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Note

Heat capacities and compressibilities of deuterium oxide-water mixtures at 298.15 K*

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In a previous study[1] of the thermodynamic properties of deuterium oxide (D_2O) + water (H_2O) mixtures, we found that the isentropic compressibilities at 298.15 K exhibit small negative deviations from ideality. As an extension of that investigation, we have measured the volumetric heat capacities of D_2O + H_2O at 298.15 K over the whole mole fraction range. These results, combined with data from the literature, were used to calculate isobaric and isochoric heat capacities, and isothermal compressibilities.

MATERIALS AND EXPERIMENTAL TECHNIQUE

Two different samples of D_2O (Merck, Sharp and Dohme reagent with specified minimum isotopic purity of 99.7 atom % D) were used. Their densities, measured at 298.15 K with an Anton Paar densimeter[2], were 1104.20 and 1104.44 kg m^{-3}. Assuming the only impurity to be H_2O and adopting a value of 1104.449 kg m^{-3} for the density of pure D_2O at 298.15 K (ref. 3), the mole fractions of D_2O in the two samples were estimated to be 0.9977 and 0.9990, respectively. Mixtures were prepared by mass, using deionized distilled H_2O. A correction for the H_2O content of the D_2O was made in calculating the mole fraction of D_2O in each mixture. The error of the mole fractions is estimated to be less than 2×10^{-4}.

Differences of volumetric heat capacity C_p/V were measured in a Picker flow calorimeter[4]. Details of this equipment and of the operating procedure have already been described[5, 6]. Since the volumetric heat capacities of the present mixtures are larger than those of the binary organic liquid mixtures studied previously[6], the flow rate was decreased from 0.01 cm^3 sec^{-1} to 0.007 cm^3 sec^{-1}. The reference liquid was H_2O in all of the measurements (single reference procedure). The precision of the

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determination of the difference of volumetric heat capacities is about 0.3% up to the limit of sensitivity of the calorimeter (5×10^{-5} J K^{-1} cm^{-3}).

RESULTS AND DISCUSSION

The measurements of volumetric heat capacity at 298.15 K are summarized in Table 1, where x_1 indicates the mole fraction of D_2O in the mixture. Each entry for $\Delta(C_p/V)$ is the average of several determinations of the difference between the volumetric heat capacity of the mixture and that of pure H_2O [4.16725 J K^{-1} cm^{-3} (ref. 7)]. The molar heat capacity C_p of each mixture was obtained from these results using the molar volume V calculated from the densities of the pure components and the molar excess volume V^E of the mixture[8].

To obtain the molar heat capacity of pure D_2O, the results for C_p were extrapolated to $x_1 = 1$ by means of least squares polynomials. This yielded a value of 84.682 J K^{-1} mol^{-1} which can be compared with the values 82.60 (ref. 9), 84.25 (ref. 10) and 84.38 (ref. 11) reported in the literature. Molar excess heat capacities C_p^E are given in the last column of Table 1 and are presented graphically in Fig. 1(a). The values of C_p^E are small and positive over the whole mole fraction range, and can be represented by the equation

$$C_p^E\ (\mathrm{J\ K^{-1}\ mol^{-1}}) = 0.082\, x_1\, (1 - x_1) \qquad (1)$$

TABLE 1

HEAT CAPACITIES OF $D_2O(1)$ + $H_2O(2)$ MIXTURES AT 298.15 K

x_1	$\Delta(C_p/V)$ ($J\ K^{-1}\ cm^{-3}$)	C_p ($J\ K^{-1}\ mol^{-1}$)	C_p^E ($J\ K^{-1}\ mol^{-1}$)
0.0	0.0	75.297[a]	0.0
0.1010	0.051210	76.250	0.005
0.1536	0.078132	76.751	0.013
0.2046	0.103652	77.227	0.010
0.3032	0.153574	78.157	0.015
0.4030	0.204634	79.109	0.030
0.4523	0.229219	79.568	0.027
0.5003	0.252730	80.008	0.015
0.5467	0.276459	80.451	0.023
0.6038	0.304929	80.983	0.019
0.7017	0.353575	81.892	0.010
0.8033	0.404389	82.842	0.006
0.8504	0.428491	83.293	0.015
0.8986	0.452294	83.739	0.008
0.9477	0.476674	84.195	0.004
0.9977	0.501636	84.663	0.003
0.9990	0.502104	84.672	−0.001
1.0		84.682[b]	0.0

[a] From ref. 7.

[b] Extrapolated value.

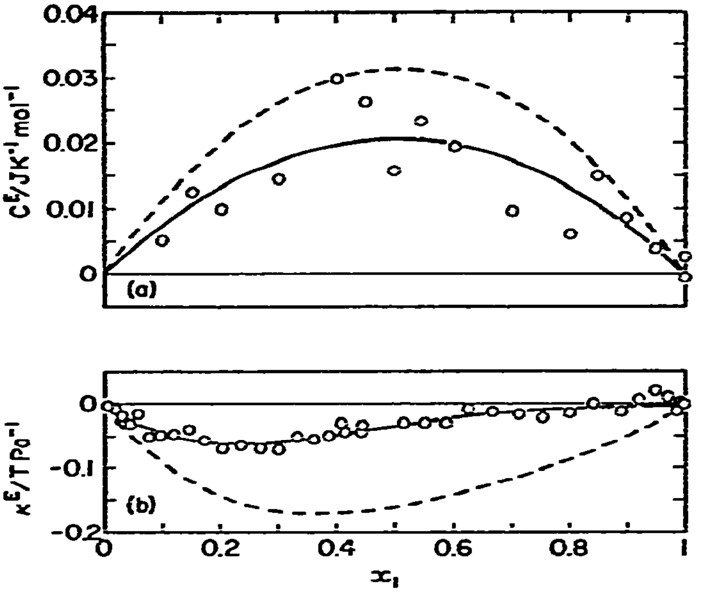

Fig. 1. Excess heat capacities and excess compressibilities of $D_2O(1) + H_2O(2)$ mixtures at 298.15 K. (a) ○, Present results for C_p^E; ———, least squares representation of C_p^E by eqn. (1); ---, curve calculated for C_v^E. (b) ○, Results for κ_S^E from ref. 1; ———, least squares representation of κ_S^E by eqn. (4); ---, curve calculated for κ_T^E.

with a standard deviation $\sigma(C_p^E) = 5 \times 10^{-3}$ J K^{-1} mol^{-1}.

Isothermal compressibilities κ_T were calculated from the isentropic compressibilities κ_S reported previously[1] using the present results for C_p and the thermodynamic relation

$$\kappa_T = \kappa_S + \alpha^2 VT/C_p \tag{2}$$

where α is the thermal expansivity and T the temperature. Values of α for the mixtures were estimated from the values of α for the pure components[3] and the variation of V^E with temperature[8]. Heat capacities at constant volume C_v were then obtained from the equation

$$C_v = C_p \kappa_S / \kappa_T \tag{3}$$

The results for the excess heat capacity at constant volume C_v^E and the excess isothermal compressibility κ_T^E are shown as broken curves in Fig. 1(a) and (b), respectively. Our previous results for κ_S^E along with their least squares representation

$$\kappa_S^E(TPa^{-1}) = x_1(1 - x_1)[-0.068 - 0.145(1 - 2x_1) - 0.108(1 - 2x_1)^2]$$
$$\sigma(\kappa_S^E) = 4 \times 10^{-3}\, TPa^{-1} \tag{4}$$

are included in Fig. 1(b) for comparison. It can be seen from Fig. 1 that C_v^E is more positive than C_p^E and that κ_T^E is more negative than κ_S^E.

Although there have been many investigations of H_2O and D_2O in the liquid state, a detailed explanation of the differences of their physical properties is still lacking. It is generally considered that D_2O is more structured than H_2O at the same temperature[12]. The present deviations of $D_2O + H_2O$ mixtures from ideality are consistent with the promotion of structure by HDO in the mixtures.

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