Part I

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MOLECULAR TRANSPORT

THERMODYNAMICS

Binary Solutions of Saturated Hydrocarbons

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It is often difficult to isolate the effect on physical properties of one specific parameter like molecular shape or intermolecular order by studying the physical properties of individual hydrocarbons. Even paraffins differ in a sufficient number of structural features so that differences in physical properties between isomers usually cannot be attributed to a change in one specific molecular parameter. However, if one studies the differences between the properties of two hydrocarbon solutions containing equal ratios of identical hydrocarbon segments, the number of varying structural features is materially decreased. Then, assuming as a first approximation, that there is no change in the intermolecular force field when two saturated hydrocarbons are mixed, it may be possible to isolate the effect of a single parameter—e.g., molecular shape. Because an investigation of solutions of trialkylmethanes reported some years ago supported this opinion (*8*), it appeared that the study of other binary hydrocarbon systems might suggest some relationships between molecular structure and physical properties and provide experimental tests of relationships which have been proposed (*1*).

For a pure hydrocarbon or solution of hydrocarbons, liquid properties such as vapor pressure and viscosity cannot be calculated as algebraic sums of contributions from the various carbon and hydrogen atoms present. However, Brønsted and Koefoed (*2*) and Schiessler and others (*8*) observed that for certain types of solutions, the physical properties appear to be a function of the number and type of submolecular segments present in the liquid without regard to the way these segments are combined to form the molecules. In 1946 Brønsted and Koefoed reported that binary solutions of normal paraffins having identical mean molecular weights had identical vapor pressures and solubility characteristics. They named the phenomenon "congruence." In the same year Schiessler and others showed that binary solutions of high molecular weight trialkylmethanes of the type

$$1 \text{ mole of } (R)_3CH + 2 \text{ moles of } (R')_3CH$$

where R is an aliphatic or alicyclic group—e.g., *n*-hexyl, cyclohexylethyl, etc.—possessed almost identical densities, refractive indices, and viscosities with the corresponding individual trialkylmethanes:

$$R\ CH(R')_2$$

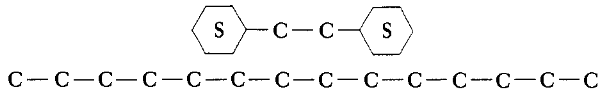
In 1953, Longuet-Higgins (*6*) provided a statistical mechanical rationalization for Brønsted's and Koefoed's observations and suggested the following generalization: "If two mixtures both containing chain molecules are such that their molecules can be divided into identical sets of fragments by cutting the chain in suitable places, then these mixtures will have identical equations of state and identical solvent properties." Both Brønsted and Longuet-Higgins restricted themselves to chain molecules, molecules which could be considered as constructed from a set of repeating units.

Table I. Hydrocarbons

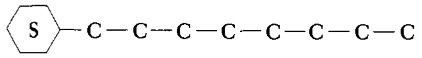
Hydrocarbon	Density G./ml. exptl.	Density 20° C. lit.	Purity, Mole %	Source[a]
n-Hexane	. . .	0.65937[b]	99.85	P-R
2-Methylpentane	0.6532	0.65315[b]	99 min.	P-P
2,2-Dimethylbutane	0.6502	0.64916[b]	. . .	P-R
2,3-Dimethylbutane	0.6617	0.66164[b]	99.87	P-R
n-Heptane	0.6839	0.68376[b]	99 min.	P-P
2,4-Dimethylpentane	0.6728	0.67270[b]	99.72	P-R
2-Methylhexane	0.6794	0.67439[b]	99.77	NBS
2,2,3,-Trimethylbutane	. . .	0.69011[b]	99.94	NBS
n-Octane	0.7027	0.70252[b]	99.76	P-R
2,2,4-Trimethylpentane	0.6920	0.69192[b]	99.95	P-R
2,3,3-Trimethylpentane	. . .	0.72619[b]	99.60	NBS
2,5-Dimethylhexane	. . .	0.69354[b]	99.70	NBS
2,2,5-Trimethylhexane	0.7073	0.70721[b]	99 min.	P-P
2,2,3,3-Tetramethylpentane	. . .	0.75666[b]	99.94	NBS
2,2,4,4-Tetramethylpentane	. . .	0.71947[b]	99.84	NBS
1,2-Dicyclohexylethane	0.8740	0.87395[c]	. . .	PSU
n-Tetradecane	0.7629	0.7628[b]	. . .	PSU
Tricyclohexylmethane	0.9474	0.9474[d]	. . .	PSU
7-*n*-Hexyltridecane	0.7878	0.7878[d]	. . .	PSU
n-Dodecane	0.7487	0.7487[d]	. . .	PSU
n-Hexadecane	0.7737	0.7737[d]	. . .	PSU

[a] P-R, Phillips Petroleum Co. research grade; P-P, Phillips Petroleum Co. pure grade; NBS, hydrocarbons prepared and purified under a joint program of American Petroleum Institute and National Bureau of Standards; PSU, Pennsylvania State University [American Petroleum Institute Research Project 42 (*9*)].
[b] (*7*).
[c] (*10*).
[d] (*9*).

In this work, only liquids composed of one or more saturated hydrocarbons were chosen, thus providing comparisons free (to a first approximation) of the difficultly isolable effects of differing intermolecular force fields. To examine the applicability of the concept of congruence and to isolate the variables of shape, volume, freedom of intramolecular rotation, etc., the properties of pairs of hydrocarbon liquids containing equal ratios of identical hydrocarbon segments were compared. For example, an equimolar solution of 1,2-dicyclohexylethane and *n*-tetradecane was compared with *n*-octylcyclohexane,

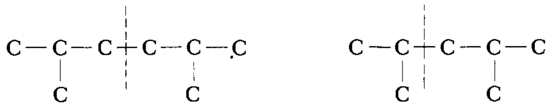


vs.



or an equimolar solution of 2,2,4-trimethylpentane and 2,5-dimethylhexane was compared with an equimolar solution of 2,2,5-trimethylhexane and 2,4-dimethylpentane

vs.



Viscosity, density, and refractive index were the physical properties determined. Density, an equilibrium property, was expected to provide information on the relative closeness of packing of pairs of liquids and on volume changes on mixing. Viscosity, a kinetic property, was chosen because it appears to be sensitive to many molecular structural parameters, including those which affect important solution properties such as vapor pressure, and because it can be determined readily over a range of temperatures with considerable accuracy. Refractive index, also an equilibrium property, is sensitive to density, and was chosen because molar refractivity is an almost purely additive rather than constitutive property.

EXPERIMENTAL

The individual hydrocarbons with their source and density are shown in Table I. The mixtures were prepared by weight. Weighings were made to 0.0001 gram, and the least amount of any component used was approximately 1.5 grams. Mole fractions are accurate to 0.1%. One property—e.g., the viscosity at 20° C.—was determined at the initiation and conclusion of the measurements on each mixture to ensure that no significant

Table II. Components and Properties of Mixtures and Corresponding Pure Compounds

Soln. No.	Component	Moles X 10^2	Viscosity, Cs. 20° C.	Viscosity, Cs. 60° C.	Density, G./Ml. 20° C.	Density, G./Ml. 40° C.	Density, G./Ml. 60° C.	ΔV^a 20° C.	Refractive Index n_D^{20}	Refractive Index n_D^{30}
1	2,5-Dimethylhexane 2,2,4-Trimethylpentane	2.066 2.067	0.720	0.494	0.6929	0.6760	0.6592	- 0.0479	1.3921	1.3875
2	2,4-Dimethylpentane 2,2,5-Trimethylhexane	4.988 4.998	0.715	0.491	0.6919	0.6749	0.6580	- 0.0468	1.3917	1.3870
3	*n*-Hexane 2,5-Dimethylhexane	1.679 1.685	0.578	. . .	0.6791	0.6615	0.6440	+ 0.0093	1.3860	. . .
4	*n*-Heptane 2,4-Dimethylpentane	4.963 4.965	0.562	0.403	0.6785	0.6609	0.6434	- 0.0104	1.3848	1.3798
5	*n*-Hexane 2,3-Dimethylbutane	5.979 5.981	0.487	0.351	0.6611	0.6421	0.6231	+ 0.0099	1.3749	1.3699
6	2,2,3-Trimethylbutane 2,5-Dimethylhexane	2.074 2.075	0.764	0.507	0.6926	0.6755	0.6584	+ 0.0016	1.3914	. . .
7	2,3-Dimethylbutane 2,2,5-Trimethylhexane	5.004 5.006	0.731	0.499	0.6892	0.6718	0.6544	+ 0.0109	1.3901	1.3866
8	2,2,4-Trimethylpentane 2,4-Dimethylpentane	3.007 3.011	0.633	0.447	0.6832	0.6658	0.6485	- 0.0031	1.3869	. . .
9	2,3,3-Trimethylpentane 2,2,3-Trimethylbutane	3.000 3.000	0.900	0.579	0.7088	0.6925	0.6761	- 0.0065	1.3998	1.3946
10	2,3-Dimethylbutane 2,2,3,3-Tetramethylpentane	4.000 4.000	0.914	0.600	0.7164	0.7004	0.6844	+ 0.0066	1.4072	1.4004
11	2,3-Dimethylbutane *n*-Octane	6.000 6.000	0.643	0.450	0.6849	0.6676	0.6503	- 0.0083	1.3904	1.3856
12	*n*-Hexane *n*-Hexadecane	4.000 4.000	1.85	1.09	0.7409	0.7260	0.7112	+ 0.0040	1.4194	1.4149
13	1,2-Dicyclohexylethane *n*-Hexane	5.000 5.000	1.86	1.09	0.7997	0.7847	0.7698	- 0.0103	1.4475	
14	1,2-Dicyclohexylethane *n*-Tetradecane	3.000 3.000	4.37	2.02	0.8140	0.7928	0.7864	+ 0.0009	1.4501	1.4461
15	Tricyclohexylmethane 7-*n*-Hexyltridecane	1.500 3.000	14.6	4.17	0.8328	0.8195	0.8062	+ 0.0097	1.4604	1.4565
16	*n*-Octane *n*-Decane	6.000 6.000	0.998	0.649	0.7180	0.7023	0.6866		1.4054	1.4012
17	*n*-Butylcyclohexane		1.64	0.954	0.7992	0.7845	0.7698		1.4408	1.4364
18	*n*-Octylcyclohexane		4.32	2.01	0.8139	0.7928	0.7864		1.4504	1.4463
19	*n*-Undecane		1.61	1.01	0.7402	0.7254	0.7106		1.4172	1.4128
20	*n*-Nonane		0.998	0.652	0.7176	0.7022	0.6864		1.4054	. . .
21	2-Methylhexane		0.561	0.400	0.6794	0.6618	0.6441		1.3849	1.3796
22	7-Cyclohexyltridecane		13.9	4.07	0.8317	0.8183	0.8048		1.4599	1.4560
23	2,2,4-Trimethylpentane		0.734	0.504	0.6920	0.6753	0.6585		1.3915	1.3868
24	2-Methylpentane		0.439	. . .	0.6532	. . .	. . .		1.3711	. . .

[a] Volume change on mixing at constant pressure in ml./mole of solution. $\sum x_i MV_i - \frac{\sum x_i MW_i}{d_{\text{soln}}}$

composition change had taken place. The compositions and properties of the mixtures are described in Table II.

The refractive indices were obtained on a Bausch and Lomb, Abbe-type instrument. Frequent checks with known standards indicated a precision to ±0.0002 unit.

The viscosities were determined in Cannon-Fenske viscometers by the standard procedure and are internally comparable to ±0.3%.

Densities were determined with a precision to ±0.0002 gram per milliliter.

DISCUSSION

Molecular Symmetry. In Table III are shown the differences in the viscosities, densities, and refractive indices at three temperatures of six pairs of liquids varying widely in molecular symmetry. In these six pairs are represented liquids composed wholly of molecules having at least a two- or threefold axis of symmetry (3, 4, and 15), liquids with one such symmetrical component and one unsymmetrical component (1 and 2), and liquids containing only unsymmetrical molecules. The physical

Table III. Congruent Mixtures

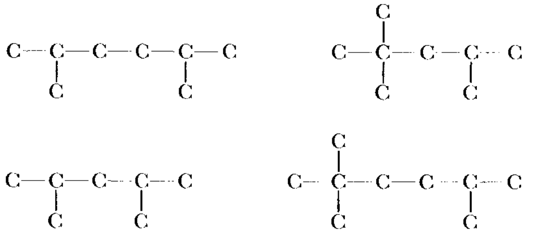
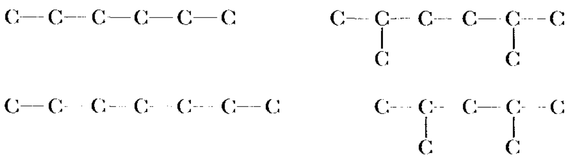
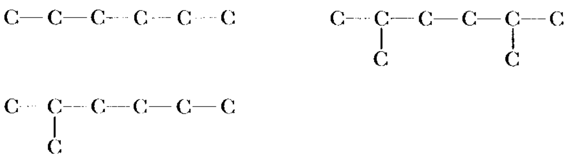
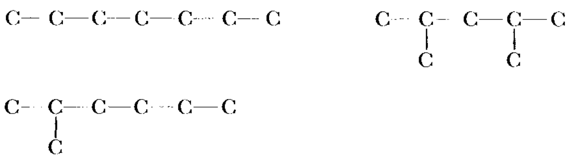
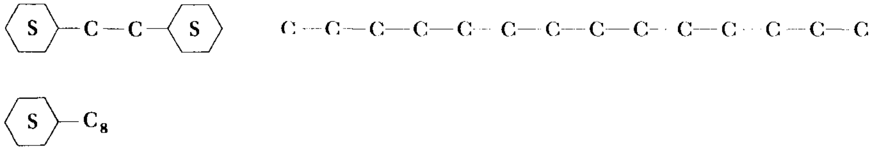
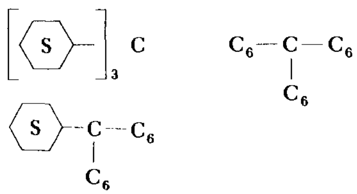
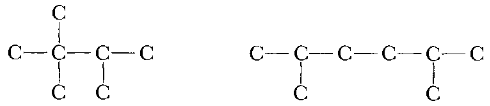
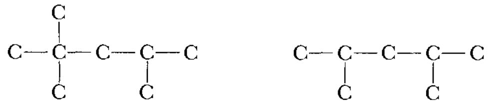
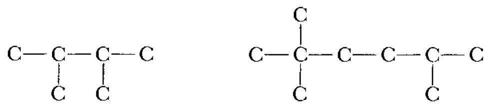
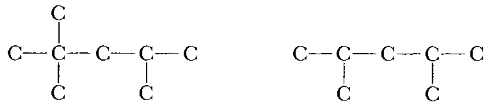
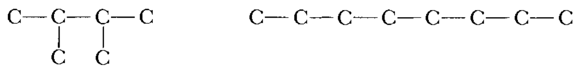
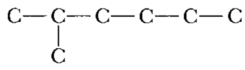
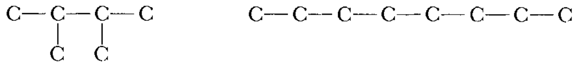
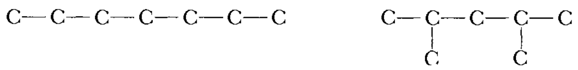
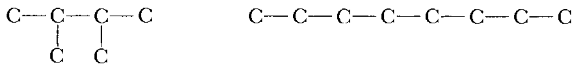
Pairs of Liquids	Structures	Viscosity Diff., % 20° C.	Viscosity Diff., % 60° C.	Density Diff., % 20° C.	Density Diff., % 40° C.	Density Diff., % 60° C.	$\Delta n_D \times 10^4$ 20° C.	$\Delta n_D \times 10^4$ 30° C.
1 and 2		0.7	0.6	0.1	0.2	0.2	4	5
3 and 4		2.8	. . .	0.1	0.1	0.1	12	. .
3 and 21		2.9	. . .	0.0	0.0	0.0	11	. .
4 and 21		0.2	0.7	0.1	0.1	0.1	1	. .
14 and 18		1.2	0.5	0.0	0.0	0.0	3	2
15 and 22		4.9	2.4	0.1	0.1	0.2	5	5
Mean		2.1	1.1	0.1	0.1	0.1	6	4

Table IV. Noncongruent Mixtures

Pairs of Liquids	Structures	Viscosity Diff., %, 20° C.	Viscosity Diff., %, 60° C.	Density Diff., %, 20° C.	Density Diff., %, 40° C.	Density Diff., %, 60° C.	$\Delta n_D \times 10^4$, 20° C.	$\Delta n_D \times 10^4$, 30° C.
6	 $C-\overset{C}{\underset{C}{C}}-\underset{C}{C}-C$ $C-\underset{C}{C}-C-C-\underset{C}{C}-C$							
and		18.7	12.6	1.4	1.4	1.5	45	. .
8	 $C-\overset{C}{\underset{C}{C}}-C-\underset{C}{C}-C$ $C-\underset{C}{C}-C-\underset{C}{C}-C$							
7	 $C-\underset{C}{C}-\underset{C}{C}-C$ $C-\overset{C}{\underset{C}{C}}-C-C-\underset{C}{C}-C$							
and		14.4	11.0	0.9	0.9	0.9	32	. .
8	 $C-\overset{C}{\underset{C}{C}}-C-\underset{C}{C}-C$ $C-\underset{C}{C}-C-\underset{C}{C}-C$							
11	 $C-\underset{C}{C}-\underset{C}{C}-C$ $C-C-C-C-C-C-C-C$							
and		13.6	11.8	0.8	0.9	1.0	55	60
21	 $C-\underset{C}{C}-C-C-C-C$							
3	 $C-C-C-C-C-C$ $C-\underset{C}{C}-C-C-\underset{C}{C}-C$							
and		10.6	. . .	0.9	0.9	1.0	46	. .
11	 $C-\underset{C}{C}-\underset{C}{C}-C$ $C-C-C-C-C-C-C-C$							
4	 $C-C-C-C-C-C-C$ $C-\underset{C}{C}-C-\underset{C}{C}-C$							
and		13.4	11.0	0.9	1.0	1.1	56	58
11	 $C-\underset{C}{C}-\underset{C}{C}-C$ $C-C-C-C-C-C-C-C$							
Mean		14.1	11.6	1.0	1.0	1.1	47	59

property congruence exhibited by these six pairs and the trialkylmethane pairs examined by Schiessler and others (*8*) suggests that the over-all symmetry of the molecules has only a minor influence on liquid properties of aliphatic hydrocarbons such as volume, viscosity, and refractive index.

Examination of Table IV leads to the same conclusion. Listed there are the properties of five pairs of liquids. Though the members of each pair possess equal ratios of identical alkyl segments, the properties of these pairs are incongruent. Just as the group exhibiting property congruence, there are solutions composed of symmetrical molecules and solutions composed of unsymmetrical molecules.

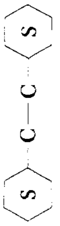
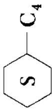
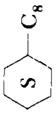
The correspondence of the physical properties of the pairs in Table III is not an artifact due to the small differences in the properties of the hydrocarbons chosen. For example, the viscosities at 20° C. of the hydrocarbons comprising solution 15, 7-*n*-hexyltridecane and tricyclohexylmethane, are 7.43 and 2690 centistokes respectively. This is a difference of approximately 360-fold. The viscosities of solution 15 and the corresponding individual hydrocarbon, 7-cyclohexyltridecane, are 14.6 and 13.9 centistokes, a difference of approximately 4%.

Intramolecular Rotation. Each of the five pairs of liquids listed in Table IV have equal ratios of identical submolecular segments, but the property differences are eight to ten times those in Table III. The only molecular structural feature common to every pair of liquids in Table IV and not possessed by any pair in Table III is the following: At least one component of each pair of liquids of Table IV contains adjacent branched carbon atoms—e.g., 2,3-dimethylbutane or 2,2,3-trimethylbutane. None of the liquids in Table III contain such a component. Apparently, the rotational barrier at the bond between adjacent branched carbon atoms is sufficiently greater than the barrier at the bond between adjacent methylene groups that the liquid properties are affected significantly. The restriction might affect the volume swept out by the molecule (and thus its density) and the number of possible configurations the molecule could assume (and thus its viscosity).

An interesting group of liquids in this connection is 3, 4, and 11. The three solutions have the same average molecular weight and identical "type" composition—that is, equal molar proportions of a normal alkane and an alkane with two methyl branches. Liquids 3 and 4 exhibit property congruence with one another and with 2-methylhexane, the individual hydrocarbon having equal ratios of the same alkyl segments. In contrast, the properties of solution 11 differ significantly from the properties of 2-methylhexane or from solutions 3 and 4. The adjacent branched carbon atoms in 2,3-dimethylbutane in solution 11 appear to be the structural feature which makes this solution different from solutions 3 and 4.

The five liquids 1, 2, 6, 7, and 8 are each composed of equal

Table V. Molecular Weight and Viscosity

Pairs of Liquids	Structures	Viscosity Diff., %		Density Diff., %			$\Delta n_D \times 10^4$, 20° C.
		20° C.	60° C.	20° C.	40° C.	60° C.	
12	C—C—C—C—C—C C—C—C—C—C—C—C—C—C—C—C—C—C—C—C—C						
and		13.3	7.6	0.1	0.1	0.1	22
19	C—C—C—C—C—C—C—C—C—C—C						
13	 C—C—C—C—C—C						
and		12.6	13.3	0.1	0.0	0.0	67
17							
14	 C—C—C—C—C—C—C—C—C—C—C—C—C—C						
and		1.1	0.5	0.0	0.0	0.0	3
18							
16	C—C—C—C—C—C—C—C C—C—C—C—C—C—C—C—C—C						
and		0.0	0.5	0.1	0.0	0.0	0
20	C—C—C—C—C—C—C—C—C						

molar proportions of an alkane with three methyl branches and an alkane with two methyl branches. Liquids 1 and 2 have similar properties. The structurally analogous pair, 7 and 8, has significantly different properties. Again, the difference appears to be due to the adjacent branching methyls in 2,3-dimethylbutane. If one accepts this explanation, the lack of property congruence of solutions 7 and 8 with 6 becomes immediately predictable. Although mixtures 9 and 10 contain equal ratios of not only identical hydrocarbon segments but also adjacent tertiary and quaternary carbon atoms, their densities and refractive indices are significantly different. (The increase of the viscosity difference with temperature suggests that at slightly higher temperatures this difference will become appreciable also.)

Intermolecular Order. Bondi suggested (*1*) that x-ray diffraction patterns of liquids indicate a significant amount of intermolecular order in the liquid, and that nonspherical molecules tend to maintain a preferred orientation with regard to each other. However, x-ray diffraction measurements of liquids may indicate merely a preferred intermolecular distance, and $q(r)$, the radial distribution function commonly used to express the x-ray diffraction data, may be essentially a purely volume-dependent function (*3*). It is difficult to envision how the molecules in an equimolar mixture—e.g., 1,2-dicyclohexylethane and *n*-tetradecane—can reproduce any reasonable short- or long-range intermolecular ordering that might occur in a liquid containing a single molecular species like *n*-octylcyclohexane. Therefore, the physical property congruence of the pairs of solutions in Table III and the solutions of trialkylmethanes examined by Schiessler and others lead to the proposal that there is relatively little intermolecular order among saturated hydrocarbon molecules in the liquid state over most of the liquid range. Alternatively, viscosity, density, and refractive index may be little affected by intermolecular ordering in nonpolar systems. Although the available data do not enable an unequivocal choice to be made, the former possibility seems more likely.

The lowest temperature at which the properties were studied, 20° C., is 40° above the melting point and approximately 250° below the boiling point of *n*-octylcyclohexane. If the explanation is correct, most intermolecular order in saturated hydrocarbons must be lost at temperatures close to the solid-liquid transition temperature.

Volume Change on Mixing. Contrary to statements in the literature (*4, 5*), when aliphatic and alicyclic hydrocarbons are mixed, the volume change at constant pressure is very small (less than 0.01%) and may be either positive or negative (Table II). This observation supports the idea of little or no intermolecular order in these liquids. Considering the molecular structures in these mixtures, the members of each pair probably do not fit into each other's "quasi-lattice."

Effect of Molecular Weight. Brønsted and Koefoed proposed (*2*) that for properties such as vapor pressure and solubility, the effect of the molecular weight of each component of a solution is directly proportional to its mole fraction in the solution. All the molecules studied by Schiessler and others were C_{25} hydrocarbons, so they made no observations bearing on this question.

In Table V are presented data on four pairs of liquids, including one (12) studied by Brønsted and Koefoed. They found that an equimolar solution of *n*-hexane and *n*-hexadecane had the same vapor pressure as the single paraffin, *n*-undecane. The viscosity, density, and refractive index differences on this same pair of liquids are shown in Table V. Like the vapor pressure, the densities (or volumes) are congruent. Surprisingly, the viscosity of this equimolar mixture is significantly greater than that of the corresponding individual hydrocarbon, *n*-undecane. If the identity of the vapor pressures and solubility properties of these two liquids indicates that the two liquids will have the same equation of state, there must be a parameter in the viscosity expression which does not appear in the equation of state.

The "weight average" molecular weight of solution 12 is

187.74, corresponding approximately to a normal paraffin of 13 carbon atoms. The kinematic viscosity of *n*-tridecane at 20° C. is 2.466 centistokes, significantly greater than the experimental value for the solution, 1.85 centistokes. Therefore, a solution of hydrocarbons differing widely in molecular weight may have a viscosity greater than that of a single hydrocarbon with the same weight average or "number average" molecular weight as the solution.

The agreement between the properties of solution 16, an equimolar mixture of *n*-octane and *n*-decane, and the analogous "chemical mixture" (20), *n*-nonane, supports the conclusion that the excess viscosity of the hexane-hexadecane solution is due to the large difference between the molecular weights of the components.

Solutions 13 and 14 further illustrate the molecular weight effect. Each of these solutions is composed of 1,2-dicyclohexylethane and a *n*-paraffin in equimolar proportions. In solution 13 the *n*-paraffin component is *n*-hexane, and there is a very significant difference in the molecular weights of the two components. As a result, there is no congruence between the properties of the "physical mixture," solution 13, and the corresponding chemical mixture, 1-butylcyclohexane (17).

In contrast, the *n*-paraffin present in solution 14 is *n*-tetradecane and thus the molecular weight disparity between the two components is of the order of 1%. The correspondence between the physical properties of solution 14 and the chemical mixture, *n*-octylcyclohexane (18), is excellent.

ACKNOWLEDGMENT

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Solubility of 1,3-Butadiene in Water

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This paper reports the solubility of 1,3-butadiene in water at pressures to 275 p.s.i.a. A summary of the light hydrocarbon-water systems studied to date is presented in Table I.

Three isotherms were investigated: 100°, 160°, and 220°F, with pressures ranging from the vapor pressure of water to the pressure at which a hydrocarbon-rich liquid phase appeared. The rocking autoclave equipment with its sampling device, which enables liquid samples to be taken under constant pressure, is identical to that used in earlier studies (*1*).

The experimental and smoothed data are shown in Tables

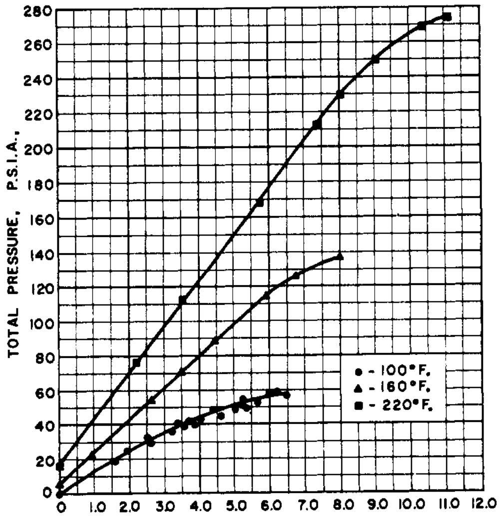

Figure 1. Concentration of 1,3-butadiene in water-rich liquid phase region *vs.* total pressure

Table I. Light Hydrocarbon-Water Systems

System	Phases Reported[a]	Temp., ° F.	Maximum Conditions Pressure, p.s.i.a.	Ref.
CH_4-H_2O	W	77	2,350	(*13*)
	W	340	10,000	(*9, 10, 19*)
	V	460	10,000	(*20*)
C_2H_6-H_2O	W	340	1,200	(*7*)
	W and V	340	10,000	(*8, 10*)
	P and *T* data	89	710	(*17*)
	V	303.7	1,000	(*23*)
C_2H_4-H_2O	W	100	7,350	(*3*)
	P and *T* data	68	882	(*11, 12*)
	V	68	570	(*12*)
C_2H_2-H_2O	W	86	570	(*15*)
C_3H_8-H_2O	3- and 2-phase regions	340	3,000	(*16*)
	H and V	187	500	(*22*)
	V	100	192	(*21*)
	V	70	120	(*14*)
	W	220	500	(*1*)
C_3H_6-H_2O	W	220	500	(*2*)
n-C_4H_{10}-H_2O	3-phase region	460	10,000	(*24*)
	3- and 2-phase regions	220	10,000	(*4, 25*)
C_4H_8-H_2O	2- and 3-phase regions	220	10,000	(*18*)
	W	291	1,000	(*5*)
	H	291	1,000	(*6*)
i-C_4H_{10}-H_2O	W	220	315	(*26*)
C_4H_6-H_2O	W	220	276	(This work)

[a] W = water-rich liquid. H = hydrocarbon-rich liquid. V = vapor.