

FLOW CALORIMETRY AND DENSITOMETRY AT HIGH TEMPERATURES *

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ABSTRACT

A review of the development of high temperature flow calorimetry is given. Some measurements of apparent molar heat capacity and volume of aqueous 1–1 electrolytes indicate that as the temperature is increased to 650 K the relative individuality of the different salts decreases. The model of a hard sphere ion in a compressible dielectric solvent predicts this behavior.

INTRODUCTION

This paper is a summary of some work carried out at the University of Delaware where the techniques of flow calorimetry and, more recently, flow densitometry have been applied to the study of aqueous solutions at temperatures up to 720 K. A brief review is given of how the flow calorimetric and densitometric techniques were developed and some recent results are presented which indicate that aqueous 1–1 electrolytes lose their relative individuality as the critical point of water is approached.

The early work of Monk and Wadsö [1], Gill and coworkers [2,3] and Picker and coworkers [4,5] showed that flow calorimeters could be used to study very small heat effects on mixing solutions with great sensitivity and speed. In a later paper, Picker et al. [6] showed that flow techniques could be used to measure the difference in volumetric heat capacity between two miscible solutions. This calorimeter revolutionized the measurement of the heat capacities of dilute solutions because of its very great sensitivity and the rapidity with which measurements could be made. The use of flow calorimetric techniques near room temperature led to the consideration of using

* Dedicated to Professor James J. Christensen in memory of his contribution to innovation in calorimetry.

these techniques for the investigation of aqueous solutions at high temperatures. At the University of Delaware we were interested in exploring the properties of electrolytes in solvents of high dielectric constant in the hope of understanding something about the unique nature of water. A natural extension of this work was to measure the properties of aqueous solutions as a function of increasing temperature since, with increasing temperature, water slowly transforms from a highly structured solvent with a high dielectric constant into a less structured solvent with a low dielectric constant. Cobble and coworkers [7,8] using standard calorimetric techniques, had already shown how interesting measurements were at high temperatures. We were convinced that flow calorimetric techniques were the easiest way to make the measurements for the following reasons. (i) There was no vapor present in equilibrium with the liquid, so there were no vapor pressure corrections. (ii) The pressures could be contained in relatively thin-walled tubing so that the calorimetric response time could still be fast. (iii) If solutions were pumped in from outside, experiments could be performed with the same speed as at room temperature. With these advantages in mind, Edwin Messikomer constructed our first flow heat of mixing calorimeter [9] and measured enthalpies of dilution of NaCl(aq) to temperatures of 100 °C. The temperature was not very high but the results showed that the principle was correct; it was just as easy to take measurements at 100 °C as at 25 °C with this calorimeter.

James Christensen and colleagues at Brigham Young University were following a similar path. Shortly after our paper on NaCl appeared, they produced a paper [10] on a flow heat of mixing calorimeter which used an isothermal plate construction and operated to 70 °C and 40 MPa. This paper was another clear indication of the advantages of flow techniques for measurements at high temperatures and showed that measurements at pressures up to 40 MPa were rapid and accurate. At the same time Wormald and coworkers [11–14] were developing flow heat of mixing calorimeters and using them to study gas and liquid mixtures at temperatures from –70 °C to 150 °C.

Our first flow calorimeter was limited to temperatures of 100 °C because of the temperature sensitivity of the thermopile elements used to detect the heat flow. James Mayrath constructed a second flow heat of mixing calorimeter using new thermopile elements to detect the heat flow [15,16]. This calorimeter had heat flow sensors that were expected to last for a while at 200 °C. We collected a large amount of data at temperatures up to 175 °C and then decided to try to obtain data at 200 °C. At 200 °C we worked with the calorimeter for 24 h a day for 5 days until it broke down. During this time the pumps were continually breaking down and needed to be repaired. Over the 5 days we were able to take 96 heat of dilution data points on eight different salts [15,17,18]. This illustrates the rapidity with which data can be taken at high temperature using these instruments.

At this point I realized that a heat capacity calorimeter based on the principles outlined by Picker et al. [6] could be used at high temperatures without having to measure the densities of the solutions at high temperatures. If the sample loop was thermostated at room temperature, and the interface between the reference and sample fluids was located in that sample loop, then all that was required was the densities of the aqueous solutions at the temperature and pressure of the sample loop. David Smith-Magowan built a high temperature heat capacity calorimeter using these principles and a preliminary description of this calorimeter was published in 1980 [16]. A complete description, together with results for aqueous NaCl at 17.7 MPa and at temperatures up to 325 °C, was published the next year [19]. In the same year Rogers and Pitzer [20] described a similar flow heat capacity calorimeter which was used to obtain data on aqueous Na₂SO₄ to 200 °C.

At the same time, developments in heat of mixing calorimeters were very rapid. Wormald and Colling [21] published a preliminary description of a calorimeter for measuring heats of mixing gases at temperatures up to 425 °C and pressures up to 12.6 MPa, with a more complete description appearing later [22]. James Christensen and colleagues at Brigham Young University were following a parallel path. In 1981 they published a description of a flow calorimeter using a Peltier cooler and an isothermal plate that operated to 150 °C and 40 MPa [23]. The speed and efficiency of this calorimeter is attested to by the large number of papers published subsequently, exploring the properties of non-electrolyte mixtures near their critical points. The next steps forward came in 1984 with two groups publishing improved heat of mixing calorimeters. Busey et al. [24] published heats of dilution of aqueous NaCl obtained using a new flow heat of mixing calorimeter which could take measurements up to 425 °C and 50 MPa. Their calorimeter consisted of a specially designed flow cell inserted into a commercial heat flow calorimeter. In the same year Christensen and Izatt [25] replaced their Peltier cooler with a controlled heat leak which allowed operation up to 400 °C and 40.5 MPa. Later, slight modifications of this calorimeter for operation with aqueous solutions up to 500 °C were published [26]. More recently, White and Biggerstaff [27,28] modified our heat capacity calorimeter for operation up to 450 °C and used it to measure the heat capacities of aqueous argon, ethylene, xenon and 0.015 M NaCl up to 450 °C. Boyette and Criss [29] built a flow heat capacity calorimeter and used it to study a variety of solutes in methanol. Archer et al. [30] have used these techniques to study surfactants.

As an offshoot of this work, Albert and Wood [31] used the same construction techniques to build a flow vibrating tube densitometer for measuring densities of solutions at high temperatures. This uses the speed of flow techniques and the sensitivity of a vibrating tube for the measurement of densities. Recently, Majer [32] has rebuilt the densitometer using platinum-rhodium tubing, adding many improvements.

As can be seen from the above there has been a rapid and parallel development of these techniques in many laboratories. One of the features that made all of these developments so rapid was the willingness of the investigators involved to share their knowledge, techniques and insights. In particular, James Christensen has always been willing to discuss his research and share ideas and methods.

With the development of these flow techniques in various laboratories we are now at a point where a large number of results on both aqueous and non-aqueous solutions at temperatures up to around 450 °C will increasingly become available.

HEAT CAPACITIES OF AQUEOUS ELECTROLYTES

Figure 1 shows the heat capacities of four 1-1 electrolytes measured in our laboratories at temperatures up to 325 °C [33-36]. Figure 2 shows more recent results for 0.015 M NaCl at temperatures up to 450 °C [28]. The basic reasons for the very large and rapidly changing apparent molar heat capacities shown in these figures are well known. The principle of corresponding states predicts that the infinite dilution apparent molar heat capacity will approach minus infinity as temperature increases towards the critical point,

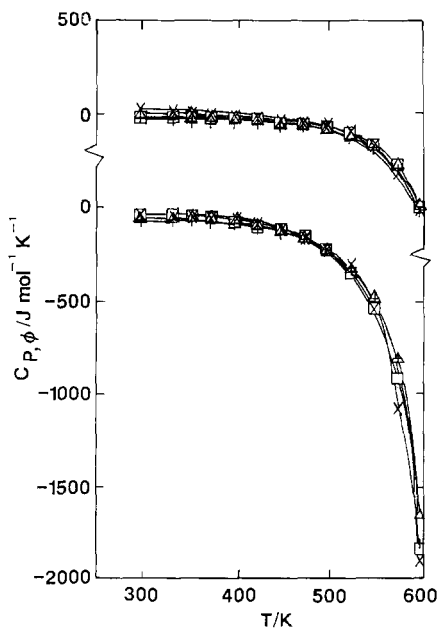


Fig. 1. Temperature dependence of $C_{p,\phi}$ ($\text{J mol}^{-1} \text{K}^{-1}$) at 17 MPa for 1-1 electrolytes at $m = 0.1 \text{ mol kg}^{-1}$ (lower curve) and $m = 3.0 \text{ mol kg}^{-1}$ (upper curve): \square , LiCl; \triangle , NaCl; \times , NaBr, $+$, KCl.

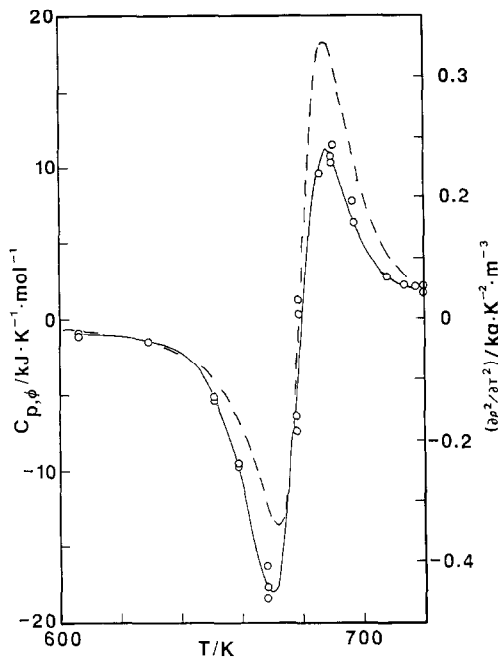


Fig. 2. Plot of $C_{p,\phi}$ for $0.0150 \text{ mol kg}^{-1} \text{ NaCl(aq)}$ and of $(\partial^2\rho/\partial T^2)_p$ against temperature at pressures near 32.2 MPa: \circ , experimental values of $C_{p,\phi}$; —, line drawn through experimental $C_{p,\phi}$ points for presentation purposes; ---, $(\partial^2\rho/\partial T^2)_p$ for H_2O calculated from the equation of state of Haar et al. [37].

and plus infinity as temperature decreases towards the critical point. At pressures above the critical pressure the behavior shown in Fig. 2 is predicted [38–40]. More recent theories involving critical point scaling laws predict the exponent with which the infinite dilution apparent molar heat capacity approaches infinity, but these theories do not predict the magnitude of the effect [41–45]. The Born equation also predicts correct infinities for both apparent molar heat capacity and apparent molar volume [19,46–49]. These aspects have been discussed fully elsewhere [41–45] and will not be discussed further here.

Figure 1 illustrates another interesting observation: to a first approximation, the heat capacities of all of these 1–1 electrolytes are very similar at high temperatures. This leads to the hypothesis that many (but not all) strong 1–1 electrolytes will behave in a similar manner. In 1980 three groups simultaneously pointed out that reactions in which the charges on the reactants and products are equal can be extrapolated to high temperatures with very good accuracy, whereas extrapolating reactions in which there is a change in the number of ions during the reaction is not accurate [50–52]. This observation implies that the heat capacities at infinite dilution of many ions with the same charge are of similar magnitude and quite different from the heat capacities of non-electrolytes. Lindsey [50] pointed out that these

ideas were not new. They received considerable attention from Gurney [53] and others in the 1930s when only data near room temperature were available. A careful observation of the data presented in Fig. 1 shows that on an absolute basis the difference between the apparent molar heat capacities for the four salts increases with increasing temperature, so that on an absolute basis the salts show more individuality at high temperature. However, on a relative basis, the opposite is true. As a fraction of the total effect the individuality decreases [34]. Because the effects at high temperature are so large, the loss of relative individuality is a useful observation.

Wood and Quint [40] pointed out that the principle of corresponding states leads directly to the expectation that the heat capacities of many 1-1 electrolytes will be similar at high temperatures, because the measurements of Marshall and Jones [54] show that the critical temperatures of a large group of aqueous 1-1 electrolytes are very similar. (The 1-1 electrolytes showing similar critical temperatures are KBr, KI, LiCl, KCl and NaCl, while HCl, HNO₃ and NH₄Cl have lower critical temperatures.) The theory of corresponding states changes the question to be asked from, "Why are the heat capacities similar?" to "Why are the critical curves similar?", but it does not give a molecular explanation.

The Born equation predicts that at infinite dilution the apparent molar heat capacities are proportional to the reciprocal of the radius of the ion, and leads to the prediction that the ratio of the apparent molar heat capacities of any two salts will be independent of temperature [19,49]. This is certainly not the case. However, if we take as our model a hard sphere ion in a compressible dielectric fluid [55,56], the prediction now is that as the compressibility increases the absolute difference between the apparent molar heat capacities of two salts becomes constant [57]. Thus, as the heat capacities become very large, the relative difference in heat capacities will become very small. The reason for this behavior of the hard sphere ion in a compressible fluid is that in a very compressible fluid, the high compressibility is only present at large distances from the ion, because the electrostatic field compresses the fluid near the ion. The large effects come from the region where the fluid is very compressible. The difference in heat capacity between two ions is due to the contribution of the region between the radius of one ion and the radius of the other. In this region the fluid is very dense and the contribution is roughly constant and independent of the bulk density. This model gives a reasonable explanation for the behavior in Fig. 1, but it needs to be tested. It accurately includes the effects of the increased compressibility of the fluid, but it does not include the effect of long-range correlations which become important very near the critical point. It is expected that this model will fail very close to the critical point [57].

An examination of Fig. 1 also shows that the concentration dependences of the heat capacities of the 1-1 electrolytes are very similar; this is predicted by corresponding states theory, together with the observed similar-

ity of the critical curves of many 1-1 electrolytes. Similarly, the conductance values of Marshall and coworkers [58-61] show that many 1-1 electrolytes have similar association constants at supercritical temperatures and pressures, implying similarities in concentration dependence, where association effects are important. Quint and Wood [56] have presented heuristic arguments that a model of two hard sphere ions in a compressible fluid will lead to this kind of behavior for association constants near the critical point. The argument is based on the fact that near the critical point of water, each ion will have a very large region of compressed water around it, with a density and dielectric constant much higher than in the bulk solvent. This allows the ions to spend appreciable amounts of time at fairly large distances from one another, and reduces the importance of contact interactions in determining the association constant.

This kind of concept has even been extended to the salting out of non-electrolytes by ions at high temperatures [34]. If the non-electrolyte is not able to penetrate the solvation sphere of the ion very frequently at temperatures near the critical point, then the interaction of the non-electrolyte with the ion at these temperatures will be relatively independent of the radius of the ion; thus, many 1-1 electrolytes will have similar salting out coefficients for a given non-electrolyte under these conditions. Unfortunately, no data are yet available to test this conjecture.

APPARENT MOLAR VOLUMES OF ELECTROLYTES AT HIGH TEMPERATURES

We have used the vibrating tube densitometer constructed at Delaware [31] to measure the densities of a variety of 1-1 electrolytes at temperatures up to and beyond the critical temperature [62,63]. We were interested in seeing if apparent molar volumes V_ϕ also become similar at high temperatures. Figures 3 and 4 show plots of the apparent molar volumes and the natural logarithm of the absolute values of the apparent molar volumes as a function of temperature for 0.025 mol kg⁻¹ solutions of four 1-1 electrolytes at 28 MPa. Since all of these electrolytes show very similar concentration dependences, it is expected that the apparent molar volume at infinite dilution will show the same trend. Figures 3 and 4 show that as the temperature increases from 600 to 650 K, the individuality of the four salts decreases dramatically, as expected from qualitative arguments based on the model of a hard sphere ion in a continuum compressible fluid. However, from 650 to 700 K, the relative individuality of the salts increases again, and is of opposite sign to that shown at low temperatures ($V_\phi(\text{LiCl}) > V_\phi(\text{CsBr})$ at high temperatures). It will take a great deal of careful and quantitative fitting of these data to find the reason for this behavior. One possible explanation which seems fairly simple is that, at low temperatures, the compressibility of the solvent is not important and so the Born equation is

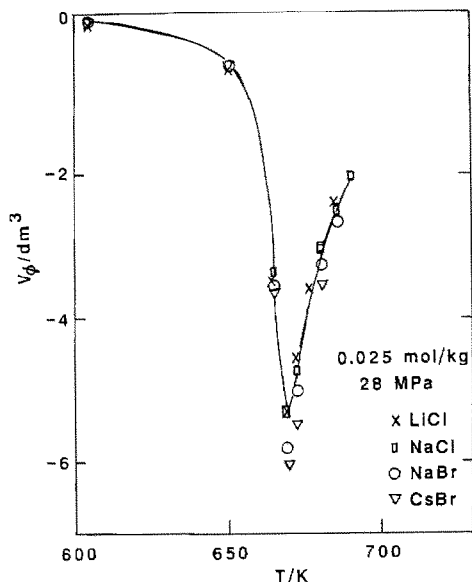


Fig. 3. Temperature dependence of V_ϕ (dm^3) for $0.025 \text{ mol kg}^{-1}$ solutions of 1-1 electrolytes at 28 MPa: \times , LiCl; \square , NaCl; \circ , NaBr; ∇ , CsBr.

reasonably accurate and the smaller ions have more negative apparent molar heat capacities than the larger ions ($V_\phi(\text{LiCl}) < V_\phi(\text{CsBr})$). At intermediate temperatures, the compressibility becomes more important and, as predicted

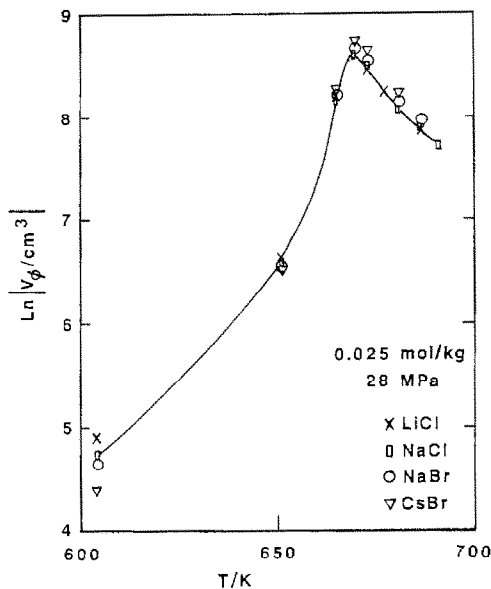


Fig. 4. Temperature dependence of $\ln|V_\phi(\text{dm}^3)|$ for $0.025 \text{ mol kg}^{-1}$ solutions of 1-1 electrolytes at 28 MPa; \times , LiCl; \square , NaCl; \circ , NaBr; ∇ , CsBr.

by the model of a hard sphere ion in a compressible fluid, the relative individualities decrease. At the highest temperatures (above 650 K), the solutions become strongly ion-paired at 0.025 M [58–61]. At contact, LiCl has a smaller distance of close approach than CsBr and, thus, a smaller dipole moment. The LiCl ion pair with its smaller dipole moment has a smaller influence on distant water molecules, and this will lead to a less negative apparent molar volume. The crossover is postulated as being due to the fact that the dependence on radius of V_ϕ of individual ions and individual ion pairs is opposite. This hypothesis must be tested with quantitative models. It should be noted that at temperatures very close to the critical point, there are other effects that become very important. Chang and Levelt Sengers [45] have shown that on the critical isotherm–isobar, \bar{V}_2 varies as $x^{-(1-1/\delta)}$ so that V_ϕ becomes infinite at $x=0$. A preliminary observation of our data does not reveal any evidence for the onset of the behaviour predicted by Sengers et al.

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