Potentiometric Determination of Apparent Ionization Constants.—Twenty-ml. aliquots of 0.01–0.02 formal amino acid in 0.05, 0.10 and 0.20 formal aqueous sodium chloride were titrated at 24.4 ± 2.1° with standard 0.2 normal hydrochloric acid or sodium hydroxide using a Beckman Model G *p*H meter equipped with No. 1170 and No. 1190E electrodes. The constants were evaluated analytically[25,26] recognizing over-lapping ionizations in the case of *p*-sulfamyl-DL-phenylalanine and correcting in every instance for the amount of acid or base added which did not react with the amino acid. As a check, several of the constants were also evaluated by the method of Speakman.[27] The reduced data summarized in Table I were obtained from thirty-three independent titrations which revealed no significant dependence of the ionization constants upon ionic strength over the range studied. The values given are believed to be accurate to within 0.05 of a *pK* unit.

Absorption Spectra.—All spectra were determined with a Beckman Model DU Quartz Spectrophotometer at a temperature of 25 ± 3° and at intervals of 2 mμ or less from the lower limit of the instrument to 280 mμ and then at 10 mμ intervals to 320 mμ.

Spectrophotometric Titrations.—The procedure of Stenstrom and Goldsmith[11] was employed using solutions approximately 0.001 formal in sulfonamide and adjusted to the desired *p*H maintaining the total ionic strength at approximately 0.12. The values found for $pK'_{SO_2NH_2}$ for benzenesulfonamide were 9.96 ± 0.05 and for *p*-toluenesulfonamide 10.21 ± 0.05.

Summary

The apparent ionization constants and ultraviolet absorption spectra of DL-phenylalanine, *o*-, *m*- and *p*-chloro- and *p*-sulfamyl-DL-phenylalanine have been determined. These nuclear substituents have been found to increase the acid strength of the ammonium group by approximately 0.2 of a *pK* unit for the chloro-compounds and by 0.5 of a *pK* unit for the *p*-sulfamido-derivative. Since these substituents effect the acid strength of the carboxyl group to a lesser degree all of the above substituted DL-phenylalanines have apparent isoelectric points which are more acidic than that of the parent amino acid.

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[27] J. C. Speakman, *J. Chem. Soc.*, 855 (1940).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

The Viscosities of Binary Liquid Mixtures: Monofluorodichloromethane and Acetone

BY J. R. LACHER, C. H. WALDEN AND J. D. PARK

Viscosity determinations on a binary liquid mixture of a haloform and a solvent containing donor atoms have been carried out by various investigators[1] and it was recognized at once that it presented a case of marked non-ideality of liquid mixtures. However, all of the early investigators in this field failed to arrive at any satisfactory treatment of the experimental results. The activated complex theory proposed by Eyring[2] does present a method of drawing certain conclusions about the viscosity process which may be expressed as follows

$$\eta = \frac{Nh}{V} \exp.\left[\frac{N_1 \Delta F_1^{\ddagger} + N_2 \Delta F_2^{\ddagger} - \dfrac{\Delta F_m}{2.45}}{RT}\right] \quad (1)$$

This formula has been applied to the benzene–phenol binary mixtures.[3] Here V is the average molar volume and $\Delta F_1^{\ddagger}$ and $\Delta F_2^{\ddagger}$ are the free energy of activation for the pure components and ΔF_m is the excess free energy of mixing. There is not sufficient information available at this time to calculate ΔF_m for the mixture treated in this paper and hence the validity of this equation cannot be checked. However, the viscosity results on the monofluorodichloromethane–acetone mixture will be discussed qualitatively on the basis of this theory. The mixture chosen for investigation was of special interest, for the heat of mixing has been determined in this Laboratory[4] and the extreme electronegativity of the fluorine atom in monofluorodichloromethane should give results differing from the less electronegative bromoform and chloroform used by others.

Experimental Details.—A Fischer–Irany type viscometer was used in these determinations. It is a modification of the Ostwald type which allows the flow to take place in a closed system. It was housed in an insulated bath equipped with windows to allow one to view the flow of the liquid. The bath was ice water for the 0° determinations and dry ice–acetone for the −40 and −80° runs. It was stirred with an electric stirrer and the temperature was determined within 0.1° with a single junction copper–constantan thermocouple. The binary mixtures were weighed out and their densities determined all in one operation by employing a special pycnometer designed in this Laboratory. It is constructed of metal and capillary tubing and designed to withstand the high vapor pressures encountered in working with certain fluorine-containing compounds at room temperature. The results at −80° are given in Table I for rounded mole fractions. The acetone used was purified by the method of Shipsey and Werner[5] using sodium iodide. Monofluorodichloromethane

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[1] O. Faust, *Z. physik. Chem.*, **79**, 97 (1912).

[2] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

[3] J. F. Kincaid, H. Eyring and A. E. Stearn, *Chem. Revs.*, **28**, 301 (1941).

[4] J. R. Lacher, J. J. McKinley and J. D. Park, THIS JOURNAL, **70**, 2598 (1948).

[5] K. Shipsey and E. A. Werner, *J. Chem. Soc.*, **103**, 1255 (1913).

was furnished us through the courtesy of Mr. R. J. Thompson of Kinetic Chemicals, Inc. It was distilled in a twenty-plate column and dried by passing repeatedly over phosphorus pentoxide.

TABLE I

DENSITY OF MONOFLUORODICHLOROMETHANE-ACETONE MIXTURE AT −80°

Mole fraction $CHCl_2F$	Density, g./ml.
0.0000	0.8996
.2500	1.0721
.5000	1.2450
.7500	1.4175
1.0000	1.5862

Discussion.—Three sets of determinations were carried out over a temperature range of 80°. They were 0, −40 and −80°. This constitutes almost the entire temperature range over which it is possible to make these measurements as the boiling point of monofluorodichloromethane is 9° (760 mm.) and the freezing point of acetone is −95°. The values of the viscosity in centipoises as a function of the mole fraction of monofluorodichloromethane at −80° are shown in Fig. 1. From curves of this kind, the viscosities at rounded mole fractions were obtained for the three temperatures. The data are given in Table II, column two, three and four. A graph of the logarithm of the viscosity at constant composition against $1/T$ gave excellent straight lines for both the pure components and the various mixtures. This would seem to preclude any strong type of association such as that in water and other hydrogen bonded liquids as these do not give a linear relationship.[2] From the equation first suggested empirically by Arrhenius and derived by both Eyring and Andrade,[2] $\eta = A \exp[-E_{vis}/RT]$ the energy of activation for viscous flow, E_{vis}, may be calculated. The values so obtained are given in Table II, column five. Using the experimental values of the constant A, the entropy of activation for viscous flow, $\Delta S^{\pm}$, was calculated from the following equation also due to Eyring

$$A = \frac{hN}{V} \exp. \left[\frac{-\Delta S^{\pm}}{R}\right]$$

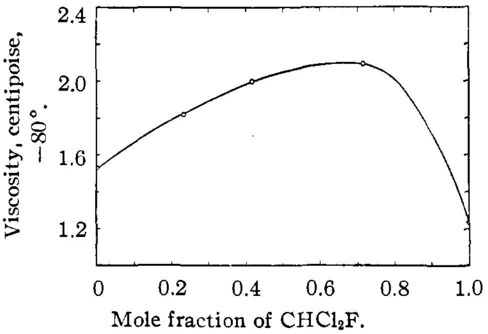

Fig. 1.

Here N is Avogadro's number, h is Planck's constant and V is the molar volume which is obtainable from the experimental density measurements. The equation assumes $p\Delta v$ is negligible in comparison with $\Delta H^{\pm}$. The entropies so calculated are also given in Table II. They are positive with monofluorodichloromethane having the smallest value. The free energy of activated flow, $\Delta F^{\pm}$, at 233°K. may be readily calculated and the results are given in Table II, column seven.

Figure 2 gives E_{vis}, $\Delta S^{\pm}$ and $\Delta F^{\pm}$ as a function of the mole fraction of monofluorodichloromethane. It is apparent that E_{vis} and $\Delta S^{\pm}$ vary with the composition in a similar way and have a maximum at about 0.75 mole fraction. The more positive $\Delta S^{\pm}$ is, the greater amount of randomness produced in going to the activated state. It takes less energy for a molecule of monofluorodichloromethane to reach the activated state necessary for viscous flow than it does for pure acetone and the various mixtures, but to reach this state the monofluorodichloromethane molecules undergo a smaller positive entropy change. The variations in E_{vis} and $\Delta S^{\pm}$ tend to counteract each other in $\Delta F^{\pm}$ with the result that the latter function is more nearly independent of the mole fraction.

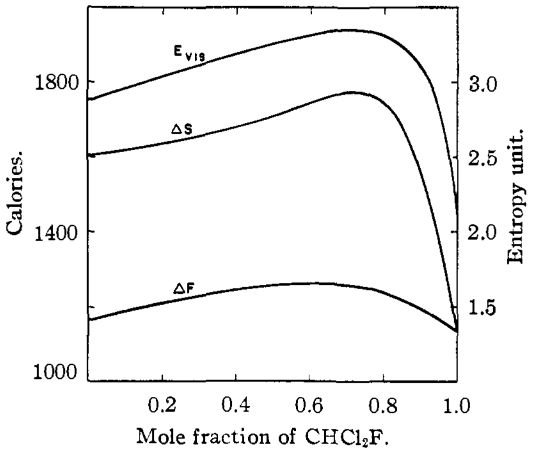

Fig. 2.

TABLE II

Mole fraction $CHCl_2F$	Viscosity, centipoise −80°	−40°	0°	E_{vis}, cal.	$\Delta S,^{\pm}$ e. u.	$\Delta F,^{\pm}$ cal.	$\Delta E_{vap.}$, cal.	$\Delta E_{vap.}/E_{vis}$	ΔF_m, cal.
0.0000	1.526	0.713	0.398	1747	2.499	1165	6577	3.75	...
.2500	1.848	.791	.453	1834	2.659	1214	6568	3.58	−113
.5000	2.042	.869	.487	1889	2.701	1259	6357	3.36	−231
.7500	2.064	.854	.473	1938	2.945	1252	5921	3.05	−242
1.0000	1.232	.664	.412	1441	1.323	1133	5260	3.65	...

Eyring has found that the ratio of the energy of vaporization to the energy of activation for flow, $\Delta E_{\text{vap}}/E_{\text{vis}}$, gives interesting information.[2] Spherical molecules require a hole one-third the size of the molecule for flow and consequently $\Delta E_{\text{vap}}/E_{\text{vis}}$ has a value of about three. Polar and elongated molecules have values of this ratio nearer four. In these cases several orientations for viscous flow are possible and the molecules tend to acquire those requiring the least E_{vis}. In making the calculations of the energy of vaporization that of acetone was taken to be 6557 cal./mole[6] and that of monofluorodichloromethane as 5260 cal./mole.[7] The energy of vaporization of the mixtures was calculated from the following equation using heat of mixing data[4]

$$\Delta E_{\text{vap}} = N_1 \Delta E_1 + N_2 \Delta E_2 + \Delta H_{\text{mix}}$$

The results of these calculations are given in Table II, column eight, together with the ratio, $\Delta E_{\text{vap}}/E_{\text{vis}}$ in column nine. The ratio is 3.75 for acetone which compares with 3.86 given by Ewell and Eyring[8] for apparently a higher temperature range.

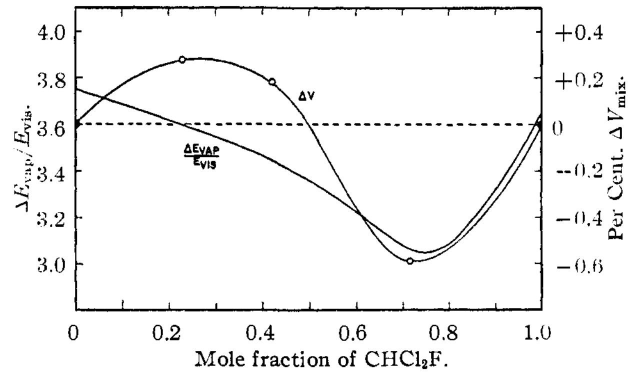

Fig. 3.

The value of 3.65 for monofluorodichloromethane is slightly lower than the value of 3.76 given for chloroform.[8] As is shown in Fig. 3, $\Delta E_{\text{vap}}/E_{\text{vis}}$ has a minimum value at a mole fraction of about 0.75. The per cent. change in volume which results when one mole of solution is produced from the pure components is also given in Fig. 3. The curve was calculated from density measurements made at −80°. A similar type of curve was noted by Hubbard[9] for chloroform–acetone mixtures. Except for a small initial rise, the volume changes are of the same general form as that given by $\Delta E_{\text{vap}}/E_{\text{vis}}$. In order to account for the curves in Figs. 2 and 3 we will assume, with Trew,[10] that acetone is a partially associated liquid and that a weak complex forms between acetone and monofluorodichloromethane. Whether this complex forms in a 1:1 ratio is not known. However, Wyatt[11] found from freezing point curves that such was the case with the analogous mixture of chloroform–acetone. When monofluorodichloromethane is added to pure acetone, the association between the acetone molecules decreases and that between the acetone and monofluorodichloromethane increases. The two effects do not balance exactly and E_{vis} and S increase slightly even though there is a slight volume increase on mixing the two pure components. At a mole fraction of 0.75 the volume change has its maximum negative value and for solutions richer in monofluorodichloromethane, E_{vis} and S fall off rapidly. Apparently the monofluorodichloromethane molecules pack in tightly with the acetone–monofluorodichloromethane complexes at this mole fraction. A maximum of activation energy is required to produce viscous flow which, when it takes place, ruptures the closely packed liquid structure and the entropy of activation is also a maximum. The fact that the viscosity is strongly dependent upon the free volume has been previously pointed out by Eyring,[2] Kottler[12] and Batschinski.[13]

Although it is not possible to test the validity of Equation I directly for this mixture, it is possible to determine what value of F_{m} is required to satisfy the equation when the experimental values of viscosity and free energy of activation for viscous flow are used. The values so obtained are included in Table II, column ten.

Summary

The viscosities of binary liquid mixtures of monofluorodichloromethane and acetone have been measured for several mole fractions and over a temperature range of −80 to 0°. The results are discussed in terms of the activated complex theory of Eyring for viscous flow.

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