

## SURFACE AND INTERFACIAL TENSIONS ALONG THE BINODAL CURVE IN THE *tert*-BUTYL METHYL ETHER–WATER–ALCOHOL TERNARY SYSTEMS AT 25 °C

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*Dedicated to Professor Eudovít Treindl on the occasion of his 70th birthday.*

The surface tensions, interfacial tensions, and densities of conjugate solutions of compositions lying in the miscibility gap were measured for three ternary systems, *viz.* *tert*-butyl methyl ether–water–ethanol, *tert*-butyl methyl ether–water–*tert*-butyl alcohol, and *tert*-butyl methyl ether–water–butan-1-ol, at 25 °C.

**Key words:** Interfacial tension; Surface tension; Density; Ternary systems; Phase equilibria.

Interfacial and surface tensions are important characteristics of the two-phase systems as they influence many physico-chemical processes. From the data for ternary systems found in literature<sup>1–17</sup> only several authors<sup>1,2,4,12,17</sup> report both, the values of the surface tensions of conjugated solutions and the interfacial tensions between them – an information important to engineers in the design of liquid–liquid contact operations.

In order to contribute to the knowledge of interfacial and surface phenomena in three-component two-phase systems, the present paper reports interfacial and surface tension values as well as the density values at 25 °C for three systems, *viz.* *tert*-butyl methyl ether–water–ethanol (denoted M–W–E), *tert*-butyl methyl ether–water–*tert*-butyl alcohol (denoted M–W–*t*B), and *tert*-butyl methyl ether–water–butan-1-ol (denoted M–W–B), very important from the industrial point of view (*e.g.* problems connected with industrial regeneration of solvents).

## EXPERIMENTAL

### Chemicals

*tert*-Butyl methyl ether was supplied by the Research Institute of Rubber, Kralupy nad Vltavou. It was dried using the 5A molecular sieve. The other chemicals, *i.e.* butan-1-ol and *tert*-butyl alcohol of analytical grade and ethanol for UV spectroscopy were supplied by Lachema Brno. *tert*-Butyl alcohol was purified by fractional crystallization. Butan-1-ol and ethanol were dried using the 4A molecular sieve and rectified on a 60-plate bubble cap column Jena, Germany. The water content in ethyl alcohol was determined by Fischer method and was taken into account when calculating the equilibrium phases composition. The purity of all chemicals was checked by measuring the normal boiling points, refraction indices at 20 °C, and densities at 25 °C. The observed results were in very good agreement with those in literature<sup>18</sup>. Redistilled water was used in all experiments.

### Methods of Measurement

The liquid-liquid equilibria determinations were performed in the same way as described previously<sup>19,20</sup>. All the measurements were carried out at  $25 \pm 0.05$  °C in conditions of equilibrium solute distribution between the two phases.

The measurements of the interfacial tensions between two phases in equilibrium were performed by the capillary rise method and the drop-volume method, surface tension of organic phases was measured by a capillary tensiometer, for the aqueous phases the drop-volume method was found to suit better. Densities of conjugate phases were measured using a Paar DMA-45 densimeter. All these techniques were described in previous communication<sup>17</sup>.

## RESULTS AND DISCUSSION

Phase diagrams for the systems under study are shown in Figs 1–3. The tie lines chosen for study in each system are numbered in the diagrams; the tie line “0” is located at the base of each diagram (*i.e.* no alcohol added). Figures 1 and 2 show the ternary equilibrium diagrams for the systems M–W–E and M–W–*t*B, respectively, with only one pair of partially miscible components (*i.e.* M–W). The diagram of M–W–B system (Fig. 3) differs from the first two, as two pairs of components, *i.e.* M–W and B–W, are partially miscible and the heterogeneous region has no critical point.

The compositions of the conjugate phases given as the molar fractions of the respective alcohol  $x_E$ ,  $x_{tB}$ , or  $x_B$  as given by the compositions at the ends of the tie, the surface tensions and densities of aqueous phases,  $\gamma^{aq}$  and  $\rho^{aq}$ , the surface tensions and densities of organic phases,  $\gamma^{org}$  and  $\rho^{org}$ , and the interfacial tensions between them,  $\gamma^{it}$ , are presented in Tables I–III.

To describe the relationship between the interfacial or surface tensions and the concentration of a solute, *i.e.* ethanol, *tert*-butyl alcohol, or butan-1-ol for the systems M–W–E, M–W–*t*B, and M–W–B, respectively, var-

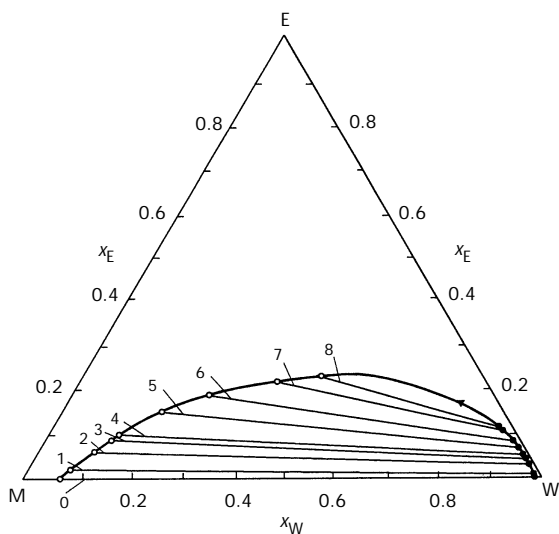


FIG. 1

Phase diagrams for M-W-E system at 25 °C: ○ aqueous phase, ● organic phase, ▼ critical point; — binodal curve, — tie lines

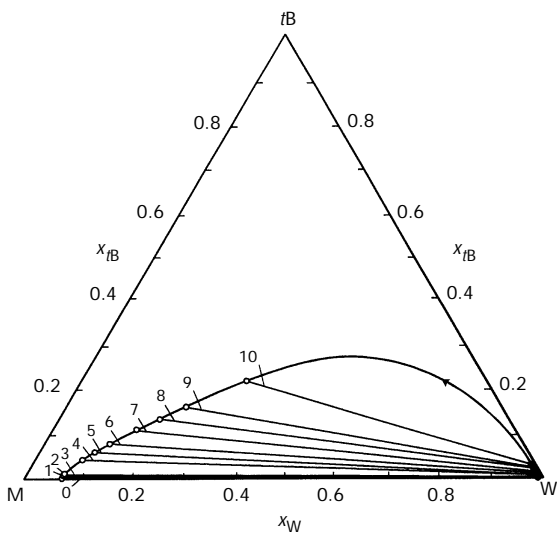


FIG. 2

Phase diagrams for M-W-tB system at 25 °C: ○ aqueous phase, ● organic phase, ▼ critical point; — binodal curve, — tie lines

TABLE I  
M-W-E system at 25 °C

Tie line No.	Aqueous phase				Organic phase				$\gamma^{it}$ mN m <sup>-1</sup>
	$x_W^{aq}$	$x_E^{aq}$	$\rho^{aq}$ g cm <sup>-3</sup>	$\gamma^{aq}$ mN m <sup>-1</sup>	$x_W^{org}$	$x_E^{org}$	$\rho^{org}$ g cm <sup>-3</sup>	$\gamma^{org}$ mN m <sup>-1</sup>	
0	0.9911	0	0.9903	52.53	0.0660	0	0.7401	18.19	10.3
1	0.9784	0.0103	0.9850	47.26	0.0772	0.0228	0.7416	18.32	8.8
2	0.9613	0.0262	0.9791	41.82	0.1000	0.0615	0.7446	18.85	7.0
3	0.9476	0.0410	0.9745	39.23	0.1252	0.0866	0.7476	19.46	5.6
4	0.9402	0.0490	0.9724	35.94	0.1369	0.1000	0.7502	19.86	4.5
5	0.9203	0.0661	0.9666	31.12	0.1868	0.1526	0.7570	20.18	3.3
6	0.9020	0.0820	0.9602	28.17	0.2570	0.1876	0.7675	20.25	1.8
7	0.8724	0.1048	0.9501	27.10	0.3759	0.2164	0.7853	20.61	0.5
8	0.8633	0.1128	0.9468	26.80	0.4510	0.2301	0.7912	20.93	-
Crit. point	0.7623	0.1652	-	-	0.7623	0.1652	-	-	-

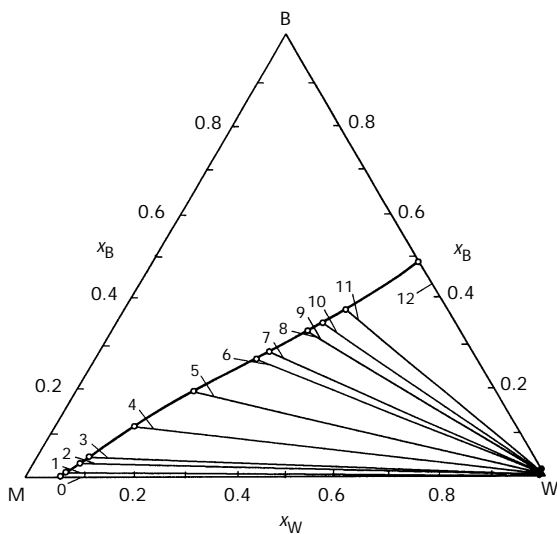


FIG. 3

Phase diagrams for M-W-B system at 25 °C: ○ aqueous phase, ● organic phase; — binodal curve, — tie lines

ious ways reported in literature<sup>4,12,14-17,21-29</sup> have been considered. The best fit was achieved if the interfacial and surface tensions were expressed as functions of mutual solubility in logarithmic coordinates<sup>16</sup> as shown in Figs 4-6. The mutual solubility defined by Donahue and Bartell<sup>30</sup> for binary systems, extended according to Paul and deChazal<sup>24</sup> and Fu *et al.*<sup>27</sup> to ternary systems, is defined by the relation

$$S = -\ln(x_M^{\text{aq}} + x_W^{\text{org}} + x_A^{\text{org}}), \quad (1)$$

where  $x_M^{\text{aq}}$  is the molar fraction of M in the aqueous phase,  $x_W^{\text{org}}$  the molar fraction of W in the organic phase, and  $x_A^{\text{org}}$  the molar fraction of the solute A (*e.g.* E, tB, B) in the organic phase. The results of the least-squares fit of

TABLE II  
M-W-tB system at 25 °C

Tie line No.	Aqueous phase				Organic phase				$\gamma^{\text{it}}$ mN m <sup>-1</sup>
	$x_W^{\text{aq}}$	$x_{tB}^{\text{aq}}$	$\rho^{\text{aq}}$ g cm <sup>-3</sup>	$\gamma^{\text{aq}}$ mN m <sup>-1</sup>	$x_W^{\text{org}}$	$x_{tB}^{\text{org}}$	$\rho^{\text{org}}$ g cm <sup>-3</sup>	$\gamma^{\text{org}}$ mN m <sup>-1</sup>	
0	0.9911	0	0.9902	52.53	0.0660	0	0.7401	18.19	10.3
1	0.9886	0.0023	0.9896	50.61	0.0692	0.0023	0.7398	18.20	9.7
2	0.9882	0.0028	0.9890	46.83	0.0728	0.0048	0.7401	18.21	9.6
3	0.9886	0.0034	0.9882	45.74	0.0715	0.0080	0.7411	18.46	9.4
4	0.9841	0.0068	0.9872	43.17	0.0909	0.0409	0.7431	18.56	8.1
5	0.9841	0.0080	0.9859	40.05	0.0936	0.0591	0.7443	18.60	7.0
6	0.9795	0.0113	0.9857	37.33	0.1227	0.0773	0.7469	18.75	6.1
7	0.9773	0.0136	0.9839	35.19	0.1545	0.1091	0.7505	18.83	5.0
8	0.9704	0.0205	0.9826	33.83	0.1954	0.1364	0.7560	19.07	4.1
9	0.9688	0.0227	0.9816	34.25	0.2295	0.1614	0.7598	19.10	3.9
10	0.9640	0.0280	0.9786	32.87	0.3204	0.2182	0.7755	19.55	2.6
Crit. point	0.9054	0.0833	-	-	0.9054	0.0833	-	-	-

the experimental data ( $\gamma$  in  $\text{mN m}^{-1}$ ) together with the mean deviation  $\delta = \Sigma|\gamma_{\text{exp}} - \gamma_{\text{calc}}|/n$  ( $n$  is the number of considered experimental points) are as follows:

### M-W-E system

$$\begin{aligned} \ln \gamma^{\text{aq}} &= 0.2062 (\ln S)^2 + 0.3664 \ln S + 3.4440, & \delta &= 0.64; n = 9 \\ \ln \gamma^{\text{org}} &= -0.0698 \ln S + 2.9840, & \delta &= 0.31; n = 9 \\ \ln \gamma^{\text{it}} &= -0.6359 (\ln S)^2 + 1.9195 \ln S + 1.0564, & \delta &= 0.17; n = 8 \end{aligned}$$

### M-W-tB system

$$\begin{aligned} \ln \gamma^{\text{aq}} &= 0.2620 (\ln S)^2 + 0.1543 \ln S + 3.5137, & \delta &= 0.80; n = 11 \\ \ln \gamma^{\text{org}} &= -0.0462 \ln S + 2.9493, & \delta &= 0.06; n = 11 \\ \ln \gamma^{\text{it}} &= 0.9480 \ln S + 1.4024, & \delta &= 0.14; n = 11 \end{aligned}$$

TABLE III  
M-W-B system at 25 °C

Tie line No.	Aqueous phase				Organic phase				$\gamma^{\text{it}}$ $\text{mN m}^{-1}$
	$x_{\text{W}}^{\text{aq}}$	$x_{\text{B}}^{\text{aq}}$	$\rho^{\text{aq}}$ $\text{g cm}^{-3}$	$\gamma^{\text{aq}}$ $\text{mN m}^{-1}$	$x_{\text{W}}^{\text{org}}$	$x_{\text{B}}^{\text{org}}$	$\rho^{\text{org}}$ $\text{g cm}^{-3}$	$\gamma^{\text{org}}$ $\text{mN m}^{-1}$	
0	0.9911	0.0000	0.9902	52.53	0.0660	0.0000	0.7401	18.19	10.3
1	0.9900	0.0010	0.9903	51.69	0.0750	0.0110	0.7423	18.24	8.9
2	0.9880	0.0030	0.9892	49.91	0.0900	0.0300	0.7465	18.61	7.7
3	0.9880	0.0030	0.9893	44.60	0.0980	0.0430	0.7491	18.92	7.4
4	0.9880	0.0040	0.9891	41.80	0.1530	0.1130	0.7563	18.95	6.5
5	0.9850	0.0050	0.9882	40.79	0.2200	0.1910	0.7686	19.61	5.2
6	0.9870	0.0060	0.9881	35.81	0.3230	0.2600	0.7842	20.70	3.9
7	0.9850	0.0100	0.9875	33.12	0.3300	0.2840	0.7905	21.00	3.6
8	0.9840	0.0110	0.9870	34.70	0.3840	0.3250	0.8019	21.77	3.4
9	0.9840	0.0110	0.9877	33.81	0.3840	0.3250	0.8023	21.65	3.3
10	0.9840	0.0113	0.9847	30.23	0.3980	0.3450	0.8076	22.20	2.7
11	0.9840	0.0114	0.9864	28.38	0.4300	0.3750	0.8153	22.55	2.3
12	0.9980	0.0020	0.9859	26.03	0.5120	0.4880	0.8443	24.23	1.5

FIG. 4  
M-W-E system: correlation of surface and interfacial tensions with mutual solubility:  
○ surface tension of aqueous phase ( $\gamma = \gamma^{aq}$ ),  
● surface tension of organic phase ( $\gamma = \gamma^{org}$ ),  
Δ interfacial tension ( $\gamma = \gamma^{it}$ )

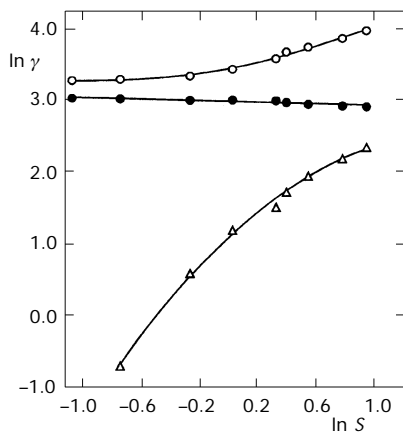


FIG. 5  
M-W-tB system: correlation of surface and interfacial tensions with mutual solubility:  
○ surface tension of aqueous phase ( $\gamma = \gamma^{aq}$ ),  
● surface tension of organic phase ( $\gamma = \gamma^{org}$ ),  
Δ interfacial tension ( $\gamma = \gamma^{it}$ )

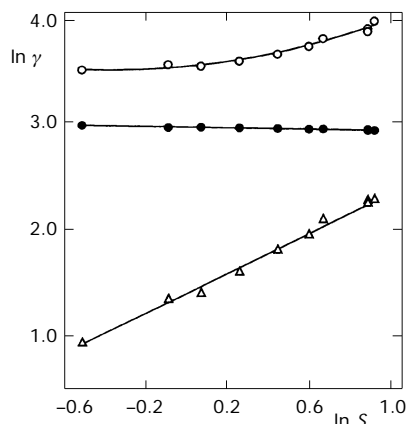
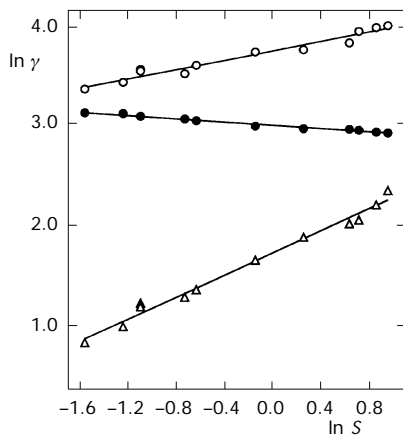


FIG. 6  
M-W-B system: correlation of surface and interfacial tensions with mutual solubility:  
○ surface tension of aqueous phase ( $\gamma = \gamma^{aq}$ ),  
● surface tension of organic phase ( $\gamma = \gamma^{org}$ ),  
Δ interfacial tension ( $\gamma = \gamma^{it}$ )



## M-W-B system

$$\ln \gamma^{\text{aq}} = 0.2257 \ln S + 3.7208,$$

$$\delta = 1.48; n = 12$$

$$\ln \gamma^{\text{org}} = -0.0873 \ln S + 2.9803,$$

$$\delta = 0.14; n = 12$$

$$\ln \gamma^{\text{it}} = 0.5423 \ln S + 1.7194,$$

$$\delta = 0.26; n = 12$$

Since the values of interfacial as well as surface tensions of the conjugate phases were obtained, the possibility of using the Antonoff rule<sup>31</sup> (the interfacial tension for two saturated liquids in equilibrium is equal to the difference in the surface tensions of the two solutions against air) for the interfacial tension prediction in ternary systems was examined. The validity of Antonoff rule for binary systems has been widely discussed. Murphy *et al.*<sup>4</sup> tested the validity of Antonoff rule for 12 ternary systems. Only for two of them agreed the experimental interfacial tensions with those calculated by Antonoff rule. In other systems the difference was as much as 30%. Good agreement between experimental and calculated values was found for the system benzene-ethyl alcohol-water<sup>17</sup> at low ethyl alcohol concentrations; for the system hexane-acetone-water<sup>17</sup> the experimental values were greater than the calculated ones (by about 15%). Figure 7 gives the comparison of the line representing the Antonoff rule with the experimental values for the title systems. As can be seen, there is a great disagreement between the measured values of interfacial tensions,  $\gamma_{\text{exp}}^{\text{it}}$ , and those calculated by Antonoff rule as the difference  $\gamma^{\text{aq}} - \gamma^{\text{org}}$ ; the calculated values are approximately 3.5 times smaller than the experimental ones. It may be concluded that the use of Antonoff rule for these ternary systems is not justified and it cannot be used even for a rough estimation of interfacial tensions.

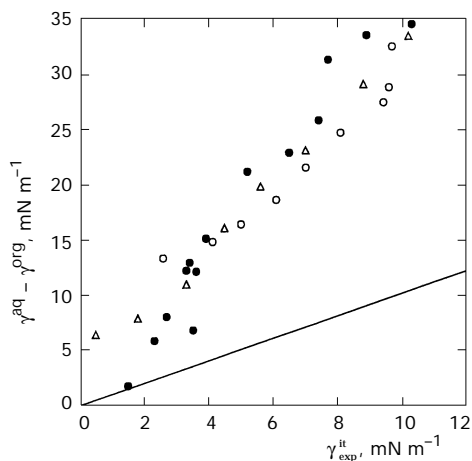


FIG. 7

The test of the Antonoff rule:  $\Delta$  M-W-E system,  $\circ$  M-W-tB system,  $\bullet$  M-W-B system, — Antonoff rule,  $\gamma^{\text{it}} = \gamma^{\text{aq}} - \gamma^{\text{org}}$



## CONCLUSIONS

The influence of ethanol, *tert*-butyl alcohol, and butan-1-ol on surface and interfacial tensions in *tert*-butyl methyl ether–water–alcohol ternary systems was investigated. With increasing concentration of alcohol in system the surface tensions of aqueous phases decrease, those of organic phases slightly increase and the interfacial tensions between aqueous and organic phases are lowered in all cases. Surface and interfacial tensions are expressed as functions of mutual solubility, calculated according to Eq. (1). Neither of ternary title systems fulfils the conditions for using the simple Antonoff rule to estimation of interface tensions from the surface tensions of saturated conjugated solutions.

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