percentages and use Equation 8, rather than use Equation 9 directly unless ±2.39% maximum error is tolerable.

Temperature Dependence of Viscosity, η, for Mixtures, between t = 25° and 50° C.

$$\eta \text{ (millipoises)} = \sum_{i=0}^{4} a_i t^i \qquad (10)$$

An equation of the fourth degree gave fairly precise computed values in this case also. Constants a_0 through a_4 were determined for different 1-propanol percents by weight and recorded in Table IV.

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Consolute Temperatures for *m*-Fluoroaniline–Hydrocarbon Systems

Coexistence Data for the Isomeric Hexanes and Pentanes

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Phase diagrams of binary liquid liquid systems involving *m*-fluoroaniline in the isomeric pentanes and hexanes were obtained, and coexistence data is presented. Consolute temperatures were determined by the cloud point method. The data was better fitted to a cubic than a quadratic equation. However, neither equation would permit theoretical predictions of solubility without empirical measurements as shown by the drift in the collected constants of both equations.

THIS STUDY was undertaken to supplement the rather fragmentary data available on the solvent power of the fluorocarbons. The critical solution temperature may be used to characterize hydrocarbons in the same manner as the melting point, specific gravity, or any representative physical property. It is useful in selecting a proper solvent for extractions and separations. Further, coexistence equilibria may be utilized to predict solubilizing effects of traces which produce a ternary system by the Crismer method (*2*). The recent ACS Monograph (*1*) stimulates interest in this area and indicates the need for further study of univestigated systems.

EXPERIMENTAL

Materials. Spectrophotometric grade, *n*-pentane, *n*-hexane 2-methylbutane, 2,3-dimethylbutane, and 2,2-dimethylbutane, were obtained from Matheson, Coleman, and Bell Division, Norwood, Ohio. Research grade 2-methylpentane, 3-methylpentane, and *m*-fluoroaniline were obtained from Aldrich Chemical Co., Milwaukee, Wisconsin. Degree of purity was confirmed by refractive indices using an Abbe refractometer.

Procedure. The usual cloud point method was used with the aid of a mechanical agitating device. Samples were measured volumetrically to within ±0.005 ml., corresponding to a maximum error of 0.005 ml. at the mole fraction 0.870. Microburets equipped with Teflon stopcocks and water jacketed when necessary were employed. Quadruplicate reproducible analyses were run. Tubes were filled almost completely and stoppered securely to minimize changes in composition caused by large vapor accumulations. Samples were thermostated at once. Mayer found that consolute temperatures rose 1° C. if solutions stood 24 to 48 hours before use (*5*). In the present study, delay also seemed to interfere with reproducibility. Heating was accomplished in a water bath with auxiliary heaters at the rate of ⅓° C. per minute. Equilibrium was approached both from the direction of increasing and decreasing temperature until confirmation was obtained from the appearance and from the disappearance of turbidity from within the limiting uncertainty determined by volumetric tolerances. A National Bureau of Standards thermometer graduated to 0.1° C. was used.

RESULTS AND DISCUSSION

Coexistence data are presented in Tables I through III with the critical solution temperature as determined by rectilinear diameter. Mole fraction rather than volume fraction was found to enhance the symmetry of the curve when temperature *vs.* composition was plotted. Inspection of volume fraction data at $V_1 = 0.500$ indicates aniline point analogs as somewhat lower than consolute temperatures, especially for 3-methylpentane.

The classical treatment of van Laar (*4*) expressed the van der Waals equation for vapor-liquid equilibria in terms of the critical constants. The equation should then be applicable to both liquids and gases, since first and second

Table I. Coexistence Data for *m*-Fluoroaniline in the Methyl Substituted Butanes

Volume Fraction Hydrocarbon, V_1 (± 0.005)	Solution Temperatures, ° C. (± 0.3)		
	2-Methylbutane	2,2-Dimethylbutane	2,3-Dimethylbutane
0.200	39.8	45.1	36.8
0.260	55.4	55.2	46.8
0.300	63.1	60.0	53.0
0.400	71.9	70.4	63.7
0.500	75.1	75.0	67.8
0.560	76.0	75.9	68.2
0.600	76.2	76.1	70.0
0.660	76.2	76.0	70.0
0.700	74.8	76.0	69.7
0.800	70.5	71.2	65.6
0.900	55.6	54.1	51.3

Table II. Coexistence Data for *m*-Fluoroaniline in the Methyl Substituted Pentanes

Volume Fraction, Hydrocarbon, V_1 (± 0.005)	Solution Temperatures, ° C. (± 0.3)	
	2-Methylpentane	3-Methylpentane
0.200	35.1	34.3
0.260	51.2	44.4
0.300	56.4	52.4
0.400	66.4	62.0
0.500	70.1	67.6
0.560	71.9	71.5
0.600	72.2	71.5
0.660	71.4	71.6
0.700	71.4	71.2
0.800	71.3	66.4
0.900	51.9	49.4

Table III. Coexistence Data for *m*-Fluoroaniline in *n*-Pentane and *n*-Hexane

Volume Fraction, Hydrocarbon, V_1 (± 0.005)	Solution Temperatures, ° C. (± 0.3)	
	n-Pentane	*n*-Hexane
0.200	31.5	37.7
0.260	47.2	46.2
0.300	56.6	52.8
0.400	64.0	62.2
0.500	68.7	64.2
0.600	70.1	64.9
0.660	70.1	64.1
0.700	69.6	64.0
0.800	65.4	59.8
0.900	52.2	47.6

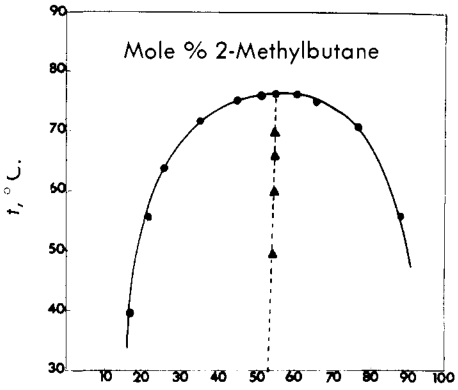


Figure 1. Solution temperature as a function of composition for 2-methylbutane and *m*-fluoroaniline

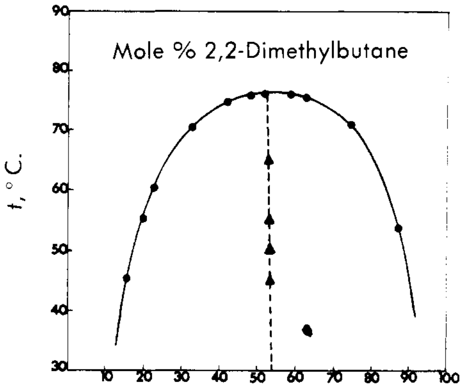


Figure 2. Solution temperature as a function of composition for 2,2-dimethylbutane and *m*-fluoroaniline

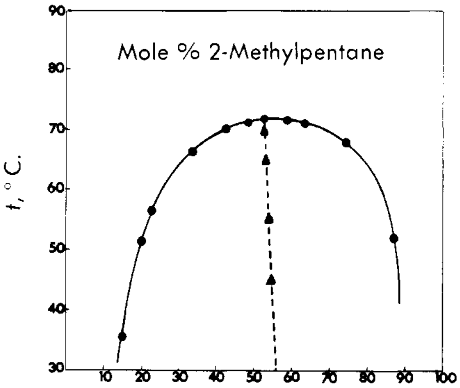


Figure 3. Solution temperature as a function of composition for 2-methylpentane and *m*-fluoroaniline

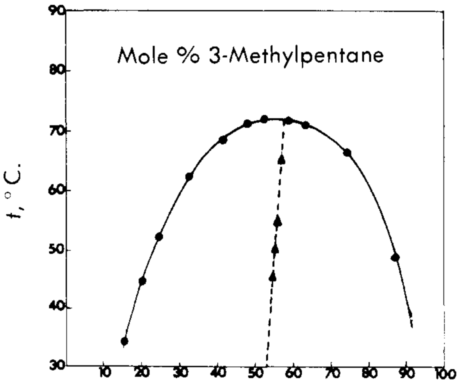


Figure 4. Solution temperature as a function of composition for 3-methylpentane and *m*-fluoroaniline

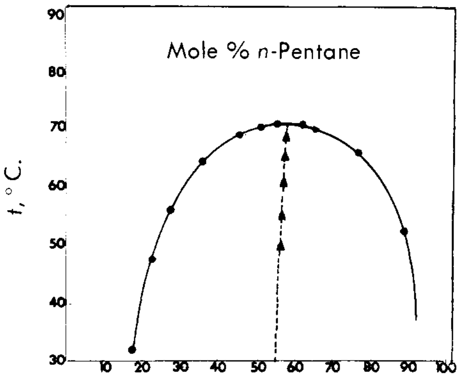


Figure 5. Solution temperature as a function of composition for *n*-pentane and *m*-fluoroaniline

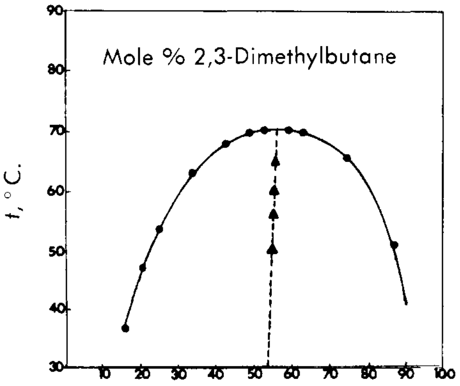


Figure 6. Solution temperature as a function of composition for 2,3-dimethylbutane and *m*-fluoroaniline

derivatives of pressure with respect to volume vanish at the critical temperature. The coexistence curve would have a parabolic shape in the region of the equivalence point. Activity, replaces pressure in van der Waals' equation according to the extension of Scatchard (*6*) and Hildebrand (*3*). The densities of the phases appear as the independent variables:

$$\frac{T_c - \mathrm{T}}{T_c} = \left[\frac{d^L - d^G}{d_c}\right]^2 k$$

In adapting to binary systems, the density may be replaced by volume or mole fraction. Any simple analytical function which simultaneously describes both phases leads to a roughly parabolic form.

However, Zimm (*7*) has found his coexistence curves well represented by a cubical equation:

$$\frac{t_c - t}{t_c} = k\left[\frac{V' - V''}{V_c}\right]^3$$

The cubical equation yields a better fit with data obtained in this study as shown by comparison of the collected constants (Table IV).

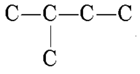
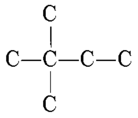
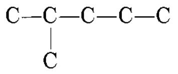
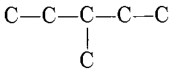
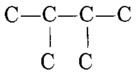
However, the drift of the collected constants with either equation indicates the necessity of experimental data for systems exhibiting a miscibility gap. The deviations from Raoult's law cannot be expressed with sufficient accuracy to predict solubility from either of the proposed equations.

Table V is a summary indicating that consolute temperatures decreased with increasing chain length in the expected manner with the exception of 2,3-dimethylbutane.

Table IV. Coexistence Curve Fitting for *n*-Hexane Constancy of Collected Constants

Temperature, °C.	Values of k	
	$t_c - t = k(N_1' - N_1'')^2$,	$t_c - t = k(N_1' - N_1'')^3$,
35	47.2	59.5
45	42.5	62.2
55	34.3	63.5
60	28.2	65.8

Table V. Summary Showing Influence of Carbon Chain Length on Critical Solution Temperature

Hydrocarbon	Structure	Critical Soln. Temp., t_c	Critical Compn., N_1
2-Methylbutane	 $\mathrm{C{-}\underset{\substack{\vert\\ C}}{C}{-}C{-}C}$	76.2	0.555
2,2-Dimethylbutane	 $\mathrm{C{-}\overset{\substack{C\\ \vert}}{\underset{\substack{\vert\\ C}}{C}}{-}C{-}C}$	76.1	0.521
2-Methylpentane	 $\mathrm{C{-}\underset{\substack{\vert\\ C}}{C}{-}C{-}C{-}C}$	72.2	0.522
3-Methylpentane	 $\mathrm{C{-}C{-}\underset{\substack{\vert\\ C}}{C}{-}C{-}C}$	71.6	0.572
n-Pentane	C—C—C—C—C	70.1	0.581
2,3-Dimethylbutane	 $\mathrm{C{-}\underset{\substack{\vert\\ C}}{C}{-}\underset{\substack{\vert\\ C}}{C}{-}C}$	70.0	0.560
n-Hexane	C—C—C—C—C—C	64.9	0.518

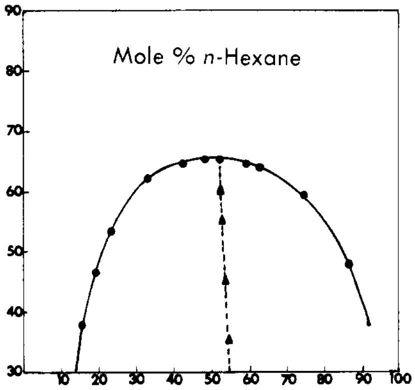


Figure 7. Solution temperature as a function of composition for *n*-hexane and *m*-fluoroaniline

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NOMENCLATURE

d = density, grams/ml.
t = °C.
T = °K.
k = constant

Subscripts

c = critical
1 = hydrocarbon

Superscripts

L = liquid
G = gas
N' = mole fraction of first phase of tie line equilibria
N'' = mole fraction of second phase
V' = volume fraction of first phase of tie line equilibria
V'' = volume fraction of second phase

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