

Fig. 5 Miscible and Partially Miscible Types of Refrigerant-Oil Solutions

pressures, for example, of refrigerant-oil solutions at a given temperature are always less than the vapor pressure of pure refrigerant at that temperature. Thus, in an evaporator the presence of dissolved oil would lead to lower suction pressures and higher evaporator temperatures than expected from pure refrigerant tables. An enthalpy diagram for R 12-oil solutions over the whole range of compositions from zero to 100 percent oil and temperatures from -40 F to 240 F has been given by Bamach.¹⁶ Spauschus¹⁴ has developed general equations for calculating thermodynamic functions of refrigerant-oil solutions and has applied these equations to the special case of R12-petroleum oil solutions.

Mutual Solubility of Oils and Refrigerants

In dealing with the lubricating and sealing problems in a compressor, the lubricating fluid is considered as a solution of refrigerant dissolved in oil. But in other parts of the refrigerant system the problem may involve a solution of oil in liquid refrigerant. In both instances, either the oil or the refrigerant could exist alone as a liquid if the other were not present, hence any distinction between the dissolving and dissolved component merely reflects a point of view. Either of the liquids

can be considered as dissolving the other and this relationship is frequently termed the *mutual solubility*.

The mutual solubility relationships are commonly expressed according to the predominant component, i.e., *oil-rich* and *refrigerant-rich* solutions. If the solution that is formed on mixing the refrigerant and oil consists of a single liquid phase, the two components are said to be *miscible*. But if two separate liquid phases appear, it does not necessarily mean that the oil and refrigerant are insoluble in each other. The two liquid phases are, themselves, solutions and although they differ in composition, both will be found to contain substantial amounts of oil and refrigerant in mutual solution. Normally, one phase will be oil-rich, the other, refrigerant-rich. The two solutions which are thus formed are, themselves, *immiscible*. Refrigerants are designated as being of high, intermediate, or low miscibility according to their mutual solubilities with oils as shown in Table 5.

Completely miscible refrigerants and oils are mutually soluble in all proportions at any temperature under consideration. Hence, a mixture of this type always forms a single liquid phase under equilibrium conditions, no matter how much refrigerant or oil may be present. Examples are Refrigerant 12 and mineral oil, and methyl chloride and mineral oil.

In completely miscible mixtures, the oil-rich compositions merge smoothly and continuously into refrigerant-rich compositions as the refrigerant content is increased from zero to 100 percent. This type of behavior is illustrated in graph (a) of Fig. 5. On this graph P_1^* and P_2^* represent the saturation pressures of pure refrigerant at temperatures t_1 and t_2 , respectively. Point E_1 represents one of the infinite number of solutions which are possible at temperature t_1 . The coordinates of E_1 are P_1 and W_1 ; these coordinates determine, respectively, the equilibrium refrigerant pressure and composition of the solution. The equilibrium refrigerant pressure P_1 is always lower than the corresponding saturation pressure (P_1^*) for

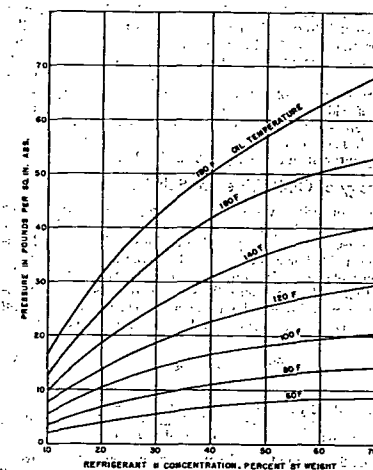


Fig. 6 Solubility of Refrigerant 11 in 300, SUV, Oil¹⁷

pure refrigerant at the given temperature, t_1 . By increasing the mixture temperature to t_2 one can shift the equilibrium to a new point, E_2 . Assuming no change in the total mass or volume of the system, the rise in temperature would be expected to vaporize a portion of the dissolved refrigerant. This transfer of dissolved refrigerant to the vapor phase should decrease the amount of refrigerant in solution and increase the refrigerant pressure. Hence point E_2 lies slightly to the left and above E_1 , but it should be noted, as before, that the pressure attained at the new temperature t_2 is always less than the saturation pressure of pure refrigerant, P_2^* at that temperature.

Four general rules may be stated for refrigerant-oil mixtures of the completely miscible type:

1. For every solution composition, there is a corresponding vapor pressure which depends only on the temperature of the solution, and increases as the temperature increases.
2. At each given temperature, the solution vapor pressure depends only on the refrigerant concentration and increases as the concentration increases, but it is always less than the saturated vapor pressure of pure refrigerant at the given temperature.
3. For every refrigerant gas pressure, there is a corresponding refrigerant solubility which depends only on the solution temperature and decreases as the temperature increases.
4. When both the pressure of the refrigerant gas and the temperature of the solution are fixed, there is only one possible solution composition under equilibrium conditions.

Partially miscible refrigerants and oils are mutually soluble only to a limited extent. Above a certain temperature known as the *critical solution temperature* (or consolute temperature) oil-refrigerant mixtures in this class are usually completely miscible. But below that temperature there is a maximum value for the solubility of the refrigerant in the oil, and also a maximum value for the solubility of the oil in the refrigerant. Between these two values an immiscible range of composition exists. The existence and breadth of the immiscible range varies with the nature of the two dissolving substances and may be strongly influenced by temperature. Examples of partially miscible mixtures are sulfur dioxide and oil, Refrigerant 22 and oil below its critical solution temperature, and Refrigerant 114 and oil below its critical solution temperature.

The behavior of partially miscible mixtures is illustrated in graph (b) of Fig. 5. Point C on this graph represents the critical solution temperature (t_c). Below this temperature three separate regions may be seen in the diagram. Reading from left to right, a family of three smooth solid line curves

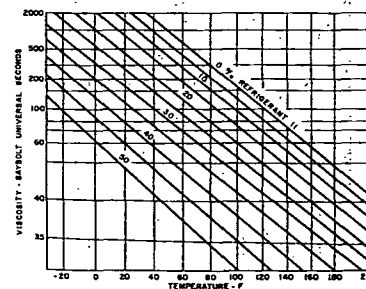


Fig. 7 Viscosity-Temperature Curves for Solutions of Refrigerant 11 in 150 SUV Naphthene Base Oil¹⁸

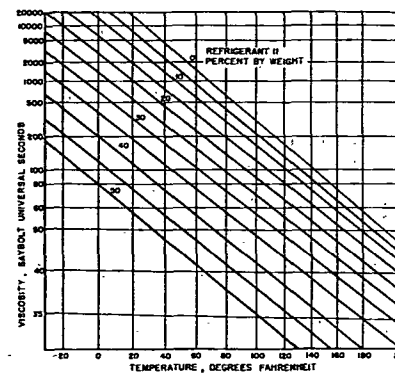


Fig. 8 Viscosity-Temperature Curves for Solutions of Refrigerant 11 in 300 SUV Naphthene Base Oil¹⁸

represents a region of completely miscible oil-rich solutions; these are followed by a wide break representing a region of partial miscibility in which two immiscible liquid phases exist; and, at the right hand side, the partially miscible region disappears into a second completely miscible region of refrigerant-rich solutions. A dome-shaped envelope (broken line curve OCR) encloses the partially miscible region; everywhere outside this dome the refrigerant and oil are completely miscible. Thus in a sense, graph (b) may be regarded as a variant of graph (a) in which the partial miscibility dome (OCR) blots out a substantial portion of the continuous solubility curves. At all points outside the dome, and especially on the left hand side, the pressure-temperature-solubility relations are treated as completely miscible mixtures. A concrete example is shown by the solubility curves for Refrigerant 22 in Fig. 23, in which a small portion of the partial miscibility region lies to the right of the broken line in the lower right hand corner.

In the partially miscible range, two important facts should be noted. One is that at a given temperature, e.g., t_1 , the two immiscible solutions which are formed are represented by two equilibrium points, e.g., E_1 and E_2 . These two solutions differ considerably in composition (W_1 and W_2) but have the same refrigerant pressure, P_1 . The solution pressure P_1 lies not far below the saturation pressure of pure refrigerant, P_1^* . Hence it is not uncommon for refrigerant-oil solutions near the partial miscibility limit to show less reduction in refrigerant pressure than is observed at the same oil concentration with refrigerants of the completely miscible type.

A second fact is that the two immiscible solutions which are formed at a given temperature within the partially miscible range retain their identity regardless of the starting composition. Thus, a mixture of composition W_2 would separate into two solutions having compositions W_1 and W_3 at temperature t_1 , and always into these same two solutions, no matter where W_2 was taken between W_1 and W_3 . The relative weights of the two solutions, i.e., the ratio of one solution layer to the other, may be computed from the lever rule: weight of oil-rich phase of composition W_1 /weight of refrigerant-rich phase of composition $W_3 = (W_2 - W_3)/(W_1 - W_3)$.