II are data for experiments 361–363 in which a very dilute butanol diffused into water; the average value of D ($\bar{C}$ = 0) is 0.976 × 10^5 cm^2 sec^{-1}, which agrees quite well with the result of 0.970 × 10^5 obtained by Lyons and Sandquist[42] at the same concentration (essentially infinite dilution).

$MgSO_4$–H_2O. This system was selected for study because Harned and Hudson[14] had already obtained diffusion data at low concentrations by means of the conductance technique.[12,13] In addition, the diffusion coefficient for $MgSO_4$–H_2O and its dependence on concentration near infinite dilution were such that one could expect experiments with the shearing diffusiometer to yield differential diffusion coefficients. Several experiments were also performed with the Gouy diffusiometer. The data are summarized in Tables III and VII, and compared with the results of Harned and Hudson[14] in Figure 5. The agreement among the three methods is quite satisfactory.

***n*-Pr_4NBr–H_2O and *n*-Bu_4NBr–H_2O.** One of the reasons for constructing the diffusion cell and the optical system used in this study was to obtain diffusion data for dilute aqueous solutions of the *n*-alkylammonium bromides which have been shown to exhibit anomalous behavior in some of their equilibrium properties.[43] Data were obtained for *n*-Pr_4NBr–H_2O with both the shearing and Gouy diffusiometers, and for the system *n*-Bu_4NBr–H_2O with the shearing optical system. The results are summarized in Tables IV, V, and VII. The system *n*-Bu_4NBr–H_2O was the last one studied and, at the beginning of these measurements, it was found that the movement of air over the tops of the two cell columns (3-mm inside diameter at the top) was causing an occasional slight oscillating motion of the boundary in the vertical direction (the center section of the cell was not isolated from the top and bottom sections). After two small glass cups were placed over the tops of the two cell columns, the results were considerably improved. Thus it is believed that the data obtained with this system provide the best test of the potential of the shearing diffusiometer.

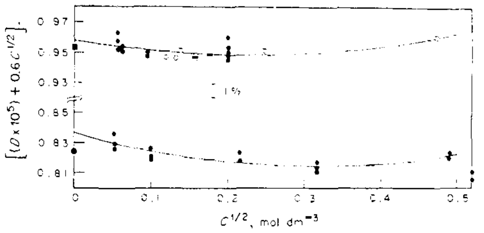

Figure 6. Diffusion data obtained with the shearing and Gouy diffusiometers for the systems *n*-Pr_4NBr–H_2O (upper) and *n*-Bu_4NBr–H_2O (lower) at 25°: ●, experiments performed with the shearing diffusiometer (see Tables IV and V); ⊙, experiments performed with the Gouy diffusiometer (see Table VII); ■, the Nernst limiting value (see eq 7). The curves drawn through the experimental points were obtained by fitting the points shown in the figure (and any other points in the same concentration range in Tables IV, V, and VII) to the equation $D = D^0 + aC^{1/2} + bC$; *e.g.*, see eq 8.

Figure 6 summarizes some of the data obtained with the system *n*-Pr_4NBr–H_2O with the Gouy and shearing diffusiometers, and also the data for the system *n*-Bu_4NBr–H_2O with the shearing optical system. As stated above it is believed that the results for this latter system are the most accurate of all the data obtained in this study. Accordingly, it was decided to fit the data in Table V, by least squares, as a function of $\sqrt{C}$ to obtain the limiting value of the diffusion coefficient at $C = 0$. This value is related to the limiting ionic conductances, λ_i^0 by the Nernst-Hartley relation

$$D^0 = \frac{2RT}{F^2}\left(\frac{\lambda_+^0\lambda_-^0}{\lambda_+^0 + \lambda_-^0}\right) \tag{7}$$

where R is the gas constant and F the Faraday constant.

For this system the data in Table V are represented with an average deviation of ± 0.3% by the equation

$$D \times 10^5 = 0.837 - 0.740_7C^{1/2} + 0.224_1C \tag{8}$$

Using the value $D^0 = 0.837 \times 10^{-5}$ and $\lambda_{Br^-}{}^0 = 78.22$,[53] eq 7 may be used to calculate $\lambda_{n\text{-}Bu_4N^+}{}^0 = 19.6_8$. This result is 1.8% higher than the value of 19.3_1 obtained by Evans and Kay[54] from conductance measurements with the same system. The difference, which is believed to be greater than the experimental error, may be due either to differences in the purity of the sample used here and the sample of Evans and Kay or by "the effects" which cause the anomalous behavior of the equilibrium properties.[43] Effects due to the concentration dependence of the diffusion coefficient and the differential refractive increment would cause the experimental results to be high (see Figure 4).

Thiourea-H_2O, Glycine Anhydride-H_2O, ε-Caprolactam-H_2O, and Mannitol-H_2O. Several experiments

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were performed with these systems for comparison with the data in the literature[40,45,55] (and the data in Table VII for thiourea). The results are summarized in Table VI, which also includes for each system the limiting diffusion coefficient, D^0, obtained by extrapolation to infinite dilution data previously measured with the Gouy diffusiometer. Since the mean concentrations used in all the experiments in Table VI were very near infinite dilution, and since the concentration dependence of each diffusion coefficient is quite small, the measured coefficients should differ negligibly from the D^0 values in the table. Inspection of the table indicates that this is indeed the case, and thus these results differ from the findings of Gary-Bobo and Weber,[56] who maintain that incorrect limiting diffusion coefficients for binary systems of nonelectrolytes are obtained by extrapolating to zero concentration data obtained with the Gouy diffusiometer.

It is believed that the experiment reported in this work indicate that differential diffusion coefficients may be measured with a precision of approximately ±0.3% with the shearing diffusiometer first proposed by Ingelstam and Bryngdahl. The data obtained are in excellent agreement with similar data obtained with both the Gouy and conductance techniques. Each of these three techniques has its advantages. As shown in this study, the shearing technique is well suited for studying systems with diffusion coefficients which are reasonably low ($\sim 10^{-5}$ cm sec^{-1}) and which depend strongly on concentration.

Acknowledgments. The authors are grateful to Messrs. K. Shepherdson and R. Weste for assistance in designing and maintaining the robot-camera circuitry, and to Miss J. Scott and Mrs. H. Robjohns for performing some of the experiments and for measuring the interferograms. This work was supported in part by a research grant from the National Institutes of Health (No. AM-06042-02).

Appendix

Nonlinear, Least-Squares Fit of Eq 5. The least-squares procedure involves finding the values of A and B so that eq 5 represents all the experimental values of $(2x)$ and t with minimum deviations. The method, a fairly standard one,[22] involves estimating first approximations A_0 and B_0 which are used in eq 5 to calculate $(2x)^2$ for the N points, the deviations of these quantities from the corresponding experimental values, and the standard deviation, σ_0. Small increments α_0 and β_0, found as described below, are then added to A_0 and B_0, respectively, and the new constants again used to calculate a set of N values of $(2x)^2$ with the corresponding standard deviation, σ_1. If $|\sigma_1 - \sigma_0| < 10^{-5}$ (or any other desired value), the iteration process is terminated; otherwise another set α_1 and β_1 is added to the new constants and the process repeated.

α and β may be found as follows. Let $y = (2x)^2$ in eq 5, and suppose A_0 and B_0 are the first estimates of A and B and that the two sets differ by amounts α and β, respectively; thus

$$A = A_0 + \alpha$$
$$B = B_0 + \beta \qquad (1A)$$

For each of the N experimental points we can write a residual r_i as the difference between y_i^{calcd} calculated using A and B, and the experimental y_i^{exptl}, giving N equations. For the ith point, the equation is

$$r_i = y_i^{\text{calcd}} - y_i^{\text{exptl}}$$

or

$$r_i + y_i^{\text{exptl}} = \frac{3(A_0 + \alpha)^2 t_i^2}{3(A_0 + \alpha)t_i - b_i^2}[1 + \ln(B_0 + \beta) - \ln t_i] - \frac{b_1^2(A_0 + \alpha)t_i}{3(A_0 + \alpha)t_i - b_1^2} \qquad (2A)$$

The right-hand side of each of the N such equations can be expanded as a Taylor series about A_0, B_0. Equation 2A, for example, becomes

$$r_i + y_i^{\text{exptl}} = f_i + \alpha(\partial f_i/\partial A_0) + \beta(\partial f_i/\partial B_0) + \ldots \qquad (3A)$$

where

$$f_i = \frac{3A_0^2 t_i^2}{3A_0 t_i - b_1^2}[1 + \ln(B_0/t_i)] - \frac{b_1^2 A_0 t_i}{3A_0 t_i - b_1^2} \qquad (4A)$$

The higher terms in eq 3A involve products of the small corrections α and β and can be ignored. f_i is essentially the value of y_i^{calcd} when A_0 and B_0 are used instead of A and B, respectively. If $R_i = f_i - y_i^{\text{exptl}}$, the N equations similar to (3A) become

$$r_1 = \alpha(\partial f_1/\partial A_0) + \beta(\partial f_1/\partial B_0) + R_1$$
$$r_2 = \alpha(\partial f_2/\partial A_0) + \beta(\partial f_2/\partial B_0) + R_2 \qquad (5A)$$
$$\ldots$$
$$r_N = \alpha(\partial f_N/\partial A_0) + \beta(\partial f_N/\partial B_0) + R_N$$

The sum S of the *squares* of the residuals is

$$S = \sum_{i=1}^{N} r_i^2 \qquad (6A)$$

and the best fit is that which yields minimum S. This requirement is satisfied if $\partial S/\partial\alpha = \partial S/\partial\beta = 0$. From eq 5A and 6A, it follows that

$$\frac{\partial S}{\partial \alpha} = \sum_{i=1}^{N}\left[2\alpha\left(\frac{\partial f_i}{\partial A_0}\right)^2 + 2\beta\left(\frac{\partial f_i}{\partial A_0}\right)\left(\frac{\partial f_i}{\partial B_0}\right) + 2R_i\left(\frac{\partial f_i}{\partial A_0}\right)\right] = 0$$

$$\frac{\partial S}{\partial \beta} = \sum_{i=1}^{N}\left[2\alpha\left(\frac{\partial f_i}{\partial A_0}\right)\left(\frac{\partial f_i}{\partial B_0}\right) + 2\beta\left(\frac{\partial f_i}{\partial B_0}\right)^2 + 2R_i\left(\frac{\partial f_i}{\partial B_0}\right)\right] = 0$$

and hence

$$\alpha\sum_{i=1}^{N}\left(\frac{\partial f_i}{\partial A_0}\right)^2 + \beta\sum_{i=1}^{N}\left(\frac{\partial f_i}{\partial A_0}\right)\left(\frac{\partial f_i}{\partial B_0}\right) + \sum_{i=1}^{N} R_i\left(\frac{\partial f_i}{\partial A_0}\right) = 0$$
$$(7A)$$
$$\alpha\sum_{i=1}^{N}\left(\frac{\partial f_i}{\partial A_0}\right)\left(\frac{\partial f_i}{\partial B_0}\right) + \beta\sum_{i=1}^{N}\left(\frac{\partial f_i}{\partial B_0}\right)^2 + \sum_{i=1}^{N} R_i\left(\frac{\partial f_i}{\partial B_0}\right) = 0$$

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These equations are linear in α and β. The derivatives in the coefficients are obtained from eq 4A; R_i is the difference between f_i in eq 4A and y_i^{exptl}. Equations 7A are solved[57] to give the corrections α and β, and these are then added to A_0 and B_0 to give A_1 and B_1. The next iteration uses A_1 and B_1 in eq 4A and 7A to obtain another set of the corrections α and β, and the process is repeated until the standard deviations of two successive iterations differ by less than a predetermined value (in this case 10^{-5}). Once the best values of A and B have been found, all the experimental times are changed by a small increment and the iteration is repeated as above. The time increment, Δt, which gives a minimum standard deviation is taken to be the "zero-time correction."

[57] The set of linear equations (7A) was solved by a standard subroutine MATRIX in the University's CDC 6400 computer. However, it can be handled by any specially written subroutine for solution of linear equations.

Nature and Effect of Solute–Solvent Interactions on Vibrational Spectra of Rotational Isomers

M. F. El Bermani, A. J. Woodward,* and Neville Jonathan

Contribution from the Department of Chemistry, The University, Southampton, England. *Received December 10, 1969*

Abstract: Infrared spectra have been measured for solutions of 1,2-dichloroethane, 1,2-dibromoethane, 1-fluoro-2-haloethanes, and β-halopropionitriles in a range of solvents having different dielectric constants. The relative intensity changes and carbon–halogen frequency shifts are correlated with the dielectric constant function $(\epsilon - 1)/(2\epsilon + 1)$. It is concluded that the nature of the solute–solvent interactions is mainly electrostatic. The usefulness of the reported correlations as aids to conformational and vibrational frequency analysis is critically assessed.

A considerable number of studies have been made of the general effect of solvent media on vibrational frequencies and intensities and of the comparative effects on rotational isomers. In the general case frequency shifts have been explained in terms of the Kirkwood–Bauer–Magat equation

$$\Delta\nu/\nu = C(\epsilon - 1)/(2\epsilon + 1) \qquad (1)$$

where $\Delta\nu$ is frequency difference between vapor and solution phases, ϵ is the dielectric constant of the solvent, and C is a constant characteristic of the solute. This relationship has subsequently been modified by a number of workers[1,2] and although the treatments are satisfactory for nonpolar solvents, the shifts in polar solvents are generally greater than those predicted and empirical corrections to account for specific or localized interactions have been made.[3] At best there is still only a semiquantitative understanding of solvent effects, and clearly the use of solutes which have rotational isomers will contribute little to a clarification of this particular problem. The purpose of this paper is more to evaluate the use which may be made of solvent effects in establishing the various conformations of rotational isomers.

Experimental Section

Infrared studies were made using a Grubb-Parsons GS2A spectrometer.

All solutes and solvents were dried and purified by standard techniques until their boiling points agreed with generally accepted values.

Solutions were run in standard 0.1-mm cells equipped with sodium chloride or potassium bromide windows. The solution concentrations were as low as practicable, and in all cases were less than 0.5 *M*.

Results and Discussion

Solvent effects can be conveniently subdivided into frequency shifts and intensity variations. These will be considered independently.

(1) Frequency Shifts. The main purpose of previous studies has been to attempt to differentiate between effects due to specific interactions and bulk dielectric solvent effects.[4,5] Additionally, a correct assignment of the bands to a particular conformation can sometimes be made. The need for this latter type of information is seen by considering compounds of the type XCH_2-CH_2Y. When X = Y in, for example, 1,2-dichloroethane, the problem is trivial since the trans conformer has a center of symmetry and the mutual exclusion principle for infrared and Raman activity applies. However, in the cases where there is not a center of symmetry, the assignment of bands to a particular conformer is not so straightforward. The usual method is to consider the solid-state spectrum of the compound, since it is often found that only the more stable conformer is present in this phase. However, there are many examples where such simplification of the spectrum does not occur on changing phase. Hence there is a need for an alternative method.

It has been established that in the case of 1,2-dichloroethane, the relative shifts of the ν(C–Cl) absorption bands are greater for the more polar conformer.[4] The so-called Bellamy–Hallam–Williams (BHW) plots of

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* Address correspondence to this author.

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