Thermochimica Acta, 90 (1985) 33–41
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

CONCENTRATION DEPENDENCE OF ACTIVITY COEFFICIENTS AT SATURATION AND AT 298.15 K EVALUATED FROM HEAT OF CRYSTALLIZATION AND SOLUBILITY DATA

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(Received 4 February 1985)

ABSTRACT

For inorganic electrolytes of $AgNO_3$, $CsNO_3$, KNO_3, $LiNO_3 \cdot 3H_2O$, $NaNO_3$, NH_4NO_3, $RbNO_3$, $TlNO_3$, $KClO_3$, K_2CrO_4, $K_2Cr_2O_7$, K_2SO_4 and $K_2S_2O_8$, the concentration dependence of activity coefficients at saturation is evaluated from heats of crystallization and from the temperature dependence of their solubilities. Calculated values are compared with those deduced from measured data. The degree of their mutual consistency differs considerably from case to case.

INTRODUCTION

Heats of dissolution and/or dilution for certain salts at high concentrations near saturation are available in the literature [1,2] or may be measured with sufficient accuracy by precise solution calorimetry [3,4]. The heat of crystallization, ΔH_c, for certain inorganic salts may thus be determined with an accuracy of a few percent [4,5]. Moreover, the literature data for highly concentrated solutions are also available for some compounds on solubility, m_s, and the temperature dependence of solubility, dm_s/dT [6–10], as well as the concentration dependence of activity and/or osmotic [11–13] coefficients, $\gamma(m)$ and/or $\phi(m)$. The thermodynamic relation between these data has been rigorously derived by Williamson [14], and repeatedly by others [15–18]. It can be represented by

$$\Delta H_c = PRQW \tag{1}$$

where $P = 1 - nm_s/K$ is the stoichiometric term for n moles of water in 1 mole of hydrate, $K = 1000/M_w$ is the number of moles of water (molar

0040-6031/85/$03.30

mass, $M_w = 18.015$), R is the universal gas constant and Q and W are terms defined by

$$Q = \frac{\mathrm{d}\ln m_s}{\mathrm{d}(1/T)} = -\frac{T^2}{m_s}\frac{\mathrm{d}m_s}{\mathrm{d}T} \tag{2}$$

where m_s is the molality at saturation and T is the temperature (K).

$$W = \nu\left[1 + \left(\frac{\partial \ln\gamma}{\partial \ln m}\right)_{P,T}\bigg|_{m_s}\right] = \nu\left[\phi + \left(\frac{\partial \phi}{\partial \ln m}\right)_{P,T}\bigg|_{m_s}\right]$$
$$= -K\left(\frac{\partial \ln a_1}{\partial m}\right)_{P,T}\bigg|_{m_s} = -K\left(\frac{\partial \ln p}{\partial m}\right)_{P,T}\bigg|_{m_s} \tag{3}$$

where ν is the stoichiometric amount of ions in a molecule of a salt, γ is the stoichiometric molal activity coefficient, ϕ is the osmotic coefficient, a_1 is the activity of water in solution, and p is the water vapor pressure over the solution. All derivatives in eqn. (3) are taken at constant pressure, P, and temperature, T, for saturation concentration.

The aim of this work was to determine the slope

$$\beta \equiv \left(\frac{\partial \ln\gamma}{\partial \ln m}\right)_{P,T}\bigg|_{m_s} \tag{4}$$

for selected salts by using heats of crystallization measured by us ($KClO_3$, KNO_3, $K_2Cr_2O_7$ and $K_2S_2O_8$–H_2O systems) or (for some nitrates) derived from the literature, and by using solubilities taken from the well-known solubility tables [6,7], or from a paper [16] which was based on other solubility publications [8–10]. Values of β calculated from these data

$$\beta = \Delta H_c[\nu RQ(1 - nm_s/K)]^{-1} - 1 \tag{5}$$

are compared with those obtained from published data for the dependencies $\phi(m)$ or $\gamma(m)$ given by Robinson and Stokes [11], which were for some cases extended to the saturation region by Voznesenskaya [12], and from critical assessment of these functions for selected uni–univalent electrolytes given by Hamer and Wu [13]. The first two sources [11,12] present their data in the form of tables, so that it is necessary to calculate the derivative of a suitable analytical approximation extrapolated (or interpolated for a few cases) to the saturation molality at 298.15 K. An algorithm of this treatment has been described previously [5]. For each of the systems described, Hamer and Wu [13] have derived a best-fit, semi-empirical, analytical formula. It was thus easy to evaluate the corresponding derivatives directly for the saturation region.

The input heats of crystallization, ΔH_c, Q, and m_s values (right-hand side of eqn. 5) used for the calculation of the concentration dependence of activity coefficients at saturation are summarized in Table 1 (columns 2–4), which also gives a comparison of resulting values of β (Table 1, column 5)

TABLE 1

A comparison of the slope, β, calculated from eqn. (5) by using published values of m_s, Q, and ΔH_c with those from published concentration dependencies of activity or osmotic coefficients

Salt	m_s (mol kg^{-1} H_2O)	Q (K)	ΔH_c (kJ mol^{-1})	β (eqn. 5)	β (from published data)
$KClO_3$	0.7016 [6]	−2965 [6] −3020 [17]	34.7±0.5 [20]	−0.2962 [6] −0.309 [17]	−0.294 [12] −0.2975 [13] −0.2993 [19]
$K_2S_2O_8$	0.2249 [23]	−4008 [23]	63.7±0.5 [22]	−0.3631 [23]	−0.32 [21]
$K_2Cr_2O_7$	0.5128 [6]	−3.616.5 [6]	59.9±0.5 [25]	−0.3354 [11]	−0.333 [12]
K_2SO_4	0.6875 [6]	−1392 [16] −1382.5 [6] −1350 [17]	20.4±0.4 [32]	−0.4124 [16] −0.4084 [11] −0.3942 [17]	−0.390 [12]
K_2CrO_4	3.341 [6]	−307 [6]	8.6±0.9 [30]	+0.124 [6]	+0.08 [12]
KNO_3	3.7896 [6]	−3183 [6] −3210 [2] −3336 [16]	20.3±0.37 [35]	−0.634 [16] −0.619 [2] −0.616 [6]	−0.585 [12] −0.567 [13]
$NaNO_3$	10.8 [6]	−781 [6] −819 [16]	13.0±3.0 [1]	+0.001 [6] −0.045 [16]	+3.90 [13] −0.19 [12] −0.44 [16]
$LiNO_3 \cdot 3H_2O$	12.45 [6]	−4032.3 [16] −2714 [6]	33.5±1.5 [36]	+0.527 [16] +1.269 [6]	+1.055 [12] +1.56 [16]
$RbNO_3$	4.52 [6]	−3607 [6] −3807 [16]	20.0±1.0 [6]	−0.666 [6] −0.684 [16]	−0.67 [12] −0.68 [16]
$CsNO_3$	1.40 [6]	−3389 [6] −3009 [16]	32.1±2.0 [1]	−0.4304 [6] −0.358 [16]	−0.4178 [13] −0.44 [12]
$AgNO_3$	15.12 [6]	−1934 [6] −1965 [16]	9.6 [17]	−0.701 [16] −0.706 [6]	−0.70 [12] −0.753 [11] −0.025 [13]
$TlNO_3$	0.42 [6]	−3490 [6] −3602 [16]	38.5 [17]	−0.3366 [6] −0.3572 [16]	−0.335 [16] −0.333 [13] −0.235 [12] −0.300 [11]
NH_4NO_3	26.8 [6]	−1936.6 [6] −1883 [16]	10.0±3 [1]	−0.689 [6] −0.681 [16]	−0.615 [16] −0.63 [12] −0.759 [13]

with those derived from published data (column 6) [11–13]. Their agreement is discussed below for each system separately.

The solubility data, the values for m_s and the slope of dm_s/dT, are usually scattered. The uncertainty in Q and m_s values is often the main factor responsible for the uncertainty in the slope, β, evaluated from eqn. (5). Reference 6 is a new version of older solubility tables [7] without any possibility for the user to estimate the experimental error of the data presented. Values of Q given by Kirgintsev and Lukyanov [16] are based on two extensive compilations [8] (see also its English version [9]) and on ref. 10. The good agreement of Q values from both the above sources [6,16] in certain cases may be a consequence of the fact that the same original data for the function $m_s(T)$ were used.

RESULTS AND DISCUSSION

The system $KClO_3$-H_2O

The heats of crystallization for this system were evaluated by Nakayama [17] from eqn. (1) as 35.19 kJ mol^{-1} using Q from ref. 9 and W derived from ref. 19. Values of Q and W taken from refs. 6 and 11 yield $\Delta H_c = 34.7 \pm 0.2$ kJ mol^{-1}. Heats of dilution and an integral heat of dissolution at infinite dilution recommended by Parker [1] yield, after differentiation, $\Delta H_c = 34.7 \pm 0.8$ kJ mol^{-1}. These values agree well with that ($\Delta H_c = 34.7 \pm 0.5$ kJ mol^{-1}) calculated from our measurements of dissolution heats in the concentrated region [20]. The β values -0.296 and -0.309 from these ΔH_c data and from Q values mentioned above [6,17] are close to those obtained from published data [12,13,19] for the function $\phi(m)$ or $\gamma(m)$. All three kinds of data are thermodynamically consistent for this system.

The system $K_2S_2O_8$-H_2O

No data on activity or osmotic coefficients near saturation concentration have been found for this system in the literature. Hu and Hepler [21] assumed that aqueous solutions of K_2SO_4 and $K_2S_2O_8$ behave similarly. According to this simplification the value of β for the K_2SO_4-H_2O system at a concentration equal to the saturation concentration of the $K_2S_2O_8$-H_2O system is -0.32. The ΔH_c and Q values necessary for calculating β for $K_2S_2O_8$ from eqn. (5) have been measured quite precisely (see ref. 22 for ΔH_c and ref. 23 for m_s and Q). From these data it follows that the calculated value of β is -0.363 and is in quite close agreement with the value assumed by Hu and Hepler [21]. The similar behavior of the K_2SO_4-H_2O and $K_2S_2O_8$-H_2O systems in the region of concentrated solutions implied by Hu and Hepler [21] was thus at least partly verified.

The system $K_2Cr_2O_7$-H_2O

The heat of crystallization evaluated from old data on the heat of dissolution published by Perreu [24] differs from that deduced by us from

Shmagin and Shidlovskiy's [26] integral heats of dissolution. Moreover, the differential and integral heats measured by Perreu [24] are inconsistent [25]. The value of ΔH_c in refs. 27 and 28 was not considered owing to the fact that this value represents the integral dissolution heat at saturation. The treatment of Shmagin and Shidlovskiy's data [26], Perreu's data [24], and our data [37] of measurement of the integral dissolution heats in concentrated solutions lead to the crystallization heats of 60.0, 60.04–60.08 and 59.4–61.1 kJ mol^{-1}, respectively. Our measurement of differential heats of dissolution [25] leads to $\Delta H_c = 59.95 \pm 0.5$ kJ mol^{-1}. This value seems to be the most probable. The slope, Q, was taken from ref. 6 (-3616.5 K) as a value representing the most probable temperature slope of the solubility. The calculated value of $\beta = -0.3354$ is consistent with the slope from directly measured activities which are listed in ref. 12.

The system K_2SO_4–H_2O

Several different estimates of ΔH_c have been published for this system. By using eqn. (1) Kirgintsev and Lukyanov [16] found $\Delta H_c = 21.06$ kJ mol^{-1}, and Nakayama [17], $\Delta H_c = 20.75$ kJ mol^{-1}. Integral heats of dissolution given in ref. 29, and data from refs. 2 and 31 yield, respectively, $\Delta H_c = 21.0 \pm 0.2$, 20.35 and 20.17 kJ mol^{-1}. The value of ΔH_c in refs. 27 and 28 was not considered for the reasons discussed for the case of the $K_2Cr_2O_7$–H_2O system. The value of ΔH_c measured by Rychlý [32] was preferred by us as probably the most reliable value of ΔH_c available for this system, owing to the extensive measurement of pseudodifferential heats. Since the value of β evaluated from eqn. (5) is about 4.5% higher than that obtained from published values for the function $\gamma(m)$ [12], the question remains as to how much of this small inconsistency is due to the Q value used and how much to the data for the $\gamma(m)$ function from refs. 11 and 12.

The system K_2CrO_4–H_2O

From the heats of dissolution given in Gmelin's Handbook [30], $\Delta H_c = 8.6$ kJ mol $^{-1}$. The value of the temperature dependence of solubility at saturation seems to be extremely low ($Q = -307$ [6]) and also the resulting β value is moderately inconsistent with that deduced from published data [12]. As in the case of the K_2SO_4–H_2O system, further data are needed to identify the sources of this inconsistency.

The system KNO_3–H_2O

Published values of ΔH_c are discrepant, see, e.g., $\Delta H_c = 16.40$ kJ mol^{-1} and $\Delta H_c = 22.8$ kJ mol^{-1} from data in refs. 33 and 34. For β value calculation we prefer the results of our own measurements [35] of pseudodifferential dissolution heats, from which $\Delta H_c = 20.3 \pm 0.2$ kJ mol^{-1}. Values of Q from all three sources [2,6,16] yield values of β about 5% higher than those taken from Hamer and Wu's critical review [13] or from previous classical sources [11,12]. The Q-value seems to be overestimated; it should be about -2800 to be consistent with the above values of ΔH_c and β taken from refs. 11–13.

The system $NaNO_3$–H_2O

Data are rare for estimation of the ΔH_c values. According to our previous paper [5] we neglect the value given by Allakhverdov et al. [34]. Values of $\Delta H_c = 7.66$ and 11.75 kJ mol^{-1} are given in refs. 27 and 28 with uncertain errors. We therefore prefer to use $\Delta H_c = 13.0 \pm 3$ kJ mol^{-1}, which may be calculated from the concentration dependence of apparent relative enthalpy, ϕ_L, and integral heat of dissolution, ΔH_0, recommended by Parker [1]. For an anhydrous salt the following holds

$$\Delta H_c = -\lim_{m \to m_s} \left[\Delta H_0 + \phi_L(m) + m \frac{d\phi_L}{dm} \right] \tag{6}$$

For ΔH_c evaluated from eqn. (6) and for both values of Q, the resulting values of β (see Table 1) approach zero. This is also true for β deduced from the data given in refs. 12 and 16. The value of β evaluated from the correlation recommended by Hamer and Wu [13] differs considerably from these values. It is evident that, close to saturation, the concentration dependencies of the activity and osmotic coefficient as given by Hamer and Wu [13] are not consistent with above data for ΔH_c and Q.

The system $LiNO_3 \cdot 3H_2O$–H_2O

We have found only one value of ΔH_c (33.5 kJ mol^{-1}) given by Tsvetkov and Tsvetkov [36]. Values of Q from other sources [6,16] differ considerably; this is probably due to the ease of formation of supersaturated solutions of lithium nitrate. The activity as well as osmotic coefficients are known even for $m = 20$ [11–13]; saturation molality, $m_s = 12.45$ [6], 12.83 [30], or 12.7 [16] so that no extrapolation was necessary. Data for ΔH_c, Q, and β for this system (Table 1) do not agree satisfactorily, so that further measurement is needed. It seems that the value $Q = -4032$ given by Kirgintsev and Lukyanov [16] is much too low.

The systems $RbNO_3$–H_2O and $CsNO_3$–H_2O

The only available data for ΔH_c were those evaluated by us from data given by Parker [1] for $CsNO_3$–H_2O by using eqn. (6), and an estimate based on eqn. (1) given in ref. 16 for $RbNO_3$–H_2O. For both salts, the Q values given by Broul et al. [6] and by Kirgintsev and Lukyanov [16] differ by 5% for $RbNO_3$ and by 10% for $CsNO_3$. Values of β calculated according to eqn. (5) more or less agree with those deduced from refs. 12 and 13.

The systems $AgNO_3$–H_2O and $TlNO_3$–H_2O

The values of ΔH_c for both systems were available from Nakayama's paper [17]. For $AgNO_3$–H_2O the value of β calculated from the correlation recommended by Hamer and Wu [13] is not consistent with the data on ΔH_c and Q given in Table 1, in contrast to the good agreement of the other data. For the system $TlNO_3$–H_2O the data listed in Table 1 are acceptably consistent, with the exception of the value of β deduced from the data given in refs. 11 and 12.

The system NH_4NO_3–H_2O

No reliable data for determining ΔH_c were found in the literature for this common salt. Parker [1] presents data for ΔH_0 and $\phi_L(m)$ only up to

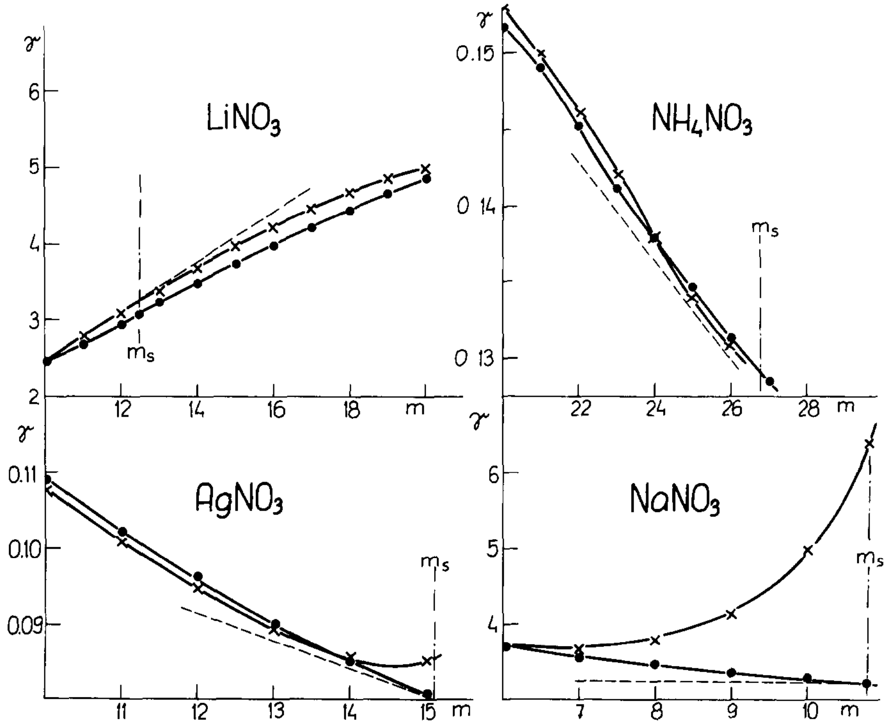

Fig. 1. Illustration of the concentration dependence of activity coefficients for $LiNO_3$, NH_4NO_3, $AgNO_3$ and $NaNO_3$–H_2O systems at 298.15 K in which the slope calculated from eqn. (5) is compared with data of Voznesenskaya [12] (●) and Hamer and Wu [13] (×). (— — —) Our results, (– · – · –) saturation molality, m_s.

$m = 20$ while the values of saturation concentration, $m_s = 26.8$ [6,12], 26.0 [16] or 25.954 [13]. Therefore, a rather high experimental error may be expected for a value evaluated from these data by using eqn. (6). With Q values from refs. 6 and 16, eqn. (5) yields values of β which lie between those derived from refs. 12, 13 and 16. The value of β evaluated from data of Hamer and Wu [13] is higher by 17% than those from refs. 12 and 16. However, until more reliable values of ΔH_c, m_s and Q are known for this system, it can hardly be decided which value of β is most reliable.

The data necessary for the evaluation of eqn. (5) are available only for a limited number of systems. However, at least for certain systems a check on the consistency is useful. Such a comparison of published and calculated data from the calorimetric measurements are presented for $LiNO_3$, NH_4NO_3, $AgNO_3$, and $NaNO_3$ in Fig. 1.

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