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Cryoscopic and Volumetric Studies in the Maleic Acid + Water System[†]

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Freezing points of aqueous solutions of maleic acid were determined. They served to obtain water activities and osmotic and activity coefficients at freezing temperatures. The integration of the Gibbs−Duhem equation was performed by taking into account the dissociation of maleic acid. Densities of (0.09831, 0.4902, and 0.9790) $\mathrm{mol\cdot kg^{-1}}$ maleic acid solutions were measured at 5 K intervals from T = (288.15 to 333.15) K, and they are compared with the literature results. From the determined densities, the apparent molar volumes, the cubic expansion coefficients, and the second derivatives of volume with respect to temperature which are interrelated with the derivatives of isobaric heat capacities with respect to pressure were evaluated. These derivatives were qualitatively correlated with the changes in the structure of water when maleic acid is dissolved in it.

Introduction

Maleic acid (*cis*-1,2-ethylenedicarboxylic acid) is an important intermediate in many fields of industrial chemistry. Its physical, but mainly chemical properties, were recently summarized by Felthouse et al.[1] (see also a comprehensive list of references therein). Due to the existence of the intermolecular hydrogen bonding in maleic acid, many properties of the acid differ considerably from those of fumaric acid, its trans isomer. In the literature, there is a relatively small number of investigations which are devoted to physical properties of aqueous solutions of maleic acid.[2−13] (solubilities, densities, viscosities, surface tensions, enthalpies, heat capacities, water activities, and dissociation constants). With relation to the behavior of atmospheric aerosols, the modeling of thermodynamic properties of maleic solutions and measurement of water activities was discussed by Clegg and Seinfeld[14] and others.[15,16]

In this work, continuing our previous cryoscopic determinations in systems with important inorganic and organic compounds,[17−21] the freezing points of maleic acid aqueous solutions are presented, as they are unknown in the literature. Using determined *freezing point lowerings* at molality m, $\theta(m) = T_{\mathrm{f.p.}}(\mathrm{H_2O}) - T_{\mathrm{f.p.}}(m)$, the water activities $a_1(m)$ and the stoichiometric osmotic coefficients of maleic acid $\phi(m)$ at freezing temperatures are reported. The integration of the Gibbs−Duhem equation served to obtain the activity coefficients $\gamma(m)$ in the maleic acid + water system.

Densities of aqueous solutions of maleic acid were determined for the first time in 1923 by Weiss and Downs,[2] but unfortunately presented only in graphical form. For a limited concentration range, Lange and Sinks[3] in 1930 correlated densities at T = 298.15 K, and Gómez et al.[8] measured densities in the T = (298.15 to 363.15) K temperature interval. Besides, at T = 298.15 K, densities were reported by us,[7] Sijpkes et al.,[11] and Hyvärinen et al.[13] The densities presented here cover lower temperatures from T = (288.15 to 333.15) K, but similarly, as for other inorganic and organic electrolytes (see for example ref 22), they are limited only to three concentrations, at nearly (0.1, 0.5, and 1.0) $\mathrm{mol\cdot kg^{-1}}$. The reason for this is that the main emphasis here is to obtain temperature dependence of volumetric properties (densities, apparent molar volumes, cubic expansion coefficients, and the change of the heat capacities with pressure) which is related to changes in the structure of water when compounds are dissolved in it.

Table 1. Experimental Freezing Temperature Lowering $\theta(m)$ of Aqueous Solutions of Maleic Acid

m / $\mathrm{mol\cdot kg^{-1}}$	$\theta(m)$ / K	m / $\mathrm{mol\cdot kg^{-1}}$	$\theta(m)$ / K	m / $\mathrm{mol\cdot kg^{-1}}$	$\theta(m)$ / K
0.0010	0.003	0.0501	0.139	1.404	2.99
0.0014	0.004	0.0769	0.215	1.987	4.05
0.0028	0.008	0.1048	0.269	3.085	5.76
0.0051	0.014	0.2459	0.599	4.13	5.18[a]
0.0075	0.021	0.5177	1.168	5.04	5.13[a]
0.0106	0.031	0.6946	1.563		
0.0250	0.076	1.009	2.23		

[a] Supersaturated solutions.

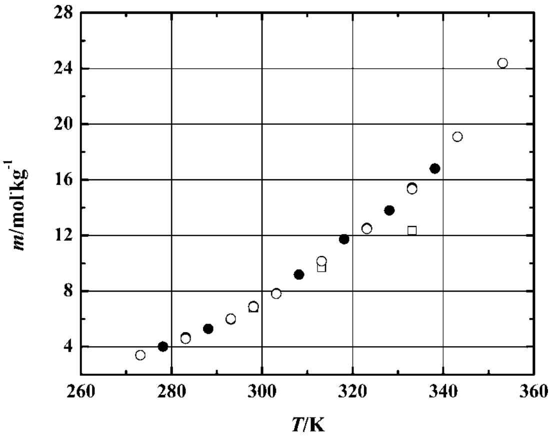

Figure 1. Solubility of maleic acid in water m as a function of temperature T. □, ref 2; ○, ref 3; ●, ref 10.

Experimental Methods

Maleic acid, HOOCCH:CHCOOH (mass fraction 99.7 %), was from BDH and used without further purification. The cryoscopic and density determinations were the same as

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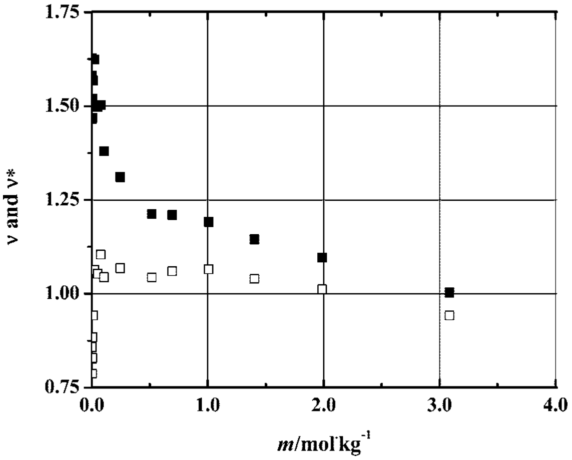

Figure 2. Apparent number of ions and undissociated molecules of maleic acid v and $v^* = v/(1 + \alpha)$ as a function of molality m. ■, v; □, v^*.

described in our previous similar investigations.[17−21] The platinum thermometer had a sensitivity of ± 0.001 K and was calibrated with double-distilled water at the tripled point (± 0.002 K). For a detailed procedure and analysis of freezing point determinations, see reviews 23−25. The uncertainty of our density measurements is $\pm\ 0.0002\ \mathrm{g \cdot cm^{-3}}$ and discussed in detail in ref 26.

Results and Discussion

Freezing Temperatures Determinations. Measured freezing-point lowerings of maleic acid solutions $\theta(m)$ are presented in Table 1. At the two highest concentrations, the measured freezing temperatures belong already to supersaturated solutions. This was clear during experiments from the behavior of cooling curves and from our analysis of the measured solubilities of maleic acid in water. There is a good agreement between reported solubilities[2,3,10] (Figure 1), and they can be correlated by

$$\begin{aligned} &\ln[m^*] = -14.317 - 12207/(T/\mathrm{K}) + 3.5695\ln(T/\mathrm{K}) \\ &\quad \sigma(m^*) = 0.29 \end{aligned} \qquad (1)$$

where m^* is the reduced molality of solution ($m^* = m/m^0$ and $m^0 = 1\ \mathrm{mol \cdot kg^{-1}}$) and $\sigma(m^*)$ denotes the standard deviation in the molality. It is worthwhile to note that the compiled values of maleic acid solubilities in the Yalkovsky and He tabulation[12] were probably incorrectly recalculated.

Freezing-point lowerings of maleic acid solutions can be represented by

$$\begin{aligned} \theta(m)/\mathrm{K} &= 2.364m^* - 0.161m^{*2} \\ \sigma(\theta)/\mathrm{K} &= 0.013 \end{aligned} \qquad (2)$$

where $\sigma(\theta)$ is the standard deviation in the temperature.

At infinite dilution, it is expected that

$$\lim_{m \to 0}(\theta/\lambda m) = v \qquad (3)$$

where $\lambda = 1.86\ \mathrm{kg \cdot mol^{-1} \cdot K}$ is the *cryoscopic constant of water*[27] and v is the number of formed ions when maleic acid is completely dissociated ($v = 3$). However, at finite concentrations, v represents the apparent number of ions and undissociated molecules in the solution. As can be observed in Figure 2 where values of v and $v^* = \mathrm{v}/(1 + \alpha)$ are plotted, the effect of dissociation is evident in a low concentration region where only the degree of the first step of dissociation α is important. Values of v as a function of m are far from the limit $v = 3$ (1:2 type-electrolyte), more close to $v = 2$ (1:1 type electrolyte), and rapidly to approach $v = 1$, i.e., to the expected value for undissociated molecules. In dilute solutions, the observed scattering of points (Figure 2) is predictable, considering that values of v are very sensitive to the accuracy in determined values of the freezing point lowerings $\theta(m)$.

Table 2. Osmotic Coefficients $\phi(m)$ and Activity Coefficients $\gamma(m)$ of Maleic Acid at the Freezing Temperatures

$\frac{m}{\mathrm{mol \cdot kg^{-1}}}$	$\phi(m)$	$\gamma(m)$	$\frac{m}{\mathrm{mol \cdot kg^{-1}}}$	$\phi(m)$	$\gamma(m)$
0.01	0.761	0.921	0.70	1.108	0.974
0.02	0.815	0.824	0.80	1.117	0.997
0.03	0.848	0.793	0.90	1.123	1.018
0.04	0.876	0.783	1.00	1.129	1.038
0.05	0.897	0.779	1.25	1.142	1.083
0.07	0.927	0.778	1.50	1.151	1.123
0.10	0.959	0.787	1.75	1.159	1.159
0.20	1.019	0.821	2.00	1.165	1.192
0.30	1.050	0.859	2.25	1.170	1.222
0.40	1.071	0.893	2.50	1.175	1.251
0.50	1.087	0.923	2.75	1.179	1.277
0.60	1.099	0.950	3.00	1.183	1.303

Using $\theta(m)$ values, it is possible to obtain the activities of water a_1 from[27]

$$-\ln a_1(m) = 9.687 \cdot 10^{-3}\theta(m)/\mathrm{K} + 4.8 \cdot 10^{-6}[\theta(m)/\mathrm{K}]^2 \qquad (4)$$

or in terms of the *stoichiometric osmotic coefficients*

$$\phi(m) = -55.508 \ln a_1 / \sum_i v_i m_i^* \qquad (5)$$

where v_I denote the stoichiometric coefficients and m_i are the molalities of the corresponding species. Maleic acid being a dibasic carboxylic acid dissociates in water in two steps

$$\begin{aligned} &\mathrm{H_2Mel} \rightarrow \mathrm{H^+} + \mathrm{HMel^{-1}};\ K_1 \\ &\mathrm{HMel^{-1}} \rightarrow \mathrm{H^+} + \mathrm{Mel^{2-}};\ K_2 \end{aligned} \qquad (6)$$

and in terms of the dissociation constants, they can be expressed as

$$K_1 = \frac{[\mathrm{H^+}][\mathrm{HMel^{-1}}]}{[\mathrm{H_2Mel}]}F_1 = \frac{m(\alpha + 2\beta)\alpha}{1 - \alpha - \beta}F_1 \qquad (7a)$$

$$K_2 = \frac{[\mathrm{H^+}][\mathrm{Mel^{2-}}]}{[\mathrm{HMel^{-1}}]}F_2 = \frac{m(\alpha + 2\beta)\beta}{\alpha}F_2 \qquad (7b)$$

where F_1 and F_2 are the corresponding quotients of activity coefficients (usually represented by the Debye−Hückel or others expressions) and α and β are the fractions of maleic anions (i.e., $m(\mathrm{HMel^{-1}}) = m\alpha$; $m(\mathrm{Mel^{2-}}) = m\beta$; $m(\mathrm{H_2Mel}) = m(1 - \alpha - \beta)$; and $m(\mathrm{H^+}) = m(\alpha + 2\beta)$). Thus, the stoichiometric osmotic coefficients take the following form if the sum in eq 4 is expressed in terms of fractions α and β

$$\phi(m) = -55.508 \ln a_1 / m^*(1 + \alpha + 2\beta) \qquad (8)$$

where $i = (1 + \alpha + 2\beta)$ is known as the *van't Hoff factor*. However, maleic acid actually can be considered as the monobasic acid because β values are very small as a result of rather large differences in dissociation constants (the fraction of maleic anions $\mathrm{HMel^{-1}}$ α becomes then the degree of dissociation). The reported K_1 and K_2 have nearly constant values $K_1 = (1.17 \pm 0.01) \cdot 10^{-2}\ \mathrm{mol \cdot kg^{-1}}$ and $K_2 = (5.46 \pm 0.03) \cdot 10^{-7}\ \mathrm{mol \cdot kg^{-1}}$ in the T = (273.15 to 313.15) K temperature range.[28,29] Values of $\phi(m)$ calculated from eq 8 are presented in Table 2. There is an alternative procedure initiated by King[30] to represent osmotic coefficients or other quantities in the case of weak electrolytes. In the present case, the King approach is based on the assumption that the logarithms of the water activities due to the undissociated molecules and to the ions are additive. However, such an assumption is inconsistent with the definition of osmotic coefficients as given in eq 5 (difference between both approaches diminishes with an increase in concentration because the fraction of maleic anions α decreases considerably with *m* as is evident from Figure 2).

From an integration of the Gibbs–Duhem equation, the activity coefficients of maleic acid at freezing temperatures can be derived by two procedures using[27]

$$-\ln\gamma(m) = j + \int_0^m j\,\mathrm{d}\ln m - 0.00054\lambda\int_0^\theta (1-j)\,\mathrm{d}\theta$$
$$j = 1 - \theta/\lambda m(1+\alpha) = 1 - v^* \qquad (9)$$

or from the Bjerrum equation

$$\ln\gamma(m) = \phi(m) - 1 + \int_0^m [\phi(m) - 1]\,\mathrm{d}\ln m \qquad (10)$$

At $m \to 0$, the results of experiments are uncertain, and therefore the numerical integration of eq 10 was performed starting from the arbitrary value of $m^{\#} = 0.01\ \mathrm{mol\cdot kg^{-1}}$ where $\phi(m^{\#}) = 0.761$ (calculated using the corresponding θ value)

$$\ln[(\gamma(m)/\gamma(m^{\#})] = \phi(m) - \phi(m^{\#}) + \int_{m^{\#}}^{m} [\phi(m) - 1]\,\mathrm{d}\ln m \qquad (11)$$

and $\gamma(m^{\#}) = 0.921$. This value of the activity coefficient was calculated from the Debye–Hückel equation

$$\ln\gamma(m^{\#}) = -A\sqrt{m^{\#}\alpha}/(1 + aB\sqrt{m^{\#}\alpha}) \qquad (12)$$

where $\alpha = 0.67$; $A = 1.1324\ \mathrm{mol^{-1/2}\cdot dm^{3/2}}$; $B = 3.248\cdot 10^7\ \mathrm{mol^{-1/2}\cdot dm^{3/2}\cdot cm^{-1}}$; and $a = 5\cdot 10^{-8}$ cm. Both numerical integrations using eq 9 or 10 gave very close consistent results. In Table 2 are presented values calculated at rounded molalities of osmotic coefficients $\phi(m)$ and the activity coefficients $\gamma(m)$ at freezing temperatures. They behave similarly to those observed in other systems with organic acids.[18,20,21]

Volumetric Properties. Determined densities $\rho(m,T)$ of aqueous (0.09831, 0.4902, and 0.9790) mol·kg^{-1} solutions of maleic acid in the T = (288.15 to 333.15) K temperature range are presented in Table 3. These densities served to determine the apparent molar volumes $V_{2,\phi}(m,T)$ from

$$V_{2,\phi}(m,T) = M_2/\rho(m,T) + 1000[1/\rho(m,T) - 1/\rho^*(T)]/m \qquad (13)$$

where $M_2 = 116.07\ \mathrm{g\cdot mol^{-1}}$ is the molecular mass of maleic acid and $\rho^*(T)$ are densities of pure water,[31]

$$\rho^*(T)/\mathrm{g\cdot cm^{-3}} = 0.999883 + 5.509202\cdot 10^{-5}t - 7.867989\cdot 10^{-6}t^2 + 5.026034\cdot 10^{-8}t^3 - 1.933126\cdot 10^{-10}t^4$$
$$t = T/\mathrm{K} - 273.15 \qquad (14)$$

and they are reported in Table 3.

As discussed above, densities of maleic acid solutions were determined mainly at T = 298.15 K, and they cover almost the entire concentration range.[7,8,11,13] If the calculated $V_{2,\phi}(m,T)$ values are compared (Figure 3), a rather reasonable agreement between various investigations is observed, but clearly the Hyvärinen et al.[13] densities which were determined in the context of surface tension measurements are less accurate. The apparent molar volumes reported here are systematically lower by about 0.5 cm^3·mol^{-1} when compared with the Manzurola and Apelblat[7] and Sijpkes et al.[11] results. However, this fact has little consequence when the temperature dependence of $V_{2,\phi}(m,T)$ is considered. The only investigation dealing with densities at various temperatures is that of Gómez et al.[8] They reported densities of concentrated solutions of maleic acid, from (0.97 to 22.2) mol·kg^{-1}, depending on solubility limits, at five temperatures, (298.15, 313.15, 333.15, 353.15, and 363.15) K. Evidently, in this case, rather wide gaps between temperatures prevent an accurate differentiation of density with respect to temperature T. The apparent molar volumes of maleic acid $V_{2,\phi}(m,T)$ from this work and the calculated values from the Gómez et al.[8] densities ($m \le 5.77\ \mathrm{mol\cdot kg^{-1}}$) are plotted in Figure 4. As can be observed, $V_{2,\phi}(m,T)$ values monotonically increase with temperature T and molality m, and there is a reasonable agreement between both investigations (if the only comparable concentration nearly m = 1.0 mol·kg^{-1} is taken into account).

Table 3. Densities $\rho(m,T)$, the Apparent Molar Volumes $V_{2,\phi}(m,T)$, the Cubic Expansion Coefficients $\alpha(m,T)$, and $T(\partial^2V/\partial T^2)_P$ of Maleic Acid Aqueous Solutions as a Function of Concentration *m* and Temperature *T*

m/mol·kg^{-1}	0.09831	0.4902	0.9790	0.09831	0.4902	0.9790
T	$\rho(m,T)$	$\rho(m,T)$	$\rho(m,T)$	$V_{2,\phi}(m,T)$	$V_{2,\phi}(m,T)$	$V_{2,\phi}(m,T)$
K	g·cm^{-3}	g·cm^{-3}	g·cm^{-3}	cm^3·mol^{-1}	cm^3·mol^{-1}	m^3·mol^{-1}
288.15	1.00324	1.01850	1.03599	73.68	75.07	75.64
293.15	1.00229	1.01726	1.03447	74.33	75.83	76.34
298.15	1.00104	1.01579	1.03274	75.29	76.52	76.99
303.15	0.99959	1.01410	1.03081	75.85	77.18	77.61
308.15	0.99791	1.01225	1.02874	76.63	77.75	78.17
313.15	0.99607	1.01018	1.02646	76.91	78.35	78.74
318.15	0.99403	1.00798	1.02406	77.40	78.86	79.26
323.15	0.99181	1.00558	1.02147	78.00	79.44	79.81
328.15	0.98941	1.00301	1.01875	78.62	80.01	80.32
333.15	0.98688	1.00036	1.01592	79.14	80.46	80.80

m/mol·kg^{-1}	0.09831	0.4902	0.9790	0.09831	0.4902	0.9790
T	$\alpha\cdot 10^6$	$\alpha\cdot 10^6$	$\alpha\cdot 10^6$	$T(\partial^2V/\partial T^2)_P$	$T(\partial^2V/\partial T^2)_P$	$T(\partial^2V/\partial T^2)_P$
K	K^{-1}	K^{-1}	K^{-1}	cm^3·K^{-1}	cm^3·K^{-1}	cm^3·K^{-1}
288.15	166	224	276	3.31	2.64	2.47
293.15	220	268	315	3.04	2.61	2.44
298.15	269	309	353	2.82	2.57	2.42
303.15	313	349	389	2.63	2.52	2.38
308.15	354	388	424	2.49	2.46	2.33
313.15	392	424	457	2.40	2.38	2.27
318.15	428	459	488	2.36	2.30	2.20
323.15	463	491	518	2.37	2.19	2.12
328.15	498	521	546	2.45	2.07	2.02
333.15	534	548	571	2.58	1.93	1.91

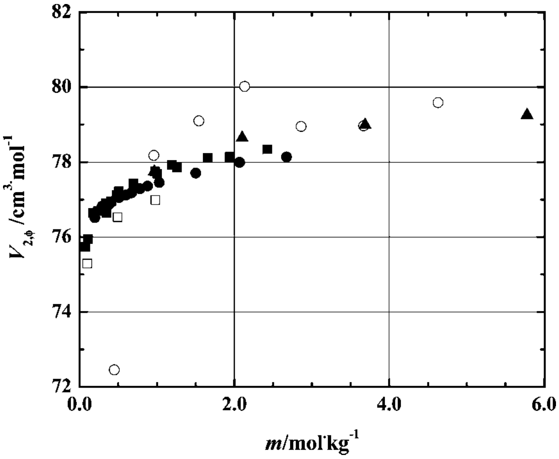

Figure 3. Apparent molar volume of maleic acid solutions $V_{2,\phi}$ as a function of concentration m at T = 298.15 K. ■, ref 7; ▲, ref 8; ●, ref 11; ○, ref 13; □, this work.

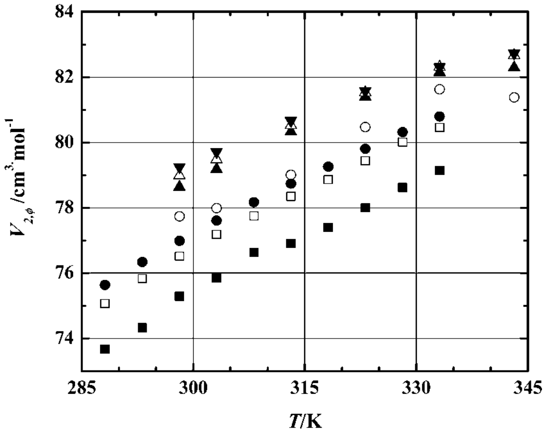

Figure 4. Apparent molar volume of maleic acid solutions $V_{2,\phi}$ as a function of temperature T. ○, $m = 0.966$ mol·kg^{-1}, ref 8; ▲, $m = 2.102$ mol·kg^{-1}, ref 8; △, $m = 3.689$ mol·kg^{-1}, ref 8; ▼, $m = 5.766$ mol·kg^{-1}, ref 8; ■, $m = 0.09831$ mol·kg^{-1}, this work; □, $m = 0.4902$ mol·kg^{-1}, this work; ●, $m = 0.9790$ mol·kg^{-1}, this work.

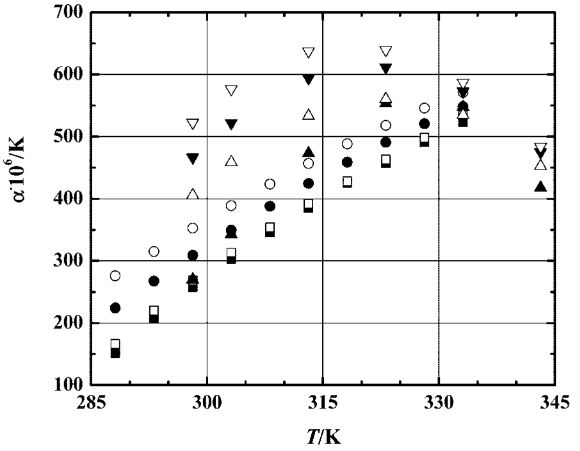

Figure 5. Cubic expansion coefficients of pure water and maleic acid solutions α·10^6 as a function of temperature T. ■, pure water, ref 26; ▲, $m = 0.966$ mol·kg^{-1}, ref 8; △, $m = 2.102$ mol·kg^{-1}, ref 8; ▼, $m = 3.689$ mol·kg^{-1}, ref 8; ▽, $m = 5.766$ mol·kg^{-1}, ref 8; □, $m = 0.09831$ mol·kg^{-1}, this work; ●, $m = 0.4902$ mol·kg^{-1}, this work; ○, $m = 0.9790$ mol·kg^{-1}, this work.

The cubic expansion coefficients of a solution (isobaric thermal expansibilities) are given by

$$\alpha(m, T) = (\partial \ln V/\partial T)_{P,m} = -[\partial \ln \rho(m, T)/\partial T]_{P,m} \quad (15)$$

and they were calculated using the polynomial fits of densities as a function of T. The results of calculations are presented in Table 3. In Figure 5 are plotted $\alpha(m,T)$ values of maleic acid solutions and those of pure water together with the cubic expansion coefficients derived by us using the Gómez et al.[8] densities. As can be observed, in the investigated temperature range, $\alpha(m,T)$ increase with temperature T and molality m and are consistent with the Gómez et al.[8] results for $m = 0.966$ mol·kg^{-1}, but their values above $T = 333.15$ K with $\partial\alpha(m,T)/\partial T < 0$ are rather questionable.

If the second derivative of volume with respect to temperature is considered, then from the Maxwell relation as applied to the differential of enthalpy

$$\mathrm{d}H = C_P\mathrm{d}T + [V - T(\partial V/\partial T)_P]\mathrm{d}P \quad (16)$$

the volumetric and thermal properties of solutions are interrelated in the following way

$$(\partial C_P/\partial P)_{T,m} = -T(\partial^2 V/\partial T^2)_{P,m} = -TV[\alpha^2 + (\partial \alpha/\partial T)_{P,m}] \quad (17)$$

or in terms of density $\rho(m,T)$

$$T(\partial^2 C/\partial T^2)_{P,m} = T(1000 + mM_2)[2(\partial \rho/\partial T)^2_{P,m}/\rho^3(\partial^2 \rho/\partial T^2)_{P,m}/\rho^2] \quad (18)$$

From determined densities, using eq 18, the products $f(m,T) = T(\partial^2 V/\partial T^2)_{P,m}$ which are equal to the change in the isobaric heat capacity with pressure, $-(\partial C_P/\partial P)_{T,m}$, were evaluated, and they are presented in Table 3.

According to Hepler[32] and Neal and Goring,[33] it is possible to obtain from the volume−temperature relations a qualitative description of changes in the structure of water when electrolyte or nonelectrolyte is dissolved in it. They postulated that the second-order derivatives of the partial molar volume of solute at infinite solution with respect to temperature indicates the structure breakers if the derivative value is negative, increases with T, and the curve is concave downward. In the case of structure makers, the second-order derivative is positive and also increases with T, but the curve is concave upward. However, the values of $T[\partial^{2-}V_2(m \rightarrow 0,T)/\partial T^2]_{P,m}$ in very dilute solutions are inaccurate, and therefore it was suggested by us[34] to replace them with $\Delta f(m,T) = f(m,T) - f(m = 0,T)$. Since the values of $f(m = 0,T)$ for pure water are known[26] and $f(m,T)$ are given in Table 3, it is possible to obtain the sign of $\Delta f(m,T)$ which gives an indication about the effect of solute on the structure of water. At three investigated molalities, $\Delta f(m,T)$ values are plotted in Figure 6. As can be seen, $\Delta f(m,T)$ is always negative indicating that for $m \leq 1.0$ mol·kg^{-1} maleic acid behaves as the structure breaking solute. However, there is a significant difference when temperature dependence and the shape of curves in dilute and moderately concentrated solutions are compared. In concentrated solutions of maleic acid, as expected for the structure breakers, the curves are concave downward, but $\Delta f(m,T)$ increases with T only up to about $T = 313$ K and at higher temperatures decreases with T (Figure 6). Such behavior was explained by Hepler by considering that pressure and temperature have a similar effect on the heat capacity when the structure of water is destroyed, and therefore at higher temperatures water starts to conduct as a "normal" liquid. On the contrary, in dilute solutions, the curvature is concave upward and $\Delta f(m,T)$ decreases with T to about $T = 313$ K and at higher temperatures increases with T. As pointed out above, maleic acid when dissolved in water acts as the

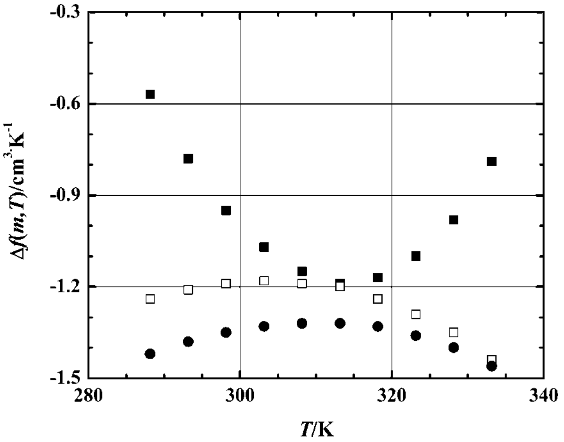

Figure 6. Values of the $\Delta f(m,T)$ function of maleic acid solutions as a function of temperature T. ■, $m = 0.09831$ mol·kg^{-1}; □, $m = 0.4902$ mol·kg^{-1}; ●, $m = 0.9790$ mol·kg^{-1}, this work.

structure breaking solute because $\Delta f(m,T) < 0$, but depending on concentration, the $\Delta f(m,T)$ curves behave differently. Probably, this could be attributed to the fact that in dilute solutions the formed in dissociation reaction ions are more important than the undissociated molecules of maleic acid.

Conclusions

Freezing-point lowerings of maleic acid aqueous solutions were measured, and they were used to evaluate the water activities and osmotic and activity coefficients at freezing temperatures.

Volumetric properties of maleic acid solutions (the apparent molar volumes, the cubic expansion coefficients, the second derivatives of volume with respect to temperature, and the isobaric heat capacities with respect to pressure) were determined from densities of (0.09831, 0.4902, and 0.9790) $\mathrm{mol \cdot kg^{-1}}$, solutions which were measured at 5 K intervals from $T = (288.15$ to $333.15)$ K.

It was found that for $m \leq 1.0\ \mathrm{mol \cdot kg^{-1}}$ maleic acid always behaves as the structure breaking solute. However, in dilute aqueous solutions, the effect of dissociation reactions is predominant.

Acknowledgment

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