# Excess Enthalpies and Liquid–Liquid Equilibrium Phase Compositions of the Nonionic Amphiphile 2-Butoxyethanol and Water

**Kyung-Hee Lim,[†] Wallace B. Whiting,[*,†] and Duane H. Smith[‡]**

Department of Chemical Engineering, West Virginia University, Morgantown, West Virginia 26506-6101, and Morgantown Energy Technology Center, U.S. Department of Energy, Morgantown, West Virginia 26507-0880

The excess enthalpies, $H^E$, for mixtures of the nonionic amphiphile $C_4H_9OC_2H_4OH$ + water were measured by isothermal flow calorimetry at atmospheric pressure and 10 temperatures over the temperature range $T - T_{lcst}$ = −0.1 to +32 K. ($T_{lcst}$ is the lower critical solution temperature.) The $H^E$ data are reported and compared to literature values. The phase boundaries between the single- and two-phase regions, determined from the $H^E$ data, are also reported and compared to data from the phase volume method and from the literature.

## Introduction

Heats of mixing or excess enthalpies (*1*) of the nonionic amphiphile 2-butoxyethanol, $C_4H_9OC_2H_4OH$, and water around and above the lower critical solution temperature, $T_{lcst}$, are reported in this paper.

Thermodynamic functions such as excess free energy, excess enthalpy, and excess volume provide a better understanding of nonideal behavior of mixtures. The nonideality is primarily caused by size effects and interactions of the molecules which comprise the mixture (*2*). While density measurements of the mixture may provide molecular size information, excess enthalpies yield information about the molecular interactions and the extent to which real mixtures deviate from ideality.

Various uses of excess enthalpy are found in, for example, calculation of other excess quantities (*3*), determination of equilibrium phase compositions (*3*), temperature dependence of activity coefficients (*3*), and also determination of critical micelle concentrations (*4*). Our excess enthalpy measurements were aimed at improving the method (*5–7*) by which equilibrium phase compositions or phase boundaries for liquid–liquid equilibria are determined. There is a unique distinction between the previous studies (*5–7*) and our method (*8, 9*). In the past the semiempirical Padé polynomial (*5*) or an enthalpy-based local-composition (EBLC) thermodynamic model (*6*) was used for the composition dependence of the excess enthalpy in the single-phase region. Although the EBLC model worked better than other models such as the UNIQUAC, NRTL, modified NRTL, and Wang–Chao models, its predictions were quite different from the measured data for certain concentration ranges (*6*). The Padé polynomial also could not yield the correct phase compositions for the 2-butoxyethanol + water system (*9*). Hence, critical scaling equations of $H^E$ for binary systems were derived and used for the phase boundary determination (*8*). The results were in good agreement with literature data and those by the phase volume method (*8*) and are reported in this paper.

Excess enthalpies for the 2-butoxyethanol + water have been reported in the literature (*10–14*). Most were measured at temperatures below $T_{lcst}$, i.e., in the single-phase region. Only several scattered measurements at 60, 80, and 100 °C (*10*) and at 65 and 85 °C (*11*) have been reported at temperatures above $T_{lcst}$. The reported values were inappropriate for determination of the phase boundaries, because they did not cover the whole composition range. Hence, we measured excess enthalpies at more than 40 compositions for each of 10 temperatures around and above $T_{lcst}$. The compositions ranged from 0.1 to 93.2 mol % amphiphile.

For comparisons of the phase boundaries determined from the $H^E$ data and the critical scaling equation, liquid–liquid phase compositions for 2-butoxyethanol + water were measured independently by the phase volume method. Recently this method was used for the phase compositions of water and the nonionic amphiphile 2-[2-(hexyloxy)ethoxy]ethanol, $C_6H_{13}(OC_2H_4)_2OH$ (*16*). In this method samples of different compositions along a tie line are prepared gravimetrically and put in a thermostatically controlled bath. After equilibrium and complete phase separation are attained, the volume of each phase is measured. According to the lever rule (*1*), the phase volume fraction is proportional to the component concentration. Hence, phase compositions are obtained through a linear regression of the phase volume fraction to the component concentration. Since in this method multiple samples are prepared along a tie line, the accuracy and the precision of the results can be greatly improved by preparation of more samples inside the two-phase region and particularly samples near the phase boundary points.

## Experimental Section

***Materials.*** The amphiphile 2-butoxyethanol, $C_4H_9OC_2H_4OH$, was from Aldrich. It is usually denoted as $C_4E_1$, where $C_4$ and $E_1$ indicate the number of carbons in the hydrophobic chain and of ethoxylate groups ($OC_2H_4$) in the hydrophilic part, respectively. The amphiphile had a stated purity of 99%, which was confirmed by gas chromatography. The amphiphile was used as received; the water was distilled and deionized.

***Excess Enthalpy Measurements.*** Excess enthalpies were measured at atmospheric pressure with a Hart Scientific isothermal flow calorimeter (Model 503, Hart Scientific, Provo, UT). The reaction vessel consisted of an equilibration coil with a "mixing wire". The wire promoted thorough mixing of the fluids as they flowed through the coil, and an equilibration coil without the wire inside gave mixing that was inadequate. The excess enthalpy during the mixing of the fluids was measured within ±0.005 J by counting the number of heat pulses of a controlled heater through the isothermal control unit. The controlled heater compensated the energy liberated or absorbed by the mixing and maintained the reaction vessel temperature constant to ±0.05 mK. We estimate the accuracy of the compositions as ±0.1 mass % and the accuracy of the excess enthalpies as ±2%. A desktop

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[†] West Virginia University.
[‡] U.S. Department of Energy.

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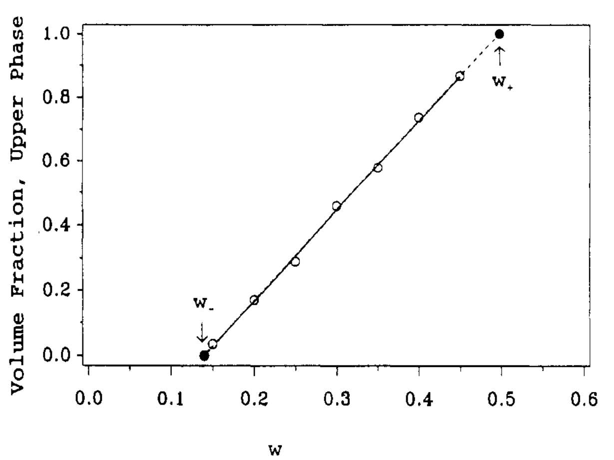

**Figure 1.** Upper phase volume fraction plotted against the mass fraction of the amphiphile at 53.99 °C. Extrapolation of the linear regression to the volume fractions of 0 and 1 yields the phase boundary points $w_-$ and $w_+$, respectively.

**Table 1. Mass fractions, $w_-$ and $w_+$, of 2-Butoxyethanol at the Phase boundaries, Determined by the Phase Volume Method**

| $T$/°C | $w_-$ | $w_+$ | $T$/°C | $w_-$ | $w_+$ |
|---|---|---|---|---|---|
| 50.03 | 0.182 61 | 0.421 13 | 57.99 | 0.117 58 | 0.552 53 |
| 51.04 | 0.166 69 | 0.448 44 | 59.95 | 0.118 83 | 0.553 33 |
| 51.77 | 0.152 88 | 0.469 43 | 62.02 | 0.115 17 | 0.562 97 |
| 52.97 | 0.146 91 | 0.475 18 | 63.86 | 0.108 55 | 0.583 39 |
| 53.99 | 0.140 00 | 0.497 65 | 65.84 | 0.109 35 | 0.589 64 |
| 54.92 | 0.136 04 | 0.514 01 | 67.85 | 0.104 83 | 0.595 83 |
| 56.02 | 0.133 97 | 0.515 54 | 69.79 | 0.107 09 | 0.612 07 |
| 56.98 | 0.123 56 | 0.545 15 | | | |

computer controlled the pumps (LC-5000 Precision Pump, ISCO Inc., Lincoln, NE) and the isothermal control unit through programmers. Details about the design and hardware of the calorimeter may be found elsewhere (*17–19*).

***Phase Volume Measurements.*** Samples of a range of known compositions were put in a microprocessor-controlled thermostat with viewing windows (Tamson Model 45, Neslab Instruments Inc., Newington, NH) for at least one day to ensure complete phase separation. Then, the volume of each phase was recorded. Since in the two-phase region the volume fraction of either phase is proportional to the amount of the amphiphile by the lever rule, linear regression of the phase volume data to the amphiphile concentration yields the phase boundary points as the compositions at which the phase volume fractions are 0 and 1, respectively (*16*) (see Figure 1). The estimated accuracy of the compositions is ±0.1 mass %.

## Results and Discussion

Liquid–liquid equilibrium phase compositions for the binary nonionic amphiphile 2-butoxyethanol ($C_4E_1$) and water were determined by the phase volume method at 15 temperatures around the lower critical solution temperature, $T_{lcst}$. The critical temperature $T_{lcst} = 48 \pm 1$ °C has been determined by various methods (*20–27*). For our data of Tables 1 and 3, $T_{lcst} = 48.6 \pm 0.4$ °C and the critical mass fraction $w_c = 0.294 \pm 0.002$ were determined with critical scaling equations as was done for 2-[2-(hexyloxy)ethoxy]ethanol + water system (*16*). At each temperature volume fractions of the upper phase were measured at several amphiphile concentrations. Figure 1 shows a typical example of the upper phase volume fraction versus amphiphile mass fraction. The measured volume fraction correlates excellently with the amphiphile mass fraction. (The correlation coefficient is 0.9993.) The amphiphile mass fractions, $w_-$ and $w_+$, of the two equilibrium phases are determined from the extrapolation of the linear regression to the phase volume fractions of 0 and 1. The quantities $w_-$ and $w_+$ denote, respectively, the amphiphile concentrations at the aqueous side (where the phase contains mainly water) and amphiphilic side (where the phase contains greater concentration of amphiphile). The values of $w_-$ and $w_+$ at different temperatures are listed in Table 1.

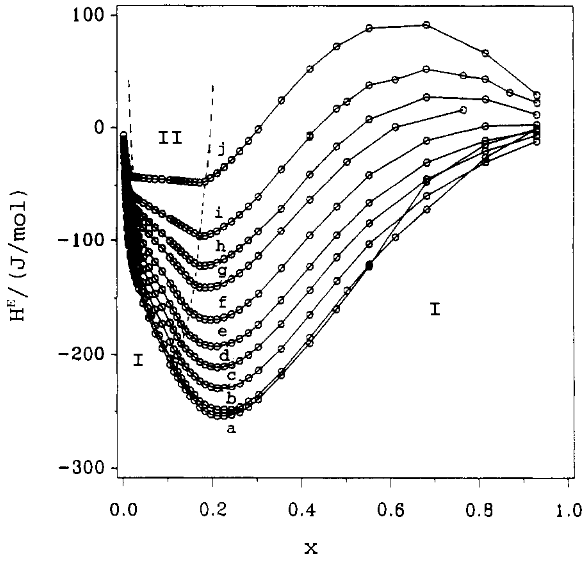

**Figure 2.** Excess enthalpy in joules per mole plotted against the mole fraction of 2-butoxyethanol ($x$) at temperatures of 48.47 (a), 48.98 (b), 50.98 (c), 52.99 (d), 54.97 (e), 57.51 (f), 60.19 (g), 62.51 (h), 65.00 (i), and 70.01 (j) °C. Roman numerals indicate the number of phases, and the filled diamond denotes the lower critical point.

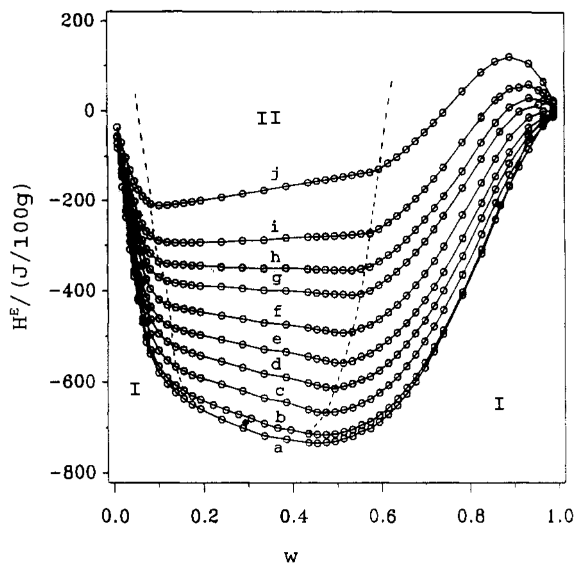

**Figure 3.** Same as in Figure 2, except that the units of the enthalpy and the concentration are joules per 100 g of the mixture, and it is plotted against the mass fraction of 2-butoxyethanol.

Excess enthalpies, $H^E$, were measured at 10 different temperatures from 48.5 to 70 °C. They are shown in Figures 2 and 3 and listed in Table 2. At lower temperatures $H^E$ is negative and large over the whole concentration range. These large negative values of $H^E$ indicate that there are considerable water + amphiphile interactions. This behavior of 2-butoxyethanol + water is similar to that of alcohol + water (*28, 29*), glycol + water (*30, 31*), and glycerol + water (*32*) mixtures. $H^E$ increases with increasing temperature and becomes positive at higher temperatures.

In Figures 2 and 3, region II is the two-phase region, which is surrounded on each side by the single-phase region, I. The

**Table 2. Measured Dependence of Excess Enthalpies, $H^E$, of $x$ 2-Butoxyethanol + (1 − $x$) Water[a]**

| $T$ = 48.47 °C | | $T$ = 48.98 °C | | $T$ = 50.98 °C | | $T$ = 52.99 °C | | $T$ = 48.47 °C | | $T$ = 48.98 °C | | $T$ = 50.98 °C | | $T$ = 52.99 °C | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $x$ | $H^E$/(J mol$^{-1}$) | $x$ | $H^E$/(J mol$^{-1}$) | $x$ | $H^E$/(J mol$^{-1}$) | $x$ | $H^E$/(J mol$^{-1}$) | $x$ | $H^E$/(J mol$^{-1}$) | $x$ | $H^E$/(J mol$^{-1}$) | $x$ | $H^E$/(J mol$^{-1}$) | $x$ | $H^E$/(J mol$^{-1}$) |
| | | | | 0.001 39 | −14.58 | 0.001 39 | −12.88 | 0.149 06 | −236.68 | 0.121 05 | −215.53 | 0.149 15 | −215.90 | 0.149 15 | −198.74 |
| 0.002 80 | −30.83 | 0.002 80 | −26.44 | 0.002 80 | −26.32 | 0.002 80 | −25.12 | 0.159 71 | −240.62 | 0.129 83 | −221.38 | 0.159 80 | −219.60 | 0.159 80 | −202.04 |
| 0.004 24 | −43.70 | 0.004 24 | −40.98 | 0.004 24 | −39.66 | 0.004 24 | −36.95 | 0.171 12 | −246.69 | 0.139 18 | −226.53 | 0.171 22 | −223.92 | 0.171 22 | −206.54 |
| 0.005 70 | −57.31 | 0.005 71 | −54.07 | 0.005 71 | −51.26 | 0.005 71 | −48.57 | 0.183 38 | −250.12 | 0.149 15 | −231.90 | 0.183 48 | −226.62 | 0.183 48 | −208.95 |
| 0.007 19 | −68.83 | 0.007 20 | −66.85 | 0.007 20 | −62.49 | 0.007 20 | −58.71 | 0.196 58 | −252.81 | 0.159 80 | −235.90 | 0.196 69 | −228.77 | 0.196 69 | −210.63 |
| 0.008 71 | −79.52 | 0.008 71 | −78.40 | 0.008 71 | −72.47 | 0.008 71 | −68.92 | 0.210 84 | −254.25 | 0.171 22 | −241.33 | 0.210 95 | −230.06 | 0.210 95 | −211.37 |
| 0.010 25 | −89.11 | 0.010 26 | −87.79 | 0.010 26 | −81.67 | 0.010 26 | −77.24 | 0.226 29 | −254.13 | 0.183 48 | −244.67 | 0.226 41 | −229.89 | 0.226 41 | −210.66 |
| 0.011 83 | −98.38 | 0.011 83 | −96.10 | 0.011 83 | −90.08 | 0.011 83 | −84.87 | 0.243 08 | −253.33 | 0.196 69 | −247.18 | 0.243 21 | −228.63 | 0.243 21 | −209.05 |
| 0.013 43 | −104.11 | 0.013 44 | −102.52 | 0.013 44 | −95.81 | 0.013 44 | −89.57 | 0.261 40 | −250.93 | 0.210 95 | −248.76 | 0.261 53 | −225.88 | 0.261 53 | −205.52 |
| 0.016 73 | −113.99 | 0.016 74 | −111.35 | 0.016 74 | −104.53 | 0.016 74 | −97.23 | 0.281 47 | −246.38 | 0.226 41 | −248.83 | 0.281 61 | −221.05 | 0.281 61 | −200.29 |
| 0.020 15 | −120.93 | 0.020 16 | −118.25 | 0.020 16 | −110.64 | 0.020 16 | −102.54 | 0.303 54 | −239.54 | 0.243 21 | −248.94 | 0.303 69 | −213.98 | 0.303 69 | −192.98 |
| 0.023 71 | −126.92 | 0.023 73 | −123.70 | 0.023 73 | −115.42 | 0.023 73 | −106.66 | 0.355 06 | −218.44 | 0.261 53 | −246.49 | 0.355 22 | −194.53 | 0.355 22 | −172.52 |
| 0.027 42 | −131.99 | 0.027 44 | −128.25 | 0.027 44 | −119.36 | 0.027 44 | −109.88 | 0.419 47 | −189.58 | 0.281 61 | −241.84 | 0.419 64 | −164.45 | 0.419 64 | −143.07 |
| 0.031 27 | −137.23 | 0.031 30 | −133.20 | 0.031 30 | −123.51 | 0.031 30 | −113.40 | 0.479 46 | −159.43 | 0.303 69 | −235.38 | 0.479 63 | −134.88 | 0.479 63 | −114.24 |
| 0.035 29 | −141.96 | 0.035 32 | −137.46 | 0.035 32 | −127.20 | 0.035 32 | −116.77 | 0.553 31 | −122.16 | 0.355 22 | −215.08 | 0.553 48 | −102.97 | 0.553 48 | −84.07 |
| 0.046 13 | −154.44 | 0.041 68 | −144.20 | 0.046 16 | −136.86 | 0.046 16 | −125.58 | 0.683 17 | −46.68 | 0.419 64 | −184.52 | 0.683 32 | −59.26 | 0.683 32 | −44.43 |
| 0.058 23 | −167.12 | 0.048 47 | −151.14 | 0.058 27 | −147.77 | 0.058 27 | −135.54 | 0.816 52 | −14.01 | 0.502 49 | −143.42 | 0.816 62 | −29.51 | 0.816 62 | −19.81 |
| 0.071 86 | −181.02 | 0.055 74 | −158.30 | 0.071 90 | −160.08 | 0.071 90 | −146.60 | 0.931 63 | −0.65 | 0.553 48 | −120.64 | 0.931 67 | −11.27 | 0.931 67 | −6.34 |
| 0.087 29 | −194.22 | 0.063 53 | −165.62 | 0.087 35 | −172.35 | 0.087 35 | −157.77 | | | 0.612 98 | −96.76 | | | | |
| 0.104 94 | −209.13 | 0.071 90 | −174.24 | 0.105 00 | −188.36 | 0.105 00 | −171.60 | | | 0.683 32 | −71.52 | | | | |
| 0.112 73 | −215.31 | 0.080 93 | −182.96 | 0.112 79 | −195.28 | 0.112 79 | −177.98 | | | 0.816 62 | −25.46 | | | | |
| 0.120 98 | −220.62 | 0.090 69 | −190.96 | 0.121 05 | −200.72 | 0.121 05 | −184.04 | | | 0.931 67 | −0.71 | | | | |
| 0.129 76 | −226.53 | 0.105 00 | −203.59 | 0.129 83 | −206.38 | 0.129 83 | −190.37 | | | | | | | | |
| 0.139 10 | −231.27 | 0.112 79 | −209.68 | 0.139 18 | −210.87 | 0.139 18 | −194.42 | | | | | | | | |

| $T$ = 54.97 °C | | $T$ = 57.51 °C | | $T$ = 60.19 °C | | $T$ = 62.51 °C | | $T$ = 54.97 °C | | $T$ = 57.51 °C | | $T$ = 60.19 °C | | $T$ = 62.51 °C | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $x$ | $H^E$/(J mol$^{-1}$) | $x$ | $H^E$/(J mol$^{-1}$) | $x$ | $H^E$/(J mol$^{-1}$) | $x$ | $H^E$/(J mol$^{-1}$) | $x$ | $H^E$/(J mol$^{-1}$) | $x$ | $H^E$/(J mol$^{-1}$) | $x$ | $H^E$/(J mol$^{-1}$) | $x$ | $H^E$/(J mol$^{-1}$) |
| 0.001 39 | −12.72 | 0.001 39 | −10.42 | 0.001 39 | −10.56 | 0.001 39 | −9.84 | 0.121 05 | −166.55 | 0.121 13 | −146.85 | 0.120 98 | −122.15 | 0.121 03 | −106.26 |
| 0.002 80 | −23.61 | 0.002 80 | −20.88 | 0.002 80 | −19.77 | 0.002 80 | −18.43 | 0.129 83 | −172.78 | 0.129 91 | −152.45 | 0.129 76 | −126.21 | 0.129 81 | −109.73 |
| 0.004 24 | −36.10 | 0.004 24 | −31.65 | 0.004 24 | −29.50 | 0.004 24 | −26.88 | 0.139 18 | −178.27 | 0.139 26 | −157.48 | 0.139 10 | −130.20 | 0.139 15 | −113.05 |
| 0.005 71 | −46.69 | 0.005 71 | −42.11 | 0.005 70 | −38.67 | 0.005 70 | −35.37 | 0.149 15 | −182.51 | 0.149 23 | −161.60 | 0.149 06 | −134.90 | 0.149 12 | −116.74 |
| 0.007 20 | −56.42 | 0.007 20 | −50.50 | 0.007 19 | −46.22 | 0.007 20 | −42.64 | 0.159 80 | −185.17 | 0.159 89 | −164.11 | 0.159 71 | −138.19 | 0.159 77 | −119.48 |
| 0.008 71 | −65.11 | 0.008 72 | −58.36 | 0.008 71 | −53.44 | 0.008 71 | −49.34 | 0.171 22 | −189.01 | 0.171 32 | −166.97 | 0.171 12 | −140.35 | 0.171 19 | −121.99 |
| 0.010 26 | −72.55 | 0.010 27 | −65.56 | 0.010 25 | −59.64 | 0.010 26 | −54.89 | 0.183 48 | −191.00 | 0.183 59 | −168.32 | 0.183 38 | −140.88 | 0.183 45 | −121.85 |
| 0.011 83 | −79.49 | 0.011 84 | −71.91 | 0.011 83 | −64.59 | 0.011 83 | −59.12 | 0.196 69 | −192.27 | 0.196 80 | −168.86 | 0.196 58 | −140.52 | 0.196 66 | −121.01 |
| 0.013 44 | −84.27 | 0.013 45 | −76.54 | 0.013 43 | −68.21 | 0.013 44 | −61.42 | 0.210 95 | −192.56 | 0.211 07 | −168.53 | 0.210 84 | −139.65 | 0.210 92 | −119.33 |
| 0.016 74 | −90.74 | 0.016 75 | −82.55 | 0.016 73 | −72.89 | 0.016 73 | −66.08 | 0.226 41 | −191.43 | 0.226 53 | −166.79 | 0.226 29 | −136.79 | 0.226 37 | −116.26 |
| 0.020 16 | −95.07 | 0.020 18 | −86.33 | 0.020 15 | −75.79 | 0.020 16 | −68.14 | 0.243 21 | −189.32 | 0.243 33 | −164.15 | 0.243 08 | −133.33 | 0.243 17 | −112.24 |
| 0.023 73 | −98.50 | 0.023 74 | −89.04 | 0.023 71 | −77.95 | 0.023 72 | −69.74 | 0.261 53 | −185.78 | 0.261 67 | −160.03 | 0.261 40 | −128.47 | 0.261 49 | −106.92 |
| 0.027 44 | −101.23 | 0.027 45 | −91.23 | 0.027 42 | −79.83 | 0.027 43 | −71.01 | 0.281 61 | −180.42 | 0.281 75 | −154.07 | 0.281 47 | −121.86 | 0.281 56 | −100.03 |
| 0.031 30 | −104.28 | 0.031 32 | −93.80 | 0.031 27 | −81.87 | 0.031 29 | −72.71 | 0.303 69 | −173.01 | 0.303 83 | −145.91 | 0.303 54 | −113.24 | 0.303 64 | −91.48 |
| 0.035 32 | −107.13 | 0.035 34 | −96.24 | 0.035 29 | −83.81 | 0.035 31 | −74.23 | 0.355 22 | −151.59 | 0.355 37 | −123.99 | 0.355 06 | −91.28 | 0.355 17 | −71.11 |
| 0.046 16 | −114.90 | 0.046 19 | −102.88 | 0.046 13 | −88.39 | 0.046 15 | −78.56 | 0.419 64 | −122.59 | 0.419 81 | −95.32 | 0.419 47 | −62.96 | 0.419 59 | −40.43 |
| 0.058 27 | −123.59 | 0.058 31 | −110.24 | 0.058 23 | −94.08 | 0.058 26 | −83.25 | 0.479 63 | −94.94 | 0.479 80 | −68.99 | 0.502 32 | −29.26 | 0.479 58 | −15.66 |
| 0.071 90 | −133.28 | 0.071 95 | −118.56 | 0.071 86 | −100.48 | 0.071 89 | −88.26 | 0.553 48 | −65.63 | 0.553 65 | −40.99 | 0.612 82 | 0.84 | 0.553 43 | 7.46 |
| 0.087 35 | −143.02 | 0.087 40 | −126.97 | 0.087 29 | −106.91 | 0.087 33 | −93.58 | 0.683 32 | −29.80 | 0.683 47 | −10.74 | 0.767 62 | 15.84 | 0.683 27 | 26.99 |
| 0.105 00 | −155.31 | 0.105 07 | −137.40 | 0.104 94 | −114.83 | 0.104 98 | −100.33 | 0.816 62 | −10.79 | 0.816 72 | 1.71 | | | 0.816 59 | 25.17 |
| 0.112 79 | −161.00 | 0.112 86 | −142.32 | 0.112 73 | −118.62 | 0.112 77 | −103.47 | 0.931 67 | −2.68 | 0.931 71 | 2.79 | | | 0.931 66 | 11.70 |

| $T$ = 65.00 °C | | $T$ = 70.01 °C | | $T$ = 65.00 °C | | $T$ = 70.01 °C | | $T$ = 65.00 °C | | $T$ = 70.01 °C | | $T$ = 65.00 °C | | $T$ = 70.01 °C | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $x$ | $H^E$/(J mol$^{-1}$) | $x$ | $H^E$/(J mol$^{-1}$) | $x$ | $H^E$/(J mol$^{-1}$) | $x$ | $H^E$/(J mol$^{-1}$) | $x$ | $H^E$/(J mol$^{-1}$) | $x$ | $H^E$/(J mol$^{-1}$) | $x$ | $H^E$/(J mol$^{-1}$) | $x$ | $H^E$/(J mol$^{-1}$) |
| | | 0.001 39 | −6.22 | 0.027 42 | −60.85 | 0.027 42 | −42.58 | 0.149 06 | −90.93 | 0.149 06 | −46.80 | 0.419 47 | −6.94 | 0.419 47 | 52.44 |
| 0.002 80 | −17.01 | 0.002 80 | −12.55 | 0.031 27 | −62.02 | 0.031 27 | −42.81 | 0.159 71 | −93.17 | 0.159 71 | −47.01 | 0.479 46 | 16.99 | 0.479 46 | 73.00 |
| 0.004 24 | −24.92 | 0.004 24 | −18.76 | 0.035 29 | −63.06 | 0.035 29 | −42.95 | 0.171 12 | −95.92 | 0.171 12 | −47.52 | 0.502 32 | 23.04 | | |
| 0.005 70 | −31.87 | 0.005 70 | −24.11 | 0.046 13 | −66.06 | 0.046 13 | −43.54 | 0.183 38 | −95.82 | 0.183 38 | −46.66 | 0.553 31 | 37.74 | 0.553 31 | 89.09 |
| 0.007 19 | −37.85 | 0.007 19 | −28.96 | 0.058 23 | −69.05 | 0.058 23 | −44.03 | 0.196 58 | −93.90 | 0.196 58 | −43.36 | 0.612 82 | 42.84 | | |
| 0.008 71 | −43.69 | 0.008 71 | −32.94 | 0.071 86 | −72.48 | 0.071 86 | −44.48 | 0.210 84 | −91.47 | 0.210 84 | −39.24 | 0.683 17 | 52.33 | 0.683 17 | 91.92 |
| 0.010 25 | −47.93 | 0.010 25 | −36.06 | 0.087 29 | −75.77 | 0.087 29 | −44.78 | 0.226 29 | −87.40 | 0.226 29 | −33.92 | 0.767 62 | 46.29 | | |
| 0.011 83 | −51.52 | 0.011 83 | −38.42 | 0.104 94 | −80.17 | 0.104 94 | −45.39 | 0.243 08 | −82.75 | 0.243 08 | −27.61 | 0.816 52 | 43.18 | 0.816 52 | 66.88 |
| 0.013 43 | −53.95 | 0.013 43 | −40.14 | 0.112 73 | −82.19 | 0.112 73 | −45.66 | 0.261 40 | −76.65 | 0.261 40 | −20.01 | 0.870 87 | 30.99 | | |
| 0.016 73 | −56.93 | 0.016 73 | −41.55 | 0.120 98 | −84.12 | 0.120 98 | −45.82 | 0.281 47 | −69.12 | 0.281 47 | −11.06 | 0.931 63 | 22.13 | 0.931 63 | 28.91 |
| 0.020 15 | −58.67 | 0.020 15 | −42.12 | 0.129 76 | −86.35 | 0.129 76 | −46.22 | 0.303 54 | −59.92 | 0.303 54 | −0.92 | | | | |
| 0.023 71 | −59.90 | 0.023 71 | −42.41 | 0.139 10 | −88.51 | 0.139 10 | −46.37 | 0.355 06 | −35.90 | 0.355 06 | 24.23 | | | | |

[a] Data are raw measurements without truncation for uncertainties described in the text.

broken lines represent the phase boundaries between regions I and II. In the two-phase region $H^E$ depends linearly on the component concentration due to the lever rule (*1*), and this linearity is seen in these figures. For a clearer display of the linear behavior of Figure 2, Figure 3 shows the data with different units for $H^E$ and concentration. At the aqueous side, the curved behavior of the single-phase region is also seen more clearly in Figure 3 than in Figure 2. The filled diamonds in the figures denote the lower critical point. The data a and b were measured at temperatures slightly below and slightly above $T_{lcst}$. Hence, the data (a) are for the single-phase region and the data (b) are for the two-phase region there the tie lines are very short. Therefore, at these temperatures the linear dependence of $H^E$ on the concentration in the two-phase region is hardly seen.

The plots in Figure 3 are more symmetric than those in Figure 2. This greater symmetry is useful in determinations of phase boundaries from excess enthalpies with the critical

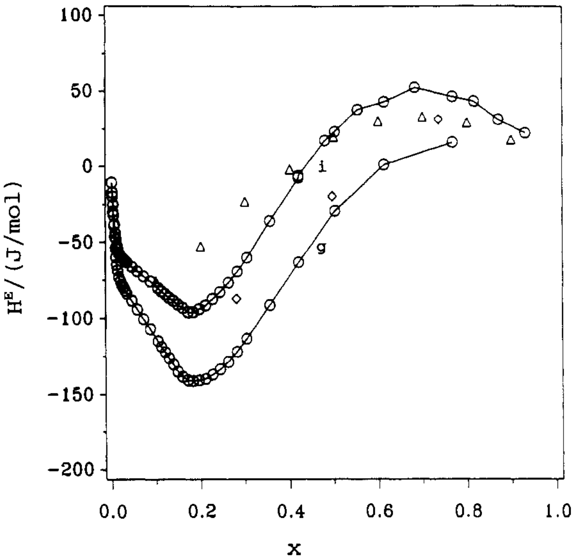

**Figure 4.** Comparison of excess enthalpies: our data (circles) at 60.19 (g) and 65.00 (i) °C; literature values at 60 (diamonds, ref 9) and 65 °C (triangles, ref 10).

**Table 3. Mass Fractions, $w_-$ and $w_+$, of 2-Butoxyethanol at the Phase Boundaries, Determined by Nonlinear Regression of $H^E_w$ to $w$**

| $T$/°C | $w_-$ | $w_+$ | $T$/°C | $w_-$ | $w_+$ |
|---|---|---|---|---|---|
| 50.98 | 0.138 | 0.464 | 60.19 | 0.115 | 0.519 |
| 52.99 | 0.131 | 0.475 | 62.51 | 0.114 | 0.520 |
| 54.97 | 0.128 | 0.487 | 65.00 | 0.115 | 0.523 |
| 57.51 | 0.122 | 0.500 | 70.02 | 0.105 | 0.542 |

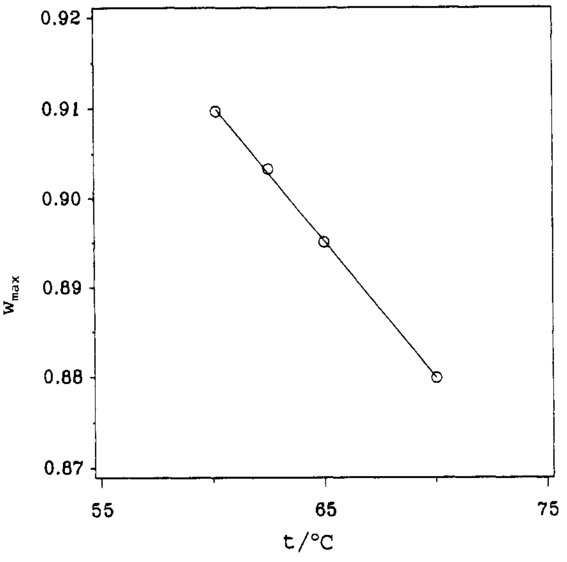

**Figure 5.** Temperature plotted against amphiphile mass fraction, $w_{max}$, at which excess enthalpy has the maximum.

scaling equations (8). The skewness of Figure 2 arises from the large disparity of the components' molecular weights. The molecular weight (118.18) of the amphiphile is 6.5 times that (18.02) of water.

The measured excess enthalpies are compared in Figure 4 to literature values calculated with thermodynamic models for 60 (*10*) and 65 (*11*) °C. At 60 °C these predicted values are larger than our data. At 65 °C they are larger at amphiphile mole fractions below 0.5 and smaller at mole fractions above 0.5. The difference between our data and the predicted values is as large as 20%. When the excess enthalpies are estimated with models, this large discrepancy is usually expected (*3*).

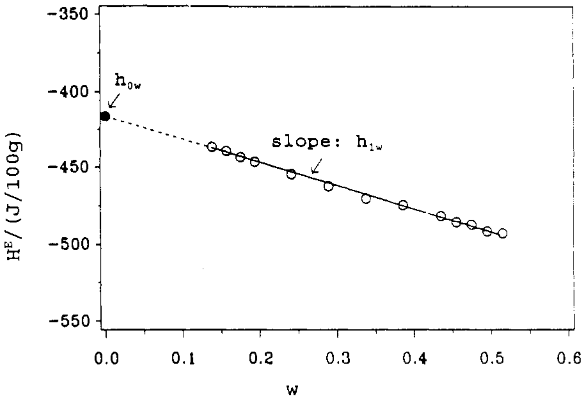

**Figure 6.** An example of linear dependence of $H^E$ on amphiphile concentration. The linear regression of the data yields the intercept, $h_{0w}$, and the slope, $h_{1w}$.

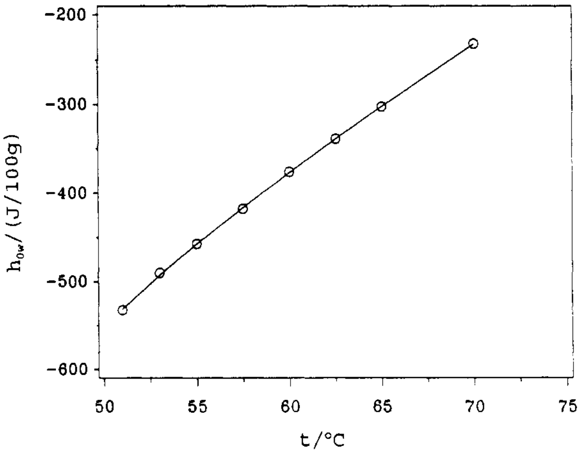

**Figure 7.** Temperature dependence of $h_{0w}$.

At temperatures lower than 57 °C, $H^E$ in the single-phase region decreases and then increases with the amphiphile concentration. The $H^E$ values are negative over the concentration range, indicating that mixing is exothermic. Above this temperature, however, $H^E$ values are positive and have maxima at high concentrations of the amphiphile. Figure 5 shows a plot of temperature vs amphiphile concentration, $w_{max}$, at which the maximum of $H^E$ takes place. The concentration $w_{max}$ decreases linearly with increasing temperature, and the correlation is excellent (correlation coefficient 0.9997).

A typical example (at 54.97 °C) of the linearity of the two-phase data is depicted in Figure 6. The correlation of $H^E$ with the amphiphile mass fraction is excellent (correlation coefficient 0.9983). From a linear regression to the data the slope, $h_{1w}$, and the $y$-intercept, $h_{0w}$, are determined and put into the critical scaling equation of enthalpy for binary mixtures to obtain phase compositions of liquid–liquid equilibria as demonstrated in ref 8.

The $y$-intercept, $h_{0w}$, depends on the temperature and fits the equation (Figure 7)

$$h_{0w}/(\mathrm{J/100\ g}) = -582 + 36.09\,(T - T_{lcst})^{1-\alpha} - 9.26\,(T - T_{lcst})$$

The parameter $h_{0w}$ changes linearly with temperature except at temperatures close to the lower critical solution temperature, $T_{lcst}$. At the latter temperatures the main contribution comes from the energy term, $(T - T_{lcst})^{1-\alpha}$, and therefore $h_{0w}$ shows nonlinear behavior. Here $\alpha$ is a universal exponent from scaling theory; the value of $\alpha$ is 0.11 (*33*).

The slope $h_{1w}$ decreases linearly with temperature according to the following equation (Figure 8)

$$h_{1w}/(\mathrm{J\ g^{-1}}) = -4.16282 - 1.51424(T/°\mathrm{C})$$

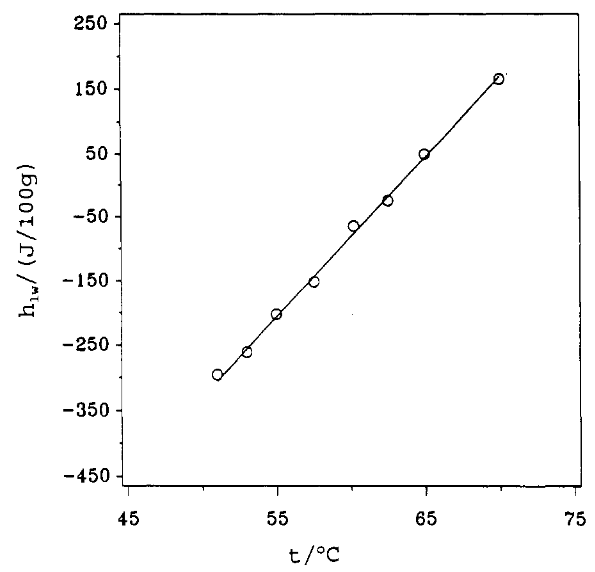

**Figure 8.** Temperature dependence of $h_{1w}$.

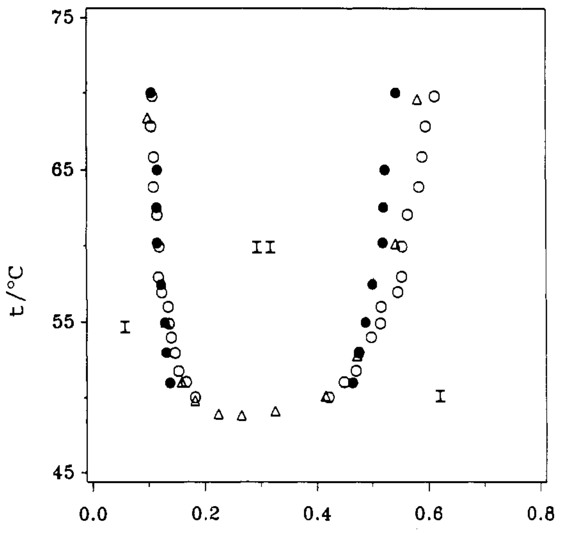

**Figure 9.** Comparison of phase boundary points from different sources: △, ref 21; ○, Table 1; ●, Table 3.

The correlation of $h_{1w}$ with temperature is excellent (correlation coefficient 0.9934). The parameter $h_{1w}$ is related to the chemical potential of the system along the critical isopleth, i.e., along the fixed composition of the lower critical point (*34*). The parameter is predicted to depend smoothly on the temperature (*34*), and the results of Figure 8 show that for the $C_4E_1$ + water system the dependence of $h_{1w}$ on temperature is, in fact, linear.

The phase compositions of the liquid–liquid equilibria for the $C_4E_1$ + water system were determined from the enthalpy data with the following critical scaling equation of $H^E$ for binary mixtures:

$$\pm\left[\frac{H^E_w - h_{0w} - h_{1w}w}{1+(f-1)w}\right]^{1/2} = h_2^{1/2}\left(\frac{fw}{1+(f-1)w} - \frac{fw_\pm}{1+(f-1)w_\pm}\right)$$

Here $H^E_w$ is the measured enthalpy in joules per gram of the mixture, $f$ [the ratio of the activity coefficients of the two components (*8*)] and $h_2$ are fitting parameters, $w$ is the amphiphile mass fraction, and $w_-$ and $w_+$ are the values of $w$ for the two equilibrium phases. From a nonlinear regression of $H^E_w$ to $w$, $w_\pm$ are obtained along with the fitting parameters. Further details on the derivation of the equation and the fitting procedure can be found elsewhere (*8*). The phase compositions, $w_\pm$, thus obtained are listed in Table 3 and plotted along with literature data and the data of Table 1 (obtained by the phase volume method) in Figure 9. The figure shows that the data are in good agreement with one another on the aqueous side, although substantive differences among the various methods exist on the amphiphilic side.

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