

# THERMODYNAMIC EVIDENCE FOR COMPLEX FORMATION BETWEEN CARBON TETRACHLORIDE AND TRIETHYLAMINE

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## Abstract

The molar excess enthalpy of the system carbon tetrachloride+triethylamine has been measured at 298.15 K. The results are consistent with complex formation between the unlike molecules and provide further evidence for the electron acceptor ability of carbon tetrachloride.

Evidence for charge-transfer complex formation between various electron donors and carbon tetrachloride as electron acceptor has been summarized elsewhere.<sup>1,2</sup> While the most compelling evidence for such an interaction is usually spectroscopic, this is often supplemented by thermodynamic results. As has been emphasized by McGlashan<sup>3</sup> and others, the excess thermodynamic functions, their temperature dependence, and other thermodynamic properties are potentially rich sources of information about complex formation in solution.

The negative (exothermic) molar excess enthalpies of carbon tetrachloride with 1,4-dioxan<sup>4</sup> and with diethyl ether, dimethyl sulphide, and pyridine<sup>5</sup> have been interpreted as an indication of strong specific interactions between donor atoms O, S, N and the CCl<sub>4</sub>. Recently<sup>6</sup> it has been suggested that the positive molar excess heat capacity at constant pressure of the system carbon tetrachloride+dimethyl sulphoxide might arise from a charge-transfer interaction between the unlike molecules. As part of an investigation of the thermodynamic properties of binary liquid mixtures containing triethylamine as one component, the molar excess enthalpy of carbon tetrachloride+triethylamine has been measured at 298.15 K.

## Experimental

The calorimeter was similar to that described by Larkin and McGlashan<sup>7</sup> and has been described elsewhere.<sup>6</sup> It is significant, in view of subsequent discussion, to observe that with this instrument mixing was complete in less than 10 s.

Carbon tetrachloride (BDH Analar) was dried over freshly activated molecular sieve (type 10 X) and then fractionally distilled in a column of 15 theoretical plates at a reflux ratio of 20 in an atmosphere of dry nitrogen. The middle fraction was degassed by successive freezing, pumping, and melting cycles and further dried over P<sub>2</sub>O<sub>5</sub>.

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<sup>1</sup> Watson, I. D., and Williamson, A. G., *J. scient. ind. Res.*, 1965, **24**, 615.

<sup>2</sup> Foster, R., "Organic Charge-Transfer Complexes," (Academic Press: New York 1969).

<sup>3</sup> McGlashan, M. L., *Pure appl. Chem.*, 1964, **8**, 157.

<sup>4</sup> McKinnon, I. R., and Williamson, A. G., *Aust. J. Chem.*, 1964, **17**, 1374.

<sup>5</sup> Gray, D. F., Watson, I. D., and Williamson, A. G., *Aust. J. Chem.*, 1968, **21**, 379.

<sup>6</sup> Fenby, D. V., Billing, G., and Smythe, D. B., *J. chem. Thermodynamics*, 1973, **5**, 49.

<sup>7</sup> Larkin, J. A., and McGlashan, M. L., *J. chem. Soc.*, 1961, 3425.

Triethylamine (BDH Laboratory Reagent) was refluxed over KOH pellets, distilled from the KOH, and then fractionally distilled in a column of 15 theoretical plates at a reflux ratio of 20. The middle fraction was dried over freshly cut sodium and degassed by vacuum sublimation.<sup>8</sup>

Both components were stored over mercury in the dark and out of contact with air.

### Results and Discussion

The study was complicated by a reaction between the components. In several cases the liquid mixture was found to be opaque at the conclusion of the experiment (approximately 10 min after mixing the liquids). In all measurements this opacity was evident within an hour of mixing the liquids.

A reaction between carbon tetrachloride and triethylamine was reported by Collins<sup>9</sup> and has been alluded to elsewhere.<sup>5,10-14</sup> On mixing these liquids Foster<sup>12</sup> reported that "the solution began to precipitate triethylamine chloride within a few minutes and the amount increased for many hours until the mixture was nearly solid. No colouration was at first observed, but gradually the mixture became yellow and finally brown." These observations were confirmed in the present study, the colouration usually appearing some hours following the mixing of the liquids. Following a suggestion that the reaction is photochemical,<sup>12-14</sup> light was excluded from the system in a number of measurements. This did not prevent the reaction from taking place although there was some evidence that it could have decreased the reaction rate.

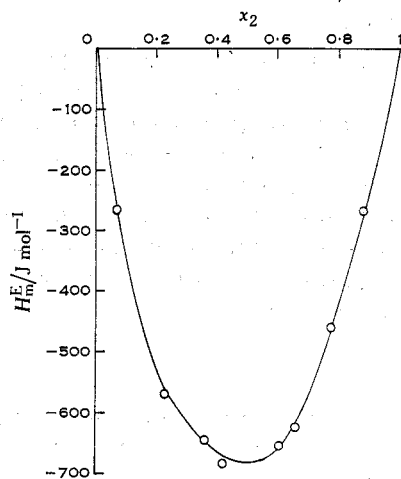


Fig. 1.—Molar excess enthalpy of carbon tetrachloride + triethylamine at 298.15 K.

For those mixtures in which opacity was not apparent or was very slight at the conclusion of the measurement, the molar excess enthalpies  $H_m^E$  at 298.15 K are given in Figure 1. The scatter is appreciably greater than in earlier work<sup>6</sup> and presumably

<sup>8</sup> Bell, T. N., Cussler, E. L., Harris, K. R., Pepela, C. N., and Dunlop, P. J., *J. phys. Chem.*, 1968, **72**, 4693.

<sup>9</sup> Collins, R. F., *Chem. Ind.*, 1957, 704.

<sup>10</sup> Cromwell, N. H., Foster, P. W., and Wheeler, M. M., *Chem. Ind.*, 1959, 228.

<sup>11</sup> Beichl, G. J., Colwell, J. E., and Miller, J. G., *Chem. Ind.*, 1960, 203.

<sup>12</sup> Foster, R., *Chem. Ind.*, 1960, 1354.

<sup>13</sup> Stevenson, D. P., and Coppinger, G. M., *J. Am. chem. Soc.*, 1962, **84**, 149.

<sup>14</sup> Kosower, E. M., *Prog. phys. org. Chem.*, 1965, **3**, 134.

arises from the reaction discussed above. Because of this no attempt was made to determine the temperature coefficient of  $H_m^E$ . The negative molar excess enthalpy is consistent with complex formation between the unlike molecules. Evidence from u.v. spectroscopic results for the formation of a charge-transfer complex between carbon tetrachloride and triethylamine has been given by Stevenson and Coppinger.<sup>13</sup> They attribute the reaction discussed above to this interaction. The solid-liquid phase diagram for carbon tetrachloride + triethylamine<sup>15</sup> indicates the formation of a 1 : 1 intermolecular compound in the solid state.

A series of six measurements in the mole fraction range 0.4–0.6 were significantly more exothermic (by approximately  $150 \text{ J mol}^{-1}$ ) than indicated in Figure 1. In these cases however the mixture was opaque at the conclusion of the measurement and it therefore seems reasonable to attribute these more negative values to the reaction between the components. The rate of temperature decrease following mixing was conspicuously smaller in a few of these measurements than in other studies involving no reaction. This can be attributed to an exothermic reaction taking place in the liquid mixture.

#### *Note Added in Proof*

L. Grote, C. Kupsch, and H. J. Bittrich (*Z. Chem.*, 1966, 6, 355) report that  $H_m^E$  for the equimolar mixture at 303 K is  $-530 \text{ J mol}^{-1}$ . Coupled with the above results at 298.15 K, this indicates that the temperature coefficient of  $H_m^E$  (the molar excess heat capacity at constant pressure) is large and positive. This conclusion is consistent with complex formation between the unlike components.

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<sup>15</sup> Schirge, H., and Bittrich, H. J., *J. prakt. Chem.*, 1966, 34, 153.