values of ν estimated from eq 3 exhibit large percent deviations from the experimental values of ν in the case of the mixtures of CH_2ClCH_2Cl with benzene, toluene, *p*-xylene, and cyclohexane.

Earlier attempts have been made to describe the dynamic viscosities, η, of binary liquid mixtures in terms of the dynamic viscosities of pure components and a parameter attributed to the intermolecular interactions between the components. According to Grunberg and Nissan (*4*), the dynamic viscosity of a binary mixture of components A and B is given by the equation

$$\ln \eta = x_A \ln \eta_A + x_B \ln \eta_B + x_A x_B d \qquad (6)$$

where η_A and η_B refer to the dynamic viscosities of the pure liquid components A and B, respectively, x_A and x_B are the mole fractions of the components A and B, respectively, in the mixture, and d is a parameter which is regarded as a measure of the strength of interaction between the two components. In order to calculate d from eq 6, the measured values of ν were converted to dynamic viscosities η by using densities which for pure liquids were those available in literature (*12*). The densities of the mixtures were obtained from the densities of pure components and the measurements on excess volumes (*1*) for the various binary mixtures. The values of d for the various binary mixtures are given in Table I which shows that the variation of the parameter d with composition of a particular mixture is not large. The values of d are positive for CH_2ClCH_2Cl–quinoline, and negative for CH_2ClCH_2Cl–benzene, CH_2ClCH_2Cl–toluene, CH_2ClCH_2Cl–*p*-xylene, and CH_2ClCH_2Cl–cyclohexane. The mean values of d for the systems CH_2ClCH_2Cl–benzene, CH_2ClCH_2Cl–toluene, CH_2ClCH_2Cl–*p*-xylene, CH_2ClCH_2Cl–quinoline, and CH_2ClCH_2Cl–cyclohexane have been found to be -0.34, -0.24, -0.22, +0.031, and -0.78, respectively. The positive values of d for CH_2ClCH_2Cl–quinoline show that CH_2ClCH_2Cl forms an intermolecular complex with quinoline in the liquid, which gives evidence in favor of our earlier conclusions (*1*–*3*). The values of d, which are slightly negative for CH_2ClCH_2Cl–benzene, CH_2ClCH_2Cl–toluene, and CH_2ClCH_2Cl–*p*-xylene, as compared with d for CH_2ClCH_2Cl–cyclohexane, indicate the existence of a weak specific interaction between CH_2ClCH_2Cl and the aromatic hydrocarbons.

Acknowledgment

We are very thankful to Professor S. C. Tripathi, Head of the Chemistry Department, Gorakhpur University, Gorakhpur, for providing laboratory facilities.

Registry No. CH_2ClCH_2Cl, 107-06-2; benzene, 71-43-2; toluene, 108-88-3; *p*-xylene, 106-42-3; quinoline, 91-22-5; cyclohexane, 110-82-7.

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Heterogeneous Equilibrium in the Quinary System $NaCl–KCl–MgCl_2–CaCl_2–H_2O$ in the 0–50 °C Temperature Range

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The quinary system $NaCl–KCl–MgCl_2–CaCl_2–H_2O$ was experimentally investigated in the 0–50 °C temperature range in a condition of equilibrium with three solid phases: sodium chloride (NaCl), carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$), and bischofite ($MgCl_2 \cdot 6H_2O$). A correlation was established between magnesium chloride concentration and the two independent variables, i.e., temperature and calcium chloride concentration. The solubilities of sodium chloride and potassium chloride were found to be low, less than 0.6 wt % NaCl and less than 0.4 wt % KCl.

Introduction

Many natural brines, such as seawater or the brines of the Dead Sea in Israel, contain sodium, potassium, calcium, and magnesium chlorides. The aqueous solubilities of these minerals are thus of great importance from both industrial and geological points of view. A large amount of experimental work has been done on binary, ternary, and quarternary subsystems of the quinary system $NaCl–KCl–MgCl_2–CaCl_2–H_2O$, and most of the results have been summarized by Linke and Seidell (*1*). However, very few equilibrium data have been published on this quinary system.

The experimental determination of the phase diagram of the quinary system $NaCl–KCl–MgCl_2–CaCl_2–H_2O$ is somewhat complicated, because a number of solid phases may appear at the various equilibria. The magnesium and calcium chlorides crystallize in a variety of hydrate forms: $MgCl_2 \cdot 12H_2O$, $MgCl_2 \cdot 4H_2O$, $MgCl_2 \cdot 2H_2O$, $CaCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 4H_2O$, and $CaCl_2 \cdot 2H_2O$. In addition, salt pairs may precipitate, such as $CaCl_2 \cdot 2MgCl_2 \cdot 12H_2O$, $2CaCl_2 \cdot MgCl_2 \cdot 12H_2O$, and $KCl \cdot MgCl_2 \cdot 6H_2O$.

For the quinary system, the Gibbs phase rule shows that at constant pressure and temperature there are four degrees of freedom. Hence, it is important that the phase diagram range

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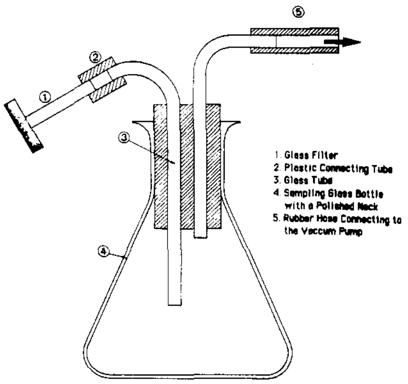

Figure 1. Sampling apparatus.

to be experimentally investigated should be clearly defined. Also, particular methods are required for the graphic presentation of the phase diagram.

In previous experimental studies of the quinary system $NaCl-KCl-MgCl_2-CaCl_2-H_2O$, the isotherms at atmospheric pressure were investigated at the following temperatures: 25 °C (*2*, *3*); 35 °C (*4*); 50 and 75 °C (*5*, *6*); 100 °C (*7*); and 110 °C (*8*). In general, in these papers schematic graphic presentations of the isotherms were presented by the methods of Jänecke (*9*) or Schreinemakers (*10*). In addition, these phase diagrams were usually based on the determination of only invariant and monovariant points. The literature thus describes the existing regimes of the various solid phases, but additional quantitative data are not sufficiently available.

The purpose of this work was to determine experimentally the phase diagram of the quinary system $NaCl-KCl-MgCl_2-CaCl_2-H_2O$ in the temperature range in which the liquid solution is saturated with the following solid phases: NaCl, $KCl{\cdot}MgCl_2{\cdot}6H_2O$, and $MgCl_2{\cdot}6H_2O$. At constant pressure this area of the quinary system has two degrees of freedom, namely, there are two independent variables. Thus, we determined the compositions of the liquid solutions (at equilibrium with the above-mentioned solid phases) as a function of calcium chloride concentration and of temperature in the range of 0–50 °C. These particular equilibrium data were sought as part of a study of the highly concentrated byproduct solutions of the Dead Sea Works. Such end brines are considered a potential source of heat storage materials by virtue of their high latent heat of solution.

Procedure and Experimental Apparatus

Materials. Analytical grade NaCl, KCl, and $MgCl_2{\cdot}6H_2O$ were supplied by Frutarom, Haifa. Analytical grade $CaCl_2{\cdot}2H_2O$ was obtained from Merck.

Procedures. A 1000 cm^3 volume of $CaCl_2$ aqueous solution of known concentration was placed in a 3000 cm^3 glass flask. The $CaCl_2$ solution was prepared by dissolving $CaCl_2{\cdot}2H_2O$ in distilled water in the appropriate weight ratio. A mixture of 50 g of KCl, 80 g of NaCl, and sufficient $MgCl_2{\cdot}6H_2O$ to supersaturate the solution at 50 °C was added.

The flask containing the mixture was placed in a thermostated (±0.1 °C) water bath (Type KT-52, Haake Corp.). The mixture was stirred continuously. The temperatures in the flask and the thermostated bath were measured by copper–constantan thermocouples. Preliminary tests showed that the system approached equilibrium within 2 h, either from undersaturation or from supersaturation. As an additional precaution, the samples from the liquid phase were taken for analysis only after the flask had been kept for at least 4 h at the fixed temperature. Samples were withdrawn via a special sampling apparatus, as shown in Figure 1. The liquid samples were sucked through a porous glass filter into a 25-cm^3 sampling bottle by means of a vacuum pump. The porous glass filter was constantly immersed in the solution for thermal equilibration. In runs in which the equilibrium temperatures were above the ambient temperature, the nonimmersed parts of the sampling apparatus were heated to a temperature above the equilibrium temperature. No crystallization occurred during the suction operation which took about 2–3 s.

Analytical Method. The compositions of the samples were determined as follows: potassium (±1%) and sodium (±1%) by flame photometry; magnesium (±1%) and calcium (±2%) by titration with EDTA. For checking the accuracy of the results, the total chloride ion concentration was determined by the Mohr method (±1%). The composition of each sample was determined as the average of two analytical measurements. At the end of each set of experiments the solid phases were identified by X-ray diffraction analysis.

Experimental Results and Discussion

The experimental data are summarized in Table IA–G. The data cover the range in which the liquid solutions are saturated with $MgCl_2{\cdot}6H_2O$ (bischofite) $KCl{\cdot}MgCl_2{\cdot}6H_2O$ (carnallite), and NaCl. In the investigated range, the solid-phase mixtures contained water and magnesium chloride in a 6:1 molar ratio ($MgCl_2{\cdot}6H_2O$, $KCl{\cdot}MgCl_2{\cdot}6H_2O$). For the convenience of graphic presentation and correlation of the equilibrium data, the concentration of the different salts in the liquid phase was also expressed as grams of salt per kilogram of "free water", as defined by

$$\mathrm{XFW} = 1000 - \mathrm{XN} - \mathrm{XK} - \mathrm{XC} - \frac{203.3}{95.23}\mathrm{XM} \qquad (1)$$

where XFW represents the concentration of H_2O in grams of free water/kilogram of solution, and XN, XK, XC, and XM, the concentrations of NaCl, KCl, $CaCl_2$, and $MgCl_2$ in grams of salt/kilogram of solution; and

$$\mathrm{FN} = 1000(\mathrm{XN}/\mathrm{XFW}) \qquad (2)$$

$$\mathrm{FK} = 1000(\mathrm{XK}/\mathrm{XFW}) \qquad (3)$$

$$\mathrm{FC} = 1000(\mathrm{XC}/\mathrm{XFW}) \qquad (4)$$

$$\mathrm{FM} = \frac{203.3}{95.23}\,1000\,\frac{\mathrm{XM}}{\mathrm{XFW}} \qquad (5)$$

where FN, FK, FC, and FM represent the concentrations of NaCl, KCl, $CaCl_2$, and $MgCl_2{\cdot}6H_2O$ in grams of salt/kilogram of free-water.

Under the conditions of our experiments, i.e., a molar ratio of water to magnesium chloride of 6:1, the amount of free water in the liquid phase in a closed system does not change as a result of crystallization or dissolution of the above-mentioned solid phases. As a result of decreasing/increasing equilibrium temperatures, there is a linear ratio between the quantity of the crystallization/dissolution of the different salts and the concentration in grams of salt/kilogram of free-water as defined in eq 1–5.

As can be seen from the experimental data, except for the last two points in Table IG where $CaCl_2{\cdot}6H_2O$ precipitated, the concentration of calcium chloride in grams of $CaCl_2$/kilogram of free water remained constant for each set of experiments. This finding verifies that $CaCl_2$ does not precipitate in the investigated range. Figure 2, a and b, shows that when the concentration is given in grams of salt/kilogram of free water, for each constant temperature curve there is a linear relationship between the decrease of "$MgCl_2{\cdot}6H_2O$" concentration and the increase of the calcium chloride concentration. By application of the least-squares method, the experimental results were found to follow the expression

$$\mathrm{FM} = -3.3422\mathrm{FC} + 0.3319T^2 + 10.734T + 2836.7 \qquad (6)$$

Table I. Composition of Solutions in Equilibrium with Sodium Chloride, Carnallite, and Bischofite

	concn of salts							
	g of salt/kg of soln				g of salt/kg of free water			
T, °C	$CaCl_2$	$MgCl_2$	KCl	NaCl	$CaCl_2$	$MgCl_2 \cdot 6H_2O$	KCl	NaCl
				A				
50	0	375.6	2.01	3.70	0	4160	10.40	19.2
35	0	366.8	1.43	3.56	0	3665	6.70	16.7
30	0	363.2	1.25	3.54	0	3496	5.65	16.1
25	0	359.6	1.06	3.45	0	3365	4.64	15.1
20	0	352.7	0.95	3.37	0	3080	3.89	13.8
15	0	351.2	0.81	3.27	0	3024	3.27	13.2
10	0	350.7	0.64	3.09	0	3002	2.57	12.4
5	0	347.2	0.54	3.00	0	2900	2.11	11.7
0	0	346.3	0.45	2.89	0	2851	1.74	11.2
				B				
50	9.5	370.3	2.06	3.65	49.2	4090	10.70	18.9
35	10.9	358.1	1.54	3.70	49.5	3474	7.00	16.8
30	11.0	351.6	1.31	3.57	47.0	3189	5.58	15.2
25	12.0	349.0	1.12	3.50	49.9	3100	4.67	14.6
20	12.7	345.2	0.92	3.30	51.2	2971	3.72	13.4
15	13.0	343.7	0.77	3.20	51.7	2922	3.07	12.7
10	13.2	340.8	0.67	3.12	52.5	2847	2.63	12.2
5	13.5	338.0	0.63	3.03	52.0	2750	2.37	11.5
0	14.0	334.7	0.47	2.96	52.1	2659	1.71	11.0
				C				
50	20.1	365.2	2.06	3.70	103.0	3993	10.50	19.0
35	23.0	350.3	1.56	3.75	102.6	3337	6.96	16.7
30	24.4	34.43	1.36	3.65	103.4	3116	5.77	15.5
25	25.9	342.7	1.08	3.56	108.7	3072	4.53	15.0
20	26.4	333.3	1.00	3.43	102.3	2758	3.84	13.5
15	26.8	330.8	0.86	3.40	101.9	2683	3.27	13.0
10	28.0	327.8	0.70	3.20	104.3	2605	2.61	11.9
5	29.4	323.9	0.60	3.16	106.7	2509	2.18	11.5
0	30.2	321.0	0.47	3.00	107.4	2437	1.70	10.7
				D				
50	41.5	347.9	2.16	3.80	198.3	3547	10.30	18.2
35	48.5	332.7	1.58	3.86	205.5	3009	6.70	16.3
30	50.3	326.0	1.50	3.78	202.5	2798	6.03	15.3
25	53.6	318.3	1.24	3.67	203.6	2576	4.71	13.9
20	54.9	314.4	0.96	3.55	202.8	2476	3.55	13.1
15	56.1	310.2	0.81	3.37	201.2	2370	2.91	12.1
10	57.4	307.6	0.65	3.28	202.7	2314	2.30	11.6
5	59.1	301.0	0.62	3.20	199.9	2169	2.10	10.9
0	59.4	301.0	0.48	3.08	201.1	2170	1.62	10.4
				E				
50	68.4	330.4	2.24	3.88	306.7	3150	10.20	17.6
35	75.1	314.9	1.68	3.88	303.7	2718	6.79	15.7
30	83.3	299.6	1.55	3.82	306.2	2351	5.70	14.0
25	85.6	295.2	1.27	3.80	307.3	2262	4.60	13.6
20	88.1	290.8	1.12	3.42	307.5	2167	3.91	13.0
15	92.2	281.9	0.92	3.56	305.6	1994	3.05	11.8
10	93.0	280.6	0.79	3.40	305.9	1970	2.60	11.2
5	95.5	276.6	0.63	3.20	307.7	1902	2.03	10.3
0	97.1	273.2	0.57	3.04	307.0	1849	1.80	9.6
				F				
50	84.8	313.6	2.41	3.81	354.0	2793	10.10	15.9
35	93.8	299.6	1.65	3.60	359.0	2445	6.31	13.8
30	96.9	294.5	1.50	3.40	355.0	2314	5.56	12.6
25	100.3	286.6	1.29	3.28	353.0	2154	4.55	11.6
20	105.8	278.6	1.02	3.09	358.0	2012	3.45	10.5
15	107.9	269.8	0.96	3.00	345.0	1843	3.07	9.76
10	108.9	271.7	0.76	2.75	353.8	1889	2.11	8.90
5	110.3	267.6	0.65	2.47	346.9	1810	2.07	7.83
0	115.0	264.4	0.55	3.27	363.0	1786	1.74	10.3
				G				
50	135.3	281.1	2.62	4.30	524.6	2326	10.20	16.7
35	156.8	251.2	1.86	4.23	519.6	1774	6.16	14.0
30	165.8	237.2	1.70	4.22	513.0	1563	5.26	13.0
25	173.0	228.6	1.40	4.15	517.4	1457	4.19	12.4
20	182.0	219.5	1.28	4.15	527.6	1355	3.71	12.0
15	183.3	212.2	1.11	4.00	510.1	1258	3.09	11.1
10	186.6	212.1	0.93	3.99	531.0	1274	2.62	11.2
5[a]	156.9	231.1	0.78	3.77	453.5	1422	2.25	10.9
0[a]	126.5	256.0	0.70	3.55	391.0	1686	2.16	11.0

[a] The solid phases contain $CaCl_2 \cdot 6H_2O$ as well.

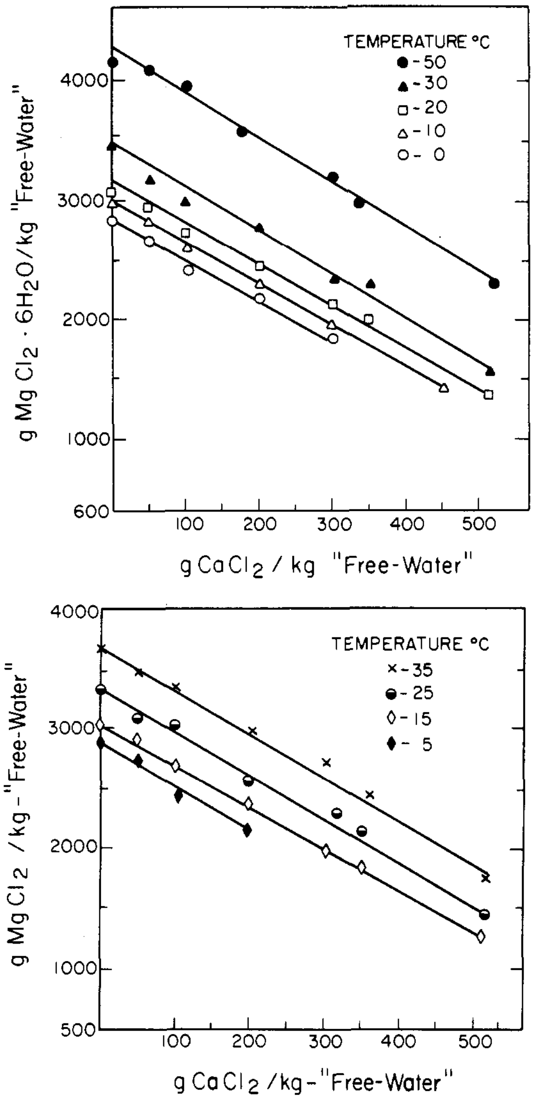

Figure 2. (a, top) Magnesium chloride concentration vs calcium chloride concentration in solutions at equilibrium with sodium chloride, carnallite, and bischofite. (b, bottom) Magnesium chloride concentration vs calcium chloride concentration in solutions at equilibrium with sodium chloride, carnallite, and bischofite.

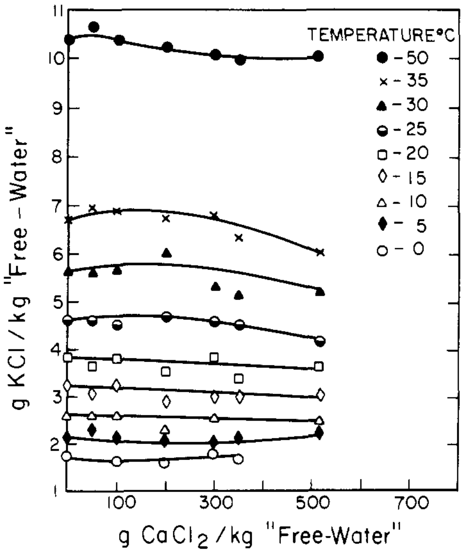

Figure 3. Potassium chloride concentration as a function of calcium chloride concentration in solutions at equilibrium with sodium chloride, carnallite, and bischofite.

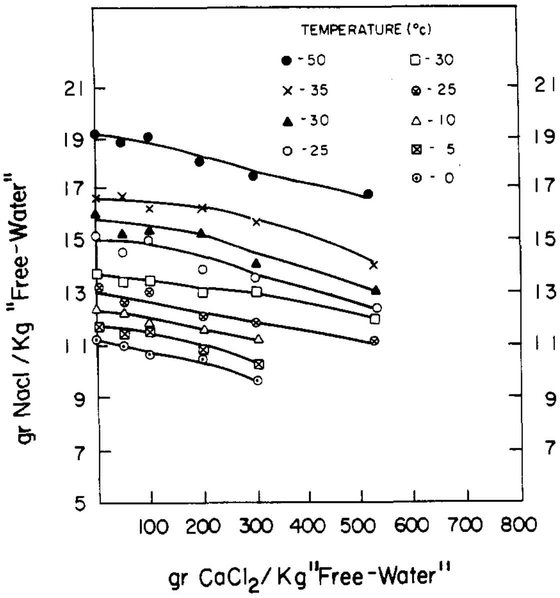

Figure 4. Sodium chloride concentration as a function of calcium chloride concentration in solutions at equilibrium with sodium chloride, carnallite, and bischofite.

Table II. Equilibrium Data in the Quaternary System NaCl-KCl-MgCl$_2$-H$_2$O Saturated with NaCl, KCl•MgCl$_2$•6H$_2$O and MgCl$_2$•6H$_2$O, Compared with Data Reported in the Literature

	concn of salts, g of salt/kg of soln			
T, °C	MgCl$_2$	KCl	NaCl	ref
50	374.7	1.3	2.8	*11*
	373.0	2.1	3.8	*12*
	375.6	2.01	3.70	this work
25	352.6	0.8	4.1	*11*
	359.6	1.06	3.45	this work
0	342.4	0.5	3.4	*11*
	346.3	0.45	2.89	this work

where T is temperature in the range 0–50 °C and FC is the concentration in the range of 0–52 g of CaCl$_2$/kg of free water. The average error E, as defined in eq 7 is 1.75%. The concentrations of potassium chloride and sodium chloride as a function of calcium chloride concentration at the different temperatures are given in Figures 3 and 4. The concentrations of sodium and potassium chloride were found to be low, less than 0.6 wt % sodium chloride and less than 0.4 wt % potassium chloride. The solubilities of these salts did not change significantly as a function of calcium chloride concentration (Figures 3 and 4).

$$E = 100\,\frac{\mathrm{FM(calcd)} - \mathrm{FM(exptl)}}{\mathrm{FM(exptl)}} \qquad (7)$$

To test the validity of the results, experimental values in the quaternary system NaCl–KCl–MgCl$_2$–H$_2$O were compared with experimental data from the literature (Table III). Our results are in fairly good agreement with the experimental measurements reported by others (*11*, *12*).

Acknowledgment

We thank Ms. Inez Mureinik for help with the manuscript and Mr. Yossi Ron for typing.

Registry No. NaCl, 7647-14-5; KCl, 7447-40-7; MgCl$_2$, 7786-30-3; CaCl$_2$, 10043-52-4.

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NEW COMPOUNDS

Tetraalkylsilanes via Hydrosilylation of 1-Alkenes

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Tetraalkylsilanes carrying one short and three long alkyl groups were synthesized via a two-step hydrosilylation procedure, which appears more suited for commercial production than previously employed Grignard or alkyllithium routes. The viscosities of two component blends were adequately treated by the ASTM D-341 procedure. The thermal stabilities of some silahydrocarbons and model paraffins, as measured by the loss of their 40 °C viscosity, were determined at 371 °C.

Synthesis of Tetraalkylsilanes

We have prepared a series of tetraalkylsilanes, referred to as silahydrocarbons to stress their hydrocarbon-like properties, via a two-step hydrosilylation procedure, and found their viscosities comparable to similar compounds prepared via the Grignard or alkyllithium routes (*1*, *2*). For example, reaction of methyldichlorosilane with 1-octene or 1-decene gave the corresponding dialkyldichlorosilanes (eq 1), which were then reduced to dialkylsilanes (eq 2), and the latter were subjected to a second hydrosilylation with 1-octene or 1-decene to give the desired silahydrocarbon (eq 3). The advantage of using a two-step hydrosilylation lies in the commercial availability of methyldichlorosilane and because the higher molecular weight dialkylsilane intermediates are not pyrophoric and are easy to handle on a large scale. Reduction of chlorosilanes was conveniently carried out with lithium aluminum hydride (LAH, 100% excess) (*3*), but less costly procedures based on sodium hydride could be developed (*4*-*9*). The catalyst used in the first reaction (eq 1) was platinum, and in the second reaction (eq 3) it was platinum or rhodium. The products were isolated by distillation in yields of ~75-86; our primary concern was to obtain purities of at least 98%.

$$CH_3SiCl_2H + H_2C{=}CHR \rightarrow CH_3SiCl_2CH_2CH_2R \qquad (1)$$

$$2CH_3SiCl_2CH_2CH_2R + LiAlH_4 \rightarrow 2CH_3SiH_2CH_2CH_2R + AlCl_3 + LiCl \qquad (2)$$

$$CH_3SiH_2CH_2CH_2R + 2H_2C{=}CHR \rightarrow CH_3Si(CH_2CH_2R)_3 \qquad (3)$$

Viscosity Correlations

A plot of viscosities against the carbon number of tetraalkylsilanes (Figure 1) for compounds listed in Table I, and some viscosities taken from the literature, gave a series of fan-shaped curves. Many of the tetraalkylsilanes had high melting points, which precluded measurement of their viscosities at temperatures below −20 °C. By synthesizing methyltrialkylsilanes, where R is a mixture of octyl and decyl groups, we found that the products were fluid even below −54 °C, the anticipated storage temperature in the Arctic region. A comparison of silahydrocarbon viscosities with a typical commercial fluid (4 mm^2/s Synfluid) is shown in Figure 2. The data show that, at temperatures above 38 °C, the viscosities for the two classes of fluids are about equivalent; at lower temperatures, however, the viscosities of silahydrocarbons were lower than those of the Synfluid.

The viscosity data for two component blends, either all silahydrocarbon (Table I) or silahydrocarbon/Synfluid mixtures (Table II), are adequately treated by the ASTM D-341 procedure, which is based on Walther's classical equations. This behavior may not be too surprising as both classes of fluids are considered to have geometries consisting of dense centers.

In our experience, D-341 procedure gave calculated viscosities that were close to the measured viscosities but the method was tedious to use without a computer. Calculations using Roegier's equation were just as effective and much simpler to carry out with a calculator. While the applicability of the Roegier's equation to untested fluids may be questionable, in our work with silahydrocarbons and Synfluids, a good correlation between the calculated and experimental viscosities was obtained at all temperatures (±2%). Calculations based on D-341 procedure showed deviations of up to ±5% at low temperature (−54 °C) (Table II), particularly when the viscosity difference between the fluids was large.

Thermal Stability

Along with viscosity, an important property of hydraulic fluids for use at elevated temperatures is the thermal stability, which is determined by exposing the fluid under nitrogen to 371 °C for 6 h and measuring the loss of its 40 °C viscosity (Penn State method) (*1*). The effect of structure of the fluid on thermal

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