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**Phase and Foam Behavior Study of CO₂-Based Foams at
Reservoir Temperature and Pressure**

**Final Report
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Executive Summary

A major objective of the Enhanced Oil Recovery Program at Morgantown Energy Technology Center (METC) is to develop technologies based on CO_2 foams, emulsions, or other fluid dispersions that will alleviate viscous fingering and mobility control problems that severely limit the production of oil by miscible CO_2 flooding. In this project, data on the phase behavior of a model surfactant/water system were generated both to help in modeling work for phase behavior and dispersion morphologies and to provide an efficient experimental methodology for determination of these data from flow calorimetric measurements.

The project consists of two separate but compatible subtasks, the results of which are described in detail in the two parts of the main body of this report.

In Part I, the excess enthalpies, H^E , for mixtures of the nonionic amphiphile 2-butoxyethanol ($\text{C}_4\text{H}_9\text{OC}_2\text{H}_4\text{OH}$) and water were measured by isothermal flow calorimetry at atmospheric pressure and ten temperatures over the temperature range $T - T_{\text{LCST}} = -0.1$ 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.

In Part II, Widom-Kadanoff scaling theory predictions are made for the temperature and composition dependence of excess enthalpies for binary mixtures. The predictions are tested with one- and two-phase heats of mixing (or excess enthalpies) measured by flow calorimetry for the system $\text{C}_4\text{H}_9\text{OC}_2\text{H}_4\text{OH}/\text{H}_2\text{O}$ over the entire composition range and at temperatures from the lower consolute temperature to about 20 kelvins above. Compositions of conjugate phases at each temperature are obtained by solving for points of intersection between fits of the scaling equations to single-phase data and fits of equations for straight lines to two-phase data. The compositions thus obtained are in excellent agreement with literature data. For all but the very highest amphiphile concentrations, the agreement of theory with the data is excellent, when a "new" order parameter is used.

The experimental work on this project was performed in the Chemical Engineering Department at West Virginia University. This project involved the collaboration of the PI's (Drs. Lim and Whiting) with Dr. Duane H. Smith of Morgantown Energy Technology Center and with Dr. Martin Ferer of the Physics Department at West Virginia University.

Part I
**Excess Enthalpies and Liquid-Liquid Equilibrium Phase Compositions
of Binary Mixtures of the Nonionic Amphiphile 2-Butoxyethanol and Water**

Introduction

Heats of mixing or excess enthalpies of binary mixtures of the nonionic amphiphile 2-butoxyethanol, $C_4H_9OC_2H_4OH$, and water around and above the lower critical solution temperature, T_{lcs} , are reported in this article. An excess function is defined as the difference between an actual quantity and the quantity for an ideal mixture at the same conditions. Since the enthalpy change for the ideal mixing is zero, the excess enthalpy and the heat of mixing are identical (1). For this reason these two terms are used interchangeably.

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 in 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 semi-empirical 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 article.

Excess enthalpies for the 2-butoxyethanol/water system have been reported in the literature (10-14). Most of the data were measured at temperatures below T_{lcs} , i.e., in the single-phase region. Only several scattered data points at 60, 80, and 100 °C (10) and at 65 and 85 °C (11) have been reported at temperatures above T_{lcs} . The reported data 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 forty compositions for each of ten temperatures around and above T_{lcs} . The compositions ranged from 0.9 to 98.9 mole percent of the amphiphile.

Various types of calorimeters such as adiabatic batch, isoperibol semi-batch, and isothermal flow calorimeters have been employed for excess enthalpy measurements. Each of these calorimeters has advantages and disadvantages. General descriptions, merits, and comparisons of these calorimeters may be found in a review article (15). A series of measurements at a given temperature was desired for our study, and isothermal flow calorimetry was suitable to meet this end. In this calorimetry there is practically no vapor space in the reaction (mixing) chamber, and this makes measurement errors due to the vapor much reduced.

For comparisons of the phase boundaries determined from the H^E data and

the critical scaling equation, liquid-liquid phase compositions for the 2-butoxyethanol and 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-hexyloxyethoxy)ethanol, $C_6H_{13}(OC_2H_4)_2OH$ (16). In this method samples of different compositions along a tieline 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, 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 tieline, 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, Utah, USA). The main components of the calorimeter are the reaction vessel, isothermal shields, air bath, the isothermal control unit, feed pumps, and flow controller programmer. Fluids were introduced by the pumps and mixed in the reaction vessel, which consisted of the isothermal plate and 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. A desk-top computer controlled the pumps (LC-5000 Precision Pump, ISCO Inc., Lincoln, Nebraska, USA) 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 known compositions were put in a microprocessor-controlled thermostat with viewing windows (Tamson Models 45, Neslab Instruments Inc., Newington, New Hampshire, USA) 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 zero and one, respectively (16) (See Figure 1.)

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 fifteen temperatures around the lower critical solution temperature, T_{lcs} . The critical temperature $T_{lcs} = 48 \pm 1$ °C has been determined by various methods (20-27). For our data of Tables I and III $T_{lcs} = 48.6 \pm 0.4$ and the critical weight fraction $w_c = 0.294 \pm 0.002$ were determined with critical scaling equations as was done for 2-(2-hexyloxyethoxy)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 weight fraction. The measured volume fraction correlates excellently with the amphiphile weight fraction. (The correlation coefficient is 0.9993.) The amphiphile weight fractions, w_u and w_l , of the two equilibrium phases are

Figure 1. Upper-phase volume fraction vs weight fraction of the amphiphile at 53.99 °C. Extrapolation of the linear regression to the volume fractions to zero and one yields the phase boundary points w_- and w_+ , respectively.

determined from the extrapolation of the linear regression to the phase volume fractions of zero and one. The quantities w_1 and w_2 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_1 and w_2 at different temperatures are listed in Table I.

Table I. Weight fractions, w_1 and w_2 , of 2-butoxyethanol at the phase boundaries, determined by the phase volume method.

Temperature (°C)	w_1	w_2
50.03	0.18261	0.42113
51.04	0.16669	0.44844
51.77	0.15288	0.46943
52.97	0.14691	0.47518
53.99	0.14000	0.49765
54.92	0.13604	0.51401
56.02	0.13397	0.51554
56.98	0.12356	0.54515
57.99	0.11758	0.55253
59.95	0.11883	0.55333
62.02	0.11517	0.56297
63.86	0.10855	0.58339
65.84	0.10935	0.58964
67.85	0.10483	0.59583
69.79	0.10709	0.61207

Excess enthalpies, H^E 's, were measured at ten different temperatures from 48.5 to 70 °C. They are shown in Figures 2 and 3 and listed in Table II. 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 the region II is the two-phase region, which is surrounded on each side by the single-phase regions, I. The broken lines represent the phase boundaries between I and II. In the two-phase region H^E depends linearly on the component concentration due to the lever rule; and this linearity is seen in these figures. For 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 and the data b are for the two-phase where the tielines 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-scaling equations (8). The skewness of Figure 2 arises from the large disparity of the components' molecular weights. The molecular weight (118.18 g/mol) of the amphiphile is 6.5 times that (18.08 g/mol, of water).

Table II. Measured dependence of excess enthalpies, H^E , of 2-butoxyethanol/water as a function of x , the mole fraction of the amphiphile.

T = 48.47 °C		T = 48.98 °C		T = 50.98 °C		T = 52.99 °C	
x	H^E (J/mol)	x	H^E (J/mol)	x	H^E (J/mol)	x	H^E (J/mol)
0.00280	-30.83	0.00280	-26.44	0.00139	-14.58	0.00139	-12.88
0.00424	-43.70	0.00424	-40.98	0.00280	-26.32	0.00280	-25.12
0.00570	-57.31	0.00571	-54.07	0.00424	-39.66	0.00424	-36.95
0.00719	-68.83	0.00720	-66.85	0.00571	-51.26	0.00571	-48.57
0.00871	-79.52	0.00871	-78.40	0.00720	-62.49	0.00720	-58.71
0.01025	-89.11	0.01026	-87.79	0.00871	-72.47	0.00871	-68.92
0.01183	-98.38	0.01183	-96.10	0.01026	-81.67	0.01026	-77.24
0.01343	-104.11	0.01344	-102.52	0.01183	-90.08	0.01183	-84.87
0.01673	-113.99	0.01674	-111.35	0.01344	-95.81	0.01344	-89.57
0.02015	-120.93	0.02016	-118.25	0.01674	-104.53	0.01674	-97.23
0.02371	-126.92	0.02373	-123.70	0.02016	-110.64	0.02016	-102.54
0.02742	-131.99	0.02744	-128.25	0.02373	-115.42	0.02373	-106.66
0.03127	-137.23	0.03130	-133.20	0.02744	-119.36	0.02744	-109.88
0.03529	-141.96	0.03532	-137.46	0.03130	-123.51	0.03130	-113.40
0.04613	-154.44	0.04168	-144.20	0.03532	-127.20	0.03532	-116.77
0.05823	-167.12	0.04847	-151.14	0.04616	-136.86	0.04616	-125.58
0.07186	-181.02	0.05574	-158.30	0.05827	-147.77	0.05827	-135.54
0.08729	-194.22	0.06353	-165.62	0.07190	-160.08	0.07190	-146.60
0.10494	-209.13	0.07190	-174.24	0.08735	-172.35	0.08735	-157.77
0.11273	-215.31	0.08093	-182.96	0.10500	-188.36	0.10500	-171.60
0.12098	-220.62	0.09069	-190.96	0.11279	-195.28	0.11279	-177.98
0.12976	-226.53	0.10500	-203.59	0.12105	-200.72	0.12105	-184.04
0.13910	-231.27	0.11279	-209.68	0.12983	-206.38	0.12983	-190.37
0.14906	-236.68	0.12105	-215.53	0.13918	-210.87	0.13918	-194.42
0.15971	-240.62	0.12983	-221.38	0.14915	-215.90	0.14915	-198.74
0.17112	-246.69	0.13918	-226.53	0.15980	-219.60	0.15980	-202.04
0.18338	-250.12	0.14915	-231.90	0.17122	-223.92	0.17122	-206.54
0.19658	-252.81	0.15980	-235.90	0.18348	-226.62	0.18348	-208.95
0.21084	-254.25	0.17122	-241.33	0.19669	-228.77	0.19669	-210.63
0.22629	-254.13	0.18348	-244.67	0.21095	-230.06	0.21095	-211.37
0.24308	-253.33	0.19669	-247.18	0.22641	-229.89	0.22641	-210.66
0.26140	-250.93	0.21095	-248.76	0.24321	-228.63	0.24321	-209.05
0.28147	-246.38	0.22641	-248.83	0.26153	-225.88	0.26153	-205.52
0.30354	-239.54	0.24321	-248.94	0.28161	-221.05	0.28161	-200.29
0.35506	-218.44	0.26153	-246.49	0.30369	-213.98	0.30369	-192.98
0.41947	-189.58	0.28161	-241.84	0.35522	-194.53	0.35522	-172.52
0.47946	-159.43	0.30369	-235.38	0.41964	-164.45	0.41964	-143.07
0.55331	-122.16	0.35522	-215.08	0.47963	-134.88	0.47963	-114.24
0.68317	-46.68	0.41964	-184.52	0.55348	-102.97	0.55348	-84.07
0.81652	-14.01	0.50249	-143.42	0.68332	-59.26	0.68332	-44.43
0.93163	-0.65	0.55348	-120.64	0.81662	-29.51	0.81662	-19.81
		0.61298	-96.76	0.93167	-11.27	0.93167	-6.34
		0.68332	-71.52				
		0.81662	-25.46				
		0.93167	-0.71				

Table II (continued)

T = 54.97 °C		T = 57.51 °C		T = 60.19 °C		T = 62.51 °C	
x	H ^g (J/mol)	x	H ^g (J/mol)	x	H ^g (J/mol)	x	H ^g (J/mol)
0.00139	-12.72	0.00139	-10.42	0.00139	-10.56	0.00139	-9.84
0.00280	-23.61	0.00280	-20.88	0.00280	-19.77	0.00280	-18.43
0.00424	-36.10	0.00424	-31.65	0.00424	-29.50	0.00424	-26.88
0.00571	-46.69	0.00571	-42.11	0.00570	-38.67	0.00570	-35.37
0.00720	-56.42	0.00720	-50.50	0.00719	-46.22	0.00720	-42.64
0.00871	-65.11	0.00872	-58.36	0.00871	-53.44	0.00871	-49.34
0.01026	-72.55	0.01027	-65.56	0.01025	-59.64	0.01026	-54.89
0.01183	-79.49	0.01184	-71.91	0.01183	-64.59	0.01183	-59.12
0.01344	-84.27	0.01345	-76.54	0.01343	-68.21	0.01344	-61.42
0.01674	-90.74	0.01675	-82.55	0.01673	-72.89	0.01673	-66.08
0.02016	-95.07	0.02018	-86.33	0.02015	-75.79	0.02016	-68.14
0.02373	-98.50	0.02374	-89.04	0.02371	-77.95	0.02372	-69.74
0.02744	-101.23	0.02745	-91.23	0.02742	-79.83	0.02743	-71.01
0.03130	-104.28	0.03132	-93.80	0.03127	-81.87	0.03129	-72.71
0.03532	-107.13	0.03534	-96.24	0.03529	-83.81	0.03531	-74.23
0.04616	-114.90	0.04619	-102.88	0.04613	-88.39	0.04615	-78.56
0.05827	-123.59	0.05831	-110.24	0.05823	-94.08	0.05826	-83.25
0.07190	-133.28	0.07195	-118.56	0.07186	-100.48	0.07189	-88.26
0.08735	-143.02	0.08740	-126.97	0.08729	-106.91	0.08733	-93.58
0.10500	-155.31	0.10507	-137.40	0.10494	-114.83	0.10498	-100.33
0.11279	-161.00	0.11286	-142.32	0.11273	-118.62	0.11277	-103.47
0.12105	-166.55	0.12113	-146.85	0.12098	-122.15	0.12103	-106.26
0.12983	-172.78	0.12991	-152.45	0.12976	-126.21	0.12981	-109.73
0.13918	-178.27	0.13926	-157.48	0.13910	-130.20	0.13915	-113.05
0.14915	-182.51	0.14923	-161.60	0.14906	-134.90	0.14912	-116.74
0.15980	-185.17	0.15989	-164.11	0.15971	-138.19	0.15977	-119.48
0.17122	-189.01	0.17132	-166.97	0.17112	-140.35	0.17119	-121.99
0.18348	-191.00	0.18359	-168.32	0.18338	-140.88	0.18345	-121.85
0.19669	-192.27	0.19680	-168.86	0.19658	-140.52	0.19666	-121.01
0.21095	-192.56	0.21107	-168.53	0.21084	-139.65	0.21092	-119.33
0.22641	-191.43	0.22653	-166.79	0.22629	-136.79	0.22637	-116.26
0.24321	-189.32	0.24333	-164.15	0.24308	-133.33	0.24317	-112.24
0.26153	-185.78	0.26167	-160.03	0.26140	-128.47	0.26149	-106.92
0.28161	-180.42	0.28175	-154.07	0.28147	-121.86	0.28156	-100.03
0.30369	-173.01	0.30383	-145.91	0.30354	-113.24	0.30364	-91.48
0.35522	-151.59	0.35537	-123.99	0.35506	-91.28	0.35517	-71.11
0.41964	-122.59	0.41981	-95.32	0.41947	-62.96	0.41959	-40.43
0.47963	-94.94	0.47980	-68.99	0.50232	-29.26	0.47958	-15.66
0.55348	-65.63	0.55365	-40.99	0.61282	0.84	0.55343	7.46
0.68332	-29.80	0.68347	-10.74	0.76762	15.84	0.68327	26.99
0.81662	-10.79	0.81672	1.71			0.81659	25.17
0.93167	-2.68	0.93171	2.79			0.93166	11.70

Table II (continued)

T = 65.00 °C		T = 70.01 °C	
x	H ² (J/mol)	x	H ² (J/mol)
0.00280	-17.01	0.00139	-6.22
0.00424	-24.92	0.00280	-12.55
0.00570	-31.87	0.00424	-18.76
0.00719	-37.85	0.00570	-24.11
0.00871	-43.69	0.00719	-28.96
0.01025	-47.93	0.00871	-32.94
0.01183	-51.52	0.01025	-36.06
0.01343	-53.95	0.01183	-38.42
0.01673	-56.93	0.01343	-40.14
0.02015	-58.67	0.01673	-41.55
0.02371	-59.90	0.02015	-42.12
0.02742	-60.85	0.02371	-42.41
0.03127	-62.02	0.02742	-42.58
0.03529	-63.06	0.03127	-42.81
0.04613	-66.06	0.03529	-42.95
0.05823	-69.05	0.04613	-43.54
0.07186	-72.48	0.05823	-44.03
0.08729	-75.77	0.07186	-44.48
0.10494	-80.17	0.08729	-44.78
0.11273	-82.19	0.10494	-45.39
0.12098	-84.12	0.11273	-45.66
0.12976	-86.35	0.12098	-45.82
0.13910	-88.51	0.12976	-46.22
0.14906	-90.93	0.13910	-46.37
0.15971	-93.17	0.14906	-46.80
0.17112	-95.92	0.15971	-47.01
0.18338	-95.82	0.17112	-47.52
0.19658	-93.90	0.18338	-46.66
0.21084	-91.47	0.19658	-43.36
0.22629	-87.40	0.21084	-39.24
0.24308	-82.75	0.22629	-33.92
0.26140	-76.65	0.24308	-27.61
0.28147	-69.12	0.26140	-20.01
0.30354	-59.92	0.28147	-11.06
0.35506	-35.90	0.30354	-0.92
0.41947	-6.94	0.35506	24.23
0.47946	16.99	0.41947	52.44
0.50232	23.04	0.47946	73.00
0.55331	37.74	0.50232	
0.61282	42.84	0.55331	89.09
0.68317	52.33	0.61282	
0.76762	46.29	0.68317	91.92
0.81652	43.18	0.76762	
0.87087	30.99	0.81652	66.88
0.93163	22.13	0.87087	
		0.93163	28.91

Table III Weight fractions, w , and w_* , of 2-butoxyethanol at the phase boundaries, determined by the phase volume method.

Temperature (°C)	w	w_*
50.98	0.138	0.464
52.99	0.131	0.475
54.97	0.128	0.487
57.51	0.122	0.500
60.19	0.115	0.519
62.51	0.114	0.520
65.00	0.115	0.523
70.02	0.105	0.542

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 per cent. When the excess enthalpies are estimated with models, this large discrepancy is usually expected (3).

At temperatures lower than 57 °C, H^E in the single-phase regions 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 weight 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 reference 8.

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

$$h_{0w} = -582 + 36.09 (T - T_{lcs})^{1-\alpha} - 9.26 (T - T_{lcs}) .$$

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

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

$$h_{1w} (J/g) = -4.16282 - 1.51424 T$$

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.

Figure 2. Excess enthalpy in joules per mole vs. mole fraction of 2-butoxyethanol at temperatures 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 gram of the mixture, and weight fraction of 2-butoxyethanol.

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) .

Figure 5. Plot of temperature vs amphiphile weight fraction, $w_{\max}$, at which excess enthalpy has the maximum.

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} .

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

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:

$$\pm \sqrt{\frac{H_w^E - h_0 w - h_1 w}{1 + (f-1)w}} = \sqrt{H_2} \left(\frac{fw}{1 + (f-1)w} - \frac{fw_i}{1 + (f-1)w_i} \right)$$

Here H_w^E is the measured enthalpy in J per g of the mixture, f [the ratio of the activity coefficients of the two components (8)] and h_i are fitting parameters, w is the amphiphile weight fraction, and w and w_i are the values of w for the two equilibrium phases. From a nonlinear regression of H_w^E to w , w_i 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_i , thus obtained are listed in Table III and plotted along with literature data and the data of Table I (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. Despite these differences our method combining enthalpy and the critical scaling equation yields far better results than other methods used in the past.

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Figure 9. Comparison of phase boundary points from different sources: Δ , ref. 21; o, Table I; and $\bullet$, Table III.

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Part II

Critical-Scaling Theory of Binary Excess Enthalpies and Its Use to Determine Liquid-Liquid Equilibrium Phase Compositions

Introduction

Liquid-liquid equilibria (LLE) long have been central to major technologies such as chemical separations and enhanced oil recovery. The uses of these technologies require a combination of careful measurements of conjugate phase compositions and equations that accurately describe the data.

Phase boundaries can be obtained by a variety of synthetic and analytical methods, some of which also give tielines. However, these measurements are tedious; and few of them give data for the thermodynamic quantities (enthalpies and entropies) that fundamentally control the phase equilibria. Thus, experimental methods that can be automated and that also provide enthalpies and/or entropies are to be greatly preferred. This preference comes not just from the fact that such measurements would provide additional data for fitting, but more fundamentally from the belief that a unified treatment incorporating enthalpy as well as phase compositions should produce a more accurate equation-of-state than that obtained by fitting phase compositions only. Current theories are most severely challenged by liquid-liquid equilibria and by systems that involve polar compounds and strong hydrogen bonding.

In recent years calorimetry has been used to measure the composition dependence of excess enthalpies in binary systems that exhibit vapor-liquid¹ and liquid-liquid equilibria^{1,3}. By the lever rule, in the two-phase regions of such systems the excess enthalpy is simply a linear function of composition; hence, phase boundaries have been obtained by visual inspection of enthalpy data to determine the composition limits for the two-phase linearity.⁴ Thus, these measurements have provided experimental enthalpies as well as phase compositions.

However, in this method the accuracy of the compositions is hampered by problems of determining exactly where the two-phase linearity begins and ends. Furthermore, the data treatments have not used the enthalpies in any thermodynamic model for the phase separation. Both limitations can be traced to the fact that for single-phase excess enthalpies no satisfactory model, which describes the temperature and composition dependence of the enthalpy, seems to exist: Expressions such as the Redlich-Kister and Padé equations provide reasonably accurate fits to the isothermal data,^{2,4,5} but lack theoretical bases and are of little help in attempts to determine phase boundaries more accurately than by visual inspection.⁶ Group contribution, non-random two-liquid (NRTL), and other methods sometimes are able to provide accurate *ad hoc* fits to the temperature dependence of excess enthalpies, but are unreliable for predictions and extensions of temperature dependencies to other chemical systems.^{1,7}

The work described here turns to scaling theory in an attempt to overcome problems caused by the lack of satisfactory equations for single-phase excess enthalpies: Expressions for the excess enthalpy are obtained from Widom-Kadanoff scaling theory.^{8,9} Excess enthalpies are measured by flow calorimetry for the binary system of water and the nonionic amphiphile 2-butoxyethanol ($C_4H_9OC_2H_4OH$) over the entire composition range and at temperatures from the lower consolute solution temperature (T_c) to about 20 °C above T_c .¹⁰ These one- and two-phase data are used to test predictions of the critical scaling theory. Except at very high amphiphile concentrations, the agreement of the theory with the data is excellent, especially when a "new" order parameter is used. Problems of obtaining phase compositions by deciding where the two-phase data deviate from linearity are avoided by solving for the points of intersection between the fits of the scaling equations to the single-phase data and the fits of equations for straight lines to the two-phase data.

Critical-Scaling Equations of Enthalpy for Binary Mixtures

The enthalpy (H) is defined in terms of internal energy (U), pressure (P), and volume (V);

$$H = U + PV \quad (1)$$

The pressure of any system can be written in terms of the partition function, Ξ , of the grand canonical ensemble,

$$P(\mu_1, \mu_2, T) V = kT \ln \Xi, \quad (2)$$

where k is Boltzmann's constant, T is the absolute temperature, and μ_i is the chemical potential of species i . The standard definition of the partition function, Ξ , is

$$\Xi = \text{Tr} (e^{-\beta \hat{H} + \beta \mu_1 N_1 + \beta \mu_2 N_2}), \quad (3)$$

where $\hat{H}$ is the Hamiltonian operator, N_i is the number of molecules of species i , $\beta_T = 1/kT$, and Tr denotes trace. The 'free energy' PV is

$$PV = -U + TS + \mu_1 (N_1 + N_2) + (\mu_2 - \mu_1) N_2, \quad (4)$$

with the differential

$$d(PV) = SdT + PdV + (N_1 + N_2) d\mu_1 + N_2 d(\mu_2 - \mu_1). \quad (5)$$

The chemical potential terms are grouped to more clearly delineate between vapor-liquid equilibria (VLE) where the total density, $(N_1 + N_2)/V$, is greatly different for conjugate phases, and liquid-liquid equilibria (LLE) where the total density is nearly constant but $N_2/(N_1 + N_2)$ differs in conjugate phases.¹¹ The internal energy $U = \langle \hat{H} \rangle$ can be determined from the ensemble average of the Hamiltonian. Then, the enthalpy can be written as a temperature derivative of $P(\mu_1, \mu_2, T)V$. Consider

$$\begin{aligned} T \frac{\partial}{\partial T} P(\mu_1, \mu_2, T) V|_{\beta_T \mu_1, \beta_T \mu_2} &= T \frac{\partial}{\partial T} kT \ln \Xi|_{\beta_T \mu_1, \beta_T \mu_2} \\ &= kT \ln \Xi + kT^2 \frac{\partial \ln \Xi}{\partial T}|_{\beta_T \mu_1, \beta_T \mu_2}, \end{aligned} \quad (6)$$

where the $\beta_T \mu_i$ are held fixed in the differentiation. The first term on the right hand side (RHS) of Eq. (6) is simply PV from Eq. (2) and the second term is the internal energy, U , since

$$\frac{\partial \ln \Xi}{\partial T}|_{\beta_T \mu_1, \beta_T \mu_2} = - \frac{\partial \beta_T}{\partial T} \frac{\text{Tr} (\hat{H} e^{-\beta_T \hat{H} + \beta_T \mu_1 N_1 + \beta_T \mu_2 N_2})}{\Xi} = \frac{1}{kT^2} U \quad (7)$$

Therefore, the RHS of Eq. (6) is equivalent to H , i.e.,

$$T \frac{\partial P(\mu_1, \mu_2 - \mu_1, T) V}{\partial T}|_{\beta_T \mu_1, \beta_T \mu_2} = U + PV = H \quad (8)$$

This expression is convenient when one works with the theory of critical phenomena since this 'free energy', $P(\mu_1, \mu_2 - \mu_1, T) V$, is the one commonly used in critical-scaling theory for LLE in binary systems. For the vicinity of a critical

point, Widom⁸ and Kadanoff⁹ hypothesized that this free energy would take the "scaling" form,¹²

$$P(T, \mu^*) V = Z_b + t^{2-\alpha} Z(z), \quad (9)$$

where

$$z = \frac{\mu^* - M(t)}{t^\Delta}. \quad (10)$$

Here, $\mu^* (= \mu_2 - \mu_1)$ is the chemical potential difference, $t = |T - T_c|/T_c$, and $M(t)$ gives the smooth variation of the chemical potential along the critical isopleth from the single-phase into the two-phase region. The critical exponents α and Δ were subsequently found to have the values $\alpha = 0.11$ and $\Delta = 1.565$ for one- and two-component fluid critical points.¹³ The function Z_b accounts for the background term and is a smooth, analytic function of temperature and chemical potential. The dependence upon μ_1 alone has been suppressed because the total number, $N_1 + N_2$, is held fixed. The critical scaling equation of enthalpy can be obtained by substitution of Eq. (9) into (8).

$$\begin{aligned} H &= T \frac{\partial PV}{\partial T} = \frac{T}{T_c} \frac{\partial PV}{\partial t} \\ &= \frac{T}{T_c} \frac{\partial Z_b}{\partial t} + \frac{T}{T_c} \left[-t^\beta \frac{dM}{dt} \frac{\partial Z}{\partial M} + (2-\alpha) t^{1-\alpha} Z(z) - \Delta t^{1-\alpha} z Z'(z) \right] \end{aligned} \quad (11)$$

Consistent with the symmetric nature of critical scaling theory,^{8,9} $Z(z)$ is an even function of z , i.e.,

$$Z(z) = A_0 + A_2 z^2 + A_4 z^4 + \dots \quad (12)$$

Hence, the quantity $(2-\alpha)Z(z) - \Delta z Z'(z)$ in the third and the fourth terms on the RHS of Eq. (11) becomes

$$\begin{aligned} (2-\alpha)Z(z) - \Delta z Z'(z) &= (2-\alpha)A_0 + (2-\alpha-2\Delta)A_2 z^2 \\ &\quad + (2-\alpha-4\Delta)A_4 z^4 + \dots \end{aligned} \quad (13)$$

The second term on the RHS of Eq. (11) is simply

$$-\frac{T}{T_c} \frac{dM}{dt} \frac{\partial Z}{\partial M} t^\beta = -\frac{T}{T_c} (OP - OP_c) M', \quad (14)$$

because

$$\frac{\partial PV}{\partial \mu^*} = OP(T, \mu^*) = OP_c + \frac{\partial}{\partial \mu^*} (t^{2-\alpha} Z(z)). \quad (15)$$

Hence, from Eqs. (11)-(14) the critical scaling form of the enthalpy is

$$\begin{aligned} \frac{T_c}{T} H &= \frac{\partial Z_b}{\partial t} - (OP - OP_c) M' \\ &\quad + t^{1-\alpha} [(2-\alpha)A_0 + (2-\alpha-2\Delta)A_2 z^2 + (2-\alpha-4\Delta)A_4 z^4 + \dots]. \end{aligned} \quad (17)$$

Use of standard thermodynamic relations allow the determination of scaling forms for other equilibrium thermodynamic properties. For example, the internal energy and the mole fraction are the appropriate derivatives of the free energy density; and the mole fraction (naively related to the order parameter, OP) is given by Eq. (15). Below a lower critical temperature, $Z'(z) \approx z$ near the critical isopleth [$\mu^* \approx M(t)$], so that

$$OP(T, \mu^*) = OP_c + A t^\beta z. \quad (17)$$

Above the lower critical temperature, $Z'(z) = \pm B + Az$ when $\mu^* = M(t) \pm \epsilon$. Hence,

$$OP(T, \mu^*) = OP_c \pm B t^\beta + A t^\beta z + \dots, \quad (18)$$

so that

$$z = \frac{OP - OP_c}{A t^\beta} + \dots, \quad (19)$$

where

$$OP_c = OP_c \pm B t^\beta. \quad (20)$$

By substituting Eq. (19) for z into Eq. (16) we obtain

$$\begin{aligned} \frac{T_c}{T} H = & \frac{\partial Z_b}{\partial t} + (2-\alpha) A_0 t^{1-\alpha} - (OP - OP_c) M' \\ & + \tilde{A}_2 t^{1-2\alpha-2\beta} (OP - OP_c)^2 + \tilde{A}_4 t^{1-2\alpha-4\beta} (OP - OP_c)^4 + \dots \end{aligned} \quad (21)$$

where $\tilde{A}_{2n}$ ($n=1, 2, \dots$) are constants determined from the constants in Eqs. (16) and (19). Because t is small, terms of high order in t are even smaller; hence $T/T_c = 1+t \sim 1$. With higher-order terms neglected $\partial Z_b/\partial t$ is approximated as

$$\frac{\partial Z_b}{\partial t} = (b_{00} + b_{01} t + \dots) + \mu^{*2} (b_{20} + b_{21} t + \dots) + \dots, \quad (22)$$

Then, Eq. (21) can be written as

$$H = h_0 + h_1 OP + h_2 (OP - OP_c)^2 + h_4 (OP - OP_c)^4 + \dots, \quad (23a)$$

where

$$h_0 = \frac{T}{T_c} [b_{00} + b_{01} t + (2-\alpha) A_0 t^{1-\alpha} + OP_c M'(t)], \quad (23b)$$

$$h_1 = \frac{T}{T_c} M'(t), \quad (23c)$$

$$h_2 = B_{20} + \tilde{A}_2 \frac{T}{T_c} t^{1-\alpha-2\beta}, \dots, \quad (23d)$$

$$h_4 = B_{40} + \tilde{A}_4 \frac{T}{T_c} t^{1-\alpha-4\beta}, \quad (23e)$$

with $\beta = 2-\alpha-\Delta = 0.325$.

In the terminology of critical phenomena, the chemical potential approximates the ordering field and a fractional concentration such as mole fraction approximates the order parameter. This critical behavior is basically symmetric in the order parameter, while liquid-liquid equilibria in real fluids show striking asymmetries in the fractional concentration. Because of the corrections to the leading scaling singularities, arising from several sources including the asymmetry, experiments did not convincingly verify these scaling relationships for two-component fluids until the early 1980's,¹⁴ more than ten years after they had been verified for a number of types of critical points in solids. Hindering the general adoption of the correct critical-point power laws is the misperception that these scaling laws only apply very close to the critical point. In actuality, it is known that symmetric systems obey the simplest scaling relations for t as large as 0.1, i.e., $T = T_c \pm 0.1 T_c$; for room temperature transitions ($T_c = 300$ K) this implies that the leading power laws will be obeyed to as much as 30 °C away from the critical point. A successful incorporation of these asymmetries into critical-scaling theory should make the theory accurate for LLE at considerable (i.e., useful) distance from the critical-point.

Several of these lowest order corrections to scaling have been included in the standard form for the miscibility gap widely used in the literature,¹² so that the order parameter should have the temperature dependence

$$OP_t = OP_c + Bt^\beta + Ct^{\beta+\Delta_1} + Dt^{1-\alpha} \quad (24)$$

This expansion includes the energy dependence ($t^{1-\alpha} = t^{0.89}$) which arises from a slight dependence of the temperature-like variable upon chemical potential, as well as the usual first correction to scaling ($t^{\beta+\Delta_1} = t^{0.91}$), in addition to the leading scaling behavior in Eq. (20).

Use of the scaling form of the free energy, Eq. (9), in the expression for the enthalpy, Eq. (8), determines the critical scaling prediction, Eqs. (23), for the enthalpy. In the two-phase region the heat of mixing (or excess enthalpy) should change linearly with OP by the lever rule:

$$H = \bar{H}_1 OP + \bar{H}_2 (1-OP) = \bar{H}_2 + (\bar{H}_1 - \bar{H}_2) OP = h_0 + h_1 OP, \quad (25)$$

where $\bar{H}_1$ and $\bar{H}_2$ are the enthalpies of phase 1 and 2, $h_0 = \bar{H}_2$, $h_1 = \bar{H}_1 - \bar{H}_2$.

For the one-phase region close enough to the miscibility gap, we assume that only the lower-order terms up to the second order in OP contribute. Then we may rewrite Eq. (23a) as

$$\pm \sqrt{H - h_0 - h_1 OP} = \sqrt{h_2} (OP - OP_t) \quad (26)$$

If a plot of the left hand side (LHS) of Eq. (26) vs OP is made, OP_t , which are the phase boundary points, are determined. Note that the coefficient, h_2 , is the same on both sides of the miscibility gap, showing the symmetry of critical scaling theory, and that scaling theory specifies the leading temperature dependence of the coefficients in Eq. (26).

The LHS of Eq. (26) is, in general, not calculated until an OP is decided. It is still a matter of some controversy in the literature whether the weight fraction, w , or mole fraction, x , or volume fraction, v , is the correct order parameter for binary mixtures.¹⁵ The transformation from weight fraction to volume fraction is instructive: If V_i is the molar volume of component i , then the volume fraction $v_i (= v)$ is given by where $f = d_i/d_1$ with d_i being the density of species i . Because the a priori preference for one type of fractional order parameter over another is not justified at present, it is appealing to work with a fractional order parameter of the form in Eq. (27):

$$v = v_1 = \frac{V_1}{V_1 + V_2} = \frac{w_1/d_1}{w_1/d_1 + w_2/d_2} = \frac{w_1 (d_2/d_1)}{1 + (d_2/d_1 - 1) w_1} = \frac{f w}{1 + (f-1) w} \quad (27)$$

$$OP = \frac{f w}{1 + (f-1) w} \quad (28)$$

where f is a fitting parameter. With this choice of the order parameter, it might seem that h_0 and h_1 cannot be determined from the two-phase data, since OP contains the parameter f , which is yet to be determined. Also, it might seem that the LHS of Eq. (26) cannot be calculated, and therefore, OP_i (i.e., the phase boundary points) cannot be determined.

However, one can circumvent these apparent problems in fitting the excess enthalpy data. We fit the data in the two-phase region to the lever rule for the enthalpy per gram, H_w^E :

$$H_w^E = \bar{H}_{1,w} w + \bar{H}_{2,w} (1 - w) = h_{0w} + h_{1w} w \quad (29)$$

where $h_{0w} = \bar{H}_{2,w}$, and $h_{1w} = \bar{H}_{1,w} - \bar{H}_{2,w}$. From the plot of H_w^E vs w the intercept, h_{0w} , and the slope, h_{1w} , are determined. We can convert from H_w^E to the excess enthalpy per unit order parameter, H_{op}^E :

$$H_{op}^E = \frac{H_w^E}{1 + (f-1) w} \quad (30)$$

The lever rule for the weight fraction, Eq. (29), then becomes the lever rule for the OP , Eq. (25):

$$\frac{h_{0w} + h_{1w} w}{1 + (f-1) w} = h_{0w} + \frac{1}{f} (h_{0w} - f h_{0w} + h_{1w}) \frac{f w}{1 + (f-1) w} \quad (31)$$

so that the constants in Eq. (25) are given by $h_0 = h_{0w}$ and $h_1 = (h_{0w} - f h_{0w} + h_{1w})/f$. Using Eqs. (30) and (31) in Eq. (26) we obtain

$$\pm \sqrt{\frac{H_w^E - h_{0w} - h_{1w} w}{1 + (f-1) w}} = \sqrt{H_2} (OP - OP_i) \quad (32)$$

The OP_i are determined from a nonlinear regression of H_w^E to Eq. (32), which has four fitting parameters (f , h_2 , OP_i , and OP).

Results

Figure 1 shows the excess enthalpy data for the 2-butoxyethanol/water system at eight temperatures as reported by Lim et al.¹⁰ The broken line represents the locus of the phase boundary points of the system. Region II is the two-phase region, which is surrounded by the single-phase region, I.

For a fixed temperature the enthalpy in the two-phase region should depend linearly on the concentration according to the lever rule, and the data in Figure 1 clearly show this linear trend. An example of this linear dependence of enthalpy on the amphiphile weight fraction is shown in Figure 2. The data points inside the two-phase region (but not those close to the phase boundary points) were chosen for the regression. The fit was good (correlation coefficient = 0.9974). For each temperature the slope, h_{1w} ($= dH_w^E/dw$), and the y-intercept, h_{0w} ,

Figure 1. Excess enthalpy vs. weight fraction of 2-butoxyethanol at the temperatures 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. The broken curve represents the loci of the phase boundaries; Roman numerals indicate the number of phases and the filled diamond denotes the lower critical point.

Figure 2. Example (at 57.51 °C) of excess enthalpy, H_e^E , vs weight fraction, w , of the amphiphile in the two-phase region. The enthalpy changes linearly with weight fraction (correlation coefficient = 0.9974) yielding the intercept h_{ow} and the slope h_{iw} .

were determined from a linear regression and put into the LHS of Eq. (32) for a nonlinear regression to obtain OP_i along with f .

If $f = 1$, OP becomes simply the weight fraction, w , (Eq. 28) and Eq. (26) or Eq. (32) becomes

$$\pm \sqrt{H_w^E - h_{0w} - h_{1w}w} = \sqrt{h_2} (w - w_i) \quad (33)$$

where w_i are the phase boundary points in weight fraction. If w is a "correct" order parameter, the plot should be a linear plot according to the above equation and w_i can be obtained from a plot of $\pm(H_w^E - h_{0w} - h_{1w}w)^{1/2}$ vs w . An example of such a plot is shown in Figure 3. The two single-phase branches are curved. Furthermore, they do not possess the same slope, as the equation dictates. By forcing the same slope in the branches, w_i are found to be 0.228 and 0.492, and these values do not represent correctly the phase boundary points (0.135 and 0.510 by the phase volume method¹⁰). These results indicate that the weight fraction is not an adequate order parameter. Hence, a new parameter OP , defined by Eq. (28), was used instead.

When the $f \neq 1$ order parameter was used, the excess enthalpy data of Figure 1 were fit by Eq. (32). Since the value of f was not known a priori, nonlinear fits of Eq. (32) to the enthalpy data were done, and f and OP_i were obtained. The value of f was found to be 3.2, and it changed little with temperature. Hence, this value of f was used for fits at different temperatures.

With f known, plots of $\pm[(H_w^E - h_{0w} - h_{1w}w)/(1 + (f-1)w)]^{1/2}$ vs OP are made similarly to Figure 3. An example of such a plot is shown in Figure 4. Here the two x-intercepts, OP_i and OP_j , refer to the aqueous and amphiphilic phase boundary points in OP units. The two branches are linear (correlation coefficient = 0.9992) and were forced to have the same slope, $h_2^{1/2}$, as predicted by Eq. (32). The phase boundary points, OP_i and OP_j , are found to be 0.3270 and 0.7574, or 0.132 and 0.494 in weight fractions, respectively. They are in good agreement with the weight fraction values 0.135 and 0.510 obtained by the phase volume method.¹⁰ Also, the plot is symmetric, as predicted by the theory. For the weight fraction of the amphiphile as the order parameter, such symmetry was broken (Figure 3).

With the values of the parameters, f , OP_i , and h_2 determined, the scaling-theory fits were compared to the experimental data in plots of the form of Figure 1. Figure 5 shows an example of such a comparison at 54.97 °C. The filled circles denoted as w_i and w_j are the phase boundary points determined at this temperature. Eqs. (29) and (32) fit the data well over the whole concentration range, except at the very highest amphiphile concentrations. We have omitted these points in the fits to get the phase boundaries. Discrepancies between the data and the fit at these concentrations might be much reduced, if higher-order terms were used in these equations. However, no attempts were made on this problem, because the region of these concentrations was far away from the phase boundaries and because phase boundary points could be determined precisely enough without fits at these concentrations.

The values of h_0 , h_1 , and h_2 are plotted vs temperature in Figures 6, 7, and 8, respectively. The parameter h_0 fits the equation

$$h_0 = -582 + 36.09 (T - T_c)^{1-\alpha} - 9.26 (T - T_c) ,$$

which keeps the three leading terms of Eq. (23b). Here, $T_c = 48.86$ °C was used, which was determined with the data in Figure 11 and Eq. (24). The main contribution to h_0 comes from the energy term, $(T - T_c)^{1-\alpha}$, and therefore h_0 shows slight nonlinear behavior.

Figure 3. Example (at 54.97 °C) of $\pm(H_w^E - h_{ow} - h_{1w}w)^{1/2}$ vs the weight fraction, w [i.e., $f = 1$ and $OP = w$, Eq. (33)].

Figure 4. Left-hand side of Eq. (32) vs OP [defined in Eq. (28)]; OP_- and OP_+ denote the aqueous and amphiphilic phase boundary points, respectively.

Figure 5. Example of fits of isothermal enthalpy data by Eq. (32) (at 54.97 °C). The two-phase data between the phase boundary points w_1 and w_2 were fit by Eq. (29).

Figure 6

Figure 6. Parameter h_0 vs temperature.

Figure 7. Parameter h_1 vs temperature.

Figure 8. Parameter h_2 vs temperature.

Figure 7 shows, experimentally, that h_1 decreases linearly with temperature. The correlation of h_1 with temperature is excellent (correlation coefficient = 0.9741). Widom¹ hypothesized that $M(t)$ (hence, h_1 through Eq. (23c)) depended smoothly on the temperature; and the results of Figure 7 show that for the 2-butoxyethanol/water system the dependence of h_1 on temperature is, in fact, essentially linear.

The temperature dependence of h_2 is shown in Figure 8. The parameter h_2 changes little at temperatures near T_c . However, as the temperature moves away from T_c , h_2 decreases as

$$h_2 = 10682 - 3596(T - T_c)^{1-\alpha-2\beta}$$

($1-\alpha-2\beta = 0.24$), which represents the two leading terms of Eq. (23d). Near T_c the h_2 values deviate from the curve described by the above equation. This deviation may arise from our neglect of all but the leading terms in Eq. (23a); close to T_c these neglected terms become large, because h_{2n} diverges for $n > 1$.

The phase boundary points, determined as illustrated by Figure 4, are plotted vs the order parameter, OP, in Figure 9 and vs the weight fraction, w , of the amphiphile in Figure 10. The coexistence curve shows better symmetry with OP than with w . The symmetry axes are $w = 0.30$ and $OP = 0.53$, respectively; and the latter is much closer to the mid-point 0.5 of the range.

The phase boundary points obtained from the enthalpy data and Eq. (32) are compared to literature data (obtained by the cloud point^{16,17}, Rayleigh scattering^{18,19} and phase volume^{10,20} methods) in Figure 11. The Figure shows that the data points are in good agreement with one another on the aqueous side, although substantive differences among the various method exists on the amphiphilic side. The solid line represents the best fit to all the data points of the critical scaling equation, Eq. (24), with OP for $f = 3.2$, i.e.,

$$OP_c = \frac{3.2w}{1+2.2w} = 0.54436 \pm 0.11761(T - T_c)^\beta + 0.0014605(T - T_c)$$

where the $t^{1-\alpha}$ and $t^{\beta+\Delta_1}$ terms of Eq. (24) are combined into t because of small difference between the exponents (0.89 and 0.91 vs 1). At 50.98 °C (close to T_c) the solid line deviates slightly from the experimental phase boundary points. This deviation may be due to our neglecting the higher-order terms in Eq. (23a).

Discussion

The enthalpy equation [Eq. (23a)] derived for binary mixtures incorporates the Widom-Kadanoff scaling of free energy and a new order parameter, OP [Eq. (28)]. The equation fit the measured enthalpy for the binary 2-butoxyethanol and water very well, and yielded phase boundary points that were in good agreement with data obtained by different methods. These results are a further confirmation that the basic theory of critical scaling is mature, sound, and well-tested.

The new order parameter worked well for both the excess enthalpies and the coexistence curve. The expression of experimental compositions in terms of OP imposed on the data the symmetry that is inherent in the theory. This order parameter is reminiscent of volume or site fraction in the Flory-Huggins model for polymer solutions,²¹ and order parameters similar to OP are found in various mixture studies.²²⁻²⁴ The value of f in OP was the same for the enthalpy and the coexistence curve, which indicates internal consistency. As shown in the

Figure 9. Phase boundary points in OP units, determined from the enthalpy data with the critical scaling equation, Eq. (32).

Figure 10. Same as in Figure 9, where the OP values at the phase boundary points are converted into the weight fraction by Eq. (28).

Figure 11. Comparison of phase boundary points by different methods; cloud point ($\square$, ref. 16; Δ , ref. 17), Rayleigh scattering ($\diamond$, ref. 18; $\circ$, ref. 19), phase volume ($\circ$, ref. 10), and this study ($\bullet$). The solid line is the best fit of the data points; see text.

Appendix, for a binary system f is equal to the ratio of the activity coefficients of the two components. Hence, the near-constancy of f over a wide range of temperatures and compositions implies a kind of very extended "Henry's law" behavior for the highly polar 2-butoxyethanol/water system.

Prior to this study we found no satisfactory theory for the composition and temperature dependence of enthalpy in the single-phase region, and therefore phase boundaries for liquid-liquid equilibria were not determined correctly. However, the critical-scaling equation of enthalpy has both composition and temperature dependencies. For the composition dependence the equation recovers the lever rule of the two-phase region; and for the single-phase region it contains an even, symmetric function of $|OP-OP_c|$, which is a measure of distance from either side of the phase boundaries. The equation describes excellently the composition dependence of enthalpy at fixed temperatures; see, as an example, Figure 5.

The temperature dependence of enthalpy in the equation [Eq. (23a)] comes naturally from the critical-scaling theory and is represented by h_0 , h_1 , and h_2 , ($j = 1, 2, \dots, n$). The predicted temperature dependencies of h_0 and h_1 (Figure 6 and Figure 7) were in good agreement with the data, and that of h_2 is in reasonable agreement with the data at all temperatures except temperatures close to T_c .

The simple approximation of keeping only the leading terms in Eq. (23a) gives good agreement with data. This agreement may be deceptive, since the higher-order terms having $h_j \sim t^{1-\alpha-2j\beta}$ ($j = 1, 2, \dots, n$) diverges more and more strongly at the critical point as j increases. Hence, they may have to be included close to the critical point. Therefore, deviations of h_2 at temperatures close to T_c can be expected, as is seen in Figure 8, for the three temperatures closest to T_c .

For determination of phase boundaries from enthalpy data, two approaches were used in the past: semi-empirical polynomials,⁶ and thermodynamic local-composition models.^{1,7}

In the first approach one fits enthalpy data in the single-phase region by Padé or Redlich-Kister polynomials,^{2,4,5} and seeks intersections of these polynomials with the straight line of the two-phase region. Although these polynomials appeared to fit the single-phase data well the intersections were unsatisfactory or did not even exist. For the 2-butoxyethanol/water system, either only one intersection was obtained or when two intersections were found, one of them did not represent the phase boundary point correctly.⁶

In the second approach^{1,7} enthalpy data at various temperatures in the single-phase region were fit by a local-composition model of enthalpy, and the temperature dependence of enthalpy was determined. By means of the Gibbs-Helmholtz identity enthalpy was integrated with respect to temperature to obtain the excess Gibbs free energy, and then the phase boundary points were obtained from the isoactivity condition. In this approach enthalpy data in the two-phase region may not be needed for the determination of the phase boundary points. This method works well for vapor-liquid equilibria (VLE),^{1,25-27} but not satisfactorily for liquid-liquid equilibria,¹ as Rowley and Battler pointed out in their treatment of the methanol/hexane system.⁷

Our method, which combines enthalpy measurements and critical-scaling theory, appears to have several advantages over previous methods. Most importantly, this new method yields significantly more accurate coexistence curves than other methods.⁶ Furthermore, the critical-scaling equation of enthalpy has fewer fitting parameters than the polynomials and local-composition models have. When two-phase data are available, Eq. (32) has four fitting parameters (f , h_2 , OP_c , and OP_c). However, polynomials or local-composition models usually need five or more fitting parameters. Also, the enthalpy equation is based on a rigorous physical theory, and therefore should give new insights to mixture phenomena.

Appendix

We show here that the condition that f is a constant for a binary system is equivalent to the condition that the ratio of the activity coefficients of the two components is constant. We have shown experimentally for the 2-butoxyethanol/water system that f is nearly constant over a wide range of temperatures and compositions. Hence (it follows), the system obey Henry's law for all but the very highest amphiphile concentration.

Consider the variable ζ_i , defined by

$$\zeta_i = \frac{e^{(\mu_i^* - \mu_i)/RT}}{\sum_j e^{(\mu_j^* - \mu_j)/RT}} \quad (A1)$$

Here μ_i is the chemical potential, μ_i^* is the standard state chemical potential of component i , and R is the gas constant.

The chemical activity, a_i , for the component i is defined by

$$\mu_i - \mu_i^* = -RT \ln a_i \quad (A2)$$

and substitution of Eq. (A2) into (A1) yields

$$\zeta_i = \frac{a_i}{\sum_j a_j} \quad (A3)$$

The variable ζ_i is analogous to the more common composition variables weight- and mole-fraction; hence, it may be termed the (chemical) activity fraction. It has some very convenient properties.^{22,28} Its values are always in the range $0 \leq \zeta_i \leq 1$; they are identical for conjugate phases and it is easy to formulate a thermodynamic potential in terms of the activity fraction that is consistent with Henry's law. The variable ζ_i is a field variable¹¹ in binary systems, and can be a hidden variable in systems of three components.²³ We have traced the appearances of ζ in the literature (almost always in a rather disguised form) to as early as van der Waals, who used it in the form of the excluded volume in his cubic equation of state.²⁴

We define the activity coefficient, γ_i , in the usual way,

$$a_i = \gamma_i x_i \quad (A4)$$

where $\gamma_i = \gamma_i(x_i)$ is a function of concentration, specifying only that the concentration variable, x_i , should be a conventional fraction concentration such as weight or mole fraction. Then the conversions back and forth between ζ and other fractional concentrations have the same form as conversions among conventional fractional concentrations [Eq. (27)]:

$$\zeta_i = \frac{f x_i}{1 + (f-1) x_i} \quad (\text{A5})$$

This can be shown as follows: Substitution of (A4) into (A3) gives

$$\zeta_i = \frac{\gamma_i x_i}{\sum_j \gamma_j x_j} \quad (\text{A6})$$

For the binary system $i/1$, substitution of $x_1 = 1 - x_i$ into (A6) gives

$$\zeta_i = \frac{(\gamma_i/\gamma_1) x_i}{1 + [(\gamma_i/\gamma_1) - 1] x_i} \quad (\text{A7})$$

and substitution of

$$f = \frac{\gamma_i}{\gamma_1} \quad (\text{A8})$$

into (A8) yields (A5). Then substitution of $\zeta_i = OP$ into (A5) gives Eq. (28):

$$OP = \frac{f x_i}{1 + (f-1) x_i}$$

However, the implications of the constancy of f are somewhat more subtle for conversions to fractional activities than for conversion between weight fractions and mole fraction or volume fractions: For the conversion to weight fractions, f is constant simply because the ratio of the molecular weights is constant; for the conversion to volume fractions f is nearly constant when the ratio of the densities is approximately constant. For the conversion to ζ , a constant f shows that the ratio of the activity coefficients is essentially constant. For liquid-liquid equilibria in ternaries, the condition of constant f leads to the condition that projections of the tielines all meet at a common point.²³

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