$$\alpha_{LL} = \{6n/[(n^2 - 1)(n^2 + 2)]\}(dn/dT) \quad (6)$$

The computed values of α_{GD} and α_{LL} are included in Table I. These are found to be smaller than the directly measured values of expansivities (α), the discrepancy being greater for α_{LL} than for α_{GD}. A similar observation has been made by Rao et al. (*22*), while analyzing their results on $Ca(NO_3)_2 \cdot 4.1H_2O + KNO_3$ mixtures, and also by Jain (*3*). In this study, the ratio α/α_{GD} has a value of 1.06 ± 0.04. This value agrees favorably with those reported earlier by Rao et al. (*22*) and Jain (*3*).

Thus, these studies further support the idea that binary mixtures containing the tetrahydrates of calcium and cadmium nitrates form an ideal molten system.

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Excess Volumes of Binary Mixtures of Isomeric Butyl Chlorides, Pivalonitrile, and Methylchloroform with Nonpolar Solvents

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Excess volumes V^E of binary mixtures of *n*-butyl chloride, *sec*-butyl chloride, *tert*-butyl chloride, pivalonitrile, and methylchloroform with benzene, carbon tetrachloride, cyclohexane, and *n*-hexane at 293.15 K have been computed from the experimental density data. Evidence exists to suggest that the respective molecular shapes of the components play a part in the determination of V^E values.

Introduction

Volume changes on mixing are of interest essentially to test theories of solution and to determine practically composition from density measurements (*1*). In this paper, we report the volumetric behavior of some polar substances (*n*-butyl chloride, *sec*-butyl chloride, *tert*-butyl chloride, pivalonitrile, methylchloroform) in nonpolar solvents (benzene, carbon tetrachloride, cyclohexane, *n*-hexane) at 293.15 K and atmospheric pressure. These measurements were made as part of a continuing study on the thermodynamic and electrical properties of liquid mixtures (*2-8*).

Experimental Section

Densities were measured with an accuracy of ±5 × 10^{-5} g cm^{-3} by the hydrostatical displacement method previously reported (*9*). The temperature was maintained at 293.15 ± 0.05

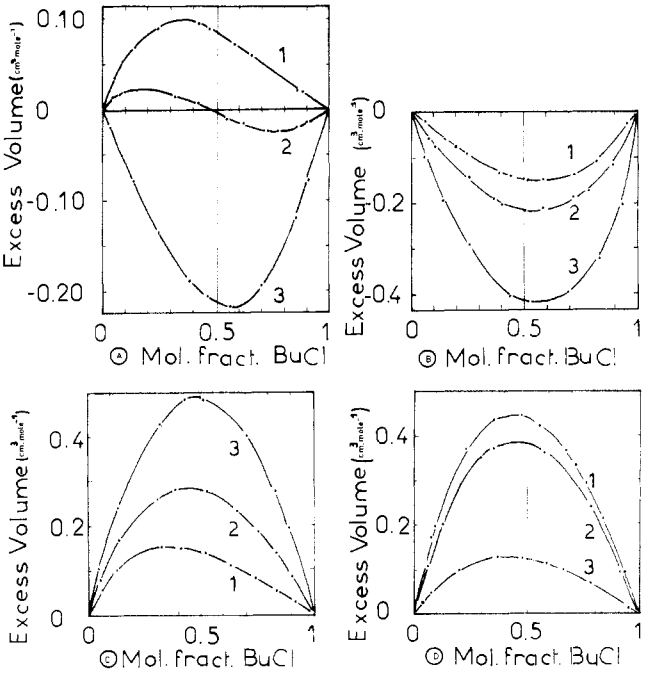

Figure 1. Molar excess volumes of mixtures of butyl chlorides ((1) *n*-butyl chloride, (2) *sec*-butyl chloride (3), *tert*-butyl chloride) with nonpolar solvents ((A) benzene, (B) carbon tetrachloride, (C) *n*-hexane, (D) cyclohexane) at 293.15 K.

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Table I. Densities d (g cm^{-3}) and Excess Volumes V^E (cm^3 mol^{-1}) of Butyl Chlorides (1)-Cyclohexane Mixtures at 293.15 K

n-butyl chloride			*sec*-butyl chloride			*tert*-butyl chloride		
x_1	d	V^E	x_1	d	V^E	x_1	d	V^E
0	0.778 56		0	0.778 53		0	0.778 53	
0.081 32	0.785 82	0.170	0.061 89	0.783 49	0.107	0.037 21	0.780 81	0.022
0.097 08	0.787 29	0.195	0.127 68	0.788 91	0.201	0.078 58	0.783 34	0.047
0.235 29	0.800 54	0.367	0.298 53	0.803 73	0.348	0.205 75	0.791 29	0.097
0.355 20	0.812 72	0.435	0.353 77	0.808 73	0.369	0.371 88	0.801 89	0.124
0.475 37	0.825 45	0.446	0.439 74	0.816 66	0.385	0.485 23	0.809 22	0.125
0.562 12	0.834 95	0.423	0.579 70	0.829 98	0.364	0.587 48	0.815 90	0.112
0.714 89	0.852 22	0.333	0.582 12	0.830 21	0.364	0.657 70	0.820 51	0.100
0.759 10	0.857 36	0.295	0.787 56	0.850 66	0.238	0.786 31	0.828 98	0.071
0.833 15	0.866 13	0.216	0.921 91	0.864 63	0.097	0.953 92	0.840 14	0.012
0.931 36	0.878 01	0.092	1	0.872 92		1	0.843 05	
1	0.886 43							

Table II. Densities d (g cm^{-3}) and Excess Volumes V^E (cm^3 mol^{-1}) of Butyl Chlorides (1)-*n*-Hexane Mixtures at 293.15 K

n-butyl chloride			*sec*-butyl chloride			*tert*-butyl chloride		
x_1	d	V^E	x_1	d	V^E	x_1	d	V^E
0	0.661 57		0	0.661 57		0	0.661 57	
0.062 02	0.672 58	0.060	0.055 03	0.670 71	0.082	0.047 06	0.668 28	0.106
0.127 80	0.684 65	0.104	0.135 42	0.684 55	0.172	0.129 66	0.680 55	0.241
0.332 14	0.724 76	0.152	0.304 72	0.715 63	0.263	0.315 40	0.709 92	0.429
0.410 27	0.741 15	0.151	0.380 37	0.730 30	0.283	0.425 50	0.728 49	0.484
0.524 83	0.766 24	0.142	0.522 28	0.759 33	0.277	0.510 60	0.743 56	0.485
0.629 91	0.790 55	0.113	0.656 17	0.788 58	0.232	0.670 02	0.773 56	0.403
0.745 00	0.818 54	0.084	0.752 70	0.810 84	0.185	0.698 50	0.779 01	0.402
0.827 31	0.839 56	0.055	0.832 74	0.830 12	0.134	0.824 98	0.804 75	0.276
0.914 36	0.862 68	0.029	0.905 36	0.848 26	0.083	0.886 93	0.817 97	0.193
1	0.886 44		1	0.872 97		1	0.843 25	

Table III. Densities d (g cm^{-3}) and Excess Volumes V^E (cm^3 mol^{-1}) of Butyl Chlorides (1)-Carbon Tetrachloride Mixtures at 293.15 K

n-butyl chloride			*sec*-butyl chloride			*tert*-butyl chloride		
x_1	d	V^E	x_1	d	V^E	x_1	d	V^E
0	1.594 07		0	1.594 07		0	1.594 07	
0.062 75	1.546 67	−0.026	0.082 58	1.530 05	−0.057	0.058 86	1.545 72	−0.096
0.150 84	1.480 86	−0.059	0.104 75	1.513 02	−0.072	0.142 28	1.477 76	−0.193
0.201 92	1.443 06	−0.075	0.257 95	1.396 72	−0.140	0.263 42	1.380 93	−0.291
0.240 52	1.414 76	−0.092	0.371 89	1.312 27	−0.187	0.374 63	1.294 18	−0.350
0.387 09	1.308 48	−0.131	0.413 95	1.281 50	−0.201	0.444 59	1.241 05	−0.403
0.444 83	1.267 17	−0.138	0.503 98	1.216 20	−0.213	0.520 09	1.184 18	−0.413
0.519 14	1.214 57	−0.149	0.583 65	1.159 20	−0.212	0.694 33	1.056 60	−0.394
0.584 11	1.168 94	−0.147	0.714 86	1.066 91	−0.187	0.833 17	0.958 40	−0.320
0.722 60	1.073 15	−0.137	0.791 29	1.014 21	−0.172	0.935 61	0.887 64	−0.201
0.825 68	1.002 98	−0.107	0.887 32	0.948 69	−0.115	1	0.843 17	
0.949 21	0.919 96	−0.023	1	0.872 95				
1	0.886 42							

Table IV. Densities d (g cm^{-3}) and Excess Volumes V^E (cm^3 mol^{-1}) of Butyl Chlorides (1)-Benzene Mixtures at 293.15 K

n-butyl chloride			*sec*-butyl chloride			*tert*-butyl chloride		
x_1	d	V^E	x_1	d	V^E	x_1	d	V^E
0	0.878 95		0	0.878 95		0	0.878 95	
0.052 67	0.879 06	0.035	0.041 21	0.878 52	0.014	0.036 67	0.877 54	−0.020
0.083 80	0.879 16	0.053	0.073 54	0.878 26	0.017	0.045 22	0.877 19	−0.022
0.143 65	0.879 51	0.069	0.096 64	0.878 08	0.019	0.135 09	0.873 91	−0.079
0.246 98	0.880 16	0.091	0.148 12	0.877 70	0.022	0.245 05	0.869 96	−0.136
0.422 54	0.881 50	0.096	0.322 27	0.876 63	0.014	0.380 82	0.865 18	−0.188
0.468 59	0.881 91	0.090	0.418 29	0.876 09	0.008	0.465 11	0.862 20	−0.204
0.581 53	0.882 91	0.073	0.543 15	0.875 49	−0.009	0.555 23	0.859 09	−0.217
0.654 84	0.883 55	0.060	0.621 83	0.875 06	−0.013	0.703 17	0.853 88	−0.195
0.856 53	0.885 28	0.021	0.725 88	0.874 56	−0.023	0.848 64	0.848 62	−0.119
0.874 29	0.885 41	0.020	0.852 32	0.873 84	−0.019	0.906 16	0.846 55	−0.079
1	0.886 39		0.900 24	0.873 55	−0.015	1	0.843 16	
			1	0.872 91				

Table V. Densities d (g cm^{-3}) and Excess Volumes V^E (cm^3 mol^{-1}) of Pivalonitrile (1)-n-Hexane, -Cyclohexane, -Carbon Tetrachloride, and -Benzene Mixtures at 293.15 K

x_1	d	V^E	x_1	d	V^E
		n-Hexane			
0	0.661 57				
0.066 69	0.666 14	0.211	0.630 04	0.717 45	0.497
0.110 40	0.669 40	0.308	0.712 62	0.726 54	0.428
0.281 35	0.683 49	0.516	0.824 36	0.739 55	0.295
0.380 14	0.692 40	0.563	0.914 40	0.750 68	0.156
0.556 32	0.709 66	0.545	1	0.761 81	
		Cyclohexane			
0	0.778 50				
0.031 85	0.777 22	0.103	0.592 23	0.764 62	0.563
0.110 30	0.774 57	0.290	0.682 03	0.763 58	0.499
0.275 08	0.770 25	0.510	0.804 89	0.762 53	0.359
0.358 07	0.768 47	0.567	0.901 34	0.762 05	0.199
0.472 95	0.766 37	0.595	1	0.761 81	
		Benzene			
0	0.878 87				
0.038 89	0.873 51	−0.019	0.557 05	0.808 35	−0.066
0.082 63	0.867 57	−0.037	0.640 04	0.799 01	−0.055
0.207 58	0.851 00	−0.068	0.797 91	0.782 06	−0.031
0.320 20	0.836 65	−0.077	0.875 79	0.774 09	−0.022
0.441 35	0.821 83	−0.072	1	0.761 81	
		Carbon Tetrachloride			
0	1.594 08				
0.049 76	1.547 90	−0.022	0.592 21	1.078 78	−0.194
0.100 06	1.501 70	−0.038	0.664 52	1.020 41	−0.180
0.272 15	1.348 58	−0.137	0.808 68	0.906 87	−0.127
0.398 99	1.239 49	−0.190	0.904 10	0.833 76	−0.076
0.479 65	1.171 62	−0.206	1	0.761 81	

Table VI. Densities d (g cm^{-3}) and Excess Volumes V^E (cm^3 mol^{-1}) of Methylchloroform (1)-n-Hexane, -Cyclohexane, -Carbon Tetrachloride, and -Benzene Mixtures at 293.15 K

x_1	d	V^E	x_1	d	V^E
		n-Hexane			
0	0.661 59				
0.037 51	0.680 81	0.071	0.563 92	0.995 64	0.274
0.136 80	0.733 73	0.178	0.705 96	1.097 30	0.231
0.257 06	0.801 58	0.250	0.781 00	1.154 55	0.194
0.378 52	0.874 65	0.270	0.843 67	1.204 56	0.141
0.453 37	0.921 96	0.289	0.974 65	0.315 74	0.005
0.479 18	0.938 87	0.272	1	1.338 03	
		Cyclohexane			
0	0.778 56				
0.031 95	0.794 71	0.052	0.597 12	1.098 68	0.282
0.072 70	0.815 48	0.107	0.707 39	1.162 12	0.238
0.243 34	0.904 45	0.247	0.810 82	1.223 06	0.169
0.381 82	0.978 84	0.298	0.897 63	1.275 17	0.104
0.493 78	1.040 45	0.309	1	1.338 05	
		Carbon Tetrachloride			
0	1.594 13				
0.120 79	1.562 17	0.008	0.547 17	1.451 85	0.007
0.259 37	1.525 94	0.009	0.695 40	1.414 28	0.002
0.378 39	1.495 16	0.008	0.792 07	1.389 93	0.001
0.482 60	1.468 25	0.014	0.962 18	1.347 39	0.005
			1	1.338 07	
		Benzene			
0	0.878 99				
0.060 53	0.909 73	0.020	0.560 62	1.148 85	0.034
0.090 82	0.925 05	0.020	0.701 82	1.211 60	0.029
0.208 48	0.983 34	0.034	0.785 75	1.248 04	0.021
0.383 96	1.067 41	0.043	0.895 22	1.294 55	0.011
0.455 74	1.100 84	0.045	1	1.338 07	
		Mesitylene			
0	0.864 92		0.696 66	1.154 67	0.449
0.062 74	0.885 98	0.095	0.756 73	1.187 46	0.381
0.107 25	0.901 36	0.164	0.848 99	1.240 25	0.319
0.324 92	0.983 32	0.389	0.912 00	1.279 42	0.199
0.453 31	1.037 40	0.464	1	1.337 97	

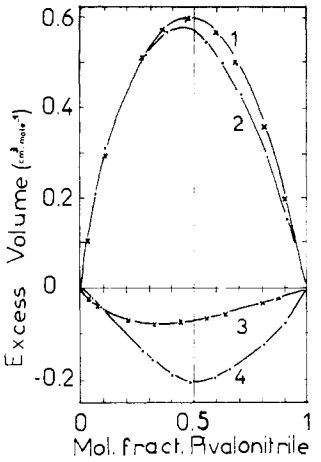

Figure 2. Molar excess volumes of mixtures of pivalonitrile with nonpolar solvents ((1) cyclohexane, (2) n-hexane, (3) benzene, (4) carbon tetrachloride) at 293.15 K.

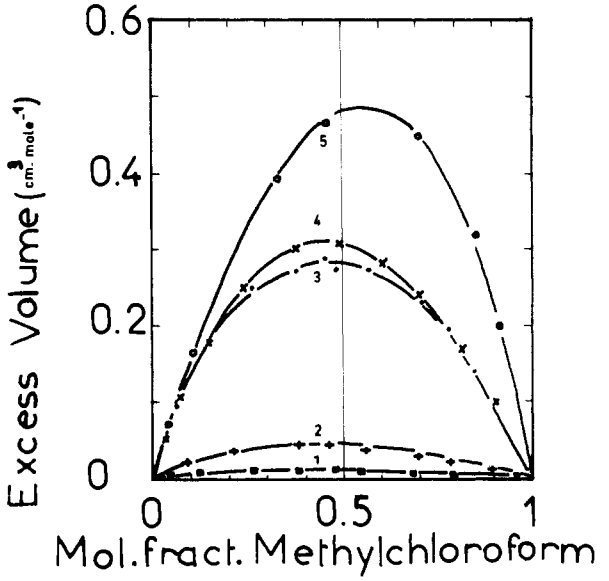

Figure 3. Molar excess volumes of mixtures of methylchloroform with nonpolar solvents ((1) carbon tetrachloride, (2) benzene, (3) n-hexane, (4) cyclohexane, (5) mesitylene) at 293.15 K.

K. Mixtures were prepared by weighing; the substances supplied by Fluka and BDH were fractionnaly distilled and dried over molecular sieves.

Results

Experimental results are tabulated in Tables I–VI; the molar excess volumes of mixing (V^E) have been calculated from experimental densities (d) and plotted as functions of mole fraction (x) (Figures 1–3).

The maximum uncertainty in excess volumes is expected to be ~0.005 cm^3 mol^{-1}. As far as we known, no V^E values have been reported in the literature for the binary liquid mixtures considered here. (*10–11*).

It appears that the volumetric effects in these solutions are governed by the respective molecular shapes of the components. This is particularly observed for the mixtures of the butyl chlorides with the apolar solvents used here, when the shape of the chain varies from the linear n-butyl chloride to the almost spherical *tert*-butyl chloride. In the n-hexane and cyclohexane mixtures, V^E values are always positive, but in the benzene and carbon tetrachloride mixtures V^E values are positive or negative. The same remarks are valid for the systems with the globular pivalonitrile or methylchloroform.

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Excess Enthalpies of Some Binary Mixtures. *n*-Alkane + Aliphatic Ether, *n*-Alkane + Hydroxy Ether, Aliphatic Ether + Hydroxy Ether†

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Measurements of excess enthalpies in a Picker flow microcalorimeter were carried out at 298.15 K for binary mixtures of *n*-heptane with di-*n*-butyl ether, diethylene glycol dimethyl ether, and 2-butoxyethanol and for 2-butoxyethanol with di-*n*-butyl ether, diethyl ether, and diethylene glycol dimethyl ether. In all cases the excess enthalpies are positive; for binary mixtures containing an ether their magnitude depends upon the molecular surface fraction of the oxygen group in the ether molecule.

Molar excess enthalpies have been reported for alcohol + ether mixtures (*1*); their interpretation in terms of a group contribution model (*2-4*) necessitates evaluation of the interchange energy parameters for the pair of contacts oxygen (-O-)/aliphatic (-CH_3 or -CH_2-) from mixtures of aliphatic ether + *n*-alkane. Also a good check for the prediction of the thermodynamic properties of mixtures containing the three functional groups oxygen, hydroxyl (-OH), and aliphatic, particularly with molecules having simultaneously the oxygen and hydroxyl groups, is thus to have available the excess enthalpies for the mixtures hydroxy ether + *n*-alkane as well as hydroxy ether + aliphatic ether. Furthermore, since celiosolves, typified here by 2-butoxyethanol, are solvents of highly technical importance, then accumulation of further information about the thermodynamic properties of such mixtures is essential to a more complete understanding of their behavior.

We report here the excess enthalpies H^E for the following systems: di-*n*-butyl ether ($CH_3(CH_2)_3O(CH_2)_3CH_3$) + *n*-heptane, diethylene glycol dimethyl ether (or diglyme, $CH_3O(CH_2)_2O(CH_2)_2OCH_3$) + *n*-heptane; 2-butoxyethanol ($CH_3(CH_2)_3O(CH_2)_2OH$) + *n*-heptane, + di-*n*-butyl ether, + diethyl ether ($H_3CH_2OCH_2CH_3$), and + diethylene glycol dimethyl ether.

Experimental Section

Excess enthalpies were determined in a Picker flow microcalorimeter (from Setaram, France). Details of the auxilliary equipment and of the operating procedure have been described previously (*1*). The calorimeter was thermostated to ±0.005 K, and the measurements were carried out at 298.15 K.

Ethers used in this work were the same as in previous works (*1*, *5*); their densities and heat capacities are given in ref *1* and *5*, respectively. *n*-Heptane (puriss.) was purchased from Fluka with a reported purity of ≥99.5 mol %, its measured density being 679.5 kg m^{-3}; 2-butoxyethanol obtained from Merck was pure grade with a reported purity of >99 mol % and had a measured density of 896.0 kg m^{-3}. Before actual measurements all liquids were dried with molecular sieves (Union Carbide Type 4 A, 2.5-1.4-mm beads from Fluka).

Results and Discussion

Experimental values of the excess enthalpies are listed in Table I; in all binaries x is the mole fraction of the first cited component.

Each set of results was fitted with a polynomial form

$$H^E = x(1 - x) \sum_{i=0}^{n-1} A_i\{U(x)\}^i \qquad (1)$$

Values of the coefficients A_i were determined by the method of (unweighted) least squares. It was found that the best fit was obtained by using two different functions $U(x)$ depending on the shape of the H^E curves: $U = 2x - 1$, $U = x^{1/2}c$. The U function used for each system is indicated in Table II, where the corresponding values of A_i, standard deviation $\sigma(H^E)$, and x range of fitting are listed.

For all of the mixtures $\sigma(H^E)/H^E_{max} < 0.013$, H^E_{max} being the maximum value of the molar excess enthalpy with respect to mole fraction x.

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