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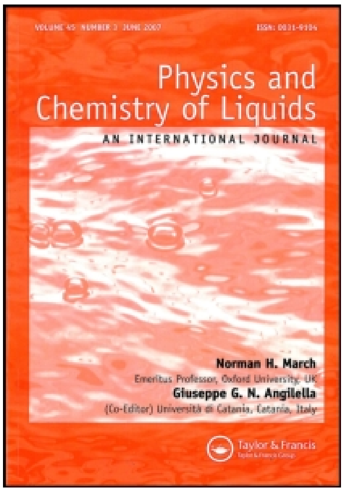

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Limited Solubility and Critical Exponents for Some Indole + Hydrocarbon Systems

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The solubility of indole *n*-octane, *n*-decane and *n*-dodecane has been measured at several temperatures. The three systems exhibit limited solubilities with upper critical solution temperatures. The critical exponents of the three systems, evaluated from the experimental data, are found to be the same within the limits of experimental error: $\beta = 0.50 \pm 0.4$.

KEY WORDS: Indole, *n*-octane, *n*-decane, *n*-dodecane, limited solubility, critical exponent

1 INTRODUCTION

Investigating the thermodynamic properties of binary solutions of indole with *n*-octane, *n*-decane and *n*-dodecane respectively, we found that these systems exhibit limited solubilities with typical critical opalescence phenomena. From the measured solubility-temperature coexistence curves, we evaluated the critical exponents for the three systems.

Critical exponents, and critical phenomena in general, have been the subject of many experimental and theoretical investigations in the last four decades.[1–8] The majority of the studies deals with the evaluation of the critical exponents from density measurements in the critical region. Occasionally, solubility versus temperature data are also used for the

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evaluation of critical exponents. For some systems, the experimentally found critical exponents are in good agreement with the ones obtained from the Renormalization Group Theory (RGT).[6–8] The criteria and conditions to be met by a system for good agreement between experiment and theory are discussed by S. C. Greer. The critical exponents for the three systems investigated in this study, $\beta = 0.50 \pm 0.04$, are in disagreement with those predicted by the RGT: $\beta = 0.325 \pm 0.010$.

2 EXPERIMENTAL

Indole supplied by the Aldrich Chemical Company, labelled as 99 +, was purified by fractional crystallization. The melting point and the boiling point of the purified product were in good agreement with the literature values.[9,10] The pure product was kept in a brown bottle under a dry nitrogen atmosphere in a refrigerator, in order to avoid polymerization. The product was checked for purity prior to each measurement. In spite of all these precautions, the quality of the product deteriorated with time. Within a couple of days, the originally white product turned first yellowish and later brownish. The chemical change had a pronounced effect on the melting point and eventually on the solubility.

Hydrocarbons of the highest commercial quality, supplied by the Aldrich Chemical Company, were repeatedly distilled in a 60 plate column, until their physical properties were found to be in good agreement with the literature values.[9–11]

A synthetic method was used for measuring the solubility. Known quantities of indole (solid) and the respective hydrocarbon (liquid) were placed in a double-jacketed saturation flask, equipped with a magnetic stirrer and an NBS calibrated mercury in glass thermometer.

A Neslab "Endocal" circulating water bath with a temperature progammer controlled the temperature in the saturation flask. The rate of temperature change was automatically reduced as the system approached the saturation point. The temperature of the saturation point was then recorded. The reproducibility of the temperature measurement was about ± 0.02°C. The saturation temperature was approached from above and from below. The temperatures reached from above and from below differed in some instances by as much as 0.08°C. Thus, the overall accuracy of the temperature measurement is about ±0.1°C. Low accuracy indeed. The relatively flat top of the curves was another source of experimental error. A minor change in temperature results in a large change in composition of the two coexisting phases. Critical opalescence phenomena were observed in all the systems.

3 RESULTS AND DISCUSSION

The solubility versus temperature data are listed in Table 1, 2, 3, and plotted in Figures 1, 2, 3. The following observations can be made from the data: (a) The coexistence curves are not symmetrical. (b) The critical solution temperature increases with the molar mass of the

Table 1 Solubility data for the indole + *n*-octane system.

Temperature °C	mol % indole	Temperature °C	mol % indole
51.27	100.0	78.21	67.00
49.80	97.86	78.55	66.06
48.65	95.82	78.85	65.18
47.80	93.85	79.65	62.30
46.90	91.35	79.77	61.48
46.35	88.72	79.92	60.68
46.15	87.56	79.86	58.74
49.80	85.71	79.95	57.90
52.77	84.48	80.02	57.09
55.90	83.29	80.10	56.30
60.07	82.00	80.23	55.30
62.25	80.78	80.29	54.91
65.72	79.07	80.36	54.14
67.78	77.43	80.39	53.86
69.24	76.69	80.39	53.10
70.07	75.86	80.40	52.36
71.24	75.07	80.42	50.72
72.75	74.50	80.43	50.00
73.04	73.55	80.44	49.31
74.03	72.94	80.12	49.17
77.44	72.06	80.44	48.64
76.29	71.76	80.12	48.47
77.51	70.26	79.93	47.67
79.91	46.98	75.91	32.33
79.91	46.32	75.55	31.64
79.97	45.45	75.59	31.29
79.98	44.79	75.34	31.38
79.64	43.35	75.16	30.42
79.58	42.71	78.11	36.03
79.76	42.26	77.65	35.55
79.51	42.12	78.29	35.13
79.50	41.53	77.41	34.80
79.68	41.35	78.19	34.37
79.64	40.51	77.17	34.08
78.64	38.42	78.07	33.65
78.48	37.59	76.86	33.39
78.30	36.80	77.84	32.96
78.48	36.69	76.67	32.73

Table 2 Solubility data for the indole + *n*-decane system.

Temperature °C	mol % indole	Temperature °C	mol % indole
51.35	100.00	81.60	72.25
50.91	99.41	81.80	71.63
50.48	98.82	82.00	70.85
50.08	95.99	82.35	69.99
49.78	97.67	82.53	68.65
49.62	97.09	82.34	68.63
49.33	96.52	82.71	67.33
48.28	94.34	82.48	66.49
47.50	91.44	82.18	66.94
53.65	89.29	82.90	66.13
58.72	87.87	82.61	65.73
62.83	86.50	83.15	64.94
70.90	83.36	82.92	64.57
71.65	82.90	83.60	63.80
73.77	81.53	83.10	63.46
76.17	80.31	83.68	62.68
76.49	79.78	83.28	62.38
79.51	76.71	83.37	61.75
79.92	76.32	83.80	61.61
80.32	75.37	83.51	60.57
80.76	74.51	83.60	59.44
81.22	73.66	83.61	58.35
81.34	72.84	83.59	57.23
83.29	56.88	83.20	46.65
83.37	56.59	83.10	44.26
83.39	55.47	83.03	45.86
83.35	55.04	82.99	45.40
83.30	54.77	82.86	44.24
83.35	53.97	81.50	42.87
83.20	53.72	80.82	39.99
83.35	53.02	80.25	38.83
83.23	52.69	78.65	36.70
83.29	52.35	78.08	36.09
83.25	51.76	77.44	35.35
83.29	48.58	76.03	33.88
83.25	50.71	71.70	30.40
83.25	50.55	66.36	25.92
83.13	49.56	57.25	20.83
83.22	48.74	44.35	11.46
83.10	48.46	37.25	7.07
83.21	48.09	31.55	5.25
83.22	47.93	28.83	3.50
83.15	47.32	9.15	1.76

Table 3 Solubility data for the indole + *n*-dodecane system.

Temperature °C	mol % indole	Temperature °C	mol % indole
51.20	100.0	87.82	70.20
50.20	98.30	88.13	68.80
49.65	96.66	88.16	67.83
48.95	95.06	88.19	66.88
48.40	94.73	88.22	65.96
48.10	93.75	88.27	64.41
50.95	92.02	88.28	63.80
57.08	91.39	88.29	63.58
65.35	89.87	88.28	62.76
73.42	87.25	88.32	61.97
76.68	85.74	88.31	61.33
80.37	84.29	88.28	60.57
82.10	82.88	88.26	60.03
83.94	81.89	88.24	59.82
84.90	80.54	88.27	59.04
85.00	79.60	88.27	58.07
85.79	78.28	87.28	56.97
86.40	77.01	87.12	54.55
86.86	75.79	86.96	53.45
86.81	74.82	86.91	52.78
87.15	73.54	86.66	51.13
87.37	72.30	86.33	49.76
87.52	71.10	86.21	48.98
85.85	48.13	75.50	32.96
85.23	47.07	70.99	28.81
84.80	45.59	64.93	24.02
84.23	44.21	60.68	21.59
83.66	42.90	46.45	13.67
81.24	40.35	44.55	11.46
79.30	37.54	36.63	7.25
77.45	35.11		

hydrocarbon. (c) The tops of the curves are relatively flat and consequently, a minor change in the temperature results in a large concentration change of the coexisting phases. (d) The solubility curves exhibit minima that are about 5°C below the melting point of the pure indole.

For the evaluation of the critical exponents we employed the following procedure: (a) A non-linear least squares curve fitting method was used for smoothing out the experimental data. Three, four and five constant equations were used in the process. The four constant equation gave the best fit. Since there is no direct need for the parameters, we do not list their values here. (b) From the derivatives, dt/dx, we evaluated the coordinates of the critical point, t_c and x_c, respectively.

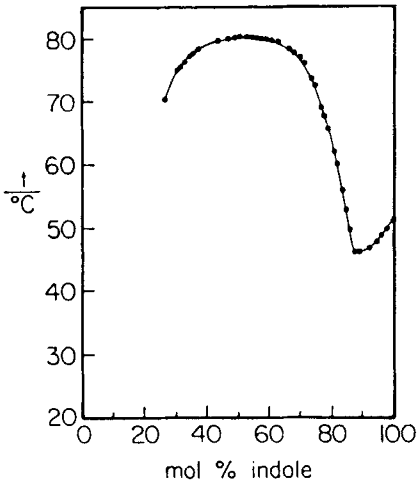

Figure 1 The Solubility Diagram of the Indole + *n*-Octane System.

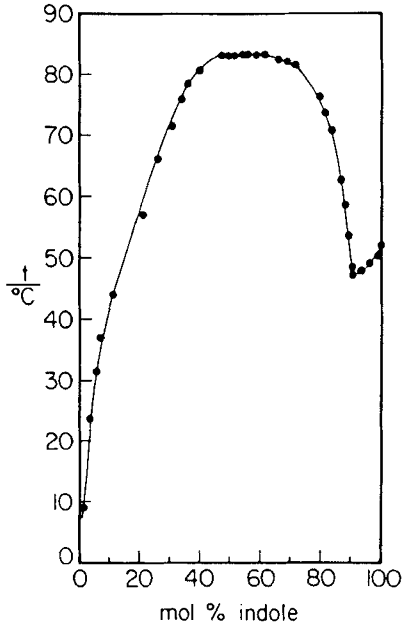

Figure 2 The Solubility Diagram of the Indole + *n*-Decane System.

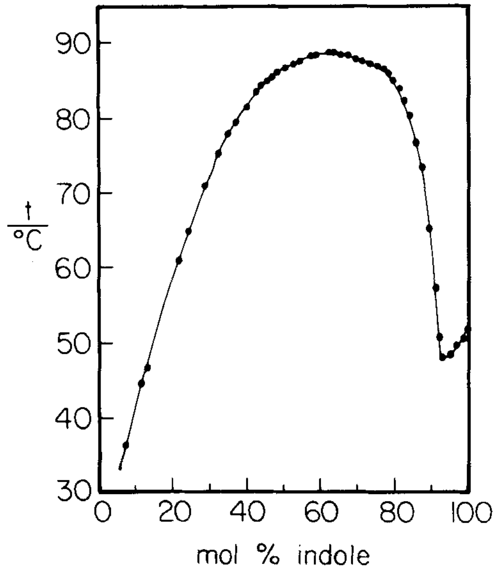

Figure 3 The Solubility Diagram of the Indole + *n*-Dodecane System.

This data are seen in Table 4. (c) From the non-linear curve fitting expressions, we evaluated x and t at 0.1°C intervals in a range of about 10°C. These results were then used for the evaluation of the critical exponents from the equation

$$\frac{x - x_c}{x_c} = k\left(\frac{T - T_c}{T_c}\right)^{\beta}$$

or better from the logarithmic form of this equation

$$\ln\left(\frac{x - x_c}{x_c}\right) = \ln k + \beta \ln\left(\frac{T - T_c}{T_c}\right)$$

where x is the mole fraction of indole and β is the critical exponent. The reduction of the temperature range to about 3°C had practically no effect on the values of the critical exponents. Critical exponents were evaluated from the data on the ascending and descending parts of the coexistence curves. The values of the critical exponents, ln k and the correlation coefficients, α, are listed in Table 5. All the correlation coefficients are equal to unity. This means that no additional terms need to be used in the last two equations. The linear expression correlates the data very well. Since the coexistence curves are not symmetrical, the discrepancy in the critical exponents obtained from the ascending and

Table 4 The criticial solution temperatures and the critical mole fractions of indole.

System	Critical solution temperature °C	Critical mole fraction x_c
Indole + *n*-octane	80.51	0.5138
Indole + *n*-decane	83.80	0.5536
Indole + *n*-dodecane	88.61	0.6386

Table 5 The critical exponents, ln *k* and the correlation coefficients for the three systems.

System	Critical exponent		ln *k*		Correlation coefficient	
	$x < x_c$;	$x > x_c$	$x < x_c$;	$x > x_c$	$x < x_c$;	$x > x_c$
Indole + *n*-octane	0.492	0.506	1.191	1.330	1.000	1.000
Indole + *n*-decane	0.462	0.536	0.890	1.464	1.000	1.000
Indole + *n*-dodecane	0.522	0.487	1.066	0.765	1.000	1.000

descending parts of the curve is expected. The use of volume fractions instead of mole fractions had practically no effect on the symmetry of the coexistence curve. An average value of 0.50 ± 0.04 represents the three systems fairly well. This value differs from the usually observed experimental and theoretical value of 0.33.[1–8]

The more or less equal values of the critical exponents prove that the three systems behave similarly in the critical region. The unusually large standard deviation (±0.04) is due to both, the nonsymmetrical shape of the coexistence curve and to the large experimental errors.

We believe that the value of 0.50 is correct for the indole + hydrocarbon systems. Repeated measurements gave, within the limits of experimental error, the same value. The value of 0.50 is justified for a fluid that obeys the van der Waals equation of state; for a fluid for which the cohesive energy-volume relationship is $U = -a/V$. It seems to be unrealistic to assume that the three systems investigated in this study behave like van der Waals fluids. However, when it comes to liquid solutions, one cannot ridicule out such behaviors.

Acknowledgements

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References

1. S. C. Greer, *Account Chem. Res.*, **11**, 427 (1978).
2. E. Stanley, *Introduction to Phase Transition and Critical Phenomena*, Oxford University Press, New York (1971).
3. J. S. Rowlinson, *Liquid and Liquid Mixtures*, Butterworths Scientific Publ., London (1959).
4. J. V. Sengers and J. M. H. Levelt Sengers, *Prog. Liquid Phys.*, **103**, 174 (1978).
5. A. L. Sengers, R. Hocken, and J. V. Sengers, *Phys. Today*, **30**, 42 (1977).
6. K. G. Wilson, *Phys. Rev. B*, **4**, 3174 (1971).
7. K. G. Wilson and J. Kogut, *Phys. Rep.*, **12**, 15 (1974).
8. S. R. Ma, *Modern Theory of Critical Phenomena*, W. A. Benjamin, Reading, Mass. (1978).
9. "Handbook of Chemistry and Physics," 48 Edition, Chemical Rubber Co., Cleveland, Ohio (1967–1968).
10. J. Timmermans, *Physico-Chemical Constants of Organic Compounds*, Elsevier Publ. Co., New York (1950).
11. A. W. Ralston, C. W. Hoerr and L. T. Crews, *J. Org. Chem.* **9**, 319 (1944).