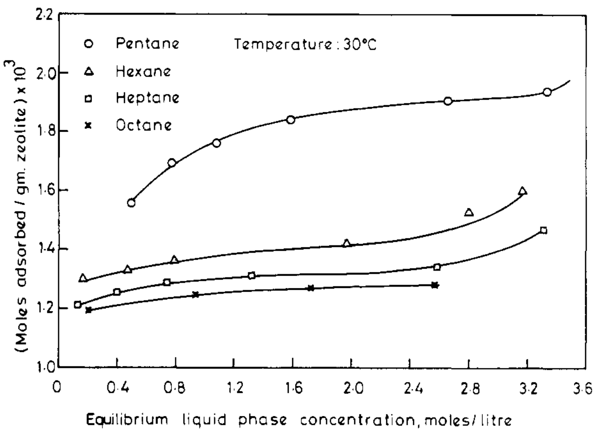

Figure 7. Adsorption isotherms of different *n*-paraffins at 30 °C.

i.e., the lower molecular weight paraffin is preferentially adsorbed. With increasing molecular weight, the effect of size diminishes. Thus, at 18 °C the equilibrium loading for *n*-pentane is 2.03 × 10^{-3} mol/g of zeolite at an equilibrium concentration of 1.6 mol/L compared to 1.62 × 10^{-3}, 1.43 × 10^{-3}, and 1.34 × 10^{-3} mol/g of zeolite for *n*-hexane, *n*-heptane, and *n*-octane, respectively. Peterson and Redlich (*3*) have also shown that liquid-phase sorbability decreases with increasing number of carbon atoms for *n*-paraffins having five or more carbon atoms. This violates Traube's rule that higher molecular weight adsorbate should be preferentially adsorbed. The reason for the preferential adsorption of lower molecular weight hydrocarbons on 5A molecular sieves is that in the zeolites both physicochemical adsorption and steric effects are important. Since type 5A molecular sieves have a pore opening of 5 Å and *n*-paraffins have a critical diameter of 4.9 Å, steric effects will play an important role. In shorter chain compounds (lower molecular weight *n*-paraffins) steric effects will be less in comparison to larger chain compounds.

Each experiment was conducted in two identical cells where initial concentration of the hydrocarbon and amount of sieves were kept same. For 95% of the runs, the deviation in the equilibrium loading between two parallel runs was less than 5%, the maximum being 9%. A few experiments were repeated somewhat separated in time and these were also found to be within 5% of each other.

In the present investigation, an experimental technique, for the liquid-phase adsorption of hydrocarbons on zeolite has been perfected. Adsorption isotherms have been measured for different liquid paraffins in the temperature range 6-42 °C. These data can be used to design single- or multiple-component adsorption plants.

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Supplementary Material Available: Tables I-IV, equilibrium adsorption data for *n*-pentane, *n*-hexane, *n*-heptane, and *n*-octane at different temperatures (4 pages). Ordering information is given on any current masthead page.

Viscosity of the Eutectic LiF-NaF-KF Melt (FLINAK)

Knut Tørklep and Harald A. Øye*

Institutt for Uorganisk Kjemi, Norges Tekniske Høgskole, Universitetet i Trondheim, N-7034 Trondheim-NTH, Norway

The viscosity of the molten eutectic mixture of LiF-NaF-KF (FLINAK) has been measured and the result can be expressed by $\eta(\mathrm{mPa\ s}) = 1.633 \exp(-2762.9T^{-1} + (3.1095 \times 10^{6})T^{-2})$.

The eutectic mixture of LiF-NaF-KF (FLINAK) is of interest as a solvent and low-pressure heat-transfer medium, because of its solvent properties, thermal stability, and extended liquid range. The present study was aimed at obtaining more reliable viscosity data for this liquid in connection with a nuclear technology program.

The experimental viscometry technique, including its application to other fluoride systems, has been described in detail elsewhere.[1-3] A specially designed high-temperature viscometer measures the period of oscillation and the damping of an oscillating Pt-Ir cylinder immersed in the liquid, using a computer-assisted digital method of timed intervals. The viscosity is calculated from fundamental viscosity equations, and no calibration against reference liquids is required.

Table I. Viscosity of FLINAK Melt Mixture, Mean Values[a]

temp, °C	viscosity, mPa s	10^3SD, mPa s
549.3	5.615	1
599.5	4.097	<1
700.3	2.535	<1
649.8	3.156	<1
497.0	8.551	1

[a] The uncertainty is given as the standard deviation (SD) of the mean.

The eutectic FLINAK mixture (29.21 wt % LiF-11.7 wt % NaF-59.09 wt % KF) was supplied by Dr. Vriesema and his group at the Laboratory for Thermal Power Engineering, Delft University of Technology (Prepared by drying under 1 Pa at 675 °C for several days after melting. The composition was thereafter checked and adjusted by using melting point determinations. The FLINAK from which the received sample was taken had been in operation for 1.5 years in Inconel-600 vessels under an argon blanket.). The sample was heated in the viscometer at 400 °C under 4 × 10^{-3} Pa prior to the measurements, which were carried out in a stream of highly purified nitrogen. The temperature was changed in a semirandom fashion in steps of 50 °C between 500 °C and 700 °C. About six determinations were made at each temperature. Results

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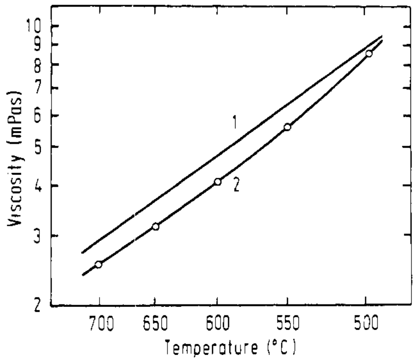

Figure 1. FLINAK viscosities (log mPa s vs. 1000/K): curve 1 according to Grimes et al.,[5] eq 4; curve 2 present results, eq 1.

(mean values) are given in Table I.

An exponential function of the second order in temperature T (K) was fitted to the entire experimental material:

$$\eta(\text{mPa s}) = 1.633 \exp(-2762.9T^{-1} + (3.1095 \times 10^6)T^{-2}) \qquad (1)$$

The standard deviation (SD) of η in the fit was 0.27%.

The densities reported by Mellors and Senderoff[4] were adopted in calculating the viscosity. The following expression, where t is degree Celsius, was derived by us from their density diagram:

$$\rho(\text{kg/m}^3) = (2.395 - (6.1 \times 10^{-4})t)10^3 \qquad (2)$$

The present viscosities may be recalculated with different densities by using the relation

$$\Delta\eta = (a + 0.005(\Delta\rho))(\Delta\rho) \qquad (3)$$

$$a = 0.852 + 0.0391\eta - 0.00158\eta^2$$

where $\Delta\rho$ is the percentage deviation of the density from eq 2 and $\Delta\eta$ is the viscosity correction in percent.

FLINAK viscosities have been measured earlier by Grimes et al.[5] They report the Arrhenius equation

$$\eta(\text{mPa s}) = 0.0400 \exp(4170/T) \qquad (4)$$

which yields viscosities 16% higher than ours at 600–650 °C (the discrepancy increases with about 2% if the density data of Grimes et al.[5] are applied to the present results through eq 3). Both results are shown as Arrhenius plots in Figure 1. While a rigid adherence to the Arrhenius rule is typical for simple liquids such as molten NaF, the present trend toward too high viscosities at lower temperatures is often observed in complex mixtures.[2,6]

The accuracy of our method in routinely performed investigations is estimated to be 0.5–1% SD,[1,2] which in this work also includes the effect of a 1 °C uncertainty in the temperature.

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Liquid–Vapor Equilibria in Binary Systems Formed by Methylcyclohexane with Chlorobenzene, Fluorobenzene, and Thiophene

M. Díaz-Peña,* A. Crespo-Colín, A. Compostizo, and I. Escudero

Departamento de Química Física, Facultad de Ciencias Químicas, Universidad Complutense, Madrid 3, Spain

Total vapor pressure at 348.15 K and liquid and vapor composition have been determined at 303.15 K by refractometry at points covering the whole range of molar concentrations for binary systems consisting of methylcyclohexane with either chlorobenzene, fluorobenzene, or thiophene. From these data the excess Gibbs free energy, G^E, for the three systems have been calculated.

As part of our systematic research on thermodynamic properties of the liquid state, we report in this paper excess Gibbs free energy values, G^E, for the three referred systems, calculated from vapor pressure data obtained at one and the same temperature for all systems. Determination of liquid and vapor composition at equilibrium was done through their refractive indexes n_D, using previously prepared calibration curves. The G^E values were determined from measurements of the four parameters, temperature, T, pressure, p, liquid-phase composition, x, and vapor-phase composition, y, and their thermodynamic consistency was checked analytically.

Experimental Section

Vapor pressure measurements were carried out by using a dynamical ebulliometer based on the work of Brown (*1*). A detailed scheme of the particular aparatus used in this work is given in ref 2. The liquids used and their source and quality were methylcyclohexane (Fluka purum), chlorobenzene (Fluka puriss), fluorobenzene (Fluka puriss), and thiophene (Fluka purum). They were further purified following conventional procedures (*3*), reaching 99.5% purity for methylcyclohexane and thiophene, 99.7% for fluorobenzene, and 99.8% for chlorobenzene. For comparison sake, in Tables I and II are included values of the

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