Heats of Mixing of Tetrahydrofuran and of Furan with Chloromethanes

SALIH DINCER and HENDRICK C. VAN NESS[1]
Chemical Engineering Department, Rensselaer Polytechnic Institute, Troy, N. Y. 12181

Heat-of-mixing data are reported for the binary systems made up of tetrahydrofuran with dichloromethane, with chloroform, and with carbon tetrachloride at 30° and 45° C. All are strongly exothermic. Data are also reported for furan with the same chloromethanes at 30° C. These heat effects are much smaller and are exothermic only in the case of furan–chloroform.

This paper reports heats of mixing for the six binary systems formed from tetrahydrofuran (THF) and from furan each with dichloromethane, with chloroform, and with carbon tetrachloride. The development of the calorimeter has been described, and the extensive data taken with it have been reported in a series of earlier papers (*2*, *4-6*, *8-11*). It is known as an isothermal dilution calorimeter, because of its truly isothermal operation and because one of the pure constituents is continually diluted by successive injections of the other constituent during a run. It is equally suited to measurements on both endothermic and exothermic systems, and allows rapid and routine collection of accurate data. The details of its operation are given by Winterhalter and Van Ness (*11*).

The materials employed were Matheson, Coleman, and Bell chromatoquality reagents, specified to have a minimum purity of 99.8 mol %, and were used as received. Data were taken for all systems at 30° C, and for the THF systems, at 45° C as well. The experimental data values, on file with the ACS Primary Publications Microfilm Depository Service (*1a*), were fit by orthogonal polynomials, from which appropriate power series expansions in mole fraction of the chloromethane were determined for $\Delta H/x_1x_2$ in joules/gram mole:

$$\Delta H/x_1x_2 = A + Bx_1 + Cx_1^2 + Dx_1^3$$

Quadratic expressions were adequate for all systems except for chloroform–THF, which required a cubic. The coefficients appropriate for each system are listed in Table I. Data for all systems at 30° C are shown in Figure 1, where the points are representative experimental values and the lines conform to the correlating equations. Also shown are the data of Murakami et al. (*3*) for furan and THF with chloroform at 25° C. The difference between the two sets of data for chloroform–furan is small, indicating little effect of temperature on the heat of mixing. For chloroform–THF the difference in the two sets of data, one at 25° C and the other at 30° C, indicates a temperature dependence for ΔH consistent with that determined by the two sets of data at 30° C and 45° C reported here.

DISCUSSION

The results reported for THF with the three chloromethanes may be compared with similar results reported by Van Ness (*8*) for tetrahydropyran (THP) with the same chloromethanes. In each case the shapes of the curves are quite similar. For carbon tetrachloride, the two curves are very close, and actually cross. For the chloroform and dichloromethane, which can form hydrogen bonds with the ethers, the THF data are somewhat more exothermic than the THP data. This difference can probably be attributed to the effect of ring size on the electron-donating ability of cyclic ethers, which is greater for a five-membered ring than for a six-membered ring (*7*).

The heats of mixing for furan with the three chloromethanes are very much less exothermic than for THF in each case. In fact, dichloromethane–furan is slightly endothermic and carbon tetrachloride–furan is somewhat more so. A considerable part of these vast differences may well be due to resonance structures in the unsaturated furan which reduce the negative charge on the oxygen atom of the ring (*1*) and thus reduce the number and strength of the hydrogen bonds formed in mixtures with chloroform and dichloromethane. In the case of carbon tetrachloride the difference, although not so great, requires some other explanation.

It should be noted that both for THF and for furan the heats of mixing shift in the negative direction (becoming less endothermic or more exothermic) in the order: carbon

Table I. Correlating Functions for $\Delta H/x_1x_2$[a]
($\Delta H/x_1x_2 = A + Bx_1 + Cx_1^2 + Dx_1^3$, J/g-mol)

Component 1	Component 2	Temp, ° C	A	B	C	D	σ, %[b]
Chloroform	Tetrahydrofuran	30	−8377.3	−6782.0	2398.5	3188.2	0.47
		45	−8141.6	−6489.9	3238.7	2061.4	0.33
	Furan	30	−473.0	−638.9	99.2	...	0.78
Dichloromethane	Tetrahydrofuran	30	−5387.9	−1040.6	2240.2	...	0.35
		45	−5267.5	−793.6	1925.2	...	0.18
	Furan	30	157.1	−243.0	126.8	...	0.82
Carbon tetrachloride	Tetrahydrofuran	30	−3327.4	635.7	251.0	...	0.28
		45	−2928.8	417.1	374.4	...	0.36
	Furan	30	1330.1	−130.8	120.5	...	0.11

[a] All raw data are given by Dincer (*1*) and are also on file with the ACS Primary Publications Microfilm Depository Service (*1a*). The numbers of data points on which the correlating functions are based range from 17 to 30, depending on the complexity of the system. [b] σ is the root-mean-square percentage deviation of the raw data points from the correlating function.

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[1] To whom correspondence should be addressed.

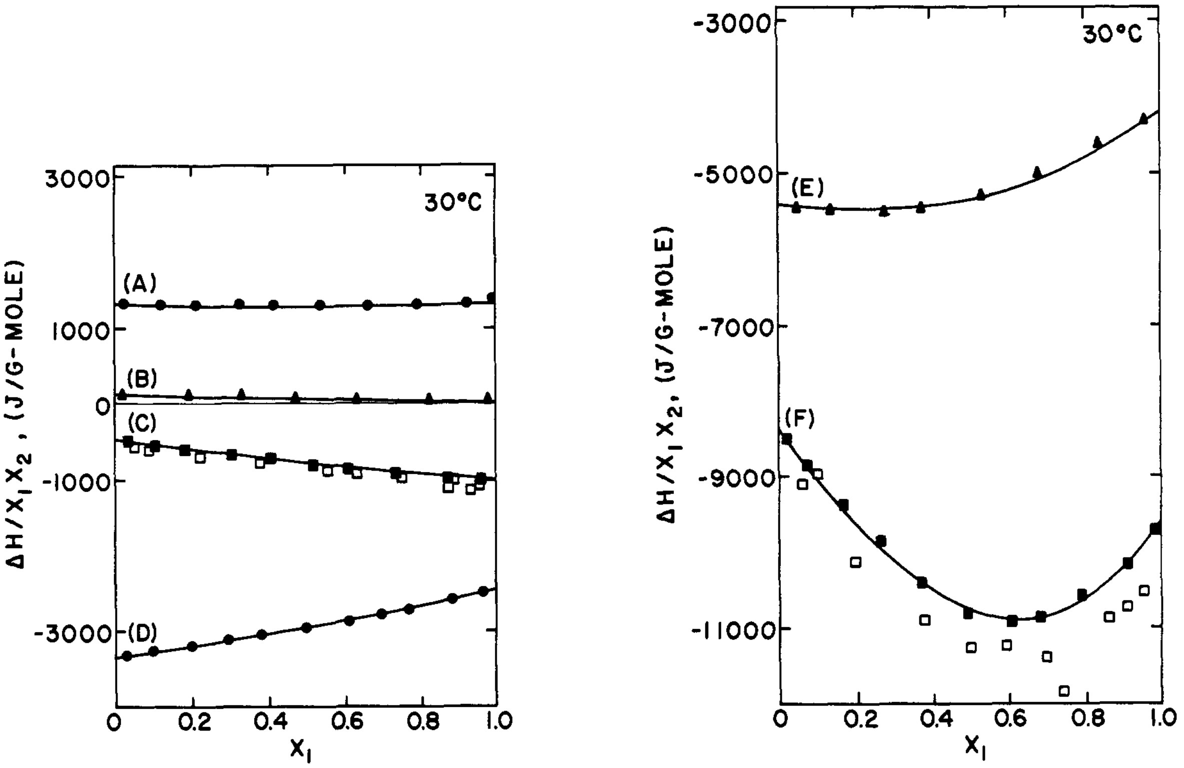

Figure 1. $\Delta H/x_1x_2$ vs. mole fraction of chloromethane at 30° C

(A) CCl_4 (1)-furan (2)
(B) CH_2Cl_2(1)-furan(2)
(C) $CHCl_3$(1)-furan(2)
(D) CCl_4(1)-THF(2)
(E) CH_2Cl_2(1)-THF(2)
(F) $CHCl_3$(1)-THF(2)

The open squares are the data of Murakami et al. (3) at 25° C

tetrachloride, dichloromethane, chloroform. This order also represents the order of increasing dipole moment and of hydrogen bond-forming propensity of the chloromethanes. For the THF systems, the effect of increasing temperature is to make the results less exothermic, but the effect is not large.

The heat-of-mixing data presented here, together with those published earlier (*8*), provide systematic results for three chloromethanes—carbon tetrachloride, chloroform, and dichloromethane—each with four cyclic ethers—1,4-dioxane, tetrahydropyran, tetrahydrofuran, and furan.

LITERATURE CITED

(1) Dincer, S., MS Thesis, Rensselaer Polytechnic Institute, Troy, N. Y., 1971.
(1a) Dincer, S., Van Ness, H. C., nine supplementary tables, "Experimental Data Values, Heats of Mixing of Tetrahydrofuran and of Furan with Chloromethanes," ACS Microfilm Depository Service.
(2) Mrazek, R. V., Van Ness, H. C., *AIChE J.*, **7**, 190 (1961).
(3) Murakami, S., Koyama, M., Fujishiro, R., *Bull. Chem. Soc. Japan*, **11**, 1540 (1968).
(4) Savini, C. G., Winterhalter, D. R., Kovach, L. H., Van Ness, H. C., *J. Chem. Eng. Data*, **11**, 40 (1966).
(5) Savini, C. G., Winterhalter, D. R., Van Ness, H. C., *ibid.*, **10**, 168 (1965).
(6) Savini, C. G., Winterhalter, D. R., Van Ness, H. C., *ibid.*, p 171.
(7) Searles, S., Tamres, M., *J. Amer. Chem. Soc.*, **73**, 3704 (1951).
(8) Van Ness, H. C., *Ind. Eng. Chem.*, **59** (9), 33 (1967).
(9) Van Ness, H. C., Kochar, N. K., Soczek, C. A., *J. Chem. Eng. Data*, **12**, 346 (1967).
(10) Van Ness, H. C., Soczek, C. A., Peloquin, G. L., Machado, R. L., *ibid.*, p 217.
(11) Winterhalter, D. R., Van Ness, H. C., *ibid.*, **11**, 189 (1966).

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