Summary

1. Phase-rule studies in the neighborhood of the critical point for ethylene have been carried out for several binary systems composed of ethylene and organic materials with low vapor pressures and melting points well above the critical temperature of ethylene. The types of phase equilibria observed have been discussed and classified.

2. Data for a number of the systems studied indicate a substantial solubility of the solid component in fluid ethylene above its critical temperature. Of these the system ethylene–naphthalene has been selected for a more extensive study of the supercritical solubility phenomenon.

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The Solubility of Naphthalene in Supercritical Ethylene

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In a previous paper[1] we have shown that, for a binary system with two components differing greatly in volatility, in which the three-phase line S–L–G cuts the critical line, the solubility of the solid in the supercritical gas phase will in general be increased over the ideal value expected on the basis of the vapor pressure of the solid.

It is our present purpose to establish a p–x section through the p–T–x diagram of the system ethylene–naphthalene for some temperatures a little higher than the critical temperature of the naphthalene-saturated solution. Previously only Cailletet types of apparatus have been used for such determinations. However these are very ill-suited for this purpose since the solubilities are mostly slight and the attainment of mixtures of very one-sided composition is of considerable practical difficulty.

We have, therefore, looked for a method enabling us to fix with satisfying accuracy these relatively slight solubilities.

The problem comes to this, that a solid-saturated fluid phase has to be prepared at a constant pressure and temperature, and a part of this has to be separated at constant pressure and temperature, and then has to be analysed. So we have developed the apparatus shown in Fig. 1, with which we could achieve our end.

The steel autoclave, A, is filled with mercury from the valve C to the T-piece D. In the steel autoclave, B, is inserted a small linen bag containing the solid substance. This bag fits closely all over the inside wall of the autoclave.

Both autoclaves are in a thermostat. In order to start the determination the valve, E, is connected with a vacuum pump and the apparatus is evacuated with valves I, G and F open (C is closed). To remove the last trace of air E is now closed, some ethylene is admitted from the cylinder K and then the apparatus is reevacuated through E. After this valve E is again closed and ethylene is passed from the cylinder K into autoclave B, until the desired pressure is attained, which is read on the pressure-gage H. Now the naphthalene is going to dissolve, causing the pressure to decrease again. Additional gas is then admitted until the desired pressure is restored. This procedure is repeated until the pressure remains constant. The required time for this varies with the pressure (at low pressures there is less solubility, consequently quicker saturation). The pressure is maintained for half an hour. Comparison experiments have proved that it makes no difference to extend this time to one or two hours.

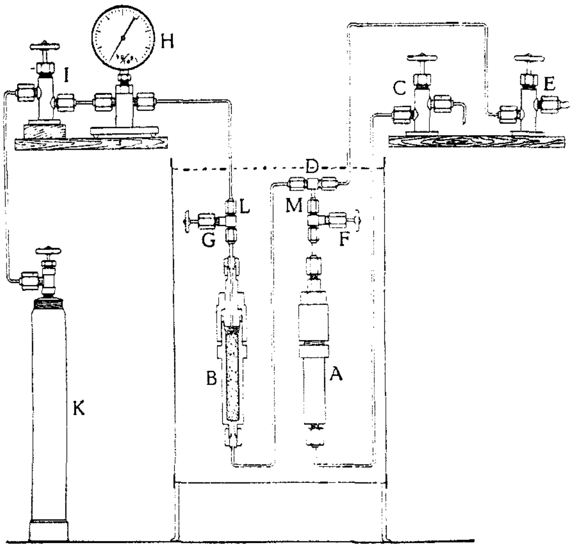

Fig. 1.—Apparatus for preparation of saturated fluid solutions.

We have now, therefore, a saturated solution in autoclave B, a part of which we must transfer into autoclave A.

The solutions in the pipe between the lower end of autoclave B and valve E are unsaturated, so that we have to displace these with saturated solution. To this end both valves E and I are somewhat opened at the same time, taking care that the pressure remains constant. The valve of cylinder

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[1] Diepen and Scheffer, THIS JOURNAL, **70**, 4081 (1948).

K is always open; the admission of gas is controlled by the easily regulated valve I.

The volume of the pipe has been measured. From a p–$(1/v)$ diagram (v = specific volume) of ethylene for various temperatures the weight of ethylene in the pipe at that given pressure and temperature is calculated. The quantity of ethylene discharging from valve E is measured and so we know when the whole of the unsaturated solution in the pipe has been replaced by saturated solution.

Both valves are then closed and the valves C and I are slowly opened. Mercury drips from valve C into a receiver, while by means of valve I the pressure is kept constant. In this way the saturated solution is displaced into the autoclave A at constant pressure and temperature.

At the top of autoclave B pure ethylene enters and needs to be saturated. In consequence too rapid a flow is not permissible. By means of comparison experiments the best rate was established at 0.5 to 1 cc. of mercury per minute. At 2 cc. of mercury per minute the same result is also attained, but then it is much more difficult to maintain a constant pressure.

For the succeeding analysis we are limited to a maximum weight of ethylene. Therefore this puts a top limit to the quantity of mercury which can stream out, and this is estimated sufficiently precisely with the help of the p–$(1/v)$ diagram of ethylene.

The valves C, I, F and G are now closed and herewith the first part of the problem, the preparation of a saturated solution and the spatial separation of a part of the solution from the solid substance, all at a constant pressure and at a constant temperature, has been solved.

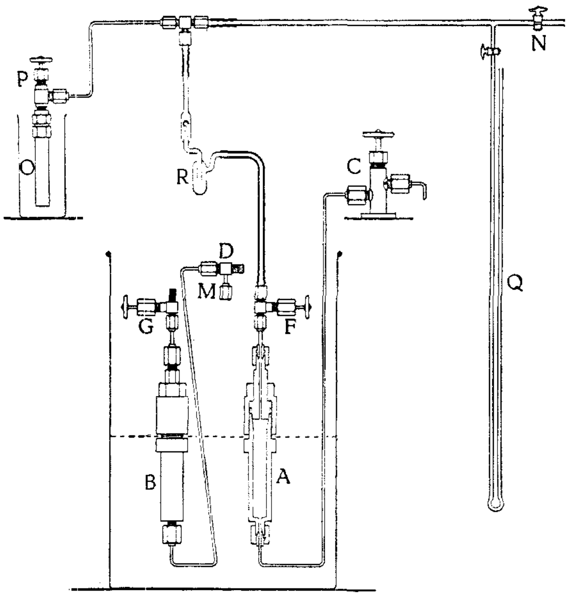

Fig. 2.—Apparatus for the determination of concentrations in fluid solutions.

Now this saturated solution has to be analyzed. For this purpose first so much mercury is run from valve C that it is only just at the bottom of the autoclave. As a result the pressure in the autoclave A is reduced and the greater part of the solid substance crystallizes. At this time the coupling L is loosened and both autoclaves are transferred to a container cooled with alcohol and solid carbon dioxide. By this procedure the pressure is lowered to about 5 atmospheres.

At this temperature the vapor pressure of the solid substance is so low and the critical point is so remote that the solubility of the solid substance in the gas phase has certainly become zero. Therefore, the solid substance has been entirely crystallized at this point.

Now the gas from bomb B is run into a large storage cylinder; in this way the ethylene is regained for the greater part. The coupling M is loosened and now the autoclave A is connected to the apparatus represented in Fig. 2.

All the air as far as the valve F is evacuated through the cock N. The valve P of the small measuring-autoclave, O, is opened while doing this.

Next the autoclave O is cooled in liquid air and valve F is slowly opened. The ethylene in autoclave A now condenses in O. The mercury carried along is collected in R. After F has been opened entirely and all the ethylene has been condensed the open manometer Q indicates a vacuum.

Valve P is now closed and the measuring-autoclave is warmed up to room temperature, after which it is weighed. The difference between full and empty weights measures the quantity of ethylene which was present in the autoclave A.

The autoclave A is now taken out of the carbon dioxide alcohol bath. It is warmed to room temperature after which it is washed out thoroughly with ether. By determining the quantity of naphthalene in this etheric naphthalene solution we evaluate the concentration of the original solid-saturated fluid solution.

For the analysis of the naphthalene solution we have applied in a somewhat modified way the method of Hilpert[2] using picric acid to precipitate naphthalene as naphthalene picrate.

Results and Discussion

The data obtained at the three temperatures, 12, 25 and 35° are shown in Table I to III and are depicted graphically in Fig. 3.

Figure 3 shows that a smooth line can be drawn through the points marking the solubilities at 12°, as well as through those for 25° and 35°, and that deviations from these lines are slight, especially at 25 and 35°. This fact demonstrates that the method developed by us gives useful results. Therefore it is our intention to apply this method further to this system and to others as well.

The results obtained thus far teach us the fol-

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(2) Hilpert, *Z. anorg. Chem.*, **29**, 58 (1916).

TABLE I

PRESSURE-COMPOSITION DATA AT 12° FOR ETHYLENE-NAPHTHALENE SYSTEM

p, atm.	C_2H_4, g.	$C_{10}H_8$, mg.	x mole %	x wt. %
103.1	7.35	266.8	0.788	3.503
98.8	7.49	268.7	.779	3.463
98.5	9.11	326.4	.777	3.459
93.8	9.09	301.4	.720	3.209
89.1	8.67	271.3	.680	3.034
89.1	9.11	282.0	.673	3.003
84.5	8.69	275.3	.688	3.071
79.8	8.63	249.5	.629	2.810
75.1	8.74	237.8	.592	2.649
70.4	9.98	242.0	.528	2.367
61.2	9.48	183.5	.422	1.899
58.4	9.29	152.6	.358	1.616
56.6	10.10	149.6	.323	1.460
55.7	9.00	130.6	.316	1.430
53.8	8.44	101.7	.263	1.191
52.9	4.19	38.6	.201	0.913
52.0	5.57	22.9	.090	.409
47.3	5.30	14.5	.060	.273
38.0	8.47	11.0	.028	.130

TABLE II

PRESSURE-COMPOSITION DATA AT 25° FOR ETHYLENE-NAPHTHALENE SYSTEM

p, atm.	C_2H_4, g.	$C_{10}H_8$, mg.	x mole %	x wt. %
98.5	6.40	272.5	0.923	4.084
98.0	6.00	250.9	.906	4.014
98.0	5.70	236.7	.900	3.987
95.3	5.03	203.6	.878	3.890
93.8	6.58	258.2	.851	3.776
92.3	8.24	327.9	.863	3.827
89.1	6.85	241.4	.765	3.404
87.8	5.29	182.7	.750	3.338
84.5	7.98	256.9	.699	3.119
83.1	4.78	145.5	.662	2.954
76.4	5.85	148.4	.552	2.474
71.7	6.61	118.9	.392	1.767
67.0	10.87	112.7	.226	1.026
67.0	11.02	110.4	.219	0.992
67.0	11.29	112.3	.217	.985
65.8	10.25	73.2	.156	.711
64.6	10.35	62.8	.133	.603
62.3	10.10	34.9	.076	.344
57.4	10.89	12.7	.026	.117
56.6	9.39	7.8	.018	.083
47.8	10.27	1.6	.003	.016

TABLE III

PRESSURE-COMPOSITION DATA AT 35° FOR ETHYLENE-NAPHTHALENE SYSTEM

p, atm.	C_2H_4, g.	$C_{10}H_8$, mg.	x mole %	x wt. %
112.9	9.85	645.0	1.412	6.140
109.0	10.30	607.0	1.273	5.565
105.7	9.80	536.5	1.183	5.186
103.1	10.91	545.5	1.082	4.762
99.4	10.21	441.0	0.936	4.141
93.8	11.21	412.0	.798	3.546
84.5	10.19	242.0	.517	2.320
84.5	10.71	247.0	.502	2.254
79.1	10.17	145.5	.312	1.410
72.3	11.08	75.6	.149	0.677
65.8	9.21	38.2	.091	.419
63.1	8.13	20.5	.055	.251
54.8	9.23	10.9	.026	.118

lowing facts regarding the system ethylene–naphthalene:

The isotherm at 12° has in the neighborhood of 0.15 to 0.2 mole % only a slight slope: $(dp/dx)_T$ = small. If the temperature falls to 11°, the temperature of the critical point, the p–x curve has a horizontal point of inflexion situated at 0.15 to 0.2 mole % naphthalene. At 25° and at 35° the slight slope occurring near the critical concentration at 12° has disappeared.

Further it appears that the isotherms for 12 and 25° intersect at about 81.5 atmospheres and 0.64 mole % naphthalene (point A) and the isotherms for 12 and 35° intersect at about 91 atmospheres and 0.71 mole % naphthalene (point B), whereas the isotherms for 25 and 35° have two intersections, namely, at about 97 atmospheres and 0.90 mole % naphthalene (point C) and at about 59.5 atmospheres and 0.04 mole % naphthalene (point D).

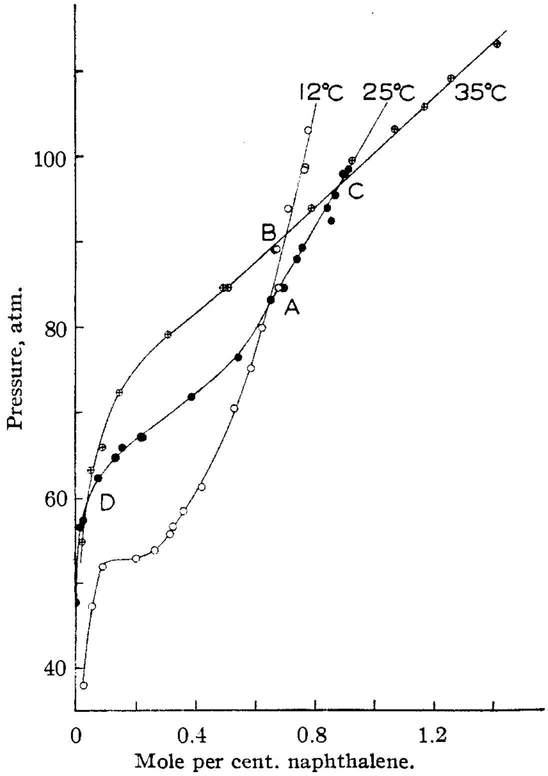

Fig. 3.—Pressure-composition sections of the system ethylene–naphthalene at 12.0, 25.0 and 35.0°.

Figure 3 makes clear that the p–x sections at various temperatures supply a bundle of curves possessing two envelopes, bounding the curves at their left and right sides. This leads to the following implications:

1. At the composition of the intersection point B (0.71 mole % naphthalene) given in Fig. 3, the pressure at 12 and 35° amounts to about 91 atmospheres, and is less at temperatures in between. Consequently at some temperature situated between 12 and 35° a point appears at which $(dp/dT)_x = 0$. This point lies on the above-mentioned envelope. A qualitative plot of the section for this composition is given in Fig. 4. (Naturally intersection with the three-phase line, S–L_2–G, is possible at higher temperatures).

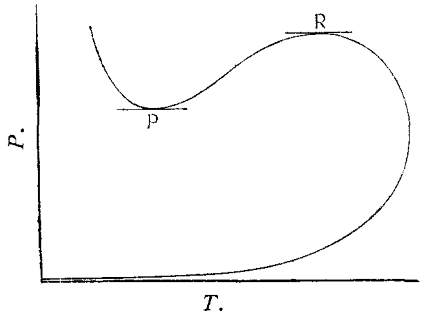

Fig. 4.—Pressure-temperature section for constant x.

Point P is the point on the envelope for the right side, *i. e.*, on the side of the higher x values, at which $(dp/dT)_x = 0$.

2. At the pressure of the intersection point B (≐91 atm.) in Fig. 3 the naphthalene concentration at 12 and 35° amounts to about 0.71 mole % and is higher at the same pressure for temperatures between. In consequence at some temperature between 12 and 35° a point occurs at which $(dx/dT)_p = 0$. This point again occurs on the above-mentioned envelope. A qualitative picture of the section for a pressure of 91 atm. is given in Fig. 5.

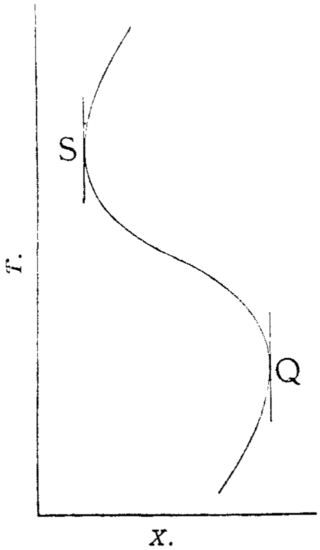

Fig. 5.—Temperature–composition section for constant p.

Point Q is the point on the envelope on the side of the higher x values, at which $(dx/dT)_p = 0$ or $(dT/dx)_p = \infty$.

3. At the composition of the intersection point D (0.04 mole % naphthalene) given in Fig. 3, the pressure at 25 and 35° amounts to about 59.5 atm. and is higher at temperatures between. Consequently at a temperature situated between 25 and 35° a point occurs at which $(dp/dT)_x = 0$. This point lies on the envelope for the left side, *i. e.*, on the side of the lower x values.

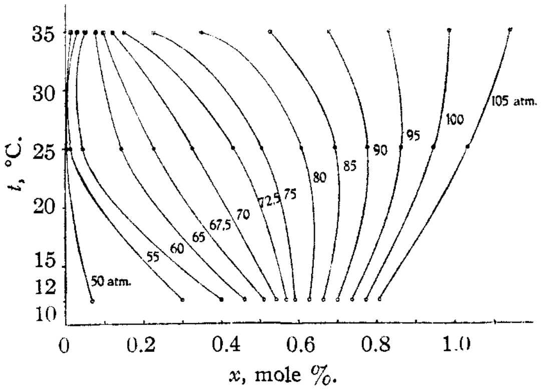

Fig. 6.—Temperature-composition sections of the system ethylene–naphthalene for various pressures.

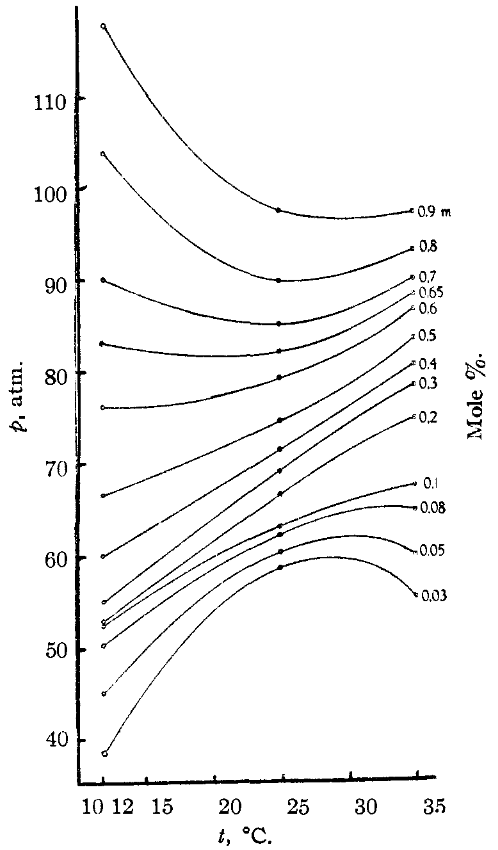

Fig. 7.—Pressure-temperature sections of the system ethylene–naphthalene for various concentrations.

TABLE IV

COMPARISON OF OBSERVED VAPOR CONCENTRATIONS OF NAPHTHALENE IN ETHYLENE WITH CALCULATED VAPOR PRESSURES

p, atm.	x mole % (expt. 12°)	x mole % (calcd. 12°)	x mole % (expt. 25°)	x mole % (calcd. 25°)	x mole % (expt. 35°)	x mole % (calcd. 35°)	$\frac{x_{\text{expt.}}}{x_{\text{calcd.}}}$ 12°	$\frac{x_{\text{expt.}}}{x_{\text{calcd.}}}$ 25°	$\frac{x_{\text{expt.}}}{x_{\text{calcd.}}}$ 35°
100.0	0.777	3.03×10^{-5}	0.950	1.08×10^{-4}	0.993	2.76×10^{-4}	25600	8800	3590
95.0	.740	3.19×10^{-5}	.866	1.14×10^{-4}	.835	2.91×10^{-4}	23200	7600	2870
90.0	.703	3.37×10^{-5}	.782	1.20×10^{-4}	.682	3.07×10^{-4}	20800	6500	2220
85.0	.666	3.57×10^{-5}	.699	1.27×10^{-4}	.530	3.25×10^{-4}	18700	5500	1630
80.0	.630	3.79×10^{-5}	.614	1.35×10^{-4}	.350	3.45×10^{-4}	16600	4500	1020
75.0	.584	4.04×10^{-5}	.506	1.44×10^{-4}	.194	3.68×10^{-4}	14500	3500	530
70.0	.530	4.33×10^{-5}	.328	1.54×10^{-4}	.160	3.94×10^{-4}	12200	2100	410
65.0	.465	4.66×10^{-5}	.144	1.66×10^{-4}	.078	4.25×10^{-4}	10000	870	180
60.0	.390	5.05×10^{-5}	.044	1.80×10^{-4}	.050	4.60×10^{-4}	7700	240	110
55.0	.296	5.50×10^{-5}	.013	1.96×10^{-4}	.028	5.02×10^{-4}	5400	66	56
53.0	.220	5.72×10^{-5}	.008	2.04×10^{-4}	.020	5.21×10^{-4}	3800	39	39
52.0	.090	5.84×10^{-5}	.006	2.08×10^{-4}	.017	5.31×10^{-4}	1540	29	32
50.0	.076	6.06×10^{-5}	.004	2.16×10^{-4}	.013	5.52×10^{-4}	1250	19	25
40.0	.034	7.59×10^{-5}	.001	2.70×10^{-4}	...	....	450	4	..

When Fig. 4 is assumed to be valid for this composition, point R is the point on the envelope for the left to which $(\mathrm{d}p/\mathrm{d}T)_x = 0$ applies.

4. At the pressure of the intersection point D (±59.5 atm.) given in Fig. 3 the naphthalene concentration at 25 and 35° amounts to about 0.04 mole % and is lower at temperatures between.

Consequently at a temperature between 25 and 35° a point appears, at which $(\mathrm{d}x/\mathrm{d}T)_p = 0$. This point lies upon the envelope for the left. If we imagine the section of Fig. 5 to be designed for this pressure, the point S will be the point on the envelope on the side of lower x values at which $(\mathrm{d}x/\mathrm{d}T)_p = 0$ or $(\mathrm{d}T/\mathrm{d}x)_p = \infty$.

Both envelopes of the p–x lines of Fig. 3 are, therefore, the loci of the points where $(\mathrm{d}p/\mathrm{d}T)_x = 0$ and $(\mathrm{d}T/\mathrm{d}x)_p = \infty$.

In Figs. 6 and 7, t–x and p–t sections, derived from the p–x figures we have found, have been drawn for different pressures and different compositions. These figures make it evident that the various types of peculiar points deduced in the foregoing discussion are all occurring.

Next we want to point out that the solubility of naphthalene at higher pressures is much greater than we would expect considering the volatility of pure naphthalene. The vapor pressure of solid naphthalene at lower pressures is known from the measurements of Schlumberger.[3] On the basis of these determinations we have calculated the vapor pressures at 12, 25 and 35° and find 0.303×10^{-4}, 1.08×10^{-4} and 2.76×10^{-4} atm., respectively.

If at these temperatures the partial pressures of naphthalene in the fluid phase were equal to the vapor pressures at the same temperature, calculated just now, then the x-values at these temperatures would be those indicated in the third, fifth and seventh columns in Table IV.

In the second, fourth and sixth columns the actual values for x according to Fig. 3 are presented. The ratio of the experimental and calculated values is to be found in the eighth, ninth and tenth columns.

Therefore, we conclude that, for instance, at 12° and 100 atm. the naphthalene concentration in the fluid phase is 25600 times as intense as it would be if the naphthalene in this phase had a pressure equal to the normal vapor pressure of the naphthalene at the same temperature. The effect of the total pressure upon the vapor pressure cannot account at all for the observed effect, which is therefore distinctly a specific solubility effect.

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Summary

An apparatus for the preparation and precise measurement of saturation concentrations of slightly volatile solids in fluids at temperatures above their critical points has been devised.

The apparatus has been used to determine the saturation concentrations of naphthalene in ethylene at 12, 25 and 35° and at various pressures. The concentrations found are as much as 25,000 times as great as those predicted from the vapor pressure of naphthalene and indicate a specific solubility effect.

Important characteristic features of the phase-rule diagrams for the ethylene–naphthalene system in the vicinity of the critical point for ethylene have been described and discussed.

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[3] Schlumberger, *J. Gasbeleucht*, **55**, 1257 (1912).