# *Effects of Nonelectrolytes on the Temperature of the Maximum Density of Water. II. Organic Compounds with Polar Groups*

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Water normally shows its maximum density at 3.98°C under atmospheric pressure, although "the temperature of the maximum density" (abbreviated as T. M. D.) is altered by foreign substances dissolved in it. In the preceding paper[1], the T. M. D.'s of dilute aqueous solutions of various alcohols were determined and several monovalent alkyl alcohols were found to elevate the T. M. D. of water when present in a low concentration. The effects of these substances on the T. M. D. of water were ascribed to the mutual interaction between the solute and water, such as the hydration and the hydrogen bondings formed between dipolar molecules. In this paper, some polar substances other than alcohols, i. e., amines, nitriles, ketones and cyclic ethers, are mainly examined in order to elucidate their influence upon the T. M. D. of water and to compare the results with those concerning alcohols already reported on[1].

## Experimental

The experiments were carried out by means of dilatometry in a manner quite similar to that described in the previous report[1]. Fourteen species were used, all of which were thoroughly purified enough for the present purpose. Pure water was prepared by distillation and by the ion-exchange method.

The elevation of the T. M. D., $\Delta T$, is defined by the following equation, in which $T_m$ indicates the T. M. D. of a solution of mole fraction $x$ of a solute and $T_{m_0}$ is that of water, namely 3.98°C.

$$\Delta T = T_m - T_{m_0} \tag{1}$$

The observed values of $\Delta T$ at various concentrations are listed in Table I. The experimental errors are within ±0.02°C.

## Discussion

Generally surveying Table I, the $\Delta T$'s are all negative, in contrast with the case of the alcohols previously observed[1]. Particularly, urea, pyridine, acetonitrile, propionitrile and 1,4-dioxane are seen to exhibit superior abilities in lowering the T. M. D. of water.

**The Excessive Elevation of the T. M. D. of an Aqueous Solution Caused by Mutual Interaction.**—If there occur no change in volume and no interaction between a solute and water on mixing the two, the T. M. D. of water should be elevated as high as $\Delta T_n$ shown by the next equation[1]. As a matter of course, judging from the equation, $\Delta T_n$ should always be negative.

$$\Delta T_n = -\frac{x}{1-x} \cdot \frac{\alpha}{2\beta} \cdot \frac{V_{s_0}}{V_{w_m}} \tag{2}$$

Here, $V_{s_0}$ and $V_{w_m}$ are the molar volumes of the solute at 0°C and of water at $T_{m_0}$ respectively, and $\alpha$ and $\beta$ are the respective coefficients of thermal expansion. The molar volumes at $\theta$°C are, therefore, expressed as:

$$V_s = V_{s_0}(1+\alpha\theta) \tag{3}$$

$$V_w = V_{w_m}\{1+\beta(\theta - T_{m_0})^2\} \tag{4}$$

Therefore, the excessive elevation of the T. M. D. of an aqueous solution, $\Delta T'$, is defined as follows:

$$\Delta T' = \Delta T - \Delta T_n \tag{5}$$

The necessary data on $\alpha$ and $V_{s_0}$ for calculating the $\Delta T_n$ for each substance are collected in Table II. For water, the following values are adopted[1,2]: $\beta = 7.80 \times 10^{-6}$ deg$^{-2}$, and $V_{w_m} = 18.016$ cc. mol$^{-1}$. The values of $\Delta T'$ derived from Eq. 5 are also shown in Table I, together

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[1] G. Wada and S. Umeda, This Bulletin, 35, 646 (1962).

[2] G. Wada, This Bulletin, 34, 955 (1961).

TABLE I. $\Delta T$ AND $\Delta T'$ AT VARIOUS MOLE FRACTIONS $x$

| Substance | $x\times10^2$ | $\Delta T$ | $\Delta T'$ |
|---|---|---|---|
| Monomethylamine | | | |
| | 0.15 | −0.14 | 0.21 |
| | 0.44 | −0.28 | 0.78 |
| | 0.72 | −0.48 | 1.26 |
| | 0.99 | −0.92 | 1.46 |
| | 1.25 | −1.28 | 1.73 |
| | 1.51 | −1.64 | 2.03 |
| | 1.68 | −1.98 | 2.10 |
| | 2.01 | −2.41 | 2.49 |
| | 2.25 | −2.87 | 2.64 |
| Dimethylamine | | | |
| | 0.14 | −0.02 | 0.71 |
| | 0.36 | −0.08 | 1.71 |
| | 0.44 | −0.10 | 2.08 |
| | 0.91 | −0.50 | 3.98 |
| | 1.16 | −1.00 | 4.76 |
| | 1.40 | −1.42 | 5.51 |
| | 1.63 | −1.94 | 6.15 |
| | 1.85 | −2.50 | 6.30 |
| | 2.09 | −3.08 | 7.34 |
| *n*-Butylamine | | | |
| | 0.08 | −0.25 | 0.11 |
| | 0.22 | −0.65 | 0.32 |
| | 0.36 | −1.08 | 0.52 |
| | 0.51 | −1.68 | 0.59 |
| | 0.64 | −2.15 | 0.62 |
| Acetamide | | | |
| | 0.08 | −0.25 | −0.12 |
| | 0.26 | −0.70 | −0.25 |
| | 0.44 | −1.16 | −0.40 |
| | 0.61 | −1.65 | −0.59 |
| | 0.81 | −2.17 | −0.70 |
| Urea | | | |
| | 0.09 | −0.42 | — |
| | 0.21 | −0.94 | — |
| | 0.43 | −1.92 | — |
| | 0.57 | −2.45 | — |
| | 0.68 | −2.89 | — |
| | 0.86 | −3.77 | — |
| Pyridine | | | |
| | 0.08 | −0.33 | −0.10 |
| | 0.20 | −0.90 | −0.34 |
| | 0.36 | −1.54 | −0.52 |
| | 0.52 | −2.26 | −0.79 |
| | 0.67 | −3.03 | −1.14 |
| Acetonitrile | | | |
| | 0.15 | −0.56 | −0.21 |
| | 0.38 | −1.42 | −0.51 |
| | 0.68 | −2.52 | −0.87 |
| | 0.81 | −3.11 | −1.13 |
| | 1.03 | −4.03 | −1.52 |
| | 1.19 | −4.77 | −1.87 |
| Propionitrile | | | |
| | 0.10 | −0.42 | −0.12 |
| | 0.28 | −0.22 | −0.38 |
| | 0.42 | −1.83 | −0.52 |
| | 0.65 | −2.97 | −0.98 |
| | 0.82 | −3.86 | −1.38 |
| Formaldehyde | | | |
| | 0.38 | −0.69 | — |
| | 0.76 | −1.49 | — |
| | 1.07 | −2.30 | — |
| | 1.41 | −3.07 | — |
| | 1.74 | −3.97 | — |
| | 2.06 | −4.77 | — |
| Acetone | | | |
| | 0.17 | −0.32 | 0.27 |
| | 0.41 | −0.96 | 0.46 |
| | 0.63 | −1.58 | 0.61 |
| | 0.88 | −2.51 | 0.59 |
| | 1.14 | −3.49 | 0.52 |
| | 1.41 | −4.42 | 0.55 |
| Tetrahydrofuran | | | |
| | 0.19 | −0.48 | 0.22 |
| | 0.36 | −0.88 | 0.46 |
| | 0.57 | −1.47 | 0.65 |
| | 0.76 | −2.06 | 0.78 |
| | 1.00 | −2.85 | 0.90 |
| | 1.21 | −3.72 | 0.83 |
| 1,4-Dioxane | | | |
| | 0.17 | −0.76 | −0.10 |
| | 0.35 | −1.43 | −0.07 |
| | 0.52 | −2.18 | −0.16 |
| | 0.70 | −3.06 | −0.35 |
| | 0.93 | −4.39 | −0.75 |
| Benzene | | | |
| | 0.007 | −0.04 | 0.00 |
| | 0.026 | −0.09 | 0.01 |
| | 0.038 | −0.12 | 0.01 |
| Tetraethylammonium bromide | | | |
| | 0.03 | −0.19 | — |
| | 0.07 | −0.41 | — |
| | 0.16 | −0.97 | — |
| | 0.24 | −1.51 | — |
| | 0.34 | −2.14 | — |
| | 0.44 | −2.77 | — |
| | 0.53 | −3.28 | — |

with those of $\Delta T$ for comparison, and the relationships between $\Delta T'$ and $x$ are pictured separately for three groups of substances in Figs. 1—3. Since $\Delta T'/x$ holds an approximate linearity with $x$ in any solute substance, $\Delta T'$ may be expressed as a second order equation with respect to $x$, both the $a$ and $b$ parameters being shown in Table II as well.

$$\Delta T' = ax + bx^2 \tag{6}$$

TABLE II. THE CHARACTERISTIC DATA FOR SUBSTANCES; COEFFICIENT OF THERMAL EXPANSION $\alpha$, MOLAR VOLUME AT 0°C $V_{s_0}$, PARAMETERS IN Eq. 6 $a$ AND $b$, AND DIPOLE MOMENT $\mu$

| Substance | $\alpha\times10^3$ deg$^{-1}$ | $V_{s_0}$ cc. mol$^{-1}$ | $a\times10^{-1}$ deg. | $b\times10^{-3}$ deg. | $\mu$ D. U. |
|---|---|---|---|---|---|
| Monomethylamine | 1.49 | 45.14 | 18.0 | − 2.9 | 1.32 |
| Dimethylamine | 2.07 | 66.27 | 51.5 | − 8.5 | 1.02 |
| *n*-Butylamine | 1.31 | 95.4 | 17.3 | −12.0 | — |
| Acetamide | 0.81 | 59.152 | − 9.4 | − 0.6 | — |
| Urea | — | — | — | — | 4.56 |
| Pyridine | 1.00 | 78.860 | −11.5 | − 7.7 | 2.22 |
| Acetonitrile | 1.32 | 51.089 | − 9.4 | − 5.4 | 3.94 |
| Propionitrile | 1.24 | 68.678 | −11.7 | − 5.9 | 4.00 |
| Formaldehyde | — | — | — | — | 2.27 |
| Acetone | 1.36 | 71.485 | 17.3 | −11.5 | 2.85 |
| Tetrahydrofuran | 1.3 | 78.96 | 15.4 | − 6.7 | 1.71 |
| 1,4-Dioxane | 1.310 | 83.03 | 1.8 | −10.6 | 0.43 |
| Benzene | 1.187 | 86.784 | 0.0 | 0.0 | 0 |

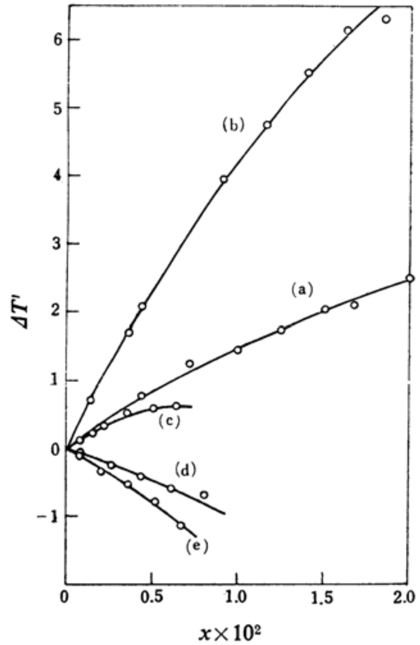

Fig. 1. Variation of $\Delta T'$ with the concentration of (a) monomethylamine, (b) dimethylamine, (c) *n*-butylamine, (d) acetamide and (e) pyridine.

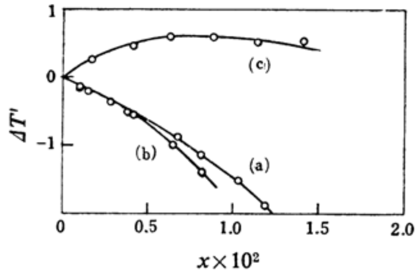

Fig. 2. Variation of $\Delta T'$ with the concentration of (a) acetonitrile, (b) propionitrile and (c) acetone.

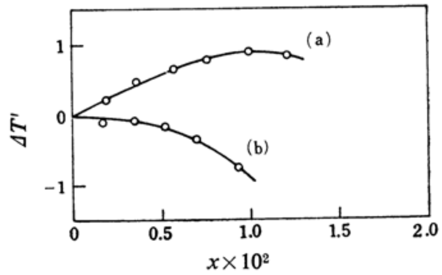

Fig. 3. Variation of $\Delta T'$ with the concentration of (a) tetrahydrofuran and (b) 1,4-dioxane.

In the cases of urea, formaldehyde and tetraethylammonium bromide, $a$ and $b$ are not known because of the lack of appropriate data for $\alpha$ and $V_{s_0}$ in the liquid state.

**The Nature of *a*.**—Since, as was mentioned in the previous paper[1], $\Delta T'$ is caused by an appreciable change in the molar volume and in the coefficient of the thermal expansion of the solute ($\Delta V_{s_0}$ and $\Delta\alpha$) on mixing a solute and water, $a$ has a nature expressed as follows:

$$a\equiv\lim_{x\to0}\left(\frac{\mathrm{d}\Delta T'}{\mathrm{d}x}\right)=-k(\alpha\Delta V_{s_0}+V_{s_0}\Delta\alpha) \tag{7}$$

As $k=(1/2)\,\beta V_{w_m}$ is taken to be constant, any changes in the volume or the coefficient of the thermal expansion of water accompanied by a transition of states in the sheaths of the hydration layer attached to the solute molecules are entirely included in $\Delta V_{s_0}$ or $\Delta\alpha$ respectively.

A polar substance in question may overcome the association between the molecules themselves and may newly establish the hydration sphere around the individual molecules when it is dissolved in water. Since water is as much compressed in the hydration sphere as in "the packed state" of pure water, the coefficient of the thermal expansion of water in this state is larger than that in the free state[1,2]. Consequently, the second term in the parenthesis on the right-hand side of Eq. 7, $V_{s_0}\Delta\alpha$, may be reasonably regarded as positive in most cases. On the other hand, $\Delta V_{s_0}$ may be either positive or negative according to whether or not the degree of the contraction of volume caused by the association of the solute due to its cohesive force in the separated state is superior to that resulting from the formation of the hydration sphere in the dissolved system. Thus, the magnitudes of $a$ are dependent upon the signs and the absolute values of $\alpha\Delta V_{s_0}$ and $V_{s_0}\Delta\alpha$ in Eq. 7.

As is illustrated in Fig. 1, the $a$ values for monomethylamine, dimethylamine and *n*-butylamine are all positive; the $a$ for dimethylamine especially is as high as that for *t*-butyl alcohol*. In the case of dimethylamine, the $|\alpha\Delta V_{s_0}|\gg|V_{s_0}\Delta\alpha|$ relation may hold because it would be least associative with a very small dipole moment (Table II); consequently, $\Delta V_{s_0}<0$ and $\Delta\alpha$ would be nearly equal to zero, as it has an extraordinarily large $\alpha$.

On the other hand, $a$ becomes negative for acetamide; this is because both $\alpha$ and $V_{s_0}$ are essentially small due to the strong formation of the intermolecular hydrogen bondings. Since this tendency occurs more severely in urea than in acetamide on account of its molecular structure, the $\Delta T$ of urea appears far lower than that of acetamide at the same mole fraction**. Unfortunately, the $a$ value for urea can not be known, for it is not liquidous. Pyridine also exhibits an excellent ability to lower the T. M. D. of water, probably due to its good hydrophilic nature.

In Fig. 2, acetonitrile and propionitrile show large negative $a$ values because of their large dipole moments. In Fig. 3, on the contrary, tetrahydrofuran and 1, 4-dioxane, which are both cyclic ethers, have positive $a$'s as in the cases of amines and acetone; this is because they have comparatively many alkyl radicals in the molecule which are of rather a hydrophobic nature and are likely to diminish the degree of hydration.

In the case of benzene, $\Delta T'$ is zero within the range of experimental error; therefore, $a=b=0$. This fact shows that benzene is a perfect non-polar liquid and that it behaves quite independently in its aqueous solution with no mutual interaction with water.

Since tetraethylammonium bromide is a kind of electrolyte, its ability to lower the T. M. D. of water is much greater than that of any polar nonelectrolyte. The relation between $\Delta T$ and $x$ shows a features similar to those of ammonium bromide[4]. Generally speaking, the lowering of the T. M. D. of water by 1-1 type electrolytes, composed of monatomic ions, seems to become greater as the size of the ion grows larger; moreover, this trend appears more effective in anions than in cations. In spite of such a tendency, it is quite strange that $N(C_2H_5)_4{}^+$ ion exhibits behavior similar to that of the simple $NH_4{}^+$ ion.

**Additivity of *a*.**—When an assumption is made that the total effect of a substance to lower the T. M. D. of water is approximately the additive sum of the nature of its individual component radicals according to their polarity, the $a$ values assigned to several radicals can be obtained by the least square method based on the observed data of relatively simple compounds, including alcohols[1], such as are taken up in Table IV. Table III shows the $a$ values thus calculated for various radicals and, as well, their radical dipole moments, between which a good parallelism is easily recognized; namely, the more polar a radical, the more negative $a$ becomes. By using the $a$ values for radicals in Table III, the $a$ values for compounds are calculated in Table IV, the agreement with the observed $a$ values being satisfactory, with errors of less than ±0.3.

TABLE III. $a$ AND DIPOLE MOMENT FOR RADICALS

| Radical | $a\times10^{-1}$ | $\mu$, D. U. |
|---|---|---|
| $-CH_3$ | 27.8 | 0.3 |
| $-CH_2-$ | 3.4 | 0 |
| $-O-$ | − 4.3 | — |
| $>NH$ (or $-NH_2$) | − 4.4 | 1.31 |
| $-OH$ | − 7.6 | 1.53 |
| $>CO$ | −37.7 | 2.5 |
| $-CN$ | −40.0 | 3.6 |

**The Nature of *b*.**—In dilute solutions of some electrolytes, an approximate linearity is established between $\Delta T$ and $x$ (Despretz's rule), but in the case of nonelectrolytes, the deviation from this linearity is considerable, from which fact the $b$ parameter in Eq. 6 originates and always exhibits a negative value. As $b$ is the coefficient of the second-order term with respect to the mole fraction, it may be related to some solute-solute interaction. When $b$ values for various substances are

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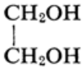
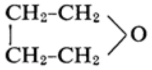
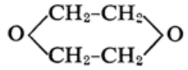
* In the case of *t*-butyl alcohol, $a=60.5$ and $\alpha=1.295$, both of which are the largest values among the observed alcohols[1].

** Urea and acetamde are far more likely to form hydrogen bondings than alcohol and acetone; the dielectric constants of their aqueous solutions are larger than that of water itself[3].

3) J. Wymann, Jr., *J. Am. Chem. Soc.*, **55**, 4116 (1933); H. Baba, *Chem. & Chem. Ind.*, **12**, 1001 (1959).

4) International Critical Tables, Vol. III, p. 107.

TABLE IV. ADDITIVITY OF $a$ FROM RADICALS

| Substance | | $a_{\mathrm{calcd}} \times 10^{-1}$ | $a_{\mathrm{obs}} \times 10^{-1}$ |
|---|---|---|---|
| Methyl alcohol | $CH_3OH$ | 20.2 | 17.3 |
| Ethyl alcohol | $C_2H_5OH$ | 23.6 | 27.3 |
| Ethylene glycol |  $CH_2OH-CH_2OH$ | − 8.4 | − 8.9 |
| Monomethylamine | $CH_3NH_2$ | 23.4 | 18.0 |
| Dimethylamine | $(CH_3)_2NH$ | 51.2 | 51.5 |
| Acetone | $CH_3COCH_3$ | 17.9 | 17.3 |
| Acetamide | $CH_3CONH_2$ | −14.3 | − 9.4 |
| Acetonitrile | $CH_3CN$ | −12.2 | − 9.4 |
| Propionitrile | $C_2H_5CN$ | − 8.8 | −11.7 |
| Tetrahydrofuran |  | 9.3 | 15.4 |
| 1, 4-Dioxane |  | 5.0 | 1.8 |

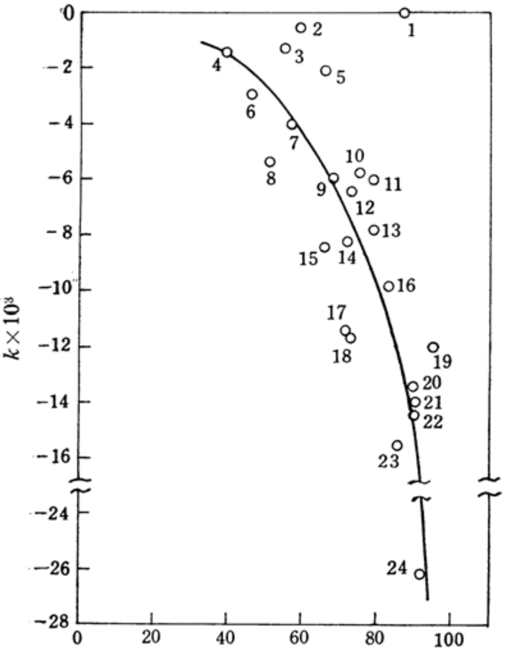


Fig. 4. Relation of $b$ against $V_{so}$. 1 : Benzene, 2 : Acetamide, 3 : Ethylene glycol, 4 : Methyl alcohol, 5 : Ethylene chlorohydrin, 6 : Monomethylamine, 7 : Ethyl alcohol, 8 : Acetonitrile, 9 : Propionitrile, 10 : Isopropyl alcohol, 11 : Tetrahydrofuran, 12 : *n*-Propyl alcohol, 13 : Pyridine, 14 : Glycerin, 15 : Dimethylamine, 16 : 1,4-Dioxane, 17 : Acetone, 18 : Propylene glycol, 19 : *n*-Butylamine, 20 : *n*-Butyl alcohol, 21 : Isobutyl alcohol, 22 : *sec*-butyl alcohol, 23 : Phenol, 24 : *t*-Butyl alcohol.

plotted against their molar volumes, as in Fig. 4, the explicit correlation is indicated, with the exception of benzene, that the larger the molar volume, the greater negative value $b$ has. Nevertheless, the mechanism of the solute-solute interaction can not be made clear at present.

## Summary

The temperature of the maximum density (T. M. D.) of aqueous solutions of various organic polar substances at various concentrations were measured dilatometrically, and the degrees of elevating the T. M. D., $\Delta T$, were estimated. The information derived from the experimental results includes :

1) At any concentration, the values of $\Delta T$ for all substances used in the present study are inevitably negative, in contrast with the cases of alkyl monovalent alcohols, reported on in the preceding paper[1]).

2) $\Delta T'$, defined as the difference between the actual elevation of T. M. D. and that when the solution is assumed to be an ideal mixture, is given by an empirical formula, $\Delta T' = ax + bx^2$, where $a$ is a characteristic constant of the solute, indicating the degree of the interaction between the solute and water ; it generally has a more negative value as the substance is more polar.

3) Benzene does not interact with water ; therefore, $\Delta T' = 0$ and $a = b = 0$ in so far as it is soluble in water.

4) An additivity correlation concerning $a$ is realized from the composing radicals, and the $a$ values assigned to respective radicals show a simple parallelism with their own polarities.

5) The $b$ parameter is negative for all substances ; the absolute value of this is greater as the molar volume becomes larger.

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