tion Postdoctoral Fellowship (awarded to C.G. Savini), and by a National Science Foundation Cooperative Fellowship (awarded to D.R. Winterhalter). The work of W.R. Gustafson and L.H. Kovach in taking much of the data reported here is appreciated.

NOMENCLATURE

ΔH = heat of mixing in joules per gram mole of solution
$\overline{\Delta H}_1, \overline{\Delta H}_2$ = partial molal heats of mixing
x_1, x_2 = mole fractions of alcohol and hydrocarbon, respectively

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Heats of Mixing for Partially Miscible Systems: Methanol–*n*-Hexane and Methanol–*n*-Heptane

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The use of an isothermal dilution calorimeter to determine the heats of mixing of partially miscible systems provides solubility data at the same time. Data are presented for the methanol–*n*-hexane system at 25°, 30°, 33.7°, 40°, 45°, and 50° C. and for the methanol–*n*-heptane system at 30°, 45°, and 60° C.

THE DATA reported in the preceding paper (*2*) pertained to alcohol-normal hydrocarbon systems which exhibited complete miscibility at room temperature and above. The data presented here were obtained with the same isothermal dilution calorimeter, and demonstrate its advantages for use with partially miscible systems. Not only are heat-of-mixing data determined, but in addition, the compositions representing miscibility limits are readily measured. This is demonstrated here for the methanol-*n*-hexane and methanol-*n*-heptane systems.

The methanol, used as received, was the Certified reagent of the Fisher Scientific Co. The lot analysis specified a boiling range of 64.4° to 65.0° C. and an assay of 99.9%. The *n*-hexane and *n*-heptane were Pure-grade reagents of the Phillips Petroleum Co., specified to have a minimum purity of 99 mole %. Chromatographic analysis showed the *n*-heptane to contain trace impurities only, and it was, therefore, used as received. The *n*-hexane contained measurable amounts of several impurities—nearly 1%—and was, therefore, purified by distillation to 99.9%.

The experimental data are shown in Figures 1 and 2. Some points at very high and very low mole fraction of methanol are omitted for clarity. Smoothed values of ΔH as read from large-scale plots are listed in Tables I and II. The methanol-*n*-hexane data have been smoothed with respect to temperature as well as with respect to composition. All results are believed to be accurate to well within ±1%.

Solubility data for the two systems considered here have been reported by Kiser, Johnson, and Shetlar (*1*). For the methanol-*n*-hexane system, agreement between the two sets of data is not particularly good. For example, at a solubility limit of methanol mole fraction equal to 0.270, the authors' find the temperature to be 25° C., whereas Kiser and coworkers give a value of about 27.5° C., some 2.5° higher.

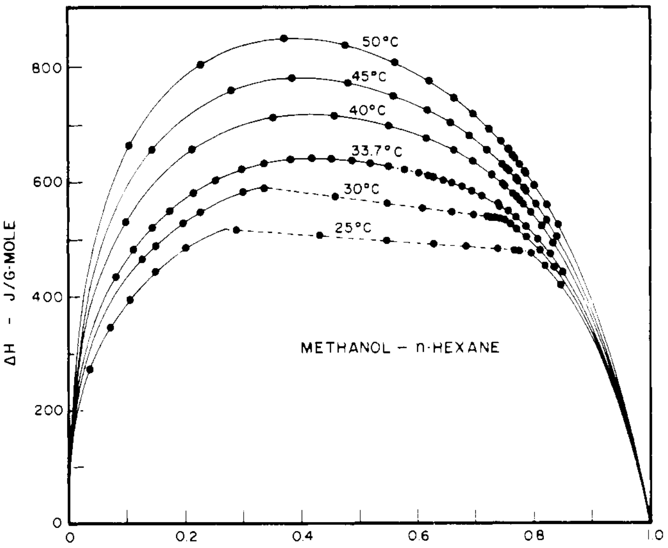

Figure 1. Heats of mixing, methanol–*n*-hexane

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Table I. Heats of Mixing

ΔH, joules/gram mole of solution

Mole Fraction, Methanol	Methanol–*n*-Hexane						Methanol–*n*-Heptane		
	25° C.	30° C.	33.7° C.	40° C.	45° C.	50° C.	30° C.	45° C.	60° C.
0.025	240	263	282	320	354	390	278	363	444
0.050	305	339	367	419	465	513	359	492	647
0.075	350	391	424	485	539	595	411	564	754
0.100	387	430	465	533	591	655	453	621	832
0.150	444	490	529	601	664	733	511	699	933
0.200	484	531	571	647	712	783	546	748	997
0.250	511	561	601	678	745	815	...	780	1036
0.300	...	584	623	700	765	837	...	798	1056
0.400	...	...	640	717	781	850	...	...	1058
0.500	...	...	636	708	768	830	...	...	1020
0.600	...	...	616	681	733	786	...	...	952
0.700	...	...	581	632	673	714	...	...	854
0.750	...	532	554	594	627	663	...	...	788
0.800	470	491	508	541	568	597	...	...	711
0.850	413	429	491	465	486	509	...	525	610
0.900	326	336	344	360	373	386	368	412	469
0.950	196	198	201	209	217	227	226	246	276

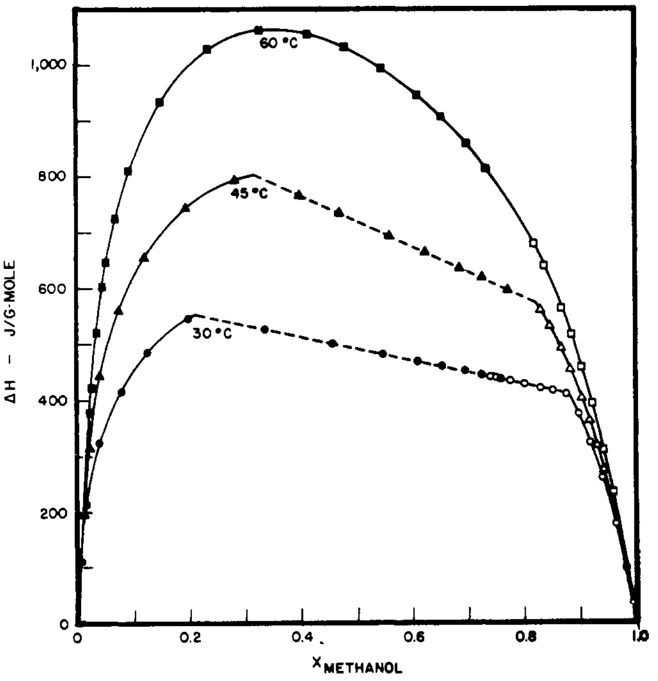

Figure 2. Heats of mixing, methanol–*n*-heptane

For a methanol mole fraction of 0.791, the temperature was again found to be 25° C., whereas Kiser and coworkers give about 23° C., some 2° lower. The authors' results indicate a critical solution temperature just in excess of 33.7° C. at a methanol mole fraction of about 0.56, whereas Kiser and coworkers give a value of 33.2° C. at an unspecified composition. It seems unlikely that these differences result from water contamination of the methanol, for the effect of water is to raise the solubility curve (*T vs. x*) very markedly at all compositions, and this is not the discrepancy observed. The hexane used by Kiser and coworkers was stated to be the Fisher Certified product. At the time of Kiser's paper, the only Fisher Certified hexane available was the Spectro grade. The authors' experience with this material has been that it contains only about 85% *n*-hexane. The present Fisher catalog states that this material contains methylcyclopentane. Moreover, the refractive indices given by Kiser and coworkers show a considerable discrepancy between their experimental value and the literature value. The differences between present solubilities and those of Kiser and coworkers are most probably the result of differences in the purities of the hexane used.

Table II. Solubilities and Heats of Mixing

t, ° C.	x'_{MeOH}	ΔH, Joules/ Gram Mole	x''_{MeOH}	ΔH, Joules/ Gram Mole
		Methanol-*n*-hexane		
25	0.270	519	0.791	478
30	0.330	592	0.745	536
33.7	0.535	630	0.590	618
		Methanol-*n*-heptane		
30	0.210	550	0.879	410
45	0.317	801	0.822	571

For the methanol-*n*-heptane system, agreement is very good with the single exception of the point at 25° C. with the lower methanol concentration. Here the purity question does not arise, and no explanation for this single discrepancy is apparent.

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