Effects of Nonelectrolytes on the Temperature of the Maximum Density of Water. I. Alcohols

By Goro WADA and Saburo UMEDA*

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The well-known fact that water exhibits its maximum density at 3.98°C under an atmospheric pressure has been discussed by one of the present authors in the previous paper[1] from the viewpoint of the two-state model stating that water holds a chemical equilibrium between the icy and the closely packed states. It may be an interesting problem how the temperature of the maximum density of water varies when a minute quantity of a foreign substance is dissolved in it. The effects of some simple electrolytes on the temperature of the maximum density have already been measured[2], and, so far as is known, electrolytes lower the temperature of the maximum density of water at a rate nearly proportional to the concentrations of electrolytes in dilute solutions, obeying the so-called Despretz's rule[3]. However, nothing is yet known about the effects of nonelectrolytes upon the temperature of the maximum density of water. The authors, therefore, intend in the present paper to find the correlation between the change in the temperature of the maximum density of water and the chemical constitution of some added organic substances, especially of various uni- and polyvalent alcohols.

Experimental

Apparatus and Procedure.—The dilatometer used for the measurement of the volume change of

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* Present address: Toppan Printing Co., Ltd., Fukushima-ku, Osaka.

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

[2] R. Wright, *J. Chem. Soc.*, **115**, 119 (1919); N. G. Wilson and R. Wright, *J. Phys. Chem.*, **35**, 624 (1934); "International Critical Tables", Vol. III, p. 107.

[3] Despretz, *Ann. chim. phys.*, [ii] **70**, 49 (1839); ibid., **73**, 296 (1840).

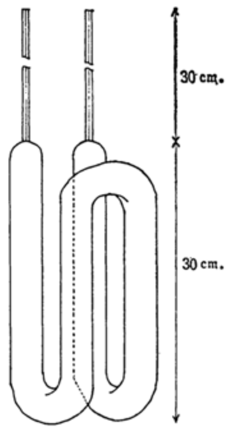

Fig. 1. Dilatometer.

aqueous solutions with temperature is shown in Fig. 1. Its shape as a whole was of a twisted-W type with a capacity of about 300 cc., to which was attached at either end a vertical capillary 0.6 mm. in inside diameter. This enabled us to detect a volume change in a solution as small as $3\times10^{-5}\%$ by observing the movement of the liquid surface in the capillary tubes as the temperature was varied. In order to fill the dilatometer with a sample solution, one of the ends of the capillaries was connected with the reservoir of a solution and the other with an aspirator. On working the aspirator, it had been verified preliminarily that no appreciable change in concentration owing to the fractional evaporation of the individual volatile components of the solution occurred during the transfer of the solution from the reservoir to the dilatometer. The height of the surface of the solution which had been introduced was adjusted to be nearly at the center of each capillary by the advance use of a thin injector.

The temperature of the thermostat was regulated within ±0.005°C. The dilatometer attained thermal equilibrium with the thermostat in half an hour. The change in volume was observed in the temperature range covering ±2°C of the temperature of the maximum density of the solution at intervals of about 0.5°C. The apparent volume of a solution does not show a minimum at its true temperature of the maximum density owing to the thermal expansion of the dilatometer itself. The changes in the casese of pure water and aqueous solutions, in the height of the liquid surface with a change in temperature near the respective temperatures of the maximum density, however, were found to be quite similar in type to each other, irrespective of the nature of the solution as long as the solution was very dilute. The temperature of the maximum density of the sample could, therefore be determined, graphically by comparing the apparent volume change of pure water with that of the sample. This method was very accurate, with a maximum error of ±0.02°C*.

Materials.—Sixteen alcohols, including uni- and polyvalent ones, were used for the experiments; these alcohols were purified by usual methods and were ascertained to be pure enough for the present purpose as judged from boiling points, melting points, densities and refractive indices. Pure water was prepared by passing distilled water obtained from an alkaline permanganate solution, through columns of ion-exchange resin.

Results

The elevation of the temperature of the maximum density ΔT is defined as

$$\Delta T = T_{\mathrm{m}} - T_{\mathrm{m_0}} \qquad (1)$$

where $T_{\mathrm{m_0}}$ represents the temperature of the maximum density of pure water and T_{m} that of a sample solution of mole fraction x of alcohol respectively. The observed values of ΔT at various concentrations of various alcohols are shown in Table I.

As examples of ternary systems, a mixture of ethyl alcohol, *tert*-butyl alcohol and water and one of *tert*-butyl alcohol, potassium chloride and water were adopted, the concentration of *tert*-butyl alcohol being kept constant at 0.10×10^{-2} mol./H_2O-mol. in the former and that of potassium chloride at 0.11×10^{-2} and 0.20×10^{-2} mol./H_2O-mol. in the latter. The results are pictured in Figs. 2 and 3.

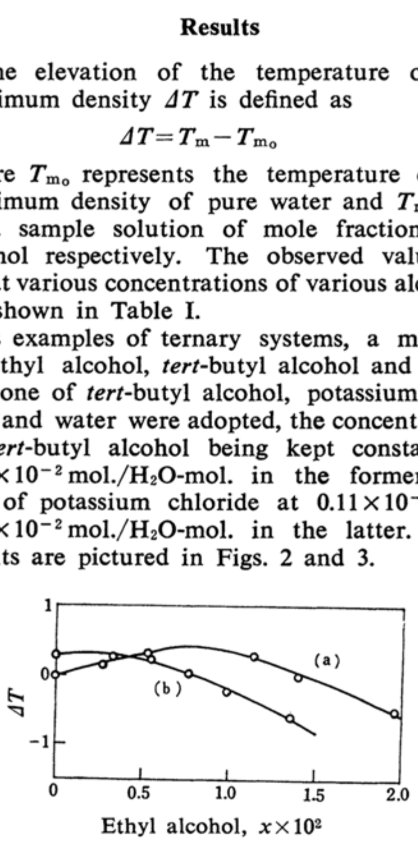

Fig. 2. The ternary system of ethyl alcohol, *tert*-butyl alcohol and water. (a) *tert*-butyl alcohol: none, (b) *tert*-butyl alcohol: 0.10×10^{-2} mol./H_2O-mol.

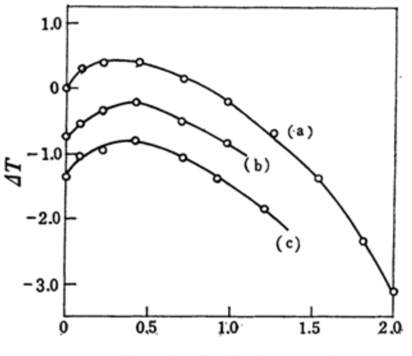

Fig. 3. The ternary system of *tert*-butyl alcohol, potassium chloride and water. (a) KCl: none, (b) KCl: 0.11×10^{-2} mol./H_2O-mol., (c) KCl: 0.20×10^{-2} mol./H_2O-mol.

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* The maximum errors ever reported in cases of electrolyte solutions were as large as ±0.2°C.

TABLE I. THE ELEVATION OF THE TEMPERATURE OF MAXIMUM DENSITY OF WATER BY VARIOUS ALCOHOLS

Substance	$x\times10^2$	ΔT	$\Delta T'$
Methyl alcohol			
	0.68	0.02	1.12
	1.00	−0.04	1.59
	1.48	−0.20	2.24
	2.05	−0.48	2.90
	2.59	−0.80	3.48
	3.17	−1.28	4.00
	3.67	−1.64	4.53
	4.21	−2.33	4.77
	4.45	−2.46	5.07
	5.26	−3.54	5.43
Ethyl alcohol			
	0.27	0.16	0.78
	0.53	0.32	1.49
	1.13	0.29	2.73
	1.38	0.00	2.97
	1.92	−0.50	3.70
	2.35	−1.13	4.03
	2.92	−1.93	4.54
	3.40	−2.94	4.60
	3.89	−4.14	4.53
n-Propyl alcohol			
	0.24	0.07	0.71
	0.48	−0.14	1.13
	0.74	−0.24	1.72
	1.00	−0.60	2.04
	1.01	−0.62	2.05
	1.48	−1.50	2.44
	1.98	−2.94	2.35
	2.48	−4.34	2.30
Isopropyl alcohol			
	0.44	0.20	1.38
	0.47	0.16	1.42
	0.56	0.32	1.78
	0.99	0.20	2.89
	1.62	−0.48	3.96
	2.15	−1.30	4.63
n-Butyl alcohol			
	0.21	−0.18	0.41
	0.41	−0.33	0.80
	0.62	−0.85	0.87
	0.84	−1.24	1.08
	1.00	−1.94	0.81
	1.24	−2.52	0.89
	1.51	−3.56	0.60
Isobutyl alcohol			
	0.21	−0.08	0.54
	0.42	−0.38	0.85
	0.71	−0.92	1.20
	0.90	−1.42	1.28
	1.24	−2.33	1.45
	1.52	−3.56	1.04
sec-Butyl alcohol			
	0.21	0.04	0.71
	0.49	−0.11	1.49
	0.76	−0.54	1.92
	1.01	−1.13	2.16
	1.25	−1.62	2.44
	1.52	−2.54	2.42
	1.79	−3.46	2.41
tert-Butyl alcohol			
	0.09	0.30	0.70
	0.22	0.40	1.36
	0.43	0.41	2.26
	0.70	0.16	3.14
	0.97	−0.20	3.96
	1.24	−0.68	4.66
	1.52	−1.36	5.17
	1.78	−2.33	5.34
	1.97	−3.11	5.39
Ethylene chlorohydrin			
	0.22	−0.37	0.04
	0.40	−0.85	−0.02
	0.65	−1.40	−0.06
	0.90	−2.04	−0.17
	1.15	−2.62	−0.23
	1.40	−3.44	−0.50
Phenol			
	0.18	−0.56	−0.15
	0.33	−1.13	−0.37
	0.49	−1.80	−0.65
	0.72	−2.92	−1.23
	0.94	−4.08	−1.88
	1.03	−4.47	−2.06
p-Nitrophenol			
	0.021	−0.23	—
	0.038	−0.37	—
	0.057	−0.49	—
Ethylene glycol			
	0.22	−0.45	−0.21
	0.43	−0.79	−0.41
	0.66	−1.23	−0.65
	0.92	−1.80	−0.95
	1.16	−2.27	−1.20
	1.44	−2.87	−1.55
	1.74	−3.54	−1.93
Propylene glycol			
	0.14	−0.05	0.21
	0.28	−0.12	0.39
	0.48	−0.35	0.51
	0.68	−0.73	0.51
	0.88	−1.17	0.45
	1.09	−1.58	0.44
	1.27	−2.17	0.18
	1.37	−2.39	0.15
	1.54	−2.76	0.07
Glycerin			
	0.18	−0.37	−0.17
	0.39	−0.95	−0.51
	0.53	−1.39	−0.78
	0.76	−1.95	−1.09
	0.92	−2.47	−1.43
	1.04	−2.97	−1.79
Saccharose			
	0.03	−0.29	—
	0.06	−0.52	—
	0.09	−0.70	—
	0.12	−1.03	—
	0.14	−1.29	—
	0.17	−1.47	—
	0.19	−1.78	—
	0.24	−2.19	—
	0.28	−2.51	—
Polyvinyl alcohol*			
	0.044	−0.00	—
	0.085	−0.13	—
	0.127	−0.10	—
	0.167	−0.10	—
	0.212	−0.16	—
	0.256	−0.27	—

* In case of polyvinyl alcohol, x represents the fraction of OH groups. The experimental errors are somewhat larger than in the case of other alcohols, caused by the special properties of its solution. The authors thank Dr. T. Mochizuki of Kurashiki Rayon Co. Ltd. for the supply of polyvinyl alcohol.

Discussion

Preliminary Considerations. — It should be pointed out with reference to Table I that although no substance which elevates the temperature of the maximum density of water has hitherto been known, methyl alcohol, ethyl alcohol, *n*-propyl alcohol, isopropyl alcohol, *sec*-butyl alcohol and *tert*-butyl alcohol are now found for the first time to be surely such substances, at least in dilute concentrations. It is especially worth attention that the ΔT of a *tert*-butyl alcohol solution reaches as high as 0.41°C at the concentration $x=0.0043$. Except for the cases mentioned above, ΔT's are usually negative, similar to those of all electrolyte solutions. Instead of obeying Despretz's rule, which states that the ΔT is proportional to the concentration, they fall off more rapidly than the change in concentration.

If a small quantity of liquid substance dissolves in water with neither an increase nor a decrease in the total volume, the resulting volume V of the aqueous solution at θ°C is expressed by

$$V=xV_s+(1-x)V_w \tag{2}$$

where V_s and V_w are the molar volumes of the solute and water respectively at θ°C. Since it is reasonably accepted that V_s increases linearly with temperature over a small temperature range of 0∼5°C, while V_w is satisfactorily expressed by a parabolic function of the temperature in the vicinity of its minimum, namely the maximum density of water, the following relations can be given:

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

$$V_w=V_{w_m}\{1+\beta(\theta-3.98)^2\} \tag{4}$$

in which V_{s_0} and V_{w_m} represent V_s at 0°C and V_w at 3.98°C respectively, and α and β are coefficients relating to the thermal expansion of the respective substances. From the condition $\mathrm{d}V/\mathrm{d}\theta=0$ at the temperature of the maximum density of the solution, we obtain

$$T_m'=-\frac{x}{1-x}\cdot\frac{\alpha}{2\beta}\cdot\frac{V_{s_0}}{V_{w_m}}+3.98 \tag{5}$$

where T_m' signifies the imaginary temperature of the maximum density of a solution if the solution were an ideal mixture without any appreciable interaction between the solute and water. The imaginary elevation of the temperature of the maximum density ΔT_n is, therefore, as follows:

$$\begin{aligned}\Delta T_n&=T_m'-T_{m_0}\\&=-\frac{x}{1-x}\cdot\frac{\alpha}{2\beta}\cdot\frac{V_{s_0}}{V_{w_m}}\end{aligned} \tag{6}$$

According to Eq. 6, ΔT_n should always be negative in ideal systems and should be approximately proportional to the solute concentration as long as the concentration is very low. Therefore, the elevation of the temperature of the maximum density of real solutions owing to mutual interaction between the solute and water, $\Delta T'$, can be defined as follows:

$$\Delta T'=\Delta T-\Delta T_n \tag{7}$$

The necessary values to estimate ΔT_n are the following: $\beta=7.80\times10^{-6}\,\mathrm{deg}^{-2}$, $V_{w_m}=18.016$ cc./mol., and α's and V_{s_0}'s for various alcohols as listed in Table II. The values of $\Delta T'$ thus obtained are shown in Table I, together with those of ΔT, the former also being approximately represented by an empirical equation of the second order with respect to the concentration

$$\Delta T'=ax+bx^2 \tag{8}$$

because $\Delta T'/x$ versus x is represented by a straight line, as are some examples shown in

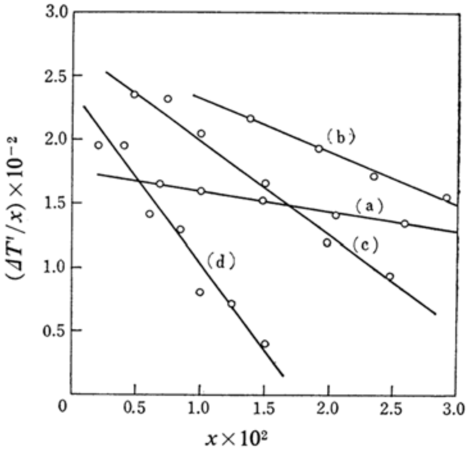

Fig. 4. Linearity of $\Delta T'/x$ against x. (a) Methyl alcohol, (b) ethyl alcohol, (c) *n*-propyl alcohol, (d) *n*-butyl alcohol.

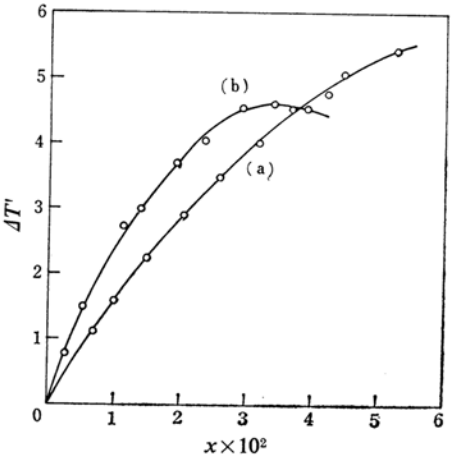

Fig. 5. Variation of $\Delta T'$ with the concentration of (a) methyl alcohol and (b) ethyl alcohol.

TABLE II. COEFFICIENTS OF THERMAL EXPANSION, MOLAR VOLUMES AND PARAMETERS a AND b FOR VARIOUS ALCOHOLS

Substance	$\alpha \times 10^3$ deg^{-1}	V_{s_0} cc. mol^{-1}	$a \times 10^{-1}$ deg.	$b \times 10^{-3}$ deg.
Methyl alcohol	1.148	39.556	17.3	− 1.5
Ethyl alcohol	1.053	57.141	27.3	− 4.1
n-Propyl alcohol	1.002	73.283	26.3	− 6.4
Isopropyl alcohol	1.01	74.993	34.1	− 5.7
n-Butyl alcohol	0.851	89.962	23.7	−13.5
Isobutyl alcohol	0.923	90.733	27.7	−14.0
sec-Butyl alcohol	1.00	90.03	36.5	−14.6
tert-Butyl alcohol	1.295	91.83	60.5	−26.2
Ethylene chlorohydrin	0.878	65.82	0.3	− 2.1
Phenol	0.752	86.181	− 5.4	−15.6
Ethylene glycol	0.464	55.139	− 8.9	− 1.3
Propylene glycol	0.70	73.33	16.3	−11.6
Glycerin	0.43	72.373	− 8.5	− 8.3

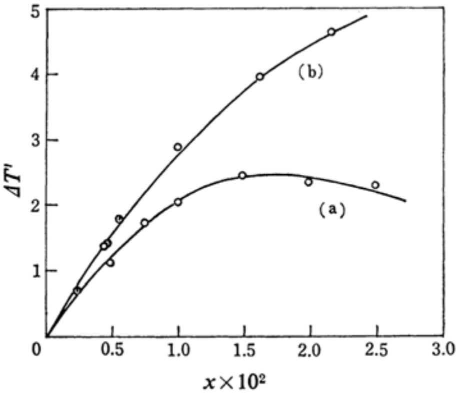

Fig. 6. Variation of $\Delta T'$ with the concentration of (a) *n*-propyl alcohol and (b) isopropyl alcohol.

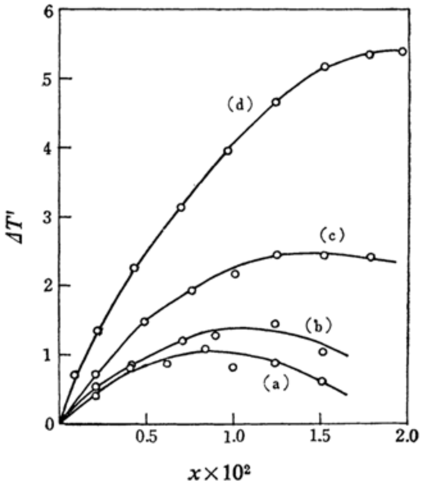

Fig. 7. Variation of $\Delta T'$ with the concentration of (a) *n*-butyl alcohol, (b) isobutyl alcohol, (c) *sec*-butyl alcohol and (d) *tert*-butyl alcohol.

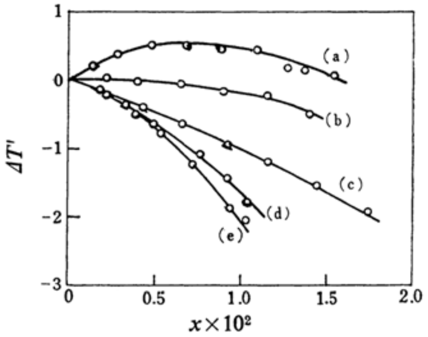

Fig. 8. Variation of $\Delta T'$ with the concentration of (a) propylene glycol, (b) ethylene chlorohydrin, (c) ethylene glycol, (d) glycerin and (e) phenol.

Fig. 4[*]. Parameters a and b obtained graphically for respective alcohols are also shown in Table II.

The General Tendency of $\Delta T'$, a and b.—In order to discuss the mutual interactions between alcohols and water, it is rather convenient to pay attention to the relationships of $\Delta T'$, instead of ΔT, with the concentration; these relationships are reproduced in Figs. 5—8. Generally speaking, the values of $\Delta T'$ for univalent alkyl alcohols are always positive, while those for polyvalent alcohols show a trend toward being negative. In the cases of propyl alcohols and butyl alcohols, the branching of the alkyl radicals is found to have a clear enhancing effect on $\Delta T'$. Moreover, it should be pointed out in Table II that a's are positive only for all univalent alcohols, while b's are negative for all alcohols adopted here, and that the absolute values of both a and b

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[*] In Fig. 4, the plots of $\Delta T'/x$ at very low concentrations of alcohols are omitted because they are subject to larger errors.

increase as the volumes of alkyl radical become larger.

Nature of a. — On mixing the solute and water, if there were no interaction between the two species, $\Delta T'$ should be zero. In reality, however, interaction occurs to some extent, so that α and V_{s_0} vary as much as $\Delta\alpha$ and ΔV_{s_0} respectively; therefore, $\Delta T'$ can be expressed as follows:

$$\Delta T' = -\frac{x}{1-x}\cdot k(\alpha\Delta V_{s_0}+V_{s_0}\Delta\alpha) \qquad (9)$$

Moreover, from Eqs. 8 and 9 one obtains the next relation:

$$a \equiv \lim_{x\to 0}\left(\frac{\mathrm{d}\Delta T'}{\mathrm{d}x}\right) = -k(\alpha\Delta V_{s_0}+V_{s_0}\Delta\alpha) \qquad (10)$$

where $k=1/2\beta V_{\mathrm{wm}}$. In these expressions, ΔV_{s_0} and $\Delta\alpha$ are assumed to include the total changes in volume and in the coefficients of the thermal expansion not only of the solute itself but also of the hydration sheaths formed round the solute molecules where the interaction wholly takes place, β and V_{wm} being regarded as constant.

Univalent alcohol is taken to exist in the form of hydrogen-bonded chains in a pure liquid state[4] but when it is dissolved in water, there occurs the breaking of the hydrogen bondings between alcohol molecules and, succeedingly, the hydration of the water molecules surrounding them. Since the energies of the hydration are higher than those of hydrogen-bond formation in case of univalent alcohols, the contraction of the volume owing to the compression by hydration exceeds the expansion owing to the breaking of hydrogen bondings and, consequently perhaps, $\Delta V_{s_0}<0$. Moreover, since water undergoes a transition from the free state (an equilibrating mixture of the icy state and the packed state[1]) to another state similar to the packed state when water hydrates to the solute molecules, $\Delta\alpha$ must be positive, because the coefficients of the thermal expansion of water of the icy state and the packed state are 1.52×10^{-4} and 1.013×10^{-3} deg^{-1} respectively[1]. Accordingly, the first term in the parenthesis in the right-hand side of Eq. 10 should be negative, while the second term is positive. In Table II, since the a's for all univalent alcohols except phenol are positive, the absolute value of the first term must be larger than that of the second term in every alcohol*. Especially, the fact that the magnitude of a for *tert*-butyl alcohol is extraordinarily large may be attributed to the greatness of α itself.

Owing to the intramolecular hydrogen bondings of ethylene chlorohydrin, ethylene glycol, propylene glycol and glycerin, and owing to the intermolecular association of phenol, they are greatly contracted by a strong cohesive force and show a relatively small V_{s_0} compared with those of non-substituted corresponding univalent alcohols in a pure state**. Consequently, ΔV_{s_0} may be nearly equal to zero or rather positive when they are dissolved in water. In such cases, the a's may be smaller than those of univalent alcohols and at last negative in certain instances, as can be seen in Table II.

Tendency of b. — Since b is, on the other hand, the parameter of the second-order term with respect to the concentration in Eq. 8, it may be related to the mutual interaction between the solute molecules themselves. However, the tendencies for b to be negative for all substances so far as have been observed and for the absolute value of b to become larger as the molecular volume of the substance is larger can not be interpreted at the present stage of investigation.

Ternary Systems. — Figure 2 illustrates the variation of ΔT with x of ethyl alcohol in curve a as a binary system and in curve b as a ternary one, *tert*-butyl alcohol being kept at a constant concentration of 0.10×10^{-2} mol./H_2O-mol. as a third substance. ΔT in the ternary system is found to be always smaller than the sum of the ΔT's which ethyl alcohol and *tert*-butyl alcohol will exhibit independently in binary systems. This fact shows that there exists a mutual interaction between the molecules of the different alcohols to disturb their individual behavior.

The situation is, on the contrary, quite different in Fig. 3. Curve a is true for *tert*-butyl alcohol only, while curves b and c correspond to the cases when potassium chloride is added to it as a third substance at 0.11×10^{-2} and 0.20×10^{-2} mol./H_2O-mol. respectively. When curve a is moved down parallel to the axis as far as -0.74 and -1.34°C, it just falls on curves b and c respectively. These distances

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[4] G. Oster and J. G. Kirkwood, *J. Chem. Phys.*, **11**, 175 (1943); R. H. Cole and W. Dannhauser, ibid., **23**, 1762 (1955); J. B. Hasted and G. W. Roderick, ibid., **29**, 17 (1958); G. P. Pimentel and A. L. McClellan, "The Hydrogen Bond", Freeman Co., San Francisco (1960).

* The fact that a tends to become larger when the alkyl chain of univalent alcohol is longer, as is seen in Table II, can be understood from the observed thermochemical data that the energy of the dissolution of $\text{-CH}_2\text{-}$ from paraffin into water is about 0.8 kcal./mol.[5] and that the longer the alkyl radical of univalent alcohol, the larger its hydration energy[6].

[5] K. Kinoshita, H. Ishikawa and K. Shinoda, This Bulletin, **31**, 1081 (1958).

[6] S. Seki and K. Suzuki, ibid., **26**, 63 (1953).

** For instance, ethylene chlorohydrin and ethylene glycol should be compared with ethyl alcohol, the former being derivatives of the latter by substituting H by Cl and OH respectively.

between the curves agree well with the ΔT's which potassium chloride exhibits when it exists alone in water at those respective concentrations. This fact indicates that *tert*-butyl alcohol and potassium chloride do not greatly influence one another in such dilute solutions.

As to the phenomena of the solvation of ions, it is known that only the hydration is overwhelmingly predominant when the concentration of alcohol is less than 10 mol. %, since water molecules are attracted to ions far more preferentially than alcohol molecules at the solvation equilibrium in ternary systems of lithium chloride-ethyl alcohol-water⁷⁾, of lithium fluoride-methyl alcohol-water⁸⁾ and of lithium fluoride-ethyl alcohol-water⁸⁾. Considering all these facts, nonelectrolytic molecules and electrolytic ions may exhibit independent behavior in dilute aqueous solutions.

Summary

The effects of various kinds of alcohol on the temperature of the maximum density of water were observed. The results revealed are as follows:

1) The change in the temperature of the maximum density due to alcohols, ΔT, is not proportional to the solute concentration, disobeying Despretz's rule and in contrast with ordinary electrolytes.

2) The ΔT for univalent aliphatic alcohols at low concentrations is generally positive; that for *tert*-butyl alcohol is the largest. The ΔT is likely to become high as the number of carbon atoms and the degree of branching in alkyl radicals increase.

3) The elevation of the temperature of the maximum density due to the interaction of alcohol and water, $\Delta T'$, depends upon the weakness of the cohesion of alcohol and the strength of the hydration of the hydrophilic molecules.

4) As the concentration of alcohol increases, there occurs a lowering of ΔT as a result of interaction between the solute molecules themselves. Similar interactions are seen between different alcohol molecules in ternary systems, but can not be seen between alcohol and electrolytic ions, where the solutes behave independently of each other. In the last case, the additivity of ΔT is realized fairly well.

Department of Chemistry
Faculty of Science
Kobe University
Mikage, Kobe

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7) G. Wada, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 77, 391 (1956).

8) G. Wada, C. Ito and K. Horie, *J. Electrochem. Soc. Japan*, 28, 58, E32 (1960).