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SOLUBILITY AND VISCOSITY OF HYDROFLUOROCARBON / ALKYL BENZENE OIL MIXTURES

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ABSTRACT

Solubility data of refrigerant/lubricant mixtures have been modeled with a cubic equation of state. The systems studied are binary mixtures of hydrofluorocarbons (R-32, R-125, R-134a and R-143a) and alkylbenzene oils (viscosity grades 15 and 32). These partially miscible mixtures are well correlated with the present model, which can be used for calculating the pressure-temperature-composition relationship for a wide range of state variables, presumably including multi-component systems. Viscosity data for these mixtures have been correlated with an empirical equation and a simple mixing rule. Using the equation of state and the empirical viscosity equation, charts of pressure-viscosity-temperature-solubility relation (Daniel charts) have been constructed.

1. INTRODUCTION

Hydrofluorocarbons (HFCs) and their mixtures have been chosen as alternative refrigerants to chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). Since HFCs are highly polar compounds, traditional non-polar lubricants such as mineral (MO) and alkylbenzene (AB) oils are barely miscible with HFCs. While polyol ester (POE), PAG, and other polar oils possess sufficient mutual solubility, they have some drawbacks with respect to MO and AB oils: hydrolysis, lubricity deterioration and high cost. With proper lubricant additives and moisture control, POE oils are now being used successfully in commercial units with HFC refrigerants. However, the successful use of AB oils for HFC refrigerants has been recently demonstrated [1, 2] using low-viscosity AB oils with low mutual miscibility. It is, therefore, important to understand the thermodynamic properties and viscosity of HFC and AB mixtures.

In our previous paper [3], we have reported the experimental solubility and viscosity data of HFC/AB binary mixtures together with some preliminary data correlation. Here, we have developed more accurate and detailed models for the solubility and viscosity of the above refrigerant/oil mixtures. With these models, miscibility limits and charts of pressure-composition-temperature-viscosity relation have been made.

2. EXPERIMENTAL DATA

The experimental apparatus and detailed procedures are given elsewhere [3]. The measured solubility and viscosity data of R-32/HAB-15, R-32/HAB-32, R-125/HAB-15, R-125/HAB-32, R-234a/HAB-15, R-134a/HAB-32, R-143a/HAB-15, and R-143a/HAB-32 mixtures are reported in Ref. [3] with preliminary data analyses, where HAB-15 and HAB-32 are branched-AB oils with viscosity grade 15 and 32, respectively. The data points were taken up to the solubility limit, by monitoring the pressure increment due to a small addition of HFC to the HFC/Oil mixture; when the solubility limit was reached, the system pressure become constant.

3. MODELING

3.1 Solubility Correlation

Solubility data are often correlated with purely empirical functions of pressure as a function of temperature and composition: $P = f(T, x)$. Such correlations require a large amount of experimental data over a wide range of T , x , and P variables in order to interpolate and/or extrapolate reliably. In addition, the use of such a correlation is quite limited, and no additional information can be obtained. However, by correlating the data using a thermodynamic equation of state (EOS), more useful information can be obtained through the thermodynamic relations from relatively small amount of experimental data.

It is well known that a cubic type of EOS can correlate $PTxy$ (pressure-temperature-compositions) of VLE (vapor-liquid equilibria) or VLLE (vapor-liquid-liquid equilibria) data with sufficient accuracy, though the density correlation, particularly for the liquid phase, is poor. In this study, we have adopted a generic RK (Redlich-Kwong) cubic EOS with a special binary mixing rule for N -component mixtures, as shown below [4,5].

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} \quad (1)$$

$$a(T) = \sum_{i,j=1}^N \sqrt{a_i a_j} (1 + t_{ij}/T) (1 - k_{ij}) x_i x_j, \quad a_i = 0.42748 \frac{R^2 T_{ci}^2}{P_{ci}} \alpha_i(T), \quad (2)$$

where $t_{ij} = t_{ji}$, and $t_{ii} = 0$.

$$\alpha_i(T) = \sum_{k=0}^{\leq 3} \beta_k \left(\frac{T_{ci}}{T} - \frac{T}{T_{ci}} \right)^k \quad (3)$$

$$k_{ij} = \frac{l_{ij} l_{ji} (x_i + x_j)}{l_{ji} x_i + l_{ij} x_j}, \quad k_{ii} = 0 \quad (4)$$

$$b = \frac{1}{2} \sum_{i,j=1}^N (b_i + b_j) (1 - m_{ij}) (1 - k_{ij}) x_i x_j, \quad b_i = 0.086640 \frac{RT_{ci}}{P_{ci}}, \quad (5)$$

where $m_{ij} = m_{ji}$, and $m_{ii} = 0$.

T_{ci} : critical temperature of i -th species.

P_{ci} : critical pressure of i -th species.

x_i : mole fraction of i -th species.

3.2 Viscosity Correlation

The viscosity, η , for a pure compound is correlated with the following empirical form:

$$\ln \eta = A + B/(T + C) + DT + ET^2 \quad (6)$$

The viscosity of N -component mixtures is modeled by:

$$\ln \eta_{mix} = \sum_{i=1}^N \xi_i^{k_i} \ln \eta_i, \quad \text{where } \xi_i = m_i^k x_i / \sum_{j=1}^N m_j^k x_j \quad (7)$$

This empirical form has been found to be sufficiently accurate for correlating the viscosity of oil/refrigerant mixtures [4,6], where $k_i = 1$. Here we treat k_i as additional adjustable parameters, as well as the k parameter. For a wide

range of temperatures, the k or k_i parameter may depend on T , and then it can be expressed as a function of T ; a linear function is often sufficient.

4. ANALYSIS

4.1 Solubility Data

The experimental solubility (PTx : pressure-temperature-liquid composition) data have been analyzed with Eqs. (1) through (5). Molecular constants of EOS for pure compounds as well as oils used here are shown in Table 1 [5]. The binary interaction parameters, l_{12} , l_{21} , m_{12} ($= m_{21}$) and t_{12} ($= t_{21}$) were optimized using a standard non-linear least-squares method with an objective function of $1 - P_{obs}/P_{calc}$, where P_{obs} is the pressure in the experimental solubility (PTx) data, and P_{calc} is the calculated pressure. The determined mixture parameters are shown in Table 2 with the average absolute deviation (AAD) % of the fit, and theoretical PTx curves are compared with experimental data in Figs. 1 (R32/HAB-15), 2 (R125/HAB-15), 3 (R134a/HAB-15), and 4 (R143a/HAB-15), respectively. Similar plots for the HAB-32 mixtures have been obtained. The horizontal lines in the Figures indicate the two liquid (VLLE) regions, which have been calculated by the present EOS model.

Table 1. Molecular Constants Used in the Present Model [5]

Compound	Molar Mass	T_c [K]	P_c [kPa]	β_0	β_1	β_2	β_3	
R-32	52.02	351.26	5782	1.0019	0.48333	-0.07538	0.0067	(*) HAB-15: Branched alkyl benzene (ISO-15) oil.
R-125	120.22	339.19	3637	1.0001	0.47736	-0.01977	-0.0177	(*) HAB-32: Branched alkyl benzene (ISO-32) oil.
R-134a	101.03	374.21	4059	1.0025	0.50532	-0.04983	0	
R-143a	84.04	346.20	3759	1.0006	0.45874	-0.04846	-0.0143	
HAB-15(*)	311	800	950	1.0	1.0	0	0	
HAB-32(*)	328	800	950	1.0	1.0	0	0	

Table 2. Determined Binary Interaction Parameters

Binary System (1)/(2)	l_{12}	l_{21}	$m_{12,21}$	$t_{12,21}$ [K]	ADD (*) [%]	
R-32/HAB-15	0.0990	0.1312	-0.1291	0	3.33	(*) AAD = Average Absolute Deviation of fitting in pressure.
R-125/HAB-15	0.0915	0.1297	-0.1570	12.2	1.88	
R-134a/HAB-15	0.1787	0.2067	-0.2585	40.25	2.90	
R-143a/HAB-15	0.0580	0.0904	-0.0900	-3.68	2.23	
R-32/HAB-32	0.1276	0.1422	-0.1536	0	2.56	
R-125/HAB-32	0.1587	0.1912	-0.2520	36.3	1.42	
R-134a/HAB-32	0.1146	0.1332	-0.1661	0	1.87	
R-143a/HAB-32	0.0153	0.0129	-0.0156	35.7	4.14	

4.2 Viscosity Data

Saturated liquid viscosity of each pure compound has been correlated with an empirical form Eq. (6), using values in the literature: R32 [8,9], R134a [10], R125 [8], R143a [8,9], HAB-15 and HAB-32 [11]. The coefficients in Eq. (6) are summarized in Table 3.

Viscosity (viscosity-composition-temperature) data in this study have been analyzed using Eq. (7), where there are at least three adjustable parameters, k , k_1 and k_2 . These parameter values were found by a trial-and-error method. First we assumed $k_1 = k_2 = 1$, and systematically varied the k value ($-1.5 \leq k \leq 1.5$). Fair fits to the experimental data were obtained with k values in the range of 0.2 - 0.6, but the values depended on temperature as well as the binary system. The system containing R-32 showed poorest fit. With a linear temperature dependence of k , the fits were improved significantly. However, the T dependence in k is inconvenient and unreliable when extrapolating beyond the experimental temperatures, especially when the measured temperature range is narrow as in the present case. In order to obtain a T -independent correlation, k_1 and k_2 values were varied as well as the k

values. Then, it was found that a temperature-independent k value could be obtained with fixed values in $k_1 = (3, 4, \text{ or } 5)$ and $k_2 = 1$. The proper k value without temperature dependence has been obtained for the present binary mixtures, and the values are given in Table 4 with the standard deviation of the fit. These deviations are somewhat smaller than those in the case of the T -dependent fit with $k_1 = k_2 = 1$.

Table 3. Coefficients for Viscosity Correlation of Pure Compound in Eq. (6).

Compound	A	B	C	D $\times 10^{-2}$	E $\times 10^{-5}$
R-32	-9.85983	258.171	-118.329	4.64362	-8.50012
R-125	-1.66528	550.000	0	-7.13348	0
R-134a	-6.04810	906.845	0	1.09872	-2.10309
R-143a	-16.0625	931.471	-180.828	0	0
HAB-15	-3.21397	778.290	-180.133	0	0
HAB-32	-3.62500	931.471	-180.828	0	0

Viscosity unit in cP and T in K.

Table 4. Determined Parameters for Viscosity of Oil-Refrigerant Mixtures in Eq.(7).

System (1)/(2)	k	k_1	k_2	$\delta \eta$ (%)
R-143a/HAB-32	-0.195	5	1	5.3
R-134a/HAB-32	-0.220	5	1	6.7
R-125/HAB-32	-0.275	5	1	4.8
R-32/HAB-32	-0.070	5	1	2.9
R-143a/HAB-15	-0.310	5	1	4.8
R-134a/HAB-15	-0.170	3	1	7.6
R-125/HAB-15	-0.255	5	1	4.5
R-32/HAB-15	-0.115	5	1	6.8

$\delta \eta$ is the standard deviation in % of the fit in the experimental and calculated viscosities.

5. RESULTS AND DISCUSSION

Solubility data are well modeled with an AAD of about 1.5-4 % in pressure. Considering the difficulty of accurate measurement for small refrigerant concentrations in oil, these average deviations from the observed data are well within the experimental error. With the present model, we can calculate the solubility limit of HFC/Oil mixtures. This is a good test for the model validity, since in the model correlation process we did not use any VLE information; the experimental data are all in the single liquid phase region, and in most of cases data points end near or at the solubility limit. The results of VLE (liquid-liquid separation) calculations are consistent with the experimental end points, as can be seen in Figs.1 through 4; at 80 °C, the experimental end points of R-32 and R-125 mixtures (Figs. 1 and 2) do not correspond the solubility limit points, which were not measured due to the high pressures involved. The miscibility limit depends on temperature, and this dependence has been calculated between $T = -40$ °C and $T = 100$ °C. HFCs are fairly miscible in the AB oils, while AB oils are hardly miscible in the HFCs: e.g., at 25 °C, HFCs are miscible in AB oils up to 13 to 18 mass %, and AB oils are miscible in HFCs only to 0.3 to 2.5 mass %, depending upon the refrigerant-oil combination. The mutual miscibility increases with decreasing the oil viscosity grade: HAB-32 vs. HAB-15. Such a trend has been observed and reported in the literature [12].

Comparisons of calculated and observed viscosity data show a standard deviation of 3 - 8 %, which is quite reasonable agreement, considering that the viscosity of pure HFCs and the oils differ by a factor of approximately 1000.

By use of the present EOS and viscosity equation, an integrated chart of the viscosity-temperature-pressure-solubility relation (Daniel chart) can be constructed. First, viscosity of any given mixture composition is simply calculated with Eq. (7) as a function of temperature. Next, the solubility limit composition of HFC, x_{lim} , in the oil-rich solution is calculated for any desired pressure by VLE calculations with the EOS model. Then, with the given pressure, ordinary bubble-point-temperature calculations with the EOS are performed for a HFC composition starting from x_{lim} to 0 % with small decrement steps; the composition and calculated temperature gives isobaric viscosity through Eq. (7). Examples of the results thus calculated are shown in Figs. 5 through 10.

6. CONCLUSION

Solubility data of partially miscible HFC/AB oil mixtures have been successfully correlated with a cubic EOS by the use of a special binary mixing rule. Mixture viscosity data are also reasonably correlated with a simple empirical equation. With these correlations, it appears that thermodynamic properties and viscosity values can be reliably calculated for a wide range of state variables (temperature, pressure, and composition).

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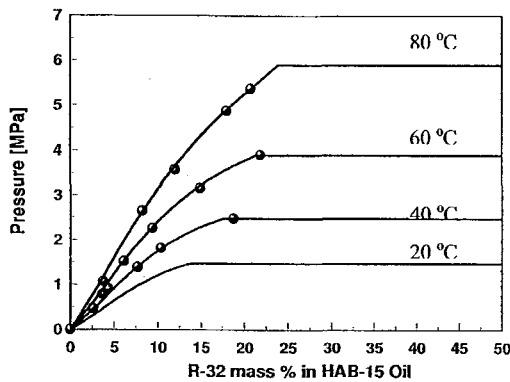


Fig. 1. Isothermal pressure composition diagram of R-32/HAB-15 mixtures. Symbols: experimental points. Lines: calculated; horizontal regions indicate VLLE.

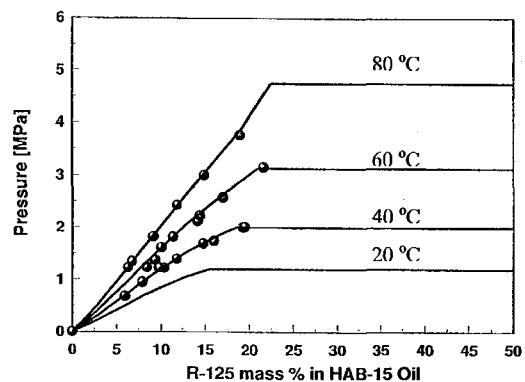


Fig. 2. R-125/HAB-15. See Fig. 1, for symbols.

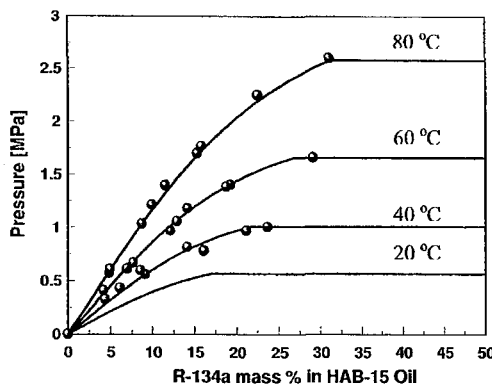


Fig. 3. R-134a/HAB-15. See Fig. 1, for symbols.

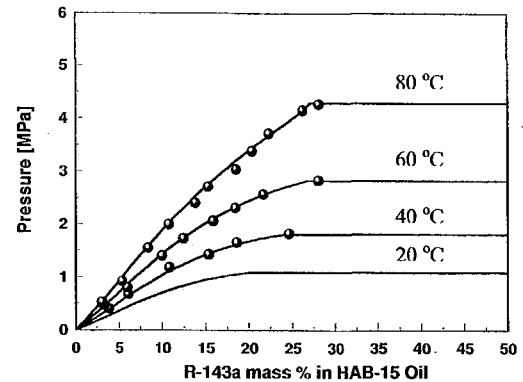


Fig. 4. R-143a/HAB-15. See Fig. 1, for symbols.

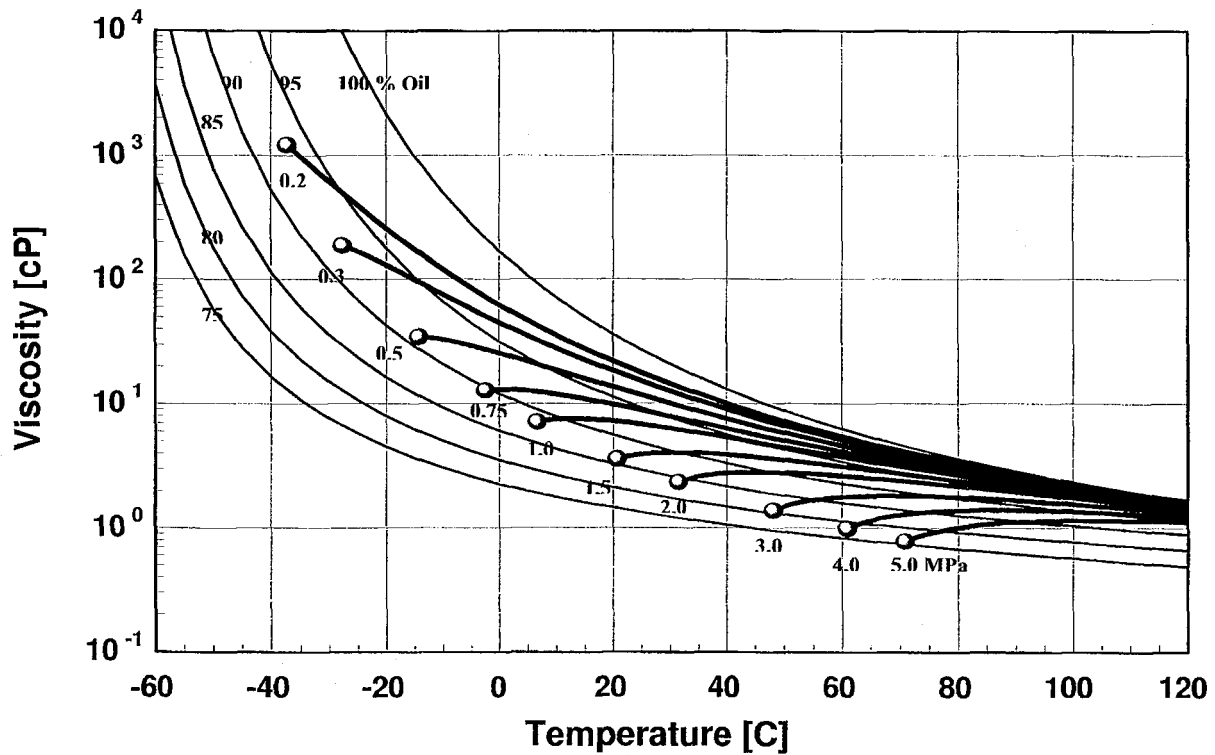


Fig. 5. Daniel chart of R-32/HAB-15. Solid circles in the isobaric curves: solubility limit points.

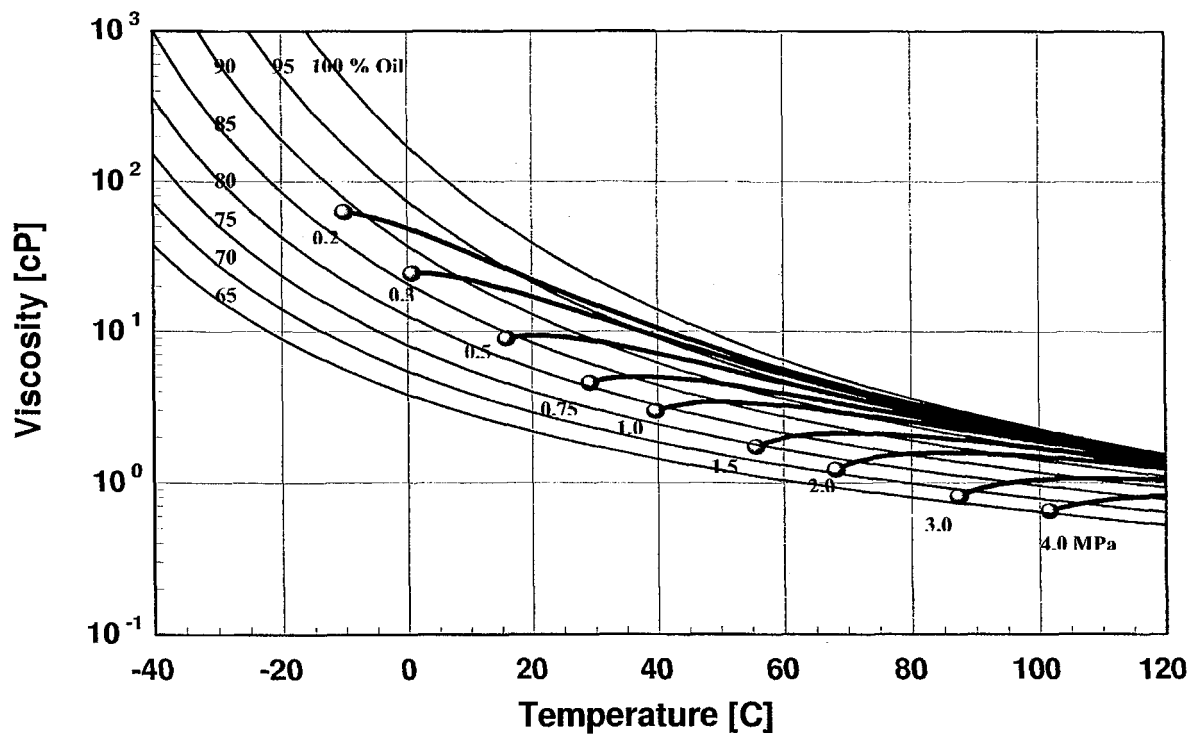


Fig. 6. Daniel chart of R-134a/HAB-15. Solid circles: solubility limit point.

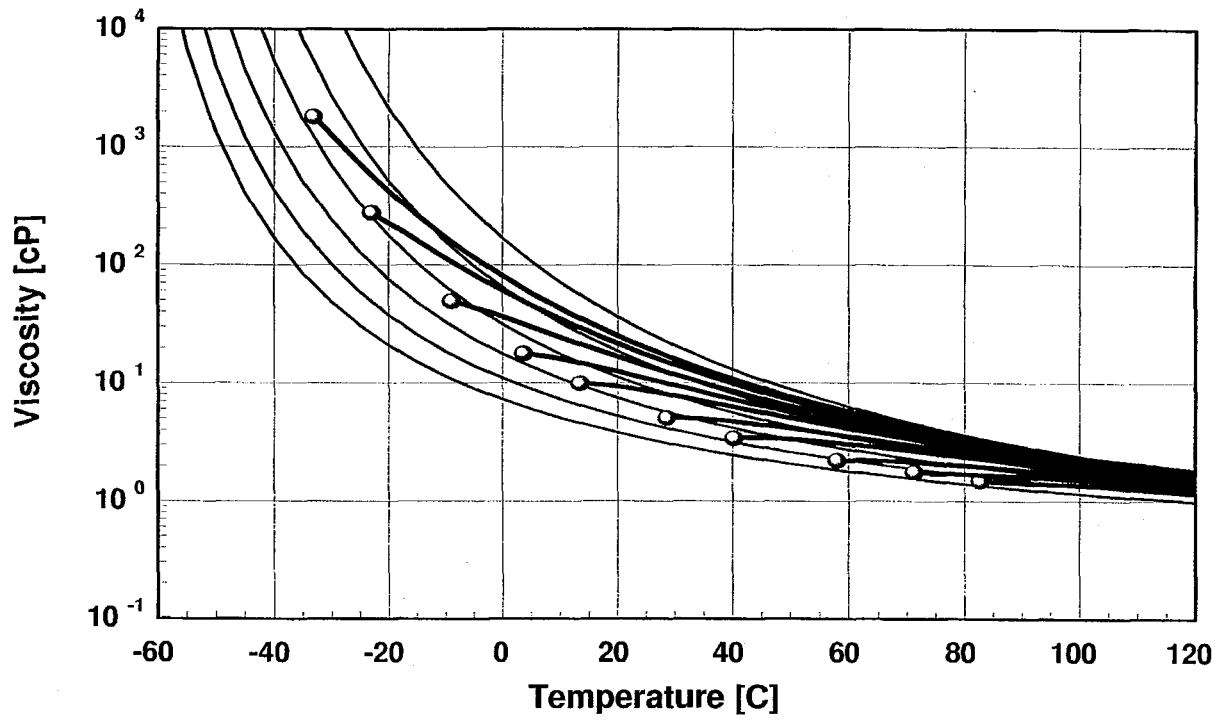


Fig. 7. Daniel chart of R-125/HAB-15. Solid circles: solubility limit points. For isobar and oil % values, see Fig. 5.

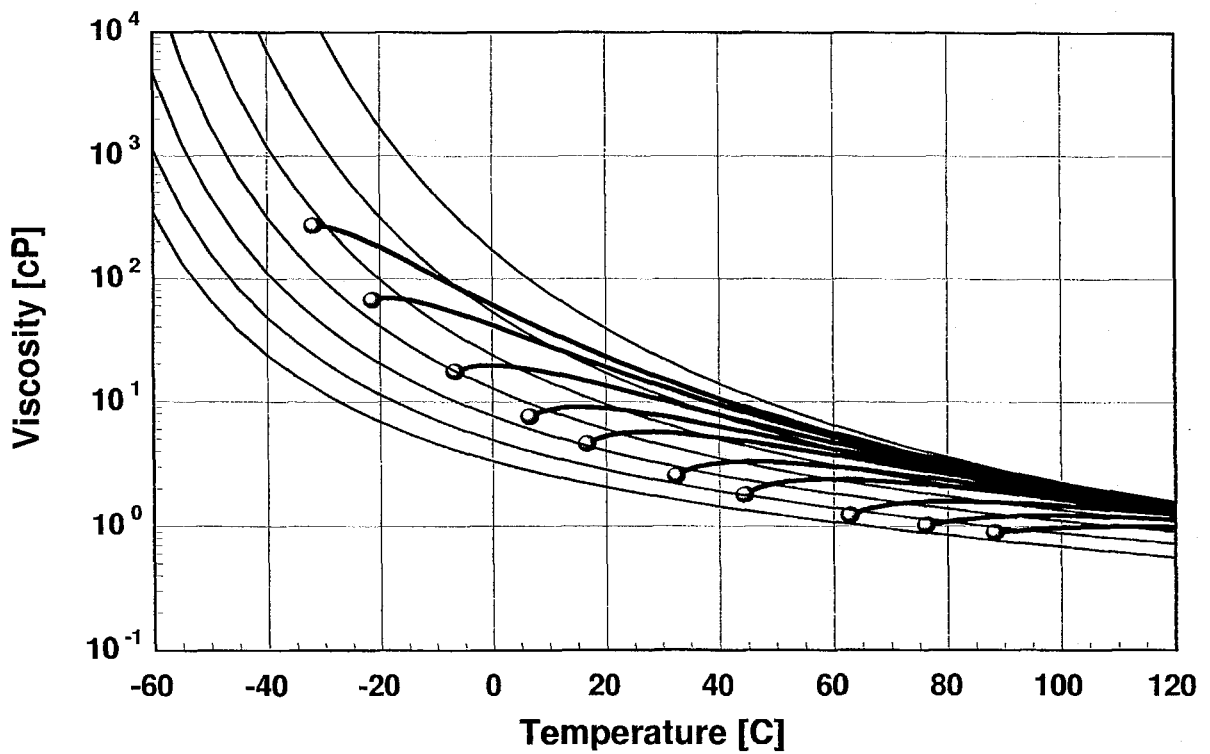


Fig. 8. Daniel chart of R-143a/HAB-15. Solid circles: solubility limit points. See Fig. 5.

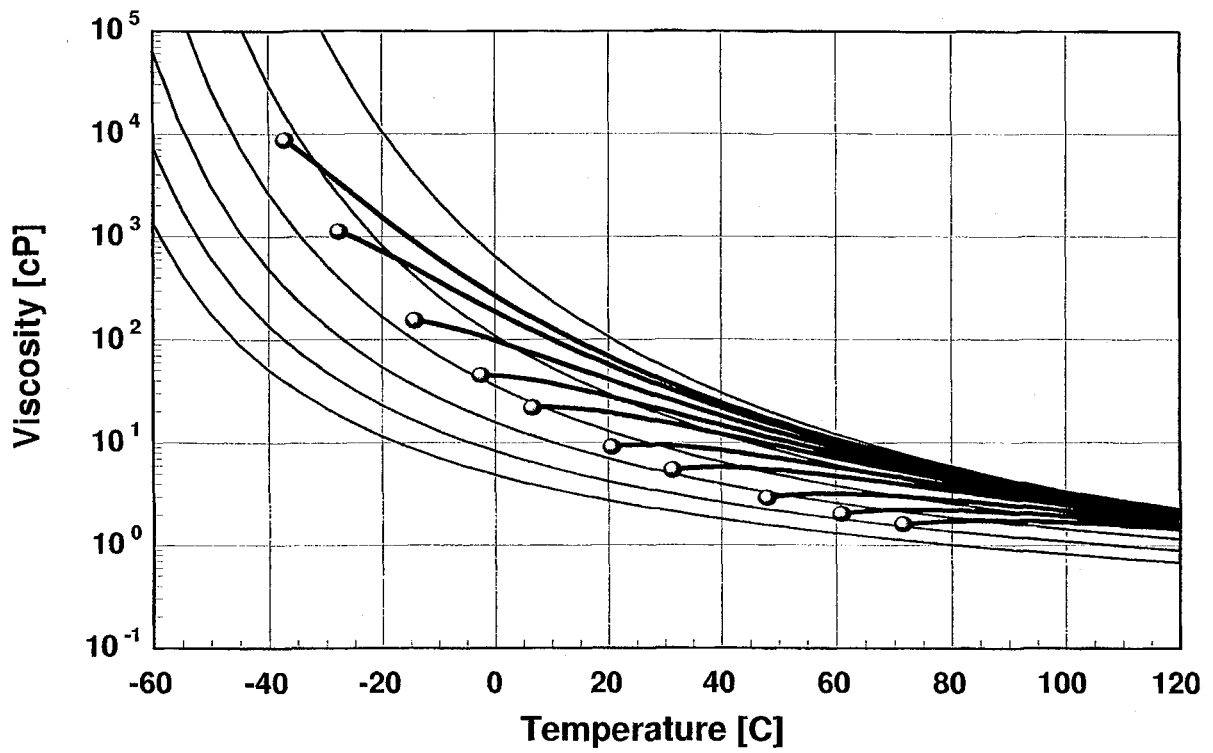


Fig. 9. Daniel chart of R-32/HAB-32. Solid circles: solubility limit points. See Fig. 5.

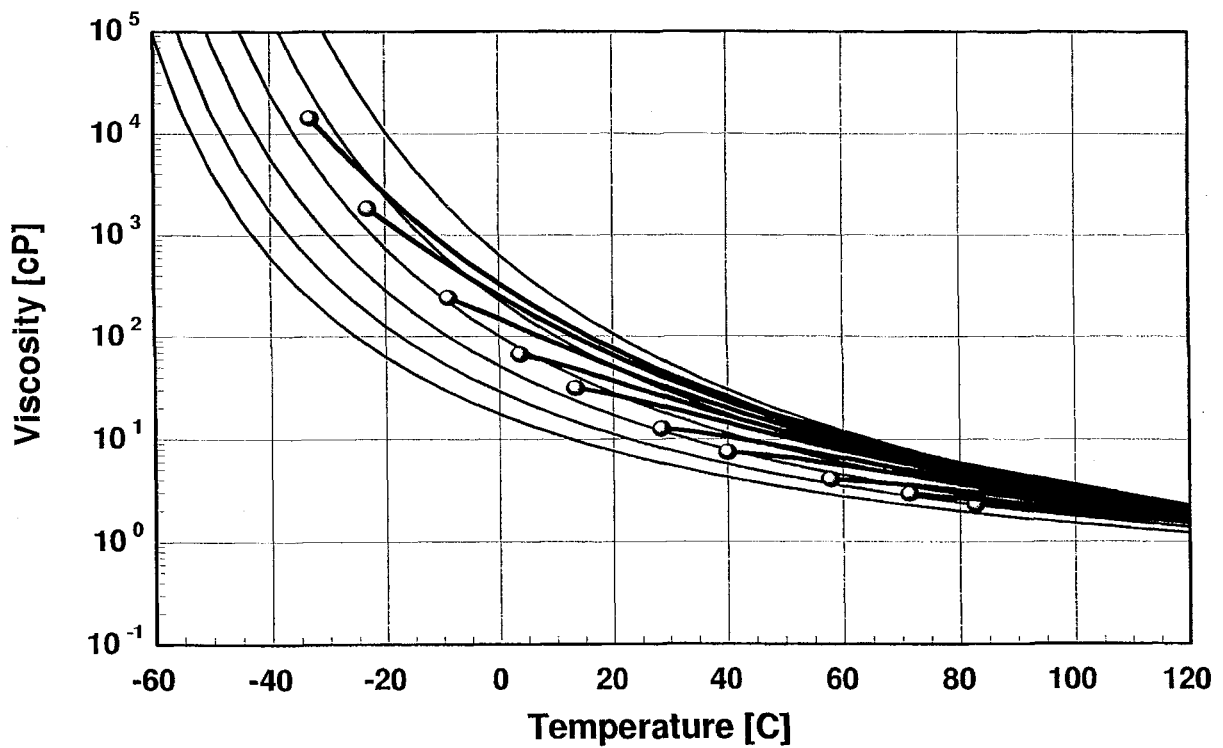


Fig. 10. Daniel chart of R-125/HAB-32. Solid circles: solubility limit points. See Fig. 5.