5. Lapidus, Leon, and Rein Luus, *A.I.Ch.E. J.*, 13, No. 1, 108 (1967).
6. Lee, E. S., *Chem. Eng. Sci.*, 21, 183 (1966).
7. Luus, Rein, and Leon Lapidus, *A.I.Ch.E. J.*, 13, No. 1, 101 (1967).
8. McGill, R., and P. Kenneth, *Am. Inst. Aeronaut. Astronaut. J.*, 2, 1761 (1965).
9. Pontryagin, L. S., V. A. Boltyanskii, R. V. Gamkrelidze, and E. F. Mishchenko, "Mathematical Theory of Optimal Processes," Wiley, New York (1962).
10. Sridhar, R., R. E. Bellman, and R. E. Kalaba, *Memorandum RM-4039-PR*, Rand Corp., (Mar., 1964).
11. Wang, C. S., and L. T. Fan, *Ind. Eng. Chem. Fundamentals*, 3, 38 (1964).

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The Gas and Liquid Solubility Relations in Hydrocarbon-Water Systems

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The typical solubility boundaries of binary simple hydrocarbon-water systems are outlined for temperatures and pressures ranging into the neighborhood of the critical point for pure water. These systems are characterized by two unique states, a critical vaporization end point and a critical solution end point. The former defines the limit of mutual solubility of two liquid phases, and the latter defines a point of complete solubility at a minimum pressure. Experimental *P-T-x* data for cyclohexane-water and *n*-hexane–water mixtures are presented.

Traditionally the solubilities of hydrocarbon-water systems are described in terms of specific phase boundaries within the liquid state. In many instances liquids dissolved in liquids are indicated (*1, 2*), while for some lighter hydrocarbons, gases dissolved in liquids may also be reported. Extensions and correlations of these data theoretically (*3* to *5*) or empirically (*6*), either within a particular hydrocarbon-water system or among systems in general, are limited in scope. Some consider only the hydrocarbon-rich phase or the solubility of water in hydrocarbon; others consider only atmospheric pressure solubilities, and nearly all are limited to temperatures below 250°C. However, when the solubility boundaries of these systems over their entire temperature range are viewed, a not altogether unexpected similarity is found.

DESCRIPTION OF THE SOLUBILITY BOUNDARIES

Qualitatively summarized in Figure 1 are the essential solubility boundaries typical of the hydrocarbon-water binary behavior up to the neighborhood of the critical temperature and pressure of pure water. In lighter outline in Figure 1 are two sets of isobaric heterogeneous phase boundaries characteristic of lower and higher pressure behavior.

Familiarly, at a constant lower pressure the solubility of water in hydrocarbon, curve *AB*, and hydrocarbon in water, curve *DE*, increases with increasing temperature when the solubility is limited by the incidence of a second liquid phase. Further increase in temperature at the same lower constant pressure shows that the solubility decreases, curves *BC* and *EF*, when the second impending phase is gaseous.

The maximum solubilities in either liquid phase at a particular lower pressure therefore occur at the temperature of point *B* or *E* when the second phase is the heteroazeotropic vapor of composition *G*. The locus of all points such as *B* and *E* forms the essential boundaries of the saturated solubility diagram. At point *H* the hydrocarbon-rich liquid and the heteroazeotropic vapor compositions become identical. This unique point is called the *critical vaporization end point* (*7*).

At a higher constant pressure the solubility of a hydrocarbon in water, although greater, is affected by increasing temperatures in the same manner as at a lower pressure. Compare curves *DLK* and *DEF*. At this same constant higher pressure the solubility of water in a hydrocarbon, although nominal at lower temperatures, increases infinitely with increasing temperature as depicted by curve *AJK*. The point *J* is located on this curve at the temperature corresponding to point *L* (the saturated solubility of hydrocarbon in water) and has no other real significance. The curve segment *JK* does appear however as the water solubility in gaseous hydrocarbons, which is more commonly referred to as a *dew-point locus*. The remainder of the curve from *J* to *A* must then be identified as a liquid-

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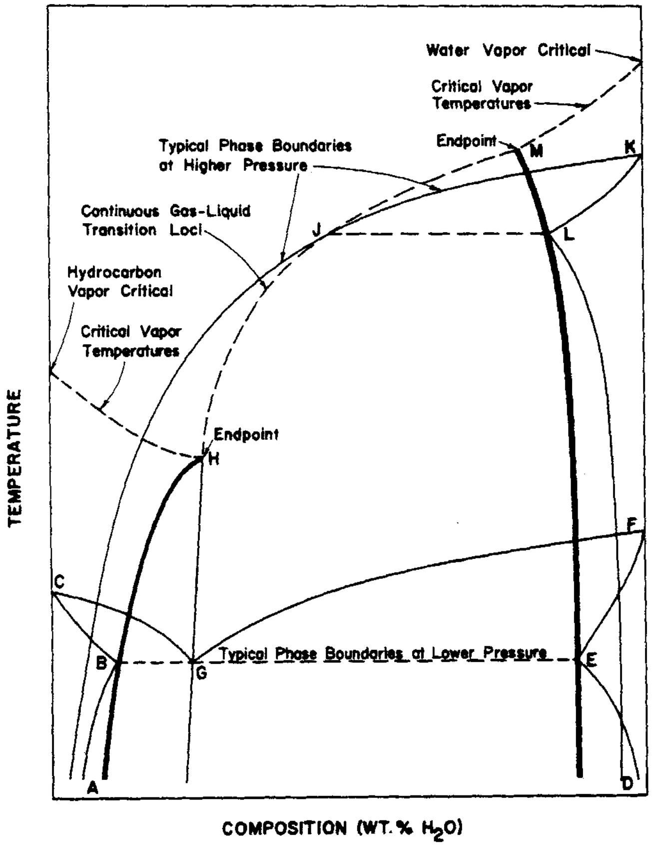

Fig. 1. A general solubility diagram for simple hydrocarbon-water systems.

liquid boundary as, indeed, it does appear on direct observation. Nevertheless, curve *AJK* is a continuous solubility boundary.

At a specific higher pressure a curve like *AJ* will join at point *M* with a boundary like *MLE* which completely envelops the two-phase liquid region. Since only a single phase exists outside this envelope, the temperature at point *M* is a critical solution temperature. There is, of course, a critical solution pressure and a critical solution composition associated with a critical solution temperature. At temperatures greater than at point *M* and at various pressures only critical vaporization phenomena occur. Presumably, at temperatures less than at point *M* other critical solution conditions exist at considerably elevated pressures. A point *M* is therefore a unique property of the system representing the lowest pressure at which a critical solution can exist. It is called the *critical solution end point.*

In general, the isothermal effect of increasing pressure is to increase the solubility of a hydrocarbon in water and to decrease the solubility of water in a hydrocarbon.

This qualitative description is a generalization based on the experimental studies of the boundaries of the cyclohexane-water and *n*-hexane–water systems along with data taken from the literature (*8* to *10*).

QUANTITATIVE EVALUATIONS

The conditions existing at the critical vapor end point for several hydrocarbon-water systems are summarized in Table 1. This unique state for each system represents the condition of temperature and pressure for the maximum solubility of water in the hydrocarbon where the hydrocarbon may be identified acceptably as a liquid. For each system the critical vapor end-point temperature is less than the corresponding critical temperature of the pure hydrocarbon, while critical pressures are related inversely.

TABLE 1. PROPERTIES AT THE CRITICAL VAPORIZATION END POINT

	Critical temp., °C.	Critical pressure, lb./sq. in. abs.	Composition wt. fraction water	Composition mole fraction water
Propane-water (*4*)	96.5	637	0.0041	0.0099
Butane-water (*15*)	152.0	637.5	0.0155	0.0483
n-Hexane–water (10)	222.0	765	0.09	0.322
Cyclohexane-water (*14*)	255.7	1,163	0.172	0.493
Benzene-water (*9*)	268.3	1,364	0.258	0.602

Among the systems the critical composition of the solubility of water increases in proportion to the critical temperature at the end point. This latter observation leads to the speculation that higher molecular weight liquid hydrocarbons will dissolve more water at this limit. An approximate relationship between maximum solubility as weight fraction of water in liquid hydrocarbon at the critical vapor end-point temperatures is shown in Figure 2.

Apparently by coincidence the critical compositions for water in the C_6-hydrocarbons can be represented by approximate simple molecular ratios. The mole ratio of water to *n*-hexane is about 1:2, for water to cyclohexane 2:2, and for water to benzene 3:2.

The second unique state, the critical solution end point, is known only for the C_6-hydrocarbon-water systems. These are summarized in Table 2 and correlated in Figure 3. This state is characterized by the temperature at the minimum pressure above which the hydrocarbon completely dissolves in liquid water. The temperatures, pressures, and compositions at the critical solution end points again follow a regular order with respect to the properties of the pure hydrocarbons. In general, the higher the crit-

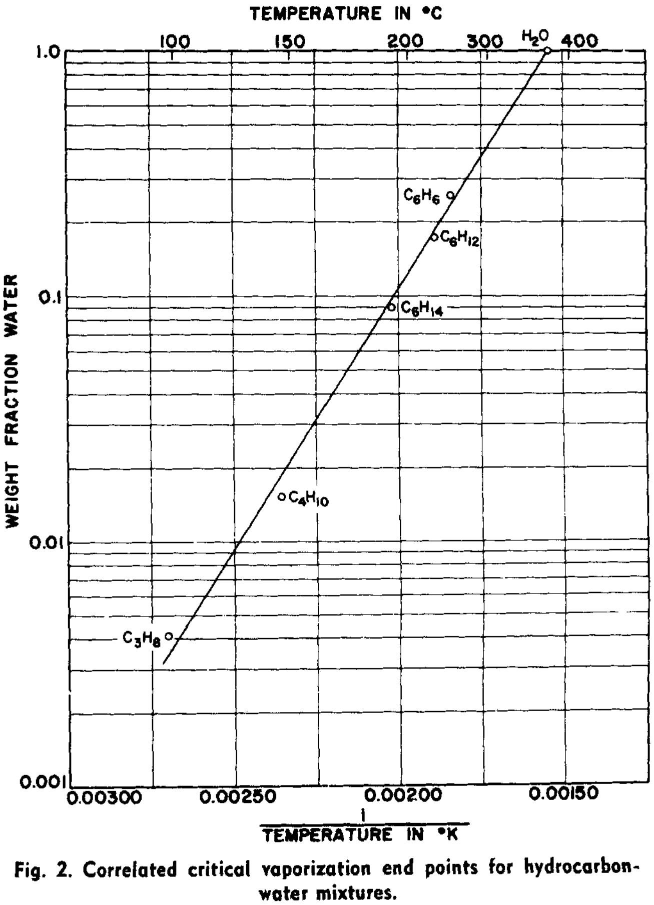

Fig. 2. Correlated critical vaporization end points for hydrocarbon-water mixtures.

TABLE 2. PROPERTIES AT THE CRITICAL SOLUTION END POINT

	Critical temp., °C.	Critical pressure, lb./sq. in. abs.	Composition weight fraction water
n-Hexane–water	368	3,280	0.95 (est)
Cyclohexane-water	360	3,260	0.913
Benzene-water (9)	306.4	2,300	0.590

ical temperature of the pure hydrocarbon the greater will be its solubility in water on approaching complete solubility. The molecular ratios of hydrocarbon to water at the critical solution end point do not reduce to simple numbers but are in the order of 1:100, 2:100, and 16:100 moles of *n*-hexane, cyclohexane, and benzene, respectively, to moles of water.

For the lighter hydrocarbons the critical solutions endpoint temperatures probably lie very near the critical temperature of water. The corresponding critical pressures should be considerably elevated above those of water. Scheffer (*11*) reported in 1913 that he was unable to find a critical condition for mixtures of ether and water in this area.

In general we may conclude that the more gaslike the hydrocarbon component is, relative to water, the poorer the mutual solubility of the two components will be. Stated another way, the lighter the hydrocarbon component the more severe must be the temperature and pressure to bring about complete solution. In all cases complete solubility represents a condition of supercriticality. Whether the remaining phase beyond the critical should be called liquid or gas is lost by default of definition even as in the case of a pure compound at pressure above its critical.

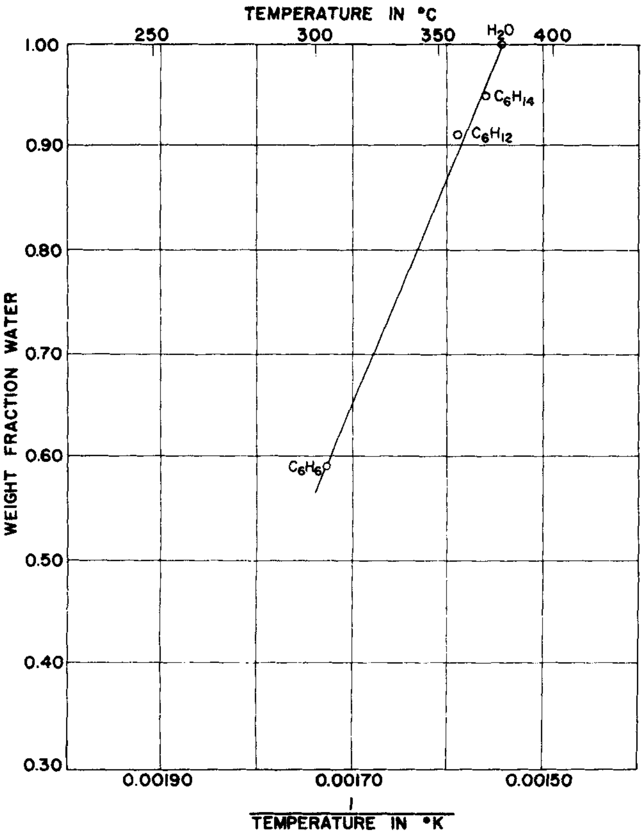

Fig. 3. Correlated critical solution end points for hydrocarbon-water mixtures.

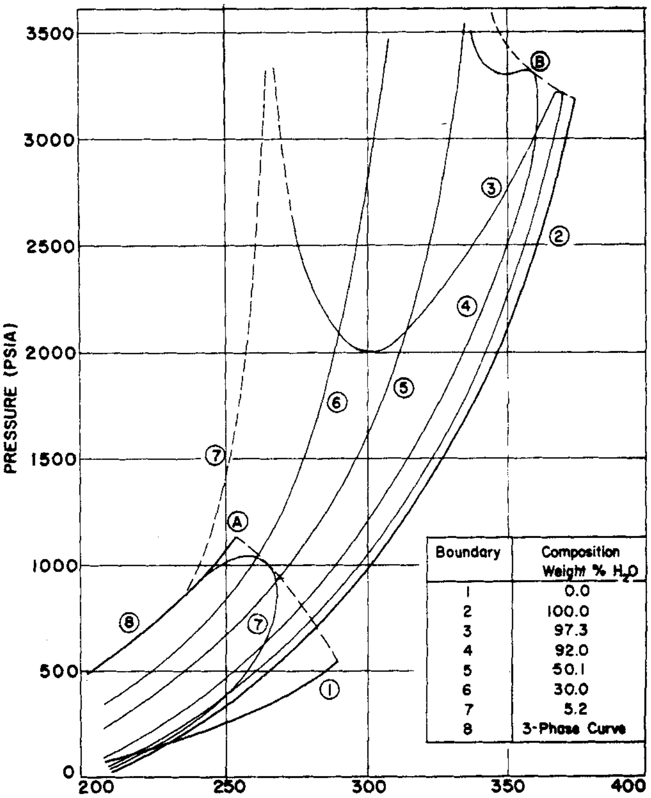

Fig. 4. Cyclohexane-water *P-T* diagram.

By means of Figures 2 and 3 the critical end points of other hydrocarbon-water systems can be assumed. With vapor pressure and critical data of the pure components along with the critical end points, a solubility diagram resembling Figure 1 will roughly approximate the solubility relations of that system.

EXPERIMENTAL METHODS AND APPARATUS

The techniques used in this experimental study were essentially those of Kay (*12*), while the apparatus was for the most part a duplicate of that reported earlier (*9*). Briefly, a small liquid sample, approximately 0.04 cc. of known composition, was confined over mercury in a heavy walled quartz capillary tube. The tube was sealed into a steel block which was a part of a closed hydraulic system containing pistons, gauges, and a mercury-to-oil interface detector. A redesign of the quartz to steel seal made it possible to pressurize the samples in excess of 3,400 lb./sq.in.gauge. Absolute control of the temperature surrounding the sample tube was maintained by condensing vapors of pure boiling organic fluids. Thus, for samples of fixed composition the pressure-temperature phase boundaries were determined by direct observation of the appearance or disappearance of a phase. Analyses of the resulting data show that for a given sample the temperature and pressure measurements are consistent within ± 0.05°C. and ± 1 lb./sq.in., respectively.

Sample preparation followed the technique described by Kay and Donham (*13*). Since the size of the complete sample was fixed, those samples whose compositions lie in the mid range were most accurate, and those approaching pure components in composition were least accurate. In some cases the latter compositions had to be adjusted by as much as 0.5% in order to be consistent with the bulk of the data.

EXPERIMENTAL RESULTS

Extensive measurement of points on the *P-T-x* phase surface boundary for the cyclohexane-water and the *n*-

TABLE 3. SELECTED CYCLOHEXANE-WATER PHASE BOUNDARIES

97.3 wt. % water		91.0 wt. % water		66.7 wt. % water		30.0 wt. % water		5.2 wt. % water		Three-phase locus*	
T, °C.	P, lb./sq. in. abs.	T, °C.	P, lb./sq. in. abs.	T, °C.	P, lb./sq. in. abs.	T, °C.	P, lb./sq. in. abs.	T, °C.	P, lb./sq. in abs	T, °C.	P, lb./sq. in. abs.
320	1,657	330	1,952	235	533	220	533	220	351	130	95
330	1,894	340	2,239	245	632	230	648	230	417	140	124
340	2,164	350	2,566	255	751	240	776	240	496	150	156
350	2,445	360	2,989	265	885	250	914	250	593	160	192
360	2,785	362	3,100	275	1,032	260	1,081	260	705	170	237
370	3,165	363.3	3,182	285	1,196	270	1,273	262	734	180	291
370.6	3,210†	362	3,236	295	1,388	280	1,492	264	765	190	357
370	3,199	360	3,255	300	1,494	290	1,764	266	803	200	433
360	2,910	359.4	3,261†	305	1,605	300	2,076	268.9	906	210	519
350	2,646	359	3,264	310	1,734	310	2,580	268	957	220	627
340	2,414	358	3,269	315	1,866			267.2	976†	230	751
330	2,209	356	3,280	320	2,000			267	980	235	818
320	2,054	354	3,294	325	2,169			263	1,024	240	890
310	1,942	352	3,308	330	2,339			261	1,027	245	968
307	1,920	350	3,329	335	2,538			260	1,024	250	1,055
304	1,916	348	3,358	340	2,765			255	1,005	255	1,148
302	1,925	346	3,405					250	980	255.7	1,162†
300	1,985							245	951		
295	2,303							243.2	939**		
292	2,540										
290	2,702										

* Common to all mixtures.
† Critical point.
** Three-phase point.

hexane–water systems were made. In total these included the measurement of temperature and pressure at the phase boundaries of eighteen samples of fixed composition for cyclohexane-water mixtures and five samples of n-hexane–water mixtures or more than 1,200 point observations. These raw data were graphically interpolated and smoothed on plots scaled 2 lb./sq.in./mm. and 0.2°C./mm. as depicted in Figure 4. P-x and T-x cross plots were prepared to test further the consistency of these data and finally to determine certain unique states of the systems. Typical smoothed data are presented in Tables 3 and 4.

TABLE 4. SELECTED n-HEXANE–WATER PHASE BOUNDARIES

98 wt. % water		84.6 wt. % water		49.43 wt. % water		14.66 wt. % water	
T, °C.	P, lb./sq. in. abs.	T, °C.	P, lb./sq. in. abs.	T, °C.	P, lb./sq. in. abs.	T, °C.	P, lb./sq. in. abs.
330	1,870	330	1,294	270	1,026	220	672
340	2,127	310	1,520	275	1,105	225	734
350	2,414	320	1,768	280	1,196	230	800
360	2,731	325	1,904	285	1,297	235	871
370	3,112	330	2,046	290	1,408	240	947
371	3,157	335	2,158	295	1,530	245	1,011
371.8	3,223*	340	2,339	300	1,660	250	1,123
371	3,214	345	2,498	305	1,798	255	1,231
370	3,193	350	2,670	310	1,946	260	1,350
360	2,939	355	2,862	315	2,120	265	1,484
350	2,715	360	3,090	320	2,324	270	1,645
340	2,527			325	2,556	275	1,873
335	2,459			330	2,832	280	2,158
332	2,433			335	3,136	285	2,522
330	2,422						
328	2,417						
326	2,420						
324	2,430						
322	2,450						
318	2,568						
315	2,790						

* Critical point.

More extensive data are available.* Original data on the n-hexane-rich region are given by Scheffer (*10*), and original data on the cyclohexane-rich region have been determined by Hayworth (*14*).

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LITERATURE CITED

1. Seidell, Atherton, "Solubilities of Inorganic and Organic Compounds," Vol. 2, 3 ed., Van Nostrand, New York (1940).
2. Katz, D. L., et al., "Handbook of Natural Gas Engineering," Chap. 5, McGraw-Hill, New York (1959).
3. Himmelblau, D. M., *J. Phys. Chem.*, **63**, 1803 (1959).
4. Kobayashi, Riki, and D. L. Katz, *Ind. Eng. Chem.*, **45**, 440 (1953).
5. Leland, T. W., Jr., J. J. McKetta, Jr., and K. A. Kobe, *ibid.*, **47**, 1265 (1955).
6. Hibbard, R. R., and R. L. Schalla, *Natl. Advisory Comm. Aeronaut. Res. Memo E52D24* (1952).
7. Roozeboom, H. W. B., "Die Heterogenen Gleichgewichte vonn Standpunkte der Phasenlehre. Pt. 2. Systeme mit Zwei Flussigne Phasen," Freidrich Vieweg & Sohn, Braunschweig (1918).
8. Reamer, H. H., R. H. Olds, B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **35**, 790 (1943).
9. Rebert, C. J., and W. B. Kay, *A.I.Ch.E. J.*, **5**, 285 (1959).
10. Scheffer, F. E. C., *Konikl. Akad. Wetenschap. Amsterdam*, **17**, 835 (1914).
11. ———, *Z. Phys. Chem.*, **84**, 728 (1913).
12. Kay, W. B., *Ind. Eng. Chem.*, **30**, 459 (1938).
13. ———, and W. E. Donham, *Chem. Eng. Sci.*, **1**, 1 (1955).
14. Hayworth, K. E., M.S. thesis, Univ. Southern California, Los Angeles (1962).
15. Reamer, H. H., R. H. Olds, B. H. Sage, and W. N. Lacey, *Ind. Eng. Chem.*, **36**, 381 (1944).

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