METHOD OF ESTIMATING SPONTANEOUS BOLTING POINTS AND CRITICAL PARAMETERS FOR BINARY MIXTURES

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A relationship is established between the temperature for vigorous spontaneous boiling and the critical parameters for solutions.

I have previously [1, 2] given a method for estimating the vigorous spontaneous boiling temperature T^* for a binary solution at a given concentration x as a function of the pressure p, which is based on approximate thermodynamic similarity between the lines for the attainable superheating $T^*(p; x = \text{const})$; input data: critical parameters p_c and T_c for pure components. The essence is as follows. A straight line is drawn in p, T coordinates joining the critical points for the components, and an auxiliary point (p_a, T_a) is defined corresponding to the concentration (in the linear approximation for $T_a = T_a(x)$). The straight line joining that point to the point $(0.1\ \text{MPa}, 0.9T_a)$ is an approximation for the required $T^*(p, x = \text{const})$ relationship. This procedure is applicable if there is marked difference between the two critical temperatures. The limits to it can be defined from measurements on $T^*(p, x)$ for systems with similar T_c in the azeotropic interval [3]. A temperature minimum is characteristic of the critical curve for solutions of that type.

Pulsed isobaric heating has been used with a platinum probe [4, 5] to examine $T^*(p, x)$ for hexane–acetone, heptane–acetone, heptane–propanol, octane–benzene [6], and hexane–methanol solutions; probe diameter 20 μm, length 2 cm, heating time to start of vigorous spontaneous boiling 35 μsec, nucleation frequency about 10^{24} ($p = 0.1$ MPa) to $10^{29}\ \text{m}^{-3}\cdot\text{sec}^{-1}$ ($p \approx p_c$).

Those superheating lines are simple in form (Fig. 1), as for the solutions previously examined [1, 2], and can be represented as straight lines to a first approximation; to predict T^* from the minimum data, we use an empirical rule concerning the similarity in the reduced temperatures $\tau_a = T_a^*/T_c = 0.89$-$0.91$ for most simple liquids [5]. My measurements [6] show that τ_a for various concentrations of six arbitrarily selected solutions having similar component T_c differed less than 1% from the τ_a for the pure components; that 1% spread is due to error in determining T_a^* and T_c (the critical temperatures were taken from [7-10]). Therefore, to approximate T^* (p; x = const) for the solution having a small critical-temperature difference ΔT_c, one can proceed as follows. The attainable superheating temperature at atmospheric pressure $T_a^*(x)$ is derived as $\bar{\tau}_a(x)T_c(x)$, in which $\bar{\tau}_a$ is the linearly interpreted τ_a for the pure components. The point on the $(p_c(x), T_c(x))$ critical curve corresponding to the set concentration is joined by a straight line to the $(0.1\ \text{MPa}; T_a^*(x))$ point, on which lie the T^* (p) for the solution. If there are no reference data on the superheating, one can assume $\bar{\tau}_a(x) = 0.9$. Table 1 gives measurements and $T^*(p)$ estimates from this scheme for octane-benzene solutions, as well as estimates from the two critical point method [1, 2]. The linear approximation is reasonably accurate. For $p \simeq p_a$, excess of T^* over the saturation temperature (superheating) is about 100 K. Error in estimating $T^*(p)$ from the two critical points increases with the depth of the minimum on the critical curve; ΔT_2 attains 30 K for the hexane–methanol system

One can use T^* (p, x) data to determine critical parameters for solutions, which are key data in similarity-theory calculations; T_c can be derived from T^* for atmospheric pressure:

$$T_c(x) = T_a^*(x)/\bar{\tau}_a(x). \tag{1}$$

(1) was tested by comparing $T_c(x)$ results from (1) with measurements [7-10]; the $T_a^*(x)$ and $\bar{\tau}_a(x)$ used in (1) were taken from [5, 6, 10, 11] (total of 12 systems). The differences from the available $T_c(x)$ measurements did not exceed 4 K, apart from the hexene–benzene system [11] (Fig. 2), where the $T_c(x)$ from (1) qualitatively reproduced the [7] critical curve but ran at lower

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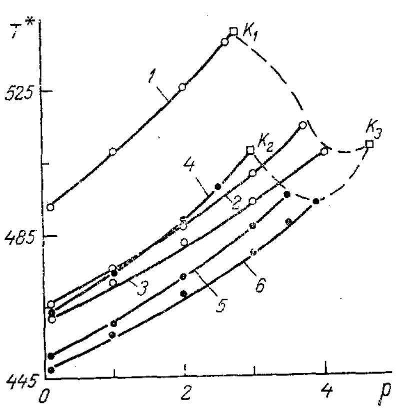

Fig. 1

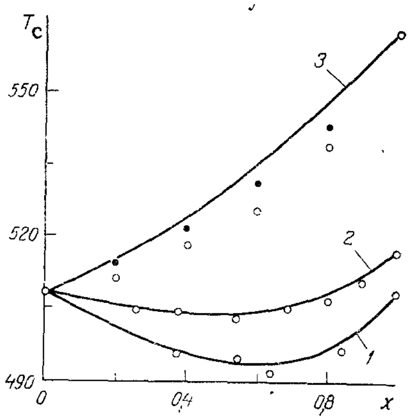

Fig. 2

Fig. 1. T^* for heptane–acetone solutions [open points: 1) $x = 0$; 2) 0.5; 3) 0.66] and hexane–acetone [filled points: 4) $x = 0$; 5) 0.37; 6) 0.64]; K_1, K_2, K_3 critical points for heptane, hexane, and acetone; dashed lines critical curves [7]; T^* in K and p in MPa.

Fig. 2. T_c as a function of molar fraction of second component; solid lines from experiment: 1) hexane–acetone; 2) hexane-perfluorobenzene; 3) hexane–benzene; open points from (1), filled points calculation from homogeneous nucleation theory.

temperatures, with $\Delta T_c(x = 0.6)$ attaining 9 K, which could be due to premature boiling because of inadequate conditions, which reduces T^*. When one uses $T_a^*(x)$ derived for the hexane–benzene system [11] with homogeneous nucleation theory and (1), $\Delta T_c(x)$ is reduced to 0.5-4.3 K.

(1) has been derived for solutions with similar component T_c; any increase in ΔT_c is usually accompanied by change in the critical curve shape, with the minimum vanishing and a pressure maximum appearing. The accuracy of (1) is reduced, since the $\tau_a(x)$ diverge from the range characteristic of pure substances, 0.89-0.91 [1, 2]. One can recommend using (1) for $T_c(x)$ for any system where the critical curve deviates from linear course in pressure by not more than 10% in p, T coordinates, which corresponds to deviation from linearity in $\tau_a(x = 0\text{-}1)$ of about 1%. The critical curves for over 200 solutions enabled me to correlate the deviation from ideal behavior in p_c ($\Delta p_c(x)$, see segment 59 in Fig. 3) and the pure-component parameters; as a rule, the condition $\Delta p_c(x)/\bar{p}_c < 0.1$ is met if the following applies:

$$\frac{\Delta T_c}{T_c^+} < \left(\frac{4-A^+}{4-A^-}-0{,}3\right)\Big/ 3{,}5. \qquad (2)$$

Here A is the Filippov similarity criterion [12] in one-parameter similarity theory; the superscripts + and − relate correspondingly to the larger and smaller T_c and A for the pure components; the difference 4 − A is correlated with basic molecular geometrical parameters that make themselves felt in macroscopic features [13], while $\Delta T_c/T_c$ is a characteristic of the component-molecule differences.

If the inequality in (2) is reversed, the [1, 2] results provide a simple method of estimating the critical pressure; input data: $T_a^*(x)$ and $T_c(x)$. Sequence: from the [1, 2] formula, $T_A(x) = T_a^*(x)/\tau_a(x)$ for the given concentration gives the auxiliary point (p_A, T_A) on the straight line joining the critical points for the components (point 8 in Fig. 3); the $T_a^*(x)$ and $T_A(x)$ points are joined by a straight line, which is extended to the intersection with the $T_c(x) = \text{const}$ line, and the abscissa for that point corresponds to the required $p_c(x)$. Figure 3 illustrates a $p_c(x)$ calculation on this scheme for the pentane-dodecane system, where the $T_a^*(x)$ data are from [14] (graphical representation), and the critical temperatures for the concentrations measured in [14] have been determined from Filippov's simple and reliable formula [15, 16]. To check the accuracy, we measured $T_a^*(x)$ and calculated $p_c(x)$ for the hexane–decane solution having a pressure maximum on the critical curve. Comparison with measurements [7] gives the error as $\Delta p_c(x)/p_c \approx 10\%$. One expects the error to increase as the pressure maximum on the critical curve rises.

TABLE 1. Comparison of Measured T^* for Octane–Benzene Solutions with Estimates from the Proposed Scheme ($\Delta T_1 = T^*_\ell - T^*$) and from the Two Critical Point Method (ΔT_2) for p in MPa and ΔT in K

p	0,1	0,5	1,0	2,0	3,0
			$x = 0,25$		
ΔT_1	1,5	2,5	3,0	3,5	0
ΔT_2	3,0	4,0	4,0	4,0	—0,5
			$x = 0,38$		
ΔT_1	2,5	3,0	4,0	4,5	1,5
ΔT_2	5,0	5,0	5,5	5,0	1,0
			$x = 0,65$		
ΔT_1	2,0	3,0	4,5	4,5	3,0
ΔT_2	5,0	6,0	6,5	5,5	3,0

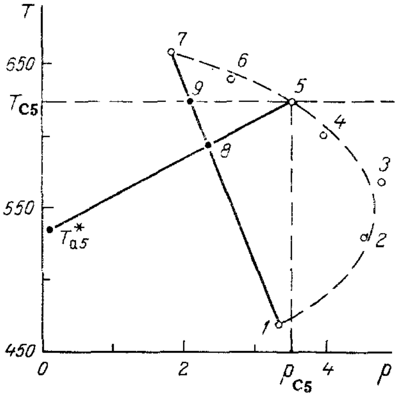

Fig. 3. Calculated critical pressures for the pentane–dodecane system derived from known $T^*_a(x)$ [14] and $T_c(x)$ [15, 16]. 1) x = 0; 2) 0.15; 3) 0.28; 4) 0.43; 5) 0.59; 6) 0.73; 7) 1; 8) auxiliary point for x = 0.59; the length of the segment between points 5 and 9 gives the deviation in the critical curve from linear with respect to pressure ($\Delta p_c(x)$).

This method of estimating $T^*(p; x = \text{const})$ for the binary solution is based on the known critical parameters for the system; one can use data on T^*_a for solutions to estimate the critical temperature or pressure.

NOTATION

T, temperature; T^*, spontaneous-boiling temperature; x, molar fraction of second component; p, pressire; $\bar{p}_c$, linearly interpolated p_c for components at given temperature; $\tau_a = T^*_a/T_c$; ΔT_c, difference in component critical temperatures; $\Delta T_c(x)$, difference between measured and calculated T_c for given x; A, similarity criterion. Subscripts: c, critical point; a, atmospheric pressure; ℓ, linear approximation.

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EVAPORATION OF BUBBLE AEROSOL DROPLETS FROM SOLID SUBSTRATES

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Evaporation-kinetic studies have been made on droplets formed under equilibrium and nonequilibrium conditions. There are differences due to the physicochemical features.

Charged droplets are formed when gas bubbles break at the surface of an aqueous electrolyte solution [1], and their compositions differ from that of the solution [2]. This is of interest to the theory of atmospheric processes [3] and also for optimizing heat and mass transfer in industry [4]. Here particular interest attaches to how small drops evaporate from solid substrates.

We used drops formed under nonequilibrium and equilibrium conditions; in the first case, the drops were made by bubble breaking at the surface, which involves highly nonequilibrium conditions, and the droplet formation speeds may be 10-100 m/sec [5]. When a bubble breaks, a cavity remains in the liquid, from which a column is ejected that breaks up into droplets. The bubbles were produced from a single capillary in distilled water, which was 2.2 cm below the surface. The generation rate was 23-25 bubbles a minute. At 50 mm from the surface there was a PTFE plate, which had been cleaned by boiling in freshly prepared chromic acid followed by repeated washing in double-distilled water and boiling in it. In the second, an MSh-10 microsyringe (scale 0.2 μl) was used in depositing a drop of distilled water slowly on the PTFE, the volume being the same. We compared results for identical-volume drops made under the two conditions. There were 40 such comparisons. The drops were selected and their parameters were measured in a saturated atmosphere in both cases. The height and base diameter were determined with an MIR-2 microscope (scale division 0.07 mm).

Table 1 gives the polynomials fitted to the volume V and side surface S in terms of the time τ; the polynomials have been fitted to minimum variance. The assumption was that the drops were spherical, which was checked from the criterion [6] $R_{ef} \ll a$, in which a is the capillary constant. The variations in volume and surface for the bubble aerosol were

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