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Ultrasonic Investigation on the Structure of Aqueous Solution of 2-Butanone

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The effect of 2-butanone on the temperature corresponding to adiabatic compressibility minimum (TACM), sound velocity maximum (TSVM) and specific acoustic impedance maximum (TSAIM) of pure water has been studied by experimentally determining the sound velocity and density of aqueous solution at different concentrations over a temperature range 34—70.5 °C. The structural contribution to the shift in TACM, TSVM, and TSAIM has been evaluated. The shift is positive throughout the concentration range studied and indicates that 2-butanone is hydrophobic in nature.

The hydrogen-bonded structure of water plays an important role in the nonideal thermodynamic behavior exhibited by aqueous nonelectrolytes. The solution structure of aqueous nonelectrolytes can be understood from the studies on the effect of these solutions on the anomalous behavior exhibited by water such as density maximum at 3.98 °C[1-3] adiabatic compressibility minimum at 64 °C,[4,5,16] sound velocity maximum at 74 °C[6,7,16] and impedance maximum[8] at 56.4 °C etc.

The physicochemical properties of water-2-butanone system has been studied extensively by various workers.[9-11] Roux et al.[9] have studied the concentration dependence of ϕ_C and ϕ_V for this system in the temperature range 4 to 40 °C. The studies on apparant molal volumes ϕ_V of various hydrophobic solutes indicate that ϕ_V decreases with concentration in the water rich region. In general, the more the hydrophobic nature of solute is the more negative would be the initial slope A_V. The apparant molal heat capacities ϕ_C decrease as a function of concentration and the decrease is more important for hydrophobic solutes. The apparant molal expansibilities ϕ_E are positive for such systems.

For water-2-butanone system, Roux et al.[9] observed a slight deviation from the typical behavior at 40 °C. Therefore an attempt has been made in the present investigation to study the temperature effect on the behavior of the solute.

The present paper deals with the studies carried out on the effect of 2-butanone on the temperature corresponding to adiabatic compressibility minimum (TACM), sound velocity maximum (TSVM), and specific impedance maximum (TSAIM) of water in order to see how the hydrophobic character of 2-butanone would change with temperature.

Experimental

Analar grade 2-butanone was used after necessary purification. The purity of the sample was checked by determining the density at 25 °C using a bicapillary pycnometer with an accuracy of 2 in 10^5. The density value, 800.44 kg m^{-3}, is in good agreement with the data available in the literature.[14] Ultrasonic velocity in pure liquid and aqueous solution was determined using a single crystal variable path interferometer working at 3 MHz with an accuracy of ±0.003%. The details of experimental technique were published elsewhere.[12] Ultrasonic velocities and densities were determined at an interval of ca. 2 °C over a temperature range of 34—70.5 °C.

Results and Discussion

The measurements of ultrasonic velocity in and density of aqueous 2-butanone solution as a function of temperature are presented in Table 1. Adiabatic compressibility ($\beta=1/u^2\rho$) and specific acoustic impedance ($z=u\rho$) are evaluated from the experimental data. The template method[12] has been employed to fix TACM, TSVM, and TSAIM with an accuracy of ±0.4 °C, ±0.2 °C, and ±0.3 °C respectively. The ultrasonic

Table 1. u and ρ at Different Temperatures for the System: Water-2-Butanone

t / °C	u / m s^{-1}	ρ / 10^3 kg m^{-3}	t / °C	u / m s^{-1}	ρ / 10^3 kg m^{-3}
	X_2=0.0082			X_2=0.0144	
45.29	1549.18	0.98754	37.83	1551.14	0.98827
47.86	1551.38	0.98640	40.05	1553.21	0.98734
50.07	1553.02	0.98540	42.01	1554.70	0.98650
52.34	1554.46	0.98433	44.13	1556.27	0.98557
54.71	1555.78	0.98319	46.40	1557.57	0.98455
56.97	1556.75	0.98208	48.44	1558.55	0.98362
59.09	1557.39	0.98100	50.78	1559.65	0.98253
61.31	1557.92	0.97985	53.04	1560.33	0.98146
63.93	1558.35	0.97846	55.16	1560.75	0.98043
66.09	1558.37	0.97728	57.58	1561.03	0.97924
68.51	1558.27	0.97593	59.85	1561.07	0.97810
70.53	1558.07	0.97478	61.96	1560.91	0.97700
	X_2=0.0108			X_2=0.0194	
42.97	1550.76	0.98590	34.05	1554.38	0.98636
45.49	1552.72	0.98482	36.72	1556.83	0.98523
48.26	1554.86	0.98358	39.29	1558.69	0.98412
50.43	1556.07	0.98258	41.86	1560.15	0.98298
52.59	1557.21	0.98156	44.23	1561.35	0.98190
54.81	1558.05	0.98049	46.40	1562.07	0.98089
57.23	1558.81	0.97923	48.66	1562.59	0.97982
59.59	1559.25	0.97808	50.78	1562.99	0.97879
61.91	1559.47	0.97687	52.89	1563.11	0.97775
64.18	1559.47	0.97565	55.01	1563.13	0.97669
66.58	1559.38	0.97433	57.33	1562.91	0.97550
68.71	1558.85	0.97314	59.24	1562.55	0.97451

velocity data have been corrected for diffraction effects.[13]

The adiabatic compressibility minimum (T_β) of the solution is given[5,12] by

$$T_\beta = \left[64 - \frac{\phi_2}{\phi_1}\frac{\alpha_\beta}{0.0032}\right]\left[1 + \frac{\phi_2}{\phi_1}\frac{\alpha_\beta^1}{0.0016}\right]^{-1} - \left[\frac{d\beta^E}{dt}\right]\left[1 + \frac{\phi_2}{\phi_1}\frac{\alpha_\beta^1}{0.0016}\right]^{-1}[\phi_1 \times 0.0032]^{-1}, \quad (1)$$

where ϕ_1 and ϕ_2 represent the volume fractions of pure water and organic solute respectively in the solution. α_β and α_β^1 are the constants of organic solute involved in adiabatic compressibility versus temperature relation given by

$$\beta_2 = \beta_2^\circ + \alpha_\beta t + \alpha_\beta^1 t^2. \quad (2)$$

The sound velocity maximum (T_u) of the solution is given[5,15] by

$$T_u = 74 - \left[\frac{\phi_2}{\phi_1}\right]^2 \frac{w_1}{w_2}\frac{\alpha_u}{0.049}\left[\frac{u_1}{u_2}\right]^3 - \frac{w_1}{\phi_1^2}\frac{u_1^3}{0.098}\left[\rho\frac{d\beta^E}{dt} + \beta^E\frac{d\rho}{dt}\right], \quad (3)$$

where w_1 and w_2 represent weight fractions of pure water and organic solute respectively in the solution. α_u is the temperature coefficient of sound velocity in the relation

$$u_2 = u_2^\circ - \alpha_u t. \quad (4)$$

The specific acoustic impedance maximum (T_z) of the solution is given[8] by

$$T_z = -\frac{\frac{7.5603\ w_1}{z_1^3} + \frac{2\alpha_z w_2}{z_2^3}}{\frac{-0.13404\ w_1}{z_1^3} + \frac{4\alpha_z^1 w_2}{z_2^3}} + \frac{\frac{1}{\rho}\left[\frac{d\beta^E}{dt} - \frac{\beta^E}{\rho}\frac{d\rho}{dt}\right]}{\frac{-0.13404\ w_1}{z_1^3} + \frac{4\alpha_z^1 w_2}{z_2^3}}, \quad (5)$$

where α_z and α_z^1 are the temperature coefficients of specific acoustic impedance in the relation

$$z_2 = z_2^\circ + \alpha_z t + \alpha_z^1 t^2 \quad (6)$$

The values of β_2°, α_β, α_β^1, u_2°, α_u, z_2°, α_z, and α_z^1 for 2-butanone are evaluated using the experimentally determined ultrasonic velocity and density data at different temperatures and the values are presented in Table 2.

In Eqs. 1, 3, and 5, first term ($T_{\beta \text{ or u or z id}}$) represents the dilution effect and second term ($\Delta T_{\beta \text{ or u or z str}}$) represents the structural contribution. ($\Delta T_{\beta \text{ or u or z str}}$) can be evaluated experimentally from the relation

$$(\Delta T_{\beta \text{ or u or z str}})_{exp} = T_{\beta \text{ or u or z exp}} - T_{\beta \text{ or u or z id}}. \quad (7)$$

The results of $(\Delta T_{\beta\ str})_{exp}$, $(\Delta T_{u\ str})_{exp}$, and $(\Delta T_{z\ str})_{exp}$ are presented in Table 3.

The variation of $[\Delta T_{\beta\ str}]_{exp}$ with mole fraction x_2 of 2-butanone is shown in Fig. 1. From this figure it is clear that the structural shifts are positive throughout the concentration range, indicating that the solute behaves as structure maker.

The concentration dependence of ϕ_C and ϕ_V of 2-butanone have been studied by Roux et al.[9] over a temperature range of 4 to 40 °C. The initial slopes are negative and become less negative as the temperature increases. The initial slopes exhibit a flat minimum around 40 °C. The slight change in the initial slopes

Table 2. Pure Liquid Parameters of 2-Butanone

$\beta_2^\circ/(10^{-11}\,m^2N^{-1})$	74.367
$\alpha_\beta/(10^{-11}\,m^2N^{-1}\,°C^{-1})$	0.3759
$\alpha_\beta^1/(10^{-14}\,m^2N^{-1}\,°C^{-2})$	6.2850
$u_2^\circ/(m\,s^{-1})$	1299.94
$\alpha_u/(m\,s^{-1}\,°C^{-1})$	4.2117
$z_2^\circ/(10^3\,kg\,m^{-2}\,s^{-1})$	1076.90
$\alpha_z/(10^3\,kg\,m^{-2}\,s^{-1}\,°C^{-1})$	−4.9216
$\alpha_z^1/(kg\,m^{-2}\,s^{-1}\,°C^{-2})$	4.916

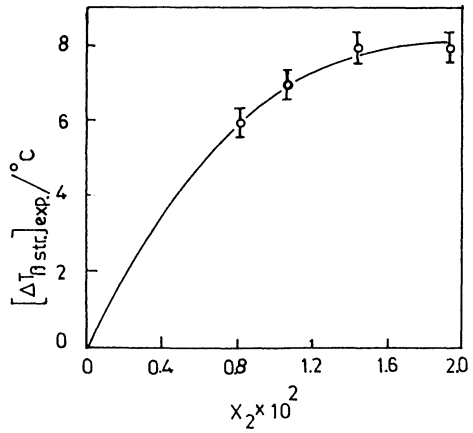

Fig. 1. Variation of $[\Delta T_{\beta\ str}]_{exp}$ with mole fraction (X_2) of 2-butanone.

Table 3. Experimental and Theoretical Values of ($\Delta T_{\beta str}$), ($\Delta T_{u\ str}$) and ($\Delta T_{z\ str}$) at Different Mole Fractions for the System: Water-2-Butanone

X_2	$(\Delta T_{\beta\ str})_{exp}$ °C	$(\Delta T_{\beta\ str})_{th}$ °C	$(\Delta T_{u\ str})_{exp}$ °C	$(\Delta T_{u\ str})_{th}$ °C	$(\Delta T_{z\ str})_{exp}$ °C	$(\Delta T_{z\ str})_{th}$ °C
0.0082	5.9±0.4	5.4	7.2±0.2	9.8	5.0±0.3	4.2
0.0108	6.9±0.4	6.1	8.2±0.2	11.5	5.6±0.3	5.2
0.0144	7.9±0.4	6.7	8.9±0.2	13.3	5.9±0.3	6.2
0.0194	7.9±0.4	7.0	9.2±0.2	14.5	6.2±0.3	7.2

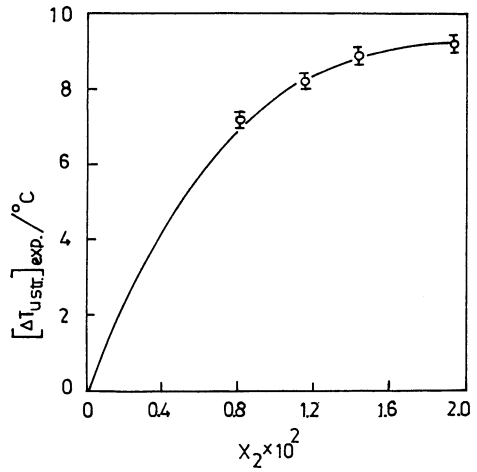

Fig. 2. Variation of $[\Delta T_{u\ str}]_{exp}$ with mole fraction (X_2) of 2-butanone.

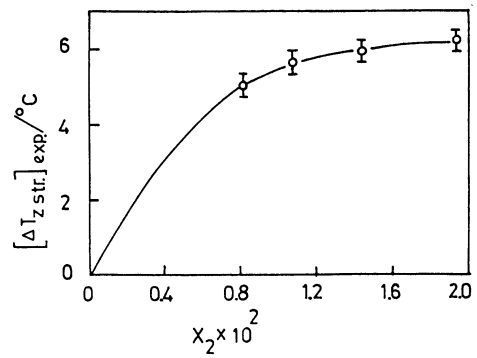

Fig. 3. Variation of $[\Delta T_{z\ str}]_{exp}$ with mole fraction (X_2) of 2-butanone.

as a function of temperature still indicate the hydrophobic character of 2-butanone (the initial slope A_V at 40 °C is -0.11 cm^3 mol^{-2} kg).

$[\Delta T_{u\ str}]_{exp}$ (Fig. 2) is positive for 2-butanone and the magnitude is found to increase with increase in the concentration, indicating structural promoting nature of solution.

The variation of $[\Delta T_{z\ str}]_{exp}$ with mole fraction x_2 is shown in Fig. 3. $[\Delta T_{z\ str}]_{exp}$ is positive and increases with increase in concentration. This trend also confirms hydrophobic character of 2-butanone. From these studies, one can infer that 2-butanone is hydrophobic throughout the temperature range of the present study.

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