

The Pressure Dependence of the Phase Diagram t-Butanol/Water

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The phase diagram t-butanol/water is studied in the temperature range between 200 and 450 K at pressures up to 200 MPa. No liquid/liquid phase separation is observed in this range. The solid/liquid phase diagram reveals the presence of a stable t-butanol/dihydrate at all pressures. At the t-butanol rich side of the diagram solid mixtures with compositions t-butanol/water ~ 5:1 and ~ 6:1 are observed.

The binary system t-butanol/water exhibits all thermodynamic properties ascribed to hydrophobic hydration and interaction in a very pronounced way and has been used in numerous experimental investigations [1–9] and in MD-simulations as a model system for these effects [10, 11].

Though the thermodynamic parameters appear to well characterize the hydrophobic effects at ambient pressure and around room temperature, it is still a matter of controversy whether application of hydrostatic pressure enhances or weakens the interaction [12, 13]. This controversy could be settled by a thorough analysis of the spin lattice relaxation rates of the various nuclei in t-butanol/water-mixtures as functions of temperature and pressure.

These studies can only be performed if the liquid/solid boundaries in the pertaining phase diagrams are known. In the literature there exist only two contradictory phase diagrams for this system at ambient pressure [14, 15]. It was therefore decided to redetermine this part of the phase diagram and to extend the experiments to pressures of 200 MPa.

Light scattering studies of liquid t-butanol/water solutions [2, 3] revealed pronounced anomalies at temperatures around 350 K, which were interpreted as the beginning of liquid/liquid phase separation unobservable at ambient pressure because of evaporation of the liquid phase. It was therefore necessary to search for a liquid/liquid phase separation in the whole p, T -range accessible to the NMR-studies. In this analysis it appeared helpful to in-

crease the potential miscibility gap by the addition of small amounts of potassium chloride.

Experimental

Substances: t-butanol (2-methyl-propanol-2) was obtained from E. Merck (Darmstadt). It was dried over molecular sieve 3 Å, redistilled and finally stored over fresh molecular sieve. In order to control the moisture content, the melting of the stock substance was determined prior to use (T_M : 298.65 K). Triply distilled water and potassium chloride p.a. (E. Merck) were used without further purification.

The solid/liquid region of the phase diagram was determined in a twin high pressure DTA cell mashed from a copper beryllium alloy. The details of the cell and the experimental procedures have been published previously [16]. Weighed and premixed quantities of both liquids were put with a syringe into the brass bellows and the bellows were sealed immediately after the filling.

The liquid/liquid phase separation was studied in a small glass capillary of the Yamada-type [17].

Results

1. Liquid/liquid phase separation

A general discussion of high pressure liquid/liquid phase separation and a phenomenological classification of the various possibilities has been given in the literature [18, 19].

The binary systems t-butanol/H₂O and t-butanol/D₂O remained completely miscible in the tempera-

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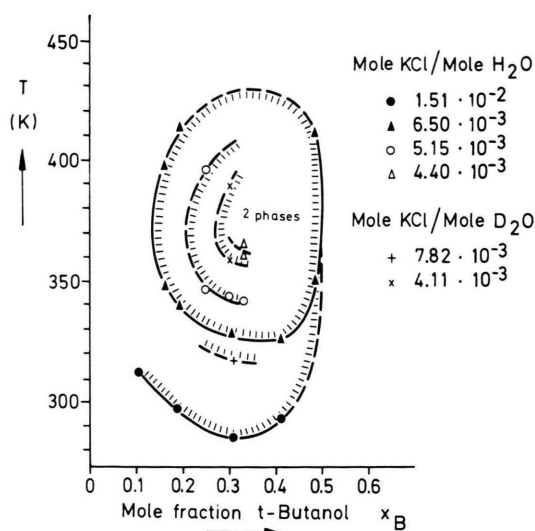


Fig. 1. Liquid/liquid phase separation in the ternary system t-butanol/water/KCl at vapour pressure.

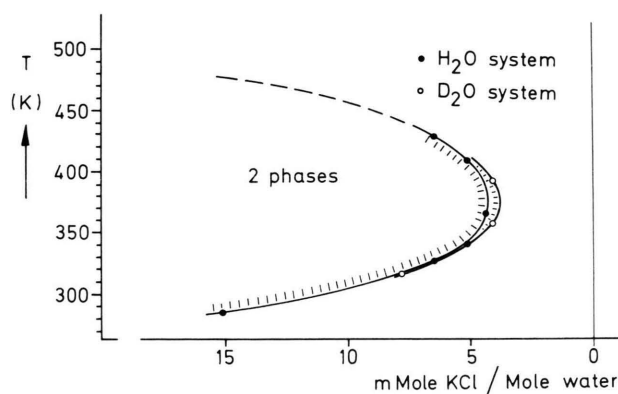


Fig. 2. Liquid/liquid phase separation in the ternary system t-butanol/water/KCl at $x_B = 0.31$ at vapour pressure.

ture range between the liquidus curves and 450 K at pressures up to 200 MPa.

Addition of small amounts of potassium chloride produced a phase separation at saturation pressure. The results are contained in Figure 1.

Figure 2 presents the data at a constant mole fraction of t-butanol ($x_B = 0.31$) in light and heavy water. These curves enclose approximately the largest extension of the solubility loop.

In order to learn about the influence, application of pressure has upon the solubility loop, some mixtures were studied as function of pressure.

Figure 3 shows two typical curves. It is obvious that pressure reduces the size of the solubility loop,

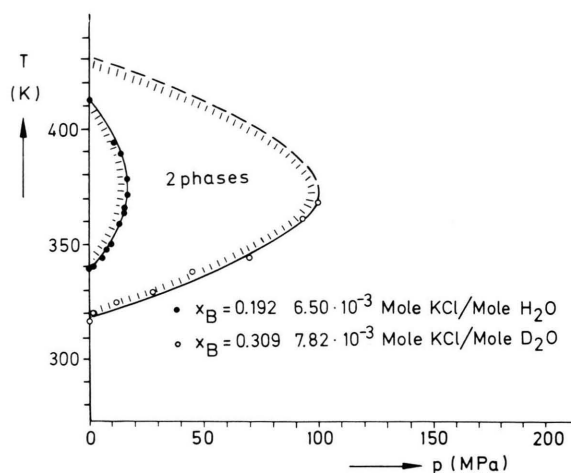


Fig. 3. Pressure dependence of liquid/liquid phase separation in the ternary system t-butanol/water/KCl.

and one can see from the data that up to a pressure of at least 500 MPa no high pressure demixing will occur in the binary system.

2. The solid/liquid phase diagram

At atmospheric pressure two controversial sets of data exist in the literature [14, 15]. They are compiled together with our data in Figure 4. Table 1 gives the ambient pressure values of the various invariant transitions, together with the physical descriptions offered by the two groups and us. Analysis of the DTA-traces is complicated by the fact that the binary system shows the tendency to produce metastable solid phases.

The broken lines in the diagrams represent the transitions that are considered metastable by the various groups. However, these assignments are by no means certain since even numerous repetitions of the DTA-experiment with one sample at a fixed pressure produced absolutely at random either transitions that fit the broken or the solid lines. This was especially pronounced at the t-butanol rich side of the phase diagram. Attempts to temper the solid phases by keeping the samples overnight and up to 48 hours a few degrees below the eutectic temperatures or at 190 K also did not remove these ambiguities. At the t-butanol rich side of the phase diagrams either the group of signals belonging to broken lines or those belonging to the solid lines did appear.

Table 1.

	Rosso	Zaugol'nikova	this work
Transition A			
Temperature	267.2 K	267 K	266.4 ± 0.7 K
Explanation	incongruent melting of t-butanol trihydrate		
Comment	stable	metastable	stable (?)
Transition B			
Temperature	263.6 K	263.8 K	262.6 ± 0.6 K
Explanation	Eutectic dihydrate/water	Peritectic of water rich hydrate	Eutectic dihydrate/water
Comment	metastable	stable	metastable (?)
Transition b			
Temperature	265 K	264.8 K	not observed
Explanation	Eutectic trihydrate/water	Peritectic of water rich hydrate	
Comment	stable	stable	
Transition C			
Temperature	not observed	260.0 K	260.5 ± 0.5 K
Explanation		Eutectic of two water rich hydrates	Eutectic trihydrate/water
Comment		stable	stable (?)
Transition D			
Temperature	269.9 K	268.9 K	268.5 ± 0.6 K
Explanation	Eutectic dihydrate/t-butanol	Eutectic dihydrate/t-butanol	Eutectic dihydrate/solid phase comp.: H_2O : t-but. $\approx 1:6$
Comment	stable	stable	stable (?)
Transition E			
Temperature	not observed		267.6 ± 0.7 K
Explanation			Eutectic dihydrate/solid phase comp.: H_2O : t-but. $\approx 1:5$
Comment			metastable (?)
Transition F			
Temperature	not observed		263.8 ± 1 K
Explanation			Solid/solid transition
Comment			metastable

Our data deviate significantly from both previous data sets especially for high t-butanol contents. It must, however, be stated that the other groups concentrated their experimental effort mainly on the water rich side of the phase diagram. Furthermore

some of the transitions that appear not clearly resolved (for instance D'' and E'') in the ambient pressure data, can be very well distinguished in the high pressure region (cf. Figs. 5 and 6). The pressure dependences of the invariant temperatures A'' to F'' are compiled in Table 2.

In order to assign the various groups of signals as unbiasedly as possible to the phase boundaries, all DTA signals were fed into a computer and tested by various criteria for similarity. Details of this assignment procedure are given in [20] and are available upon request.

The pressure dependence of the composition of the four eutectics observed in the phase diagrams is given in Figure 7. It appears remarkable that only the eutectic connected with the transition C'' does not change its composition with pressure, while the composition of all other eutectics varies significantly with pressure.

Discussion

For the liquid phase of the t-butanol/water system it could be shown that it is completely miscible in the whole range of the liquid phase at saturation pressure. Pilot studies of the ternary system t-butanol/water/potassium chloride exclude also the possibility of high pressure demixing for the binary phase at pressures below at least 500 MPa. The study of the liquid/solid phase boundary and the comparison with data published for ambient pressure reveal discrepancies between the three sets of data (cf. Fig. 4) that were claimed to have been resolved by the studies of Zaugol'nikova et al [15]. The data presented here cast considerable doubt upon this claim, since it appears impossible to decide, which of the transitions observed are stable resp. metastable. Attempts to temper the probes for periods of up to 48 h at ambient as well as high pressure did not lead to an unequivocal assignment. In order to settle this open question it appears necessary to study repeatedly the structure of solid probes while tempering them for periods of months. It seems especially interesting to perform such spectroscopic or diffraction studies in the water rich region of the phase diagram, since here the very strong anomaly of the phase diagram around $x_B \approx 0.067$ appears to indicate the presence of a hydrate with a t-butanol/water ratio of approx. 1:14.

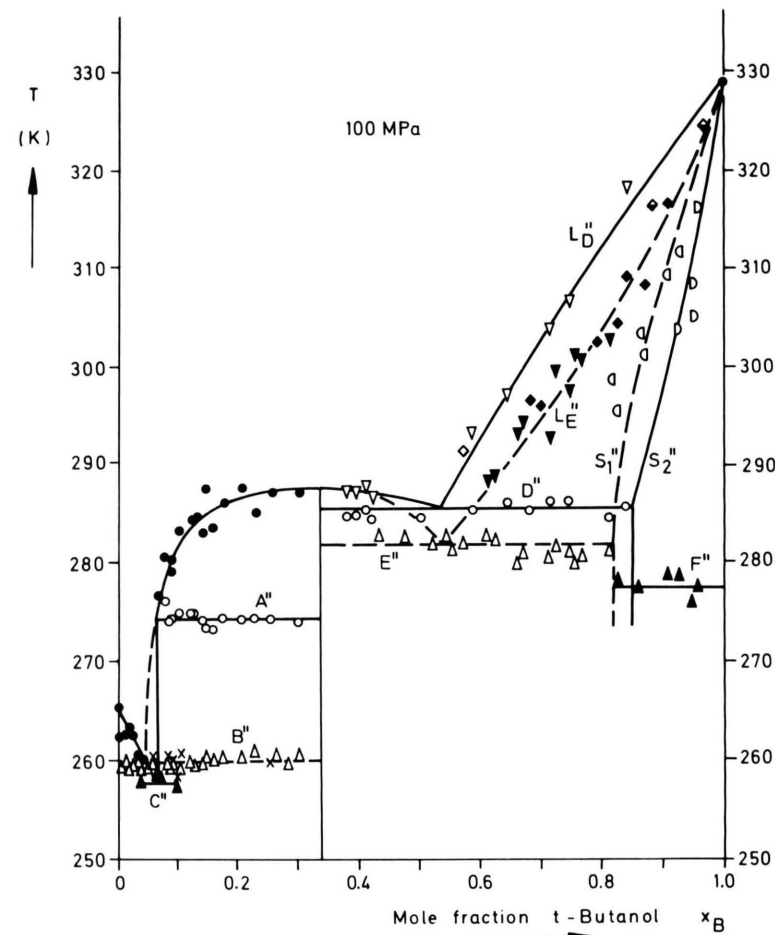
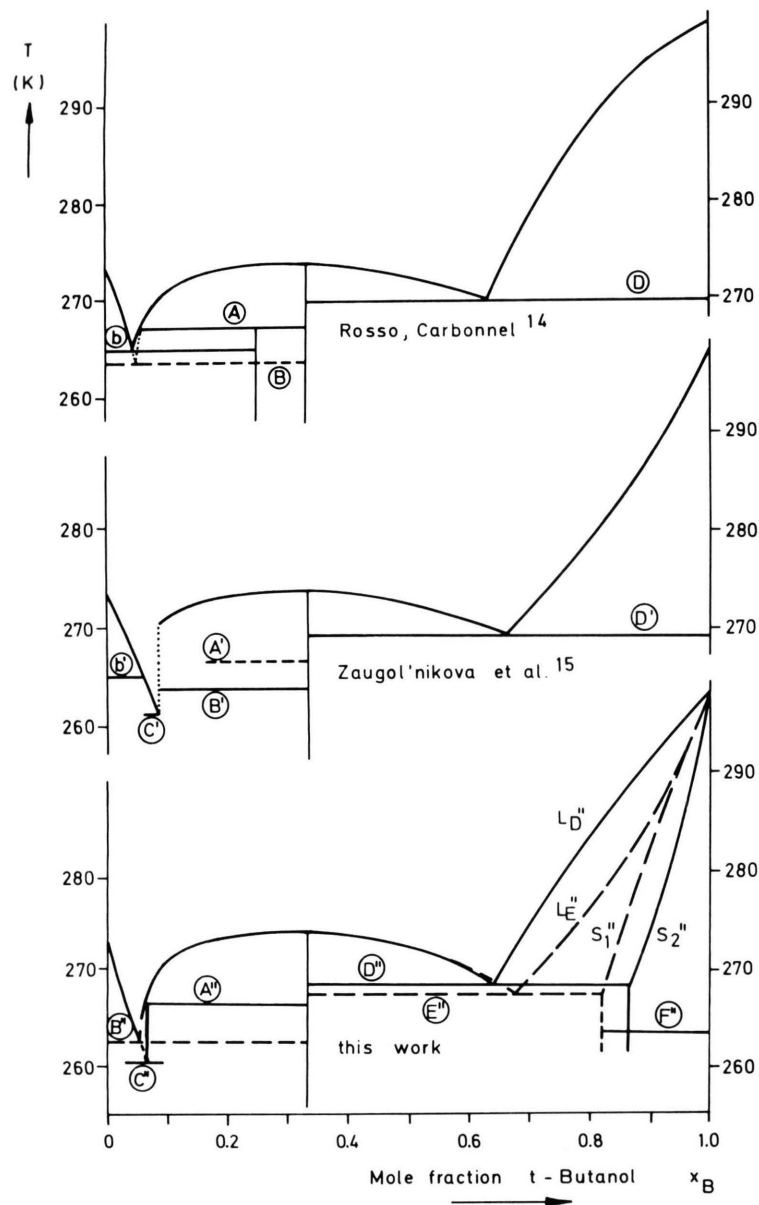


Fig. 5. Phase diagram of the binary system t-butanol/water at 100 MPa.

Fig. 4. Comparison of the ambient pressure phase diagrams for the system t-butanol/water. Solid lines: Transitions considered stable. Broken lines: Transitions considered metastable.

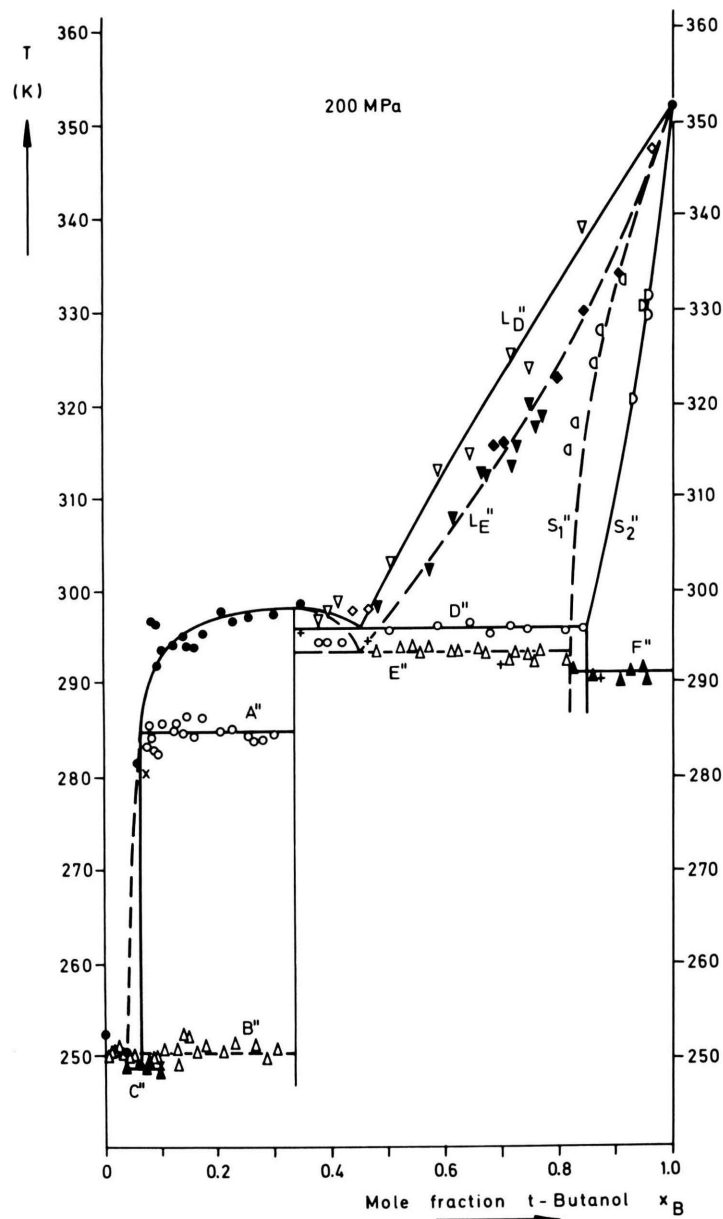
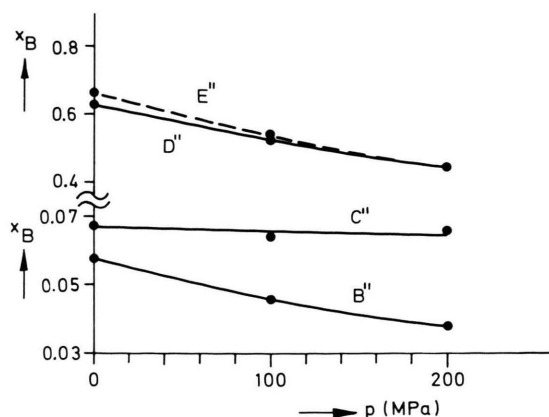


Table 2. Description of the pressure dependence of the various invariant transition temperatures and the melting pressure of the pure substances and the dihydrate by polynomials of the form $T_{tr}(p) = T_0 + AP + BP^2$.

Compound	Phase transition	Pressure Range	T_0 K	A (MPa ⁻¹ ·K)	B (10 ⁻⁴ MPa ⁻² ·K)	RMSD (K)
H ₂ O	melting	0.1–200	273.2	–0.0542	–2.437	0.15
t-butanol	melting	0.1–225	298.7	0.3465	–4.006	0.7
dihydrate	melting	0.1–200	273.9	0.1444	–1.236	0.49
A	incongruent melting of trihydrate	0.1–200	266.4	+0.0662	+1.339	0.73
B	Eutectic dihydrate/water	0.1–200	262.6	+0.0022	–3.125	0.56
C	Eutectic trihydrate/water	0.1–200	260.5	–0.0004	–2.868	0.38
D	Eutectic dihydrate/solid phase: H ₂ O: t-but. ≈ 1:6	0.1–200	268.5	+0.1997	–3.129	0.59
E	Eutectic dihydrate/solid phase: H ₂ O: t-but. ≈ 1:5	0.1–200	267.2	+0.1559	–1.348	0.73
F	solid/solid trans.	0.1–200	263.8	+0.1367	–0.006	1.08

Fig. 6. Phase diagram of the binary system t-butanol/water at 200 MPa.



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Fig. 7. Pressure dependence of the composition of the four eutectics in the phase diagram t-butanol/water.

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