Marian Woldan, Stefania Taniewska-Osińska

DENSIMETRIC INVESTIGATIONS OF WATER-ACETAMIDE SYSTEM WITHIN THE TEMPERATURE RANGE 25-85°C

The density of aqueous acetamide solutions was measured over the temperature range 25-85°C. From the obtained density data apparent molal volume of acetamide in water and volume expansibility coefficient were calculated. The analysis of changes of these functions in relation to acetamide concentration and temperature allowed to conclude on breaking effect of acetamide on water structure.

The thermodynamic investigations of electrolyte solutions in molten acetamide showed certain similarity of the molten acetamide to water used as electrolyte solvents. It seems possible that this similarity is due to the existence of the partially disturbed three-dimensional network of H-bonds in both solvents [1].

The present paper deals with the densimetric investigations of acetamide aqueous solutions which we intend to use as electrolyte solvents. We have measured the density of water-acetamide system in the temperature range 25-85°C. Density values of the solutions enable the calculation of apparent molal volume of the solute and the volume expansibility coefficient of the investigated solutions. The concentration and temperature effect on the calculated quantities makes it possible to draw certain conclusions on the effect of the dissolved substance on the solvent.
Experimental

Reagents

The solutions used for investigations were prepared by mixing the weighted amounts of twice distilled water with acetamide. Analytical grade acetamide "Xenon-Lódź" product previously crystallized from methanol and dried for about 50 hours at the temperature 60°C was used for the investigations. The melting temperature of acetamide was 81-82°C which is in accordance with literature data [2-5].

Apparatus

The density measurements of the investigated solutions were performed with the use magnetic densimeter constructed in our laboratory, basing on the description included in the works of Millero and Franks [6-8]. The densimeter applied by us consisted of a glass vessel (Pyrex) of 100 ml capacity, glass float with a magnetic core attached to it by means of polyethylene and a support made of brass, containing two solenoids in its lower part. The subsidiary upper solenoid served to move the float into the magnetic field of the lower measuring solenoid. The densimeter was used in a wide temperature range therefore the solenoids were insulated by polystyrene and epoxy resin. The weight of the float was 21.3933 g and its volume at the temp. 25°C was 22.6995 ml. The densimeter was placed in a thermostate bath keeping the desired temperature with accuracy to ±0.02°C.

The Density Measurements

The densimeter filled with solution was thermostated for about 60 min. By means of subsidiary solenoid the float is moved to the bottom of the glass vessel of densimeter and the current in the measuring solenoid is switched on. The intensity
of the current slowly decreases up to the moment when the float is detached from the bottom of the vessel. The measurement was being repeated till the current intensity at the moment of detachment of the float became reproducible. The densimeter was calibrated using twice distilled water as the standard liquid. The current intensity was determined by measuring the voltage drop on the standard resistance (1Ω) by means of digital voltmeter of the V 534 type by Mera-Tronic.

The density of the solution was calculated from the formula:

\[ d = \frac{W + w + f_i}{V + w/d_{pt}} \]  

where:

- \( W \) - the weight of float
- \( w \) - the weight of platinum rings loading the float
- \( f \) - solenoid constant
- \( i \) - current intensity in the measuring solenoid at the moment of departure of the float from the bottom,
- \( V \) - volume of the float
- \( d_{pt} \) - platinum density

The solenoid constant and the float volume are determined by measuring the standard liquid density. The measurements carried out for aqueous NaCl and NaI solutions were in agreement with literature data with accuracy to \( \pm 1 \times 10^{-5} \text{g/cm}^3 \) (NaCl [9], NaI [10]).

**Results**

The results of density measurements of acetamide solutions in water at the temperatures 25°C, 40°C, 60°C, 75°C and 85°C are given in Table 1.

The density of the investigated solutions was used to calculate the apparent molal volume \( 
\Phi_v \) of acetamide in water using the well-known formula:
<table>
<thead>
<tr>
<th>wt %</th>
<th>$X_{\text{AcNH}_2}$</th>
<th>25°C</th>
<th>40°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$d$</td>
<td>$\phi_v$</td>
<td>$d$</td>
</tr>
<tr>
<td></td>
<td>g/cm³</td>
<td>cm³/mole</td>
<td>g/cm³</td>
</tr>
<tr>
<td>1</td>
<td>0.0031</td>
<td>0.99769</td>
<td>55.56</td>
</tr>
<tr>
<td>2</td>
<td>0.0062</td>
<td>0.99831</td>
<td>55.56</td>
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<td>3</td>
<td>0.0158</td>
<td>1.00022</td>
<td>55.51</td>
</tr>
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</tr>
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<td>1.00335</td>
<td>55.42</td>
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<td>0.0510</td>
<td>1.00695</td>
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</tr>
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<td>7</td>
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<td>1.01029</td>
<td>55.37</td>
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<td>8</td>
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<td>1.01374</td>
<td>55.35</td>
</tr>
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<td>0.1155</td>
<td>1.01715</td>
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<td>1.02378</td>
<td>55.38</td>
</tr>
<tr>
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<td>0.2336</td>
<td>1.03024</td>
<td>55.43</td>
</tr>
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<td>12</td>
<td>0.3137</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>0.4155</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td>0.6333</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>0.8527</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>16</td>
<td>1.00</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 1

Densimetric investigations of water-acetamide in the temperature range 25–85°C (g/cm³)
\[
\Phi_{V_{AcNH_2}} = \frac{1000(d_o - d)}{md_o} \frac{M_{AcNH_2}}{d} 
\]

where:

- \(M_{AcNH_2}\) - the molecular weight of \(AcNH_2\)
- \(m\) - the concentration of \(AcNH_2\) in water in moles per 1000 g of water
- \(d_o\) - the density of water
- \(d\) - the density of the solution

The obtained values \(\Phi_{V_{AcNH_2}}\) are shown in Table 1.

The concentration dependence of \(\Phi_{V}\) can be described by the polynomial [11]:

\[
\Phi_{V} = \Phi_{V}^o + A_v m + B_v \cdot m^2 + \ldots 
\]

where:

- \(\Phi_{V}^o\) - apparent molal volume of nonelectrolyte in the infinitely diluted solution.

In the case of the average concentrated solutions the equation (3) can be applied [12]:

\[
\Phi_{V} = \Phi_{V}^o + A_v \cdot m 
\]

The value of \(A_v\) slope is interesting because according to Mac Millan-Mayer's solution theory it refers to the interactions among nonelectrolyte molecules [13-16].

The values \(\Phi_{V}^o\) obtained by extrapolation of the equation (4) up to \(m = 0\) are given in Table 2. For comparison the values of \(\Phi_{V}^o\) and \(A_v\) for other nonelectrolytes have been also placed in this Table [17-22].

The volume expansibility coefficient of the examined acetamide solutions in water was calculated from the formula:

\[
\alpha = - \frac{1}{d} \cdot \left(\frac{\partial d}{\partial T}\right)_{P,x} 
\]

The derivative \(\partial d/\partial T\) was calculated analytically knowing the values of the coefficients of the equation \(d = a + bt + \ldots\)
+ct² representing the dependence of density on temperature. The obtained values of volume expansibility coefficients of acetamide solutions in water are given in Table 3.

Table 2
Partial molal volumes $\Phi^o_V$ of nonelectrolytes in water

<table>
<thead>
<tr>
<th></th>
<th>$\Phi^o_V$ cm³ • mole⁻¹</th>
<th>Av cm³ • kg • mole⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>38.6</td>
<td>0.06 [17, 18]</td>
</tr>
<tr>
<td>NMF</td>
<td>56.87 (25°)</td>
<td>-0.15</td>
</tr>
<tr>
<td></td>
<td>57.45 (35°)</td>
<td>-0.15</td>
</tr>
<tr>
<td></td>
<td>57.95 (45°)</td>
<td>-0.11 [12]</td>
</tr>
<tr>
<td>AcNH₂</td>
<td>55.61 (25°)</td>
<td>-0.123 [11]</td>
</tr>
<tr>
<td></td>
<td>55.6 (25°)</td>
<td>-0.11</td>
</tr>
<tr>
<td></td>
<td>56.2 (40°)</td>
<td>-0.05</td>
</tr>
<tr>
<td></td>
<td>57.2 (60°)</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>58.0 (75°)</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>58.5 (85°)</td>
<td>0.01</td>
</tr>
<tr>
<td>CH₃COCH₃</td>
<td>66.92 (25°)</td>
<td>-0.370 [11]</td>
</tr>
<tr>
<td></td>
<td>67.0 [17]</td>
<td></td>
</tr>
<tr>
<td>DMSO</td>
<td>68.92 (25°)</td>
<td>-0.262 [11]</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>38.3 [19, 20]</td>
<td>-0.2</td>
</tr>
<tr>
<td>CO(NH₂)₂</td>
<td>44.24 (25°)</td>
<td>0.116 [17, 21, 22]</td>
</tr>
<tr>
<td></td>
<td>44.8 (60°)</td>
<td>-0.07</td>
</tr>
<tr>
<td></td>
<td>43.8</td>
<td></td>
</tr>
</tbody>
</table>
Table 3

Volume expansibility coefficient of aqueous acetamide solutions
\(10^6 \alpha [\text{deg}^{-1}]\)

<table>
<thead>
<tr>
<th>wt % AcNH₂</th>
<th>X AcNH₂</th>
<th>25°C</th>
<th>40°C</th>
<th>60°C</th>
<th>75°C</th>
<th>85°C</th>
</tr>
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<tr>
<td>1</td>
<td>0.0031</td>
<td>289</td>
<td>390</td>
<td>519</td>
<td>621</td>
<td>691</td>
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<tr>
<td>2</td>
<td>0.0062</td>
<td>293</td>
<td>391</td>
<td>522</td>
<td>622</td>
<td>694</td>
</tr>
<tr>
<td>5</td>
<td>0.0158</td>
<td>308</td>
<td>403</td>
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<td>634</td>
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</tr>
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<td>0.0258</td>
<td>328</td>
<td>421</td>
<td>547</td>
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<td>711</td>
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<tr>
<td>10</td>
<td>0.0328</td>
<td>342</td>
<td>432</td>
<td>556</td>
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<td>715</td>
</tr>
<tr>
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<td>459</td>
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<td>602</td>
<td>687</td>
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<td>25</td>
<td>0.0922</td>
<td>450</td>
<td>524</td>
<td>626</td>
<td>703</td>
<td>756</td>
</tr>
<tr>
<td>30</td>
<td>0.1155</td>
<td>491</td>
<td>555</td>
<td>646</td>
<td>714</td>
<td>762</td>
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<td>554</td>
<td>613</td>
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<td>757</td>
<td>801</td>
</tr>
<tr>
<td>50</td>
<td>0.2336</td>
<td>635</td>
<td>680</td>
<td>740</td>
<td>788</td>
<td>821</td>
</tr>
<tr>
<td>60</td>
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<td>-</td>
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<td>769</td>
<td>825</td>
<td>864</td>
</tr>
<tr>
<td>70</td>
<td>0.4155</td>
<td>-</td>
<td>700</td>
<td>783</td>
<td>850</td>
<td>895</td>
</tr>
</tbody>
</table>

Discussion

Fig. 1 illustrates the dependence of density of aqueous acetamide solutions on concentration and temperature. As it is seen on the plot the density of aqueous acetamide solutions increases with the growth of acetamide (AcNH₂) concentration in the solution and it decreases with the temperature growth. The range of rectilinear relation \(d = f(\text{wt} \%)\) decreases with the temperature growth. At the temp. 85°C higher than acetamide melting temperature (81-82°C) the curve \(d = f(\text{wt} \%)\) has a maximum for the solutions containing 85 weight % of AcNH₂ i.e. about 63.33 mole % of AcNH₂. Thus it may be presumed that the solution containing two acetamide molecules falling on one water molecule has maximum packing of molecules.
The X-ray [23-25] and spectroscopic [26-27] investigations showed that in solid state acetamide three-dimensional network of NH...O hydrogen bonds occurs. In liquid acetamide a strong association was observed [28-30]. It is justifiable, because each acetamide molecule can form hydrogen bond both as donor and acceptor of proton. It follows from the spectroscopic investigations [26-27] that energy of hydrogen bonding in acetamide is close to the bonding energy in water. The length of bondings is also similar: 2.76 Å in water and 2.86 Å in acetamide. So it is probable that the bond between water and acetamide molecules differs only a little from the bondings in pure components.

Assuming that at the temp. 85°C, near the melting point of AcNH$_2$ (81-82°C) its three-dimensional structure will be only slightly disturbed it may be presumed that water molecules can built in acetamide structure interstitials.

If all the vacancy of acetamide structure were filled with
water molecules it follows from the crystallographic analysis [31] that one water molecule should fall on two acetamide molecules. It corresponds with the solution with the composition 66.6 mole % of AcNH$_2$, which is in agreement with the placement of maximum on the d = f(x) curve obtained in this work. Apparent molal volumes of some nonelectrolytes in water have been calculated, using the data on the density of the examined so-

Fig. 2. The apparent molar volume of nonelectrolytes as a function of the mole fraction of nonelectrolyte in water
solutions of acetamide in water and literature data concerning other nonelectrolytes. The obtained results are presented as the function \( \Phi_v = f(x) \) on Fig. 2.

As it is seen from Table 1 and from Fig. 2c the course of concentration relation changes with the growth of temperature. At the temp. 25°C this relation shows small minimum in the solution with concentration \( \sim 10 \text{ mole} \% \text{ AcNH}_2 \). The minimum decreases with the growth of temperature and starting from 60°C it does not exist any more.

In case of aqueous solutions of urea (U) [17, 21, 22, 32-34] and formamide (F) [17, 18] (Fig. 2a, 2b) \( \Phi_v \) increases with the growth of nonelectrolyte concentration minimum does not occur. In the remaining systems presented on Fig. 2 minimum appears on curve \( \Phi_v = f(x) \).

According to many authors [11, 35-36] minimum appearing on curve \( \Phi_v = f(x) \) is characteristic for hydrophobic substances. It seems that the depth of minimum may be treated as a measure of hydrophobic character of nonelectrolyte. It is seen from Fig. 2 that methanol (MeOH), dimethylsulphoxide (DMSO) and dimethylformamide (DMF) show almost analogous minima at about 15 mole \% of nonelectrolyte content in water. Thus it can be presumed that these substances display similar hydrophobic character and have similar influence on water structure.

According to Avédikian, Perron and Desnoyers [35] these substances probably order water structure within the concentration range 0-15 mole \% of nonelectrolyte while in more concentrated solutions they disorder it, because of the formation of mixed hetero-associates. The greatest minimum can be observed in case of aqueous t-BuOH solutions. Strong hydrophobic interactions between t-butanol and water is undoubtedly connected with greater number of methyl groups in a molecule of this alcohol in comparison to the above mentioned substances.

Applying the above criterion of hydrophobility it can be easily observed that acetone (AcT) displays hydrophobic character intermediate between t-BuOH and DMSO, DMF and MeOH. Stronger hydrophobic character of AcT in comparison to MeOH is probably caused by the presence of two methyl groups in AcT. The weaker hydrophobic character of DMSO and DMF in comparison to
AcT is probably caused by higher dipole moment of these substances (DMSO - 3.96, DMF - 3.86, AcT - 2.76) [11].

In case of NMF-H$_2$O system (NMF-N-methylformamide) [12] and AcNH$_2$-H$_2$O (25°, 40°C) a small minimum occurs, which may be the proof of a very weak hydrophobic substances of these compounds. With the temperature growth the hydrophobic character of AcNH$_2$ and NMF decreases. Above 60°C in case of AcNH$_2$ the hydrophilic character begins to dominate. Similarly, on the basis of course of $\Phi_v = f(x)$ curve of aqueous formamide solutions it can be observed that the hydrophilic character of this compounds prevails. The replacement of hydrogen in amine group by methyl group in amine group (F-NMF) increases, as it can be presumed the hydrophobic character of nonelectrolyte. The presence of methyl group at carboxyl carbone (F and AcNH$_2$) has a similar effect but it is slightly smaller ($\Phi_{v,NMF}$ grows more the solution concentration growth than $\Phi_{v,AcNH_2}$). The last of the discussed nonelectrolytes - urea(U) shows a strong hydrophilic character. Urea introduced to water causes water structure disordering [37].

Because of the hydrophobic character the discussed nonelectrolytes can be arranged in the following way:

$$U < F < AcNH_2 < NMF < MeOH < DMSO < DMF < AcT < t-BuOH$$

The examined AcNH$_2$ exhibits very small hydrophobic and hydrophilic interactions with water. Comparing the results of the analysis of $\Phi_v$ and thermodynamic values both of binary mixtures and electrolyte solutions in these mixtures we can observe some discrepancies. As for as DMF is concerned it follows from the thermodynamic analysis [18] that this substance disturbs water structure. A similar order of the hydrophobic character may be observed when the values $A_v$ given in Table 2 are discussed. The smallest absolute values $A_v$ were obtained for AcNH$_2$ and F which according to literature [19-22], points to the greater capability of hydrogen bond formation among AcNH$_2$ and F molecules in comparison to the remaining substances. Certain information about the effect of the dissolved substance on the solvent structure can be obtained from the analysis of the dependence of volume expansibility coefficient $\alpha$ on the
concentration of the solution and on the temperature. It follows from works of Krumgalz [38, 39] and Baron [40] that the increase of temperature or introduction of some electrolytes breaking the solvent structure cause the increase of the values of the above mentioned coefficient. Solvent structure ordering electrolytes, on the other hand, cause the lowering of the coefficient $\alpha$ value.

In order to get additional information about acetamide effect on water structure the values of aqueous acetamide solution coefficient $\alpha$ were calculated over the temperature range 25-85°C (formula 5). As it is seen from Fig. 3 the volume expansibility coefficient $\alpha$ of aqueous acetamide solutions grows with the increase of the concentration of the solution and its temperature.

![Graph](attachment:image.png)

**Fig. 3.** The volume expansibility coefficient as function of the concentration and temperature

It follows that the more concentrated solutions expands more than the diluted ones, which may point to the disordering effect of the introduced acetamide on water structure. At a higher temperature the values of the coefficient $\alpha$ are also greater, since the solution expands more easily because of more inten-
sive thermal motions of the molecules. At the same time the ef-
fect of the dissolved substance on the value of coefficient $\alpha$
decreases, as the $\alpha = f(x)$ curve slope indicates.

Quite obviously there exists a temperature at which the
coefficient $\alpha$ does not depend on the concentration of the
solution, whereas above this temperature the coefficient $\alpha$
will decrease with the growth of concentration of the solution.
This temperature may be called the inversion temperature. At this
temperature the effect of disordering the solvent structure com-

pensate with the effects of solvation, association etc. From the
course of the relation $\alpha = f(T)$ of aqueous acetamide solutions
it follows that the inversion temperature is in this case
$123^\circ C$, so it is above water boiling temperature. It also fol-

laws that over the temperature range $0-100^\circ C$ acetamide weakly
disorders water structure.

The above opinion is in agreement with the conclusions aris-
ing from the analysis of the course of relation of the excess
of the relative partial molal entropy of water in aqueous acet-

am ide solutions on concentration and temperature [41] and is
compliant with the conclusion from the dielectric permittivity
of AcNH$_2$-H$_2$O system [42-44]. Gonczarow et al. [42, 43] claim
that AcNH$_2$ molecule can without greater difficulty built in
water structure if this molecule occupies one interstitial hole
and three lattice nodes. The acetamide molecule forms hydrogen
bonds with water molecules slightly changing the length of hydro-
gen bonds and the angles between them. According to the above
mentioned authors [42, 43] these bondings are a bit weaker than
the hydrogen bondings in pure water. Unlike water molecules,
the polar groups of AcNH$_2$ molecules cannot form four hydrogen
bonds, so in the new structure of H$_2$O-AcNH$_2$ system there will
be much more broken hydrogen bonds than in pure water.

Then tetrahedric structure occurs constructed from water and
acetamide, which is gradually destructed at higher AcNH$_2$ con-
tent in the solution. The opinion about breaking water structure
by AcNH$_2$ molecules is also expressed by Christoffers and Kege-
les who examined the diffusion coefficient of acetamide in
water at the temp. $25^\circ C$ [45].
REFERENCES

[38] Krumgalz B.S., Mishchenko K.P.,


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DENSYMETRYCZNE BADANIA UKŁADU WODA-ACETAMID W ZAKRESIE TEMPERATURY 25-85°C

Zmierzono gęstość wodnych roztworów acetamidu w zakresie temp. 25-85°C. Na podstawie otrzymanych badanych gęstości obliczono wartość poznanej molowej objętości acetamidu w wodzie oraz współczynnik rozszerzalności objętościowej danych roztworów. Analiza zmian wymienionych wielkości w zależności od stężenia acetamidu i temperatury pozwoliła wypuścić wniosek o niszczącym wpływ acetamidu na strukturę wody.

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DENSYMETRISCHE ERFAHRUNGEN EINES WASSER-ACETAMID-SYSTEMS IN DEM TEMPERATURENINTERVERAL 25-85°C