J. Chem. Eng. Data 1981, 26, 172–174

Correlation of Surface- and Interfacial-Tension Data for Two Ternary Systems: Benzene–Water–Ethanol and *n*-Hexane–Water–Ethanol

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Interfacial tensions measured by Ross and Patterson are consistent with the theory of interfacial tensions near critical points proposed by Fleming, Vinatieri, and Glinsmann. Fits to the experimental data were obtained with tension scale factors of 45 and 56 mN/m for the two ternary systems studied by Ross and Patterson, values consistent with scale factors for other nonsurfactant systems. Systems containing surfactants exhibit scale factors of ~10 mN/m. The tension data of Ross and Patterson allow checks of the generalized Antonoff's rule as proposed by Widom. For certain compositions the experimental data violate the rule by more than the stated uncertainty, suggesting an undetected error in the tension measurements. Another uncertainty is the possibility of an isopycnic in the benzene–water–ethanol system, beyond which the densities of the aqueous and organic phases may be reversed, leading to uncertainty in the identification of the surface tensions.

Introduction

Recently, Ross and Patterson (*1*) published the results of surface- and interfacial-tension measurements in two ternary systems. These measurements were conducted along with tie-line and density measurements for the systems benzene–water–ethanol and *n*-hexane–water–ethanol as their respective plait points were approached. It is the purpose of this note to make three observations concerning Ross and Patterson's paper: (1) The interfacial-tension data for the two ternary systems can be interpreted in terms of the theory recently proposed (*2*) for multicomponent systems near critical points. (2) The surface- and interfacial-tension values violate the generalized Antonoff's rule (*3*) as formulated by Widom (*4*, *5*). (3) The benzene–water–ethanol system may possess an isopycnic (*6*) for compositions near the plait point.

Interfacial-Tension Theory

Recently (*2*), we presented a theory of interfacial tensions in multicomponent systems near critical points. This theory, a consequence of the scaling theory of critical phenomena, is closely related to that presented for the quantitative interpretation of phase-volume behavior of such systems (*7*). Here we show that the theory can be applied to the data of Ross and Patterson.

In ref *7*, it was shown that the volume (or mass) fraction of the disappearing phase in a ternary system is given as a function of an overall composition variable by eq 1. C is the

$$F = \tfrac{1}{2}\{1 - [(\bar{C}^0 - C^0)/(C - C^0)]^{\beta/(1-\alpha)}[1 + \lambda(C - \bar{C}^0)]\} \qquad (1)$$

composition being varied, $\bar{C}^0$ is the composition at which the phase disappears, λ is a parameter related to the behavior away from the disappearance point, and C^0 is a parametric composition such that $|\bar{C}^0 - C^0|^{\beta/(1-\alpha)}$ is proportional to the distance that the composition path passes to the critical (plait) point. β is the coexistence curve critical exponent, and α is the specific heat critical exponent. These exponents have "universal" values for all fluid–fluid critical points, these values being the same as for Ising-like spin systems (*8*). For our purposes it is sufficient to take $\alpha = {}^1/_8$ and $\beta = {}^5/_{16}$.

In ref *2*, it was shown that the interfacial tension corresponding to eq 1 is given by eq 2, where γ_0 is a scale factor

$$\gamma = \gamma_0|C - C^0|^{2\upsilon/(1-\alpha)} \qquad (2)$$

and υ is the critical exponent describing the divergence of the correlation length. The exponent υ enters because the correlation length and the interfacial width diverge with the same exponent (*9*, *10*). For our purposes υ will be taken equal to ${}^5/_8$. Equation 2 has only one adjustable parameter if the parameters in eq 1 are known. Since these can be determined by an nonlinear least-squares fit to phase–volume data, one can determine γ_0 by a simple linear regression on the tension data.

For the two ternary systems discussed in ref *1*, the mass fractions of the phases at 20.0 °C were determined from the measured tie lines, using the lever rule, for linear paths passing near the plait point of these systems. For the benzene–water–ethanol system, the path is the straight line passing through $C_{H_2O} = C_{C_6H_6} = 0.5$, $C_{EtOH} = 0$ and $C_{C_6H_6} = 0.573$, $C_{H_2O} = 0.089$, $C_{EtOH} = 0.338$. For the *n*-hexane–water–ethanol system the corresponding points are $C_{H_2O} = C_{C_6H_6} = 0.5$, $C_{EtOH} = 0$ and $C_{n\text{-hex}} = 0.487$, $C_{H_2O} = 0.042$, $C_{EtOH} = 0.471$. The mass fractions were fit to eq 1 as a function of ethanol concentration $C \equiv C_{EtOH}$ in order to determine C^0. For the system containing benzene, $C^0 = 0.342$, while for the *n*-hexane system $C^0 = 0.471$. With these values of C^0, γ_0 was determined by regression on the tension data. For the benzene system $\gamma_0 = 45.5$, while for the *n*-hexane system $\gamma_0 = 56.3$. The corresponding fits to the tension data are given in Figures 1 and 2. The agreement between the experiments and eq 2 is excellent for both examples. The values of γ_0 obtained for these systems are of the same order of magnitude as the value of 38.0 obtained for the chloroform–acetone–water system in ref 2 and are much larger than the values between 4 and 14 obtained there for surfactant systems of the type employed in tertiary oil recovery (*11*, *12*). As emphasized in ref 2, these lower values of γ_0 are manifestations of the surface activity of the surfactant molecule.

Generalized Antonoff's Rule

Recently (*4*, *5*), Widom proposed that, for three fluid phases in equilibrium, the three interfacial tensions between independent pairs of phases satisfy the triangle inequality

$$\gamma_{max} \leq \gamma_{med} + \gamma_{min} \qquad (3)$$

where γ_{max} is the largest of the three tensions, γ_{min} is the smallest, and γ_{med} is the median tension. Widom has given strong thermodynamic arguments for the inequality and has recently provided a molecular derivation (*13*) of it. The original statement of Antonoff's Rule (*3*) was made with the inequality in eq 3 replaced by an equality. Widom (*5*) argued that the equality may indeed be satisfied asymptotically as a fluid tricritical point (*14*) is approached.

For the Ross and Patterson systems the three phases are the two liquid phases and the vapor phase (mostly air), and the three interfacial tensions are the liquid–liquid tension and the two surface tensions. The values of these tensions for the two systems as determined by Ross and Patterson are tabulated in Tables I and II along with the corresponding values of $\gamma_{med} + \gamma_{min} - \gamma_{max}$. This combination should be positive if inequality 3 is satisfied. We see that for both systems violations occur,

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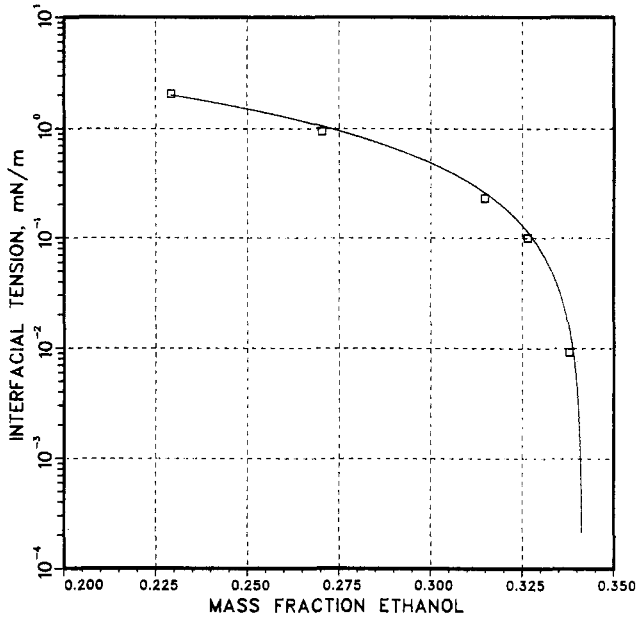

Figure 1. Interfacial tension in the benzene-water-ethanol system. The symbols represent the experimental data, and the curve is the theoretical prediction.

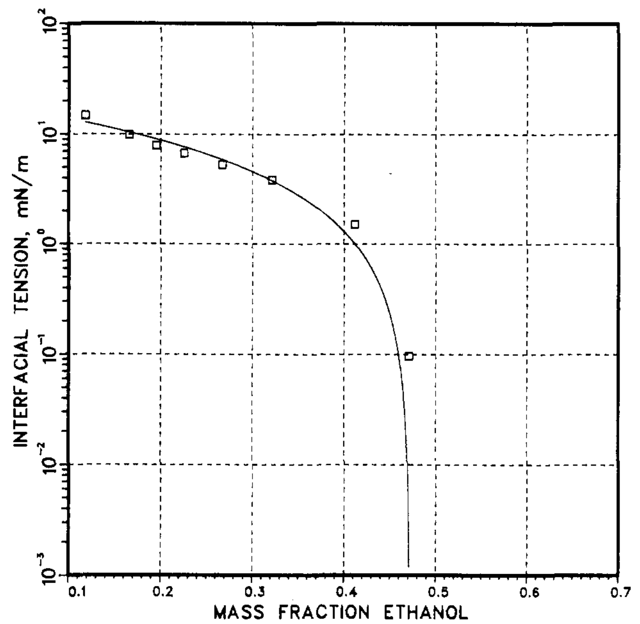

Figure 2. Interfacial tension in the hexane-water-ethanol system. The symbols represent the experimental data, and the curve is the theoretical prediction.

Table I. Interfacial Tensions for Benzene-Water-Ethanol at 20 °C

tie line no.	γ_{aq}, mN/m	γ_{org}, mN/m	γ_{int}, mN/m	$\gamma_{med} + \gamma_{min} - \gamma_{max}$, mN/m
0	62.15	28.69	34.08	0.62
1	41.93	28.02	15.90	1.99
2	32.30	28.53	7.03	3.26
3	28.31	28.55	3.76	3.52
4	27.12	28.58	2.06	0.6
5	26.34	28.02	0.94	−0.74
6	26.00	26.52	0.230	−0.29
7	26.15	26.00	0.100	−0.05
8	26.28	25.80	0.0092	−0.47

Table II. Interfacial Tensions for Hexane-Water-Ethanol at 20 °C

tie line no.	γ_{aq}, mN/m	γ_{org}, mN/m	γ_{int}, mN/m	$\gamma_{med} + \gamma_{min} - \gamma_{max}$, mN/m
0	66.32	18.1	49.75	1.53
1	37.11	18.5	14.70	−3.91
2	31.5	18.5	9.82	−3.18
3	30.18	18.5	7.83	−3.85
4	28.14	18.4	6.67	−3.07
5	27.93	18.5	5.26	−3.97
6	26.68	18.7	3.82	−4.16
7	23.74	18.8	1.50	−3.44
8	18.9	18.7	0.096	−0.104

Table III. Densities of the Phases for Benzene-Water-Ethanol at 20 °C

tie line no.	aqueous-phase density		organic-phase density	
	measured	"calcd"	measured	"calcd"
0	0.9980	0.9982	0.8792	0.8792
1	0.9756	0.9670	0.8781	0.8787
2	0.9572	0.9390	0.8764	0.8772
3	0.9403	0.9197	0.8747	0.8755
4	0.9201	0.9007	0.8712	0.8735
5	0.8977	0.8816	0.8695	0.8709
6	0.8713	0.8632	0.8650	0.8659
7	0.8652	0.8588	0.8631	0.8642
8	0.8608	0.8562	0.8603	0.8611

in some cases being greater than 4 mN/m for the hexane system. The interfacial-tension measurements should be carefully reassessed in order to be sure of their violation of the inequality. The apparent violations of the inequality may be a consequence of the fact that all three phases were not in contact while the tensions were being measured.

Possible Isopycnic in the System Benzene-Water-Ethanol

An isopycnic (*6*) tie line in a two-phase system is one which connects phases having the same density. Such a situation might be expected to occur in the system benzene-water-ethanol because "aqueous phase" compositions near the plait point contain large amounts of ethanol which is less dense than either water or benzene. In order to see how this can happen, we "calculate" the densities of the phases by using the measured tie lines and the bulk densities of the pure components (0.9982 g/cm^3 for water, 0.8792 g/cm^3 for benzene, and 0.7895 g/cm^3 for ethanol, all at 20 °C, as given in Table II of ref *1* and assuming "volume additivity". This assumption is not rigorously valid but might help to identify general trends. The calculated and measured densities are compared in Table III. Note that the organic phase is "calculated" to be the more dense phase for tie lines 6, 7, and 8. Also note that the calculated organic-phase densities are in good agreement with experiment. The aqueous-phase densities are in poorer agreement with experiment, but negative excess volumes are well-known for aqueous solutions.

Although these "calculated" densities are not of sufficient accuracy to confirm an inversion of densities, they do suggest that the published identifications should be checked. Note that an inversion of densities will invert the identification of the surface tensions with aqueous and organic phases but that it will have no consequence on the violation of Antonoff's rule.

Conclusions

We have shown that the experimental interfacial tensions measured by Ross and Patterson (*1*) are in excellent agreement with the theory of ref *2*. We have also noted that the three-phase interfacial tensions measured by these authors violate the generalized Antonoff's rule (*3*) as formulated by Widom (*4*). Finally we have suggested that an isopycnic (*6*) might be observed in the system benzene-water-ethanol.

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Received for review January 31, 1980. Accepted December 2, 1980.

Critical Evaluation of Thermodynamic Properties of Mixing for Solid Cobalt-Platinum Alloys between 1000 and 1400 K

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The most recent compilation of the thermodynamic properties of mixing for cobalt-platinum alloys was published in 1973 by Hultgren et al. but does not include all of the experimental results now available, particularly Miner's; moreover, Hultgren's tables present only the Gibbs energy of components, without enthalpy or entropy data. We have made a new critical evaluation that leads to the best values of total and partial enthalpy, entropy, and Gibbs energy of cobalt and platinum, in solid alloys, in the temperature range 1000-1400 K. These results are presented in three tables and shown in several figures.

1. Introduction

We have determined the thermodynamic properties of stoichiometric defects in cobalt oxide by means of measurements of the electronic conductivity as a function of composition, the latter being imposed by contacting the oxide with a cobalt-platinum alloy. To be able to use these conductivity measurements, we require, in addition to other data, thermodynamic data of mixing for cobalt-platinum alloys. The most recent compilation, published in 1973 by Hultgren et al. (*1*), does not include all of the experimental results now available; moreover, Hultgren's tables present only the Gibbs energy of components, without enthalpy or entropy data. This paper reports the results of the critical evaluation we have been led to make, for total and partial Gibbs energy, enthalpy, and entropy of components.

2. History

The first activity measurements on solid cobalt-platinum alloys were made by Oriani (*2*) in 1953. By measuring the emf of cells having a molten LiCl-KCl eutectic as electrolyte and working between 973 and 1173 K, he found a negative deviation for cobalt activities and a positive deviation for those of platinum. In addition he found positive enthalpies of mixing, which is in complete disagreement with all further measurements, notably those he carried out with Murphy (*3*) in 1962, using differential calorimetry for the dissolution of liquid tin at ~913 K. They found a total molar enthalpy of mixing ΔH^M of -9500 J mol^{-1} at $x_{Co} = 0.3$ and -1690 J mol^{-1} at $x_{Co} = 0.153$ for disordered alloys of cobalt-platinum. The values published in cal mol^{-1} have been converted to J mol^{-1} on the basis of 1 cal = 4.184 J.

Rudman and Averbach (*4*), using X-ray measurements of the short-distance order parameters for Co-Pt alloys and assuming a quasi-chemical model of the interaction between the closest neighbors, calculate the total molar enthalpies of mixing to fit the expression $\Delta H^M = Ax_{Co}x_{Pt}$ in which $A = -(35600 \pm 1300)$ J mol^{-1}. If such an expression were developed from the measurements of Oriani and Murphy (*3*), the value of A would be $-44\,800$ J mol^{-1}.

In 1964 Schwerdtfeger and Muan (*5*) measured the activity of cobalt in Co-Pt alloys at 1473, 1573, and 1673 K, with compositions ranging from 3 to 100 at. % of cobalt of two complementary techniques: (1) A sample of a Co-Pt alloy was suspended in a thermobalance under a partial pressure of oxygen which was slowly increased by small increments until the alloy was oxidized and its weight increased. (2) A mixture of Co-Pt alloy and the oxide CoO was maintained at equilibrium at a constant temperature under a fixed partial pressure of oxygen; then the temperature was brought rapidly to ambient temperature and the composition of the alloy was determined.

King (*6*) and Miner (*7*) measured the activities of solid cobalt-platinum alloys from 10 to 90 at. % cobalt and temperature between 1073 and 1273 K for King and between 1173 and 1473 K for Miner. They both used solid electrolyte cells which may be schematized by the following: $|\text{Pt,air}|(\text{ZrO}_2)_{0.85}(\text{CaO})_{0.15}|\text{Co-Pt,CoO}|$ for King (*6*); $|\text{Co,CoO}|(\text{ThO}_2)_{0.85}(\text{Y}_2\text{O}_3)_{0.15}|\text{Co-Pt,CoO}|$ for Miner (*7*).

These cells differ not only by the solid electrolyte used (zirconia stabilized with CaO or thoria stabilized with yttrium oxide) and by the partial pressure of oxygen used as reference (air or Co-CoO equilibrium mixture) but also in the way they were constructed, which will be dealt with later.

In 1966 Winters (*8*) used the Knudsen effusion technique to determine the vapor pressure of cobalt above six Co-Pt alloys at composition from 50 to 100 at. % cobalt at 1693 K. The thermodynamic mixing data for the Co-Pt solution at atomic fractions of Co less than 0.5 have been obtained by extrapolation. The total Gibbs energy of mixing ΔG^M goes through a minimum at -1700 J mol^{-1} for $x_{Co} = 0.55$. This same Knudsen effusion technique was used by Alcock and Kubik (*9*) in 1968 to measure the activities of cobalt in liquid Co-Pt alloys from 40 to 80 at. % cobalt at 1823-1923 K; it was also used in 1978 for the same purpose by Chegodaev et al. (*10*).

Smith and Masson also give cobalt activity in Co-Pt-Rh alloy (*11*), by equilibrating the alloys with cobalt oxide and oxygen of known pressure.

Other work was done on this alloy, especially with regard to low-temperature specific heat for studies of magnetic anomalies (*12*, *13*). Phase diagrams with ordered solids were also studied.

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