Limiting Partial Molar Volumes (V_{23}^∞) in Solvent (1) – [Solute (2) + Solute (3)] Systems and the Effects of Ionic Hydration on V_{23}^∞

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Abstract

Ionic hydration and electrostriction are very important phenomena in various fields such as medical science, biochemistry, and chemical engineering. The present study is the first to focus on these parameters at infinite dilution. Limiting partial molar volumes (V_{23}^∞) in a solvent (1) – [solute (2) + solute (3)] system were measured at several solute compositions x_3 [$=n_3/(n_2+n_3)$] at 30.00 ± 0.05 °C. When the mixed solutes (2 and 3) only slightly ionized, V_{23}^∞ were observed on the additivity line. This result was attributed to the fact that only solvent (1) molecules can exist around an isolated solute (2) molecule or an isolated solute (3) molecule at infinite dilution. However, V_{23}^∞ in water – [pyridine + fatty acid (acetic acid, propionic acid, or butyric acid)] systems negatively deviate from the additivity line. By measuring electrical conductivity (κ) and mixing enthalpy (ΔH_{mix}), the negative deviations of V_{23}^∞ from the additivity line were attributed to the ionic hydration of pyridine and the fatty acid. As a result, by measuring V_{23}^∞ at several solute compositions, the electrostriction in water – [pyridine + fatty acid] systems was observed. Conversely, V_3^∞ in all 14 [solvent (1) + solvent (2)] – solute (3) systems deviated in complicated ways from the additivity line. Unfortunately, we could not clarify the reason behind this deviation because numerous factors had to be considered. Thus, it was confirmed that the behavior of V_3^∞ is much more complicated than that of V_{23}^∞ . The solvents used to study V_{23}^∞ and V_3^∞ are as follows: water, pyridine, acetic acid, propionic acid, butyric acid, benzene, acetone, chloroform, methanol, ethanol, DMF, carbon tetrachloride, isobutylamine, isobutyl alcohol, *n*-heptane, and *n*-octane.

Keywords Limiting partial molar volume · Electrical conductivity · Mixing enthalpy · Ionic hydration · Electrostriction

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1 Introduction

Recently, we experimentally studied the effects of the vol% of voids (i.e., empty spaces) in a solvent and the repulsive solute–solvent interactions, on limiting partial molar volumes (V_2^∞) in solvent (1)–solute (2) systems at infinite dilution [1]. In the present paper, we experimentally studied the behavior of V_{23}^∞ in solvent (1)–[solute (2) + solute (3)] systems at an infinite dilution. Furthermore, for comparison, the behavior of V_3^∞ in [solvent (1) + solvent (2)]–solute (3) systems has been investigated.

Generally, V_2^∞ in solvent (1)–solute (2) systems is defined by Eq. 1 at an infinite dilution.

$$V_2^\infty \equiv \left(\frac{\partial V}{\partial n_2} \right)_{T,P,n_1} \quad (1)$$

where V is the volume of the system, n_1 and n_2 denote the numbers of moles of solvent (1) and solute (2), respectively, and T and P denote the temperature (K) and pressure (Pa), respectively. In Eq. 1, V_2^∞ is the limiting value when n_2 approaches zero. That is, $V_2^\infty \equiv \lim_{n_2 \rightarrow 0} V_2$. Therefore, V_2^∞ corresponds to the volume increment of the system when 1 mol of solute (2) is dissolved in a large amount of solvent (1) under constant temperature and pressure.

V_{23}^∞ in solvent (1)–[solute (2) + solute (3)] systems can be expressed by Eq. 2 at infinite dilution.

$$V_{23}^\infty \equiv \left(\frac{\partial V}{\partial n_{23}} \right)_{T,P,n_1} \quad (2)$$

where V is the volume of the system, n_1 and n_{23} are the mole number of solvent (1) and the mixed solutes (2 and 3), respectively. V_{23}^∞ corresponds to the volume increment of the system when 1 mol of the mixed solutes (2 and 3) is dissolved in a large amount of solvent (1) under constant temperature and pressure. In Eq. 2, V_{23}^∞ is the limit value when n_{23} approaches zero. That is, $V_{23}^\infty \equiv \lim_{n_{23} \rightarrow 0} V_{23}$. Therefore, V_{23}^∞ at infinite dilution will reflect the volume occupied by a single hypothetical mixed molecule with average properties. Thus, it can be considered that V_{23}^∞ reflects the volume occupied by one isolated solute (2) molecule or by one isolated solute (3) molecule at an infinite dilution.

In this study, V_{23}^∞ in each solvent (1)–[solute (2) + solute (3)] system were measured at several solute compositions (x_3) at 30.00 ± 0.05 °C. Here x_3 can be expressed as follows:

$$x_3 = \frac{n_3}{n_2 + n_3} \quad (3)$$

where n_2 and n_3 are mole numbers of solute (2) and solute (3), respectively.

When the mixed solutes (2 and 3) are slightly ionized, V_{23}^∞ values were observed on the additivity line. However, V_{23}^∞ in water–[pyridine + fatty acid] systems deviated negatively from the additivity line. As pyridine and fatty acids are a weak organic base and a weak organic acid, respectively, they are expected to ionize according to the acid–base chemistry in water at an infinite dilution. Therefore, the reason for the negative deviation of V_{23}^∞ from the additivity line was investigated by measuring the electrical conductivity (κ) and mixing enthalpy (ΔH_{mix}).

For comparison, V_3^∞ in each [solvent (1) + solvent (2)] – solute (3) system was measured at several solvent compositions (x_2) at 30.00 ± 0.05 °C. Here, V_3^∞ and x_2 can be expressed by Eqs. 4 and 5, respectively.

$$V_3^\infty = \left(\frac{\partial V}{\partial n_3} \right)_{T, P, n_{12}} \quad (4)$$

$$x_2 = \frac{n_2}{n_1 + n_2}. \quad (5)$$

2 Experimental

2.1 Chemicals

Organic solvents of JIS special grade (purity: $\geq 99\%$) purchased from Kanto Chemical Co., Inc. and ion-exchanged water purchased from Kishida Chemical Co., Ltd. were used without further purification. Experimental samples were prepared by weight.

2.2 Calculation of V_{23}^∞

$V_{23}^\infty/\text{cm}^3 \cdot \text{mol}^{-1}$ values were calculated using an equation of the approximation curve of ρ vs. C plot, where $\rho/\text{g} \cdot \text{cm}^{-3}$ is the density of the solution and $C/\text{g} \cdot \text{cm}^{-3}$ is the mass concentration of the solute. Here, the approximation curve of ρ vs. C plot was calculated by the least-squares method. The instrument used for density measurements was a Lipkin–Davison type pycnometer with a capacity of 5 cm^3 . The volume scale of the pycnometer was calibrated using degassed ion-exchanged water with an apparent density of $0.99449 \text{ g} \cdot \text{cm}^{-3}$, i.e., $0.99565 \text{ g} \cdot \text{cm}^{-3}$ subtracted by air density $0.00116 \text{ g} \cdot \text{cm}^{-3}$. V_{23}^∞ in each solvent (1) – [solute (2) + solute (3)] system was determined at several x_3 at 30.00 ± 0.05 °C.

Detailed methods for measuring ρ and calculating V_{23}^∞ are presented in previous research [1]. For example, the extrapolation procedure and the graph (ρ vs. C plot) for calculating V_2^∞ in the acetic acid (1) – pyridine (2) system are given in Fig. 1 of the previous paper [1]. In this graph, V_2^∞ in the acetic acid (1) – pyridine (2) system is given as $50.9 \text{ cm}^3 \cdot \text{mol}^{-1}$.

The measurement precision of V_{23}^∞ was estimated to be within 1% by referring to both the V_2^∞ values reported by several other researchers [2] and the reproducibility of V_2^∞ of water in 23 different solvents where V_2^∞ of water in the respective solvent was measured twice by us [1].

2.3 Measurement of Electrical Conductivity (κ)

$\kappa/\text{mS} \cdot \text{cm}^{-1}$ values of a solution comprising solvent (1) (95 wt%) and [solute (2) + solute (3)] (5 wt%) were measured at several x_3 at 30 °C using a conductivity meter (ECT-estr 11) purchased from the AS ONE Corporation. The operation of this instrument was extremely simple because the κ values are directly shown. The κ data can be considered to be approximately the values at infinite dilution because of the small value of 5 wt% of [solute (2) + solute (3)]. The precision of the used conductivity meter was $1 \mu\text{S} \cdot \text{cm}^{-1}$.

Fig. 1 Dependence of V_{23}^{∞} in solvent (1)–[solute (2)+solute (3)] systems, where the mixed solutes (2 and 3) only slightly ionized, on x_3 at 30.00 ± 0.05 °C. Here, x_3 is the solute composition expressed by the following equation: $x_3 = n_3/(n_2 + n_3)$, where n_2 and n_3 are mole numbers of solute (2) and solute (3), respectively

2.4 Measurement of Mixing Enthalpy (ΔH_{mix})

Mixing enthalpy (ΔH_{mix})/kJ·mol^{−1} values were measured by mixing 5 g of [solute (2) + solute (3)] into 95 g of solvent (1) at several x_3 at 27 °C. Here, ΔH_{mix} corresponds to the dissolution enthalpy of the mixed solutes (2 and 3), when 1 mol of them is dissolved into a large amount of solvent (1). The detailed method for measuring ΔH_{mix} is presented in a previous study [1]. A schematic of the apparatus used for measuring ΔH_{mix} is shown in Fig. 2 of our previous paper [1]. As shown in this figure, all ΔH_{mix} were measured in a measurement room with temperature of 27 °C. Thus, the measurement temperature of H_{mix} was unfortunately different from those of V_{23}^{∞} , V_3^{∞} and κ . The measurement precision of ΔH_{mix} was estimated to be $\pm 5\%$ by referring to both the ΔH_{mix} values reported by several other researchers [3] and the reproducibility of the ΔH_{mix} values obtained by us [1].

Fig. 2 Dependence of V_{23}^{∞} in water – [pyridine + fatty acid] systems on x_3 at 30.00 ± 0.05 °C

3 Results and Discussion

The numerical results of $V_{23}^{\infty}/\text{cm}^3\cdot\text{mol}^{-1}$, $-\Delta V_{23}^{\infty}/\text{cm}^3\cdot\text{mol}^{-1}$, $\kappa/\text{mS}\cdot\text{cm}^{-1}$, $\Delta H_{\text{mix}}/\text{kJ}\cdot\text{mol}^{-1}$, and $V_3^{\infty}/\text{cm}^3\cdot\text{mol}^{-1}$ are presented in Tables 1, 2, 3, 4, and 5, respectively.

3.1 Dependence of V_{23}^{∞} on x_3

Figure 1 shows the variation of V_{23}^{∞} in solvent (1) – [solute (2) + solute (3)] systems, where the mixed solutes (2 and 3) can hardly ionize, on x_3 at 30.00 ± 0.05 °C. Here, by measuring κ , we were able to determine that the mixed solutes (2 and 3) were only slightly ionized. All V_{23}^{∞} values in Fig. 1 were observed on the additivity line, which means the line connecting the point of V_{23}^{∞} value at $x_3=0$ and the point of V_{23}^{∞} value at $x_3=1$. These experimental results can be explained as follows. Only solvent (1) molecules can exist around an isolated solute (2) molecule or an isolated solute (3) molecule at infinite dilution. In theory, even if x_3 is changed, the volume occupied by one isolated solute (2) molecule or one isolated solute (3) molecule at infinite dilution should not change. As a result, all V_{23}^{∞} in Fig. 1 were observed on the additivity line.

However, as shown in Fig. 2, V_{23}^{∞} in water – [pyridine + fatty acid (acetic acid, propionic acid, or butyric acid)] systems deviated negatively from the additivity line. By measuring the κ and ΔH_{mix} values, we attempted to clarify the reason why V_{23}^{∞} deviated from the additivity line.

3.2 Dependences of $-\Delta V_{23}^{\infty}$ and κ on x_3 (in the Case of Water – [Pyridine + Fatty Acid] Systems)

Figures 3 and 4 show the dependence of $-\Delta V_{23}^{\infty}$ and κ on x_3 , respectively, in the case of water – [pyridine + fatty acid] systems. Here, $-\Delta V_{23}^{\infty}/\text{cm}^3\cdot\text{mol}^{-1}$ is the magnitude of the negative deviation of V_{23}^{∞} from the additivity line. The κ values are considered to be almost proportional to the number of ions. It was found from Figs. 3 and 4 that the shape of the approximation curve of $-\Delta V_{23}^{\infty}$ was substantially similar to the curve of κ . All approximation curves of $-\Delta V_{23}^{\infty}$ and κ had a maximum at $x_3 \approx 0.5$. The $-\Delta V_{23}^{\infty}$ values at $x_3=0$ and 1 were naturally zero. The κ values at $x_3=0$ and 1 were nearly zero and very small, respectively.

From the above experimental results, certain conclusions were drawn. At $x_3=0.5$, all pyridine and fatty acid molecules easily ionize in water, but at $x_3 \neq 0.5$, the excess pyridine or fatty acid molecules are only slightly ionized. Therefore, $-\Delta V_{23}^{\infty}$ was proportional to the number of ions of pyridine and the fatty acid. Furthermore, $-\Delta V_{23}^{\infty}$ caused by one pyridine ion is nearly equal to that caused by one fatty acid ion. Therefore, it was concluded from the results of $-\Delta V_{23}^{\infty}$ and κ that negative deviations of V_{23}^{∞} from the additivity line resulted from the ionization of pyridine and the fatty acid.

The $-\Delta V_{23}^{\infty}/V_{23}^{\infty}$ ratio at $x_3=0.5$, calculated from Figs. 2 and 3, is 8.6% (for acetic acid), 8.6% (for propionic acid), and 7.0% (for butyric acid). These large values indicate that the negative deviations of V_{23}^{∞} from the additivity line are considerable. Here, the relatively small value of 7.0% (butyric acid) may be due to the smallest κ value and the largest van der Waals volume of butyric acid.

Table 1 Numerical results of V_{23}^{∞} in solvent (1)–[solute (2)+solute (3)] systems at several x_3 [$=n_3/(n_2+n_3)$] at 30.00 ± 0.05 °C (refer to Figs. 1 and 2)

System	x_3	$V_{23}^{\infty} (\text{cm}^3 \cdot \text{mol}^{-1})$
Benzene – [acetone + chloroform]	0	74.3
	0.200	75.7
	0.400	77.6
	0.600	78.6
	0.800	80.8
	1	82.2
Acetone – [pyridine + acetic acid]	0	79.9
	0.248	74.1
	0.466	68.3
	0.664	63.1
	0.840	58.2
	1	53.9
Water – [acetone + methanol]	0	66.8
	0.377	55.9
	0.644	48.2
	0.845	42.5
	1	38.1
Water – [acetone + pyridine]	0	67.1
	0.156	68.4
	0.329	70.6
	0.525	72.5
	0.747	75.1
	1	77.2
Water – [acetone + acetic acid]	0	66.8
	0.246	63.3
	0.492	60.2
	0.743	55.9
	1	52.3
Water – [pyridine + fatty acid]		
Water – [pyridine + acetic acid]	0	77.7
	0.248	67.9
	0.466	60.6
	0.664	56.4
	0.840	53.9
	1	52.3
Water – [pyridine + propionic acid]	0	77.7
	0.211	72.4
	0.416	68.4
	0.616	66.8
	0.811	67.1
	1	68.6

Table 1 (continued)

System	x_3	V_{23}^{∞} (cm ³ ·mol ⁻¹)
Water – [pyridine + butyric acid]	0	77.6
	0.184	75.3
	0.375	75.1
	0.575	76.2
	0.783	79.4
	1	84.4

Table 2 Numerical results of $-\Delta V_{23}^{\infty}$ in water (1) – [pyridine (2) + fatty acid (3)] systems at several x_3 at 30.00 ± 0.05 °C (refer to Fig. 3)

System	x_3	$-\Delta V_{23}^{\infty}$ (cm ³ ·mol ⁻¹)
Water – [pyridine + acetic acid]	0	0
	0.20	3.0
	0.40	4.5
	0.60	4.7
	0.80	3.2
	1	0
Water – [pyridine + propionic acid]	0	0
	0.20	3.5
	0.40	5.4
	0.60	5.6
	0.80	3.9
	1	0
Water – [pyridine + butyric acid]	0	0
	0.20	2.8
	0.40	5.0
	0.60	5.1
	0.80	3.2
	1	0

3.3 Dependence of ΔH_{mix} on x_3

As shown in Fig. 5, ΔH_{mix} were observed on the additivity line in water – [solute (2) + solute (3)] systems, where the mixed solutes (2 and 3) only slightly ionized. However, as shown in Fig. 6, ΔH_{mix} deviated negatively from the additivity line in water – [pyridine + fatty acid] systems. Here, ΔH_{mix} corresponds to the dissolution enthalpy of the mixed solutes (2 and 3), namely pyridine and the fatty acid, when 1 mol of the mixed solutes (2 and 3) was dissolved into a large amount of water, as mentioned in Sect. 2.

Generally, as ΔH_{mix} decreases, the attractive interaction between solute and solvent molecules increases [1]. Therefore, the above experimental results indicate that V_{23}^{∞} negatively deviated from the additivity line because of the strong attractive ion–H₂O interaction (i.e., ionic hydration). Generally, ionic hydration breaks the water structure and therefore decreases the distance between the ion and H₂O molecule [4–9]. Hence, it can be concluded that ionic hydration largely decreased the volume of the aqueous solution.

Table 3 Numerical results of κ of a solution comprising of water (1) (95 wt%) and [pyridine (2)+fatty acid (3)] (5 wt%), at several x_3 at 30 °C (refer to Fig. 4)

Solution (or system)	x_3	($\kappa/\text{mS}\cdot\text{cm}^{-1}$)
Water – [pyridine + acetic acid]	0	0.01
	0.248	9.00
	0.468	13.90
	0.662	12.70
	0.837	7.60
Water – [pyridine + propionic acid]	1	1.28
	0	0.01
	0.207	6.80
	0.415	10.80
	0.614	10.50
Water – [pyridine + butyric acid]	0.809	6.60
	1	0.95
	0	0.01
	0.183	5.70
	0.374	9.10
	0.573	9.40
	0.779	6.20
	1	0.88

From the measurement results of κ and ΔH_{mix} , it was concluded that the negative deviation of V_{23}^∞ from the additivity line resulted from the ionic hydration of pyridine and the fatty acid. Therefore, by measuring V_{23}^∞ at several x_3 values, we can observe electrostriction [4–9] in water – [pyridine + fatty acid] systems. Here, electrostriction is generally a phenomenon where the volume of a solid or liquid in an electric field (E) decreases in proportion to E^2 .

3.4 Behavior of V_3^∞ in [Solvent (1) + Solvent (2)] – Solute (3) Systems

For comparison, the behavior of V_3^∞ in [solvent (1) + solvent (2)] – solute (3) systems was evaluated using a method similar to that used herein. In this case, however, V_3^∞ in each ternary system was measured at several solvent compositions ($x_2 = n_2/(n_1 + n_2)$). The 14 systems examined include: [methanol + DMF]–carbon tetrachloride, [isobutylamine + isobutyl alcohol]–water, [water + acetone]–methanol, [methanol + acetone]–benzene, [water + pyridine]–methanol, [chloroform + *n*-heptane]–acetone, [water + pyridine]–acetic acid, [acetone + *n*-octane]–benzene, [benzene + *n*-heptane]–acetone, and [ethanol + chloroform]–benzene, among others.

V_3^∞ in all 14 systems deviate in a complex manner from the additivity line. For example, the behaviors of V_3^∞ in [methanol + DMF]–carbon tetrachloride, [isobutylamine + isobutyl alcohol]–water, and [water + acetone]–methanol systems are shown in Fig. 7a, b, and c, respectively. However, we could not clarify the reasons why V_3^∞ deviated in these ways from the additivity line because the following factors had to be considered: (a) the preferential solvation of solute (3); (b) the coordination number of the solute (3) molecule; (c) the packing density of the mixed solvent (1 and 2) molecules around the solute (3)

Table 4 Numerical results of ΔH_{mix} measured by mixing 5 g of [solute (2) + solute (3)] into 95 g of solvent (1) at several x_3 at 27 °C (refer to Figs. 5 and 6)

System	x_3	ΔH_{mix} (kJ·mol ⁻¹)
Water – [acetone + methanol]	0	– 8.73
	0.312	– 7.93
	0.548	– 7.33
	0.732	– 6.86
	0.879	– 6.47
	1	– 6.17
Water – [acetone + DMF]	0	– 8.72
	0.165	– 9.61
	0.346	– 10.57
	0.543	– 11.60
	0.760	– 12.75
	1	– 14.04
Water – [acetic acid + acetone]	0	– 0.99
	0.205	– 2.48
	0.408	– 3.45
	0.608	– 4.90
	0.805	– 6.34
	1	– 7.75
Water – [pyridine + acetone]	0	– 7.21
	0.254	– 7.96
	0.475	– 8.03
	0.671	– 8.65
	0.845	– 8.69
	1	– 9.20
Water – [pyridine + fatty acid]		
Water – [pyridine + acetic acid]	0	– 7.88
	0.247	– 8.65
	0.467	– 7.59
	0.664	– 4.42
	0.840	– 2.62
	1	– 0.49
Water – [pyridine + propionic acid]	0	– 7.88
	0.205	– 8.48
	0.415	– 7.67
	0.615	– 6.34
	0.810	– 3.75
	1	– 0.62
Water – [pyridine + butyric acid]	0	– 7.86
	0.182	– 8.05
	0.374	– 8.21
	0.574	– 7.01
	0.782	– 4.29
	1	– 0.72

Table 5 Numerical results of V_3^∞ in [solvent (1) + [solvent (2)] – solute (3)] systems at several x_2 [$=n_2/(n_1 + n_2)$] at 30.00 ± 0.05 °C (refer to Figs. 7 (a), (b), and (c))

System	x_2	V_3^∞ (cm ³ ·mol ⁻¹)
[Methanol + DMF] – carbon tetrachloride	0	101.6
	0.098	95.1
	0.226	95.3
	0.396	95.7
	0.637	96.8
	1	95.1
[Isobutylamine + isobutyl alcohol] – water	0	9.52
	0.197	6.46
	0.396	13.5
	0.596	13.7
	0.796	12.3
	1	16.5
[Water + acetone] – methanol	0	38.08
	0.072	37.98
	0.171	38.36
	0.316	38.94
	0.552	40.12
	1	40.57

Fig. 3 Dependence of $-\Delta V_{23}^\infty$ on x_3 at 30.00 ± 0.05 °C in the case of water – [pyridine + fatty acid] systems. Here, $-\Delta V_{23}^\infty$ is the magnitude of the negative deviation of V_{23}^∞ from the additivity line

molecule; and (d) the voids (i.e., empty spaces) in the mixed solvents (1 and 2). Therefore, it was confirmed that the variation of V_3^∞ is much more complicated than that of V_{23}^∞ .

4 Conclusion

Ionic hydration and electrostriction are very important phenomena in fields including medical science, biochemistry and chemical engineering. The present research about V_{23}^∞ focused on these parameters at infinite dilution. Thus, we were able to obtain clear information about these parameters at infinite dilution, as described below.

Fig. 4 Dependence of κ on x_3 at 30 °C in the case of water – [pyridine + fatty acid] systems

Fig. 5 Dependence of ΔH_{mix} on x_3 at 27 °C in the case of water – [solute (2) + solute (3)] systems, where the mixed solutes (2 and 3) could hardly ionize

Fig. 6 Dependence of ΔH_{mix} on x_3 at 27 °C in the case of water – [pyridine + fatty acid] systems

The V_{23}^{∞} values in solvent (1) – [solute (2) + solute (3)] systems, where the mixed solutes (2 and 3) only slightly ionized, were observed on the additivity line. This result indicated that only solvent (1) molecules can exist around an isolated solute (2) molecule or an isolated solute (3) molecule at infinite dilution. Therefore, even if x_3 is changed at infinite dilution, the volume occupied by one isolated solute (2) molecule or one isolated solute

Fig. 7 Dependence of V_3^∞ in [solvent (1) + solvent (2)] – solute (3) systems on x_2 at 30.00 ± 0.05 °C. Here, x_2 is the solvent composition expressed by the following equation: $x_2 = n_2/(n_1 + n_2)$, where n_1 and n_2 are mole numbers of solvent (1) and solvent (2), respectively

(3) molecule must not change. Consequently, all V_{23}^{∞} values were observed on the additivity line.

However, V_{23}^{∞} in water – [pyridine + fatty acid (acetic acid, propionic acid, or butyric acid)] systems negatively deviate from the additivity line. From the measurement results of κ and ΔH_{mix} , the negative deviations of V_{23}^{∞} from the additivity line were attributed to the ionic hydration of pyridine and the fatty acid. Therefore, by measuring V_{23}^{∞} at several x_3 values, we can observe electrostriction in water – [pyridine + fatty acid] systems.

Conversely, V_3^{∞} in all 14 [solvent (1) + solvent (2)] – solute (3) systems deviated in complex ways from the additivity line. However, we could not clarify the reasons for this because numerous factors had to be considered. Thus, it was confirmed that the behavior of V_3^{∞} is much more complicated than that of V_{23}^{∞} . We intend to consider the behavior of V_3^{∞} in each [solvent (1) + solvent (2)] – solute (3) system in more detail by experiment and theory in the future.

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Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interest.

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