

intermolecular attractive forces exceed the thermal and surface forces, which tend to prevent clustering, irreversible formation of a new phase occurs. If this approach is valid, it would permit an estimation of the  $T_N$  without performing the usual droplet experiment of Turnbull and Cormia (15). The temperature corresponding to an infinite viscosity,  $T_N$ , is obtained from an analysis of the liquid surface tension data. The surface tension data for the liquids in Table I were plotted as a function of temperature and extrapolated to lower temperatures by assuming  $(\partial\gamma/\partial T)$  to be constant. In general, the plots of  $\gamma$  vs.  $T$  were sufficiently linear to warrant such an approximation. The temperature at which  $\gamma = \gamma_N$ , is defined as  $T_N$ . The values of  $T_N$  for a variety of liquids are listed in Table I.

Several interesting correlations are immediately apparent from the foregoing analysis. Apparently,  $T_N$  represents a temperature below which there is no liquid phase but only a crystalline or glassy state.

The intercept for argon suggests that a considerably greater lowering of the temperature of the liquid could be effected before homogeneous nucleation occurs, but, apparently heterogeneous nucleation cannot be avoided (2, 9). It is possible that heterogeneous nucleation has not been avoided in the case of KBr where  $T_N < T^*$ . Equation 1, as well as Equation 2, indicates a functional relationship of  $\eta_l - \eta_v$  which is different from that in the usually accepted Williams, Landel, Ferry (16) equation.

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#### NOMENCLATURE

- A =  $\gamma_N$   
 B = constant, gram/cm.-sec. (poise)

- $T$  = temperature, °K.  
 $T^*$  = temperature of homogeneous nucleation, °K.  
 $T_c$  = critical temperature, °K.  
 $T_M$  = melting temperature, °K.  
 $T_N$  = temperature where  $\eta_l = \infty$ , °K.  
 $\gamma$  = surface tension, dynes/cm.  
 $\gamma_N$  = surface tension at  $T_N$ , dynes/cm.  
 $\eta_l$  = absolute liquid viscosity, gram/cm.-sec. (poise)  
 $\eta_v$  = absolute vapor viscosity, gram/cm.-sec. (poise)  
 $\eta_c$  = absolute critical viscosity, gram/cm.-sec. (poise)

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## Densities of Potassium Hydroxide Solutions

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Densities of aqueous solutions of potassium hydroxide are reported for the temperature range 60° to 161° C. and the concentration range 0 to 77.1% by weight.

**A** KNOWLEDGE of the properties of aqueous potassium hydroxide solutions at relatively high temperatures and concentrations is of value in the design and operation of fuel cells and batteries. Density data for potassium hydroxide solutions for the temperature range 0° to 70° C. and a concentration range of 0 to 50 wt.% have been reported by Akerlof and Bender (1), and Kelly, Borza, and Harriger (3) have reported densities at lower temperatures (-54° to 0° C.) for the same concentration range.

#### EXPERIMENTAL

Solutions were prepared from reagent grade KOH containing less than 1% carbonate. Solutions were analyzed for both total alkalinity and carbonate content to check

against buildup of potassium carbonate. Concentrations in Table I are total alkalinity reported as weight per cent KOH. Aqueous solutions of concentrations below the saturation value at room temperature were stored in polyethylene bottles. More concentrated solutions were stored in Teflon bottles and kept in an oven at temperatures varying from 80° to 140° C., the temperature used depending on the concentration.

The method used to determine densities was the hydrostatic weighing method of Kohlrausch, and the usual precautions were taken (2). A silver plummet was used, and was electroplated with pure silver to reduce corrosion. The plummet was calibrated at temperatures up to 100° C. using water and following the procedure described by Bauer and Lewin (2); plummet volumes at higher temperatures were

Table I: Densities of KOH Solutions

Temperature, °C.	Concn., Wt.% KOH	Number of Measurements	Density, G./Cc.
59.9	6.17	16	1.0381 ± 0.0001
	11.50	15	1.0863 ± 0.0002
	20.90	9	1.1758 ± 0.0002
	27.80	10	1.2448 ± 0.0001
	36.00	11	1.3294 ± 0.0002
	43.00	10	1.4080 ± 0.0001
	47.20	10	1.4560 ± 0.0001
	50.37	10	1.4957 ± 0.0001
79.9	6.17	9	1.0269 ± 0.0001
	11.50	10	1.0746 ± 0.0001
	20.90	9	1.1652 ± 0.0001
	27.80	10	1.2329 ± 0.0001
	36.00	10	1.3180 ± 0.0001
	43.00	10	1.3973 ± 0.0001
	47.20	9	1.4442 ± 0.0008
	50.37	10	1.4848 ± 0.0001
99.2	36.0	14	1.3073 ± 0.0001
	43.0	14	1.3858 ± 0.0001
	43.97	9	1.3969 ± 0.0001
	55.4	15	1.5324 ± 0.0001
120.5	59.46	15	1.5809 ± 0.0001
	55.4	20	1.5205 ± 0.0001
	59.46	18	1.5683 ± 0.0001
141	65.1	13	1.6342 ± 0.0001
	53.9	11	1.4901 ± 0.0001
	55.72	16	1.5160 ± 0.0001
	59.71	10	1.5622 ± 0.0001
161.4	65.1	10	1.6268 ± 0.0001
	64.68	16	1.6086 ± 0.0001
	72.25	16	1.7046 ± 0.0001
	77.1	16	1.7652 ± 0.0001

calculated by extrapolating values determined at lower temperatures using a power series in temperature for the volumetric expansion coefficient. Calibration of the plummet was repeated at frequent intervals during the measurements, and a small decrease in volume with time was observed at the higher temperatures. Solutions to be studied were maintained at the required temperature in an oil bath controlled to 0.02°C.

To prevent a rapid change in concentration by evaporation, an atmosphere of nitrogen presaturated with water vapor at a partial pressure equal to the equilibrium vapor pressure of the KOH solution was maintained over the surface of the sample studied. This was achieved by first passing the nitrogen stream through a series of presaturators containing pure water, and maintained at a temperature such that the vapor pressure of water was nearly equal to the known vapor pressure of the KOH solution (4) at the temperature under study. Final equilibration of the nitrogen stream was attained by passing it through a presaturator containing the KOH solution under study at the temperature of the density measurement. As a check against possible changes in concentration, a number of density measurements were made on the same sample and examined for any drift in density with time. At the higher temperatures, concentrations were determined by titration before and after an experiment.

## RESULTS

The measured densities are shown in Table I. The uncertainties listed are the standard deviations from the arithmetic mean. The analysis accuracy was estimated to be 0.2% of the concentration value.

The data at 59.9° and 79.9°C. may be compared with hydrometer readings (4); agreement between the two sets of data is within 0.07% for almost all points.

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# Vapor-Liquid Equilibria at 60°C. for *n*-Hexane-Alkyl Amines and 1-Hexene-Alkyl Amines

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**E**FFECTIVE separation of close boiling hydrocarbon mixtures often necessitates an uneconomical number of trays in a fractionator. An extractive distillation process may reduce the cost of the separation by changing the volatility characteristics of the mixture through the addition of a polar compound (solvent) to the hydrocarbon mixture. The solvent, if effective, will selectively interact with one or more of the hydrocarbon components. The solution complexities resulting from the interactions are difficult to define theoretically and quantitatively. This investigation is a por-

tion of an experimental program at The University of Texas to determine the influence of various types of polar compounds in modifying the solution nonideality.

Binary vapor-liquid equilibrium data were determined at 60°C. for *n*-butylamine, diethylamine, *n*-hexylamine, di-*n*-propylamine, diisopropylamine, and triethylamine with each of the hydrocarbons, *n*-hexane and 1-hexene.

## EXPERIMENTAL

**Materials.** All materials used for the experimental work were checked for purity by a Beckman GC-2 gas chroma-

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