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its upper limit for negligible solvent flow permeation of the equivalent sphere. The difference between the value of a observed to apply in Eq. (32) and 0.50 should be ascribed primarily to the influence of long range interference and to the heat of dilution of the polymer segments with solvent molecules.

At sufficiently low molecular weights the decrease in φ with further decrease in chain length must

become significant. On the other hand, α^3 varies as Z raised to a power which diminishes as the chain length becomes small (see above). The dependences of these two factors (φ and α^3) on Z are such as to compensate (partially at least) one another so as to preserve the empirical relationship (32) with a fixed exponent a down to lower molecular weights than would be possible if either of the two factors alone entered in Eq. (33).

Theory of the Thermal Diffusion of Electrolytes in a Clusius Column

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A theory is presented which accounts approximately for the apparently anomalous difference between the thermal diffusion coefficients of an ion in the presence and in the absence of other electrolytes; the theory is based on the existence of an electric field parallel to the thermal gradient in the electrolyte as a consequence of the variation in mobility among the various ions present. It is pointed out also that some data on the behavior of electrolytes in a Clusius column are at variance with the Debye exponential law concerning the steady-state distribution of solute.

AN apparent anomaly in the thermal diffusion of electrolytes was reported by Gillespie and Breck¹ and by Hirota² in 1941. In experiments with the Clusius column³ these workers found that one⁴ of a mixture of two electrolytes was transported into the upper reservoir, contrary to its behavior when it was the only solute; the other electrolyte of the mixture was transported as usual into the lower reservoir, but to a greater extent than when it was the only solute. Prior to this work no instances of the thermal diffusion of an electrolyte against the temperature gradient had been recorded in the literature.

A similar but less striking effect has long been known to occur in the ordinary diffusion of mixtures of electrolytes;^{4,5} the more mobile of two mixed electrolytes diffuses more rapidly, the less mobile more slowly, than each diffuses alone. Vinograd and McBain⁶ accounted for the effect quantitatively in terms of an electrostatic field set up by the diffusion of ions of different mobilities. It occurred to one of us (G.G.) that the results of Gillespie and Breck and of Hirota could be similarly explained.

* Shell Development Company, Emeryville, California.

** Contribution No. 1222.

¹ L. J. Gillespie and S. Breck, *J. Chem. Phys.* **9**, 370 (1941).

² K. Hirota, *Bull. Chem. Soc. (Japan)* **16**, 232 (1941).

³ K. Clusius and G. Dickel, *Naturwiss.* **26**, 546 (1938).

⁴ In these experiments the two electrolytes have a common ion.

⁵ T. Graham, *Phil. Trans. Roy. Soc. (London)* **805** (1850); J. W. McBain and C. R. Dawson, *J. Am. Chem. Soc.* **56**, 52 (1934).

⁶ J. R. Vinograd and J. W. McBain, *J. Am. Chem. Soc.* **63**, 2008 (1941).

We present herewith approximate treatments of the behavior of the mixed electrolytes in the pure Soret effect and in the Clusius column; the analysis accounts approximately for the anomalies referred to above.

THE SORET EFFECT

Let the thermal gradient lie along the x axis. At the steady state the flux f_i of the i 'th ionic species across any plane in the solution normal to x will vanish, i.e.

$$f_i = -D_i dc_i/dx - D_i' c_i dT/dx + \nu_i u_i c_i E = 0 \quad (1)$$

where D_i is the ordinary diffusion coefficient, D_i' is the thermal diffusion coefficient, c_i is the concentration in equivalents per unit volume, u_i is the equivalent mobility, ν_i is the sign of the ionic charge, and E is the local field postulated to arise from the difference in ionic mobilities. Let us substitute $RTu_i = FD_i$, where F is the Faraday; multiply Eq. (1) by ν_i/D_i and sum over all ions. Applying the approximate neutrality condition $\sum \nu_i dc_i/dx = 0$ we obtain

$$(EF/RT) \sum c_i = (dT/dx) \sum \nu_i c_i D_i' / D_i \quad (2)$$

and

$$\frac{d \ln c_i}{dx} = \left(-\frac{D_i'}{D_i} + \frac{\nu_i \sum \nu_i c_i D_i' / D_i}{\sum c_i} \right) \frac{dT}{dx} \quad (3)$$

For non-electrolytes the Soret coefficient, σ , is equal to the ratio $-D'/D$. We shall call this ratio for individual ions the intrinsic Soret coefficient σ_i^* .

The observed Soret coefficient σ_i for an ion in an electrolyte is therefore

$$(d \ln c_i / dx)(dx / dT) = \sigma_i = \sigma_i^* - \nu_i \sum \nu_j c_j \sigma_j^* / \sum c_i \quad (4)$$

For a single electrolyte AX this becomes

$$\sigma_{AX} = \sigma_A = \sigma_X = 1/2(\sigma_A^* + \sigma_X^*) \quad (5)$$

For a mixture of electrolytes AX and BX

$$\begin{aligned} \sigma_A &= \sigma_{AX} + [c_B / (c_A + c_B)](\sigma_{AX} - \sigma_{BX}) \\ \sigma_B &= \sigma_{BX} + [c_A / (c_A + c_B)](\sigma_{BX} - \sigma_{AX}) \end{aligned} \quad (6)$$

Equations (6) predict effects of the type observed by Gillespie and Breck and by Hirota. The electrolyte which has the higher Soret coefficient alone will have an enhanced Soret coefficient in the mixture; that with the lower Soret coefficient alone will have a diminished coefficient in the mixture and may even have the sign of its coefficient reversed if the difference between σ_{AX} and σ_{BX} is sufficiently great. Unfortunately no data are available for a direct test of these equations.

THERMAL DIFFUSION WITH CONVECTION

In the Clusius column a thermal gradient is maintained between two parallel vertical walls set close together; a convection current is thereby superimposed on the thermal diffusion current and the solute diffusing to the cold wall is carried to the bottom of the column and concentrated there.

Let the vertical coordinate be y with origin at the bottom of the column of height h . Let the temperature gradient be parallel to the coordinate x with origin mid-way between the walls, separated by a distance $2a$.

A material balance for an element of volume of height dy and unit width extending normal to the y axis from $x=0$ to $x=a$ leads at the steady state to

$$\begin{aligned} -D_i \partial c_i / \partial x - D_i' c_i \partial T / \partial x + \nu_i D_i c_i F E_x / RT \\ - \int_0^a v_y(x) [\partial c_i(x) / \partial y] dx = 0 \end{aligned} \quad (7)$$

where v_y is the vertical component of the convection current and all concentrations unless otherwise specified refer to the values at $x=0$. Effects of diffusion arising from $D \partial c / \partial y$ have been neglected as small compared to $v_y \partial c / \partial y$.

Since $\partial c / \partial y$ is not likely to vary markedly with x , we may to a good approximation replace the integral in (7) with $a \bar{v}_y \partial c / \partial y$ where \bar{v}_y is the mean velocity of the convection current between $x=0$ and a .

The field E may be evaluated as before in any one of several ways; the accuracy and convenience of the result depends on which of the terms is eliminated in the summation. We choose to elimi-

nate $\sum \nu_j \partial c_j / \partial y$ and obtain

$$\frac{FE}{RT} = \frac{\sum \nu_i D_i \partial c_i / \partial x + (\partial T / \partial x) \sum \nu_i D_i' c_i}{\sum D_i c_i} \quad (8)$$

whence

$$\begin{aligned} a \bar{v}_y \partial c_i / \partial y = - \left(D_i \partial c_i / \partial x - \frac{\nu_i D_i c_i \sum \nu_j D_j \partial c_j / \partial x}{\sum D_j c_j} \right) \\ - \frac{\partial T}{dx} \left(D_i' c_i - \frac{\nu_i D_i c_i \sum \nu_j D_j' c_j}{\sum D_j c_j} \right) \end{aligned} \quad (9)$$

A consideration of the divergence of the flux in a volume element of cross section $dy dx$ at $x=0$ indicates that $\partial c_i / \partial x$ at $x=0$ is small. To a fair approximation we may set $(\partial c_i / \partial x)_0$ equal to $\varphi c_i \sigma_i dT / dx$ for all ions, where φ is a constant lying between zero and unity and σ_i is defined by Eq. (4). This relation has been shown by de Groot⁷ to hold approximately in the thermal diffusion of non-electrolytes in the Clusius column. Substitution of this approximation in (9) by means of Eq. (3) leads to

$$\frac{\partial c_i}{\partial y} = \frac{-(1-\varphi)dT/dx}{a \bar{v}_y} \left(D_i' c_i - \frac{\nu_i D_i c_i \sum \nu_j D_j' c_j}{\sum D_j c_j} \right) \quad (10)$$

Equation (10) can be integrated for the case of a single electrolyte, AX , if the dependence on y ⁸ of the mobilities, thermal diffusion coefficients, and average convection velocity can be neglected. Application of the conservation condition

$$\int_0^h c dy = h c_0,$$

where c_0 is the initial concentration of electrolyte, then leads to

$$\begin{aligned} R_{AX} = \ln(c_b / c_t)_{AX} = \left(\frac{c_b - c_t}{c_0} \right)_{AX} \\ = K_{AX} h \left(\frac{D_A' u_X + D_X' u_A}{u_A + u_X} \right) \end{aligned} \quad (11)$$

where R is called the enrichment. The quantities c_b and c_t are respectively the concentrations at the bottom and top of the column; K_{AX} is a constant whose magnitude depends on the dimensions of the apparatus and on the density, thermal expansion coefficient, and viscosity of the solution.

⁷ S. R. de Groot, *L'Effet Soret* (N.V. Noord-Hollandsche Uitgevers Maatschappij, Amsterdam, 1945), p. 107.

⁸ The dependence on y either may be explicit or may be implicit through dependence on c .

TABLE I.

Solution	Ion	Expt.	Enrichment		$(c_b - c_i)/c_0$		Observer
			c_b/c_i Theory	Soret*	Expt.	Theory	
1 N HCl	H ⁺ , Cl ⁻	1.22					Hirota**
1 N NaCl	Na ⁺ , Cl ⁻	1.047					
1 N NH ₄ Cl	NH ₄ ⁺ , Cl ⁻	1.010					
0.5 N HCl	H ⁺	1.34	1.43 ^{a,c}	1.32			Gillespie and Breck
0.5 N NaCl	Na ⁺	0.97	0.95 ^{a,c}	0.97			
0.5 N HCl	H ⁺	1.42	1.51 ^{a,c}	1.34			
0.5 N NH ₄ Cl	NH ₄ ⁺	0.89	0.88 ^{a,c}	0.89			
1 N HCl	H ⁺ , Cl ⁻	9.4			1.60		
1 N FeCl ₂	Fe ⁺⁺ , Cl ⁻	1.30			0.23		
1 N HCl	H ⁺	39.	72. ^{a,c}	25.	1.90	4.30 ^{a,c}	
1 N FeCl ₂			296. ^{a,d}			2.74 ^{a,d}	
			20.4 ^{b,c}			3.01 ^{b,c}	
			36.4 ^{b,d}			2.74 ^{b,d}	
	Fe ⁺⁺	0.92	0.40 ^{a,c}	0.48	-0.10	-0.92 ^{a,c}	
			0.55 ^{a,d}			-0.52 ^{a,d}	
			0.55 ^{b,c}			-0.59 ^{b,c}	
			0.62 ^{b,d}			-0.44 ^{b,d}	

* Enrichment assumed proportional to effective Soret coefficient.

** All measurements by Hirota listed above were made after his column had been running for two hours. The two-hour values did not differ greatly from the equilibrium values in these cases for which both were obtained; e.g. for 1 N NaCl, 1 N NH₄Cl and 1 N HCl the equilibrium values were respectively 1.048, 1.010, and 1.25 as compared to values of 1.047, 1.010 and 1.22 at two hours.

^a Using $R = \ln(c_b/c_i)$.

^b Using $R = (c_b - c_i)/c_0$.

^c Approximate integration, Eq. (13).

^d Exact integration, Eq. (14).

In the integration of Eq. (10) for a mixture of two electrolytes, AX and BX, it is convenient to substitute $c_X = c_A + c_B$, and to substitute for the expressions in $u_i D_j'$ in terms of the quantities $R_{ij}' = R_{ij} K_m / K_{ij}$. Equation (10) becomes for this case

$$-\frac{\partial c_A}{\partial y} = \frac{c_A}{h} \left\{ \frac{(u_A + u_X) R_{AX}' c_A + [(u_A + u_X)(u_B + u_X) R_{AX}' - u_A(u_B + u_X) R_{BX}'] c_B / u_X}{(u_A + u_X) c_A + (u_B + u_X) c_B} \right\}. \quad (12)$$

A similar expression for $\partial c_B / \partial y$ is obtained by interchanging the subscripts A and B.

These expressions can be integrated approximately if the fraction in curly brackets is assumed to be constant, giving

$$R_A = \frac{[(u_A + u_X) R_{AX}'] c_A + [(u_A + u_X)(u_B + u_X) R_{AX}' - u_A(u_B + u_X) R_{BX}'] c_B / u_X}{(u_A + u_X) c_A + (u_B + u_X) c_B} \quad (13)$$

and the corresponding expression for R_B . When the enrichments are great enough to invalidate this approximation, an exact integration may be made. Variables may be separated in terms of the parameter, $V = c_A / c_B$. Integration of dV/dy and dc_B/dV yields

$$\frac{y + y_0}{h} = \frac{u_X(u_A - u_B) \ln(1 + V)}{(u_A + u_X)(u_B + u_X)(R_{AX}' - R_{BX}')} + \frac{u_X \ln V}{(u_A + u_X)(R_{AX}' - R_{BX}')} \quad (14)$$

and

$$\ln k c_B = \frac{[u_A(u_B + u_X) R_{BX}' - u_B(u_A + u_X) R_{AX}'] \ln(1 + V) + u_X(u_B + u_X) R_{BX}' \ln V}{(u_A + u_X)(u_B + u_X)(R_{AX}' - R_{BX}')}$$

where y_0 and k are integration constants determined by the ratio and absolute magnitudes of the initial concentrations respectively. The limits of integration y_i and y_b are determined by the relation $y_i - y_b = h$.

In obtaining Eq. (12) from Eq. (11) it has been assumed that the quantities u and D' for each ion are constant. This assumption is justified even

approximately only if the solutions of AX, BX, and of the mixture have the same ionic strength. Fortunately, this requirement is met in the experiments of Hirota. For dealing with more complicated situations such as are presented by the experiments of Gillespie and Breck a more complex equation corresponding to Eq. (12) can be obtained in which the values u and D' corresponding to the different

ionic strengths enter specifically. The variations in mobilities with ionic strength can be predicted fairly well, but no adequate theory appears to be available for the prediction of variations in D' .

APPLICATION TO EXPERIMENT

The experimental enrichments obtained by the authors cited are compared in Table I with the values predicted by means of Eqs. (13), (14), with substitution of the concentrations corresponding to the initial composition of the solutions, of mobilities corresponding to infinite dilution and a temperature midway between those of the hot and cold walls and of $R_{AX}'=R_{AX}$ and $R_{BX}'=R_{BX}$. We have presented the results of the approximate integration, Eq. (13), for all of the experiments. The more exact integration, Eq. (14), was computed only for the experiments of Gillespie and Breck, in which the enrichments were large. In this computation K_m was assumed equal to K_{AX} ; this may be only a rough approximation.

In the data presented by Gillespie and Breck, $\ln c_b/c_t$ does not equal $(c_b - c_t)/c_0$ for single electrolytes; that is, the variation of concentration with height is not purely exponential as predicted by Eq. (11). This complication may contribute to the disagreement between these data and the approximate theory presented here. It is not possible to choose at this time between the substitution of $\ln c_b/c_t$ and $(c_b - c_t)/c_0$ for the enrichment R . For the experiments of Gillespie and Breck we have made calculations using both values. It will be seen that the agreement is much better with Hirota's data, as is to be expected from the arguments given above.

It also may be mentioned that the results obtained by Gillespie and Breck and by Hirota can be accounted for by assuming that the enrichments of the various ions are proportional to their corrected Soret coefficients as given by Eq. (6). The enrichments computed on the basis of this assumption are given in column 3 of Table I; we are unable to present a detailed explanation for their excellent agreement with the experimental results, although the result perhaps may be a natural consequence of the small separations obtained together with good equilibration along the temperature gradient.

APPENDIX

The Apparent Distribution of Solute in Gillespie and Breck's Column

Evidence will now be presented which suggests that the concentration of solute at the steady state in Gillespie and Breck's apparatus approximates

TABLE II.

Solution	$\frac{c_b - c_t}{c_0}$		c_b/c_t	
	Expt.	Expt.	Linear	Exponential
0.5 M FeCl ₂	0.22	1.29	1.25	1.25
0.5 M BaCl ₂ } Ba ⁺⁺	0.44	1.64	1.57	1.55
+1 M HCl } H ⁺	1.06	3.9	3.26	2.88
1 M HCl	1.60	9.4	9.0	4.95
1 M HCl } +0.5 M FeCl ₂ } H ⁺	1.90	39.	39.	6.69

more closely a linear dependence on the vertical coordinate than the exponential dependence which was predicted by Debye⁹ and which also follows from the treatment presented here.

Applying the conservation condition to a column without reservoirs as used by Gillespie and Breck we have for the exponential distribution,

$$c = U(x) \exp(\alpha y),$$

the consequence

$$(c_b - c_t)/c_0 = \ln(c_b/c_t) \tag{14}$$

where c_0 is the initial concentration.

For a linear distribution of concentration up the column,

$$c = U(x)(1 + \beta y),$$

$$(c_b - c_t)/c_0 = 2(c_B/c_t - 1)/(c_B/c_t + 1). \tag{15}$$

The experimental values of $(c_b - c_t)/c_0$ and c_b/c_t , which were both reported by Gillespie and Breck, are presented in Table II together with the values of c_b/c_t calculated by means of Eqs. (14) and (15) from the experimental values of $(c_b - c_t)/c_0$. The results shown in Table II indicate that the distribution of solute up the column is certainly not exponential and may be roughly linear.

We are unable to account for the apparently linear distribution; a function linear in y is not a valid solution for the differential equation which applies to a column in which only laminar convection occurs. Possibly in Gillespie and Breck's apparatus v_y varied appreciably with y . It is quite possible, also, that the apparent agreement with a linear distribution is purely coincidental; indeed, some of their data appear to require a dependence of c on y whose curvature is of the opposite sign from that of the exponential.

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⁹ P. Debye, Ann. d. Phys. 36, 284 (1939).