

Heats of Mixing for the Partially Miscible System Ethanol-*n*-Tetradecane

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Heats of mixing for the partially miscible system ethanol-*n*-tetradecane have been determined with an isothermal dilution calorimeter at 15°, 20°, 25°, 30°, 35°, and 40° C. Solubility data for this system were evaluated from the curves of ΔH vs. x_{a2} and are also reported. The changes of heat capacity accompanying mixing were calculated from experimental data.

AN EXTENSIVE, systematic collection of heats of mixing data is necessary for the eventual formulation of a comprehensive theory, capable of rigorous quantitative prediction of the behavior of nonideal solutions. In a preceding paper (4), heats of mixing data were reported for systems of *n*-alkanes plus *n*-alcohols at 20°, 25°, and 30° C., exhibiting complete miscibility at these temperatures. Some of the systems in this category show partial miscibility at or near room temperature. Heats of mixing for some of such partially miscible systems have been reported (7).

The objective of this paper is to present heats of mixing data for the ethanol-*n*-tetradecane system at 15°, 20°, 25°, 30°, 35°, and 40° C. At 35° and 40° C. the system is completely miscible, but at the four lower temperatures, regions of partial miscibility occur.

EXPERIMENTAL

These data were obtained with the isothermal dilution calorimeter, without vapor space, described previously (4). The experimental and computation procedures were also identical to those described in that paper.

The materials employed were analytical grade chemicals (Table I). Further purification was not considered necessary (6). Refractive indexes were measured by a Bausch & Lomb refractometer (ABBE-36) and found to agree with literature values. Since, for ethanol, the most probable impurity present is water, it was determined quantitatively by the Karl Fischer method and found to represent approximately 0.002% by weight.

RESULTS

Experimental data are listed in Table II. An error analysis was performed (5), and the results are believed to be accurate within 1 to 2%. The experimental data are also plotted in Figures 1 and 2. Figure 1 covers the range of mole fractions of ethanol from 0.05 to 0.9. Figure 2, drawn on a larger scale, presents heats of mixing data at higher ethanol concentrations, between mole fractions of 0.7 to 1.0. For the range of ethanol concentrations between 94 and 100 mole %, the temperature effect on the heats of mixing is very slight (Figure 2). The regions of partial miscibility in Figures 1 and 2 correspond to the straight broken lines. By locating the end points of these lines, one can estimate the partial miscibility limits at the temperature in question.

Since it is easier to draw smooth curves, passing through experimental points, on a plot of $\Delta H/x_{a2}x_{a14}$, an auxiliary graph (not shown) was constructed and used to interpolate additional points in the plots of ΔH vs. x_{a2} (Figures 1 and 2). From these interpolated values, graphs similar to Figures 1 and 2 were constructed and the partial miscibility limits were evaluated by locating the end points of straight lines corresponding to the regions of partial miscibility. It was found that the critical solution temperature (CST) was just in excess of 34.9° C. at a mole fraction of ethanol

of 0.77. (The CST is defined as the highest temperature at which the two liquid phases can coexist.) This value was also confirmed by turbidity determinations as follows: A series of solutions with molar concentration of ethanol ranging from 0.70 to 0.82 was prepared and heated to approximately 36° C. The temperature was then allowed to drop gradually, and the temperature at which turbidity first appeared, indicating separation of a second liquid phase, was recorded. The solution for $x_{a2} = 0.77$ was the one for which turbidity appeared at the highest temperature, 34.9° C.

It becomes increasingly difficult to determine the partial miscibility limits as the temperature is raised toward the CST (Figures 1 and 2). Therefore, the precision of the partial miscibility limits decreases as the temperature approaches the CST. Table III shows the partial miscibility limits for the temperatures at which heats of mixing were obtained. The system ethanol-*n*-tetradecane is completely miscible at 35° and 40° C., and the experimental curves of ΔH vs. x_{a2} do not exhibit straight sections.

Figure 3 is a sample of a cross plot of Figures 1 and 2, which permits easy interpolation for values of ΔH at temperatures other than experimental. Since the values of ΔH for a given temperature first increase with the mole fraction of ethanol and then decrease (Figures 1 and 2), the curves in a graph of the type of Figure 3 will cross each other, if the graph is to encompass the complete range of values of Figures 1 and 2. For clarity, a series of graphs of the type of Figure 3 was drawn.

CHANGE OF HEAT CAPACITY DURING MIXING

Consider the isothermal mixing of two components to form 1 mole of solution of a given composition. The change of heat capacity accompanying this process is:

$$\Delta C_p = C_{p, sol} - (x_{a2}C_{p, a2} + x_{a14}C_{p, a14}) \quad (1)$$

Assuming that ΔC_p is represented by the polynomial expression:

$$\Delta C_p = A + BT + CT^2 \quad (2)$$

the following equations can be obtained from basic thermodynamic relations (8):

$$\Delta H^E = \Delta H = AT + BT^2/2 + CT^3/3 + D \quad (3)$$

$$\Delta G^E = -AT \ln T - BT^2/2 - CT^3/6 + D + IT \quad (4)$$

$$\Delta S^E = A \ln T + BT + CT^2/2 + (A - I) \quad (5)$$

Table I. Specifications of Materials

Materials	Supplier	Specifications
Ethanol (C ₂ H ₅ OH)	Canlab Co.	200% proof, anhydrous
<i>n</i> -Tetradecane (<i>n</i> -C ₁₄ H ₃₀)	Matheson, Coleman and Bell Co.	99 mole % purity

Table II. Heats of Mixing for System $C_2H_5OH-n-C_{14}H_{30}$ at 15°, 20°, 25°, 30°, 35°, and 40° C.
Joules per Gram Mole

15° C.			20° C.			25° C.		
x_{a2}	$x_{a2}x_{h14}$	ΔH	x_{a2}	$x_{a2}x_{h14}$	ΔH	x_{a2}	$x_{a2}x_{h14}$	ΔH
0.0664	6356	394	0.0676	7019	442	0.0653	7912	483
0.1539	4115	536	0.1571	4524	599	0.1488	5112	648
0.2675	3179	623	0.2692	3536	696	0.2557	3972	756
0.4216	2460	600	0.4237	2782	679	0.4072	3198	772
0.5929	2092	505	0.5949	2346	565	0.5925	2644	638
0.7181	2139	433	0.7198	2386	481	0.7127	2648	542
0.7844	2336	395	0.7859	2601	438	0.7780	2817	486
0.8256	2591	373	0.8318	2909	407	0.8208	3080	453
0.8376	2689	366	0.8371	2947	402	0.8297	3147	445
0.8902	3391	332	0.8860	3624	366	0.8870	3921	393
0.9341	4675	288	0.9315	4759	304	0.9321	4946	313
0.9660	5531	182	0.9645	5541	190	0.9649	5743	195
0.9827	6055	103	0.9819	6104	109	0.9810	6233	116
0.9912	6322	55	0.9909	6472	58	0.9910	6695	60
30° C.			35° C.			40° C.		
0.0525	9792	487	0.0721	9256	619	0.0580	11282	616
0.1455	5701	709	0.1312	6712	765	0.1286	7485	839
0.2537	4374	828	0.2116	5272	880	0.2078	5905	972
0.4050	3580	863	0.3073	4443	946	0.3024	4946	1043
0.5761	3089	754	0.4327	3860	948	0.4184	4308	1048
0.7039	3027	631	0.5803	3476	846	0.5183	4006	1000
0.7732	3211	563	0.7005	3470	728	0.5890	3883	940
0.8222	3509	513	0.7403	3547	682	0.6667	3850	855
0.8267	3539	507	0.7852	3670	619	0.7308	3916	770
0.8880	4273	425	0.8265	3905	560	0.7812	4045	691
0.9327	5178	325	0.8298	3923	554	0.8251	4240	612
0.9652	5954	200	0.8845	4483	458	0.8498	4505	575
0.9823	6334	110	0.9306	5300	342	0.8927	4962	475
0.9911	6728	60	0.9641	5894	204	0.9338	5594	346
0.9957	7078	30	0.9817	6512	117	0.9656	6317	210
			0.9905	7342	69	0.9858	6963	98

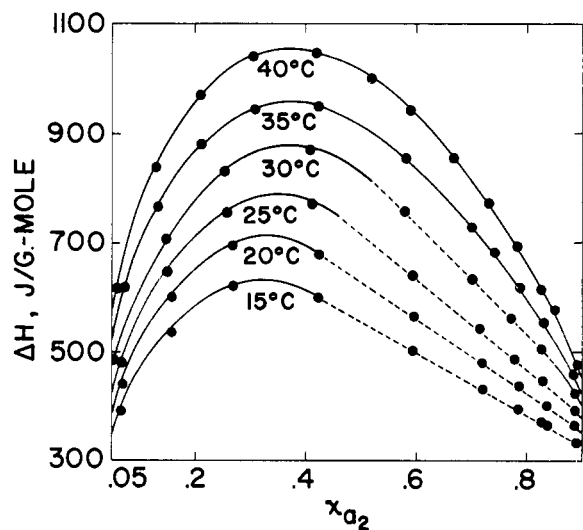


Figure 1. Heats of mixing for system $C_2H_5OH-n-C_{14}H_{30}$ Joules/gram mole

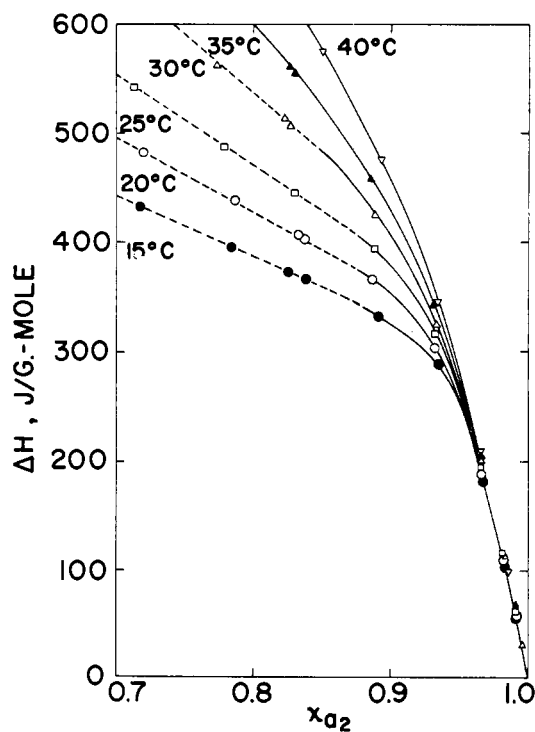


Figure 2. Heats of mixing for system $C_2H_5OH-n-C_{14}H_{30}$ Joules/gram mole

Plots of ΔH vs. t (Figure 3) yield smooth curves for the system studied. Using a series of these plots in conjunction with Equation 3, constants A , B , C , and D were determined by applying the method of least squares, using a digital computer (Table IV).

The change of heat capacity accompanying mixing has been reported (1, 9) in terms of the dimensionless ratio,

Table III. Partial Miscibility Limits for System Ethanol-*n*-Tetradecane

Temp., °C.	Lower x_{a2}	Higher x_{a2}
15	0.42	0.88
20	0.43	0.87
25	0.46	0.87
30	0.52	0.85

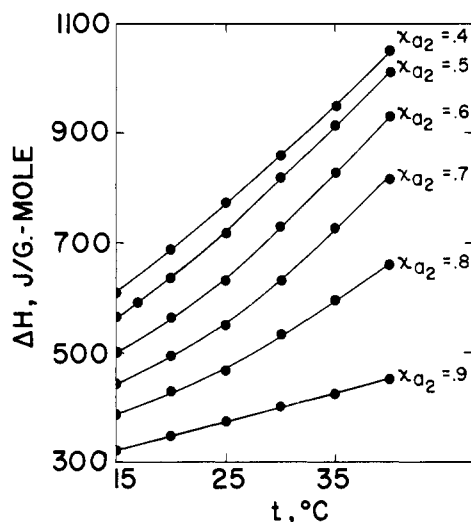


Figure 3. Heats of mixing for system $C_2H_5OH-n-C_{14}H_{30}$ As a function of temperature

$\Delta C_p/R$. Figure 4 presents values of this ratio at 20° and 40° C., calculated from Equation 2, using the values of the constants reported in Table IV. From Figure 4 it can be seen that at 20° C., C has very little effect upon the values of $\Delta C_p/R$, but, as temperature increases, the values of $\Delta C_p/R$ calculated with the constants from Table IV become increasingly different. Smooth curves were drawn (Figure 4) to encompass these points.

Since $\partial(\Delta H)/\partial T = \Delta C_p$, this means that, in effect, the values of $\Delta C_p/R$ were obtained by differentiation of heats of mixing data with respect to temperature. Therefore, the accuracy of these values is only of the order of 10 to 20%.

The constant I , in Equations 4 and 5, can be calculated if excess free energies of mixing for the system are available. Excess free energies can be, for instance, calculated from total pressure measurements (2, 3). Since such data are

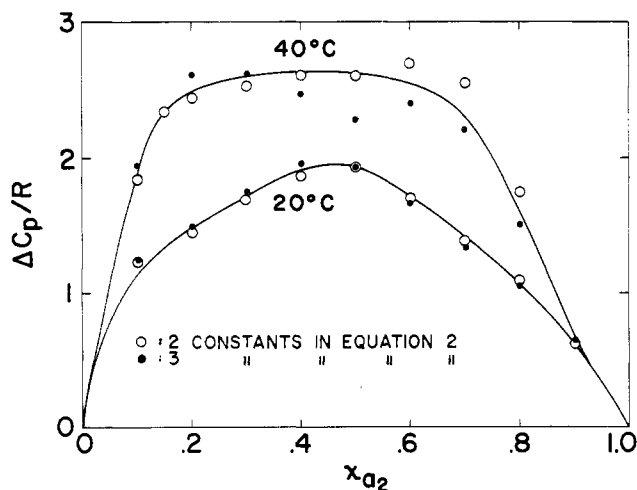


Figure 4. $\Delta C_p/R$ for system $C_2H_5OH-n-C_{14}H_{30}$

Table IV. Coefficients of Equation 3 for System $C_2H_5OH-n-C_{14}H_{30}$

x_{a2}	A, J./G. Mole ° K.	B, J./G. Mole, ° K. ²	C, J./G. Mole, ° K. ³	D, J./G. Mole
$C = 0$				
0.1	-63.0082	0.250000		8257.34
0.2	-97.2481	0.372857		13129.18
0.3	-77.2310	0.311428		9957.73
0.4	-64.4459	0.272851		7854.55
0.5	-65.1859	0.277142		7839.16
0.6	-112.3775	0.431429		14969.25
0.7	-131.3566	0.487143		18069.26
0.8	-72.2087	0.277143		9687.08
0.9	4.8447	0.001429		-1133.37
$C \neq 0$				
0.1	679.8582	-4.6940	0.008222	-66120.92
0.2	1689.6474	-11.5196	0.019778	-165780.72
0.3	1521.3112	-10.2862	0.017556	-150709.18
0.4	464.0743	-3.1563	0.005556	-46385.75
0.5	-2193.4001	14.4412	-0.023556	220923.00
0.6	-2340.4587	15.2621	-0.024667	238012.92
0.7	-2279.6491	14.7848	-0.023779	233163.39
0.8	-1678.4083	10.9670	-0.017778	170505.10
0.9	65.0774	-0.39944	0.000667	-7164.05

not available in the literature for the system ethanol-*n*-tetradecane, it was not possible to calculate ΔG^E and ΔS^E for this system.

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NOMENCLATURE

- A = constant, joules (gram mole)⁻¹ (° K.)⁻¹
- B = constant, joules (gram mole)⁻¹ (° K.)⁻²
- C = constant, joules (gram mole)⁻¹ (° K.)⁻³
- $C_{p,a2}$ = heat capacity at constant pressure for ethanol, joules (gram mole)⁻¹ (° K.)⁻¹
- $C_{p,n14}$ = heat capacity at constant pressure for *n*-tetradecane, joules (gram mole)⁻¹ (° K.)⁻¹
- $C_{p,sol}$ = heat capacity at constant pressure for solution ethanol-*n*-tetradecane, joules (gram mole)⁻¹ (° K.)⁻¹
- D = constant, joules (gram mole)⁻¹
- I = constant, joules (gram mole)⁻¹ (° K.)⁻¹
- R = universal gas constant, joules (gram mole)⁻¹ (° K.)⁻¹
- t = temperature, ° C.
- T = absolute temperature, ° K.
- x_{a2} = mole fraction of ethanol
- x_{n14} = mole fraction of *n*-tetradecane
- ΔC_p = heat capacity change of mixing, joules (gram mole)⁻¹ (° K.)⁻¹
- ΔH = heat of mixing, joules (gram mole)⁻¹
- ΔG^E = excess free energy, joules (gram mole)⁻¹
- ΔS^E = excess entropy, joules (gram mole)⁻¹ (° K.)⁻¹

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