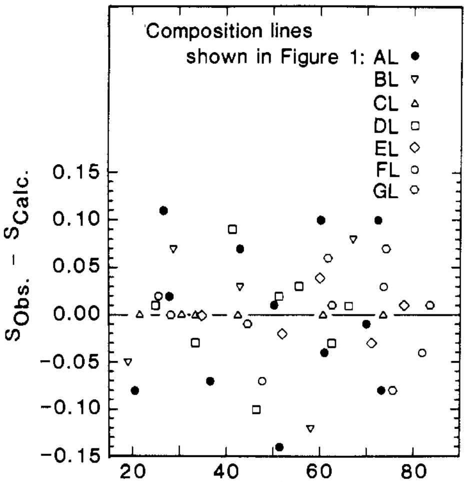

Figure 3. Differences between the observed and calculated (from eq 1 using the regression coefficients given in Table III) solubilities of $FeCl_2 \cdot 4H_2O$ and halite (in weight percent of $FeCl_2$).

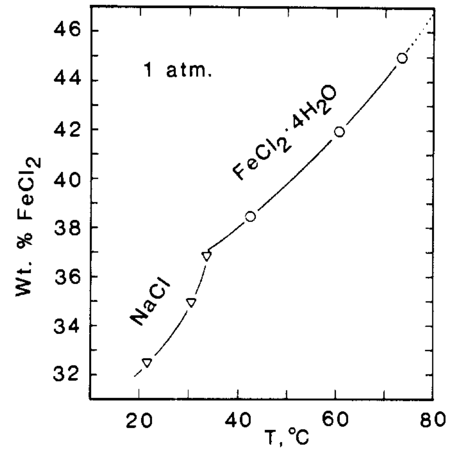

Figure 4. Solubilities of halite (triangles) and $FeCl_2 \cdot 4H_2O$ (circles) determined along the composition line CL shown in Figure 1. The solid curves are least-squares regression lines. $FeCl_2 \cdot 4H_2O$ is metastable with respect to $FeCl_2 \cdot 2H_2O$ at temperatures above 74.6 °C.

Celsius. The coefficients, a_i, for the regression equation are listed in Table III. The differences between the observed and calculated solubilities (in weight percent) are summarized in Figure 3; the maximum difference is 0.14.

Of the seven composition lines studied, line CL is the only one involving two solids. The results are shown in Figure 4. Halite and $FeCl_2 \cdot 4H_2O$ coexist at 33.8 °C with halite being stable at lower temperatures and $FeCl_2 \cdot 4H_2O$ at higher temperatures.

Table IV. Isothermal Solubilities Calculated from Eq 1 for (a) $FeCl_2 \cdot 4H_2O$ and (b) Halite along Seven Composition Lines

comp line[a]	isothermal solubility, wt % $FeCl_2$ 25 °C	50 °C	70 °C
	(a) $FeCl_2 \cdot 4H_2O$		
AL	38.56	42.15	45.80
BL	37.43	41.10	45.30
CL		39.78	44.12
	(b) Halite		
CL	33.25		
DL	30.00	36.15	
EL	23.70	27.60	33.10
FL	14.35	17.50	21.20
GL	3.67	5.35	7.48

[a] Composition lines shown in Figure 1.

Isothermal solubilities of halite and $FeCl_2 \cdot 4H_2O$ at 25, 50, and 70 °C in the ternary system $NaCl-FeCl_2-H_2O$ were calculated from eq 1 by using the data listed in Table III. The results are given in Table IV and plotted in Figure 1. The solubility data in the binary system $NaCl-H_2O$ are from Potter and Clynne (*3*). The dashed curve IJ shown in Figure 1 is the trace of the isothermal invariant points between 25 and 70 °C where solutions coexist with two solids.

Conclusions

The solubility relations in the ternary system $NaCl-FeCl_2-H_2O$ are presented between 25 and 70 °C at 1 atm. The range of deviation of the measured solubilities from the smoothed curves is 0.00-0.14 in weight percent of $FeCl_2$.

Registry No. NaCl, 7647-14-5; $FeCl_2$, 7758-94-3.

Literature Cited

(1) Naumov, V. B.; Shapenko, V. V. *Geochem. Int.* **1980**, *17*, 125.
(2) Grant, J. N.; Halls, C.; Sheppard, S. M. F.; Avila, W. *Min. Geol. Spec. Issue* **1980**, *No. 8*, 151.
(3) Potter, R. W., II; Clynne, M. A. *J. Res. U.S. Geol. Surv.* **1978**, *6*, 701.
(4) Clynne, M. A.; Potter, R. W., II. *J. Chem. Eng. Data* **1979**, *24*, 338.
(5) Chou, I. M.; Lee, R. D. *J. Chem. Eng. Data* **1983**, *28*, 390.
(6) Schimmel, F. A. *Z. Anorg. Chem.* **1928**, *176*, 285.

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Excess Volumes of the Water/Methanol, *n*-Heptane/Ethyl Acetate, *n*-Heptane/*n*-Butyraldehyde, and *n*-Heptane/Isobutyraldehyde Systems

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Excess volumes at 298.15 K have been measured by means of a vibrating tube densimeter for the binary mixtures of water with methanol, and *n*-heptane separately with ethyl acetate, *n*-butyraldehyde, and isobutyraldehyde. Partial molar volumes have also been calculated.

Introduction

Few thermodynamic data have been published for systems containing hydrocarbons with either aldehydes or esters. This may be attributed to the difficulty involved in working with these compounds. Aldehydes are oxidized rapidly in the presence of air while esters are hygroscopic.

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Table I. Comparison of Measured Densities with Literature Values

component	ρ, g cm^{-3} this work	ρ, g cm^{-3} lit.[a]
n-heptane	0.679 541	0.679 51
methanol	0.786 846	0.787 065
ethyl acetate	0.893 966	0.894 55
butyraldehyde	0.796 315	0.796 4
isobutyraldehyde	0.783 387	0.783 6

[a] Literature value for methanol is taken from Grolier (*4*); all others from Riddick and Bunger (*7*).

In a continuing effort to measure the thermodynamic properties of mixtures of hydrocarbons with aldehydes and esters, we now report the excess volumes of the following binary systems: *n*-heptane/*n*-butyraldehyde, *n*-heptane/isobutyraldehyde, and *n*-heptane/ethyl acetate. These data and the vapor–liquid equilibrium data reported in previous papers (*1*, *2*) will be useful in developing a better understanding of polar–nonpolar interactions.

Most of the excess volume data obtained from densimeter measurements have been obtained by operating the densimeter under flow conditions (*3–6*). This requires the thermostating of all parts through which sample is flowing and, in addition, the instrument may be sensitive to changes in flow rate (*5*). Partly to avoid this problem, and partly because of the nature of the systems under investigation, we have used an Anton Paar densimeter (Model DMA 512) operating under static (no flow) conditions. The water/methanol system, for which accurate excess volumes have already been reported (*4*), was used in this study to test the densimeter operating in this manner.

Experimental Section

The ethyl acetate and methanol used were available in high purity from Fisher Scientic Co. The *n*-heptane used was "ultrapure grade" obtained from Alfa Products. Further purification was not necessary since no secondary peaks were found from gas-chromatographic analysis, and the pure-component density measurements proved satisfactory (see Table I). The aldehydes, obtained from Alfa Products, needed purification. The main impurities were water and oxidation products. Because of rapid oxidation in the presence of air, the aldehydes were distilled under an inert atmosphere of nitrogen (Matheson, purity greater than 99.99%) as described prevously (*1*, *2*). Nitrogen and water distilled in our laboratory were used for calibration of the densimeter.

Solutions were prepared gravimetrically by weighing the components to 0.1 mg on an analytical balance. A septum-capped vial of approximately 5-cm^3 capacity was used. The two components were injected into the vial without allowing any vapor to escape. The sample was immediately transferred to the densimeter by using a hypodermic syringe and care was taken to avoid introducing any air bubbles. This procedure effectively reduced errors from evaporation, contamination, and oxidation. The vapor space in the vial was usually less than 1 cm^3. Because of similarities in vapor pressures of the components, no significant error was introduced in composition from evaporation into this small vapor space.

Density measurements were made with an Anton Paar Model DMA 512 external measuring cell (densimeter). This cell can be used for density measurements under extreme pressure (up to 400 bar) and temperature (up to 150 °C) conditions. The sample chamber is a stainless tube with a wall thickness of about 0.3 mm and an inside diameter of 2.4 mm. The tube is in a brass housing which is thermostated by the circulating water from a constant-temperature bath. Temperature control is achieved with an Exacal Model 200 constant-temperature bath circulator with built-in stainless steel reservoir, external circulating pump, and temperature control system. The unit is designed to maintain precise temperature control (±0.01 °C) of the bath fluid by cycling an immersion heater. The constant-temperature bath is coupled to an Endocal Model 350 refrigeration system. The sample tube is excited by two magnetic dynamic converters in connection with an electronic control and amplifier circuit which guarantees a constant amplitude of the oscillator tube.

The density determination is based on measuring the period of oscillation of the vibrating U-shaped sample tube, which is filled with sample liquid or through which the sample liquid flows continuously. The following relationship exists between the period τ and the density ρ:

$$\rho = A + B\tau^2 \tag{1}$$

where A and B are instrument constants which are determined by calibration with fluids of known density.

To measure the period, we have used an Anton Paar Model DMA 60 processing unit. This unit has a built-in time base which gives pulses every 0.000 01 s. The period meter measures the time for a preselected number of oscillator periods by counting the number of clock pulses. In this way, it is possible to perform period measurements of high resolution quickly. The position of the "period select switch" determines the compromise between resolution and measurement time. All measurements in this work were taken with period select switch at 10 K; this corresponds to measurement time of approximately 35 s. Temperature equilibration was judged by the stability in the period measured. Usually the period was found to be stable within 1 part in 10^7. The time taken for equilibration was typically 10–15 min, and periods were averaged over 5 min after this time.

To check the validity of eq 1 under our operating conditions, we calibrated the instrument with distilled water [ρ(298.15 K) = 0.997047 g cm^{-3}] and with nitrogen gas [ρ(298.15 K) = 0.0011456 g cm^{-3}] and then determined the density of the pure components used in this study. Water and nitrogen gas were chosen as calibrating fluids since they span a wide density range, they can be obtained in high purity, and their densities are well established. Density measurements for pure components are summarized in Table I and a comparison with literature values is made. In general, agreement to four decimal places is obtained. This is considered satisfactory for the determination of excess volumes of the systems used in this study, especially since aldehydes and ethyl acetate are chemically unstable.

All measurements were made in the "static mode". The U-shaped sample tube was equipped with the valves at entry (top) and at exit (bottom). After the sample was introduced, the valve at the bottom was closed, and the sample was pressurized from the top. The pressure was then released and the end of the tube was exposed to atmospheric pressure. The valve at the top was then closed to stop evaporation. This procedure ensured a bubble-free sample inside the tube. The presence of bubbles was indicated by the fluctuations in the period measured.

Densities of the pure components were measured before preparing sample mixtures to ensure the purity of the components used. For aldehydes, it was necessary to use only freshly distilled samples. When samples were changed, the sample tube was cleaned with acetone and dried by using the built-in air pump for at least 20 min. This was the time necessary for the period of the empty sample tube to return to its previous value. Contrary to what is reported for measurements under flow conditions (*6*), we found it necessary to clean and dry the sample tube after every run.

Table II. Experimental Densities ρ, Excess Volumes V^E, and Partial Molar Volumes V_1 and V_2 for Water (1)/Methanol (2) System at 298.15 K

x_1	ρ, g cm^{-3}	V^E, cm^3 mol^{-1}	V_1, cm^3 mol^{-1}	V_2, cm^3 mol^{-1}
0.1162	0.806 655	−0.3883	15.314	40.650
0.1744	0.817 256	−0.5578	15.604	40.559
0.2221	0.825 959	−0.6688	15.871	40.483
0.2425	0.829 631	−0.7066	15.996	40.454
0.2841	0.837 504	−0.7855	16.190	40.374
0.3729	0.855 031	−0.9174	16.563	40.159
0.3737	0.855 248	−0.9203	16.561	40.153
0.4186	0.864 245	−0.9581	16.758	40.029
0.5266	0.887 222	−1.0032	17.162	39.602
0.6119	0.905 376	−0.9496	17.486	39.201
0.7220	0.929 537	−0.7904	17.801	38.563
0.8261	0.953 126	−0.5476	17.979	37.925
0.8509	0.957 522	−0.4476	18.040	37.990
0.8829	0.965 942	−0.3704	18.042	37.731
0.9489	0.981 906	−0.1490	18.078	37.831
0.9881	0.993 202	−0.0316	18.074	38.065

Table III. Experimental Densities ρ, Excess Volumes V^E, and Partial Molar Volumes V_1 and V_2 for *n*-Heptane (1)/Ethyl Acetate (2) System at 298.15 K

x_1	ρ, g cm^{-3}	V^E, cm^3 mol^{-1}	V_1, cm^3 mol^{-1}	V_2, cm^3 mol^{-1}
0.0613	0.872 694	0.2544	151.277	98.574
0.0875	0.864 061	0.3572	151.099	98.601
0.1409	0.847 438	0.5323	150.614	98.664
0.1658	0.840 108	0.5979	150.374	98.692
0.1660	0.840 005	0.6041	150.407	98.699
0.1786	0.836 498	0.6199	150.208	98.697
0.2550	0.815 427	0.8057	149.748	98.848
0.2605	0.813 855	0.8346	149.784	98.884
0.3031	0.803 027	0.9051	149.506	98.973
0.3114	0.800 903	0.9277	149.488	99.007
0.4293	0.773 630	1.0498	148.845	99.344
0.4705	0.764 789	1.0810	148.675	99.517
0.5109	0.756 511	1.0934	148.505	99.697
0.5723	0.744 516	1.0964	148.281	100.034
0.5981	0.739 789	1.0723	148.166	100.154
0.6404	0.732 149	1.0476	148.035	100.441
0.6838	0.724 708	0.9940	147.897	100.736
0.7342	0.716 393	0.9240	147.780	101.171
0.7414	0.715 220	0.9156	147.770	101.252
0.7999	0.706 285	0.7740	147.636	101.736
0.8051	0.705 498	0.7633	147.631	101.800
0.8515	0.698 863	0.6143	147.545	102.169
0.8801	0.694 819	0.5331	147.531	102.577
0.9108	0.690 774	0.4019	147.487	102.746
0.9710	0.683 070	0.1427	147.463	103.377

The excess volumes V^E were calculated from the following equation (*4*):

$$V^E = \frac{x_1M_1 + x_2M_2}{\rho} - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2} \tag{2}$$

where x_1 and x_2 are the mole fractions, M_1 and M_2 are the molecular weights, and ρ_1 and ρ_2 are the densities of the two components, and ρ is the density of mixture calculated from eq 1.

Results

Excess volumes were determined at 298.15 K for the water/methanol, *n*-heptane/ethyl acetate, *n*-heptane/butyraldehyde, and *n*-heptane/isobutyraldehyde systems. The results are given in Tables II–V. The equation used to express the dependence of the excess volume on composition was

$$V^E_{\text{calcd}}(\text{cm}^3\ \text{mol}^{-1}) = x_1x_2 \sum_{l=0}^{3} a_l(x_1 - x_2)^l \tag{3}$$

Table IV. Experimental Densities ρ, Excess Volumes V^E, and Partial Molar Volumes V_1 and V_2 for *n*-Heptane (1)/Isobutyraldehyde (2) System at 298.15 K

x_1	ρ, g cm^{-3}	V^E, cm^3 mol^{-1}	V_1, cm^3 mol^{-1}	V_2, cm^3 mol^{-1}
0.0341	0.777 176	0.0789	149.776	92.045
0.1062	0.764 910	0.2396	149.624	92.048
0.1321	0.760 594	0.3182	149.723	92.084
0.1902	0.751 915	0.4203	149.386	92.107
0.2362	0.745 320	0.5168	149.252	92.178
0.2646	0.741 575	0.5526	149.087	92.208
0.3802	0.727 455	0.6938	148.615	92.455
0.4285	0.722 159	0.7311	148.446	92.590
0.4303	0.721 995	0.7279	148.430	92.587
0.5017	0.714 795	0.7526	148.207	92.802
0.5823	0.707 427	0.7436	148.002	93.071
0.5937	0.706 455	0.7373	147.973	93.106
0.6424	0.702 375	0.7169	147.884	93.303
0.7376	0.695 133	0.6268	147.726	93.721
0.7820	0.692 092	0.5556	147.650	93.914
0.7953	0.691 224	0.5301	147.628	93.969
0.8857	0.685 559	0.3548	147.531	94.642
0.9222	0.683 463	0.2665	147.507	95.078
0.9720	0.680 969	0.0870	147.452	94.984

Table V. Experimental Densities ρ, Excess Volumes V^E, and Partial Molar Volumes V_1 and V_2 for *n*-Heptane (1)/Butyraldehyde (2) System at 298.15 K

x_1	ρ, g cm^{-3}	V^E, cm^3 mol^{-1}	V_1, cm^3 mol^{-1}	V_2, cm^3 mol^{-1}
0.0413	0.787 999	0.0780	149.296	90.541
0.0427	0.787 536	0.1029	149.815	90.564
0.1051	0.775 831	0.2160	149.356	90.565
0.1082	0.775 225	0.2276	149.399	90.573
0.1439	0.768 864	0.3026	149.332	90.602
0.1924	0.760 824	0.3803	149.116	90.634
0.2772	0.748 046	0.4799	148.727	90.705
0.3584	0.736 786	0.5879	148.528	90.874
0.3955	0.732 081	0.6173	148.411	90.951
0.4145	0.729 705	0.6378	148.373	91.007
0.4639	0.723 885	0.6667	148.240	91.136
0.4998	0.719 880	0.6793	148.148	91.238
0.5664	0.712 957	0.6759	147.977	91.428
0.5685	0.712 761	0.6732	147.968	91.429
0.6213	0.707 609	0.6648	147.868	91.628
0.6526	0.704 694	0.6550	147.817	91.765
0.6708	0.703 046	0.6475	147.790	91.853
0.6903	0.701 382	0.6260	147.747	91.916
0.7019	0.700 351	0.6233	147.738	91.992
0.7042	0.700 113	0.6292	147.745	92.029
0.7604	0.695 459	0.5798	147.674	92.365
0.7968	0.692 728	0.5147	147.607	92.519
0.8163	0.691 297	0.4800	147.579	92.626
0.8212	0.690 992	0.4610	147.561	92.599
0.8593	0.688 243	0.3984	147.533	92.920
0.8626	0.687 989	0.3971	147.536	92.985
0.8771	0.686 987	0.3691	147.527	93.130
0.9156	0.684 450	0.2806	147.504	93.551
0.9409	0.682 954	0.1948	147.473	93.603

The coefficients a_l are listed in Table VI along with the standard deviations $\sigma(V^E)$ and $\sigma(a_l)$, and the maximum deviation δ_m for each system. The $\sigma(V^E)$, $\sigma(a_l)$, and δ_m were calculated from the following equations:

$$\sigma(V^E) = [\textstyle\sum(V^E_{\text{calcd}} - V^E)^2/(N - n)]^{1/2} \tag{4}$$

$$\sigma(a_l) = [SP(J,J)]^{1/2} \tag{5}$$

$$\delta_m = \max |V^E_{\text{calcd}} - V^E| \tag{6}$$

where

$$S = [\textstyle\sum W_l\{(V^E_{\text{calcd}} - V^E)/x_1x_2\}^2/(N - n - 1)]$$

N = number of direct experimental values, n = number of coefficients a_l, W_l = weighting of each data point, and $P(J,J)$

Table VI. Values[a] of the Coefficients a_i for Eq 3, the Standard Deviations $\sigma(V^E)$ and $\sigma(a_i)$,[b] and the Maximum Deviations δ_m

system	a_0	a_1	a_2	a_3	$\sigma(V^E)$	δ_m
water/methanol	-4.0034 (0.024)	-0.177 56 (0.088)	0.541 39 (0.071)	0.604 81 (0.182)	0.008	0.016
water/methanol (Grolier)	-4.041 (0.02)	-0.428 (0.07)	0.644 (0.077)	0.990 (0.16)	0.008	0.016
n-heptane/ethyl acetate	4.3762 (0.014)	0.536 82 (0.047)	0.526 55 (0.051)	-0.298 65 (0.117)	0.008	0.015
n-heptane/butyraldehyde	2.6896 (0.014)	0.559 58 (0.050)	0.317 24 (0.040)	0.191 77 (0.105)	0.008	0.018
n-heptane/isobutyraldehyde	0.30166 (0.018)	0.251 07 (0.068)	0.048 95 (0.08)	0.490 38 (0.187)	0.007	0.014

[a] All values in cm^3 mol^{-1}. [b] Shown in parentheses.

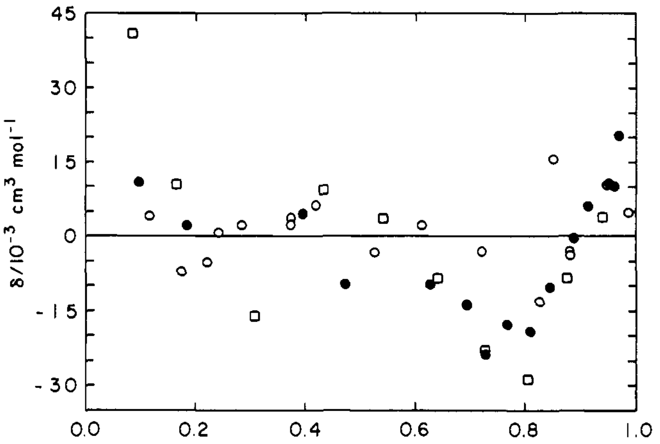

Figure 1. Deviations δ from eq 3 for water (1)/methanol (2) system at 298.15 K: (□) Mikhail (*9*); (●) Grolier (*4*); (○) this work.

= elements of the coefficient matrix in the least-squares analysis (*8*). The weighing factor W_i was unity for each point between mole fractions of 0.12 and 0.88, and zero elsewhere. This was done to improve the overall fit of the data as including the points at the ends of the concentration range tended to distort the fit because of their heavy weighting with the $(x_1x_2)^{-1}$ term.

We have also calculated the partial molar volumes V_1 and V_2 from the following equations (*5*):

$$V_1 = V_1^* + V^E/x_1 + x_1x_2[\partial(V^E/x_1)/\partial x_1]_{T,P} \quad (7)$$

$$V_2 = V_2^* + V^E/x_2 + x_1x_2[\partial(V^E/x_2)/\partial x_2]_{T,P} \quad (8)$$

where V_1^* and V_2^* are the molar volumes of the pure components. The values for the first two terms on the right-hand side of eq 7 and 8 were obtained directly from the experimental data. The last term in each equation was obtained by differentiating the fitted equation (3).

Discussion

Experimental measurements of V^E are included in Tables II-V. For the water/methanol system V^E is negative over the entire composition range. For all other systems V^E is always positive. In Figure 1, a deviation plot is given which compares our results for the water/methanol system with those of Grolier (*4*) and Mikhail (*9*). The agreement is best with the results of Grolier, who used a vibrating tube densimeter under flow conditions with a temperature control of ±0.001 K. Indeed, the agreement between Grolier's data and ours is excellent. Also, our standard deviation $\sigma(V^E)$ and the maximum deviations δ_m are of the same magnitude as those reported by Grolier. In Figure 2 our results for the *n*-heptane/ethyl acetate system are compared with those published by Grolier (*10*). Again, excellent agreement is obtained. Figure 2 also contains the V^E vs. composition plots for the other systems that we have studied. The precision of the results for these other systems is comparable to that of the test system of water/methanol.

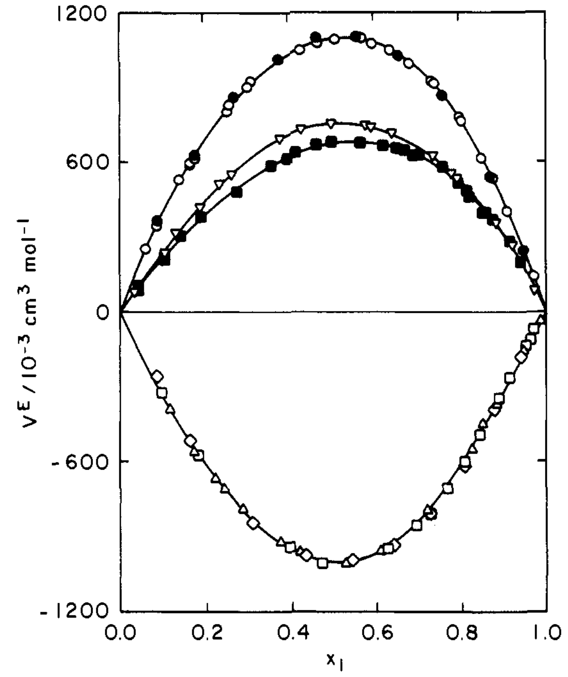

Figure 2. Excess volumes at 298.15 K for the mixtures studied here. The data for the water (1)/methanol (2) system are represented by ◇ for Mikhail (*9*), □ for Grolier (*4*), and △ for our results. The *n*-heptane (1)/ethyl acetate (2) data are given by ● for Grolier (10) and ○ for our results. Our results for *n*-heptane (1)/butyraldehyde (2) are given by ■ and for *n*-heptane (1)/isobutyraldehyde (2) by △.

The present work not only provides the first accurate data for the excess volumes of the hydrocarbon/oxyhydrocarbon systems studied here, but also demonstrates the capabilities of the vibrating tube densimeter operating in a static mode. Very accurate densities, and hence excess molar volumes, are obtained with relative ease, in a short time, and with small quantities of the constituent liquids.

Acknowledgment

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Glossary

A, *B*	instrument constants, eq 1
a_i	coefficients, eq 3
M	molecular weight
N	number of experimental values
n	number of coefficients, eq 3
P(*J*,*J*)	elements of coefficient matrix in least-squares analysis
V^E	excess volume, cm^3 mol^{-1}
V	partial molar volume, cm^3 mol^{-1}
V^*	molar volume, cm^3 mol^{-1}
W_i	weighing factor of point *i*
x	mole fraction

ρ	density, g cm^{-3}
τ	period of oscillation
σ	standard deviation
δ	deviation between calculated and experimental values, cm^3 mol^{-1}

Registry No. Methanol, 67-56-1; heptane, 142-82-5; ethyl acetate, 141-78-6; butyraldehyde, 123-72-8; isobutyraldehyde, 78-84-2.

Literature Cited

(1) Eng, R.; Sandler, S. I. *J. Chem. Eng. Data* **1984**, *29*, 156.
(2) Shealy, G. S.; Sandler, S. I. *J. Chem. Thermodyn.*, in press.
(3) Wilhelm, E.; Grolier, J. P. E.; Karbalai Ghassemi, M. H. *Monatsh. Chem.* **1978**, *109*, 369.
(4) Grolier, J. P. E.; Karbalai Ghassemi, M. H.; Inglese, A. *Int. Data Ser., Ser. B* **1977**, Guideline 2c.
(5) Goates, J. R.; Otts, J. B.; Moellmer, J. F. *J. Chem. Thermodyn.* **1977**, *9*, 249.
(6) Takenaka, M.; Tanaka, R.; Murakami, S. *J. Chem. Thermodyn.* **1980**, *12*, 849.
(7) Riddick, J. A.; Bunger, E. B. "Organic Solvents. Physical Properties and Methods of Purification"; Wiley-Interscience: New York, 1970.
(8) Davies, O. L.; Goldsmith, P. L. "Statistical Methods in Research and Production"; Hafner Publishing Co.: New York, 1972.
(9) Mikhail, S. Z.; Kimel, W. R. *J. Chem. Eng. Data* **1961**, *6*, 533.
(10) Grolier, J. P. E.; Ballet, D.; Viallard, A. *J. Chem. Thermodyn.* **1974**, *6*, 895.

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Excess Enthalpies of Binary Mixtures of 2,4-Dimethylpentane with *n*-Hexane, *n*-Heptane, *n*-Octane, and *n*-Dodecane[†]

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Calorimetric measurements of excess enthalpies are reported for binary mixtures of 2,4-dimethylpentane with *n*-hexane, *n*-heptane, *n*-octane, and *n*-dodecane at 298.15 K. The results for the mixtures containing *n*-hexane and *n*-octane are much lower than previous estimates of excess enthalpies obtained from vapor–liquid equilibria.

The effect of chain branching on the excess thermodynamic properties of binary mixtures has been investigated previously in our laboratory by measuring excess enthalpies for mixtures of *n*-heptane (*1*), *n*-octane (*2*), and *n*-dodecane (*3*) with each of the five hexane isomers. The present paper reports the results of similar measurements for mixtures of a branched isomer of *n*-heptane, 2,4-dimethylpentane (2,4-DMP), with the *n*-alkanes: *n*-hexane, *n*-heptane, *n*-octane, and *n*-dodecane.

Experimental Section

Excess molar enthalpies, H_m^E, were determined at 298.15 K in a modified LKB flow microcalorimeter. Details of the equipment and its operation have been described previously (*1*, *4*). For most of the measurements the error in the determination of H_m^E is estimated to be less than 0.5%. However, it may be somewhat higher for small H_m^E (<10 J mol^{-1}).

Sources of the component liquids and purities specified by the manufacturers are summarized in Table I. In all cases the liquids were used without further purification. Densities, measured at 298.15 K in an Anton Paar densimeter, are also listed in Table I along with values from the literature (*5*) for comparison.

Results and Discussion

The experimental values of H_m^E, measured for the four 2,4-DMP–*n*-alkane systems at 298.15 K, are given in Table II. In all cases, x is the mole fraction of 2,4-DMP.

Table I. Sources, Purities, and Densities, $\rho(T = 298.15\ \text{K})$, of the Component Liquids

liquid	source and purity	ρ/(kg m^{-3}) obsd	ρ/(kg m^{-3}) lit. (*5*)
2,4-dimethylpentane	Phillips Petroleum Co., Research Grade, 99.72 mol %	668.44	668.32
n-hexane	Phillips Petroleum Co., Research Grade, 99.95 mol %	654.92	654.84
n-heptane	Phillips Petroleum Co., Pure Grade, >99 mol %	679.67	679.46
n-octane	Aldrich Chemical Co., Gold Label, >99 mol %	698.61	698.62
n-dodecane	Phillips Petroleum Co., Pure Grade, >99 mol %	745.23	745.18

The parameters of the smoothing equation

$$H_m^E/(\text{J mol}^{-1}) = x(1-x)[1-k(1-2x)]^{-1}\sum_{j=1}^{m} h_j(1-2x)^{j-1} \qquad (1)$$

were fitted to each set of results by the method of least squares with each point assigned unit weight. The skewing factor k was set equal to zero except for the mixture with *n*-dodecane. In the latter instance fewer coefficients h_j were needed to fit the results adequately when k was also treated as an adjustable parameter. The values of h_j and k, obtained from the least-squares analyses, are listed in Table III, along with the standard deviations, s, of the representations.

The experimental results and their representations by eq 1 are plotted in Figure 1. For each mixture, H_m^E is positive throughout the mole fraction range and is appreciably greater than the H_m^E for the corresponding *n*-heptane–*n*-alkane mixture (*1*, *6*, *7*).

We are not aware of any comparable previous calorimetric studies of the present mixtures. Values of H_m^E for 2,4-DMP with *n*-hexane at 293.15 K and with *n*-octane at 303.15 K have been estimated by Davison and co-workers (*8*, *9*) from measurements of vapor–liquid equilibria over the range 283.15–313.15 K. Allowing for the differences of temperature, these values of H_m^E are very much larger than our calorimetric results and it appears that the discrepancies must be attributed

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