

published data, these data were summarized by an Arrhenius relationship.

Extensive data have been reported for density, viscosity, N_2O solubility, and N_2O diffusivity for various aqueous amine solutions, aqueous mixtures of alkanolamines, and solutions of MDEA in water/ethanol.

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Glossary

| | |
|-----------|--|
| C | concentration |
| D | diffusivity |
| Ha | Hatta number (see eq 2) |
| k_{app} | apparent pseudo-first-order reaction rate constant |
| k_L | liquid-phase mass-transfer coefficient |
| m | dimensionless solubility (see eq 4) |
| T | temperature |

Greek Letters

| | |
|--------|-----------|
| η | viscosity |
| ρ | density |

Amine Abbreviations

| | |
|-------|---|
| AMP | 2-amino-2-methyl-1-propanol |
| DEA | diethanolamine |
| DEMEA | diethylmonoethanolamine |
| DGA | diglycolamine, 2-(2-aminoethoxy)ethanol |
| DIPA | diisopropanolamine |
| DMMEA | dimethylmonoethanolamine |
| MDEA | <i>N</i> -methyldiethanolamine |
| MEA | monoethanolamine |
| MMEA | methylmonoethanolamine |

MOR morpholine, 1-oxa-4-azacyclohexane
TEA triethanolamine

Registry No. COS, 463-58-1; CO_2 , 124-38-9; N_2O , 10024-97-2; MEA, 141-43-5; DEA, 111-42-2; MMEA, 109-83-1; AMP, 124-68-5; TEA, 102-71-6; MDEA, 105-59-9; DMMEA, 108-01-0; DEMEA, 100-37-8; DGA, 929-06-8; morpholine, 110-91-8; sulfolane, 126-33-0.

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Excess Volumes of Mixtures of Alkanes with Carbonyl Compounds

Anwel Qin, Dolly E. Hoffman, and Petr Munk*

Department of Chemistry and Biochemistry and Center for Polymer Research, The University of Texas at Austin, Austin, Texas 78712

Excess volumes of mixing were measured at 20 °C for mixtures of three linear alkanes (hexane, heptane, and octane) and cyclohexane with five alkyl acetates (methyl, ethyl, propyl, butyl, and amyl acetates) and two ketones (acetone and 2-butanone). The whole composition range was studied for all 28 binary systems. For a given alkane, the excess volume decreases with the increasing size of the carbonyl compound. For a given carbonyl compound, the excess volume increases with the size of the alkane. The excess volumes for a given pair are distinctly larger for mixtures dilute in the carbonyl compound than for mixtures dilute in the alkane component. This is a result of the nonregular nature of mixtures of compounds having strongly interacting dipoles with nonpolar alkanes.

Among the excess thermodynamic functions of mixing, the excess volume of mixing is understood the least, yet it may reveal details of molecular interaction in liquid mixtures that are

Table I. Densities ρ of Pure Solvents at 20 °C

| solvent | ρ /(g cm ⁻³) | |
|----------------|-------------------------------|------------|
| | this work | lit. |
| methyl acetate | 0.933 89 | 0.9342 (3) |
| ethyl acetate | 0.900 96 | 0.9003 (3) |
| propyl acetate | 0.887 58 | 0.8883 (3) |
| butyl acetate | 0.881 68 | 0.8813 (3) |
| amyl acetate | 0.877 76 | 0.8766 (3) |
| acetone | 0.791 38 | 0.7898 (4) |
| 2-butanone | 0.805 61 | 0.8049 (4) |
| hexane | 0.659 87 | 0.6594 (5) |
| heptane | 0.684 03 | 0.6838 (6) |
| octane | 0.702 78 | 0.7025 (7) |
| cyclohexane | 0.778 84 | 0.7786 (8) |

manifested by other thermodynamic properties to a minor extent or not at all. In our laboratory, we are accumulating extensive thermodynamic data concerning mixtures and utilizing the methods of densitometry, calorimetry, light scattering, and inverse gas chromatography (1, 2). The experiments are performed under very consistent conditions that allow extensive

Table II. Densities ρ , Molar Excess Volumes V^E , Equation 2, Relative Changes in Volume ΔV , Equation 3, Coefficients a_i , Equation 4, b_i and c , Equation 5, and Standard Deviations $\sigma(V^E)$, Equation 6, and $\sigma(\Delta V)$, Equation 7 for Carbonyl Compound (1) + Alkane (2) Mixtures at 20 °C

| φ_1 | x_1 | $\rho/(\text{g cm}^{-3})$ | $V^E/(\text{cm}^3 \text{mol}^{-1})$ | $\Delta V/10^{-2}$ | φ_1 | x_1 | $\rho/(\text{g cm}^{-3})$ | $V^E/(\text{cm}^3 \text{mol}^{-1})$ | $\Delta V/10^{-2}$ |
|--|-------|---------------------------|-------------------------------------|--------------------|-------------|-------|---------------------------|-------------------------------------|--------------------|
| Methyl Acetate (1) + Hexane (2) | | | | | | | | | |
| 1.000 | 1.000 | 0.93389 | | | 0.400 | 0.524 | 0.76077 | 1.201 | 1.158 |
| 0.799 | 0.867 | 0.87971 | 0.498 | 0.578 | 0.302 | 0.416 | 0.73442 | 1.230 | 1.126 |
| 0.705 | 0.797 | 0.84627 | 0.726 | 0.809 | 0.196 | 0.286 | 0.70686 | 1.096 | 0.945 |
| 0.599 | 0.711 | 0.81615 | 0.919 | 0.977 | 0.101 | 0.155 | 0.68319 | 0.765 | 0.624 |
| 0.505 | 0.627 | 0.78959 | 1.092 | 1.109 | 0.000 | 0.000 | 0.65989 | | |
| $a_0 = 4.867; a_1 = 0.951; a_2 = 0.485; a_3 = 0.209; \sigma(V^E/x_1x_2) = 0.048 \text{ cm}^3 \text{mol}^{-1}$ $c = -0.528; b_0 = 4.432 \times 10^{-2}; b_1 = -0.561 \times 10^{-2}; \sigma(\Delta V/\varphi_1\varphi_2) = 0.036 \times 10^{-2}$ | | | | | | | | | |
| Methyl Acetate (1) + Heptane (2) | | | | | | | | | |
| 1.000 | 1.000 | 0.93388 | | | 0.398 | 0.550 | 0.77422 | 1.325 | 1.210 |
| 0.895 | 0.940 | 0.90426 | 0.313 | 0.375 | 0.309 | 0.452 | 0.75253 | 1.336 | 1.150 |
| 0.796 | 0.878 | 0.87686 | 0.599 | 0.685 | 0.203 | 0.320 | 0.72783 | 1.188 | 0.951 |
| 0.700 | 0.812 | 0.85125 | 0.834 | 0.907 | 0.109 | 0.185 | 0.70683 | 0.853 | 0.636 |
| 0.601 | 0.736 | 0.82538 | 1.042 | 1.074 | 0.000 | 0.000 | 0.68403 | | |
| 0.503 | 0.651 | 0.80031 | 1.208 | 1.176 | | | | | |
| $a_0 = 5.350; a_1 = 0.155; a_2 = 0.531; a_3 = 0.021; \sigma(V^E/x_1x_2) = 0.044 \text{ cm}^3 \text{mol}^{-1}$ $c = -0.557; b_0 = 4.738 \times 10^{-2}; b_1 = -1.341 \times 10^{-2}; \sigma(\Delta V/\varphi_1\varphi_2) = 0.030 \times 10^{-2}$ | | | | | | | | | |
| Methyl Acetate (1) + Octane (2) | | | | | | | | | |
| 1.000 | 1.000 | 0.93388 | | | 0.401 | 0.579 | 0.78609 | 1.377 | 1.204 |
| 0.902 | 0.949 | 0.90777 | 0.312 | 0.374 | 0.300 | 0.468 | 0.76352 | 1.395 | 1.128 |
| 0.800 | 0.892 | 0.88159 | 0.618 | 0.699 | 0.208 | 0.350 | 0.74381 | 1.260 | 0.944 |
| 0.698 | 0.825 | 0.85592 | 0.885 | 0.943 | 0.102 | 0.188 | 0.72206 | 0.851 | 0.580 |
| 0.503 | 0.674 | 0.80928 | 1.269 | 1.192 | 0.000 | 0.000 | 0.70278 | | |
| $a_0 = 5.595; a_1 = -0.349; a_2 = 0.630; a_3 = -0.175; \sigma(V^E/x_1x_2) = 0.036 \text{ cm}^3 \text{mol}^{-1}$ $c = -0.593; b_0 = 4.801 \times 10^{-2}; b_1 = -1.811 \times 10^{-2}; \sigma(\Delta V/\varphi_1\varphi_2) = 0.025 \times 10^{-2}$ | | | | | | | | | |
| Methyl Acetate (1) + Cyclohexane (2) | | | | | | | | | |
| 1.000 | 1.000 | 0.93389 | | | 0.406 | 0.482 | 0.82904 | 1.454 | 1.543 |
| 0.905 | 0.929 | 0.91482 | 0.387 | 0.476 | 0.301 | 0.370 | 0.81394 | 1.385 | 1.421 |
| 0.801 | 0.845 | 0.89494 | 0.754 | 0.900 | 0.202 | 0.257 | 0.80082 | 1.180 | 1.172 |
| 0.705 | 0.765 | 0.87755 | 1.039 | 1.207 | 0.097 | 0.127 | 0.78835 | 0.732 | 0.701 |
| 0.616 | 0.686 | 0.86225 | 1.247 | 1.412 | 0.000 | 0.000 | 0.77887 | | |
| 0.504 | 0.580 | 0.84398 | 1.407 | 1.540 | | | | | |
| $a_0 = 5.815; a_1 = 0.331; a_2 = 0.685; a_3 = 0.347; \sigma(V^E/x_1x_2) = 0.020 \text{ cm}^3 \text{mol}^{-1}$ $c = -0.616; b_0 = 6.168 \times 10^{-2}; b_1 = -2.637 \times 10^{-2}; \sigma(\Delta V/\varphi_1\varphi_2) = 0.020 \times 10^{-2}$ | | | | | | | | | |
| Ethyl Acetate (1) + Hexane (2) | | | | | | | | | |
| 1.000 | 1.000 | 0.90096 | | | 0.391 | 0.462 | 0.74829 | 0.903 | 0.782 |
| 0.799 | 0.842 | 0.84911 | 0.416 | 0.404 | 0.298 | 0.361 | 0.72621 | 0.890 | 0.750 |
| 0.700 | 0.757 | 0.82428 | 0.556 | 0.525 | 0.200 | 0.251 | 0.70373 | 0.778 | 0.636 |
| 0.599 | 0.666 | 0.79903 | 0.716 | 0.659 | 0.100 | 0.129 | 0.68115 | 0.529 | 0.419 |
| 0.498 | 0.570 | 0.77429 | 0.828 | 0.740 | 0.000 | 0.000 | 0.65990 | | |
| $a_0 = 3.497; a_1 = 1.094; a_2 = 0.675; a_3 = -0.009; \sigma(V^E/x_1x_2) = 0.071 \text{ cm}^3 \text{mol}^{-1}$ $c = -0.573; b_0 = 2.959 \times 10^{-2}; b_1 = -0.554 \times 10^{-2}; \sigma(\Delta V/\varphi_1\varphi_2) = 0.051 \times 10^{-2}$ | | | | | | | | | |
| Ethyl Acetate (1) + Heptane (2) | | | | | | | | | |
| 1.000 | 1.000 | 0.90097 | | | 0.390 | 0.489 | 0.76203 | 1.063 | 0.867 |
| 0.906 | 0.935 | 0.87833 | 0.256 | 0.253 | 0.300 | 0.391 | 0.74315 | 1.032 | 0.810 |
| 0.801 | 0.858 | 0.85359 | 0.516 | 0.493 | 0.201 | 0.274 | 0.72284 | 0.892 | 0.670 |
| 0.702 | 0.779 | 0.83078 | 0.726 | 0.669 | 0.101 | 0.144 | 0.70304 | 0.589 | 0.422 |
| 0.602 | 0.694 | 0.80822 | 0.893 | 0.792 | 0.000 | 0.000 | 0.68405 | | |
| 0.500 | 0.600 | 0.78576 | 1.013 | 0.863 | | | | | |
| $a_0 = 4.250; a_1 = 0.244; a_2 = 0.483; a_3 = 0.273; \sigma(V^E/x_1x_2) = 0.006 \text{ cm}^3 \text{mol}^{-1}$ $c = -0.572; b_0 = 3.445 \times 10^{-2}; b_1 = -1.158 \times 10^{-2}; \sigma(\Delta V/\varphi_1\varphi_2) = 0.015 \times 10^{-2}$ | | | | | | | | | |
| Ethyl Acetate (1) + Octane (2) | | | | | | | | | |
| 1.000 | 1.000 | 0.90097 | | | 0.398 | 0.523 | 0.77464 | 1.158 | 0.900 |
| 0.904 | 0.940 | 0.87951 | 0.283 | 0.278 | 0.306 | 0.423 | 0.75710 | 1.120 | 0.829 |
| 0.803 | 0.871 | 0.85733 | 0.558 | 0.526 | 0.199 | 0.293 | 0.73730 | 0.974 | 0.678 |
| 0.702 | 0.797 | 0.83603 | 0.780 | 0.702 | 0.101 | 0.157 | 0.71982 | 0.631 | 0.414 |
| 0.601 | 0.715 | 0.81522 | 0.960 | 0.825 | 0.000 | 0.000 | 0.70279 | | |
| 0.501 | 0.625 | 0.79485 | 1.095 | 0.897 | | | | | |
| $a_0 = 4.625; a_1 = -0.047; a_2 = 0.425; a_3 = -0.071; \sigma(V^E/x_1x_2) = 0.034 \text{ cm}^3 \text{mol}^{-1}$ $c = -0.565; b_0 = 3.592 \times 10^{-2}; b_1 = -1.355 \times 10^{-2}; \sigma(\Delta V/\varphi_1\varphi_2) = 0.025 \times 10^{-2}$ | | | | | | | | | |
| Ethyl Acetate (1) + Cyclohexane (2) | | | | | | | | | |
| 1.000 | 1.000 | 0.90094 | | | 0.397 | 0.421 | 0.81800 | 1.177 | 1.135 |
| 0.901 | 0.909 | 0.88563 | 0.358 | 0.362 | 0.299 | 0.320 | 0.80691 | 1.095 | 1.045 |
| 0.804 | 0.819 | 0.87117 | 0.664 | 0.667 | 0.197 | 0.213 | 0.79620 | 0.889 | 0.840 |
| 0.696 | 0.717 | 0.85609 | 0.916 | 0.910 | 0.103 | 0.112 | 0.78720 | 0.567 | 0.530 |
| 0.601 | 0.625 | 0.84323 | 1.081 | 1.064 | 0.000 | 0.000 | 0.77885 | | |
| 0.498 | 0.523 | 0.83019 | 1.173 | 1.142 | | | | | |
| $a_0 = 4.727; a_1 = 0.570; a_2 = 0.515; a_3 = 0.456; \sigma(V^E/x_1x_2) = 0.017 \text{ cm}^3 \text{mol}^{-1}$ $c = -0.559; b_0 = 4.564 \times 10^{-2}; b_1 = -1.721 \times 10^{-2}; \sigma(\Delta V/\varphi_1\varphi_2) = 0.026 \times 10^{-2}$ | | | | | | | | | |

Table II (Continued)

| φ_1 | x_1 | $\rho/(\text{g cm}^{-3})$ | $V^E/(\text{cm}^3 \text{mol}^{-1})$ | $\Delta V/10^{-2}$ | φ_1 | x_1 | $\rho/(\text{g cm}^{-3})$ | $V^E/(\text{cm}^3 \text{mol}^{-1})$ | $\Delta V/10^{-2}$ |
|---|-------|---------------------------|-------------------------------------|--------------------|-------------|-------|---------------------------|-------------------------------------|--------------------|
| Propyl Acetate (1) + Hexane (2) | | | | | | | | | |
| 1.000 | 1.000 | 0.887 42 | | | 0.406 | 0.436 | 0.748 55 | 0.594 | 0.480 |
| 0.903 | 0.913 | 0.864 24 | 0.136 | 0.117 | 0.296 | 0.323 | 0.723 85 | 0.577 | 0.459 |
| 0.801 | 0.820 | 0.840 12 | 0.270 | 0.229 | 0.197 | 0.218 | 0.701 91 | 0.491 | 0.386 |
| 0.604 | 0.634 | 0.794 25 | 0.462 | 0.382 | 0.000 | 0.000 | 0.659 82 | | |
| 0.504 | 0.535 | 0.770 92 | 0.556 | 0.455 | | | | | |
| $a_0 = 2.277; a_1 = 0.945; a_2 = 0.255; a_3 = -0.142; \sigma(V^E/x_1x_2) = 0.039 \text{ cm}^3 \text{mol}^{-1}$ $c = -0.407; b_0 = 1.807 \times 10^{-2}; b_1 = 0.064 \times 10^{-2}; \sigma(\Delta V/\varphi_1\varphi_2) = 0.029 \times 10^{-2}$ | | | | | | | | | |
| Propyl Acetate (1) + Heptane (2) | | | | | | | | | |
| 1.000 | 1.000 | 0.887 78 | | | 0.400 | 0.459 | 0.761 06 | 0.777 | 0.588 |
| 0.899 | 0.919 | 0.865 78 | 0.195 | 0.166 | 0.303 | 0.356 | 0.741 69 | 0.737 | 0.545 |
| 0.801 | 0.837 | 0.844 56 | 0.391 | 0.325 | 0.207 | 0.249 | 0.722 81 | 0.636 | 0.459 |
| 0.703 | 0.751 | 0.823 60 | 0.545 | 0.443 | 0.101 | 0.125 | 0.702 65 | 0.403 | 0.283 |
| 0.497 | 0.557 | 0.780 70 | 0.748 | 0.580 | 0.000 | 0.000 | 0.684 05 | | |
| $a_0 = 3.096; a_1 = 0.304; a_2 = 0.214; a_3 = 0.587; \sigma(V^E/x_1x_2) = 0.040 \text{ cm}^3 \text{mol}^{-1}$ $c = -0.402; b_0 = 2.307 \times 10^{-2}; b_1 = -0.259 \times 10^{-2}; \sigma(\Delta V/\varphi_1\varphi_2) = 0.049 \times 10^{-2}$ | | | | | | | | | |
| Propyl Acetate (1) + Octane (2) | | | | | | | | | |
| 1.000 | 1.000 | 0.887 77 | | | 0.406 | 0.491 | 0.773 00 | 0.879 | 0.631 |
| 0.903 | 0.929 | 0.868 01 | 0.251 | 0.212 | 0.303 | 0.381 | 0.754 45 | 0.848 | 0.587 |
| 0.797 | 0.847 | 0.847 01 | 0.453 | 0.370 | 0.203 | 0.265 | 0.736 85 | 0.721 | 0.481 |
| 0.699 | 0.766 | 0.827 89 | 0.633 | 0.502 | 0.105 | 0.143 | 0.720 05 | 0.476 | 0.305 |
| 0.596 | 0.675 | 0.808 07 | 0.786 | 0.603 | 0.000 | 0.000 | 0.702 77 | | |
| 0.498 | 0.584 | 0.789 95 | 0.848 | 0.629 | | | | | |
| $a_0 = 3.519; a_1 = 0.268; a_2 = 0.467; a_3 = -0.205; \sigma(V^E/x_1x_2) = 0.082 \text{ cm}^3 \text{mol}^{-1}$ $c = -0.721; b_0 = 2.538 \times 10^{-2}; b_1 = -1.445 \times 10^{-2}; \sigma(\Delta V/\varphi_1\varphi_2) = 0.054 \times 10^{-2}$ | | | | | | | | | |
| Propyl Acetate (1) + Cyclohexane (2) | | | | | | | | | |
| 1.000 | 1.000 | 0.887 36 | | | 0.398 | 0.383 | 0.815 15 | 0.940 | 0.849 |
| 0.901 | 0.905 | 0.875 40 | 0.284 | 0.248 | 0.304 | 0.291 | 0.805 53 | 0.868 | 0.788 |
| 0.808 | 0.798 | 0.862 46 | 0.541 | 0.476 | 0.204 | 0.194 | 0.795 82 | 0.706 | 0.645 |
| 0.703 | 0.689 | 0.849 46 | 0.748 | 0.662 | 0.108 | 0.102 | 0.787 30 | 0.451 | 0.415 |
| 0.592 | 0.576 | 0.836 40 | 0.889 | 0.793 | 0.000 | 0.000 | 0.778 83 | | |
| 0.499 | 0.483 | 0.826 01 | 0.944 | 0.847 | | | | | |
| $a_0 = 3.745; a_1 = 0.828; a_2 = 0.556; a_3 = 0.309; \sigma(V^E/x_1x_2) = 0.013 \text{ cm}^3 \text{mol}^{-1}$ $c = -0.552; b_0 = 3.390 \times 10^{-2}; b_1 = -1.209 \times 10^{-2}; \sigma(\Delta V/\varphi_1\varphi_2) = 0.005 \times 10^{-2}$ | | | | | | | | | |
| Butyl Acetate (1) + Hexane (2) | | | | | | | | | |
| 1.000 | 1.000 | 0.881 65 | | | 0.402 | 0.400 | 0.747 48 | 0.271 | 0.207 |
| 0.908 | 0.907 | 0.860 99 | 0.038 | 0.029 | 0.296 | 0.294 | 0.723 79 | 0.308 | 0.235 |
| 0.808 | 0.807 | 0.838 69 | 0.076 | 0.058 | 0.201 | 0.200 | 0.702 92 | 0.283 | 0.216 |
| 0.703 | 0.701 | 0.815 18 | 0.109 | 0.083 | 0.095 | 0.094 | 0.679 93 | 0.177 | 0.135 |
| 0.505 | 0.502 | 0.770 41 | 0.237 | 0.181 | 0.000 | 0.000 | 0.659 88 | | |
| $a_0 = 0.916; a_1 = 1.172; a_2 = 0.543; a_3 = -0.265; \sigma(V^E/x_1x_2) = 0.036 \text{ cm}^3 \text{mol}^{-1}$ $c = -0.415; b_0 = 0.730 \times 10^{-2}; b_1 = 0.414 \times 10^{-2}; \sigma(\Delta V/\varphi_1\varphi_2) = 0.051 \times 10^{-2}$ | | | | | | | | | |
| Butyl Acetate (1) + Heptane (2) | | | | | | | | | |
| 1.000 | 1.000 | 0.881 77 | | | 0.390 | 0.416 | 0.758 30 | 0.543 | 0.387 |
| 0.896 | 0.906 | 0.860 32 | 0.150 | 0.113 | 0.301 | 0.324 | 0.740 96 | 0.514 | 0.363 |
| 0.797 | 0.814 | 0.839 98 | 0.272 | 0.202 | 0.198 | 0.215 | 0.720 93 | 0.430 | 0.300 |
| 0.699 | 0.720 | 0.819 92 | 0.372 | 0.274 | 0.096 | 0.106 | 0.701 72 | 0.268 | 0.185 |
| 0.603 | 0.628 | 0.800 49 | 0.465 | 0.339 | 0.000 | 0.000 | 0.684 04 | | |
| 0.511 | 0.538 | 0.782 21 | 0.515 | 0.372 | | | | | |
| $a_0 = 2.106; a_1 = 0.616; a_2 = 0.292; a_3 = 0.102; \sigma(V^E/x_1x_2) = 0.026 \text{ cm}^3 \text{mol}^{-1}$ $c = -0.451; b_0 = 1.492 \times 10^{-2}; b_1 = -0.176 \times 10^{-2}; \sigma(\Delta V/\varphi_1\varphi_2) = 0.014 \times 10^{-2}$ | | | | | | | | | |
| Butyl Acetate (1) + Octane (2) | | | | | | | | | |
| 1.000 | 1.000 | 0.881 70 | | | 0.396 | 0.559 | 0.770 21 | 0.522 | 0.440 |
| 0.904 | 0.948 | 0.863 43 | 0.117 | 0.132 | 0.295 | 0.447 | 0.752 46 | 0.526 | 0.413 |
| 0.796 | 0.883 | 0.842 99 | 0.240 | 0.257 | 0.196 | 0.321 | 0.735 45 | 0.462 | 0.336 |
| 0.701 | 0.819 | 0.825 35 | 0.337 | 0.343 | 0.100 | 0.176 | 0.719 11 | 0.310 | 0.208 |
| 0.601 | 0.744 | 0.806 96 | 0.427 | 0.410 | 0.000 | 0.000 | 0.702 78 | | |
| 0.502 | 0.661 | 0.789 05 | 0.493 | 0.445 | | | | | |
| $a_0 = 2.131; a_1 = -0.122; a_2 = 0.189; a_3 = 0.026; \sigma(V^E/x_1x_2) = 0.016 \text{ cm}^3 \text{mol}^{-1}$ $c = -0.510; b_0 = 1.771 \times 10^{-2}; b_1 = -0.493 \times 10^{-2}; \sigma(\Delta V/\varphi_1\varphi_2) = 0.013 \times 10^{-2}$ | | | | | | | | | |
| Butyl Acetate (1) + Cyclohexane (2) | | | | | | | | | |
| 1.000 | 1.000 | 0.881 60 | | | 0.404 | 0.357 | 0.814 45 | 0.841 | 0.721 |
| 0.902 | 0.883 | 0.869 63 | 0.283 | 0.220 | 0.297 | 0.257 | 0.803 99 | 0.756 | 0.662 |
| 0.809 | 0.777 | 0.858 58 | 0.502 | 0.397 | 0.198 | 0.168 | 0.794 90 | 0.601 | 0.536 |
| 0.708 | 0.665 | 0.846 88 | 0.686 | 0.554 | 0.100 | 0.084 | 0.786 48 | 0.369 | 0.336 |
| 0.607 | 0.558 | 0.835 66 | 0.800 | 0.659 | 0.000 | 0.000 | 0.778 83 | | |
| 0.505 | 0.455 | 0.824 82 | 0.848 | 0.714 | | | | | |
| $a_0 = 3.331; a_1 = 0.881; a_2 = 0.573; a_3 = 0.580; \sigma(V^E/x_1x_2) = 0.027 \text{ cm}^3 \text{mol}^{-1}$ $c = -0.522; b_0 = 2.863 \times 10^{-2}; b_1 = -0.873 \times 10^{-2}; \sigma(\Delta V/\varphi_1\varphi_2) = 0.020 \times 10^{-2}$ | | | | | | | | | |

Table II (Continued)

| φ_1 | x_1 | $\rho/(\text{g cm}^{-3})$ | $V^E/(\text{cm}^3 \text{mol}^{-1})$ | $\Delta V/10^{-2}$ | φ_1 | x_1 | $\rho/(\text{g cm}^{-3})$ | $V^E/(\text{cm}^3 \text{mol}^{-1})$ | $\Delta V/10^{-2}$ |
|--|-------|---------------------------|-------------------------------------|--------------------|-------------|-------|---------------------------|-------------------------------------|--------------------|
| Amyl Acetate (1) + Hexane (2) | | | | | | | | | |
| 1.000 | 1.000 | 0.877 77 | | | 0.398 | 0.368 | 0.745 53 | 0.195 | 0.142 |
| 0.901 | 0.889 | 0.855 91 | 0.039 | 0.027 | 0.301 | 0.275 | 0.724 43 | 0.204 | 0.151 |
| 0.805 | 0.784 | 0.834 80 | 0.070 | 0.049 | 0.205 | 0.185 | 0.703 51 | 0.176 | 0.131 |
| 0.706 | 0.679 | 0.813 07 | 0.099 | 0.069 | 0.104 | 0.093 | 0.681 95 | 0.121 | 0.091 |
| 0.601 | 0.570 | 0.789 99 | 0.146 | 0.104 | 0.000 | 0.000 | 0.659 84 | | |
| 0.498 | 0.466 | 0.767 26 | 0.186 | 0.134 | | | | | |
| $a_0 = 0.664; a_1 = 0.627; a_2 = 0.354; a_3 = 0.016; \sigma(V^E/x_1x_2) = 0.031 \text{ cm}^3 \text{mol}^{-1}$ $c = -0.420; b_0 = 0.510 \times 10^{-2}; b_1 = 0.177 \times 10^{-2}; \sigma(\Delta V/\varphi_1\varphi_2) = 0.022 \times 10^{-2}$ | | | | | | | | | |
| Amyl Acetate (1) + Heptane (2) | | | | | | | | | |
| 1.000 | 1.000 | 0.877 77 | | | 0.399 | 0.396 | 0.759 25 | 0.394 | 0.268 |
| 0.899 | 0.898 | 0.857 54 | 0.107 | 0.072 | 0.306 | 0.303 | 0.741 38 | 0.376 | 0.256 |
| 0.704 | 0.702 | 0.819 02 | 0.261 | 0.177 | 0.193 | 0.191 | 0.719 92 | 0.311 | 0.212 |
| 0.603 | 0.600 | 0.798 98 | 0.330 | 0.224 | 0.098 | 0.097 | 0.702 03 | 0.194 | 0.133 |
| 0.497 | 0.494 | 0.778 40 | 0.377 | 0.256 | 0.000 | 0.000 | 0.684 03 | | |
| $a_0 = 1.487; a_1 = 0.670; a_2 = 0.314; a_3 = -0.019; \sigma(V^E/x_1x_2) = 0.017 \text{ cm}^3 \text{mol}^{-1}$ $c = -0.425; b_0 = 1.018 \times 10^{-2}; b_1 = -0.030 \times 10^{-2}; \sigma(\Delta V/\varphi_1\varphi_2) = 0.015 \times 10^{-2}$ | | | | | | | | | |
| Amyl Acetate (1) + Octane (2) | | | | | | | | | |
| 1.000 | 1.000 | 0.877 76 | | | 0.403 | 0.425 | 0.770 66 | 0.525 | 0.336 |
| 0.899 | 0.907 | 0.859 25 | 0.149 | 0.099 | 0.302 | 0.322 | 0.753 28 | 0.495 | 0.313 |
| 0.802 | 0.816 | 0.841 61 | 0.274 | 0.182 | 0.199 | 0.214 | 0.735 74 | 0.411 | 0.258 |
| 0.708 | 0.726 | 0.824 59 | 0.372 | 0.244 | 0.102 | 0.111 | 0.719 45 | 0.265 | 0.165 |
| 0.603 | 0.625 | 0.805 96 | 0.453 | 0.295 | 0.000 | 0.000 | 0.702 78 | | |
| 0.498 | 0.521 | 0.787 42 | 0.505 | 0.325 | | | | | |
| $a_0 = 2.048; a_1 = 0.493; a_2 = 0.303; a_3 = 0.147; \sigma(V^E/x_1x_2) = 0.013 \text{ cm}^3 \text{mol}^{-1}$ $c = -0.513; b_0 = 1.305 \times 10^{-2}; b_1 = -0.305 \times 10^{-2}; \sigma(\Delta V/\varphi_1\varphi_2) = 0.007 \times 10^{-2}$ | | | | | | | | | |
| Amyl Acetate (1) + Cyclohexane (2) | | | | | | | | | |
| 1.000 | 1.000 | 0.877 76 | | | 0.402 | 0.329 | 0.813 45 | 0.771 | 0.636 |
| 0.906 | 0.875 | 0.866 91 | 0.257 | 0.180 | 0.300 | 0.238 | 0.803 75 | 0.691 | 0.587 |
| 0.803 | 0.749 | 0.855 36 | 0.478 | 0.346 | 0.199 | 0.153 | 0.794 75 | 0.544 | 0.476 |
| 0.705 | 0.635 | 0.844 49 | 0.640 | 0.479 | 0.099 | 0.074 | 0.786 34 | 0.319 | 0.287 |
| 0.602 | 0.524 | 0.833 59 | 0.737 | 0.571 | 0.000 | 0.000 | 0.778 82 | | |
| 0.502 | 0.424 | 0.823 34 | 0.784 | 0.627 | | | | | |
| $a_0 = 3.014; a_1 = 1.117; a_2 = 0.605; a_3 = 0.385; \sigma(V^E/x_1x_2) = 0.018 \text{ cm}^3 \text{mol}^{-1}$ $c = -0.368; b_0 = 2.507 \times 10^{-2}; b_1 = -0.295 \times 10^{-2}; \sigma(\Delta V/\varphi_1\varphi_2) = 0.009 \times 10^{-2}$ | | | | | | | | | |
| Acetone (1) + Hexane (2) | | | | | | | | | |
| 1.000 | 1.000 | 0.791 44 | | | 0.402 | 0.545 | 0.705 71 | 0.994 | 1.000 |
| 0.900 | 0.941 | 0.776 02 | 0.219 | 0.285 | 0.306 | 0.440 | 0.693 49 | 1.014 | 0.962 |
| 0.799 | 0.876 | 0.760 90 | 0.427 | 0.530 | 0.210 | 0.321 | 0.681 73 | 0.945 | 0.842 |
| 0.702 | 0.807 | 0.746 73 | 0.615 | 0.729 | 0.101 | 0.167 | 0.669 43 | 0.679 | 0.561 |
| 0.607 | 0.733 | 0.733 39 | 0.771 | 0.869 | 0.000 | 0.000 | 0.659 87 | | |
| 0.498 | 0.638 | 0.718 35 | 0.915 | 0.972 | | | | | |
| $a_0 = 4.042; a_1 = 0.489; a_2 = 0.833; a_3 = 0.484; \sigma(V^E/x_1x_2) = 0.009 \text{ cm}^3 \text{mol}^{-1}$ $c = -0.682; b_0 = 3.862 \times 10^{-2}; b_1 = -1.321 \times 10^{-2}; \sigma(\Delta V/\varphi_1\varphi_2) = 0.029 \times 10^{-2}$ | | | | | | | | | |
| Acetone (1) + Heptane (2) | | | | | | | | | |
| 1.000 | 1.000 | 0.791 52 | | | 0.401 | 0.572 | 0.719 75 | 1.073 | 1.025 |
| 0.894 | 0.944 | 0.777 51 | 0.256 | 0.331 | 0.300 | 0.461 | 0.709 25 | 1.109 | 0.983 |
| 0.795 | 0.886 | 0.765 04 | 0.480 | 0.587 | 0.196 | 0.327 | 0.699 27 | 1.017 | 0.830 |
| 0.699 | 0.822 | 0.753 20 | 0.681 | 0.789 | 0.099 | 0.180 | 0.690 83 | 0.738 | 0.553 |
| 0.592 | 0.743 | 0.740 73 | 0.863 | 0.937 | 0.000 | 0.000 | 0.684 02 | | |
| 0.500 | 0.666 | 0.730 34 | 0.991 | 1.013 | | | | | |
| $a_0 = 4.422; a_1 = 0.186; a_2 = 0.976; a_3 = 0.262; \sigma(V^E/x_1x_2) = 0.023 \text{ cm}^3 \text{mol}^{-1}$ $c = -0.738; b_0 = 4.052 \times 10^{-2}; b_1 = -1.890 \times 10^{-2}; \sigma(\Delta V/\varphi_1\varphi_2) = 0.022 \times 10^{-2}$ | | | | | | | | | |
| Acetone (1) + Octane (2) | | | | | | | | | |
| 1.000 | 1.000 | 0.790 83 | | | 0.401 | 0.597 | 0.730 73 | 1.102 | 1.008 |
| 0.905 | 0.955 | 0.780 00 | 0.244 | 0.315 | 0.303 | 0.490 | 0.722 57 | 1.130 | 0.950 |
| 0.800 | 0.898 | 0.768 59 | 0.494 | 0.599 | 0.199 | 0.355 | 0.714 62 | 1.040 | 0.794 |
| 0.702 | 0.839 | 0.758 57 | 0.696 | 0.793 | 0.102 | 0.201 | 0.708 03 | 0.768 | 0.531 |
| 0.596 | 0.766 | 0.748 28 | 0.881 | 0.934 | 0.000 | 0.000 | 0.702 78 | | |
| 0.499 | 0.688 | 0.739 34 | 1.013 | 1.001 | | | | | |
| $a_0 = 4.510; a_1 = -0.156; a_2 = 1.080; a_3 = -0.140; \sigma(V^E/x_1x_2) = 0.001 \text{ cm}^3 \text{mol}^{-1}$ $c = -0.818; b_0 = 4.030 \times 10^{-2}; b_1 = -2.525 \times 10^{-2}; \sigma(\Delta V/\varphi_1\varphi_2) = 0.024 \times 10^{-2}$ | | | | | | | | | |
| Acetone (1) + Cyclohexane (2) | | | | | | | | | |
| 1.000 | 1.000 | 0.791 74 | | | 0.395 | 0.490 | 0.774 57 | 1.100 | 1.208 |
| 0.899 | 0.929 | 0.787 18 | 0.314 | 0.415 | 0.299 | 0.386 | 0.774 04 | 1.058 | 1.117 |
| 0.797 | 0.852 | 0.783 23 | 0.590 | 0.751 | 0.195 | 0.805 | 0.774 25 | 0.907 | 0.917 |
| 0.699 | 0.774 | 0.780 17 | 0.800 | 0.986 | 0.111 | 0.156 | 0.775 27 | 0.662 | 0.645 |
| 0.602 | 0.690 | 0.777 74 | 0.959 | 1.140 | 0.000 | 0.000 | 0.778 83 | | |
| 0.501 | 0.597 | 0.775 85 | 1.064 | 1.218 | | | | | |
| $a_0 = 4.394; a_1 = 0.065; a_2 = 0.970; a_3 = 0.415; \sigma(V^E/x_1x_2) = 0.006 \text{ cm}^3 \text{mol}^{-1}$ $c = -0.867; b_0 = 4.896 \times 10^{-2}; b_1 = -3.558 \times 10^{-2}; \sigma(\Delta V/\varphi_1\varphi_2) = 0.027 \times 10^{-2}$ | | | | | | | | | |

Table II (Continued)

| φ_1 | x_1 | $\rho/(\text{g cm}^{-3})$ | $V^E/(\text{cm}^3 \text{mol}^{-1})$ | $\Delta V/10^{-2}$ | φ_1 | x_1 | $\rho/(\text{g cm}^{-3})$ | $V^E/(\text{cm}^3 \text{mol}^{-1})$ | $\Delta V/10^{-2}$ |
|--|-------|---------------------------|-------------------------------------|--------------------|-------------|-------|---------------------------|-------------------------------------|--------------------|
| 2-Butanone (1) + Hexane (2) | | | | | | | | | |
| 1.000 | 1.000 | 0.805 51 | | | 0.405 | 0.498 | 0.714 67 | 0.637 | 0.578 |
| 0.905 | 0.933 | 0.790 67 | 0.125 | 0.135 | 0.312 | 0.398 | 0.701 32 | 0.647 | 0.566 |
| 0.805 | 0.857 | 0.774 92 | 0.262 | 0.275 | 0.199 | 0.266 | 0.685 42 | 0.590 | 0.493 |
| 0.715 | 0.785 | 0.761 00 | 0.380 | 0.387 | 0.100 | 0.139 | 0.672 15 | 0.420 | 0.337 |
| 0.601 | 0.687 | 0.743 76 | 0.502 | 0.491 | 0.000 | 0.000 | 0.659 86 | | |
| 0.507 | 0.600 | 0.729 64 | 0.581 | 0.548 | | | | | |
| $a_0 = 2.541; a_1 = 0.646; a_2 = 0.540; a_3 = 0.583; \sigma(V^E/x_1x_2) = 0.009 \text{ cm}^3 \text{mol}^{-1}$ $c = -0.595; b_0 = 2.190 \times 10^{-2}; b_1 = -0.292 \times 10^{-2}; \sigma(\Delta V/\varphi_1\varphi_2) = 0.040 \times 10^{-2}$ | | | | | | | | | |
| 2-Butanone (1) + Heptane (2) | | | | | | | | | |
| 1.000 | 1.000 | 0.805 48 | | | 0.396 | 0.517 | 0.727 33 | 0.762 | 0.651 |
| 0.892 | 0.931 | 0.790 68 | 0.193 | 0.206 | 0.293 | 0.404 | 0.715 19 | 0.764 | 0.619 |
| 0.798 | 0.866 | 0.778 17 | 0.346 | 0.356 | 0.201 | 0.292 | 0.704 64 | 0.699 | 0.538 |
| 0.693 | 0.787 | 0.764 38 | 0.499 | 0.490 | 0.092 | 0.142 | 0.692 88 | 0.463 | 0.335 |
| 0.601 | 0.711 | 0.752 65 | 0.611 | 0.576 | 0.000 | 0.000 | 0.684 02 | | |
| 0.499 | 0.619 | 0.739 87 | 0.708 | 0.636 | | | | | |
| $a_0 = 3.068; a_1 = 0.441; a_2 = 0.625; a_3 = 0.251; \sigma(V^E/x_1x_2) = 0.006 \text{ cm}^3 \text{mol}^{-1}$ $c = -0.688; b_0 = 2.539 \times 10^{-2}; b_1 = -0.958 \times 10^{-2}; \sigma(\Delta V/\varphi_1\varphi_2) = 0.008 \times 10^{-2}$ | | | | | | | | | |
| 2-Butanone (1) + Octane (2) | | | | | | | | | |
| 1.000 | 1.000 | 0.805 67 | | | 0.404 | 0.551 | 0.739 26 | 0.833 | 0.681 |
| 0.904 | 0.944 | 0.794 10 | 0.193 | 0.207 | 0.302 | 0.439 | 0.729 10 | 0.840 | 0.644 |
| 0.806 | 0.883 | 0.782 76 | 0.365 | 0.372 | 0.198 | 0.310 | 0.719 26 | 0.760 | 0.543 |
| 0.702 | 0.811 | 0.771 04 | 0.536 | 0.519 | 0.095 | 0.160 | 0.710 11 | 0.517 | 0.343 |
| 0.597 | 0.729 | 0.759 50 | 0.674 | 0.616 | 0.000 | 0.000 | 0.702 77 | | |
| 0.500 | 0.645 | 0.749 23 | 0.775 | 0.672 | | | | | |
| $a_0 = 3.381; a_1 = 0.218; a_2 = 0.649; a_3 = 0.050; \sigma(V^E/x_1x_2) = 0.024 \text{ cm}^3 \text{mol}^{-1}$ $c = -0.727; b_0 = 2.686 \times 10^{-2}; b_1 = -1.291 \times 10^{-2}; \sigma(\Delta V/\varphi_1\varphi_2) = 0.016 \times 10^{-2}$ | | | | | | | | | |
| 2-Butanone (1) + Cyclohexane (2) | | | | | | | | | |
| 1.000 | 1.000 | 0.805 76 | | | 0.405 | 0.451 | 0.782 69 | 0.901 | 0.904 |
| 0.907 | 0.922 | 0.801 09 | 0.247 | 0.272 | 0.302 | 0.344 | 0.780 44 | 0.854 | 0.840 |
| 0.698 | 0.736 | 0.792 03 | 0.668 | 0.708 | 0.197 | 0.229 | 0.778 80 | 0.716 | 0.690 |
| 0.603 | 0.647 | 0.788 55 | 0.794 | 0.827 | 0.100 | 0.118 | 0.778 06 | 0.476 | 0.449 |
| 0.506 | 0.553 | 0.785 45 | 0.875 | 0.895 | 0.000 | 0.000 | 0.778 86 | | |
| $a_0 = 3.568; a_1 = 0.468; a_2 = 0.679; a_3 = 0.364; \sigma(V^E/x_1x_2) = 0.020 \text{ cm}^3 \text{mol}^{-1}$ $c = -0.722; b_0 = 3.589 \times 10^{-2}; b_1 = -1.888 \times 10^{-2}; \sigma(\Delta V/\varphi_1\varphi_2) = 0.009 \times 10^{-2}$ | | | | | | | | | |

intercorrelation of results. Our ultimate goal is the development of a comprehensive theory of mixtures that would explain simultaneously all the important aspects of liquid mixtures. In the present study, we are reporting our measurements of excess volume of mixing of alkanes with carbonyl compounds. In order to be able to correlate the experimental results with the chemical nature of the components, we have selected for our measurements compounds grouped into chemical families. Thus, our carbonyl compounds were represented by five linear esters (methyl, ethyl, propyl, butyl, and amyl acetates) and two ketones (acetone and 2-butanone). The hydrocarbon family included three linear alkanes (hexane, heptane, and octane) and cyclohexane. Mixtures of each carbonyl compound were studied with each hydrocarbon (28 systems). For each system, the dependence of the excess volume on concentration was measured.

Experimentally, we are measuring the masses m_i and the densities ρ_i of the components and the densities ρ_m of the mixtures. The volume fractions φ_i , the molar excess volumes V^E , and the relative changes in volume ΔV are then calculated as

$$\varphi_i = (m_i/\rho_i)/(m_1/\rho_1 + m_2/\rho_2) \quad (1)$$

$$V^E = [(m_1 + m_2)/\rho_m - m_1/\rho_1 - m_2/\rho_2]/(m_1/M_1 + m_2/M_2) \quad (2)$$

$$\Delta V \equiv V^E/(x_1V_1^\circ + x_2V_2^\circ) = [(m_1 + m_2)/\rho_m - m_1/\rho_1 - m_2/\rho_2]/(m_1/\rho_1 + m_2/\rho_2) \quad (3)$$

where x_i , M_i , and V_i° are mole fraction, molar mass, and molar volume of pure component i , respectively.

Experimental Section

Materials. All hydrocarbons and carbonyl compounds were obtained from Aldrich Chemical Co. and used as supplied. The average measured densities are listed in Table I, together with some literature data.

Apparatus and Procedure. The densities were measured by an Anton Paar digital precision density meter (Model DMA 02C) at 20 °C. The temperature was controlled using a Tronac precision temperature controller (Model 1040) capable of keeping the temperature constant within 0.001 °C. Typically, all mixtures belonging to a given system (including both pure components) were measured during one session; the instrument was calibrated with air and water during every session. While the experimental precision (reproducibility of measured densities during a session) was better than one unit in the fifth decimal place, the accuracy of the measurement was much worse. The accuracy may be judged from the values of density for a given pure compound (as listed in Table II) measured in different sessions. We ascribe this variation to an occasional use of solvents from different manufacturer's lots and, possibly, to deterioration of the solvent (hygroscopy) over a longer period of time. This variation very rarely reaches beyond the fifth decimal place. However, we believe that this variation does not influence appreciably the measured values of excess volume because the mixtures were prepared always shortly before the measurement and the pure components were remeasured together with the mixtures. Thus, these systematic experimental errors essentially cancelled out in the computation of the excess volume.

Our experimental data are listed in Table II for all our systems.

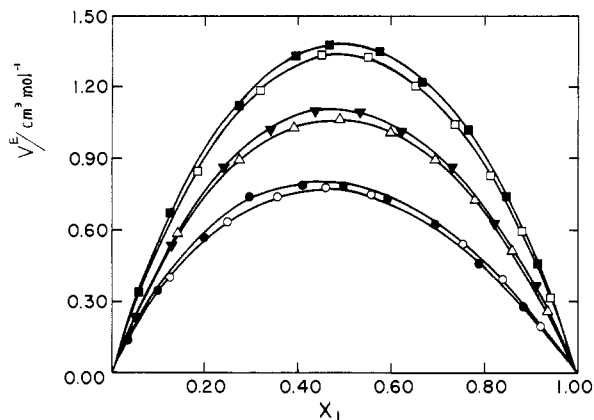


Figure 1. Molar excess volume V^E for carbonyl compounds (1)-heptane (2) mixtures at 20 °C as a function of the mole fraction x_1 of the carbonyl compound: \square , methyl acetate; \blacksquare , methyl acetate (25 °C, ref 9); Δ , ethyl acetate; \blacktriangledown , ethyl acetate (25 °C, ref 9); \circ , propyl acetate; \bullet , propyl acetate (25 °C, ref 9).

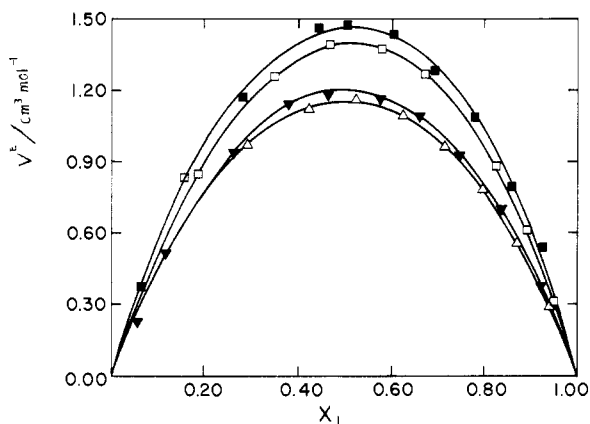


Figure 2. Molar excess volume V^E for carbonyl compounds (1)-octane (2) mixtures at 20 °C as a function of the mole fraction x_1 of the carbonyl compound: \square , methyl acetate; \blacksquare , methyl acetate (25 °C, ref 9); Δ , ethyl acetate; \blacktriangledown , ethyl acetate (25 °C, ref 9).

Discussion

Experimental data of V^E are usually correlated by the following power series

$$V^E/x_1x_2 = \sum a_j(x_2 - x_1)^j \quad (4)$$

For correlation, ΔV can also be expressed mathematically by means of a power series. However, we found that fitting ΔV with a hyperbolic function is more satisfactory. The hyperbolic function reads

$$\Delta V/\varphi_1\varphi_2 = [b_0 + b_1(\varphi_2 - \varphi_1)]/[1 + c(\varphi_2 - \varphi_1)] \quad (5)$$

The correlation coefficients obtained by least-squares fitting are collected in Table II together with the statistical deviations of the fits, $\sigma(V^E/x_1x_2)$ and $\sigma(\Delta V/\varphi_1\varphi_2)$, which have the definitions as follows

$$\sigma(V^E/x_1x_2) = \left[\sum (V_{\text{calc}}^E/x_1x_2 - V^E/x_1x_2)^2 / (N - n - 1) \right]^{1/2} \quad (6)$$

$$\sigma(\Delta V/\varphi_1\varphi_2) = \left[\sum (\Delta V_{\text{calc}}/\varphi_1\varphi_2 - \Delta V/\varphi_1\varphi_2)^2 / (N - n - 1) \right]^{1/2} \quad (7)$$

where N is the number of experimental points and n is the number of coefficients.

We were able to compare some results of our systems with literature data (9-14) for the compositional dependence of V^E .

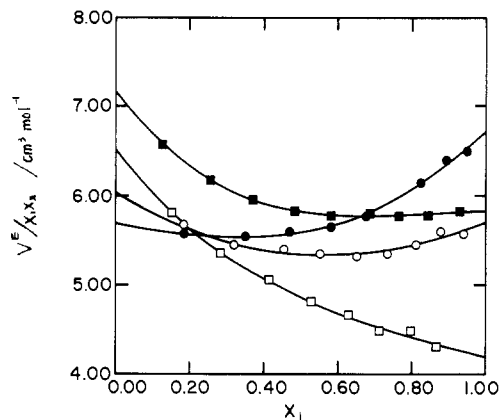


Figure 3. Variation of V^E/x_1x_2 , eq 4, with mole fraction x_1 of methyl acetate for methyl acetate (1)-alkane (2) mixtures at 20 °C: \square , hexane; \circ , heptane; \bullet , octane; \blacksquare , cyclohexane.

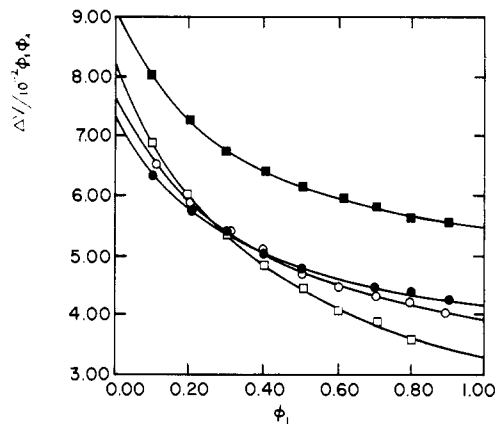


Figure 4. Variation of $\Delta V/\varphi_1\varphi_2$, eq 5, with volume fraction φ_1 of methyl acetate for methyl acetate (1)-alkane (2) mixtures at 20 °C: \square , hexane; \circ , heptane; \bullet , octane; \blacksquare , cyclohexane.

The literature data were measured at 25 °C. In Figures 1 and 2, some literature data are compared with our results. For all of these systems but one, the values calculated from our interpolation formula (eq 4 and Table II) were lower than the values obtained from the literature formula. The magnitudes vary from 2 to 8%, but the majority lie between 2 and 4%. The magnitude and the sign of this difference can be explained by the fact that our experimental temperature was 5 °C lower than the temperature quoted in the references.

The relative change of volume in mixing ΔV seems to be a more relevant quantity than the excess molar volume V^E . Its dependences on composition for similar pairs of solvents follow a similar pattern, while the corresponding dependences for V^E quite often do not. This is clearly demonstrated in Figures 3 and 4, where the compositional dependences of V^E/x_1x_2 and $\Delta V/\varphi_1\varphi_2$ are depicted for mixtures of methyl acetate with three alkanes and cyclohexane.

Comparison among $\Delta V/\varphi_1\varphi_2$ of different systems reveals several interesting features. When a given alkane is mixed with a series of alkyl acetates, their values of $\Delta V/\varphi_1\varphi_2$ decrease regularly with the increasing size of the alkyl group (Figure 5). Mixtures with ketones show a similar trend (Figure 5). The positive excess volumes reflect the dissimilarity between non-polar alkanes and polar carbonyl compounds. For systems of a given ester with different alkanes (Figure 4), the excess volumes increase with increasing length of the alkane. This seems to be an effect of the size of the alkane molecules that influences their free volumes. There is also a quite significant increase of excess volume when going from linear alkanes to

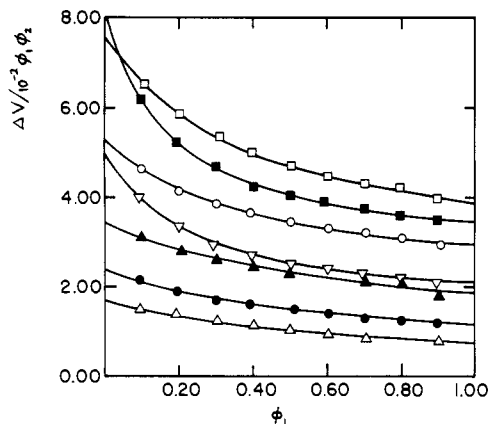


Figure 5. Variation of $\Delta V/\phi_1\phi_2$, eq 5, with volume fraction ϕ_1 of carbonyl compounds for carbonyl compounds (1)—heptane (2) mixtures at 20 °C: \square , methyl acetate; \circ , ethyl acetate; \blacktriangle , propyl acetate; \bullet , butyl acetate; \blacktriangle , amyl acetate; \blacksquare , acetone; ∇ , 2-butanone.

cycloalkanes (cyclohexane in the present case).

$\Delta V/\phi_1\phi_2$ increases sharply in the region of lower concentration of the carbonyl compound. For ketones this increase is sharper than for alkyl acetates, as is apparent from Figure 5 and from the larger negative value of the fitting parameter c (Table II). This phenomenon reflects the nonregular nature of mixtures of carbonyl compounds with alkanes. The increase of volume is caused by alkane molecules disrupting the interactions of the highly dipolar molecules of the carbonyl compounds. When only a small amount of alkane is added, the carbonyl molecules rearrange themselves to preserve a larger proportion of paired dipoles than would be allowed by regular mixing. With the progressing amount of alkane being added, these "excess" dipolar pairs are disrupted as well, increasing the value of the excess volume in this concentration range.

Conclusions

Systematic measurement of compositional dependences of the excess volume of mixing on the composition for families of related pairs of compounds may reveal basic effects governing

interactions among molecules. In the present study, it was found that mixtures of carbonyl compounds with alkanes exhibit a distinct nonregularity. Due to the strong interaction among the polar molecules, the number of interacting dipolar pairs disrupted by added nonpolar alkane molecules is less than would be expected for regular (random) mixing.

Registry No. Hexane, 110-54-3; heptane, 142-82-5; octane, 111-65-9; cyclohexane, 110-82-7; methyl acetate, 79-20-9; ethyl acetate, 141-78-6; propyl acetate, 109-60-4; butyl acetate, 123-86-4; amyl acetate, 628-63-7; acetone, 67-64-1; 2-butanone, 78-93-3.

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Excess Volume of Mixtures of Alkanes with Aromatic Hydrocarbons

Anwei Qin, Dolly E. Hoffman, and Petr Munk*

Department of Chemistry and Biochemistry and Center for Polymer Research, The University of Texas at Austin, Austin, Texas 78712

The excess volumes of 22 binary mixtures of aromatic hydrocarbons and alkanes are reported. The excess volume of systems with the same alkane decreases with increasing size and number of substituents on the benzene ring. For systems with the same aromatic hydrocarbon it increases with the length of the alkanes. Systems with benzene or cyclohexane as one of the components show larger excess volumes than the other systems, and the dependence of their $\Delta V/\phi_1\phi_2$ values on composition is noticeably asymmetric.

During recent years we have been using various methods such as light scattering, inverse gas chromatography, densito-

metry, and calorimetry to accumulate extensive thermodynamic data concerning binary mixtures in order to develop a comprehensive theory which could interpret all the important aspects of liquid mixtures (1, 2). As part of this work, we are reporting in the present paper the measurements of excess volume of mixing of alkanes and aromatic hydrocarbons. The alkanes used were three linear alkanes (hexane, heptane, and octane) and cyclohexane. The aromatic hydrocarbons included benzene, toluene, ethylbenzene, *p*-xylene, *o*-xylene, and *m*-xylene. Altogether 22 systems were prepared, and, for each system, the dependence of the excess volume on concentration was studied.

The molar excess volume of mixing V^E is defined as

$$V^E = V - x_1V^{\circ}_1 - x_2V^{\circ}_2 \quad (1)$$

where V is the volume of 1 mol of the mixture and x_i and V°_i

* To whom correspondence should be addressed at the Department of Chemistry.