

Isothermal diffusion measurement on the system water-sodium salicylate-sodium chloride at 25° at one composition

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The main and cross-term diffusion coefficients for the system water-sodium-salicylate-sodium chloride have been measured at the composition 0.05 g cc⁻¹, and the results indicate that sodium chloride is effective in producing a flow of sodium salicylate at this concentration. Density, refractive index, partial specific volumes and gravitational data are also reported. The system has been assumed to be 3-component.

THE Gouy interferometric technique has been used to measure the main and cross-term diffusion coefficients for the system water-sodium salicylate-sodium chloride. The initial results indicate that the flow interaction of both solutes is taking place. Such studies provide basic information about diffusional processes in the system and may be of use in describing the flow of these substances in a biological environment.

Theory

In an isothermal system where there are more than two components and where the components do not diffuse independently, the solute flows can be described by the expression (Baldwin, Dunlop & Gosting, 1955)

$$(J_i)_v = - \sum_{j=1}^r (D_{ij})_v \frac{\partial \rho_j}{\partial x} \quad (i = 1, 2, \dots, r) \quad \dots \quad (1)$$

in which ρ_i is the concentration of component i in g cc⁻¹, $(D_{ij})_v$ are the diffusion coefficients corresponding to the volume fixed reference frame and have the units of cm sec⁻¹, and J_i is the flow of component i in units of g cm² sec⁻¹. The summation is taken over r solutes.

Thus the flow of sodium salicylate which in this paper has been given the subscript 1 is described by the equation

$$(J_1)_v = - D_{11} \frac{\partial \rho_1}{\partial x} - D_{12} \frac{\partial \rho_2}{\partial x} \quad \dots \quad (2)$$

and the flow of sodium chloride, which has been given subscript 2

$$(J_2)_v = - D_{21} \frac{\partial \rho_1}{\partial x} - D_{22} \frac{\partial \rho_2}{\partial x} \quad \dots \quad (3)$$

For the small concentration differences used in these differential diffusion experiments, the volume fixed reference frame can be considered to be identical with the cell (or apparatus)—fixed reference frame (Kirkwood, Baldwin & others, 1960). Because of its greater ionic radius, the salicylate ion would be expected to diffuse slower than the smaller sodium and

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chloride ions. Furthermore, from *a priori* considerations of ionic mobilities the flow of salicylate $(J_1)_v$ produced by the flow of sodium chloride will be large and the cross-term diffusion coefficient $(D_{12})_v$ finite. Conversely, the flow of sodium chloride $(J_2)_v$ due to the salicylate gradient will be small and the cross-term diffusion coefficient $(D_{21})_v$ correspondingly small but non-zero.

APPARATUS

The optical beam of the diffusimeter consists of two rigid cast-iron beds, of uniform box-like construction 3.2 m and 1.8 m in length, purchased from Hilger and Watts. These kinematically mounted beds rest on a platform of braced iron girders whose weight is evenly distributed on eight Barrymount type SM4-8 spring mountings. This method of support ensures that the rigid substructure has a minimal sensitivity to extraneous vibration. Light from a water-cooled 100 watt mercury-vapour G.E.C. lamp passes through a Wratten No. 77A filter which isolates the mercury green line at 5460.7 Å before being brought to a focus on a Hilger and Watts source slit (1 division = 0.005 mm). The image of the slit is focussed on a photographic plate by a 101.5 cm focal length acromatic doublet objective lens, 11 cm in diameter and corrected to $\frac{1}{8}$ th wavelength at 5460.7 Å.

The water bath has a capacity of 100 litres and is controlled to better than $(25 \pm 0.01^\circ)$. It has four optical flat windows 2 cm thick, 11 cm in diameter and corrected to $\frac{1}{20}$ th of a wavelength at 5460.7 Å. The frame holding the 11 cm Tiselius cell is similar to that described by Gosting, Hanson & others (1949), and by Dunlop & Gosting (1953; 1955).

Experimental

A rough boundary was formed in the Tiselius cell between the upper solution A and the lower more dense solution B. This crude boundary was then brought down through the cell and sharpened at the optic axis position by siphoning off the liquids through a stainless-steel capillary at a rate of approximately 1.4 to 1.6 ml/min. When 80 ml of liquid had been collected the flow was stopped, the capillary was withdrawn and the top and bottom sections of the Tiselius cell were closed. Photographs of the interference pattern were taken at times t' after stopping the flow from the stainless-steel capillary. Usually 10 to 12 photographs were taken on Kodak Ortho 800 plates. Measurements of the distance of the fringe minima from the optic axis were made to 0.001 mm using a Gaertner M2001P toolmakers' microscope, and C_t , the maximum displacement of light according to ray optics at time t' is found by the customary extrapolation procedure. For each photograph a preliminary value of D_a' , the reduced height-area ratio, was calculated using the relation

$$D_a' = \frac{J_m^2 \lambda^2 b^2}{C_t^2 t' 4\pi} \dots \dots \dots (4)$$

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where J_m is the total number of fringes in the pattern, $\lambda = 5460.7 \times 10^{-8}$ and b is the optical lever distance from the centre of the Tiselius cell to the photographic plate emulsion ($b = 260.1973$ cm).

The integral number of fringes was counted directly from an early pattern, the fractional part being measured using horizontal Rayleigh slits. A plot of D'_a versus $\frac{1}{t} = 0$ was made using a least-squares procedure to obtain a value of D_a the reduced-height area ratio, corrected for any initial imperfections in the boundary. Values of the starting time correction Δt , obtained from the slope of this graph varied between 6.7 and 14.5 sec. A fringe-deviation graph was plotted of Ω_j the average value of the reduced fringe deviation against $f(\zeta)$ the reduced fringe number, where

$$\Omega_j = e^{-(\zeta)^2} - Y_j/C_t \quad \dots \quad \dots \quad \dots \quad (5)$$

in which Y_j is the fringe displacement from the optic axis and

$$f(\zeta) = \frac{j + 0.75}{J_m} \quad \dots \quad \dots \quad \dots \quad (6)$$

in which j has an integral value greater than 6.

The area of the fringe deviation graph Q where

$$Q = \int_0^1 \Omega_j df(\zeta) \quad \dots \quad \dots \quad \dots \quad (7)$$

was calculated using Simpson's 1/3rd rule. Mean values of Ω_j were read at intervals of 0.025 along the $f(\zeta)$ axis from a large scale fringe-deviation graph and calculation of the four diffusion coefficients $(D_{ij})_v$ was then made by the method of Fujita & Gosting (1960).

A set of four experiments were made with α_1 equal to approximately 0.0, 0.2, 0.8 and 1.0 where α_1 the refractive index fraction is defined by

$$\alpha_1 = \frac{R_i \Delta \rho_1}{\sum_{j=1} R_j \Delta \rho_j} \quad (i = 1, 2) \quad \dots \quad \dots \quad \dots \quad (8)$$

and where R_1 and R_2 , the refractive index increments are given by

$$n(\rho_1, \rho_2) = n(\tilde{\rho}_1, \tilde{\rho}_2) + R_1(\rho_1 - \tilde{\rho}_1) + R_2(\rho_2 - \tilde{\rho}_2) \quad \dots \quad (9)$$

In equation (9), $n(\rho_1, \rho_2)$ is the refractive index of the solutions with the concentrations of the solutes ρ_1, ρ_2 ; $n(\tilde{\rho}_1, \tilde{\rho}_2)$ is the refractive index of the solution when $\rho_1 = \tilde{\rho}_1$ and $\rho_2 = \tilde{\rho}_2$. In all experiments $\Delta \rho_1 + \Delta \rho_2 = 0.01$ g cc⁻¹ which gave a convenient number of fringes ($J \simeq 90$).

The concentration increment between upper and lower solutions

$$\Delta \rho_1 = [(\rho_1)_B - (\rho_1)_A] \quad (i = 1, 2) \quad \dots \quad \dots \quad (10)$$

The first two experiments were made with α_1 equal to zero and unity respectively. Sufficient data were then available to solve the equation

$$\frac{\lambda}{a} \left(\frac{J_m}{\Delta \rho_1 + \Delta \rho_2} \right) = \left(\frac{\Delta \rho_1}{\Delta \rho_1 + \Delta \rho_2} \right) (R_1 - R_2) + R_2 \quad \dots \quad (11)$$

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simultaneously for R_1 and R_2 . In equation (11), the internal width, a , of the diffusion cell, is 2.4979 cm. These values of the refractive index increments were then used to calculate the concentrations required to yield solutions for which $\alpha_1 = 0.2$ and $\alpha_1 = 0.8$.

By inserting the four experimentally determined values of α_1 and D_a in equation (12), and applying a least squaring procedure, values for the coefficients I_a and S_a were obtained together with a smoothed value for D_a .

$$\frac{1}{\sqrt{D_a}} = I_a + S_a\alpha_1 \quad \dots \quad (12)$$

Fujita & Gosting (1960) have shown that the term $Q/\sqrt{D_a}$ can be related to the four diffusion coefficients and α_1 by the following expression

$$E = \frac{Q}{\sqrt{D_a}} = E_0 + E_1\alpha_1 - E_2\alpha_1^2 \quad \dots \quad (13)$$

Since I_a and S_a are themselves functions of $(D_{ij})_v$, it is necessary to use a method of successive approximations to derive accurate values for E_0 , E_1 and E_2 , from which the four $(D_{ij})_v$ values can be calculated.

By measuring the slope of the graph $\frac{E - E_0}{\alpha_1}$ a first approximation for E_2 is obtained, the preliminary value for E_0 being taken as the experimental value of $Q/\sqrt{D_a}$ at $\alpha_1 = 0$.

After rearrangement of terms, equation (13) will yield first approximations for the ratios E_0/E_2 and E_1/E_2 , which can be smoothed by a least squaring procedure and from which approximate values of $(D_{ij})_v$ can be derived. Since $E_2 \propto S_a^2$ (Fujita & Gosting, 1960) an improved value of E_2 can then be computed together with subsequent values of E_0/E_2 and E_1/E_2 , until the values of $(D_{ij})_v$ from two successive calculations agree to within (0.0001×10^{-5}) . These calculations were carried out using the Atlas computer of the University of London Institute of Computer Science.

MATERIALS

Sodium salicylate and Analar sodium chloride were purchased from British Drug Houses Ltd. The molecular weights were taken to be 160.11 and 58.45 respectively.

SOLUTIONS

To prepare these solutions at the appropriate concentrations it was necessary to predict the densities of the solutions within a few parts in a hundred thousand. Previous experiments on the binary system water-sodium salicylate (unpublished) showed that the densities could be predicted in the region of $\bar{\rho}_1 = 0.05 \text{ g cc}^{-1}$ by the equation

$$d = 0.99724_3 + 0.4056_5\rho_1 - 0.00049_3\rho_1^2 + 0.00021_3\rho_1^3 \quad \dots \quad (14)$$

which was obtained by the method of least squares.

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The density of a 0.05 g cc⁻¹ solution of sodium chloride was estimated using the relation (Woolf, Miller & Gosting, 1962)

$$d = d_0 + \frac{C_2}{1000} (M_2 - d_0\phi_2) \quad \dots \quad (15)$$

in which d_0 the density of pure water at 25° was taken as 0.997048 g cc⁻¹, c_2 is the molar concentration and M_2 the molecular weight of sodium chloride. ϕ_2 , the partial molal volume was calculated from the formula (Harned & Owen, 1958)

$$\phi_2 = 16.50 + 2.034 C_2^{1/2} + 0.0121 C_2^{3/2} \quad \dots \quad (16)$$

In this way the contributions of sodium chloride and sodium salicylate to the density of a solution containing 0.05 g cc⁻¹ of each solute could be estimated. The predicted value was tested experimentally and the differences between the two values was noted, and for solutions at other concentrations ($\alpha_1 = 0$, $\alpha_1 = 1$) the difference was subtracted from the predicted densities using equations (15) and (16).

The density of each ternary mixture was measured in triplicate at 25°C ± 0.01 using matched, single stem, Pyrex glass pycnometers which were weighed against a calibrated, sealed tare of similar shape filled with air-free double distilled water, whose density was taken as 0.997048 g cc⁻¹.

By applying multilinear regression analysis to the density data obtained from the measurement of the two solutions in which $\alpha_1 = 0$ and $\alpha_1 = 1$ respectively the expression

$$d = 0.99854_8 + 0.39713_8\rho_1 + 0.65696_0\rho_2 \quad \dots \quad (17)$$

was obtained for the density of a ternary water–sodium salicylate–sodium chloride solution. This relationship was used to predict the densities of solutions in which $\alpha_1 = 0.2$ and $\alpha_1 = 0.8$. Analysing the density data from experiments (10–12) in a similar way produced a refined expression

$$d = 0.99855_0 + 0.39341_3\rho_1 + 0.66044_0\rho_2 \quad \dots \quad (18)$$

for the density of the solution in terms of ρ_1 and ρ_2 . The average deviation of values predicted by equation (18) and the experimentally obtained density measurements is ±0.0018%.

All solutions were prepared by weighing in air and were subsequently corrected for weight *in vacuo*.

The partial specific volumes of solvent and solutes were calculated using equations (Dunlop & Gosting, 1959)

$$\bar{v}_i = \frac{1 - H_i}{d - (H_1\rho_1 + H_2\rho_2)} \quad (i = 1, 2) \quad \dots \quad (19)$$

$$d = \rho_0 + \rho_1 + \rho_2 \quad \dots \quad (20)$$

$$\bar{v}_0\rho_0 + \bar{v}_1\rho_1 + \bar{v}_2\rho_2 = 1 \quad \dots \quad (21)$$

where d is the density of the solution in g cc⁻¹, H_i is a density derivative

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and the subscripts 0, 1 and 2 refer to water, sodium salicylate and sodium chloride respectively. The partial specific volume and density results are reported in Table 1.

TABLE 1. PARTIAL SPECIFIC VOLUME AND DENSITY DATA FOR THE SYSTEM: WATER-SODIUM SALICYLATE-SODIUM CHLORIDE AT 25°C

Experiment No.	9	10	11	12
$(\rho_1)_A$	0.044864 ₃	0.046198 ₆	0.049167 ₈	0.050005 ₈
$(\rho_2)_A$	0.049845 ₇	0.048802 ₆	0.045829 ₉	0.045023 ₆
d_A	1.04910 ₆	1.04896 ₆	1.04813 ₇	1.04796 ₆
$(\rho_1)_B$	0.054833 ₈	0.053801 ₇	0.050826 ₆	0.050000 ₂
$(\rho_2)_B$	0.049886 ₇	0.051197 ₇	0.054165 ₆	0.055025 ₆
d_B	1.05309 ₄	1.05354 ₄	1.05428 ₆	1.05457 ₆
H_1	0.393 ₄	0 = H ₂ O 1 = Salicylate 2 = NaCl A = upper solution B = lower solution		
H_2	0.660 ₄			
\bar{v}_0	1.0014 ₄			
\bar{v}_1	0.607 ₆			
\bar{v}_2	0.340 ₁			

Units: concentrations (ρ_1, ρ_2) , g cc⁻¹;
 partial specific volumes (\bar{v}_i), cc g⁻¹
 density (d_A, d_B), g cc⁻¹.

Discussion

The values for the refractive index derivatives R_1 and R_2 , $(D_{ij})_V$ and areas of the fringe deviation graphs are reported in Table 2. (Lines 8-9, 10-13, and 4 respectively.)

TABLE 2. DIFFUSION DATA FOR TERNARY SYSTEM WATER-SODIUM SALICYLATE-SODIUM CHLORIDE AT 25° AT ONE COMPOSITION

	Experiment No.	9	10	11	12
1	J _{expt.}	90.13	85.78	75.90	71.80
2	J _{calc.}	90.16	85.77	74.95	71.92
3	Q _{expt.} × 10 ⁴	12.24	25.85	10.88	-44.88
4	D _A × 10 ⁶	0.7860 ₆	0.8673 ₉	1.2358 ₉	1.4060 ₉
5	D _A calc. × 10 ⁶	0.7845 ₇	0.8697 ₁	1.2334 ₉	1.4072 ₆
6	α_1	0.9967	0.7991	0.1996	- 0.0007
7	R ₁	0.19706	0 = H ₂ O 1 = Salicylate 2 = NaCl $\bar{\rho}_1 = 0.05$ $\bar{\rho}_2 = 0.05$		
8	R ₂	0.15731			
9	$(D_{11})_V \times 10^6$	0.768 ₆ ± 0.001 ₉			
10	$(D_{12})_V \times 10^6$	0.076 ₇ ± 0.001 ₈			
11	$(D_{21})_V \times 10^6$	0.029 ₉ ± 0.003 ₈			
12	$(D_{22})_V \times 10^6$	1.258 ₄ ± 0.003 ₄			
13					

Units: Densities ρ_i , g cc⁻¹;
 Reduced height: Area ratio D_A, g cm² sec⁻¹;
 Diffusion coefficients $(D_{ij})_V$, g cm² sec⁻¹ corresponding to a volume-fixed frame of reference;
 Refractive index derivatives R_i, cc g⁻¹.

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The Tiselius cell was found to have a small positive area Q' when fringe deviation graphs were plotted for data obtained from the binary system water-sodium salicylate (unpublished). Values of Q measured for the ternary system were then adjusted by subtracting 0.2×10^{-4} from each observed value.

The range of accuracy indicated for the values of $(D_{1j})_v$ were calculated by changing the value of Q by its anticipated error of $\pm 1 \times 10^{-4}$ and evaluating the corresponding values for the diffusion coefficients. As $\rho_2 \rightarrow 0$ at constant ρ_1 , the main diffusion coefficient $(D_{11})_v$ approaches $(D_1)_m$, the binary mutual diffusion coefficient for water-sodium salicylate. Similarly, as $\rho_1 \rightarrow 0$ at constant ρ_2 , $(D_{22})_v$ approaches $(D_2)_m$, the binary mutual diffusion coefficient for water-sodium chloride. Measurement of these limiting values of $(D_{11})_v$ and $(D_{22})_v$ will involve further experiments on this system at other compositions combined with data obtained from tracer diffusion studies. The literature value (Vitagliano & Lyons, 1955) for $(D_2)_m$ at this concentration is $1.456_0 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$, whilst the result obtained from preliminary experiments carried out on the binary system water-sodium salicylate for a mean concentration of 0.05 g cc^{-1} is $0.913_9 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$. These values may be compared with lines 13 and 10 respectively of Table 2.

Since $(D_{12})_v$ and $(D_{21})_v$ are both positive and significantly different from zero, a concentration gradient of either solute contributes significantly to the flow of the other solute. In particular, at solute concentrations of 0.05 g cc^{-1} a concentration gradient of sodium chloride is about $\frac{1}{10}$ th as effective in producing a flow of salicylate as the concentration gradient of sodium salicylate.

Clearly, because of the difference in the ionic mobilities of the ions involved, electrostatic potential gradients are set up in the system due to the flows. In experiment (12) the Cl^- ions tend to move faster than the Na^+ ions and in this process some Na^+ ions were transported with salicylate $^-$ ions. Similarly, some Cl^- ions were transported with Na^+ ions in experiment (9).

In ternary systems the condition

$$\rho_B > \rho_A \quad \dots \quad (22)$$

does not by itself ensure that

$$\left(\frac{\partial \rho}{\partial x}\right)_t > 0 \quad \dots \quad (23)$$

The latter inequality is a necessary and sufficient condition for the gravitational stability (G_α , G_β) of the diffusing columns of liquid.

G_α and G_β have been calculated using equations (24-30) derived by Wendt (1962).

$$G_\alpha = H_1 K_1^- + H_2 K_2^- \quad \dots \quad (24)$$

$$G_\beta = H_1 K_1^+ + H_2 K_2^+ + \sqrt{\sigma_- / \sigma_+} (H_1 K_1^- + H_2 K_2^-) \quad (25)$$

where

$$K_1^{\pm} = \pm \frac{[(D_{22} - D_{11} \pm U)\Delta\rho_1 - 2D_{12}\Delta\rho_2]}{4U} \quad \dots (26)$$

$$K_2^{\pm} = \pm \frac{[(D_{11} - D_{22} \pm U)\Delta\rho_2 - 2D_{21}\Delta\rho_1]}{4U} \quad \dots (27)$$

$$\sigma_{\pm} = \frac{(D_{11} + D_{22} \pm U)}{2S^2} \quad \dots (28)$$

and

$$U = [(D_{22} - D_{11})^2 + 4D_{12}D_{21}]^{1/2} \quad \dots (29)$$

$$S = (D_{11}D_{22} - D_{12}D_{21})^{1/2} \quad \dots (30)$$

The values obtained are summarized in Table 3.

Because $G_{\alpha} \geq 0 \quad \dots (31)$

$G_{\beta} > 0 \quad \dots (32)$

these diffusion columns are gravitationally stable.

G_{α} decreases rapidly with increase in $\Delta\rho_1$ and decrease in $\Delta\rho_2$, and since $\Delta\rho_1 + \Delta\rho_2 \simeq 0.01$ convective mixing would occur if $\Delta\rho_2$ were only slightly less than the lowest figure reported. In contrast, G_{β} decreases less rapidly with decrease in $\Delta\rho_2$. Thus, for the condition $G_{\beta} < 0$ to obtain, $\Delta\rho_2$ would have to be considerably smaller than its lowest value in Table 3.

TABLE 3. DATA FOR THE GRAVITATIONAL STABILITY FOR THE EXPERIMENTS REPORTED

Experiment No.	9	10	11	12
$\Delta\rho_1$	0.009969 ₉	0.007603 ₁	0.001659 ₁	-0.000005 ₉
$\Delta\rho_2$	0.000041 ₉	0.002395 ₁	0.008336 ₉	0.010001 ₇
G_{α}	0.00022 ₄	0.00101 ₄	0.00301 ₉	0.00357 ₉
G_{β}	0.00192 ₉	0.00206 ₁	0.00241 ₉	0.00250 ₇

Units: concentration ρ_i , g cc⁻¹;
 G_{α} and G_{β} , g cc⁻¹

1 = Salicylate
 2 = NaCl

$\tilde{\rho}_1 = 0.05$
 $\rho_2 = 0.05$

A non-Gaussian refractive-index curve could arise from hydrolysis of the sodium salicylate producing a multicomponent system, from the concentration dependence of the solute diffusion coefficients or because refractive index and concentration are not linearly related. Unfortunately, the Goüy fringes are not markedly sensitive to skewed distributions, but it is hoped that further investigation may enable more definite conclusions to be reached about the physical state of the system.

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