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Enthalpic Interaction Coefficients of *N*,*N*′-Hexamethylenebisacetamide in Aqueous Glucose and Sucrose Solutions at 298.15 K[†]

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The enthalpies of dilution of *N*,*N*′-hexamethylenebisacetamide in aqueous glucose and sucrose solutions have been measured by using a mixing-flow microcalorimeter at 298.15 K. The enthalpic interaction coefficients (h_2, h_3, h_4) in the range of the saccharide molality, (0 to 2.0) mol·kg^{-1}, have been calculated according to the McMillan−Mayer model. The results show that the enthalpic pairwise interaction coefficients h_2 of *N*,*N*′-hexamethylenebisacetamide in both the saccharide solutions are positive and become less positive with the increase of the saccharide molality. The value of h_2 in aqueous glucose solutions is larger than that in aqueous sucrose solutions of the same molality. The effects of the two saccharides on h_2 are discussed in terms of the solute−solute and solute−solvent interactions.

Introduction

To humans, cancer is the second killer in all types of diseases. Research on various cancers and antitumor drugs has been ongoing for years.[1−3] Among various antitumor drugs, *N*,*N*′-hexamethylenebisacetamide (HMBA), a small polar molecule compound, cannot only induce differentiation of leukemia cells but also could lead to a variety of tumor cells to normal differentiation.[4,5] At the present, people have done a series of research on the function of HMBA to Burkitt lymphoma Raji cells, malignant pleural mesothelioma, and so forth.[6,7] Also, HMBA is usually used to cooperate with other antitumor drugs to get a better effect on differentiation.[8,9] However, so far the induced differentiation mechanism of HMBA is not demonstrated clearly. On the other hand, glucose and sucrose are important biological substances in the bodies of animals and plants, and hence the drug getting into living body most probably interacts with the sugars. Although there have been many reports about the thermodynamic properties of aqueous glucose and sucrose solutions,[10−13] there are no reports on the thermodynamic properties of HMBA in the above saccharide solutions to our knowledge.

As an important part of our serial investigations, the present work is aimed at measuring the enthalpies of dilution of HMBA in aqueous glucose and sucrose solutions by using flow microcalorimetry. After analyzing the data, the homogeneous enthalpic interaction coefficients of HMBA have been obtained. These important thermodynamic parameters can be applied to understand the solute−solute and solute−solvent interactions.[14−16]

Experimental Section

Reagents. HMBA was purchased from Aldrich, and the mass fraction purity is better than 0.98; glucose and sucrose were analytical reagents with mass fraction purities of > 0.99 which were respectively gained from Tianjin Chemical Reagent Co. and Tianjin Damao Reagent Co., Ltd. All of the reagents were stored over P_2O_5 in a vacuum desiccator for 72 h at room temperature prior to use. Twice-distilled water was deionized by passing through a quartz sub-boiling purifier before use in the preparation of solutions. The saccharide solutions and the HMBA solutions were prepared by weight using a Mettler Toledo AG 135 analytical balance with a precision of ± 0.00001 g. The molality ranges of the aqueous saccharide and HMBA solutions were (0 to 2.0) mol·kg^{-1} and (0.05 to 0.32) mol·kg^{-1}, respectively. All of the solutions were degassed with ultrasonic waves and used within 12 h after preparation.

Calorimetric Measurements. The enthalpies of dilution for HMBA in the saccharide solutions at 298.15 K were measured with a 2277-204 measuring cylinder and a Thermometric 2277 thermal activity monitor (Thermometric, Sweden). The solutions of HMBA and the saccharide were pumped through the mixing-flow vessel of a calorimeter using VS2-10R MIDI dual-channel pumps. The flow rates were obtained from the mass of the samples delivered in 6 min. The variation in the flow rates was less than 0.1 % both before and after a complete dilution experiment. Further information about this apparatus, associated equipment, and the experimental procedure has been reported already.[17−21]

The enthalpies of dilution $\Delta_{\text{dil}}H_{\text{m}}$ can be obtained from the following equation[22]

$$\Delta_{\text{dil}}H_{\text{m}} = -P(1 + m_{\text{i}}M)/m_{\text{i}}f_2 \tag{1}$$

in which P is the dilution thermal power of the solute, m_{i}, M, and f_2 are the initial molality, the molar mass of HMBA, and the flow rate of HMBA solution, respectively. The uncertainties of P, m_{i}, and f_2 were ± 0.2 μW, ± 0.0001 mol·kg^{-1}, and ± 0.002 mg·s^{-1}, respectively. The relative mean deviations of all of the $\Delta_{\text{dil}}H_{\text{m}}$ values for duplicate runs at each initial molality were within 1 %. The final molality m_{f} can be calculated from the following equation

$$m_{\text{f}} = m_{\text{i}}f_2/[f_1(1 + m_{\text{i}}M) + f_2] \tag{2}$$

where f_1 is the flow rate of diluent (water or aqueous solution of glucose or sucrose).

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Table 1. Molar Enthalpies of Dilution $\Delta_{\mathrm{dil}}H_{\mathrm{m}}$ of HMBA in Water and Aqueous Glucose Solutions at 298.15 K[a]

m_{i} / mol·kg^{-1}	m_{f} / mol·kg^{-1}	$\Delta_{\mathrm{dil}}H_{\mathrm{m}}$ / J·mol^{-1}	δ / J·mol^{-1}	m_{i} / mol·kg^{-1}	m_{f} / mol·kg^{-1}	$\Delta_{\mathrm{dil}}H_{\mathrm{m}}$ / J·mol^{-1}	δ / J·mol^{-1}
m(glucose) = 0.0000 mol·kg^{-1}							
0.0500	0.0263	−41.61 ± 0.37	−0.03	0.2000	0.1048	−210.23 ± 0.19	−0.13
0.0800	0.0422	−75.42 ± 0.07	−0.02	0.2200	0.1148	−233.33 ± 0.21	−0.03
0.1000	0.0525	−98.36 ± 0.09	0.10	0.2500	0.1300	−267.58 ± 0.24	0.07
0.1200	0.0631	−120.66 ± 0.11	0.01	0.2800	0.1454	−301.65 ± 0.27	0.04
0.1500	0.0784	−155.24 ± 0.14	−0.06	0.3000	0.1554	−324.89 ± 0.29	0.01
0.1800	0.0941	−188.27 ± 0.17	0.06	0.3200	0.1650	−349.31 ± 0.31	−0.04
m(glucose) = 0.3000 mol·kg^{-1}							
0.0500	0.0243	−41.64 ± 0.37	0.02	0.2000	0.0968	−216.02 ± 1.94	0.01
0.0800	0.0386	−75.66 ± 0.68	−0.04	0.2200	0.1050	−243.05 ± 2.19	−0.04
0.1000	0.0485	−97.88 ± 0.88	0.01	0.2500	0.1190	−279.72 ± 2.52	0.00
0.1200	0.0580	−121.49 ± 1.09	0.01	0.2800	0.1329	−316.29 ± 2.85	0.00
0.1500	0.0725	−156.86 ± 1.41	0.00	0.3000	0.1432	−337.79 ± 3.04	−0.01
0.1800	0.0863	−194.06 ± 1.75	0.01	0.3200	0.1508	−365.05 ± 3.29	−0.01
m(glucose) = 0.6000 mol·kg^{-1}							
0.0500	0.0251	−31.56 ± 0.28	0.00	0.2000	0.0988	−182.45 ± 1.64	−0.01
0.0800	0.0402	−58.28 ± 0.52	−0.06	0.2200	0.1093	−203.62 ± 1.83	−0.04
0.1000	0.0501	−77.18 ± 0.69	0.02	0.2500	0.1235	−238.90 ± 2.15	0.11
0.1200	0.0601	−96.61 ± 0.87	0.08	0.2800	0.1378	−275.05 ± 2.48	0.01
0.1500	0.0750	−127.23 ± 1.15	−0.05	0.3000	0.1467	−300.85 ± 2.71	−0.08
0.1800	0.0900	−158.76 ± 1.43	−0.03	0.3200	0.1564	−325.19 ± 2.93	0.02
m(glucose) = 0.9000 mol·kg^{-1}							
0.0500	0.0250	−20.94 ± 0.19	−0.04	0.2000	0.0983	−160.88 ± 1.45	−0.04
0.0800	0.0398	−45.33 ± 0.41	0.04	0.2200	0.1077	−182.31 ± 1.64	0.05
0.1000	0.0497	−62.81 ± 0.57	0.04	0.2500	0.1224	−214.12 ± 1.93	0.04
0.1200	0.0598	−80.56 ± 0.73	0.05	0.2800	0.1357	−248.63 ± 2.24	0.02
0.1500	0.0739	−110.19 ± 0.99	−0.05	0.3000	0.1455	−270.11 ± 2.43	0.01
0.1800	0.0887	−140.11 ± 1.26	−0.06	0.3200	0.1549	−292.19 ± 2.63	−0.02
m(glucose) = 1.2000 mol·kg^{-1}							
0.0500	0.0241	−18.09 ± 0.16	0.01	0.2000	0.0954	−147.19 ± 1.32	−0.04
0.0800	0.0385	−39.98 ± 0.36	−0.01	0.2200	0.1042	−168.25 ± 1.51	0.03
0.1000	0.0477	−56.25 ± 0.51	0.02	0.2500	0.1175	−200.05 ± 1.80	0.02
0.1200	0.0576	−72.66 ± 0.65	−0.02	0.2800	0.1322	−230.11 ± 2.07	−0.02
0.1500	0.0712	−100.21 ± 0.90	0.06	0.3000	0.1411	−251.49 ± 2.26	−0.01
0.1800	0.0853	−128.63 ± 1.16	−0.04	0.3200	0.1495	−273.62 ± 2.46	0.01
m(glucose) = 1.5000 mol·kg^{-1}							
0.0500	0.0245	−8.82 ± 0.08	0.00	0.2000	0.0957	−119.53 ± 1.08	−0.03
0.0800	0.0390	−27.13 ± 0.24	−0.01	0.2200	0.1057	−135.85 ± 1.22	0.12
0.1000	0.0480	−41.12 ± 0.37	0.07	0.2500	0.1184	−163.76 ± 1.47	0.06
0.1200	0.0576	−55.64 ± 0.50	−0.08	0.2800	0.1331	−189.51 ± 1.71	−0.09
0.1500	0.0722	−78.22 ± 0.70	−0.03	0.3000	0.1423	−207.41 ± 1.87	−0.16
0.1800	0.0867	−102.18 ± 0.92	−0.02	0.3200	0.1519	−224.28 ± 2.02	0.14
m(glucose) = 2.0000 mol·kg^{-1}							
0.0500	0.0246	16.81 ± 0.15	−0.03	0.1800	0.0880	−63.68 ± 0.57	0.00
0.0800	0.0395	1.24 ± 0.01	−0.01	0.2000	0.0981	−77.62 ± 0.70	−0.01
0.1000	0.0495	−10.11 ± 0.09	0.12	0.2200	0.1064	−93.63 ± 0.84	−0.05
0.1200	0.0592	−22.72 ± 0.20	−0.05	0.2500	0.1212	−115.31 ± 1.04	0.11
0.1500	0.0731	−43.11 ± 0.39	−0.01	0.2800	0.1349	−138.24 ± 1.24	−0.05

[a] The symbols m_{i} and m_{f} represent the initial and final molalities of HMBA, respectively; the symbol δ is defined as $\delta = \Delta_{\mathrm{dil}}H_{\mathrm{m}} - \Delta_{\mathrm{dil}}H_{\mathrm{m}}$(calcd), where $\Delta_{\mathrm{dil}}H_{\mathrm{m}}$(calcd) was calculated using eq 5 with coefficients obtained by fitting the data at the corresponding m(glucose).

Results and Discussion

The excess enthalpy concept is the foundation of the thermodynamic formula of dilution enthalpies for a solution with molality m. If we regard the aqueous glucose or sucrose solutions as the "solvent" of HMBA, the molar excess enthalpy of a solution $H_{\mathrm{m}}^{\mathrm{E}}$ can be written as a power series in m with coefficient h_n by

$$H_{\mathrm{m}}^{\mathrm{E}} = L_{2\varphi} = h_2 m + h_3 m^2 + h_4 m^3 + ... \qquad (3)$$

where $H_{\mathrm{m}}^{\mathrm{E}}$ is the molar excess enthalpy; $L_{2\varphi}$ is the relative apparent molar enthalpy; and h_2, h_3, h_4, and so forth represent the enthalpic coefficients of pairwise, triplet, quart, and so forth higher-order interactions between solvated solute species.

So the molar dilution enthalpy ($\Delta_{\mathrm{dil}}H_{\mathrm{m}}$) of a nonelectrolytic solute from an initial molality m_{i} to a final molality m_{f} can be written as:

$$\begin{aligned}\Delta_{\mathrm{dil}}H_{\mathrm{m}} = H_{\mathrm{m}}^{\mathrm{E}}(m_{\mathrm{f}}) - H_{\mathrm{m}}^{\mathrm{E}}(m_{\mathrm{i}}) = {} & \\ h_2(m_{\mathrm{f}} - m_{\mathrm{i}}) + h_3(m_{\mathrm{f}}^2 - m_{\mathrm{i}}^2) + {} & \\ h_4(m_{\mathrm{f}}^3 - m_{\mathrm{i}}^3) + ... & \end{aligned} \qquad (4)$$

in which $H_{\mathrm{m}}^{\mathrm{E}}$ (m_{i}) and $H_{\mathrm{m}}^{\mathrm{E}}$ (m_{f}) are the molar excess enthalpies of the solute in the solutions before and after dilution, respectively.

According to the McMillan−Mayer theory[23−25] and the relationship between relative apparent molar enthalpy $L_{2\varphi}$ with the relative partial molar enthalpy L_2, $L_2 = L_{2\phi} + m(\partial L_{2\phi}/\partial_{\mathrm{m}})_{T,P,n_1}$, the following equation can be obtained.

$$L_2 = 2h_2 m + 3h_3 m^2 + 4h_4 m^3 + ... \qquad (5)$$

Tables 1 and 2 list the experimental values of dilution enthalpies ($\Delta_{\mathrm{dil}}H_{\mathrm{m}}$) and the initial and final molalities (m_{i} and m_{f}) of HMBA in different aqueous glucose or sucrose solutions.

Table 2. Molar Enthalpies of Dilution $\Delta_{\mathrm{dil}}H_{\mathrm{m}}$ of HMBA in Aqueous Sucrose Solutions at 298.15 K[a]

m_{i} / mol·kg^{-1}	m_{f} / mol·kg^{-1}	$\Delta_{\mathrm{dil}}H_{\mathrm{m}}$ / J·mol^{-1}	δ / J·mol^{-1}	m_{i} / mol·kg^{-1}	m_{f} / mol·kg^{-1}	$\Delta_{\mathrm{dil}}H_{\mathrm{m}}$ / J·mol^{-1}	δ / J·mol^{-1}
m(sucrose) = 0.3000 mol·kg^{-1}							
0.0500	0.0267	−31.53 ± 0.28	0.05	0.2000	0.1052	−186.13 ± 1.68	0.00
0.0800	0.0430	−59.46 ± 0.54	−0.11	0.2200	0.1154	−208.89 ± 1.88	−0.02
0.1000	0.0530	−80.16 ± 0.72	0.00	0.2500	0.1306	−243.59 ± 2.19	−0.05
0.1200	0.0635	−100.48 ± 0.90	0.06	0.2800	0.1459	−278.78 ± 2.51	0.00
0.1500	0.0792	−131.72 ± 1.19	−0.01	0.3000	0.1561	−302.46 ± 2.72	0.04
0.1800	0.0947	−164.36 ± 1.48	0.05	0.3200	0.1670	−324.76 ± 2.92	−0.02
m(sucrose) = 0.6000 mol·kg^{-1}							
0.0500	0.0237	−24.94 ± 0.22	−0.04	0.2000	0.0935	−174.43 ± 1.57	−0.06
0.0800	0.0378	−51.42 ± 0.46	0.04	0.2200	0.1028	−196.56 ± 1.77	0.07
0.1000	0.0470	−70.36 ± 0.63	0.05	0.2500	0.1155	−232.83 ± 2.10	0.04
0.1200	0.0566	−89.52 ± 0.81	−0.04	0.2800	0.1299	−266.74 ± 2.40	0.00
0.1500	0.0698	−121.24 ± 1.09	−0.03	0.3000	0.1416	−284.44 ± 2.56	0.00
0.1800	0.0845	−151.99 ± 1.37	−0.01	0.3200	0.1476	−315.15 ± 2.84	−0.02
m(sucrose) = 0.9000 mol·kg^{-1}							
0.0500	0.0235	−18.64 ± 0.17	−0.27	0.2000	0.0923	−146.03 ± 1.31	−0.18
0.0800	0.0375	−39.79 ± 0.36	0.31	0.2200	0.1016	−164.55 ± 1.48	0.37
0.1000	0.0469	−55.17 ± 0.50	0.55	0.2500	0.1148	−194.69 ± 1.75	0.16
0.1200	0.0562	−72.15 ± 0.65	0.07	0.2800	0.1270	−226.36 ± 2.04	0.03
0.1500	0.0699	−98.85 ± 0.89	−0.19	0.3000	0.1370	−244.49 ± 2.20	−0.03
0.1800	0.0839	−126.25 ± 1.14	−0.39	0.3200	0.1463	−263.39 ± 2.37	−0.06
m(sucrose) = 1.2000 mol·kg^{-1}							
0.0500	0.0239	−11.67 ± 0.11	0.02	0.2000	0.0938	−118.92 ± 1.07	0.01
0.0800	0.0384	−29.02 ± 0.26	−0.02	0.2200	0.1032	−135.54 ± 1.22	0.00
0.1000	0.0476	−42.15 ± 0.38	−0.03	0.2500	0.1165	−161.68 ± 1.46	−0.02
0.1200	0.0567	−56.33 ± 0.51	−0.02	0.2800	0.1300	−187.87 ± 1.69	−0.01
0.1500	0.0707	−78.58 ± 0.71	0.01	0.3000	0.1386	−205.56 ± 1.85	0.01
0.1800	0.0846	−102.39 ± 0.92	0.03	0.3200	0.1475	−222.76 ± 2.00	0.01
m(sucrose) = 1.5000 mol·kg^{-1}							
0.0500	0.0241	−5.06 ± 0.05	−0.06	0.2000	0.0938	−97.83 ± 0.88	−0.03
0.0800	0.0380	−20.06 ± 0.18	0.10	0.2200	0.1030	−112.22 ± 1.01	0.02
0.1000	0.0476	−31.20 ± 0.28	0.03	0.2500	0.1160	−134.76 ± 1.21	0.04
0.1200	0.0569	−43.41 ± 0.39	−0.03	0.2800	0.1301	−155.78 ± 1.40	0.03
0.1500	0.0712	−62.60 ± 0.56	−0.05	0.3000	0.1395	−169.41 ± 1.52	0.04
0.1800	0.0850	−83.24 ± 0.75	−0.02	0.3200	0.1479	−183.57 ± 1.65	−0.04
m(sucrose) = 2.0000 mol·kg^{-1}							
0.0500	0.0248	−2.14 ± 0.02	0.06	0.1800	0.0887	−63.48 ± 0.57	−0.01
0.0800	0.0396	−13.88 ± 0.12	−0.14	0.2000	0.0980	−74.91 ± 0.67	−0.05
0.1000	0.0494	−22.47 ± 0.20	0.02	0.2200	0.1079	−85.84 ± 0.77	−0.04
0.1200	0.0593	−31.86 ± 0.29	0.09	0.2500	0.1220	−102.51 ± 0.92	0.06
0.1500	0.0739	−47.41 ± 0.43	−0.03	0.2800	0.1357	−118.96 ± 1.07	−0.01

[a] The symbols m_{i} and m_{f} represent the initial and final molalities of HMBA, respectively; the symbol δ is defined as $\delta = \Delta_{\mathrm{dil}}H_{\mathrm{m}} - \Delta_{\mathrm{dil}}H_{\mathrm{m}}(\mathrm{calcd})$, where $\Delta_{\mathrm{dil}}H_{\mathrm{m}}(\mathrm{calcd})$ was calculated using eq 5 with coefficients obtained by fitting the data at the corresponding m(sucrose).

Table 3. Enthalpic Interaction Coefficients of HMBA in Water and Aqueous Glucose Solutions at 298.15 K[a]

m (glucose) / mol·kg^{-1}	h_2 / J·kg·mol^{-2}	h_3 / J·kg^2·mol^{-3}	h_4 / J·kg^3·mol^{-4}	SD / J·mol^{-1}
0.0000	2485 ± 10	−493 ± 37	632 ± 56	0.07
0.3000	1976 ± 3	1153 ± 11	−1704 ± 17	0.02
0.6000	1544 ± 8	1387 ± 32	−904 ± 48	0.06
0.9000	1279 ± 6	1952 ± 25	−1979 ± 38	0.05
1.2000	1014 ± 4	2278 ± 17	−2358 ± 26	0.04
1.5000	823 ± 11	2150 ± 46	−2341 ± 70	0.10
2.0000	675 ± 12	2135 ± 53	−2594 ± 90	0.07

[a] The h_n values are reported as the value ± standard error, the latter of which was given by the computer during the multiple linear regression analysis. SD = standard deviation.

Table 4. Enthalpic Interaction Coefficients of HMBA in Aqueous Sucrose Solutions at 298.15 K[a]

m (sucrose) / mol·kg^{-1}	h_2 / J·kg·mol^{-2}	h_3 / J·kg^2·mol^{-3}	h_4 / J·kg^3·mol^{-4}	SD / J·mol^{-1}
0.3000	1846 ± 7	980 ± 28	−618 ± 43	0.05
0.6000	1380 ± 5	1675 ± 20	−1464 ± 31	0.04
0.9000	994 ± 21	2196 ± 86	−2538 ± 133	0.18
1.2000	727 ± 2	2296 ± 9	−2581 ± 15	0.02
1.5000	558 ± 6	2380 ± 24	−3060 ± 37	0.05
2.0000	382 ± 13	2315 ± 58	−3267 ± 33	0.08

[a] The h_n values are reported as the value ± standard error, the latter of which was given by the computer during the multiple linear regression analysis. SD = standard deviation.

The difference between the experimental values and the corresponding calculated values are also included. Tables 3 and 4 give the coefficients of eq 4 and the standard deviations, which are all obtained from the least-squares analysis of experimental results. The relationship between relative partial molar enthalpy L_2 obtained from eq 5 and molality m of the aqueous glucose or sucrose solutions are shown in Figures 1 and 2, respectively. From the two figures, it can be observed that the relative partial molar enthalpy L_2 is nearly linear with the saccharide molality m in lower molality ranges, which indicates that the interactions between two HMBA molecules make the dominate role in these dilute solutions. Furthermore, because of the fact that the interactions among three or more solute molecules are very complicated, it is hard to show regularity of higher order coefficients with increasing molality of saccharide in aqueous solutions.[26] As a result, we only discuss the enthalpic pairwise coefficients h_2 here.

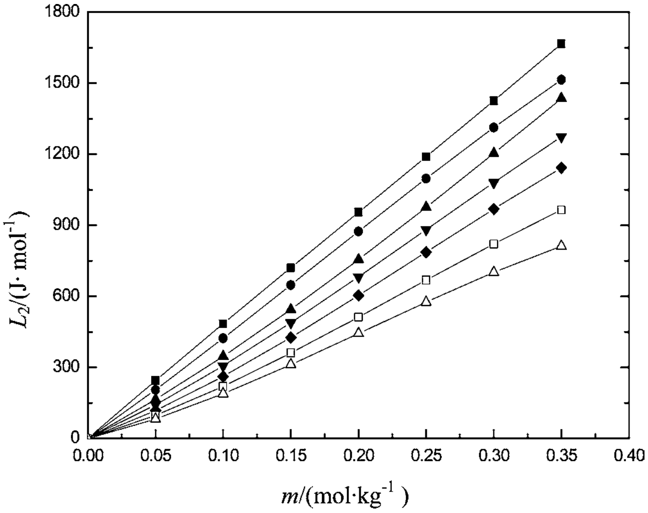

Figure 1. Relative partial molar enthalpy L_2 of HMBA versus the molality m of glucose in aqueous solutions at 298.15 K. ■, m(glucose) = 0.0000 mol·kg^{-1}; ●, m(glucose) = 0.3000 mol·kg^{-1}; ▲, m(glucose) = 0.6000 mol·kg^{-1}; ▼, m(glucose) = 0.9000 mol·kg^{-1}; ◆, m(glucose) = 1.2000 mol·kg^{-1}; □, m(glucose) = 1.5000 mol·kg^{-1}; △, m(glucose) = 2.0000 mol·kg^{-1}.

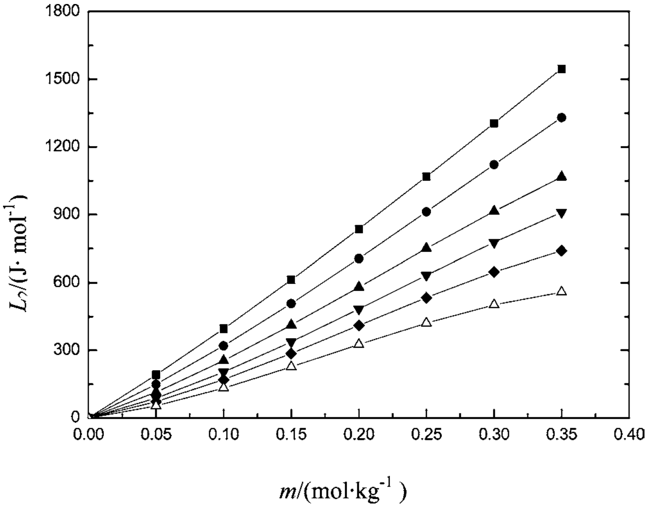

Figure 2. Relative partial molar enthalpy L_2 of HMBA versus the molality m of sucrose in aqueous solutions at 298.15 K. ■, m(sucrose) = 0.3000 mol·kg^{-1}; ●, m(sucrose) = 0.6000 mol·kg^{-1}; ▲, m(sucrose) = 0.9000 mol·kg^{-1}; ▼, m(sucrose) = 1.2000 mol·kg^{-1}; ◆, m(sucrose) = 1.5000 mol·kg^{-1}; △, m(sucrose) = 2.0000 mol·kg^{-1}.

From Tables 3 and 4 and the corresponding plots in the Supporting Information, we can see that the values of pairwise enthalpic coefficients h_2 for HMBA in both the saccharide solutions are positive, and the values of h_2 for HMBA in aqueous glucose solutions are always larger than that in aqueous sucrose solutions of the same molalities. This can be explained from the solute−solute and solute−solvent interactions: (i) hydrophobic−hydrophobic interaction between the hexamethylenes of two HMBA molecules (positive contribution to h_2); (ii) formation of two types of intermolecular hydrogen bonds (negative contribution to h_2), one of which is caused by interaction between the carbonyl group (proton acceptor) in one HMBA molecule and the amino group (proton donor) in another HMBA molecule, and the other is caused by the interaction of the carbonyl oxygen in the HMBA molecule with the hydroxyl group in the saccharide molecule; (iii) hydrophobic−hydrophilic interaction between the apolar group and the hydroxyl group (positive contribution to h_2); and (iv) partial desolvation of the diluted species (positive contribution to h_2).

The overall effect on h_2 reflects the competitive equilibrium among the above effects. The positive values of h_2 testify that the hydrophobic−hydrophobic interaction, hydrophobic−hydrophilic interaction, and partial desolvation predominate over the hydrogen-bond interaction. In addition, the values of h_2 in aqueous glucose solutions are larger than those in aqueous sucrose solutions of the same molalities. This may be due to the fact that, for solutions of the same molality, aqueous sucrose solutions contain about twice the number of OH groups compared to aqueous glucose solutions, which leads to larger hydrogen-bond interactions in sucrose solutions than those in glucose solutions.

The data in Tables 3 and 4 also show that the value of h_2 for HMBA in the aqueous saccharide solution becomes less with the increase of the saccharide molality. This change trend is in accordance with the influence of the number of the OH groups on the values of h_2 as discussed above. The higher the molality of glucose or sucrose is, the stronger the hydrogen bond interaction between the carbonyl oxygen in HMBA molecule and the hydroxyl groups in the saccharide molecule is, and the more negative of the contribution to the enthalpy will be.

Conclusion

The enthalpies of dilution of HMBA in aqueous glucose and sucrose solutions have been measured by using a mixing-flow microcalorimeter at 298.15 K. Experimental enthalpies of dilution varying with the molalitiy of HMBA were correlated with the virial expansion equation. The enthalpic interaction coefficients (h_2, h_3, h_4) in the equations were obtained, and the values of the enthalpic pairwise interaction coefficient h_2 have been discussed. The different numbers of hydroxyl groups in the molecules of the two saccharides make a contribution to the different values of h_2.

Supporting Information Available:

Plot of enthalpic pairwise interaction coefficients h_2 of HMBA versus the molality m of glucose and sucrose in aqueous solutions at 298.15 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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