Anomalies in the Density Curves of Alkyldiamine-Water Systems[1]

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Introduction

The only previous works reported on alkyldiamine-water systems were those done by Elgort (1) in 1929, and Ust-Kachkintzev (6) in 1934, on the system ethylenediamine-water. Elgort's melting point curve indicated the existence of a monohydrate expressed as a distorted maximum, and a dihydrate as a concealed maximum. An opposite relationship occurred in the viscosity curve, where the dihydrate is a distinct maximum, and faint maximums occur corresponding to a monohydrate and semihydrate. The density isotherms occurred as convex curves with slight inflections at those positions corresponding to the three hydrates. Incomplete data in the 70-100 mole percent water region indicated a broad maximum and a possible minimum.

The purpose of this work was to determine density isotherms of several alkyldiamine-water systems in those regions where hydrate formation occurs, and to investigate further the apparent maximum found in the region of higher water concentration. From this data apparent molal volumes were calculated, considering both water and the alkyldiamine as solvents, and temperature effects on these relationships tested.

Experimental

The alkyldiamines used were Matheson, Coleman, and Bell and contained up to 3% water as the main impurity. They were dried by refluxing over calcium hydride for four hours, followed by distilling twice over fresh calcium hydride using an atmosphere of dry nitrogen. Due to the extreme hygroscopic nature of the alkyldiamines, stock solutions were prepared containing 5-10 weight percent water by direct distillation into a tared flask containing a known weight of distilled water.

Densities were obtained by means of an accurate Westphal-type balance. The balance was constructed from a Sargent model LCB chainomatic balance by replacing the left pan with a glass displacement bob suspended by a fine platinum wire through a hole drilled in the balance table. The balance was mounted over a water bath thermostatically controlled to $\pm0.005°C$ by a mercury thermoregulator. The stock alkyldiamine-water solution was placed in a sample flask, and the weight of the displacement bob recorded after thermal equilibrium had been reached. Water was then added by means of a weight burette in quantities such that the density could be taken in intervals of 1-2 weight percent water. Stock solutions were used immediately after preparation, and fresh glass-distilled water was used, thus eliminating

gas bubble formation. Duplicate runs were made in all cases, and values agreed within ±0.00005 gm ml⁻¹.

All weights taken with the chainomatic balance were corrected for air bouyancy and the surface tension effect on the platinum wire was found to be negligible.
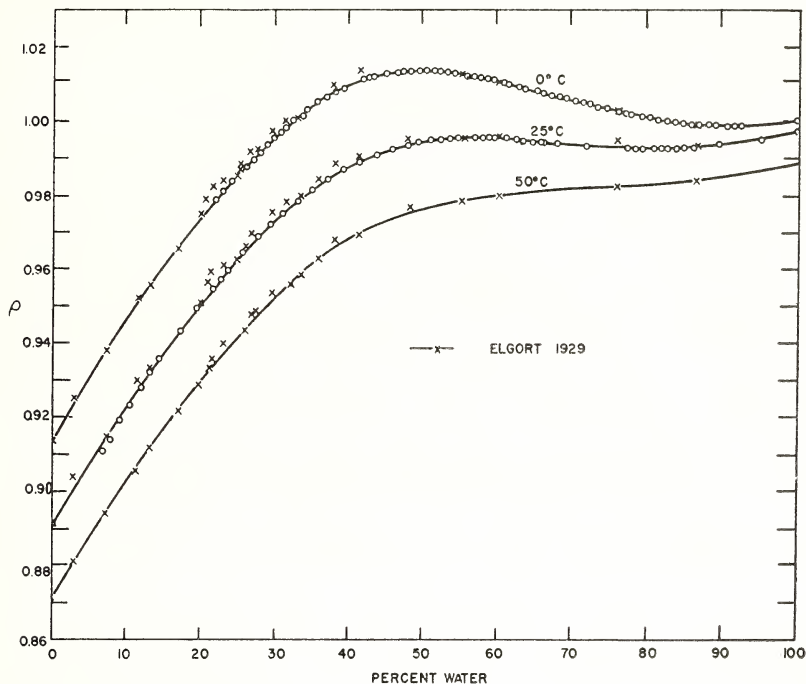

Figure 1. Plot of density in gm ml⁻¹ vs. weight percent water for ethylenedi-amine-water mixtures.

Results and Discussion

Density isotherms for ethylenediamine-water mixtures at 0[2], 25, and 50°C are shown in Figure 1. The maximums reported by Elgort corresponding to the proposed hydrate formations were not found in our data, and replicate runs failed to indicate their existence. A pronounced maximum does occur which shifts to higher water percentage regions as temperature increases, and becomes more pronounced as temperature is decreased. A distinct minimum is present in the 25°C isotherm, but is not evident in the 0° or 50° isotherms.

To determine if the effect was due to hydrogen-bonding between water and the nitrogens in the alkyldiamine, a series of densities were taken for ethylenediamine-methyl alcohol mixtures at 25°C. The result was a smooth convex curve displaying no pecularities for the entire

2. Data at 0°C was partially taken by Charles Bronick of this laboratory.

range. To determine the effect of the structure of the alkyldiamine, densities were taken for methylethylenediamine and trimethylenediamine-water mixtures at 0° and 25°. These results are shown graphically in Figure 2. In both cases the results are similar to those for the ethylenediamine-water isotherms, with the maximum being reduced in amplitude and shifted to the higher water percent region.
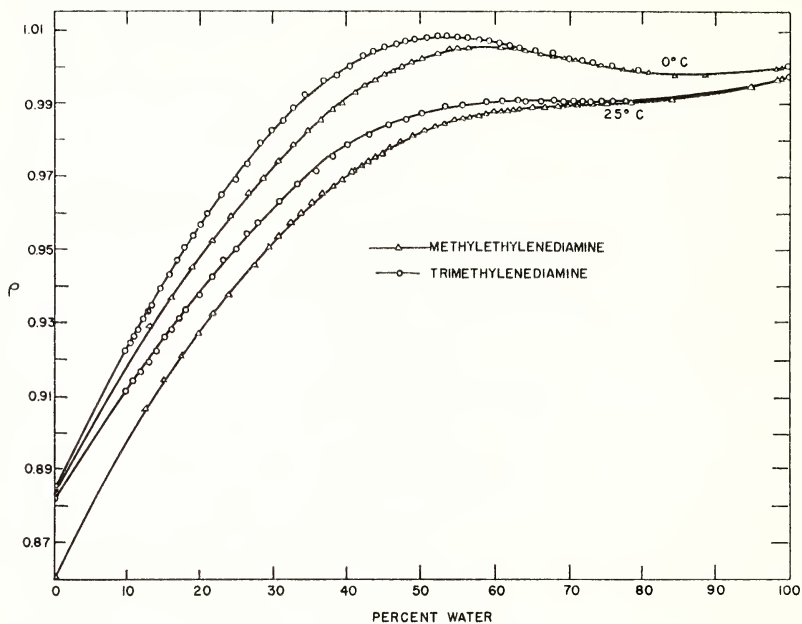

Figure 2.   Density vs. weight percent water for methylethylenediamine and trimethylenediamine water mixtures at 0° and 25°.

In order to understand more fully the significance of the density isotherms, the apparent molal volumes were calculated, both for water and the alkyldiamines as solvents. The apparent molal volume, Φ_{v_2}, can be calculated from the relationship,

$$\Phi_{v_2} = \frac{1000\ (d_o - d)}{m d_o d} + \frac{M_2}{d} ,$$

where d_o is the density of the pure solvent, M_2 is the molecular weight of the solute, and d is the density of the solution at a concentration m, in molality. The major source of error in apparent molal volumes arises from the $(d_o - d)$ term in the equation. Slight errors in either d_o or d at low concentration will cause a large deviation in Φ_{v_2}. The densities used in our calculation for the pure alkyldiamines are given in Table I. Those values found in our laboratory were obtained using 50 ml. pycnometers, using methods which have been described previously (5).

When water was considered the solvent and the apparent molal volume of the alkyldiamines calculated, the resulting plots were similar to those shown for ethylenediamine in Figure 3. No simple function
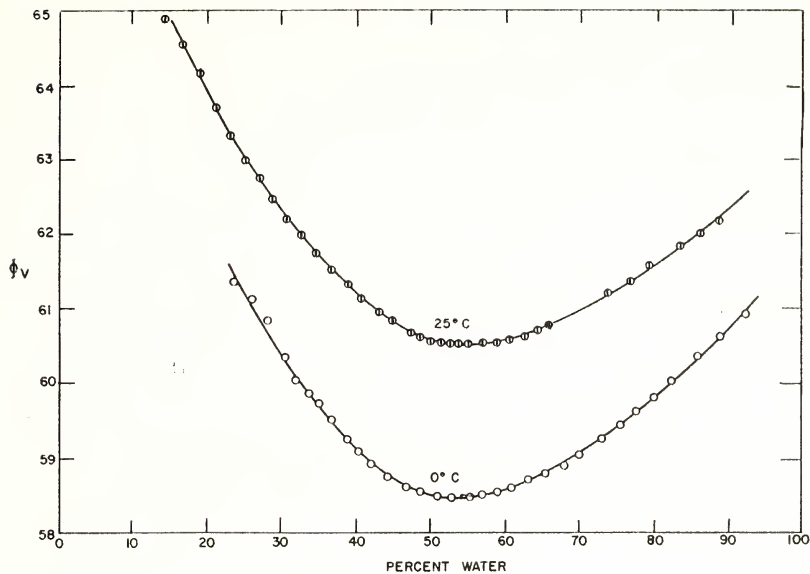
Figure 3. Apparent molal volume of ethylenediamine vs. weight percent water.

could be found to describe the curves, although all displayed the striking minimum which, within experimental error, corresponded to the maximum in the density isotherm for the corresponding system.

Earlier work in this laboratory (2,4) has shown that Masson's Rule (3) for apparent molal volumes holds for the ethylenediamine solvent system in the case of strong electrolytes. The rule can be expressed as,
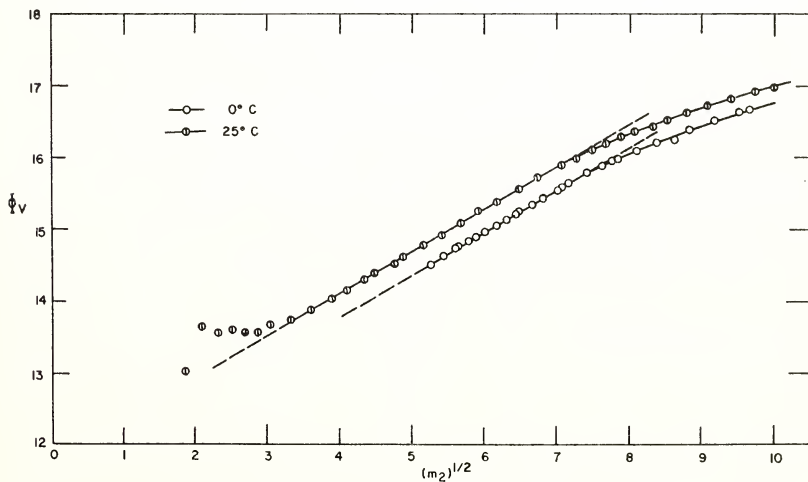
$$\Phi_{V_2} = \Phi_{V_2}o + K(m)^{1/2}$$

Figure 4. Apparent molal volume of water in ethylenediamine as a function of $(m)^{1/2}$.

where $\Phi_{v_2}o$ is the partial molal volume at infinite dilution and K is the Masson constant.

Masson's work also indicated that deviations from this relationship occur at concentrations corresponding to a hydrate formation in many cases. Calculations of apparent molal volumes for water using the alkyldiamines as solvents give results which appear to obey Masson's rule. This is shown in Figure 4 for ethylenediamine.

In all cases the curves deviated from linearity at a concentration which corresponded to the maximum in the density isotherm.

A summary of the results for the three alkyldiamines studied is given in Table 2.

From our results it appears that an ordered structure corresponding to a weak hydrate solvent shell may be occurring in solutions of alkyldiamines. This would account for the maximums in the density isotherms and their dependence on temperature. Further studies with NMR should indicate if a semi-stable hydrate is present and give an insight into its nature.

TABLE I
Densities of Pure Alkyldiamines

Alkyldiamine	Temperature	Density	Reference
ethylenediamine	0°C	0.91411	Timmermans (5)
	25°C	0.8922	this laboratory
	50°C	0.8793	Elgort (1)
methylethylenediamine	0°C	0.8845	by extrapolation
	25°C	0.8826	this laboratory
trimethylenediamine	0°C	0.8851	by extrapolation
	25°C	0.8597	this laboratory

TABLE II
Constants Derived from Density Data

Alkyldiamine	Temp.	ρ max.	Mole % Water at Maximum ρ	K	$\Phi_{v_2}o$
ethylenediamine	0°	1.01341	77.15	1.715	11.46
	25°	0.99533	80.52	1.717	11.78
	50°	(0.978)[1]	(83.7)	(1.73)	(12.0)
methylethylenediamine	0°	1.00763	82.66	1.32	10.3
	25°	(0.990)	89.73[2]	1.97	12.8
trimethylenediamine	0°	1.00632	85.13	1.68	10.8
	25°	(0.985)	92.31[2]	1.69	10.95

1. Values in parenthesis are uncertain.
2. Mole percent water corresponding to minimum in Φ_{v_2} curve for the alkyldiamine in water.

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