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Excess Enthalpies for Binary Mixtures of Chloroform with Alcohols

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With 1 Figure and 2 Tables

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Abstract

Excess enthalpies have been measured at 25°C and 35°C for the ethanol-chloroform, 1-propanol-chloroform, 2-propanol-chloroform, and 1-butanol-chloroform solutions by use of a Van Ness type dilution calorimeter. A new equation, based on a continuous association model of alcohol (Mecke-Kempton model), is proposed to express the experimental data for these solutions with good accuracy.

Introduction

The work described in this paper forms part of a programme of investigating properties of associated solutions. We have measured excess enthalpies of solutions of chloroform with ethanol, 1-propanol, 2-propanol, and 1-butanol at 25 and 35°C. Those for methanol and chloroform at 35°C have been reported by MOELWYN-HUGHES and MISSEN [1] and those for ethanol-chloroform solutions at 30 and 50°C by SHATAS et al. [2].

There are several attempts to formulate thermodynamic functions of solutions of alcohols and inert solvents under the assumption that the alcohols form linear hydrogen-bonding polymers by successive chemical reactions. One of them is an association model of the Mecke-Kempton type suggested by WIEHE and BAGLEY [3]. WIEHE et al. [4] have extended the model to involve interacting solvents, excluding solvents that are both electron donating and electron withdrawing such as chloroform. They neglected physical effects in the model and took the ratio of molar volumes of alcohol and solvent as an adjustable parameter. Their theory could not represent correctly the excess enthalpy of mixing curve. In this work a new association model that involves chemical, physical, and size effects is presented for calculating the excess enthalpies of alcohol/active solvent liquid mixtures.

Model of Nonathermal Mixtures

Using the local volume fractions suggested by WILSON [5] and the combinatorial factor of Flory-Huggins, NAGATA [6] presented a simplified UNIQUAC equation for the molar excess Gibbs free energy according to the method of ABRAMS and PRAUSNITZ

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[7] who have derived their model, called UNIQUAC (universal quasi-chemical).

$$\begin{aligned} g^E &= g^E \text{ (combinatorial)} + g^E \text{ (residual = physical)} \\ &= RT[x_1 \ln(\phi_1/x_1) + x_2 \ln(\phi_2/x_2)] + RT[-x_1 \ln(\phi_1 + \phi_2\tau_{21}) \\ &\quad - x_2 \ln(\phi_2 + \phi_1\tau_{12})] \end{aligned} \quad (1)$$

where

$$\tau_{21} = \exp[-(u_{21} - u_{11})/RT], \quad \tau_{12} = \exp[-(u_{12} - u_{22})/RT] \quad (2)$$

In the nonathermal Flory-Huggins equation, the physical contribution term to the excess Gibbs free energy is given by the Scatchard-Hildebrand equation. On the other hand, the physical term of eq. (1) is expressed by a two-parameter equation.

The total enthalpy of formation of the chemical complexes from alcohol (*A*) and solvent (*B*) monomer units is

$$h_c = h_A \sum_{i=1}^{\infty} (i-1)(n_{A_i} + n_{A_i B}) + h_{AB} \sum_{i=1}^{\infty} n_{A_i B} \quad (3)$$

where h_A is the enthalpy of formation of an alcohol hydrogen bond, h_{AB} the enthalpy of formation of an alcohol-solvent bond, and $n_{A_i B}$ is the mole number of a chemical complex $A_i B$.

The definition of the excess enthalpy gives

$$h^E = h_c^E + h_p^E = [h_c - x_A h_c^0]_{\text{chemical}} + [\partial(g_p^E/T)/\partial(1/T)]_{\text{physical}} \quad (4)$$

where h_c^0 is the value of h_c for pure alcohol and $x_A (= x_1)$ is the analytical mole fraction of alcohol.

The independent chemical equilibria and equilibrium constants are, respectively, defined by

$$A_i + A_1 = A_{i+1}, \quad K_A = \phi_{A_{i+1}}/(\phi_{A_i} \phi_{A_1}), \quad (5a \text{ and } b)$$

$$A_i + B = A_i B, \quad K_{AB} = \phi_{A_i B}/(\phi_{A_i} \phi_{OB}) \quad (6a \text{ and } b)$$

Thus, the final expression for the excess enthalpy is

$$\begin{aligned} h^E &= \frac{h_A x_1}{K_A \phi_1} \{ \phi_1 \ln(1 + K_A) + \ln(1 - K_A \phi_{A_1}) - K_{AB} \phi_{OB} f \} + \frac{h_{AB} x_1 K_{AB}}{K_A \phi_1} \phi_{OB} f \\ &\quad - R \left[\frac{x_1 \phi_2}{(\phi_1 + \phi_2 \tau_{21})} \frac{\partial \tau_{21}}{\partial(1/T)} + \frac{x_2 \phi_1}{(\phi_2 + \phi_1 \tau_{12})} \frac{\partial \tau_{12}}{\partial(1/T)} \right] \end{aligned} \quad (7)$$

where ϕ_{A_1} , the volume fraction of alcohol monomer, and ϕ_{OB} , that of solvent monomer, are obtained from the following relations in which V is the true molar volume of the solution

$$\phi_1 = \phi_A = \sum_{i=1}^{\infty} \phi_{A_i} + \sum_{i=1}^{\infty} \frac{n_{A_i B} V_{A_i}}{V} = \frac{\phi_{A_1} (1 + K_{AB} \phi_{OB})}{1 - K_A \phi_{A_1}} - \frac{K_{AB} \phi_{OB} V_B f}{K_A V_A}, \quad (8)$$

$$\phi_2 = \phi_B = \sum_{i=0}^{\infty} \frac{n_{A_i B} V_B}{V} = \phi_{OB} \left(1 + \frac{V_B K_{AB} f}{V_A K_A} \right), \quad (9)$$

$$f = \sum_{i=1}^{\infty} \frac{(K_A \phi_{A_1})^i}{i + (V_B/V_A)} \quad (10)$$

Experimental Section

Chemically pure materials were purified for experimental work. The alcohols were distilled over drying materials: ethanol (calcium oxide), propanols (anhydrous copper sulfate), 1-butanol (calcium oxide). Chloroform was distilled in a packed column.

Table 1. Excess enthalpies for binary systems, J mol⁻¹

| Ethanol(1)-chloroform(2) | | | | 1-Propanol(1)-chloroform(2) | | | |
|--------------------------|--------|--------|--------|-----------------------------|--------|--------|--------|
| 25°C | | 35°C | | 25°C | | 35°C | |
| x_1 | h^E | x_1 | h^E | x_1 | h^E | x_1 | h^E |
| 0.0105 | 80.7 | 0.0172 | 155.1 | 0.0261 | 227.5 | 0.0291 | 239.6 |
| 0.0234 | 161.7 | 0.0381 | 304.7 | 0.0674 | 445.0 | 0.0777 | 494.4 |
| 0.0410 | 247.0 | 0.0538 | 389.8 | 0.1431 | 589.5 | 0.1612 | 664.0 |
| 0.0626 | 317.9 | 0.0822 | 494.8 | 0.1810 | 601.5 | 0.2493 | 667.4 |
| 0.0786 | 342.1 | 0.1154 | 559.2 | 0.2399 | 573.8 | 0.2931 | 631.5 |
| 0.0930 | 360.3 | 0.1270 | 573.2 | 0.2963 | 510.8 | 0.3686 | 526.4 |
| 0.1233 | 377.6 | 0.1396 | 584.3 | 0.3631 | 403.0 | 0.4341 | 404.2 |
| 0.1425 | 377.8 | 0.1538 | 592.1 | 0.4333 | 263.1 | 0.4853 | 295.2 |
| 0.1683 | 371.4 | 0.1747 | 595.2 | 0.5332 | 36.2 | 0.5097 | 233.5 |
| 0.1963 | 353.4 | 0.1826 | 595.4 | 0.5694 | -47.8 | 0.5302 | 193.1 |
| 0.2442 | 302.2 | 0.1976 | 590.1 | 0.6113 | -141.8 | 0.5562 | 126.4 |
| 0.2897 | 232.1 | 0.2137 | 580.3 | 0.6547 | -232.6 | 0.6065 | 9.8 |
| 0.3530 | 115.9 | 0.2328 | 564.6 | 0.7132 | -334.5 | 0.6637 | -113.8 |
| 0.3946 | 29.6 | 0.2533 | 542.7 | 0.7649 | -394.3 | 0.7448 | -256.6 |
| 0.4146 | -13.4 | 0.2774 | 511.6 | 0.8299 | -411.5 | 0.7980 | -311.3 |
| 0.4406 | -70.9 | 0.3057 | 469.0 | 0.8816 | -364.3 | 0.8897 | -291.9 |
| 0.4902 | -185.3 | 0.3281 | 431.0 | 0.9444 | -214.6 | 0.9414 | -197.9 |
| 0.5307 | -276.9 | 0.3543 | 382.4 | 0.9829 | -76.9 | 0.9774 | -88.0 |
| 0.5960 | -420.3 | 0.3846 | 320.9 | | | | |
| 0.6541 | -526.7 | 0.4227 | 138.0 | | | | |
| 0.7099 | -595.2 | 0.4626 | 46.8 | | | | |
| 0.7362 | -613.5 | 0.5032 | 49.5 | | | | |
| 0.7707 | -622.6 | 0.5519 | -67.1 | | | | |
| 0.8101 | -605.7 | 0.5951 | -167.5 | | | | |
| 0.8614 | -532.1 | 0.6144 | -210.9 | | | | |
| 0.9198 | -369.2 | 0.6473 | -280.5 | | | | |
| 0.9485 | -257.4 | 0.6690 | -322.5 | | | | |
| 0.9802 | -106.7 | 0.6924 | -363.5 | | | | |
| 0.9919 | -45.1 | 0.7209 | -405.5 | | | | |
| | | 0.7507 | -438.7 | | | | |
| | | 0.7676 | -449.6 | | | | |
| | | 0.7984 | -461.0 | | | | |
| | | 0.8300 | -453.9 | | | | |
| | | 0.8660 | -419.8 | | | | |
| | | 0.8971 | -364.1 | | | | |
| | | 0.9220 | -301.5 | | | | |
| | | 0.9423 | -239.1 | | | | |
| | | 0.9632 | -162.8 | | | | |
| | | 0.9822 | -83.0 | | | | |

Table 1 (Continued)

| 2-Propanol(1)-chloroform(2) | | | | 1-Butanol(1)-chloroform(2) | | | |
|-----------------------------|--------|--------|--------|----------------------------|--------|--------|--------|
| 25°C | | 35°C | | 25°C | | 35°C | |
| x_1 | h^E | x_1 | h^E | x_1 | h^E | x_1 | h^E |
| 0.0304 | 258.8 | 0.0299 | 251.9 | 0.0178 | 161.6 | 0.0228 | 209.3 |
| 0.0853 | 550.9 | 0.0532 | 418.5 | 0.0725 | 467.6 | 0.0545 | 420.6 |
| 0.1285 | 675.6 | 0.0757 | 541.4 | 0.1421 | 606.5 | 0.1148 | 639.4 |
| 0.1736 | 746.3 | 0.1043 | 658.1 | 0.2101 | 620.4 | 0.2035 | 732.4 |
| 0.2082 | 772.0 | 0.1474 | 780.6 | 0.2736 | 580.2 | 0.2958 | 684.8 |
| 0.2320 | 778.9 | 0.1884 | 851.0 | 0.3293 | 507.9 | 0.3503 | 615.6 |
| 0.2604 | 777.2 | 0.1908 | 851.3 | 0.3850 | 414.5 | 0.3945 | 542.6 |
| 0.2953 | 763.7 | 0.2227 | 881.5 | 0.4299 | 327.2 | 0.4375 | 461.9 |
| 0.3291 | 739.7 | 0.2495 | 893.6 | 0.4680 | 247.4 | 0.4692 | 398.2 |
| 0.3852 | 678.3 | 0.2832 | 895.9 | 0.5300 | 101.8 | 0.5080 | 315.0 |
| 0.4644 | 556.4 | 0.3258 | 879.6 | 0.5938 | -38.1 | 0.5656 | 186.3 |
| 0.5171 | 456.1 | 0.4101 | 796.9 | 0.6631 | -176.8 | 0.6289 | 45.5 |
| 0.5472 | 392.5 | 0.4875 | 674.5 | 0.7082 | -251.7 | 0.7053 | -106.8 |
| 0.6375 | 201.6 | 0.5762 | 696.5 | 0.7809 | -333.3 | 0.7696 | -202.6 |
| 0.7222 | 22.5 | 0.6833 | 252.3 | 0.8282 | -347.0 | 0.8301 | -248.8 |
| 0.7682 | -63.6 | 0.7826 | 38.0 | 0.9149 | -260.6 | 0.9040 | -220.1 |
| 0.8121 | -129.3 | 0.8322 | -46.9 | 0.9629 | -135.6 | 0.9648 | -107.4 |
| 0.8577 | -172.6 | 0.8806 | -100.4 | | | | |
| 0.8843 | -177.1 | 0.8980 | -104.6 | | | | |
| 0.9100 | -171.4 | 0.9379 | -95.6 | | | | |
| 0.9479 | -130.8 | 0.9777 | -48.6 | | | | |
| 0.9844 | -49.4 | | | | | | |

Refractive indices of the purified materials were measured by a Shimadzu Pulfrich refractometer at 25°C; chloroform, 1.4427; ethanol, 1.3594; 1-propanol, 1.3835; 2-propanol, 1.3750; 1-butanol, 1.3971. The isothermal semicontinuous dilution calorimeter [8], which was originally designed by VAN NESS, was used to obtain the excess enthalpies for chloroform-alcohol solutions at 25 and 35°C. Table 1 presents experimental data for four binary systems. Figure 1 illustrates the data graphically. Our data for the ethanol-chloroform system seem to be consistent with the data of SHATAS et al. [2] at 30 and 50°C.

Data Reduction

Considering the totality of the data, we have selected for h_A the value of -6 kcal mol^{-1} and for h_{AB} the value of $-5.9 \text{ kcal mol}^{-1}$. At 50°C, K_A is 450 for methanol, 190 for ethanol, 110 for 1-propanol, 85 for 2-propanol, and 95 for 1-butanol. The van't Hoff equation fixes the temperature dependence of the chemical equilibrium constant

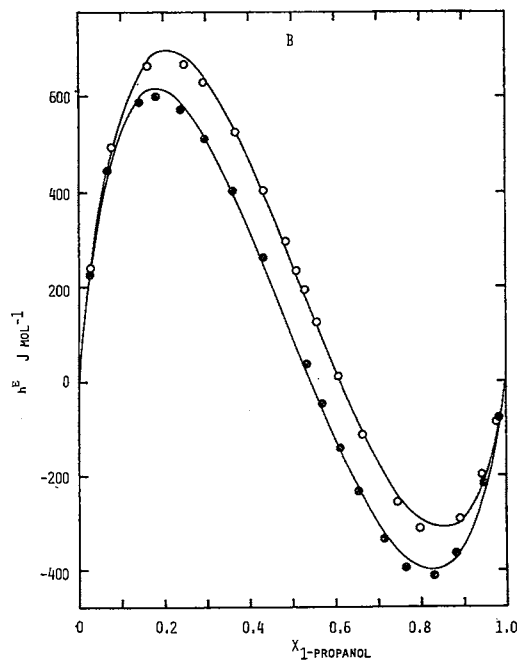
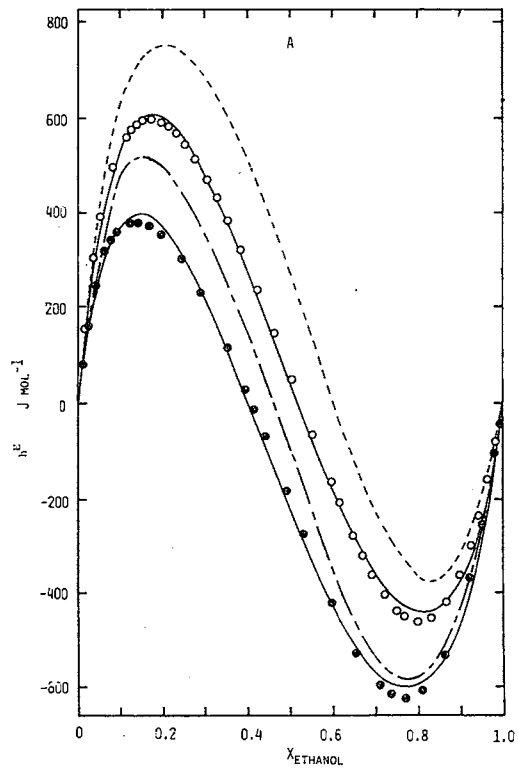
$$\partial \ln K / \partial \ln (1/T) = -h/R \quad (11)$$

K_{AB} at 50°C is 350 for the methanol-chloroform system, 150 for the ethanol-chloroform, 85 for the 1-propanol-chloroform, 70 for the 2-propanol-chloroform, and 75 for the

Table 2. Calculated results for five binary systems

| System (1-2) | K_{AB} at 50°C | h_{AB} (kcal mol ⁻¹) | Temp. °C | No. of data points | Abs. arith. mean dev. (cal mol ⁻¹) | C_1 C_2 (cal mol ⁻¹) | D_1 D_2 (cal K ⁻¹ mol ⁻¹) | Ref. |
|-----------------------|---------------------|---------------------------------------|-------------|-----------------------|--|--|---|-----------|
| Methanol-chloroform | 350 | -5.9 | 35 | 10 | 3.6 | 1700.69 -247.97 | -5.2218 4.9218 | [1] |
| Ethanol-chloroform | 150 | -5.9 | 25 | 29 | 4.5 | 1190.86 137.21 | -4.2534 6.9634 | This work |
| 1-Propanol-chloroform | 85 | -5.9 | 25 | 18 | 3.7 | 1335.03 105.20 1130.34 | -5.5125 6.0643 -5.8752 | This work |
| 2-Propanol-chloroform | 70 | -5.9 | 25 | 22 | 2.4 | 357.57 1096.60 300.17 1042.78 | 6.4153 -5.6529 5.6437 -5.1110 | This work |
| 1-Butanol-chloroform | 75 | -5.9 | 25 | 17 | 3.1 | 669.76 1069.08 702.23 974.61 429.34 1081.87 469.24 | 5.7741 -5.1226 4.9722 -6.2744 6.0894 -6.1853 5.3366 | This work |

1 cal = 4.1868 J.



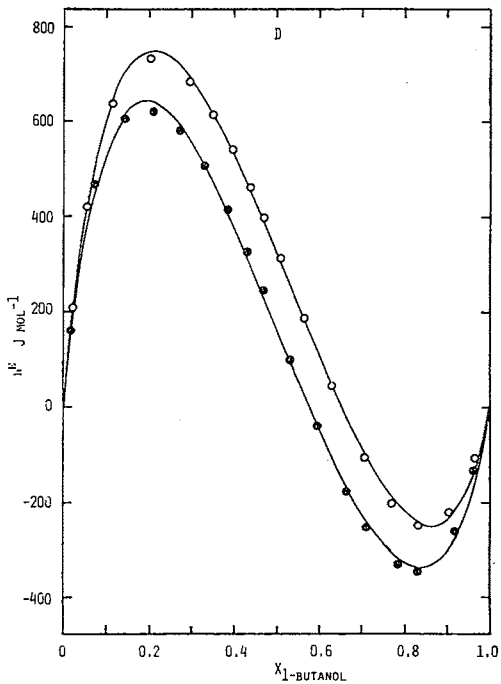
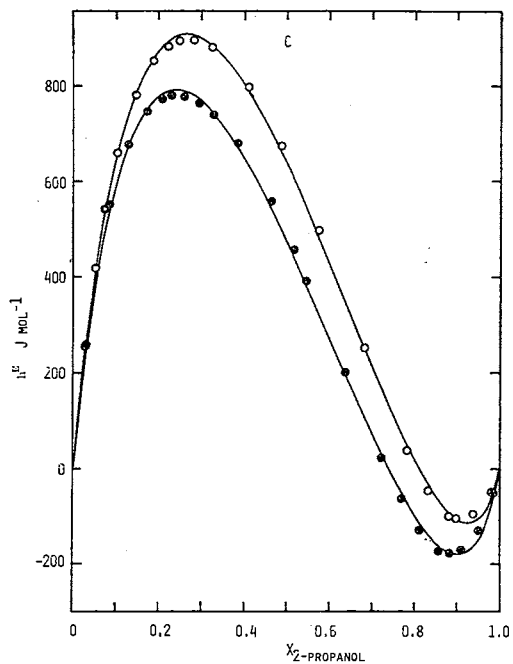


Fig. 1. Comparison of calculated and experimental excess enthalpies for four alcohol-chloroform systems: calculated (—); experiment: this work, (●) 25°C, (○) 35°C; (A) ethanol(1)-chloroform(2), Shatas et al. [2], (—) 30°C, (.....) 50°C, smoothed data were obtained by an empirical equation given in ref. [2]; (B) 1-propanol(1)-chloroform(2); (C) 2-propanol(1)-chloroform(2); (D) 1-butanol(1)-chloroform(2)

1-butanol-chloroform. We assumed that the physical interaction parameters vary linearly with temperature

$$u_{ji} - u_{ii} = C_i + D_i(T - 273.15) \quad (12)$$

The simplex method [9] was used to obtain the constants C_i and D_i for each system. Data reduction for five binary alcohol-chloroform systems is listed in Table 2.

It is not easy for the previous associated solution theories to represent well the excess enthalpy curves for solutions including alcohols and active solvents. The excess enthalpy data of the alcohol-chloroform systems having endo- and exothermic regions provide a particularly severe test for the associated solution theories. Figure 1 compares the calculated values with the experimental results, showing that the present approach solves this problem with good accuracy. Detailed calculated results of thermodynamic properties for many alcohol-active solvent systems by use of the present theory are available in a separate publication [10].

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