SOLUBILITIES OF ETHYLENE IN HEXANE, CYCLOHEXANE, AND BENZENE UNDER PRESSURE

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In view of the fact that compressed hydrocarbon gases are beginning to be applied as solvents in various processes in the chemical and petroleum-processing industries [1, 2], it is necessary to have information regarding the solubilities of individual unsaturated hydrocarbon gases in hydrocarbons of various classes at high pressures. Also, this information is necessary both for the calculation of the solubilities of mixtures of unsaturated hydrocarbon gases in liquids and for the development of the theory of the solubility of gases in liquids under pressure, which is still insufficiently advanced.

<table>
<thead>
<tr>
<th>Substance</th>
<th>B.p. (°C at 760 mm)</th>
<th>a^20</th>
<th>n^20</th>
<th>Molar volume* (cc/mole)</th>
<th>Latent heat of vaporization* at b.p. (cal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>68,8</td>
<td>0.6601</td>
<td>1.3758</td>
<td>130.7</td>
<td>6900</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>80,9</td>
<td>0.7801</td>
<td>1.4271</td>
<td>108.1</td>
<td>7185</td>
</tr>
<tr>
<td>Benzene</td>
<td>79,5</td>
<td>0.8788</td>
<td>1.5017</td>
<td>88.9</td>
<td>7353</td>
</tr>
</tbody>
</table>

*Data from literature.

In the present paper, we report results of a study of the solubilities of ethylene in liquid hexane, cyclohexane, and benzene at 35-150° under pressures of 100-120 atm. In choosing hydrocarbons of different nature but containing the same number of carbon atoms as solvents, we had the object of determining the effect of the nature of the solvent on the solubility of a given gas. Such information can be applied in the elucidation of the molecular mechanism of the solution of gases in liquids under pressure. The solubilities of ethylene in hexane, cyclohexane, and benzene under pressure were studied in the apparatus described in [3].

EXPERIMENTAL

The ethylene used in this investigation had a purity of 97.1%; it contained 2.9% of ethane as impurity. Its specific gravity with respect to air was 0.9748. The characteristics of the hydrocarbons are given in the table.

The method of investigating the solubility of ethylene in liquid hydrocarbons consisted in the determination of the saturation pressure and the corresponding specific volume for a series of mixtures of ethylene and liquid hydrocarbon of known composition. The exact value of the saturation pressure for each mixture investigated and the corresponding specific volume was determined from the break in v=f(P,t) curves, which were plotted on large-scale diagrams. Curves for the solubilities of ethylene in hexane, cyclohexane, and benzene were constructed from the results and are presented in Figures 1-3. From these figures it will be seen that a crude linear
relation between the solubility of ethylene and pressure is found only in the ethylene-hexane system. In contrast, the ethylene-benzene system shows the greatest departure from the linear relation, even at high temperatures.

The curves for the solubility of ethylene in cyclohexane have an intermediate character over the whole range of temperature and pressure investigated. The graphs (Figures 1-3) show that the solubility of ethylene in the hydrocarbons investigated falls with rise in temperature at constant pressure. At given temperature and pressure, the solubility of ethylene falls along the series hexane—cyclohexane—benzene.

It is interesting to trace the connection of the regularity observed in the solubilities of ethylene in hexane, cyclohexane, and benzene with the molecular constants of these hydrocarbons. In the theoretical treatment of questions of solubility of gases in liquids, it is necessary to account for: 1) interaction forces between molecules of the gas; 2) interaction forces between molecules of the liquid; and 3) interaction forces between molecules of dissolved gas and solvent molecules. As we have investigated the solubilities of one particular gas in different liquids, we shall confine ourselves to a consideration of the factors in the secondary category. There are no data in the literature characterizing the interaction forces between ethylene molecules and molecules of hexane, cyclohexane, and benzene.

An idea of the molecular field of a liquid, which is a function of its nature, can be obtained indirectly from the values of the latent heat of vaporization, the molar volume, the surface tension, etc. The data in the table enable us to follow the changes in these constants among the hydrocarbons under consideration. It will be seen that in the series \( n-C_6H_{14} \rightarrow C_6H_{12} \rightarrow C_6H_6 \) there is a lowering of molar volume and a rise in latent heat of vaporization. If we regard the mechanism of the solution of ethylene as being, to the first approximation, the incorporation of molecules of a gas into a complex of molecules of a liquid, on the basis of the data in the table, we may suppose that the solubility of ethylene should fall in the series hexane—cyclohexane—benzene.

The results of the investigation of the solubilities of ethylene in these liquids are in good agreement with this supposition. The experimentally determined specific volumes corresponding to saturation pressures at various temperatures were recalculated as molar volumes \( V_M \). By way of example, in Fig. 4 we give the relation of the molar volume of the ethylene-cyclohexane system to the mole fraction \( N_2 \) of ethylene at 30°, 50°, 75°, 100°, and 125°. It will be seen from Fig. 4 that at 30° and 50° \( V_M \) diminishes linearly with increase in the ethylene content of the liquid phase right up to \( N_2 = 0.65-0.70 \). With further increase in \( N_2 \), the sign of the slope reverses and \( V_M \) rises with increase of \( N_2 \) at a given temperature; the rise is steeper the higher the temperature. An analogous relation of \( V_M \) to \( N_2 \) is observed also in the ethylene-benzene system. It must be pointed out, however, that for this system at \( t = 30° \) and 50° a linear fall in \( V_M \) with rise in \( N_2 \) occurs up to \( N_2 = 0.55-0.65 \).

For the ethylene-hexane system, the linear reduction in molar volume with rise in the ethylene content of the solution at \( t = 30° \) and 50° is observed over the whole range of ethylene concentrations investigated. At higher temperatures, the character of the relation of \( V_M \) to \( N_2 \) is analogous to that described above.