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Viscosities of Saturated Alcohol Vapors at Room Temperature

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IN CONNECTION with a study of the reactions of sodium with alcohols, the coefficients of viscosity of several low molecular weight alcohols were needed at room temperature and at or below their equilibrium vapor pressures. Since no data could be found for the butanols, and the values of the coefficients for the other alcohols had to be extrapolated from higher pressures and from temperatures above the boiling points, it was decided to determine their values under the conditions described above.

EXPERIMENTAL

Isopropyl alcohol was reagent grade from Baker and Adamson Co. The isobutyl alcohol was an Eastman Kodak product. *n*-Butyl alcohol was from Merck, and *n*-propyl, *sec*-butyl and *tert*-butyl alcohol were all from Matheson, Coleman and Bell. The alcohols were all distilled four times in vacuo, taking the middle third each time and discarding the rest. The infrared spectra showed no impurities. They were analyzed on a model 20 Barber-Coleman vapor phase chromatrograph using a 12 ft., ⅛in o.d. column packed with 20% Armeen D (octadecenyl amine) from Armour Co., on chromosorb. The usual sample size was 0.5 Ul. The accuracy of the analysis is estimated to be 0.2%. The minimum purities of the alcohols were found to be: *n*-propyl alcohol, 99.4%; isobutyl alcohol, 99%; and all others, 99.8%.

Carbon dioxide was obtained from a tank and purified by four bulb-to-bulb distillations, retaining only the middle third each time. No further analysis was performed.

The capillary used was of glass attached to a conventional vacuum system and was calibrated by allowing carbon dioxide, the coefficient of viscosity of which was known (*2*), to flow through it for a measured length of time, collecting it in a liquid nitrogen cooled, tared bulb and weighing it. By using the Poiseuille expression, the capillary constant was determined. The Poiseuille equation was used to calculate the coefficient of viscosity by similarly allowing the alcohol vapor to flow through the capillary for a known length of time, at a given temperature, and weighing the amount of alcohol taken. Flow conditions were such that no correction was needed for nonstreamline flow, nor for end effects.

RESULTS AND DISCUSSION

The range of experimental temperatures was 296° to 302° K. and the coefficients were corrected to 298° K. by assuming a half-power dependence on the temperature. Five runs were made in each determination and column two of Table I gives the results along with the average deviation. Original data may be found elsewhere (*3*).

The viscosities of the vapors of methyl, ethyl, and the propyl alcohols were determined by Titani (*3*) and fitted by the Sutherland expression. For comparison, column three of Table I gives values of the viscosity extrapolated to 298° K. from the data of Titani using the expression given by him. These data are considered applicable only above the boiling points and, for *n*-propyl alcohol, it can be seen that the value determined at 298° K. in this work is over 3% lower than the value extrapolated from the high temperature data (above 390° K.). For isopropyl alcohol, the present value is less than 2% lower than the extrapolated value which is within experimental uncertainty. Because of

Table I. Coefficients of Viscosity of Alcohols at 298° K. (Micropoise) and Collision Diameters (Angstroms)

Alcohol	This Work	Titani (*4*)	σ_2, Angstroms
methyl	...	95.49	(5.27)
ethyl	...	85.77	(6.09)
n-propyl	72.9 ± 1.0	75.31	7.06
isopropyl	75.7 ± 1.9	76.88	6.93
n-butyl	64.3 ± 1.6	...	7.92
isobutyl	67.4 ± 1.0	...	7.73
sec-butyl	68.7 ± 1.8	...	7.66
tert-butyl	73.7 ± 1.3	...	7.40

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the long range of temperature extrapolation, the experimental value is expected to be lower than the extrapolated one in view of the temperature dependence of the Sutherland "constant" over a wide range of temperatures (*1*).

The molecular diameters, σ, shown in the last column of Table I were calculated from the viscosity data using the smooth hard elastic sphere model (*1*). For methanol and ethanol, the coefficients of viscosity from Titani were used and the others from the values determined in this work. The expected trends of increasing diameter with increasing chain length, and the systematic reduction due to chain branching are seen to be in evidence.

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Distribution Coefficients for Certain Actinide and Fission Product Chlorides in the Immiscible Salt System: LiCl–KAlCl$_4$

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Two nearly immiscible molten salt phases, KAlCl$_4$ and LiCl, are obtained in the ternary system: LiCl–KCl–AlCl$_3$. Metal chlorides and oxychlorides dissolve in and distribute between these two solvent phases in practical amounts. The distribution data show that potentially useful separations can be achieved by partitioning solutes between these phases. The distribution coefficients range from 18.1 for Cs$^+$ to 0.014 for Sr^{+2}.

THE TERNARY SALT SYSTEM, LiCl–KCl–AlCl$_3$, exists as two immiscible phases over an appreciable composition and temperature range (*2*). Compositions which yield two liquid phases can be obtained from 350° to 775° C. Below 350°, solid separation commences in one or both phases. Above 775°, the consolute temperature, only a single liquid phase exists.

The principal constituent of the phase of lower density is the complex, KAlCl$_4$. The phase of higher density is mainly LiCl. The phases have a small mutual solubility.

Metal chlorides and oxychlorides dissolve and distribute in the partly immiscible phases. Large quantities of solute coalesce the phases, but this does not occur until as much as 25 to 30 weight per cent of solute has been added.

The immiscible phases are highly mobile liquids, about as fluid as water. They disperse and disengage with ease. Molten salts are resistant to radiation damage, and this system may find application in separations processing of intensely radioactive materials. With this in mind, attention was focused on determination of the distribution coefficients of a number of fission product and actinide element chlorides and oxychlorides. From these data the separations capability of a practical process can be deduced.

The immiscible phases constitute pairs of conjugate ternary solutions with variable composition. Figure 1 is an isothermal section through the isobaric prism. Compositions indicated by asterisks on each tie line yield immiscible phases of composition indicated by open circles at the points of intersection of the tie lines and the binodal curve. The compositions indicated by solid circles and connected by a heavy dashed line are typical of the compositions used in this work. These compositions provided an excess of chloride ion over that needed to complex AlCl$_3$. This leads to a solvent less susceptible to hydrolysis by atmospheric moisture and reduces competition between AlCl$_3$ and added solute for available chloride ion. Such competition could have a marked effect on the composition of the distributing solute.

EXPERIMENTAL

A weighed quantity of anhydrous solute was added to a known quantity of premelted immiscible phases. The solvent phases contained in an open 200 mm. × 25 mm. Vycor test tube were heated by a Lindbergh Model Cr-15 Pot Furnace. Addition of the solute would normally disturb the temperature equilibrium; while temperature equilibrium was being reestablished, the system was stirred to disperse the phases and assist dissolution of the solute. Stirring was done manually with a quartz thermocouple protection tube enclosing a chromel-alumel thermocouple connected through a bucking variable potentiometer to a 0–2 mv. scale recorder. With this arrangement temperatures could be measured to ±0.5° at 625° C.

When temperature equilibrium was reestablished, stirring was stopped to permit the phases to disengage. Approximately 2.0 ml. was then withdrawn from each 25 ml. phase with pipettes preheated to the equilibration temperature. The molten samples were quenched by pouring them onto a stainless steel plate, after which they were weighed, dissolved in 3*M* HCl, and analyzed for the distributing cation and solvent metal ions. The large conversion factors needed to convert these data to weight per cent metal chloride multiplies small analytical errors. The