Temperature dependence of liquid/liquid and liquid/gas interfacial tensions in binary liquid mixtures with a miscibility gap: Study of the system 2-butoxyethanol/water in the vicinity of its lower critical point

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Abstract
Experimental data obtained with a 2-butoxyethanol/water mixture are used to present current concepts used to describe the temperature dependence of liquid/liquid and liquid/gas interfacial tension of binary liquid mixtures with a miscibility gap.

1. Introduction

It is the aim of this contribution to present current concepts used to describe the temperature dependence of liquid/liquid and liquid/gas interfacial tensions in binary liquid mixtures with a miscibility gap based on experimental data obtained with the system 2-butoxyethanol (abbreviated by C_4E_1)/water in the vicinity of its lower critical point.

2. Liquid/liquid interfacial tension

A homogeneous mixture of C_4E_1 and water (index, $\beta\gamma$) of critical composition is prepared. Its temperature is raised to approach its lower critical temperature. At T_c the mixture reaches a point of marginal thermodynamic stability. When the temperature is increased further ($T > T_c$) it is brought into the thermodynamic instable region of its phase diagram and separates into two coexisting liquid phases of different compositions (index, β; index, γ; $\rho_\beta < \rho_\gamma$; ρ, density). The interfacial tension between the two liquids is measured as function of temperature using the pendant drop method. This method appears to be the method of choice for this type of measurements because the results are not influenced by wetting phenomena at solid/liquid interphases. The experimental set up and details of the experimental procedures used to obtain the data discussed here are described in [1]. The value of the interfacial tension $\sigma_{\beta,\gamma}$ between the liquid phases coexisting at a certain temperature ($T > T_c$) is obtained from the shape of the liquid/liquid contour line of a drop of phase γ pending from the tip of a hypodermic needle positioned within phase β. From the shape factor of the contour line determined with an image processing system the value of the square of the capillary length $a_{\beta,\gamma}$ ($a^2_{\beta,\gamma} = 2 \sigma_{\beta,\gamma}/(\Delta\rho\ g)$); $\Delta\rho = \rho_\gamma - \rho_\beta$; g, standard acceleration of free fall) is obtained. When the difference of the density $\Delta\rho$ of the coexisting phases is known as function of $|T-T_c|$ from independent measurements the value of $\sigma_{\beta,\gamma}$ can be calculated.

It is well established [2][3][4] that close to the critical temperature (i. e. lim $T \rightarrow T_c$) the temperature dependence of the liquid/liquid interfacial tension $\sigma_{\beta,\gamma}$ of binary liquid mixtures (as well as one-component fluids) can be represented by a power law of the form:

$$\sigma_{\beta,\gamma} = \sigma_o\ t^{\,\mu} \qquad\qquad (1)$$

t is the reduced temperature ($t = |(T - T_c)/T_c|$). It is assumed that the critical exponent μ has the universal value calculated on the basis of the renormalization group theory ($\mu = 1.26$) [5][6] [7]. σ_o is the system specific critical amplitude.

According to eq. (1) $\sigma_{\beta,\gamma}$ converges to zero at the critical temperature. The values of μ found experimentally for binary liquid mixtures (and for one-component fluids) are consistent with the predictions of the theory. The critical amplitude σ_0 of binary mixtures of low molar mass components has values in the range 5 mN m^{-1} < σ_0 < 140 mN m^{-1} [2][3][4].

The two-scale-factor universality introduced by Stauffer et al. [8] asserts that the singular part of the free energy of a volume element of size ξ^3 (ξ is the correlation length of local concentration fluctuations which diverges approaching the critical T_c, i. e. $\xi = \xi_0 \mid t \mid^{-\nu}$; universal value, $\nu = 0.630$) is a finite quantity which is universal for all binary liquid mixtures (and one-component fluids). The authors predict that separate universal ratios exist for σ_0 and ξ_0 and for σ_0 and the critical amplitude $A_{0,v}$ of the heat capacity at constant pressure per unit volume. The critical amplitude ratios $R_{\sigma,\xi}$ and $R_{A,\sigma}$ are expressed by eqs. (2) and (3) [2].

$$R_{\sigma,\xi} = [\sigma_0(\xi_0^+)^2]/(k_B T_c) \qquad (2)$$
$$R_{A,\sigma} = [(A_0^+ \rho_c N_L)/(M\,R)]^{2/3} [k_B T_c/\sigma_0] \quad (3)$$

M is the mean molar mass of the mixture and R the universal gas constant. k_B is the Boltzmann constant and N_L the Avogadro number. A_0^+ is the system specific critical amplitude of the molar heat capacity at constant pressure $C_{P,m}$ (i. e. $C_{P,m}/R = A_0^+ \mid t \mid^{-\alpha}$, $\alpha = 0.11$) in the homogeneous phase (index, +). ξ_0^+ is the corresponding system specific critical amplitude correlation length of local composition fluctuations in the homogeneous phase.

$R_{\sigma,\xi}$ and $R_{A,\sigma}$ are expected to have universal values for binary liquid mixtures (and for one-component systems)[9]. The literature has been reviewed in this respect with the conclusion that the available experimental data for one- and two-component systems are consistent with the two-scale-factor universality. The theoretical value of $R_{\sigma,\xi}$ based on Monte-Carlo simulation ($R_{\sigma,\xi} = 0.36 \pm 0.01$; [10]) is close to the median value of $R_{\sigma,\xi}$ calculated from experimental data (median $R_{\sigma,\xi}$ (exp) = 0.386[2][3][4]). The same is true for the theoretical value of $R_{A,\sigma}$ (= 0.75 $\pm$0.03) [11] which is close to the median value of $R_{A,\sigma}$ calculated from the experimental data (median $R_{A,\sigma}$ (exp) = 0.77)) [2][3][4].

The existence of the two amplitude ratios is very useful from an experimental point of view. The two-scale-factor universality can be used to estimate the values of the critical amplitude σ_0 for phase separated binary liquid metallic systems for which it is difficult to measure $\sigma(|T-T_c|)$ directly (e. g. binary alloys [12]).

3. Liquid/gas interfacial tension

A situation is considered in which a homogeneous C_4E_1/water mixture (index $\beta\gamma$) of critical composition is in equilibrium with a gaseous phase (index α). The gaseous phase is formed by air in equilibrium with the liquid mixture. At the lower critical temperature of the mixture the condensed phase becomes critical (point of marginal thermodynamic stability, liquid/liquid critical interphase at $T_c + \delta T$). But the vapour phase remains non-critical (non-critical interfaces, α,β and α,γ; see Fig. 1). Presently, studies of the temperature dependence of $(\sigma_{\alpha,\beta} - \sigma_c)$, $(\sigma_{\alpha,\gamma} - \sigma_c)$ and $(\sigma_{\alpha,\beta\gamma} - \sigma_c)$ approaching the critical temperature as well as of the difference of interfacial tensions $(\sigma_{\alpha,\beta} - \sigma_{\alpha,\gamma})$ (or $\sigma_{\alpha,\gamma} - \sigma_{\alpha,\beta}$) are of considerable interest [7][13]. σ_c is the interfacial tension at the critical temperature (lim T$\rightarrow$T$_c$, $\sigma_{\alpha,\beta\gamma} = \sigma_{\alpha,\beta} = \sigma_{\alpha,\gamma} = \sigma_c$). The experimental determination of the singular contributions $(\sigma_{i,j} - \sigma_c)$ is difficult because they are small compared with the non-singular background contributions. The same is true for the determination of the difference $(\sigma_{\alpha,\beta} - \sigma_{\alpha,\gamma})$ (or $\sigma_{\alpha,\gamma} - \sigma_{\alpha,\beta}$) as function of temperature. Usually the difference $(\sigma_{\alpha,\beta} - \sigma_{\alpha,\gamma})$ (or $\sigma_{\alpha,\gamma} - \sigma_{\alpha,\beta}$) is small.
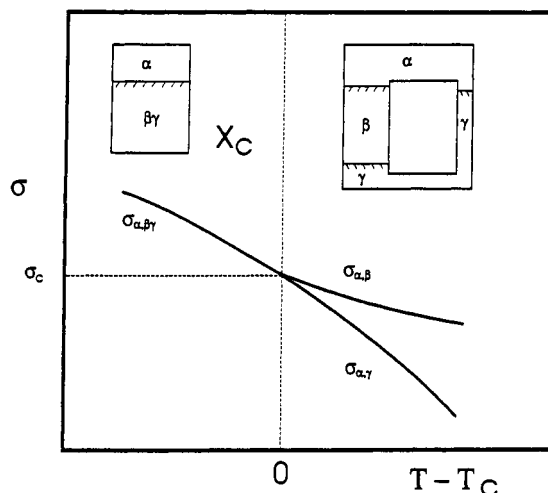
Fig. 1: Theoretically expected temperature dependence of the liquid/gas interfacial tension σ of a binary liquid mixture of critical composition in the vicinity of its lower critical point. T_c the critical temperature. α is the gas phase and ($\beta\gamma$) the homogeneous binary mixture at temperatures below the crititical temperature. At temperatures above T_c two liquid phases β and γ coexist.
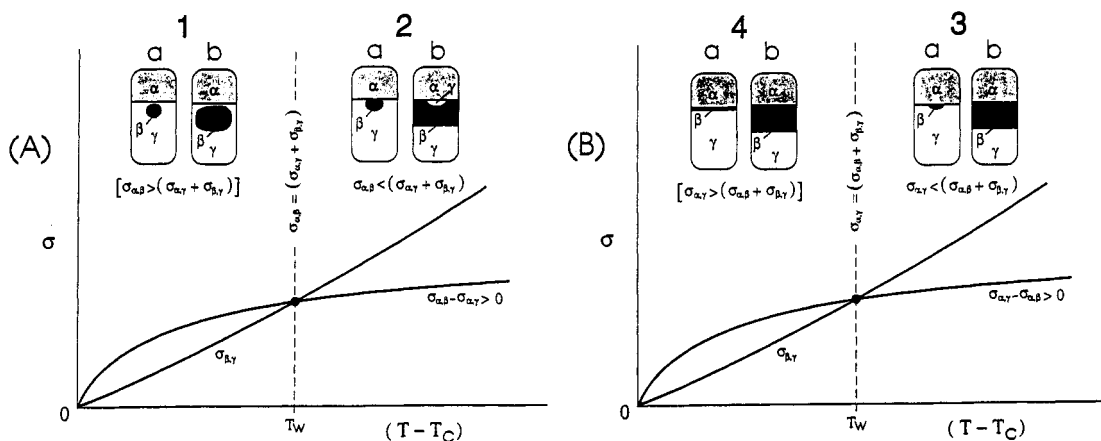

Fig. 2: Schematic presentation of transitions from partial wetting with three phases (gas, two liquid phases) in equilibrium at a line of mutual contact to complete wetting near a lower critical point. With complete wetting the line of mutual contact of the three phases in equilibrium is absent. T_w is the wetting temperature and T_c the critical temperature. σ is the interfacial tension. α marks the gas phase and β and γ the two coexisting liquid phases. Figure 2A refers to a system in which at temperatures $T > T_w$ the inequality $\sigma_{\alpha,\beta} < (\sigma_{\alpha,\gamma} + \sigma_{\beta,\gamma})$ holds. Figure 2B refers to a system in which the inequality $\sigma_{\alpha,\gamma} < (\sigma_{\alpha,\beta} + \sigma_{\beta,\gamma})$ holds for $T > T_w$. In the Figures (a) the volume of phase β is small compared this that of phase γ. In Figures (b) the volumes of the phases β and γ have about the same value. Wetting transitions can occur if the critical exponent β_1 characterizing the temperature dependence of $(\sigma_{\alpha,\beta} - \sigma_{\alpha,\gamma})$ (i. e. $(\sigma_{\alpha,\beta} - \sigma_{\alpha,\gamma}) \sim (T - T_c)^{\beta_1}$) is smaller than the critical exponent μ characterizing the temperature dependence of $\sigma_{\beta,\gamma}$ (i. e. $\sigma_{\beta,\gamma} \sim (T - T_c)^{\mu}$; $\mu > \beta_1$).

The theoretically expected variation of $(\sigma_{i,j} - \sigma_c)$ with temperature for a mixture of critical composition near its lower critical temperatures is shown schematically in Fig. 1. Following arguments given by Gomez et al. [14][15][16] the three $\sigma_{\alpha,\beta}$ (T), $\sigma_{\alpha,\gamma}$ (T) and $\sigma_{\alpha,\beta\gamma}$(T) curves have a common tangent near T_c and deviate from it proportionally to $|T - T_c|^\mu$ (see eqs. (4) - (6)). In the vicinity of the critical point the temperature dependence of $\sigma_{\beta,\gamma}$ is given by eq. (1).

$$\sigma_{\alpha,\beta} - \sigma_c = A \cdot (T - T_c) + C_0 \cdot (|T - T_c|)^\mu \qquad (4)$$

$$\sigma_{\alpha,\gamma} - \sigma_c = A \cdot (T - T_c) + C_1 \cdot (|T - T_c|)^\mu \qquad (5)$$

$$\sigma_{\alpha,\beta\gamma} - \sigma_c = A \cdot (T - T_c) + C_2 \cdot (|T - T_c|)^\mu \qquad (6)$$

It is predicted that the critical amplitudes σ_0, C_0, C_1, and C_2 obey universal ratios (e. g. $C_2/C_1 = -0.83$) [17]. Furthermore it is predicted [18][19] that in a finite temperature range $T_c < T \leq T_w$ (T_w is called wetting temperature) eq. (7) holds (Antonow's rule [20]).

$$\sigma_{\alpha,\beta} = \sigma_{\alpha,\gamma} + \sigma_{\beta,\gamma} \qquad (7)$$

Here it is assumed that the system has a lower critical point for which away from T_c the inequality $\sigma_{\alpha,\beta} < (\sigma_{\alpha,\gamma} + \sigma_{\beta,\gamma})$ holds. At the wetting temperature, Neumann's triangle [20] formed by the three interfacial tensions $\sigma_{\alpha,\beta}$, $\sigma_{\alpha,\gamma}$, and $\sigma_{\beta,\gamma}$ degenerates to a line: The altitude of the triangle, measured from the vertex of the triangle opposite to its longest side (in eq. 7: $\sigma_{\alpha,\beta}$) vanishes. At T_w phase γ begins spread at the interphase α,β and wets the interface α,γ completely. At temperatures $T > T_w$ phase γ wets the interphase α,γ only partially. Figure 2 shows schematically the changes taking place at T_w for two types of systems. They differ in their interfacial properties at temperatures away from the critical temperature. Figure 2A refers to: $\sigma_{\alpha,\beta} < (\sigma_{\alpha,\gamma} + \sigma_{\beta,\gamma})$ (e. g. C_4E_1/water) and Fig. 2B to: $\sigma_{\alpha,\gamma} < (\sigma_{\alpha,\beta} + \sigma_{\beta,\gamma})$ (e. g. methanol, (water)/cyclohexane; upper critical point [21][22][23][24]).

Experimental results of measurements of the interfacial tensions $\sigma_{\alpha,\beta}$, $\sigma_{\alpha,\gamma}$ and $\sigma_{\alpha,\beta\gamma}$ in a C_4E_1/water mixture of critical composition ($x_c = 0.0598$, mole fraction of C_4E_1; $T_c = 49.395$ °C) as function of temperature are shown in Fig. 3 [25]. The data are obtained by analyzing the contour line of a gas bubble attached to the tip of a hypodermic needle pointing upward (inverted pendant drop method). The bubble is positioned within phase β and phase γ respectively. The temperature dependence of the interfacial tensions shown in Fig. 3a are in qualitative agreement with the theoretical predictions shown schematically in Fig. 1. Similar results are reported in the literature for another system [26][27]. It turns out that the interfacial tension $\sigma_{\alpha,\beta}$ between the C_4E_1 rich phase β and its vapour phase α is larger than the interfacial tension $\sigma_{\alpha,\gamma}$ of the water rich phase γ and its vapour phase α. The same conclusion has been drawn from elipsometric measurements in the system C_4E_1/ aqueous NaCl solution by Hirtz et al. [28]. The difference between $\sigma_{\alpha,\beta}$ and $\sigma_{\alpha,\gamma}$ is small. This can be expected for an aqueous solution of a component which is the first member of a homologous series on non-ionic tensides of the type C_iE_j. The $\sigma_{\alpha,\beta\gamma}$ versus composition curve of the system C_4E_1/water at ambient temperatures exhibits a plateau region at compositions $x > 0.02$ [29]. The question whether in the system C_4E_1/water there exists a transition from partial wetting to complete wetting of the interphase α,γ cannot be answered on the basis of the interfacial tension measurements. If a wetting temperature T_w does exist the temperature difference $(T_w - T_c)$ must be small (estimated $(T_w - T_c) < 1$ K). For experimental reasons reliable $\sigma_{\alpha,\beta}$ and $\sigma_{\alpha,\gamma}$ data cannot be obtained in this temperature range with the inverted drop method.

A search for this wetting transition in the system C_4E_1/water is based on a method used first systematically by Kahlweit et al. [22][30]. This method allows to determine the sign of

the difference of interfacial tensions ($\sigma_{\alpha,\beta} - \sigma_{\alpha,\gamma}$) in three phase equilibrium α,β,γ at a given temperature from microscopic observations of the shape (contour line) of drops of phase β at the interface α,γ. At temperatures $(T - T_c) > 1K$ the contour line of the drops of phase β at the interface α,γ of the system C_4E_1/water observed in cylindrical sealed vials (internal diameter 25 mm, height 40 mm) corresponded to that shown in Fig. 2A, position 2a. The contact angle Θ_γ (angle between the line representing the interface α,γ and the curved line representing the interface β,γ extending across phase γ) has a value smaller than 90° (i. e. $(\sigma_{\alpha,\beta} - \sigma_{\alpha,\gamma}) > 0$). Caused by the convex curvature of the interface α,γ the droplets of the phase β which have a lower density than phase γ were moved along the
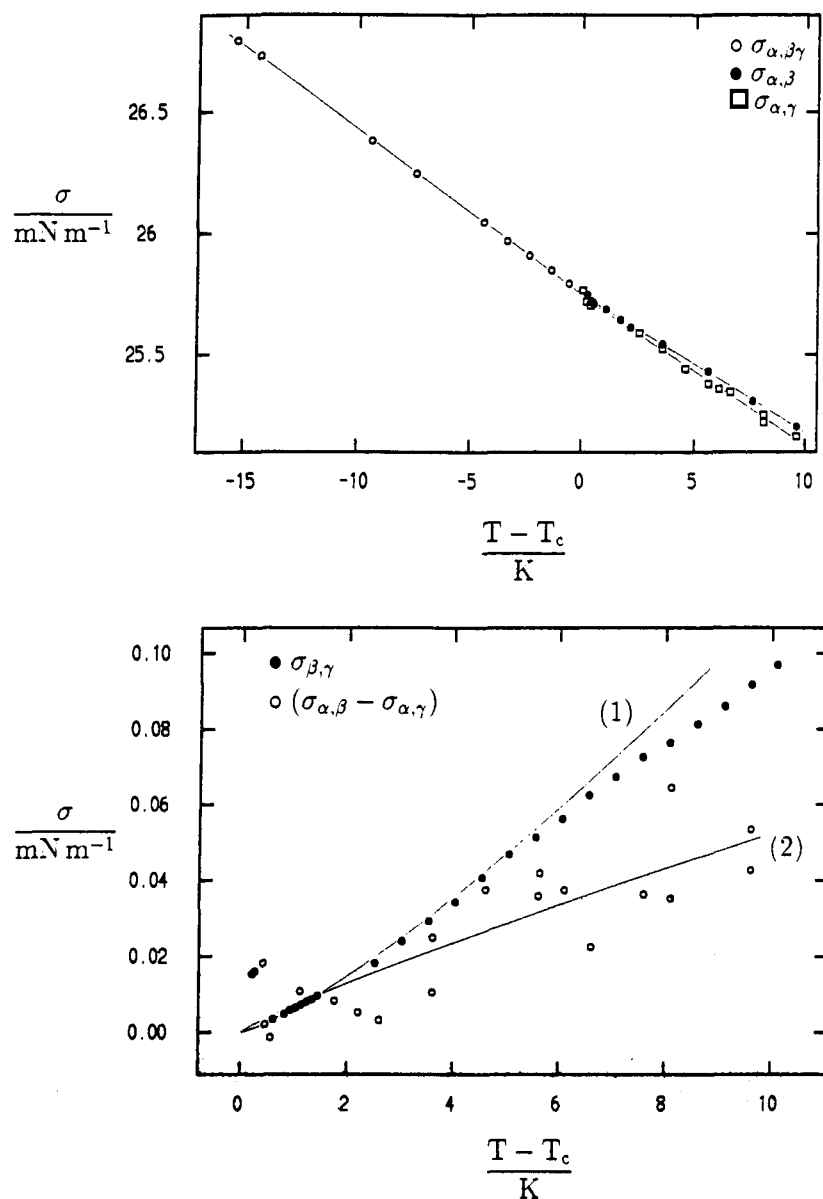

Fig. 3: Plots of the experimentally determined interfacial tensions $\sigma_{\alpha,\beta\gamma}$, $\sigma_{\alpha,\beta}$, and $\sigma_{\alpha,\gamma}$ of a C_4E_1/water mixture of critical composition as function of the temperature difference $(T - T_c)$. The drawn out lines in Fig. 3b represent the function $\sigma_{\beta,\gamma} = \sigma_0 [(T-T_c)/T_c]^\mu$ with $\sigma_0 = (8.7 \pm 0.5)$ mN m^{-1}, $\mu = 1.26$ (fixed) and $T = 322.545.K$ (fixed) (curve 1) and $(\sigma_{\alpha,\beta} - \sigma_{\alpha,\gamma}) = \sigma_{0,\Delta}[(T - T_c)/T_c]^{\beta_1}$ with $\sigma_{0,\Delta} = (1.2 \pm 0.2)$ mN m^{-1} and $\beta_1 = (0.9 \pm 0.2)$ (curve 2). The experimental $\sigma_{\alpha,\beta}$ and $\sigma_{\alpha,\gamma}$ data are compiled in Table 1.

interface driven by buoyancy forces until they reached the point of three phase contact α,γ glass. Decreasing the temperature difference $(T - T_c)$ (but still $(T-T_c) > 1K$) resulted in a decrease of the thickness of drops of the phase β of equal volume and an increase of three phase contour line α,β,γ. The value of the contact angle Θ_γ continued to have a value smaller than 90°. These findings are in agreement with the experimentally determined interfacial tension data shown in Fig. 3b: the difference $(\sigma_{\alpha,\beta} - \sigma_{\alpha,\gamma})$ has a positive value.

TABLE 1. Experimental data of the interfacial tension $\sigma_{\alpha,\beta}$ and $\sigma_{\alpha,\gamma}$ of the system C_4E_1/water at different temperature differences $(T - T_c)$. $\delta\sigma = \pm 0.005$

$(T-T_c)/K$	$\sigma_{\alpha,\beta}/mN\ m^{-1}$	$(T-T_c)/K$	$\sigma_{\alpha,\gamma}/mN\ m^{-1}$
0.255	25.75	0.055	25.77
0.455	25.75	0.205	25.72
0.555	25.71	0.405	25.70
1.105	25.69	2.605	25.59
1.755	25.64	3.605	25.52
2.205	25.61	4.605	25.44
3.605	25.54	5.631	25.38
5.605	25.43	6.105	25.36
7.605	25.31	6.605	25.35
9.605	25.20	8.105	25.25
		9.605	25.16

There are indications that close to T_c a wetting transition from partial wetting of the α,γ interphase by phase γ to complete wetting could exist. They come from observations of characteristic changes of the buoyancy driven movement of droplets of phase β along the α,γ interface formed by a gas bubble attached to the tip of the hypodermic needle (inverted "pendent drop") positioned within phase γ (densities $\rho_\beta < \rho_\gamma$). The droplets originate from a small amount of phase β adhering to the outer surface of the hypodermic needle. At temperatures in the range $1.5\ K < (T - T_c) < 9.6\ K$ the droplets of phase β move along the α,γ interface in the direction of the apex of the gas bubble remain attached to the interface after reaching it. At temperatures in the range $0.05 < (T- T_c) < 0.7\ K$ the droplets of phase β remain attached to the α,γ interface only for a short distance of migration starting from the line of three phase contact at the tip of the needle. Soon they detach from the α,γ interface and raise through phase γ driven the buoyancy force. These observations can be interpreted as a hint that close to T_c $((T -T_c) < 1K)$ the interface α,β is completely wetted by phase γ (see Fig. 2, position 1a).

A more detailed analysis of the properties of the non-critical gaseous/liquid interfaces of the system C_4E_1/water cannot be carried out by measurements of the interfacial tensions alone. Other techniques (e. g. grazing incident X-ray, neutron scattering [34], and ellipsometry [35]) have to be used to probe the concentration profiles of the components of the mixtures close to non-critical interfaces.

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