NONCLASSICAL BEHAVIOUR OF BINARY MIXTURES IN GAS–LIQUID CRITICAL REGION AND ITS QUANTITATIVE DESCRIPTION

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Dedicated to late Academician Eduard Hála.

The gas–liquid critical region is described by means of an exponential relation, parameters of which are independent of system. It can be used for the prediction of nonclassical fluid phase behaviour. The isothermal vapour–liquid equilibrium data on the sulphur hexafluoride–pentane system measured in neighbourhood of the critical point of SF_6 are presented.

Phase behaviour of fluids can easily be described using simple procedures; in most cases. the equation of state provides a good quantitative description of gas–liquid coexistence region within a large range of both temperature and pressure. However, the problems appear in the critical region. It was found out a century ago that phase equilibrium data resist there any attempt to correlate them using the (classical) approach via equation of state.

In general, phase transition phenomena reflect in various properties (thermo-dynamical, magnetical. electrical, etc.) and are investigated by physicists. We concentrate here on the phenomenological and quantitative description concerning fluid systems in critical region.

Steep changes of physico-chemical properties take place when approaching the critical point. This singularity can be best described by the exponential function

$$\lim_{z \to 0} \ln |f(z)|/\ln |z| = \beta , \qquad (1)$$

where $f(z)$ is the vanishing fluid phase property, z is the independent variable, and β is a so-called critical exponent. Function $f(z)$ is not necessarily continuous at $z = 0$ and may have different numerical values for limit to the right and to the left.

Processing of the available experimental data has confirmed that various transition phenomena can be described by means of Eq. (1) in a realistic way. Some cases which we meet with among fluid systems can be pointed out:

1. Coexistence curve vapour–liquid for pure compounds. Since the difference of orthobaric densities vanishes at the critical point, Eq. (*1*) can be rewritten as

$$\varrho_L - \varrho_V = k|T_c - T|^\beta ,\qquad (2)$$

where ϱ_L and ϱ_V are the densities of coexisting liquid (L) and vapour (V) phases at temperature T, respectively, k is the proportionality constant, and T_c is the critical temperature. The experiments yielded value $\beta = 0.32 \pm 0.01$.

2. Liquid–liquid equilibrium in binary mixtures. Assuming that the density is proportional to concentration, we can write similarly

$$x' - x'' = k'|T - T_c|^\beta ,\qquad (3)$$

where x's denote the mole fractions of component in the coexisting liquid phases, k' is the proportionality constant (not equal to k in Eq. (*2*)), and T is the temperature of the system approaching the upper critical solution temperature T_c to the left. The same expression is valid for the lower critical solution temperature and the temperature approaching the critical point to the right. There is a lot of experiments around the upper critical solution temperature leading to the value of β within the range 0·32 to 0·35.

3. Vapour–liquid equilibrium in binary mixtures. Analogously to liquid–liquid equilibria both the liquid and vapour phase can be characterized by composition. The difference of concentrations of coexisting phases is equal to zero at the critical point. Therefore, the similar expression was suggested[1] for an isothermal system

$$y_1 - x_1 = c|P_c - P|^\beta ,\qquad (4)$$

where x_1 and y_1 are the mole fractions of more volatile component in the liquid and vapour phase, respectively, c is the proportionality constant, P is the pressure and P_c is the critical pressure of the mixture (at the given constant temperature).

Since the critical exponent β is equal approximately to $1/3$ both for pure compound and for binary immiscible systems, the same value may be expected also for vapour–liquid equilibrium (case 3). Moreover, this assumption is justified for all the cases mentioned above because they conform with the same phenomenological description. The value $\beta = 0.33$ corresponding to the coexistence curve of the third order, expresses so-called nonclassical behaviour in contrast to $\beta = 0.50$ resulting from any equation of state of the van der Waals type (yielding the second order parabolic curve).

The parameters c and β in Eq. (*4*) have not yet been thoroughly evaluated. Nevertheless, the additional data were required in order to generalize the conclusions that could be hitherto drawn from the existing data on systems of light paraffins.

EXPERIMENTAL

The vapour–liquid equilibria in the sulphur hexafluoride(1)–pentane(2) system were measured in near critical region of SF_6. The measurements were carried out in the high pressure static cell described by Wagner and Wichterle[2]; more details concerning the measurement of this particular system can be found elsewhere[3]. Three isotherms were measured slightly above the critical temperature of pure SF_6 ($T_{c1} = 318·67$ K), namely at $T - T_{c1} = 0·48, 2·48$, and $9·90$ K; the concentrations cover the critical region only. New data are summarized in Table I. Accuracy of the measurement is 0·02 mole per cent in composition, 0·001 MPa in pressure and 0·01 K in temperature.

TABLE I

Vapour–liquid equilibrium in the sulphur hexafluoride(1)–pentane(2) system

x_1	y_1	P, MPa
	$T = 319·15$ K	
0·4242	0·8243	2·446
0·7959	0·8942	3·316
0·8701	0·9223	3·500
0·9105	0·9453	3·592
0·9424	0·9616	3·671
0·9602	0·9700	3·707
0·9729	0·9774	3·741
0·9759	0·9800	3·750
0·990	0·990	3·783[a]
	$T = 321·15$ K	
0·8524	0·9070	3·596
0·9061	0·9288	3·726
0·9297	0·9389	3·773
0·9333	0·9412	3·787
0·9369	0·9416	3·794
0·947	0·947	3·802[a]
	$T = 328·57$ K	
0·7758	0·8429	3·845
0·7907	0·8437	3·893
0·8018	0·8359	3·927
0·8096	0·8342	3·930
0·8138	0·8335	3·932
0·8128	0·8281	3·933
0·822	0·822	3·937[a]

[a] Critical pressure.

RESULTS

Composition difference $(y_1 - x_1)$ versus pressure difference $\Delta P = P_c - P$ in logarithmic scales exhibits a linear dependence for $\Delta P < 0.05$ MPa (at constant temperature). The slope of this line is $\beta = 0.33$ with estimated error ± 0.03 when using all available data[1,4-7]. The proportionality constant c in Eq. (4) is equal to the value of composition difference at $\Delta P = 1$; its dimension is $[P^{-1/3}]$ due to the fact that $\beta = 1/3$.

Preliminary results led to the conclusion that the constant c is proportional to the "temperature distance" from the critical temperature T_{c1} of pure more volatile component. To be sure that the proposed expressions are valid more generally, we checked them with the sulphur hexafluoride–pentane system consisting of significantly different types of molecules. It was found out that the correlation (using the Redlich–Kwong–Soave equation of state with common mixing rules) of the data[3] measured in the whole concentration range resulted in the interaction parameter which was one of the greatest ever known. Thus, if the data on this system agree with the proposed relations, one could assume that the vast amount of other systems would comply with the model since their behaviour would be somewhere between behaviour of ideal and very nonideal system.

The dependence of parameter c is presented in Fig. 1. It can be seen that even for the sulphur hexafluoride–pentane system, the results agree well with the proposed model. Then, the simple expression can be derived for the temperature dependence of constant c

$$c = 0.004(T - T_{c1}) , \tag{5}$$

with the numerical coefficient evaluated as a slope of the line shown in Fig. 1.

The relations (4) and (5) lead to the expression
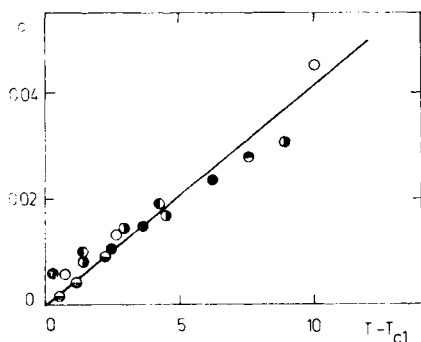
$$y_1 - x_1 = 0.004(T - T_{c1}) |P_c - P|^\beta , \tag{6}$$

FIG. 1

Temperature dependence of consant c.
● Methane–ethane[1], ◑ methane–ethane[4], ◐ methane–propane[5], ◒ ethane–butane[7], ◓ ethane–propane[6], ○ sulphur hexafluoride––pentane (this work)

which can be considered as independent of system and is able to describe the coexistence region around the critical point of the more volatile component within the limits estimated as follows: composition difference $y_1 - x_1$ ...0 to 5 mole per cent, pressure difference ΔP ... 0 to 0·1 MPa, temperature distance $T - T_{c1}$ ... 0 to 15 K. The classical approach to the description can be exploited outside these limits.

CONCLUSIONS

The proposed method makes possible the reliable description of that part of coexistence region which cannot be done by the classical procedures based on equation of state. Moreover, it is capable of predicting the phase equilibrium of any system in near critical region based on critical data only. Even though the available data give sufficient evidence for the proposed method, a further measurement of additional vapour–liquid equilibria in neighbourhood of critical point would be encouraged.

REFERENCES

1. Wichterle I., Chappelear P. S., Kobayashi R.: J. Comput. Phys. 7, 606 (1971).
2. Wagner Z., Wichterle I.: Fluid Phase Equil. 33, 109 (1987).
3. Wagner Z., Berg J.: Fluid Phase Equil., in press.
4. Wichterle I., Chappelear P. S., Kobayashi R.: J. Chem. Eng. Data 17, 4 (1972).
5. Wichterle I., Chappelear P. S., Kobayashi R.: J. Chem. Eng. Data 17, 9 (1972).
6. Mikšovský J., Wichterle I.: Collect. Czech. Chem. Commun. 40, 365 (1975).
7. Lhoták V., Wichterle I.: Fluid Phase Equil. 6, 229 (1981).

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