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Benzene–Methanol Association. The Excess Molar Enthalpy and Second Virial Cross Coefficients of (Benzene + Methanol)(g) and (Cyclohexane + Methanol)(g)

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New measurements of the excess molar enthalpy H_m^E of $\{xCH_3OH + (1-x)C_6H_6\}(g)$ and $\{xCH_3OH + (1-x)C_6H_{12}\}(g)$ measured at standard atmospheric pressure over the temperature range 363.2 to 433.2 K are reported. These measurements supplement earlier measurements made over the range 454.2 to 523.0 K at pressures up to 4.0 MPa. The nonideality of the methanol vapor is described using a quasi chemical model model in which only dimer and tetramer association equilibria are considered. The values of H_m^E for the (methanol + cyclohexane)(g) mixture were found to agree well with values calculated using the association model. For (methanol + benzene)(g) the experimental values of H_m^E were found to be approximately 20% smaller than values calculated from the model and this was attributed to weak association between the unlike molecules. A quasi-chemical model used to describe the association between the unlike molecules yielded a value of the equilibrium constant $K_{12}(298.15\ K) = 0.22\ MPa^{-1}$, and a value for the enthalpy of the methanol–benzene association of $\Delta H_{12} = -13\ kJ \cdot mol^{-1}$. Second virial cross-coefficients B_{12} for methanol–cyclohexane and methanol–benzene have been derived from the H_m^E measurements.

KEY WORDS: benzene methanol association; excess molar enthalpy; flow calorimetry; heat of mixing; gas mixtures; second virial cross-coefficient.

1. INTRODUCTION

Vapor- phase measurements of the excess molar enthalpy H_m^E of a number of (water + hydrocarbon)(g) mixtures made using a flow mixing calorimeter operating at pressures close to atmospheric have been reported. The

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values of H_m^E for mixtures of $(yH_2O+(1-y)C_nH_{2n+2})(g)$ for $n=1$ to 8 and for the mixture $(yH_2O+(1-y)C_6H_{12})(g)$ [1] could all be fitted by a model in which the cross-term second virial coefficient B_{12} and the cross-term isothermal Joule–Thomson coefficient ϕ_{12} were calculated by combining the Stockmayer potential parameters $\varepsilon/k=233$ K, $\sigma=0.312$ nm, and $t^*=1.238$ for water with Kihara potential parameters for the hydrocarbon. Unlike the H_m^E measurements on (water + cyclohexane), similar measurements on (water + benzene) [2] could not be fitted by this model. For this mixture the H_m^E measurements were found to be about 20% smaller than expected, and this was attributed to a specific association between water and benzene. This association caused values of $B_{12}$for the water-benzene interaction to be much more negative than expected, and to fit these values it was necessary to increase the well depth of the water–benzene potential by 35% [1]. As these low-pressure H_m^E measurements were made only over the limited range of temperature 363.15 to 393.15 K, additional low-pressure H_m^E measurements were made over the temperature range 403.15 to 453.15 K and these have been reported recently [3]. The new measurements were analyzed with a quasichemical model in which the water–benzene interaction was described by an equilibrium constant K_{12} and an enthalpy of association ΔH_{12} derived from the temperature dependence of K_{12}. In this model intermolecular potentials were used to calculate the contribution to the interaction energy arising from dispersion forces. The values were found to be $K_{12}(298.12\ \text{K})=0.208\ \text{MPa}^{-1}$ and $\Delta H_{12}=-11.3\ \text{kJ}\cdot\text{mol}^{-1}$, and these relate to the specific pairwise interaction between the water and the benzene molecules. For comparison a similar analysis of the second virial coefficient of pure water vapor yields $K_{11}(298.15\ \text{K})=0.4085\ \text{MPa}^{-1}$ and $\Delta H_{11}=-18.15\ \text{kJ}\cdot\text{mol}^{-1}$. Again, these figures apply to the specific (hydrogen bonding) interaction between pairs of water molecules, the contribution from dispersion forces having been estimated separately.

In addition to the above low-pressure measurements a parallel series of measurements using a high-temperature, high-pressure flow mixing calorimeter have also been made. Most of these measurements extend up to temperatures of 698.2 K and pressures in the region of 10 MPa. The mixtures studied include steam with C_1 to C_8 n-alkanes, cyclohexane, and benzene [4]. The measurements were analyzed with a cubic equation of state [5], which was constrained to give correct second virial coefficients. Again, the values of H_m^E for water–benzene were found to be less endothermic than those predicted on the basis of the equations which correctly predicted the results for water–cyclohexane. The inclusion of association terms in the model yielded $K_{12}(298.15\ \text{K})=0.179\ \text{MP}^{-1}$ and $\Delta H_{12}=-12.3\ \text{kJ}\cdot\text{mol}^{-1}$ for the water–benzene interaction.

High-pressure H_m^E measurements for mixtures of (methanol + cyclohexane) and (methanol + benzene) at temperatures up to 523.0 K and pressures up to 4 MPa have been reported [6]. For the methanol–benzene interaction the quasi-chemical model yields $K_{12}(298.15\ \mathrm{K}) = 0.177\ \mathrm{MPa}^{-1}$ and $\Delta H_{12} = -14.7\ \mathrm{kJ \cdot mol^{-1}}$. Similar measurements for (ethanol + cyclohexane) and (ethanol + benzene) have been made over the range 453.5 to 522.9 K at pressures up to 4.5 MPa^{-1}, and for the ethanol–benzene interaction the quasi-chemical model yields $K_{12}(298.15\ \mathrm{K}) = 0.219\ \mathrm{MPa}^{-1}$ and $\Delta H_{12} = -14\ \mathrm{kJ \cdot mol^{-1}}$. Experience with the measurements on steam mixtures showed the importance of obtaining H_m^E measurements over as wide a temperature range as possible. As the model used for the analysis of the measurements at high pressures and temperatures over 450 K is slightly different from that used for the measurements at low pressures ($p^\ominus = 0.101325$ MPa) and temperatures below 450 K, two slightly different values of ΔH_{12} were obtained from the two data sets. This is also likely to be true for measurements on (methanol + benzene) for which no low-pressure H_m^E measurements have yet been reported.

We now report new measurements of H_m^E for (methanol + cyclohexane)(g) and (methanol + benzene)(g) at $p^\ominus$ made with our low-pressure flow mixing calorimeter over the temperature range 363.2 to 433.2 K. The results of these experiments are combined with values of $H_m^E(p^\ominus)$ derived from high-temperature, high-pressure measurements to obtain further information about the methanol–benzene interaction, and hence about the second virial cross-coefficients.

2. EXPERIMENTAL PROCEDURE

The differential flow-mixing calorimeter was of the same design as that described previously [8]. Analytical reagent-grade methanol was dried by distillation over calcium hydride and was at least 0.998 CH_3OH. Thiophen-free analytical grade benzene of purity 0.995 C_6H_6 was dried and distilled before use, as was the analytical-grade cyclohexane of purity 0.998 C_6H_{12}.

All measurements were made at ambient atmospheric pressure over the approximate range of mole fraction $y = 0.4$ to 0.6. Usually five measurements were made at each temperature. These were corrected to standard atmospheric pressure $p^\ominus$ and values of H_m^E ($y = 0.5$) were obtained from plots of $H_m^E(y)/4y(1-y)$ against y. Mean values of $H_m^E(y = 0.5, p = p^\ominus)$ and the uncertainty σH_m^E on this quantity are listed for temperatures in the range 363.3 to 433.2 K in columns 2 and 3 of Tables I and II, and are plotted (as circles) against temperature in Figs. 1 and 2.

Table I. Excess Molar Enthalpy $H^{\mathrm{E}}_{\mathrm{m}}(p^{\circ})$ of $(0.5\ CH_3OH + 0.5\ C_6H_{12})(g)$ and Related Quantities

T (K)	$H^{\mathrm{E}}_{\mathrm{m}}(p^{\circ})$ $(J \cdot mol^{-1})$	$\sigma H^{\mathrm{E}}_{\mathrm{m}}$ $(J \cdot mol^{-1})$	$-\phi_{11}$ $(cm^3 \cdot mol^{-1})$	$-\phi_{22}$ $(cm^3 \cdot mol^{-1})$	$-\phi_{12}$ $(cm^3 \cdot mol^{-1})$	$-B_{11}$ $(cm^3 \cdot mol^{-1})$	$-B_{22}$ $(cm^3 \cdot mol^{-1})$	$-B_{12}$ $(cm^3 \cdot mol^{-1})$
363.2	146	7	3549	3271	954	673	998	294
368.2	133	4	3306	3156	927	635	967	285
373.2	118	3	3086	3048	902	600	938	276
378.2	107	2	2887	2947	878	569	911	268
383.2	102	2	2705	2852	855	539	884	260
393.2	88	2	2389	2678	812	487	835	245
403.2	77	2	2125	2524	773	442	790	231
413.2	70	1	1901	2385	735	403	749	218
423.2	63	1	1710	2259	702	369	711	206
433.2	57	2	1547	2145	668	339	676	195
473.2	44	2	1054	1775	561	250	558	156
483.2	41	2	1001	1700	538	234	533	147
493.2	38	2	928	1629	516	219	509	140
503.2	36	1	863	1564	497	205	487	132
513.2	34	1	805	1502	477	192	467	125
523.2	32	1	752	1445	458	181	447	118

Table II. Excess Molar Enthalpy $H^E_m(p^\circ)$ of $(0.5\,CH_3OH + 0.5\,C_6H_6)(g)$ and Related Quantities

T (K)	$H^E_m(p^\circ)$ ($J \cdot mol^{-1}$)	σH^E_m ($J \cdot mol^{-1}$)	$-\phi_{11}$ ($cm^3 \cdot mol^{-1}$)	$-\phi_{22}$ ($cm^3 \cdot mol^{-1}$)	$-\phi_{12}$ ($cm^3 \cdot mol^{-1}$)	$-B_{11}$ ($cm^3 \cdot mol^{-1}$)	$-B_{22}$ ($cm^3 \cdot mol^{-1}$)	$-B_{12}$ ($cm^3 \cdot mol^{-1}$)
363.2	119	4	3549	3112	954	673	915	424
368.2	104	3	3306	2994	927	635	885	409
373.2	92	2	3086	2883	902	600	857	395
378.2	82	2	2887	2781	878	569	831	382
383.2	76	2	2705	2685	855	539	806	370
393.2	66	1	2389	2510	812	487	759	346
403.2	57	1	2125	2355	773	442	717	325
413.2	51	1	1901	2218	735	403	678	306
423.2	46	1	1710	2094	702	369	642	288
433.2	40	2	1547	1982	668	339	609	272
473.2	31	2	1084	1625	561	250	499	218
483.2	29	2	1001	1553	538	234	476	207
493.2	26	1	928	1486	516	219	454	196
503.2	25	2	863	1424	497	205	434	186
513.2	24	2	805	1366	477	192	415	177
523.2	23	1	752	1311	458	181	397	168

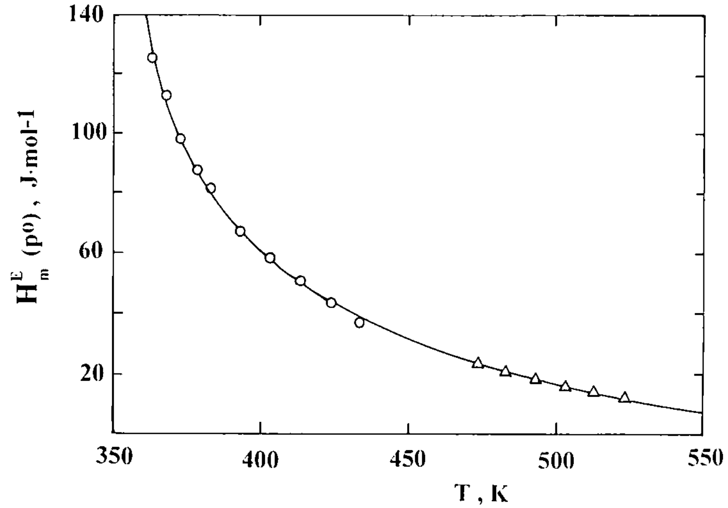

Fig. 1. The excess molar enthalpy $H^{E}_{m}(p^{\circ})$ at standard atmospheric pressure p° for $(0.5CH_3OH + 0.5C_6H_{12})(g)$. (○) Measurements made with the low-pressure differential flow mixing calorimeter (Table 1). (△) Values of $H^{E}_{m}(p^{\circ})$ obtained by extrapolating to $p = p^{\circ}$ measurements made with a single-stage mixing calorimeter operating at high temperatures and pressures. The extrapolation is shown in Fig. 3a. The curve through the points was calculated from the association model with $\xi = 0.92$ as described in the text.

3. VALUES OF $H^{E}_{M}(P^{0})$ FROM HIGH-PRESSURE MEASUREMENTS

The high-pressure H^{E}_{m} measurements reported previously [7] extend over the temperature range 454.2 to 523.0 K and pressures up to 4.0 MPa. These measurements were made using a single mixing calorimeter rather than a differential arrangement, but at high pressures the speed of flow through the calorimeter is much less than at low pressures and the Joule–Thomson effect in the calorimeter is consequently negligible. Using this calorimeter it is difficult to make accurate measurements at pressures much below 0.5 MPa because H^{E}_{m} diminishes as the pressure is reduced and the error due to temperature fluctuations in the fluidized alumina bath surrounding the calorimeter increases in inverse proportion to the pressure. The best way to extrapolate the high-pressure excess enthalpies to standard atmospheric pressure is to plot graphs of (H^{E}_{m}/p) against p. The measurements at pressures up to 2 MPa and at temperatures from 463.2 to 523.2 K reported previously [7] are plotted this way in Fig. 3. Values of

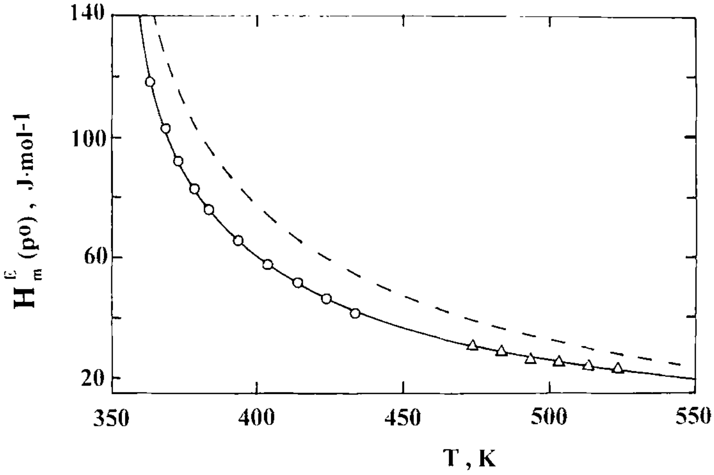

Fig. 2. The excess molar enthalpy $H^E_m(p^\circ)$ at standard atmospheric pressure p° for $(0.5CH_3OH + 0.5C_6H_6)(g)$. (○) Measurements made with the low-pressure differential flow mixing calorimeter (Table II). (△) Values of $H^E_m(p^\circ)$ obtained by extrapolating to $p = p^\circ$ measurements made using a single-stage mixing calorimeter operating at high temperatures and pressures. The extrapolation is shown in Fig 3b. The dashed curve was calculated from the association model with $\xi = 0.92$, which fits the measurements on $(0.5CH_3OH + 0.5C_6H_{12})(g)$ shown in Fig. 1 to within the uncertainty on the measurements. The continuous curve was calculated by including additional terms to describe the specific association between methanol and benzene, for which the interaction energy was found to be $\Delta H_{12} = -13$ kJ·mol^{-1}.

$H^E_m(p = p^\circ, y = 0.5)$ obtained by graphical extrapolation to 0.101 MPa are listed in Tables I and II and plotted (as triangles) in Figs. 1 and 2.

4. ASSOCIATION MODEL

The H^E_m measurements on (water + cyclohexane)(g) and (water + benzene)(g) reported previously were analysed with pair potentials for the pure components and for water in its interaction with hydrocarbon. This could be done for these water mixtures only because an extensive database of H^E_m measurements made on 12 mixtures of gases which do not associate with steam was available, and this information made it possible to obtain parameters of the Stockmayer potential for water in its interaction with normal fluids [1]. A similar database for methanol mixtures is not available, and Stockmayer potential parameters for methanol in its interaction with hydrocarbon are not known. Furthermore, the extent of association in methanol vapor is greater than that for steam, and to describe the

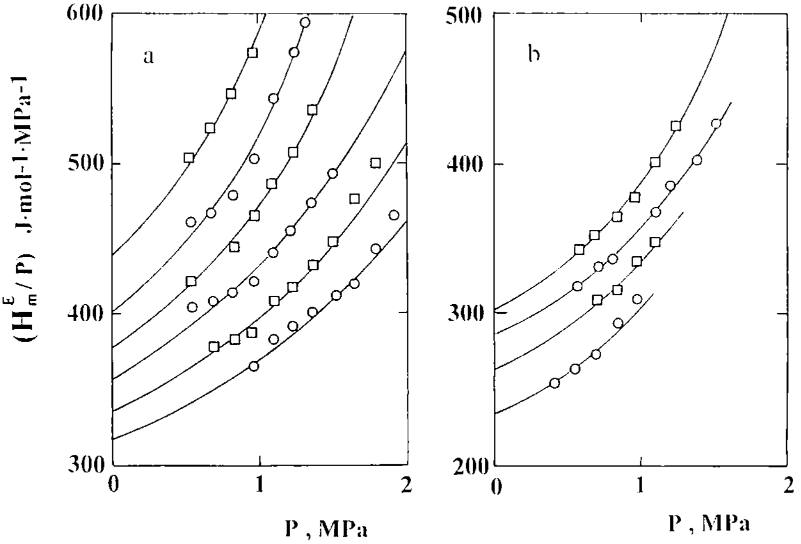

Fig. 3. Measurements of $H^E_m(p^o)$ for $(0.5CH_3OH + 0.5C_6H_6)(g)$ (a) and $(0.5CH_3OH + 0.5C_6H_6)(g)$ (b), plotted in the form H^E_m/p against p to facilitate extrapolation to $p = p^o$. The experimental values are reported in Ref. 7, and the extrapolated values are listed in Tables I and II.

nonideality at temperatures around 373 K it is necessary to take account of the fourth virial coefficient as well as the second. For the above reasons we analyze the H^E_m measurements using a quasi-chemical model which describes the properties of methanol in terms of association equilibria and which can be extended by the addition of further terms which describe the specific interaction between methanol and benzene.

We previously [10] made use of the quasi-chemical model in the form developed by Ginell [11], who gave expressions for the second, third, and fourth virial coefficients B, C, and D in terms of equilibrium constants K_2, K_3, and K_4 for the association of molecules into clusters of two, three, and four molecules, respectively. Ginell's equations differ from the earlier equations of Woolley [12] in that they include terms which are a crude estimate of the hard-sphere second, third, and fourth virial coefficients. We found, as others have done [13, 14], that the nonideality of methanol could be fitted adequately by considering the formation of dimers and tetramers only, and the inclusion of a trimer term was not necessary This procedure uses K_4 as a "catch-all" term which approximates trimer, tetramer, and higher n-mer formation with adequate accuracy. With K_3 set to zero, the first three virial coefficients are

$$B = B_h - K_2 RT \tag{1}$$

$$C = B_h^2 - (21/16)\, B_h K_2 RT + 4K_2^2 (RT)^2 \tag{2}$$

$$D = B_h^3 = (13/8)\, B_h^2 K_2 RT + (89/16)\, B_h K_2^2 (RT)^2 - (20K_2^3 + 3K_4)(RT)^3 \tag{3}$$

Here B_h is the second virial coefficient of a homomorph which approximates the nonspecific forces between the methanol molecules. Differentiation of B, C, and D with respect to temperature gives

$$\phi_o = B - T(dB/dT) \tag{4}$$

$$\Psi = C - (T/2)\, dC/dT) \tag{5}$$

$$\Lambda = D - (T/3)(dD/dT) \tag{6}$$

Differentiation of Eq. (1) yields

$$\phi_o = \phi_h + K_2\, \Delta H_2 \tag{7}$$

Here ΔH_{12} is the enthalpy of formation of the dimer, which is a negative quantity, and ϕ_o is the zeropressure isothermal Joule–Thomson coefficient. Differentiation of Eq. (2) yields

$$\Psi = B_h \phi_h - (21/32)[\phi_h - \Delta H_2 B_h (RT)^{-1}]\, K_2 RT - 4\Delta H_2 K_2^2 RT \tag{8}$$

and differentiation of Eq. (3) yields

$$\begin{aligned} \Lambda = {} & B_h^2 \phi_h - (1/48)[52 B_h \phi_h - 26\Delta H_2 B_h^2 (RT)^{-1}]\, K_2 (RT) \\ & + (1/48)[89\phi_h - 178\Delta H_2 B_h (RT)^{-1}]\, K_2 (RT)^2 \\ & + [20K_2^2 \Delta H_2 + K_4 \Delta H_4](RT)^2 \end{aligned} \tag{9}$$

For a fluid a low densities the residual molar enthalpy H_m^R is given by

$$H_m^R = RT[\phi/V_m) + (\Psi/V_m) + (\Lambda/V_m) + \cdots] \tag{10}$$

and for a binary mixture of components 1 and 2 the excess molar enthalpy H_m^E is given by

$$H_m^E = H_m^R - y_1 H_1^R - y_2 H_m^R \tag{11}$$

where the first term on the right-hand side refers to the mixture. Equation (11) can be written

$$\begin{aligned} H^E_m = {} & [(\phi/V_m) + (\Psi/V_m^2) + (\Lambda/V_m^3)] \\ & - y_1[(\phi_{11}/V_{m1}) + (\Psi_{111}/V_{m1}^2) + (\Lambda_{1111}/V_{m1}^3)] \\ & - y_2[(\phi_{22}/V_{m2}) + (\Psi_{222}/V_{m2}^2) + (\Lambda_{2222}/V_{m2}^3)] \end{aligned} \qquad (12)$$

In Eq. (12) ϕ, Ψ, and Λ refer to the mixture and are given by the equations

$$\phi = y_1^2\phi_{11} + 2y_1y_2\phi_{12} + y_2^2\phi_{22} \qquad (13)$$

$$\Psi = y_1^3\Psi_{111} + 3y_1^2y_2\Psi_{112} + 3y_1y_2^2\Psi_{122} + y_2^3\Psi_{222} \qquad (14)$$

$$\Lambda = y_1^4\Lambda_{1111} + 4y_1^3y_2\Lambda_{1112} + 6y_1^2y_2^2\Lambda_{1122} + 4y_1y_2^3\Lambda_{1222} + y_2^4\Lambda_{2222} \qquad (15)$$

V_m is the molar volume of the mixture at the experimental pressure p calculated by iterative solution of the equation

$$p = (RT/V_m)(1 + B/V_m + C/V_m^2 + D/V_m^3) \qquad (16)$$

The mixture virial coefficients B, C, and D were calculated from equations of similar form to Eqs. (13)–(15). The molar volumes V_{m1} and V_{m2} of the pure components at pressure p were calculated in similar fashion.

It is not possible to calculate all the terms in Eqs. (14) and (15), nor is it necessary to do so. The focus of interest is the term ϕ_{12}, and hence B_{12}, in Eq. (14). As pair potentials for methanol in its interaction with hydrocarbon are not available, the corresponding-states correlation of Pitzer and Curl [15] or that of Tsonopoulos [16] can be used. A corresponding-states correlation will adequately represent B_{22} and ϕ_{22} for benzene or cyclohexane and can be used to calculate similar properties for the chosen homomorph. To develop the quasi-chemical model for methanol the nonspecific forces between two methanol molecules were estimated by assuming them to be the same as the forces between two fluoromethane molecules. This choice of homomorph was used previously [6] and it is useful to recall the reasons for the choice. The molar masses of methanol and fluoromethane are the same, and the polarizabilities α and dipole moments μ are similar. For methanol $\alpha = 32.5 \times 10^{-25}$ cm$^3 \cdot$molecule^{-1} and $\mu = 1.70$ D, and for fluoromethane $\alpha = 35.0 \times 10^{-25}$ cm$^3 \cdot$molecule^{-1} and $\mu = 1.85$ D. The closeness of these electrical properties suggests that the nonideality of the fluoroalkane should approximate the nonspecific forces of the corresponding alcohol fairly well, though clearly the dipole–dipole interaction energy will be a little stronger for the homomorph than for methanol. As this energy diminishes with an increase in temperature, fluoromethane will be a better model for methanol at high temperatures.

In its interaction with cyclohexane, methanol forms no hydrogen bond. In our model this interaction is represented by the interaction between cyclohexane and fluoromethane, and the appropriate cross-terms B_{12} and ϕ_{12} were calculated using the following combining rules, in which subscript h refers to the homomorph.

$$T_{\mathrm{ch2}} = \xi(T_{\mathrm{ch}} T_{\mathrm{c2}})^{1/2} \tag{17}$$

$$V_{\mathrm{ch2}} = [V_{\mathrm{ch}})^{1/3} + (V_{\mathrm{c2}})^{1/3}]/8 \tag{18}$$

$$\omega_{\mathrm{h2}} = (\omega_{\mathrm{h}} + \omega_2)/2 \tag{19}$$

$$p_{\mathrm{ch2}} = Z_{\mathrm{ch2}} R T_{\mathrm{ch2}} / V_{\mathrm{ch2}} \tag{20}$$

where

$$Z_{\mathrm{ch2}} = 0.291 - 0.08\omega_{\mathrm{h2}} \tag{21}$$

Equation (21) is due to Pitzer [17]. The interaction parameter ξ was calculated from the formula [18]

$$\xi = 2[(V_{\mathrm{ch}} V_{\mathrm{c2}})^{1/2} (V_{\mathrm{h2}})^{-1}](I_{\mathrm{h}} I_2)^{1/2} (I_{\mathrm{h}} + I_2)^{-1} \tag{22}$$

This formula was used previously for water–alkane interactions [19]. Here I is the ionization energy.

At temperatures around 373 K the contribution to the enthalpy of mixing arising from Eqs. (14) and (15) is about 5%, and at temperatures around 473 K it is about 1%. We therefore made some simplifications, the first of which was to set all terms in Eq. (14) to zero, and the second of which was to set all terms except the first in Eq. (15) to zero. This term is related to K_4 and ΔH_4, parameters which characterize tetramer formation in methanol, and it is by far the biggest of the five terms in Eq. (15). In analyzing similar measurements on (steam + hydrocarbon) mixtures [20], these same approximations were made and found to be adequate. These simplifications have no consequences for Eqs. (1)–(3), which were used as written.

5. ANALYSIS OF THE (METHANOL + CYCLOHEXANE) $H^{\mathrm{E}}_{\mathrm{M}}$ MEASUREMENTS

Measurement [10] of $H^{\mathrm{E}}_{\mathrm{m}}$ for (methanol + nitrogen)(g) over the temperature range 338.2 to 423.5 K at pressures up to 0.098 MPa were analyzed in terms of the above association model and values of the second virial coefficient of methanol were obtained. These values were found to be consistent with the pressure derivative of the isobaric heat capacity obtained from heat capacity measurements. [13, 14, 21–23]. At temperatures above 373 K the values of B derived from the H_m^E measurements were found to be in good agreement with values obtained from (pVT) studies. Below 373 K it is evident that most of the second virial coefficients obtained using (pVT) techniques are wrong, probably because of large adsorption errors. The model for the analysis of the (methanol + nitrogen) H_m^E measurements, which used fluoromethane as a homomorph for methanol, yielded K_2 (298.15 K) = 0.624 MPa^{-1} and $\Delta H_2 = -18\text{kJ}\cdot\text{mol}^{-1}$ for dimer formation and K_4 (298.15 K) = 569 MPa^{-3} and $\Delta H_4 = -94.3$ kJ $\cdot\text{mol}^{-1}$ for tetramer formation. We have subsequently found that the parameters K_2 (298.15 K) = 0.63 MPa and $\Delta H_2 = -17\text{kJ}\cdot\text{mol}^{-1}$ give a slightly improved fit, and in this work we use these better parameters.

Measurements of the isothermal Joule–Thomson coefficient of benzene and cyclohexane have been made by Francis et al. [24] and Wormald [25] using throttling calorimeters of quite different design. The measurements are in good agreement with each other and are consistent with the best measurements of the second virial coefficient made using (pVT) techniques. While the measurements can be fitted by the corresponding-states correlation of McGlashan and Potter [26], this correlation is of little use in the present application, as any corresponding-states correlation used must also fit the second virial coefficient of fluoromethane. We therefore turned to the correlation of Pitzer and Curl [15] and its modified form suggested by Tsonopoulos [16]. Since these correlations were developed much more work on the nonideality of benzene and cyclohexane vapors has been done, and it is now clear that many of the virial coefficient measurements on which the correlations were based are in error. At temperatures below 400 K the Tsonopoulos correlation gives values of B, and more importantly ϕ, which are too negative. The correlation of Pitzer and Curl is better, and using the acentric factor $\omega = 0.212$ an adequate, though not perfect, fit to values of ϕ for benzene is obtained. For cyclohexane $\omega = 0.213$, but this choice gives values of ϕ which are about 5% too negative, and to fit the measurements of ϕ it is necessary to use $\omega = 0.17$.

The above parameters now allow us to calculate H_m^E for (methanol + cyclohexane)(g). The value of the interaction parameter calculated from Eq. (22) is $\xi = 0.96$, and using this value the above model gives values of H_m^E which agree with the measurements at temperatures below 450 K to within 2% but which are 5% less than the values obtained from the high-pressure, high-temperature measurements. The calculated value of ξ depends on the properties assumed for the homomorph. Although the ionization energy of fluoromethane $(I = 12.6$ eV) is greater than that

($I = 10.8$ eV) for methanol, this makes little difference to the value of ξ, it is the ratio of the critical volumes which has the biggest effect. As there is no way of knowing what the critical volume of methanol might be in the absence of hydrogen bonding, we treated ξ as an adjustable parameter and found that the choice $\xi = 0.92$ gives values of $H^{\mathrm{E}}_{\mathrm{m}}(p^{\circ})$ which agree with experiment over the full temperature range to within the uncertainty on the measurements. The continuous curve shown in Fig. 1 was calculated using $\xi = 0.92$. As can be see from Fig. 1, the curve is an excellent fit to the measurements made using the low-pressure differential flow mixing calorimeter at temperatures up to 433.2 K and to the values of $H^{\mathrm{E}}_{\mathrm{m}}(p^{\circ})$ derived from the high-pressure measurements in the temperature range 473.2 to 523.2 K.

6. ANALYSIS OF THE (METHANOL+BENZENE) $H^{\mathrm{E}}_{\mathrm{M}}$ MEASUREMENTS

The first step was to make adjustments to the association model similar to those made for (methanol + cyclohexane). Equation (22) gives $\xi = 0.96$, the same as for (methanol + cyclohexane), and so the same adjusted parameter $\xi = 0.92$ is appropriate to (methanol + benzene). Putting the critical parameters for benzene, together with $\omega = 0.212$, into the above equations yields values of $H^{\mathrm{E}}_{\mathrm{m}}(p^{\circ})$ which are shown as the dashed curve in Fig. 2. The calculated values are approximately 15 J · mol^{-1} greater than the experimental values, and this suggests that the endothermic mixing process is offset by an exothermic methanol–benzene interaction. To describe this interaction the terms for B_{12} and ϕ_{12} were modified to include new parameters, K_{12} and ΔH_{12}, such that

$$B_{12} = B_{\mathrm{h}2} - (RTK_{12})/2 \tag{23}$$

$$\phi_{12} = \phi_{\mathrm{h}2} + (K_{12}\Delta H_{12})/2 \tag{24}$$

These equations were used previously [27] to fit measurements on mixtures of gases which strongly associate. $B_{\mathrm{h}2}$ and $\phi_{\mathrm{h}2}$ were calculated from the correlation of Pitzer and Curl [15] by combining parameters for fluoromethane and benzene and using $\xi = 0,92$ as described above. The $H^{\mathrm{E}}_{\mathrm{m}}(p^{\circ})$ measurements shown in Fig. 2 are fitted to within experimental error by the parameters K_{12} (298.15 K) = 0.22 MPa^{-1} and $\Delta H_{12} = -13$ kJ · mol^{-1}. Our previous analysis of high-temperature, high-pressure $H^{\mathrm{E}}_{\mathrm{m}}$ measurements on (methanol + benzene)(g) was made using a cubic equation of state with added association terms [6], and this yielded K_{12} (298.15 K) = 0.1773 MPa and $\Delta H_{12} = -14.7$ kJ · mol^{-1}. These parameters are almost the same, but as the cubic equation generates different values for the nonideality of the homomorph, it would be surprising if the values obtained were any closer than they are. Our new values, obtained from measurements over a much wider temperature range and derived from the virial equation rather than a cubic equation, are to be preferred.

Second virial cross-coefficients obtained from the analysis are not sensitive to the choice of homomorph. At 373 K the calculated value of $H^E_m(p^\circ)$ for an equimolar (cyclohexane + fluoromethane) mixture is 43 J · mol^{-1}, and at 523 K it is 18 J · mol^{-1}. The experimental values of $H^E_m(p^\circ)$ for (cyclohexane + methanol) at these temperatures are 118 and 32 J · mol^{-1}, respectively, and the difference between the two sets of figures is the contribution to H^E_m from hydrogen bonding. At 373 K more than 80% of the B_{12} term arises from the specific forces between the unlike molecules. Changing the choice of homomorph does not greatly affect the values of B_{12} for the simple reason that, if a smaller molecule is chosen, the values of K_{12} and ΔH_{12} will compensate by being larger so that the sum of the nonspecific and specific contributions will remain about the same.

Second virial cross-coefficients for cyclohexane–methanol and benzene–methanol derived from the parameters used in the above analysis are listed in Tables I and II. To facilitate comparison with other work, the

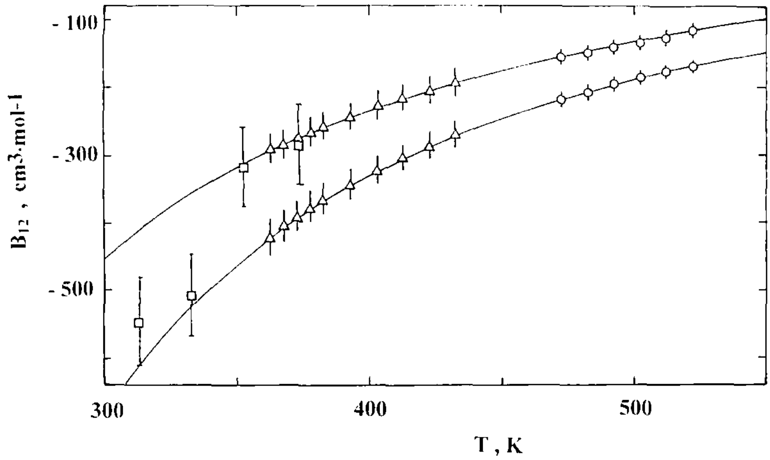

Fig. 4. Second virial cross-coefficients for methanol–cyclohexane (upper curve) and methanol–benzene (lower curve). (○, △) Tables I and II. (○) derived from measurements made with a high-pressure flow mixing calorimeter; (△) derived from measurements made using a low-pressure flow mixing calorimeter; (□) values obtained from a pVT experiment [29]. Curves were calculated from Eqs. (25) and (26).

second virial coefficients B_{11} and B_{22} and isothermal Joule–Thomson coefficients ϕ_{11} of methanol and ϕ_{22} of benzene or cyclohexane and the cross-coefficients ϕ_{12} are also listed. In their compilation of virial coefficients, Dymond and Smith [28] list no second virial cross-coefficients for cyclohexane–methanol and only one set, due to Knoebel and Edmister [29], for benzene–methanol. These are compared with the measurements obtained in this work in Fig. 4. The uncertainty in our values of B_{12} obtained from measurements made using the low-pressure flow mixing calorimeter at temperatures below 450 K is estimated to be $\pm 20\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$, and the uncertainty on the values of B_{12} at higher temperatures is $\pm 10\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$. Knoebel and Edmister used a low-pressure pVT apparatus, and they report their uncertainty to be $\pm 50\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$. Figure 4 shows that their values of B_{12} at 313 and 333 K are in satisfactory agreement with ours, but their values at 353 and 373 K are closer to those for methanol–cyclohexane rather than methanol–benzene. For convenience of calculation we have fitted our second virial cross-coefficients to equations of square-well form. For methanol–cyclohexane,

$$B_{12} = 405.5 - 270.5(\exp 345.2/T)) \tag{25}$$

and for methanol–benzene,

$$B_{12} = 240.8 - 137.4(\exp 570.2/T)) \tag{26}$$

where B_{12} is in $\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$ and T is in K.

7. METHANOL–BENZENE ASSOCIATION

Of particular interest is the comparison of the values of K_{12} and ΔH_{12} for the benzene–methanol interaction with those of the benzene–ethanol and benzene–water interactions. In a parallel publication [30] we report similar measurements on the (ethanol + cyclohexane) and (ethanol + benzene) mixtures. These were analyzed the same way, using fluorethane as a homomorph for ethanol. The specific ethanol–benzene interaction association energy was found to be similar to that for methanol–benzene and is much the same as the value for water–benzene reported previously [4]. For water–benzene $K_{12} = 0.21\ \mathrm{MPa}^{-1}$ and $\Delta H_{12} = -(12 \pm 1.5)\ \mathrm{kJ} \cdot \mathrm{mol}^{-1}$. For methanol–benzene $K_{12} = 0.22\ \mathrm{MPa}^{-1}$ and $\Delta H_{12} = -(13 \pm 1.5)\ \mathrm{kJ} \cdot \mathrm{mol}^{-1}$. For ethanol–benzene $K_{12} = 0.28\ \mathrm{MPa}^{-1}$ and $\Delta H_{12} = -(14 \pm 1.5)\ \mathrm{kJ} \cdot \mathrm{mol}^{-1}$. The uncertainties in the values of K_{12} (298.15 K) are about 5%. It is possible that these energies may bear comparison with information obtained from low-temperature molecular beam experiments designed to study the formation of van der Waals complexes. For example lines in the microwave spectrum of a jet-cooled (water + benzene)(g) mixture show that water forms a van der Waals complex with benzene in which the water molecule rotates freely above the plane of the ring, with both hydrogen atoms pointing towards the ring [31]. The binding energy of the complex has been calculated and found to be $-15.8\ \text{kJ} \cdot \text{mol}^{-1}$. Structures of similar complexes formed between methanol and benzene have deduced, and binding energies calculated [32]. Comparison of the calculated binding energy for the water–benzene complex with that obtained from the association model is to some extent justifiable only because Stockmayer potential parameters for water in its interaction with a nonpolar fluid have been obtained [1] and there is no need to fall back on the homomorph approach. To use fluoromethane and fluoroethane as homomorphs, which hopefully provide a reasonable approximation to the nonspecific forces for methanol and ethanol, is much less satisfactory. Both homomorphs probably overestimate the nonspecific forces, with the consequence that the values of ΔH_{12} obtained for the methanol–benzene and ethanol–benzene interactions are likely to be too small.

The uncertainties in the values of ΔH_{12} arising from the choice of fluoromethane and fluoroethane as homomorphs can be considerably reduced by approaching the problem another way. This is based, first, on the fact that the measurements of (benzene + cyclohexane) vapor [8] show that H_{m}^{E} is less than $1\ \text{J} \cdot \text{mol}^{-1}$ and, second, on the fact that the values of B_{12} for water–benzene and water–cyclohexane calculated using the Stockmayer potential with parameters appropriate to water–nonpolar fluid interaction are quite close together. For example [2], at temperatures around 363 K the calculated value of B_{12} for water–benzene is $-120\ \text{cm}^3 \cdot \text{mol}^{-1}$ and for water–cyclohexane it is $-130\ \text{cm}^3 \cdot \text{mol}^{-1}$. The fresh approach to the analysis is to assume that the difference between the values of B_{12} for methanol–benzene and methanol–cyclohexane listed in Tables I and II is due entirely to the specific methanol–benzene interaction. From Table I we see that at temperature $T_1 = 363$ K, B_{12} (methanol–cyclohexane) = $-294\ \text{cm}^3 \cdot \text{mol}^{-1}$, and at $T_2 = 523$ K, $B_{12} = -118\ \text{cm}^3 \cdot \text{mol}^{-1}$. From Table II we see that $T_1 = 363$ K, B_{12} (methanol–benzene) $= -424\ \text{cm}^3 \cdot \text{mol}^{-1}$, and at $T_2 = 523$ K, $B_{12} = -168\ \text{cm}^3 \cdot \text{mol}^{-1}$. At T_1 the difference $(\delta B_{12})_1 = (-294) - (-424) = 130\ \text{cm}^3 \cdot \text{mol}^{-1}$, and at T_2 the difference $(\delta B_{12})_2 = (-118) - (-168) = 50\ \text{cm}^3 \cdot \text{mol}^{-1}$. The quasi-chemical formula $(\delta B_{12}) = RTK_{12}/2$ gives $K_{12} = 0.0861\ \text{MPa}^{-1}$ at 363 K and $K_{12} = 0.023\ \text{MPa}^{-1}$ at 523 K. Finally, ΔH_{12} is obtained from

$$\ln[\delta H_{12})_2/(\delta H_{12})_1] = -(\Delta H_{12}/R)(T_2^{-1} - T_1^{-1}) \qquad (27)$$

Equation (27) gives $\Delta H_{12} = -13.0\ \mathrm{kJ \cdot mol^{-1}}$ for the methanol–benzene interaction. A similar analysis of the (ethanol + benzene)(g) measurements [30] yields $\Delta H_{12} = -14.98\ \mathrm{kJ \cdot mol^{-1}}$ for the ethanol–benzene interaction, and analysis of (water + benzene)(g) measurements [3] yields $\Delta H_{12} = -12.05\ \mathrm{kJ \cdot mol^{-1}}$. These values are close to those obtained above using the homomorph approach and go some way toward justifying the choice of fluoromethane for this purpose.

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