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Excess Molar Enthalpies and Excess Molar Volumes of Dimethyl Carbonate + Seven Alkyl Acetates at 298.15 K

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Excess molar enthalpies and excess molar volumes of dimethyl carbonate + seven alkyl acetates have been determined at 298.15 K and at atmospheric pressure using a flow microcalorimeter and a digital density meter. Values of excess enthalpies and excess volumes increase as the chain length of the acetate molecule is increased. In contrast, the mixtures containing dimethyl carbonate + vinyl acetate show the lowest values. The experimental results have been correlated using the Redlich−Kister equation and have been qualitatively discussed.

Introduction

This paper is part of our investigations on the thermodynamic properties of binary liquid mixtures containing esters of carbonic acid used as solvents in many important industrial extractions, in the synthesis of pharmaceuticals, and in agricultural chemistry.

As a continuation of our research program, we report here the excess molar enthalpies, H_m^E, and the excess molar volumes, V_m^E, of binary mixtures containing dimethyl carbonate + seven alkyl acetates, that is, vinyl-, methyl-, ethyl-, propyl, butyl-, pentyl-, and hexyl acetate at 298.15 K and at atmospheric pressure. An attempt is made to provide a qualitative interpretation of the nature of molecular interactions between the components.

A survey of the literature reveals no previous studies of both H_m^E or V_m^E for these mixtures.

Experimental Section

Chemicals. All chemicals used were of analytical grade. Dimethyl carbonate (DMC), propyl acetate, butyl acetate, pentyl acetate and hexyl acetate were purchased from Aldrich Chemical Co., while vinyl acetate, methyl acetate, and ethyl acetate were Fluka products. All purity grades of chemicals vary in the range from 99 mol % (DMC) to a maximum of 99.7 mol % (butyl acetate). DMC was fractionally distilled as indicated in a previous paper (Francesconi and Comelli, 1996). Alkyl acetates were used without further purification: a GLC analysis did not detect any appreciable impurity peak. The purities of the chemicals were also checked by comparing the measured densities of the pure compounds with those reported in literature, (see Table 1).

Before measurements, the chemicals were kept in dark bottles, dried over molecular sieves (Union Carbide, type 4A, $^1/_{16}$ in. pellets), and degassed by ultrasound (Ultrasonic bath , Hellma, type 460, Milan).

Apparatus. The excess molar enthalpies, H_m^E, were determined using an LKB flow-microcalorimeter (LKB, model 2107, Produkter AB, Bromma, Sweden) equipped with two automatic burets (ABU, Radiometer, Copenhagen, Denmark) to pump pure liquids into the mixing cell of the calorimeter; details of the equipment and its operating procedure have been described previously (Monk and Wadso, 1968; Francesconi and Comelli, 1986). The instrument was thermostated to ±0.01 K and controlled by calibrated thermoresistors inside the calorimeter.

Table 1. Comparison between Measured Densities, ρ, and Literature Data for Pure Components at 298.15 K

component	ρ/g·cm^{-3} this paper	ρ/g·cm^{-3} lit.
dimethyl carbonate	1.063 33	1.063 059[a]
vinyl acetate	0.925 77	0.925 5[b]
methyl acetate	0.926 63	0.927 0[c]
ethyl acetate	0.894 38	0.894 3[b]
propyl acetate	0.883 33	0.883 1[d]
butyl acetate	0.876 20	0.876 36[e]
pentyl acetate	0.872 09	0.871 9[e]
hexyl acetate	0.868 56	0.868 42[f]

[a] Negadi et al. (1993). [b] Kato (1988). [c] Martin et al. (1994). [d] Benito et al. (1994). [e] Riddick et al. (1986). [f] El-Banna (1997).

Mole fractions x_1 of DMC (component 1) were determined from fluxes with an accuracy of $\pm 2 \times 10^{-4}$. The estimated uncertainty in H_m^E is in the range 0.5−1 J.

The calorimeter accuracy was checked against literature data of the system hexane + cyclohexane (Gmehling, 1993), which exhibited a deviation from our measurements of less than 0.5% in the central range of mole fraction.

Excess molar volumes, V_m^E, were determined from density values that were measured by a digital density meter (Anton Paar, model DMA 60, Graz, Austria) equipped with a measuring cell type 602. Densities have been determined with an accuracy of 1×10^{-5} g·cm^{-3}, leading to V_m^E values with an estimated error of ±0.003 cm^3·mol^{-1}.

Details of the operating procedure have been described elsewhere. (Fermeglia and Lapasin, 1988).

Before each set of measurements, the density meter was calibrated with doubly distilled and degassed water and dry air at atmospheric pressure. The temperature was kept constant at ±0.005 K using an external bath (Heto, type 01 DBT 623, Birkerød, Denmark), and temperature was detected with a digital thermometer (Anton Paar DT-25).

Solutions were prepared by mass using a Mettler balance (model AE 160) with an accuracy of ±0.0001 g, charging

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Table 2. Excess Molar Enthalpies, H_m^E, of Dimethyl Carbonate + Alkyl Acetates at 298.15 K

x_1	H_m^E/ J·mol^{-1}	x_2	H_m^E/ J·mol^{-1}	x_1	H_m^E/ J·mol^{-1}	x_2	H_m^E/ J·mol^{-1}
Dimethyl Carbonate (1) + Vinyl Acetate (2)							
0.0437	−4.2	0.6222	−43.3	0.2679	−36.5	0.8978	−10.6
0.0838	−11.2	0.6871	−37.8	0.3544	−43.6	0.9294	−6.0
0.1207	−16.3	0.7671	−29.5	0.4226	−46.3	0.9634	−2.7
0.1546	−21.2	0.8145	−23.9	0.5233	−46.3		
0.2153	−30.2	0.8682	−15.1				
Dimethyl Carbonate (1) + Methyl Acetate (2)							
0.0378	−0.1	0.5860	−9.7	0.2393	−9.9	0.8830	0.7
0.0729	−0.8	0.6537	−7.6	0.3206	−12.1	0.9189	1.9
0.1055	−2.4	0.7390	−4.1	0.3862	−13.1	0.9577	0.9
0.1359	−4.6	0.7906	−2.8	0.4855	−11.9		
0.1909	−8.1	0.8499	−0.4				
Dimethyl Carbonate (1) + Ethyl Acetate (2)							
0.0426	7.4	0.6356	40.0	0.2793	30.1	0.9029	17.0
0.0883	12.1	0.6993	36.7	0.3677	34.8	0.9331	11.9
0.1269	17.3	0.7772	31.6	0.4367	37.6	0.9654	6.1
0.1623	21.1	0.8230	27.9	0.5376	40.8		
0.2252	26.2	0.8747	21.4				
Dimethyl Carbonate (1) + Propyl Acetate (2)							
0.0538	33	0.6718	171	0.3127	151	0.9161	56
0.1021	60	0.7319	156	0.4056	173	0.9425	41
0.1457	82	0.8037	123	0.4764	183	0.9704	21
0.1853	104	0.8452	104	0.5771	184		
0.2544	130	0.8912	73				
Dimethyl Carbonate (1) + Butyl Acetate (2)							
0.0612	49	0.7012	257	0.3428	245	0.9260	85
0.1153	92	0.7578	232	0.4389	279	0.9494	60
0.1636	131	0.8112	190	0.5105	288	0.9741	32
0.2068	166	0.8622	151	0.6101	284		
0.2812	213	0.9037	110				
Dimethyl Carbonate (1) + Pentyl Acetate (2)							
0.0684	58	0.7254	341	0.3699	338	0.9337	110
0.1280	114	0.7789	302	0.4682	382	0.9548	75
0.1804	164	0.8409	239	0.5400	399	0.9769	38
0.2269	210	0.8757	199	0.6378	389		
0.3057	280	0.9136	138				
Dimethyl Carbonate (1) + Hexyl Acetate (2)							
0.0755	86	0.6622	485	0.3289	376	0.8869	244
0.1404	160	0.7462	424	0.3951	434	0.9216	170
0.1968	225	0.7967	378	0.4949	486	0.9400	127
0.2462	288	0.8546	292	0.5665	503	0.9522	109

Table 3. Densities, ρ, and Excess Molar Volumes, V_m^E, of Dimethyl Carbonate + Alkyl Acetates at 298.15 K

x_1	ρ/g·cm^{-3}	V_m^E/ cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	V_m^E/ cm^3·mol^{-1}
Dimethyl Carbonate (1) + Vinyl Acetate (2)					
0.0442	0.931 64	−0.030	0.5637	1.001 96	−0.160
0.1007	0.939 11	−0.060	0.6014	1.007 18	−0.155
0.1976	0.952 07	−0.106	0.6625	1.015 67	−0.143
0.2269	0.956 00	−0.115	0.7073	1.021 91	−0.132
0.3123	0.967 53	−0.141	0.7997	1.034 88	−0.100
0.3893	0.978 01	−0.156	0.8836	1.046 74	−0.064
0.4333	0.984 02	−0.160	0.9354	1.054 11	−0.037
0.4874	0.991 43	−0.162	0.9840	1.061 04	−0.010
0.5193	0.995 82	−0.161			
Dimethyl Carbonate (1) + Methyl acetate (2)					
0.0129	0.928 46	−0.004	0.5256	1.001 24	−0.065
0.0977	0.941 01	−0.028	0.5642	1.006 47	−0.064
0.1167	0.943 78	−0.031	0.6279	1.015 0	−0.058
0.1862	0.953 84	−0.046	0.6847	1.022 6	−0.053
0.2227	0.959 06	−0.050	0.7768	1.034 67	−0.040
0.2805	0.967 27	−0.058	0.8581	1.045 23	−0.027
0.3486	0.976 84	−0.063	0.9204	1.053 22	−0.016
0.4149	0.986 08	−0.066	0.9745	1.060 11	−0.005
0.4884	0.996 17	−0.066			
Dimethyl Carbonate (1) + Ethyl Acetate (2)					
0.0628	0.903 72	−0.015	0.6185	0.993 43	−0.060
0.1250	0.913 14	−0.029	0.6665	1.001 81	−0.055
0.2449	0.931 71	−0.049	0.7316	1.013 36	−0.048
0.3792	0.953 19	−0.061	0.7914	1.024 18	−0.041
0.4591	0.966 34	−0.064	0.8767	1.039 88	−0.025
0.4946	0.972 23	−0.063	0.9168	1.047 43	−0.018
0.5650	0.984 19	−0.062	0.9823	1.059 92	−0.004
0.5800	0.986 76	−0.060			
Dimethyl Carbonate (1) + Propyl Acetate (2)					
0.0151	0.885 31	0.003	0.6038	0.977 72	0.056
0.1409	0.902 42	0.027	0.6518	0.986 68	0.054
0.2986	0.925 71	0.048	0.7065	0.997 69	0.049
0.3624	0.935 78	0.054	0.7701	1.010 77	0.042
0.4388	0.948 37	0.057	0.8155	1.020 47	0.036
0.4997	0.958 85	0.058	0.9049	1.040 52	0.021
0.5412	0.966 21	0.057	0.9446	1.049 84	0.012
0.5692	0.971 30	0.057	0.9768	1.057 62	0.006
Dimethyl Carbonate (1) + Butyl Acetate (2)					
0.04720	0.881 75	0.028	0.6422	0.974 87	0.156
0.1566	0.895 46	0.082	0.6887	0.984 34	0.148
0.2182	0.903 72	0.108	0.7305	0.993 44	0.137
0.3608	0.924 61	0.149	0.7957	1.008 44	0.116
0.4158	0.933 39	0.158	0.8341	1.017 85	0.097
0.4830	0.944 73	0.164	0.9177	1.039 67	0.053
0.5180	0.950 93	0.165	0.9494	1.048 51	0.035
0.5687	0.960 29	0.163	0.9825	1.058 08	0.014
0.6059	0.967 44	0.160			
Dimethyl Carbonate (1) + Pentyl Acetate (2)					
0.0504	0.877 92	0.041	0.6775	0.974 27	0.225
0.1365	0.887 66	0.102	0.7112	0.981 78	0.213
0.2545	0.902 40	0.169	0.7551	0.992 07	0.194
0.3310	0.912 97	0.203	0.7908	1.000 95	0.173
0.4240	0.927 06	0.231	0.8626	1.020 15	0.130
0.4981	0.939 38	0.243	0.9202	1.037 15	0.080
0.5552	0.949 67	0.243	0.9507	1.046 74	0.053
0.5964	0.957 53	0.240	0.9863	1.058 60	0.016
0.6428	0.966 91	0.233			
Dimethyl Carbonate (1) + Hexyl Acetate (2)					
0.0380	0.872 19	0.040	0.6921	0.969 97	0.299
0.1708	0.886 16	0.159	0.7362	0.980 41	0.278
0.2782	0.899 10	0.234	0.7713	0.989 29	0.257
0.3601	0.910 18	0.276	0.8148	1.001 04	0.227
0.4523	0.924 09	0.309	0.8820	1.021 12	0.162
0.5246	0.936 31	0.317	0.9280	1.036 41	0.107
0.5891	0.948 26	0.322	0.9606	1.048 13	0.061
0.6183	0.954 08	0.317	0.9929	1.060 46	0.015
0.6649	0.963 91	0.307			

the heavier component first to minimize the error due to vaporization and following the same procedure used by Fermeglia and Lapasin (1988). Buoyancy corrections due to air and evaporation of solvents were taken into account to achieve greater accuracy in measurements.

The test mixture benzene + cyclohexane was used to check the apparatus, and our results show a discrepancy of less than 0.5% from those in the literature (Wilhelm, 1985) over the central range of mole fraction x_1 of DMC.

V_m^E values have been determined from density measurements using the following equation:

$$V_m^E/\text{cm}^3\text{·mol}^{-1} = (x_1M_1 + x_2M_2)/\rho - x_1M_1/\rho_1 - x_2M_2/\rho_2 \quad (1)$$

where x_i, M_i, and ρ_i are the mole fraction, molar mass, and density of component i, respectively.

Results and Discussion

The excess molar enthalpies, H_m^E, and the excess molar volumes, V_m^E, at 298.15 K and at various mole fractions are reported in Tables 2 and 3 and in Figures1 and 2. The excess properties were fitted to the Redlich−Kister relation

$$Q_m^E = x_1x_2\sum_{k\geq 0} a_k(x_1 - x_2)^k \quad (2)$$

where $Q_m^E = H_m^E/(\text{J·mol}^{-1})$ or $V_m^E/(\text{cm}^3\text{·mol}^{-1})$ with all points weighted equally, x_1 and x_2 are the mole fractions of components, and a_k are the adjustable parameters

Table 4. Adjustable Parameters, a_k, and Standard Deviations, $\sigma(Q^E_m)$, for H^E_m (in J·mol^{-1}) and V^E_m (in cm^3·mol^{-1}) of Dimethyl Carbonate (1) + Alkyl Acetates (2) at 298.15 K

acetates	function	a_0	a_1	a_2	a_3	a_4	$\sigma(Q^E_m)$
vinyl acetate	H^E_m	−187.5	13.6	12.8	6.4	119.8	0.4
	V^E_m	−0.6485	0.0260				0.0008
methyl acetate	H^E_m	−46.7	39.9	13.7	−24.0	75.5	0.3
	V^E_m	−0.2641	0.0542				0.0005
ethyl acetate	H^E_m	159.1	40.0	25.4	−27.9		0.4
	V^E_m	−0.2543	0.0063				0.0005
propyl acetate	H^E_m	743.1	126.6	−35.3	−105.8		1.5
	V^E_m	0.2332	0.0073				0.0004
butyl acetate	H^E_m	1160.7	215.8	−109.7			2.1
	V^E_m	0.6612	0.0649				0.0011
pentyl acetate	H^E_m	1571.7	504.2	−314.4			3.1
	V^E_m	0.9689	0.1529	0.0085			0.0010
hexyl acetate	H^E_m	1963.0	705.6	−233.3			3.9
	V^E_m	1.2688	0.2908	0.1182			0.0014

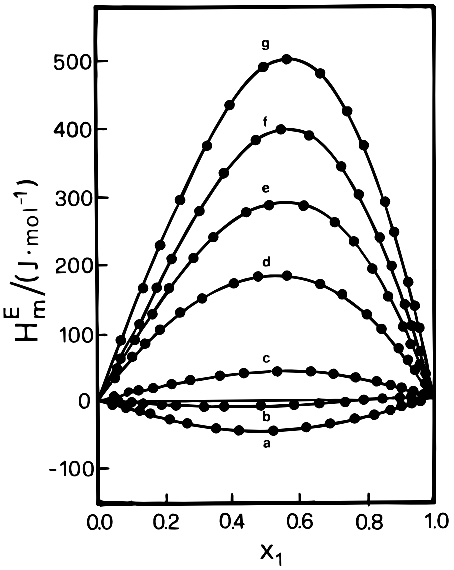


Figure 1. Excess molar enthalpies, H^E_m, at 298.15 K of dimethyl carbonate + vinyl acetate (a), + methyl acetate (b), + ethyl acetate (c), + propyl acetate (d), + butyl acetate (e), + pentyl acetate (f), and + hexyl acetate (g). Closed circles, experimental points; solid lines, calculated with eq 2.

evaluated by the method of least squares.

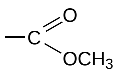
The values of the parameters, together with their standard deviations $\sigma(Q^E_m)$, are reported in Table 4.

Figures 3 and 4 represent $H^E_m(x_1=0.5)$ or $V^E_m(x_1=0.5)$, the equimolar excess enthalpy of H^E_m or V^E_m plotted against the number n_R of the alkyl groups in the acetate molecules.

Values of equimolar H^E_m or V^E_m for DMC + vinyl acetate mixture are not represented in these figures.

If we consider the series from methyl to hexyl acetate, both H^E_m and V^E_m increase regularly as the molecular size of the ester is increased. The first elements of the series show negative or very low values. The lowest values of H^E_m and V^E_m are given by vinyl acetate.

The near zero values of H^E_m for DMC + methyl acetate are due to the great similarity of the two molecules, having the following molecular structure as a common part:



$$-C(=O)OCH_3$$

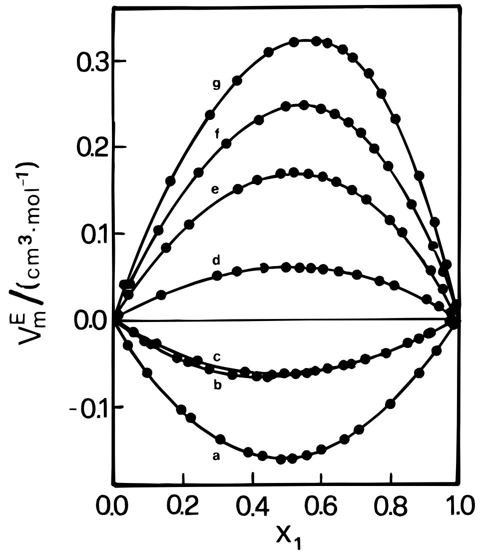


Figure 2. Excess molar volumes, V^E_m, at 298.15 K of dimethyl carbonate + alkyl acetate mixtures. Symbols and letters are the same indicated in Figure 1.

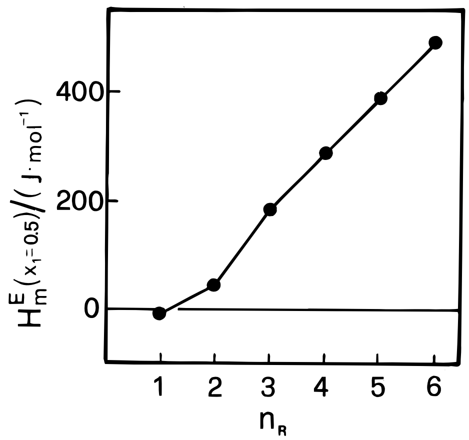


Figure 3. Values of equimolar $H^E_m(x_1=0.5)$ at 298.15 K as a function of the numbers of C-atoms, $\mathbf{n}_R$, in the alkyl substituent.

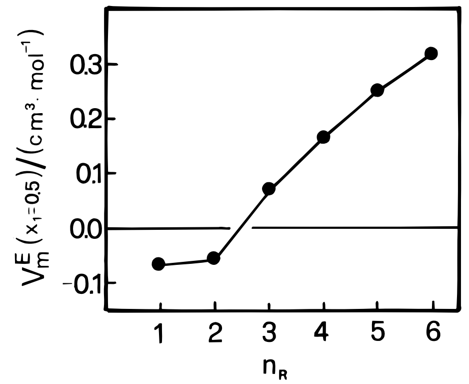


Figure 4. Values of equimolar $V^E_m(x_1=0.5)$ at 298.15 K as a function of the numbers of C-atoms, n_R, in the alkyl substituent.

The different calorimetric behavior between vinyl acetate and alkyl acetates follows from the stronger interaction of the C=O group of DMC with the π electrons of the vinyl group than with those of the alkyl groups.

Furthermore, the dipole−dipole interactions cannot explain the behavior of the H^E_m or V^E_m curves, since dipole moments of alkyl acetates show an erratic variation as a function of the number of C atoms.

Interpretation of V^E_m curves is more difficult since the contributions of packaging of molecules in the mixture and of steric effects are not easily predictable.

Similar H_m^E and V_m^E trends were observed for the mixtures of DMC + chloroalkenes or *n*-alkyl ketones (Comelli and Francesconi, 1994; Francesconi and Comelli, 1995a,b).

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