Table I shows the daily average ΔOD resulting for each oxalate increment in a sequence of oxalate increments. There is no obvious correlation between sequence position and ΔOD. A least-squares fit was made with each day's set of observations to give a fitted estimate of K_1, as shown in Table II. (Individual optical density changes were used to make the estimates instead of average optical density changes.) An average of the values of K_1 in Table II is 2669 ± 332 (SEM) M^{-1}, if the average of the different days' sets of measurements are given equal weight. Entry 3 in Table II is more than three standard deviations from the mean; excluding it lowers the average to 2341 ± 60 (SEM) M^{-1}, which we take as the estimate of K_1 resulting from this study. This stability constant, estimated by oxalate and murexide competition, is 15% less than the 2741 M^{-1} estimated by calcium oxalate solubility (*1*). The two estimates of the stability constant of calcium oxalate are essentially in agreement, and the difference between them is probably due to error in measuring the 11 measurements necessary in these competition studies.

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Diffusion and Viscosity in $CHCl_3$-CH_3COOH System at 25°C

Vincenzo Vitagliano,[1] Adriana Zagari, and Roberto Sartorio
Istituto Chimico, Universita di Napoli, Naples, Italy

Sets of mutual diffusion coefficients and viscosity data are presented for the chloroform-acetic acid system at 25°C. The experimental data are compared with those given by Leffler's equation for diffusion coefficients. Equations for fitting density, refractive index, and viscosity data are given.

Sets of mutual diffusion coefficients and viscosity data are presented for the chloroform-acetic acid system at 25°C. The experimental data fit Leffler's equation (*5*) for diffusion coefficients in the range of dilute chloroform solutions by assuming that acetic acid is a dimer.

Experimental

Materials. Freshly distilled, reagent-grade acetic acid (A) (C. Erba, Milan) was used. The chloroform (C), reagent grade (C. Erba, Milan), was shaken several times with double-distilled water (ratio 1:2) to eliminate ethyl alcohol, kept over anhydrous calcium chloride for a few hours, and then passed through a basic alumina column to eliminate the last alcohol traces. It was used immediately for diffusion or viscosity runs. Purity was controlled by gas chromatography.

Solutions. All solutions for diffusion and viscosity runs were made by weighing both components. No correction for the weighing in vacuum was applied.

Viscosity. Viscosity measurements were made at 25° ± 0.01 by using an Ubbelhode microviscometer (volume ≃ 1 ml; running times: water, 243.6 sec; C, 97.8 sec; A, 294.4 sec; water viscosity was taken from "Handbook of Chemistry and Physics" (*4*), 0.8937 cP at 25°C. No kinetic correction was needed. Experimental results are given in Table I. Densities were computed from the data of Campbell et al. (*2*) fitted with the following equation:

$$d_{25} = 1.04405 + 0.56191\,X_1 - 0.16317\,X_1^2 + 0.03782\,X_1^3 \pm 0.00065 \quad (1)$$

where X_1 is the stoichiometric mole fraction of chloroform.

The experimental viscosity data have been fitted with the following equation:

$$\eta = 1.1442 - 1.4576\,X_1 + 1.8221\,X_1^2 - 1.5190\,X_1^3 + 0.5435\,X_1^4 \pm 0.0046 \text{ cP} \quad (2)$$

Diffusion. Diffusion experiments were carried out at 25° ± 0.02 by using the Gouy interferometric technique (*3, 8*) with a mercury source lamp (Wratten 11 + Wratten 22 A filters, λ = 546.1 nm). A single-channel cell (*8*) was used with a Teflon-glass stopcock to avoid lubrication problems. The initial boundary was made with the syphoning technique (*3, 8*) at the level of the diffusiometer optical axis. The experimental results are collected in Table II.

From the refractive index increments given in Table II, we have computed the refractive indexes of the system A-C as a function of the C mole fraction. The results are in good agreement with Campbell's data (*2*). The $\Delta n/\Delta X_1$ experimental data fit the following equation:

$$\Delta n/\Delta X_1 = 0.08282 - 0.00380\,X_1 - 0.04562\,X_1^2 + 0.02960\,X_1^3 \pm 0.00055 \quad (3)$$

at λ = 546.1 nm

(The data of runs 8a, 9, and 17a,b were not used in computing Equation 3). By integrating Equation 3, an equation for the refractive index has been obtained which fits Campbell's data:

$$n_{25} = 1.37046 + 0.08282\,X_1 - 0.00190\,X^2 - 0.01521\,X_1^3 + 0.00740\,X_1^4 \pm 0.00020 \quad (4)$$

at λ = 589.3 nm

Campbell's data fit the following equation:

$$n_{25} = 1.37029 + 0.08821\,X_1 - 0.02919\,X_1^2 + 0.02947\,X_1^3 - 0.01551\,X_1^4 \pm 0.00014 \quad (5)$$

Our $\Delta n/\Delta X_1$ data have been measured at 546.1 nm and can fit the refractive index data at 589.3 nm because the integration constant 1.37046 corresponds to the chloroform refractive index at 589.3 nm, and the refractive

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[1] To whom correspondence should be addressed.

index dispersion of A and C in the range 540–590 nm must be similar.

Discussion

The change of diffusion coefficients with composition in binary systems cannot be predicted rigorously by any theoretical or semiempirical equations.

Recently Vignes (7) suggested an exponential equation relating the limiting diffusion coefficients of each component to the actual diffusion coefficients and to the mole fractions of components:

$$D = (D_1^\circ)^{(1-x_1)} \cdot (D_2^\circ)^{x_1} \cdot [1 + \frac{\partial \ln f_1}{\partial \ln X_1}] \qquad (6)$$

where D is the Fickian diffusion coefficient at component 1 mole fraction X_1, D_1° and D_2° are the limiting diffusion coefficients of components 1 and 2 at infinite dilution, and the last factor on the right side is the thermodynamic factor, f_1, the activity coefficient in a mole fraction scale. Vignes' equation accounts fairly well for the diffusion coefficient behavior as a function of composition for a variety of systems. Leffler improved Vignes' equation by accounting also for the solution viscosity (5):

$$D = (D_1^\circ\eta_2^\circ)^{(1-x_1)} \cdot (D_2^\circ\eta_1^\circ)^{x_1} \cdot [1 + \frac{\partial \ln f_1}{\partial \ln X_1}]/\eta \qquad (7)$$

where η is the solution viscosity, and η_1° are the viscosities of pure components.

Leffler showed that his equation holds for a variety of systems with not too strong interactions between components, and that the agreement is somewhat better than that obtained by using Vignes' equation.

To test Leffler's equation on the system A–C, an equation for the thermodynamic factor is required. Good activity data on the A–C system are not available in the literature. The only available data are the vapor-pressure measurements taken by Campbell et al. (2). We computed the chloroform activities, $a_1 = p_1/p_1^\circ$, from Campbell's vapor-pressure data. These activities fit a simple "regular-like solution" equation (6):

$$a_1 = X_1 \exp [w(1 - X_1)^2] \qquad (8)$$

If we assume that A is a dimer (Table III):

$$a_1 = X_D \exp [-0.070(1 - X_D)^2] \pm 0.0052 \qquad (8a)$$

where X_D is the chloroform mole fraction on the assumption that acetic acid is a dimer:

$$X_D = \frac{X_1}{X_1 - 0.5(1 - X_1)} \qquad (9)$$

X_1 is the stoichiometric mole fraction of C. Actually the $w = -0.070$ parameter does not correspond to that computed from the experimental heat of mixing (1) in dilute C solutions:

$$w = -567/nRT \qquad (10)$$

where n is the average aggregation of A (for $n = 2$, $w = -0.48$).

By using an average aggregation $n = 2.4$, the best fitting of the experimental activities is obtained with $w = -0.40$, which corresponds to the w value given by Equation 10. Unfortunately, the agreement is much worse than that obtained by using Equation 8a, and it was not possible to use this n value for computing the thermodynamic factor.

From Equation 8a, the thermodynamic factor is:

$$1 + \frac{\partial \ln f_1}{\partial \ln X_1} = 1 + 0.0140\, X_D\, (1 - X_D) \qquad (11)$$

Table I. Viscosities of $CHCl_3$–CH_3COOH System at 25°C

Run no.	X_1	η
1	0.0000	1.139
2	0.0468	1.087
3	0.1013	0.997
4	0.1021	1.022
5	0.1487	0.954
6	0.2030	0.925
7	0.2312	0.882
8	0.2997	0.837
9	0.3403	0.805
10	0.4207	0.759
11	0.4784	0.731
12	0.5017	0.717
13	0.5627	0.680
14	0.6215	0.657
15	0.7312	0.613
16	0.8031	0.589
17	0.8931	0.560
18	1.0000	0.533

Table II. Diffusion Coefficients of $CHCl_3$–CH_3COOH System at 25°C

Run no.	$\bar{X}_1$	ΔX_1	X_D	J_m	$\Delta n/\Delta X_1$	$D \times 10^5$	$D_L \times 10^5$
1	0.0098	0.0197	0.0194	a 74.35 b 74.25	0.0824 0.0823	1.437[a] 1.431	1.432
2	0.0508	0.0193	0.0967	73.60	0.0833	1.459	1.460
3	0.0654	0.0199	0.1228	74.80	0.0821	1.461	1.469
4	0.1347	0.0167	0.2374	63.15	0.0826	1.515	1.511
5	0.2055	0.0270	0.3409	98.80	0.0799	1.559	1.548
6	0.2824	0.0165	0.4404	59.65	0.0790	1.613	1.584
7	0.3527	0.0140	0.5215	49.70	0.0775	1.676	
8	0.3600	0.0195	0.5294	a 63.60 b 68.15	0.0712 0.0763	1.688 1.681	
9	0.4391	0.0159	0.6102	57.45	0.0789	1.725	
10	0.4427	0.0219		a 109.50 b 109.15	0.0750 0.0747	1.711 1.696	
11	0.5102	0.0188		62.65	0.0728	1.727	
12	0.5104	0.0169		55.95	0.0723	1.733	
13	0.5749	0.0190		a 62.15 b 62.15	0.0714 0.0714	1.782 1.776	
14	0.5821	0.0256		82.00	0.0700	1.769	
15	0.6498	0.0197		a 62.30 b 62.28	0.0691 0.0690	1.771 1.781	
16	0.7011	0.0132		42.00	0.0695	1.776	
17	0.8119	0.0590		a 164.25 b 164.56	0.0608 0.0609	1.788 1.794	
18	0.9306	0.0195		56.65	0.0634	1.813	
19	0.9603	0.0197		a 57.20 b 56.95	0.0634 0.0631	1.820 1.818	
20	0.9881	0.0239		68.95	0.0630	1.838	
21	0.9910	0.0180		52.05	0.0632	1.846	

[a] Independent diffusion runs carried out on the same solutions.

Table III. Comparison Between Experimental and Computed Activities for $CHCl_3$–CH_3COOH System

X_1	a_1	$(a_1)_c$[a]	X_D
0.0851	0.1567	0.149	0.157
0.107	0.187	0.184	0.193
0.134	0.229	0.227	0.236
0.208	0.335	0.334	0.344
0.282	0.421	0.430	0.440
0.314	0.465	0.468	0.478
0.528	0.679	0.686	0.691
0.746	0.856	0.854	0.855

[a] $(a_1)_c$, activity computed through Equation 8a.

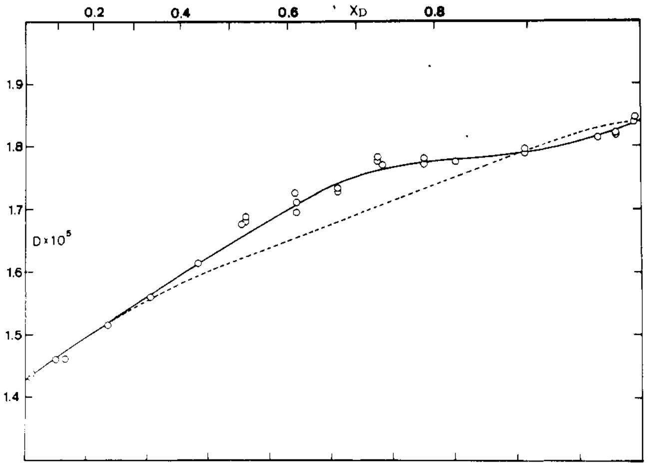

Figure 1. Diffusion coefficients of $CHCl_3$–CH_3COOH system at 25°C

—O—Experimental data; ---- Leffler's equation

We have computed the diffusion coefficients given by Equation 7 by use of the experimental limiting diffusion coefficients and viscosities

$$D_1^\circ = 1.425 \times 10^{-5} \text{ and } D_2^\circ = 1.840 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$$

$$\eta_2^\circ = 1.1442 \text{ and } \eta_1^\circ = 0.5332 \text{ cP}$$

and the thermodynamic factor given by Equation 11. The results are shown in Figure 1. Equation 7 describes the experimental data well, up to a chloroform stoichiometric mole fraction of about 0.2, $X_D \simeq 0.33$.

Actually, the A–C system is far from being a simple system; strong interactions certainly exist between solvent-solvent and solvent-solute molecules. These interactions are most probably responsible for the nonmonotonic behavior of the diffusion coefficients in the range $0.5 < X_1 < 0.8$ (Figure 1), but in the absence of an accurate set of thermodynamic data covering all of the composition range $0 < X_1 < 1$, any speculation would not have much meaning. However, Leffler's equation can be used as a limiting expression which fits the experimental data in a wide range of composition where *A* plays the role of solvent. In this range neither of the existing species should change much with composition nor should the interactions among them. Furthermore, the assumption that acetic acid is a dimer must not be far from accurate.

Nomenclature

$\bar{X}_1$ = average mole fraction of chloroform
ΔX_1 = mole fraction difference between lower and upper solution of each run
X_D = mole fraction of chloroform on the assumption that acetic acid is a dimer (Equation 10)
J_m = no. of Gouy fringes
Δn = refractive index difference between lower and upper solution: $\Delta n = \lambda J_m/a = 2.184 \times 10^{-5} J_m$, where $a = 2.500$ is the diffusion cell thickness, and $\lambda = 546.1$ nm is the mercury green line
D = diffusion coefficient, cm² sec⁻¹
D_L = diffusion coefficient computed by Equation 7
$(a_1)_c$ = activity computed through Equation 8a

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