

SHORT COMMUNICATIONS

VOLUMES OF MIXING OF HALOMETHANE-ETHER MIXTURES

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Introduction

There now exists an amount of evidence, mainly from the shapes of solid-liquid equilibrium curves,¹⁻³ but also from heats of mixing measurements^{4,5} which suggests that carbon tetrachloride forms weak molecular complexes with aromatic, and oxygen-, nitrogen-, and sulphur-containing molecules. There is also an indication from solid-liquid equilibrium curves and elsewhere^{6,7} that CFCl_3 and CBrCl_3 might also form such complexes. We have decided to measure the thermodynamic properties of solutions of these substances with donor solvents with a view to further understanding the nature of the halogen-donor interaction. Here we report our results for the volumes of mixing of these two substances, and carbon tetrachloride, with diethyl ether at 0°C and 10°C.

Experimental

Commercial grade carbon tetrachloride and fluorotrichloromethane were fractionally distilled twice through a column of about 20 theoretical plates. They were degassed and stored in sealed ampoules. Bromotrichloromethane was taken from a freshly opened bottle obtained from the Aldrich Chemical Company. It was degassed, and allowed to stand over mercury for a week before use. It was then distilled, and, after degassing, was stored in a sealed ampoule. Peroxide-free diethyl ether was purified using the method of Gray.⁴ It was distilled under an atmosphere of nitrogen on the 20 plate column, and stored in sealed ampoules.

Apparatus

The volume of mixing was measured directly, using a mixing vessel similar to that of Larkin and McGlashan,⁸ and the same technique as that of Kershaw and Malcolm.⁹ The apparatus was immersed in a water thermostat, stable to $\pm 0.005^\circ\text{C}$. The maximum error is believed to be 1%.

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¹ Goates, J. R., Ott, J. B., and Mangelson, N. F., *J. chem. Engng Data*, 1964, **2**, 330.

² Kennard, S. M. S., and McCusker, P. A., *J. Am. chem. Soc.*, 1948, **70**, 3375.

³ Wyatt, W. F., *Trans. Faraday Soc.*, 1929, **25**, 43.

⁴ Gray, D. F., Watson, I. D., and Williamson, A. G., *Aust. J. Chem.*, 1968, **21**, 379.

⁵ McGlashan, M. L., Stubbley, D., and Watts, H., *J. chem. Soc. (A)*, 1969, 673.

⁶ Goates, J. R., Ott, J. B., and Oyler, D. E., *Trans. Faraday Soc.*, 1966, **62**, 1511.

⁷ Stevenson, D. P., and Coppinger, G. M., *J. Am. chem. Soc.*, 1962, **84**, 149.

⁸ McGlashan, M. L., and Larkin, J. A., *J. chem. Soc.*, 1961, 3425.

⁹ Kershaw, R. W., and Malcolm, G. N., *Trans. Faraday Soc.*, 1968, **64**, 323.

Results and Discussion

As a test of our technique, we measured the volumes of mixing of carbon tetrachloride and diethyl ether at 25°C and compared our results with the smoothed results of Beath¹⁰ who used a different apparatus. The result, shown in Figure 1, indicates that the agreement is satisfactory.

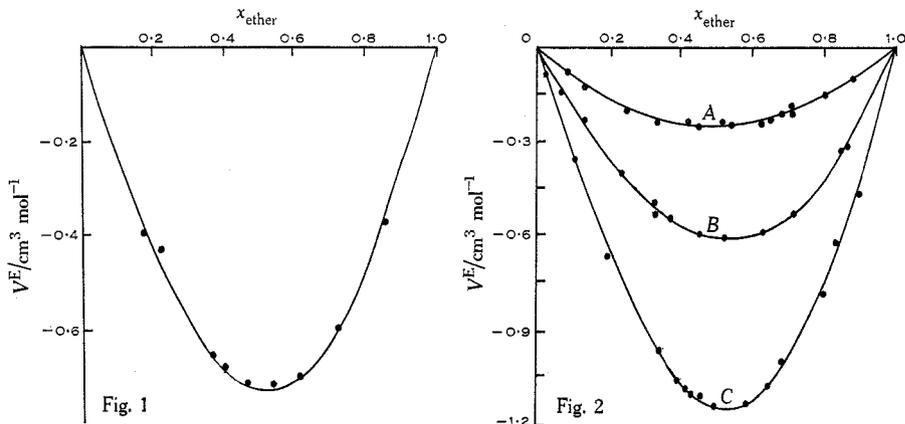


Fig. 1.—The volume of mixing of carbon tetrachloride and diethyl ether at 25°C. The dots represent the experimental points, and the curve is the best fit of Beath's data.

Fig. 2.—The volume of mixing curves (A) CFCl_3 , (B) CCl_4 , (C) CBrCl_3 with diethyl ether at 0°C. The dots represent the experimental points, and the curve is the best fit as given by equation 1.

Our measured volumes of mixing for the various systems at 0°C and 10°C are shown in Table 1. The data at 0°C were fitted with equations of the type

$$V^E/\text{cm}^3 \text{ mol}^{-1} = x_1 x_2 \sum_{n=0}^n V_n (x_1 - x_2)^n \quad (1)$$

where x_1 is the mole fraction of diethyl ether. The choice of n was taken as that for which

$$\sigma = [\sum d_1^2 / (m - n)]^{1/2}$$

was smallest. Here d_1 and m refer respectively to the difference between experimental and calculated values, and the number of measurements.

The values of the parameters for n up to 3 are:

| | V_0 | V_1 | V_2 | σ |
|--------------------------------------|---------|--------|--------|----------|
| $\text{CFCl}_3\text{-Et}_2\text{O}$ | -1.0392 | 0.0786 | | 0.008 |
| $\text{CBrCl}_3\text{-Et}_2\text{O}$ | -4.5405 | 1.0870 | 0.3460 | 0.02 |
| $\text{CCl}_4\text{-Et}_2\text{O}$ | -2.4733 | 0.4361 | 0.1513 | 0.02 |

Comparisons between the curves as given by equation (1) and experimental data are shown in Figure 2.

¹⁰ Beath, L. A., and Williamson, A. G., *J. chem. Thermodynamics*, 1969, **1**, 51.

Initial experiments with CBrCl_3 and diethyl ether produced a faint yellow solution on standing. The chemical reaction causing this appeared to be catalysed by light. It was found that provided the solution was thoroughly degassed, and the mixing was carried out in subdued light, a reproducible volume of mixing was obtained, and no change occurred after mixing even up to 6 hr afterwards.

TABLE I
VOLUME OF MIXING CHANGES IN HALOMETHANE-ETHER SYSTEMS
 ΔV in $\text{cm}^3 \text{mol}^{-1}$

| Halo- methane | At 0°C | | | | At 10°C | | | |
|------------------|--------------------|-------------|--------------------|-------------|--------------------|-------------|--------------------|-------------|
| | x_{ether} | $-\Delta V$ |
| CFCl_3 | 0.102 | 0.083 | 0.646 | 0.260 | 0.269 | 0.186 | 0.468 | 0.247 |
| | 0.168 | 0.140 | 0.664 | 0.240 | 0.383 | 0.242 | 0.541 | 0.247 |
| | 0.278 | 0.213 | 0.711 | 0.224 | 0.388 | 0.226 | 0.626 | 0.235 |
| | 0.347 | 0.237 | 0.730 | 0.206 | 0.422 | 0.239 | 0.691 | 0.188 |
| | 0.450 | 0.245 | 0.731 | 0.224 | 0.424 | 0.241 | | |
| | 0.475 | 0.250 | 0.823 | 0.154 | | | | |
| | 0.550 | 0.256 | 0.910 | 0.085 | | | | |
| | 0.577 | 0.263 | | | | | | |
| CBrCl_3 | 0.040 | 0.116 | 0.516 | 1.13 | 0.274 | 0.84 | 0.541 | 1.20 |
| | 0.102 | 0.321 | 0.583 | 1.14 | 0.369 | 1.05 | 0.614 | 1.17 |
| | 0.209 | 0.68 | 0.649 | 1.10 | 0.381 | 1.00 | 0.674 | 1.15 |
| | 0.357 | 0.97 | 0.695 | 1.02 | 0.383 | 0.95 | 0.710 | 1.04 |
| | 0.417 | 1.06 | 0.812 | 0.81 | 0.452 | 1.22 | | |
| | 0.444 | 1.08 | 0.839 | 0.65 | | | | |
| | 0.451 | 1.09 | 0.896 | 0.496 | | | | |
| | 0.474 | 1.09 | | | | | | |
| CCl_4 | 0.077 | 0.157 | 0.513 | 0.634 | 0.368 | 0.564 | 0.503 | 0.611 |
| | 0.158 | 0.243 | 0.630 | 0.596 | 0.389 | 0.601 | 0.513 | 0.651 |
| | 0.249 | 0.403 | 0.676 | 0.566 | 0.451 | 0.625 | 0.535 | 0.649 |
| | 0.363 | 0.534 | 0.728 | 0.521 | 0.455 | 0.612 | 0.536 | 0.625 |
| | 0.381 | 0.572 | 0.844 | 0.349 | 0.473 | 0.661 | 0.638 | 0.617 |
| | 0.446 | 0.625 | 0.861 | 0.329 | 0.494 | 0.639 | 0.663 | 0.607 |
| | | | | | | | | |

The magnitude and sign of the volume of mixing obtained are consistent with the formation of weak molecular complexes and in the case of carbon tetrachloride-diethyl ether mixtures corroborates other evidence from phase diagrams and enthalpies of mixing. However, for the other systems this cannot be regarded as strong evidence, for it is well known that some non "reacting" systems also contract on mixing.¹¹

We are currently investigating other thermodynamic mixing functions and pure component properties so that a detailed theoretical analysis can be made on these systems.

¹¹ Englert-Chwoles, A., *J. chem. Phys.*, 1955, **23**, 1168.