V^E of Binary Mixtures Containing 3-Pentanone or 3-Heptanone with 1-Chloroalkanes at 298.15 K

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The excess volumes, V^E, of the binary mixtures formed by a 3-alkanone (3-pentanone, 3-heptanone) and a 1-chloroalkane (from 1-chlorobutane to 1-chlorooctane) were determined from densities measured using a vibrating-tube densimeter at 298.15 K. All the systems studied exhibit positive excess volumes over the whole range of concentrations except for the 3-heptanone + 1-chlorobutane for which all the experimental V^E values are negative. The excess molar volumes increase as the 1-chloroalkane chain increases and as the 3-ketone chain decreases. This behavior is similar to that found previously for excess molar enthalpies for 2-ketone + 1-chloroalkane mixtures.

Introduction

Systematic studies of the excess Gibbs energy, G^E, the excess enthalpy, H^E, and the excess volume, V^E, provide important information for better understanding of the molecular liquid structure and intermolecular interactions of the liquid mixtures. In the case of ketone + 1-chloroalkane systems, Garcia et al. (*1*) and Pico et al. (*2*) have recently measured H^E values of mixtures where the chain lengths of the 1-chloroalkane and of the ketone have been changed systematically. In the last paper, Pico et al. (*2*) used the H^E values to test the redetermine new interaction parameters of the UNIFAC group-contribution model.

The lack of experimental V^E values for alkanone + 1-chloroalkane mixtures led us to initiate a systematic investigation of excess molar volumes for these mixtures. The experimental excess volumes reported in the present paper and other forthcoming publications will be used to characterize the interactions between the carbonyl and chloro groups in the framework of the Nitta-Chao (*3*) model. We present here the excess molar volumes of the binary mixtures of an alkanone (3-pentanone and 3-heptanone) and a 1-chloroalkane (from 1-chlorobutane to 1-chlorooctane) at 298.15 K and atmospheric pressure.

Experimental Section

Materials. The sources and mole fraction purities of the chemicals were 1-chlorobutane and 3-pentanone (Fluka, >0.995), 1-chloropentane and 1-chlorohexane (Fluka, >0.99), 1-chloroheptane (Aldrich, >0.99), and 3-heptanone (Fluka, >0.97). All liquids were used without further purification, but prior to the actual measurements, they were dried over molecular sieves (Union Carbide Type 4A from Fluka) and partially degassed. Their densities measured as described below agree well with the literature values, as can be seen in Table 1.

Volumetric Measurements. Binary mixtures were prepared by mass with a probable error in the mole fraction of less than 3×10^{-5}. The excess molar volumes were determined from densities of the pure liquids and mixtures, measured with an Anton Paar digital precision densimeter (model DMA 60/602) in static mode. The vibrating-tube temperature was regulated to better than 0.01 K using a Haake F3 thermostat with a digital thermometer (Anton Paar DT 100-20). Before each series of measurements, the apparatus was calibrated with double-distilled and degassed water and *n*-heptane (Fluka, mole fraction 0.995). The error in the determination of V^E was estimated to be better than ± 0.002 cm^3·mol^{-1}.

Table 1. Densities ρ of Pure Components at 298.15 K

	ρ/(g·cm^{-3})	
	this work	literature
3-pentanone	0.809 25	0.809 41 (*4*), 0.809 45 (*5*)
3-heptanone	0.814 12	0.813 76 (*4*), 0.813 44 (*5*)
1-chlorobutane	0.880 87	0.880 88 (*6*), 0.880 95 (*5*)
1-chloropentane	0.876 82	0.876 92 (*7*), 0.876 96 (*2*)
1-chlorohexane	0.873 27	0.873 33 (*7*), 0.873 07 (*2*)
1-chloroheptane	0.871 08	0.870 98 (*8*), 0.871 5 (*9*)
1-chlorooctane	0.868 72	0.868 65 (*7*), 0.868 72 (*2*)

Results and Discussion

The excess molar volumes V^E at 298.15 K for all the binary mixtures are listed in Table 2. The composition dependence of V^E has been calculated in accordance with the smoothing equation

$$V^E/(\text{cm}^3\cdot\text{mol}^{-1}) = x(1-x)\sum_{p=0}^{q} A_p(2x-1)^p \qquad (1)$$

where x is the mole fraction of the 3-alkanone. The values of the coefficients A_p determined by the method of least squares with all points equally weighted and the standard deviations s are shown in Table 3. The number of coefficients was determined using an F-test (*10*) for the validity of an additional term.

The experimental results for V^E are plotted against x in Figures 1 and 2, together with the curves calculated with eq

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Table 2. Excess Molar Volumes V^E of x Alkanone + (1 − x) Chloroalkane at 298.15 K

x	V^E/ (cm³·mol⁻¹)	x	V^E/ (cm³·mol⁻¹)	x	V^E/ (cm³·mol⁻¹)	x	V^E/ (cm³·mol⁻¹)	x	V^E/ (cm³·mol⁻¹)	x	V^E/ (cm³·mol⁻¹)
3-Pentanone + 1-Chlorobutane											
0.036 16	0.0067	0.174 58	0.0253	0.397 45	0.0390	0.556 07	0.0386	0.772 44	0.0258	0.890 74	0.0141
0.093 24	0.0153	0.202 88	0.0281	0.471 24	0.0402	0.630 14	0.0356	0.806 10	0.0228	0.908 50	0.0118
0.143 22	0.0215	0.343 85	0.0379	0.507 07	0.0398	0.691 54	0.0323	0.830 93	0.0205	0.943 25	0.0079
3-Pentanone + 1-Chloropentane											
0.056 86	0.0181	0.230 88	0.0675	0.395 19	0.0957	0.533 61	0.1021	0.660 36	0.0912	0.847 52	0.0504
0.131 63	0.0416	0.265 95	0.0754	0.441 43	0.1003	0.593 15	0.0989	0.777 59	0.0689	0.892 53	0.0368
0.182 01	0.0561	0.329 25	0.0875	0.463 11	0.1013	0.630 36	0.0953	0.811 55	0.0604	0.958 26	0.0149
3-Pentanone + 1-Chlorohexane											
0.065 36	0.0349	0.257 62	0.1075	0.415 50	0.1349	0.631 61	0.1308	0.831 04	0.0804		
0.126 67	0.0633	0.305 84	0.1183	0.458 01	0.1379	0.667 53	0.1246	0.888 68	0.0569		
0.186 90	0.0865	0.336 28	0.1238	0.481 00	0.1385	0.738 45	0.1081	0.920 35	0.0429		
0.205 62	0.0919	0.378 85	0.1311	0.524 63	0.1386	0.782 63	0.0965	0.941 77	0.0319		
3-Pentanone + 1-Chloroheptane											
0.047 00	0.0295	0.292 53	0.1377	0.558 18	0.1731	0.710 41	0.1484	0.831 34	0.1036	0.954 49	0.0338
0.184 40	0.0998	0.378 67	0.1588	0.616 45	0.1669	0.741 57	0.1401	0.866 93	0.0859		
0.235 49	0.1194	0.434 17	0.1682	0.654 09	0.1623	0.791 29	0.1220	0.902 78	0.0672		
3-Pentanone + 1-Chlorooctane											
0.095 32	0.0579	0.398 01	0.1878	0.598 34	0.2025	0.732 19	0.1709	0.877 45	0.0964		
0.174 93	0.1010	0.407 75	0.1905	0.617 38	0.1996	0.753 06	0.1629	0.918 98	0.0674		
0.277 81	0.1489	0.490 10	0.2032	0.670 36	0.1899	0.800 79	0.1415	0.956 73	0.0377		
0.355 85	0.1762	0.535 86	0.2053	0.708 40	0.1791	0.823 47	0.1294				
3-Heptanone + 1-Chlorobutane											
0.037 32	−0.0075	0.173 67	−0.0235	0.401 07	−0.0426	0.551 94	−0.0436	0.777 45	−0.0266		
0.102 95	−0.0162	0.237 72	−0.0305	0.463 44	−0.0436	0.597 95	−0.0406	0.825 84	−0.0221		
0.129 83	−0.0205	0.356 29	−0.0388	0.494 92	−0.0428	0.707 86	−0.0349	0.928 85	−0.0108		
3-Heptanone + 1-Chloropentane											
0.044 13	0.0036	0.176 24	0.0100	0.432 79	0.0158	0.646 10	0.0134	0.745 52	0.0112	0.872 50	0.0058
0.107 25	0.0076	0.229 96	0.0120	0.457 20	0.0163	0.705 75	0.0114	0.794 36	0.0095	0.938 50	0.0041
3-Heptanone + 1-Chlorohexane											
0.045 89	0.0089	0.300 77	0.0388	0.449 56	0.0461	0.620 78	0.0409	0.764 42	0.0304	0.947 92	0.0071
0.119 02	0.0191	0.355 86	0.0432	0.531 54	0.0455	0.661 12	0.0388	0.820 54	0.0248		
0.168 63	0.0273	0.427 42	0.0453	0.568 59	0.0440	0.714 64	0.0357	0.870 48	0.0187		
3-Heptanone + 1-Chloroheptane											
0.032 60	0.0107	0.190 49	0.0459	0.361 20	0.0719	0.558 86	0.0768	0.742 85	0.0635	0.947 81	0.0169
0.066 73	0.0179	0.234 93	0.0558	0.433 27	0.0765	0.575 77	0.0761	0.795 43	0.0557		
0.136 62	0.0349	0.274 95	0.0611	0.454 42	0.0762	0.598 27	0.0764	0.834 52	0.0478		
0.174 55	0.0437	0.311 28	0.0662	0.490 26	0.0785	0.623 55	0.0741	0.875 09	0.0384		
3-Heptanone + 1-Chlorooctane											
0.028 87	0.0119	0.251 79	0.0779	0.473 97	0.1031	0.626 20	0.0979	0.810 36	0.0702		
0.144 86	0.0518	0.344 65	0.0943	0.515 81	0.1019	0.724 71	0.0867	0.850 59	0.0591		
0.210 62	0.0689	0.401 44	0.1002	0.591 41	0.0999	0.759 68	0.0819	0.958 62	0.0204		

Table 3. Coefficients A_i and Standard Deviations s According to Equation 1 for x Alkanone + (1 − x) Chloroalkane

	A_0	A_1	A_2	A_3	s/ (cm³·mol⁻¹)
3-pentanone +					
1-chlorobutane	0.1592	−0.0229	0.0037		0.0002
1-chloropentane	0.4086	0.0166	−0.0622		0.0003
1-chlorohexane	0.5554	0.0038	0.0312		0.0004
1-chloroheptane	0.6918	0.0652	0.0220		0.0006
1-chlorooctane	0.8153	0.1443	−0.0462		0.0002
3-heptanone +					
1-chlorobutane	−0.1728	0.0109	0.0191		0.0011
1-chloropentane	0.0632	−0.0118			0.0005
1-chlorohexane	0.1811	−0.0191			0.0007
1-chloroheptane	0.3119	0.0157	0.0259	0.0343	0.0008
1-chlorooctane	0.4123	0.0061	0.0637	0.0657	0.0007

1. We have not found any previously published values of V^E with which to compare our own results.

The experimental excess volumes are positive for all the systems except for 3-heptanone + 1-chlorobutane where all the V^E values are negative. The V^E–x curves are symmetrical. In Figure 3, the equimolar excess molar volumes are plotted against n, the number of carbon atoms in the 1-chloroalkane.

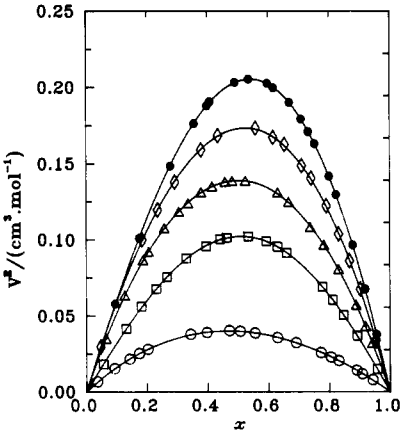

Figure 1. Excess molar volumes V^E at 298.15 K of 3-pentanone + 1-chloroalkane *vs* the alkanone mole fraction x: ○, 1-chlorobutane, □, 1-chloropentane, △, 1-chlorohexane, ◇, 1-chloroheptane, ●, 1-chlorooctane.

The excess molar volumes increase as the 1-chloroalkane chain increases and as the ketone length decreases. The same characteristics are exhibited by the excess molar enthalpies

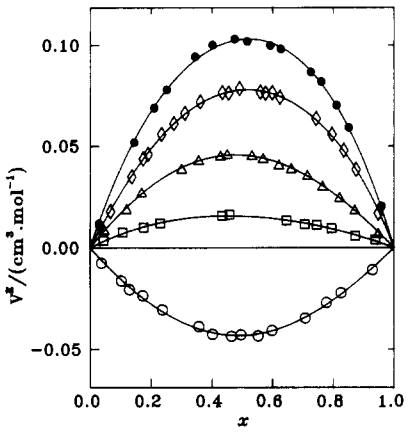

Figure 2. Excess molar volumes V^E at 298.15 K of 3-heptanone + 1-chloroalkane *vs* the alkanone mole fraction x: ○, 1-chlorobutane, □, 1-chloropentane, △, 1-chlorohexane, ◇, 1-chloroheptane, ●, 1-chlorooctane.

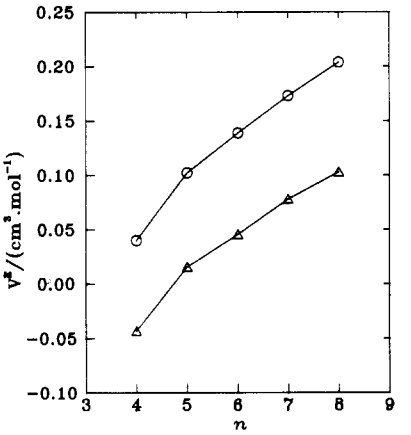

Figure 3. Excess molar volumes V^E at equimolar composition for 3-alkanone + 1-chloroalkane against n, the number of carbons of the 1-chloroalkane: ○, 3-pentanone, △, 3-heptanone.

of other (ketone + 1-chloroalkane) systems (*1*, *2*). This behavior is also very similar to that observed for H^E and V^E of ester + 1-chloroalkane (*7*, *8*, *11*) and ketone + alkane (*12*, *13*), and has been explained in terms of the formation of interactions between unlike molecules and the breaking of interactions between like molecules (*7*, *8*, *11–13*).

Moreover, in the case of excess molar volumes, a more efficient packing in the mixture than in the pure liquids gives rise to a decrease of volume. The observed sequences can be explained in terms of the ease with which the 1-chloroalkanes can fit into the volume left free by the ketone molecules: this ease of insertion increases as the length of the ketone chain increases and decreases as the length of the 1-chloroalkane increases.

Registry Numbers Supplied by Author. 3-Pentanone, 96-22-0; 3-heptanone, 106-35-4; 1-chlorobutane, 109-69-3; 1-chloropentane, 543-59-9; 1-chlorohexane, 544-10-5; 1-chloroheptane, 629-06-1; 1-chlorooctane, 111-85-3.

Literature Cited

(1) García, I.; Cobos, J. C.; González, J. A.; Casanova, C. *Thermochim. Acta* **1988**, *128*, 209.
(2) Pico, J. M.; Menaut, C. P.; Fernández, J.; Legido, J. L.; Paz Andrade, M. I. *J. Solution Chem.* **1991**, *20*, 115.
(3) Nitta, T.; Turek, E.A.; Greenkorn, R. A.; Chao, K. C. *AIChE J.* **1977**, *23*, 144.
(4) Benson, G. C.; Handa, Y. P. *Int. Data Ser., Sel. Data Mixtures, Ser. A* **1980**, 66.
(5) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*; 4th ed.; Wiley-Interscience: New York, 1986; Vol. II.
(6) Muñoz Embid, J.; Berro, C.; Otin, S.; Kehiaian, H. V. *J. Chem. Eng. Data* **1990**, *35*, 266.
(7) Ortega, J.; Matos, J. S.; Paz-Andrade, M. I.; Fernández, J. *J. Chem. Eng. Data* **1987**, *32*, 464.
(8) Ortega, J. *Ber. Bunsen-ges. Phys. Chem.* **1989**, *93*, 730.
(9) Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*; Elsevier: Amsterdam, 1965.
(10) Bevington, P. *Data Reduction and Error Analysis for the Physical Sciences*: McGraw-Hill: New York, 1969.
(11) Matos, J. S.; Ortega, J.; Garcia, M. V. *J. Chem. Eng. Data* **1988**, *33*, 260.
(12) Kehiaian, H. V.; Grolier, J.-P. E.; Kechavarz, M. R.; Benson, G. C.; Kiyohara, O.; Handa, Y. P. *Fluid Phase Equilib.* **1981**, *7*, 95.
(13) Grolier, J.-P. E.; Benson, G. C. *Can. J. Chem.* **1984**, *62*, 949.

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