Densities, Refractive Indices, and Excess Molar Volumes of Water + Methanol + Hexyl Acetate and Its Binary Submixtures at 298.15 K

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Densities and refractive indices were measured throughout the miscible region for water + methanol + hexyl acetate, water + methanol, and hexyl acetate + methanol at 298.15 K and atmospheric pressure. Derived excess volumes were correlated using Redlich–Kister polynomials.

Introduction

We report densities, refractive indices, and excess volumes in the miscible region for water + methanol + hexyl acetate at 298.15 K and atmospheric pressure. In spite of the potential of hexyl acetate as a solvent for recovery of methanol from aqueous dilute solutions, no measurements of this ternary mixture have appeared in the open literature. The measured excess volumes have been correlated using Redlich–Kister polynomials.

Experimental Section

Materials. Reagent grade water was obtained with a Milli-Q Plus system. Methanol (from Merck) was >99.7 mass % pure, and hexyl acetate (from Aldrich) >99.1 mass % pure. Since small concentrations of impurities have no influence on the properties studied (in particular, they do not affect excess volume results) (*1*, *2*), both compounds were used without further purification. Table 1 lists the densities and refractive indices of all three components together with values found in the literature (*3*).

Apparatus. Mixtures were prepared by mass using a Mettler AE 240 balance with a precision of ±0.000 01 g. Densities were measured to a precision of ±0.000 01 g·cm^{-3} in an Anton Paar DMA 60 digital vibrating tube densimeter with a DMA 602 measuring cell, and refractive indices to a precision of ±0.0001 in an Atago RX-1000 refractometer. Temperature was kept at 25.00 ± 0.02 °C with a Heto Therm ultrathermostat.

Results and Discussion

The molar volumes V of mixtures were calculated as usual from the expression

$$V = \sum x_i M_i / d \qquad (1)$$

where x_i is the mole fraction of component i in the mixture, M_i its molecular weight, and d the measured density of the mixture, and excess molar volumes V^E from

$$V^E = V - \sum x_i V_i \qquad (2)$$

where V_i is the molar volume of pure component i. Molar refractions R were calculated using the Lorentz–Lorenz equation:

$$R = V(n_D^2 - 1)/(n_D^2 + 2) \qquad (3)$$

where n_D is the refractive index of the mixture and ΔR the deviation of R from a mole fraction average of the molar refraction of the pure components, from

$$\Delta R = R - \sum x_i R_i \qquad (4)$$

where R_i is the molar refraction of pure component i.

Table 2 lists the measured values of d and n_D together with the corresponding values of V^E and ΔR (results are included both for mixtures with all three components present and for the binary subsystems water + methanol and hexyl acetate + methanol). Figures 1 and 2 show isolines for d and n_D in the miscible region of the ternary system, together with the binodal curve established in previous work (*4*). Figure 3 shows the dependence of V^E on the mole fractions of water and hexyl acetate, and Figure 4 the corresponding V isolines (computed using a standard program). Figure 5 compares our V^E results for water + methanol with previously published data (*6–9*).

Table 1. Densities (d) and Refractive Indices (n_D) of Pure Components at 298.15 K

component	d/(g·cm^{-3}) exptl	d/(g·cm^{-3}) lit. (*3*)	n_D exptl	n_D lit. (*3*)
water	0.9970	0.997 04	1.3324	1.332 50
methanol	0.7866	0.786 64	1.3264	1.326 52
hexyl acetate	0.8686	0.868 1	1.4069	
			1.4092[a]	1.409 6[a]

[a] At 293.15 K.

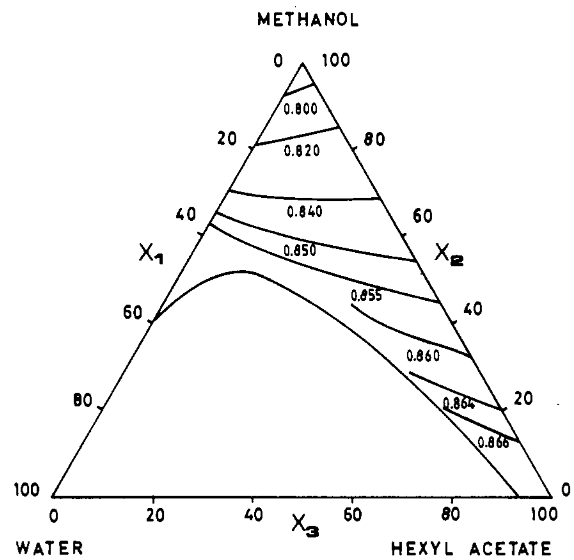

Figure 1. Density isolines for water (1) + methanol (2) + hexyl acetate (3) at 298.15 K and atmospheric pressure.

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Table 2. Densities d, Refractive Indices n_D, Excess Volumes V^E, and ΔR Values for Water (1) + Methanol (2) + Hexyl Acetate (3) at 298.15 K

x_1	x_2	$d/(g\cdot cm^{-3})$	n_D	V^E $(cm^3\cdot mol^{-1})$	$\Delta R/(cm^3\cdot mol^{-1})$	x_1	x_2	$d/(g\cdot cm^{-3})$	n_D	$V^E/(cm^3\cdot mol^{-1})$	$\Delta R/(cm^3\cdot mol^{-1})$
0.0000	1.0000	0.786 59	1.3264	0.000	0.000	0.0000	0.0000	0.868 59	1.4069	0.000	0.000
0.0716	0.9284	0.799 01	1.3288	−0.267	−0.006	0.0476	0.9524	0.794 82	1.3281	−0.183	−0.004
0.1203	0.8797	0.807 60	1.3303	−0.423	−0.010	0.0426	0.8522	0.818 21	1.3537	−0.098	0.010
0.1612	0.8388	0.814 96	1.3316	−0.539	−0.013	0.0377	0.7552	0.832 44	1.3689	−0.065	0.019
0.2145	0.7855	0.824 78	1.3331	−0.672	−0.016	0.0331	0.6627	0.841 83	1.3789	−0.054	0.023
0.2609	0.7391	0.833 56	1.3344	−0.772	−0.018	0.0283	0.5668	0.848 94	1.3863	−0.048	0.025
0.3054	0.6946	0.842 19	1.3356	−0.853	−0.020	0.0234	0.4677	0.854 46	1.3921	−0.042	0.023
0.3550	0.6450	0.852 05	1.3369	−0.927	−0.022	0.0188	0.3771	0.858 40	1.3962	−0.036	0.020
0.4096	0.5904	0.863 18	1.3382	−0.986	−0.023	0.0150	0.3004	0.861 15	1.3991	−0.030	0.016
0.4584	0.5416	0.873 33	1.3392	−1.018	−0.024	0.0100	0.1998	0.864 15	1.4022	−0.024	0.011
0.4943	0.5057	0.880 91	1.3398	−1.028	−0.024	0.0055	0.1105	0.866 37	1.4045	−0.019	0.006
0.5604	0.4396	0.895 03	1.3407	−1.016	−0.023	0.1500	0.8500	0.812 95	1.3312	−0.508	−0.012
0.6063	0.3937	0.904 93	1.3410	−0.982	−0.023	0.1345	0.7620	0.830 09	1.3561	−0.340	−0.001
0.6562	0.3438	0.915 73	1.3411	−0.922	−0.021	0.1194	0.6767	0.840 73	1.3708	−0.250	0.008
0.7040	0.2960	0.926 12	1.3408	−0.842	−0.020	0.1044	0.5919	0.848 09	1.3806	−0.196	0.014
0.7484	0.2516	0.935 81	1.3403	−0.749	−0.018	0.0894	0.5064	0.853 49	1.3876	−0.155	0.015
0.7958	0.2042	0.946 25	1.3394	−0.632	−0.015	0.0757	0.4288	0.857 22	1.3924	−0.122	0.013
0.8468	0.1532	0.957 74	1.3381	−0.487	−0.012	0.0616	0.3488	0.860 28	1.3963	−0.092	0.008
0.8984	0.1016	0.969 87	1.3364	−0.327	−0.009	0.0457	0.2587	0.863 06	1.3998	−0.062	0.000
0.9455	0.0545	0.981 73	1.3346	−0.175	−0.005	0.0326	0.1846	0.864 98	1.4022	−0.044	−0.005
1.0000	0.0000	0.997 06	1.3325	0.000	0.000	0.0185	0.1050	0.866 74	1.4044	−0.029	−0.008
0.0000	0.9503	0.800 65	1.3405	0.025	0.011	0.2457	0.7543	0.830 66	1.3342	−0.741	−0.018
0.0000	0.8992	0.811 79	1.3516	0.038	0.019	0.2200	0.6752	0.841 80	1.3593	−0.517	−0.003
0.0000	0.8545	0.819 65	1.3594	0.043	0.025	0.1949	0.5984	0.849 03	1.3735	−0.387	0.007
0.0000	0.8056	0.826 77	1.3664	0.041	0.029	0.1714	0.5261	0.853 91	1.3824	−0.306	0.013
0.0000	0.7531	0.833 12	1.3726	0.036	0.032	0.1486	0.4561	0.857 46	1.3886	−0.244	0.015
0.0000	0.7037	0.838 14	1.3774	0.028	0.034	0.1236	0.3793	0.860 42	1.3936	−0.185	0.015
0.0000	0.6561	0.842 29	1.3814	0.019	0.034	0.1012	0.3108	0.862 50	1.3971	−0.137	0.013
0.0000	0.6006	0.846 44	1.3854	0.009	0.034	0.0755	0.2316	0.864 47	1.4004	−0.089	0.010
0.0000	0.5689	0.848 53	1.3874	0.003	0.033	0.0529	0.1624	0.865 92	1.4027	−0.055	0.006
0.0000	0.4970	0.852 67	1.3914	−0.007	0.031	0.0318	0.0977	0.867 11	1.4045	−0.032	0.003
0.0000	0.4466	0.855 16	1.3938	−0.013	0.029	0.3430	0.6570	0.849 64	1.3366	−0.911	−0.021
0.0000	0.3952	0.857 40	1.3960	−0.017	0.026	0.3269	0.6261	0.851 19	1.3499	−0.764	−0.014
0.0000	0.3447	0.859 37	1.3979	−0.020	0.023	0.3102	0.5943	0.853 28	1.3601	−0.663	−0.007
0.0000	0.2869	0.861 37	1.3998	−0.021	0.020	0.2935	0.5622	0.855 32	1.3680	−0.589	−0.001
0.0000	0.2473	0.862 61	1.4010	−0.020	0.018	0.2765	0.5296	0.857 06	1.3743	−0.524	0.004
0.0000	0.2008	0.863 95	1.4023	−0.019	0.015	0.3923	0.6077	0.859 62	1.3377	−0.970	−0.023
0.0000	0.1503	0.865 28	1.4036	−0.016	0.011	0.3797	0.5882	0.858 96	1.3472	−0.856	−0.019
0.0000	0.1080	0.866 30	1.4046	−0.013	0.009	0.3677	0.5697	0.859 22	1.3547	−0.782	−0.016
0.0000	0.0492	0.867 60	1.4059	−0.007	0.004	0.3548	0.5497	0.859 70	1.3612	−0.715	−0.012

Table 3. Coefficients and Standard Deviations of the Excess Volume-composition curves fitted to the data for the binary systems

system	$A_0/(cm^3\cdot mol^{-1})$	$A_1/(cm^3\cdot mol^{-1})$	$A_2/(cm^3\cdot mol^{-1})$	$A_3/(cm^3\cdot mol^{-1})$	$\sigma/(cm^3\cdot mol^{-1})$
water + methanol	−4.1148	−0.1325	0.5078	0.6222	0.001
hexyl acetate + methanol	−0.0277	−0.2629	0.2721	−0.1329	0.001

Table 4. Coefficients and Standard Deviations of the ΔR–Composition Curves Fitted to the Data for the Binary Systems

system	$A_0/(cm^3\cdot mol^{-1})$	$A_1/(cm^3\cdot mol^{-1})$	$A_2/(cm^3\cdot mol^{-1})$	$\sigma/(cm^3\cdot mol^{-1})$
water + methanol	−0.0952			0.001
hexyl acetate + methanol	0.1239	−0.0768	0.0403	0.001

Table 5. Coefficients and Standard Deviations of the Excess Volume–Composition and ΔR–Composition Surfaces Fitted to the Data for the Ternary System

property	$A/(cm^3\cdot ol^{-1})$	$B_1/(cm^3\cdot mol^{-1})$	$B_2/(cm^3\cdot mol^{-1})$	$B_3/(cm^3\cdot mol^{-1})$	$C_1/(cm^3\cdot mol^{-1})$	$C_2/(cm^3\cdot mol^{-1})$	$C_3/(cm^3\cdot mol^{-1})$	$D_1/(cm^3\cdot mol^{-1})$	$D_2/(cm^3\cdot mol^{-1})$	$D_3/(cm^3\cdot mol^{-1})$	$\sigma/(cm^3\cdot mol^{-1})$
V^E	−3.0216	−15.0761	−9.7954	5.2807	−37.1854	4.0476	14.2640	−16.3716	−0.5216	−15.4910	0.002
ΔR	0.5350	−0.1104	0.8601	0.9705	−3.4206	1.9575	−7.0600				0.002

The V^E and ΔR data were correlated using Redlich–Kister polynomials for ternary systems (5):

$$Q_{123} = Q_{12} + Q_{32} + Q_{13} + x_1x_2x_3\{A + B_1(x_1 - x_2) + B_2(x_3 - x_2) + B_3(x_3 - x_1) + C_1(x_1 - x_2)^2 + C_2(x_3 - x_2)^2 + C_3(x_3 - x_1)^2 + ...\} \quad (5)$$

where Q_{123} is the dependent quantity (here V^E or ΔR), x_i is the mole fraction of component i in the ternary mixture, Q_{ij} is the Redlich–Kister polynomial fitted to the data for binary mixtures of components i and j, and A, B_i, C_i, etc. are the coefficients to be optimized. The optimized coefficients and standard deviations of the binary polynomials

$$Q_{ij} = x_ix_j\sum_k A_k(x_i - x_j)^k \qquad k = 0, 1, 2, ..., n \quad (6)$$

are listed in Tables 3 and 4 for $Q = V^E$ and $Q = \Delta R$, respectively (Q_{31} is taken to be identically zero, since water and hexyl acetate are practically immiscible), and those of the ternary polynomials in Table 5. All polynomials were fitted by least squares, using Student's t test to estimate the significance of

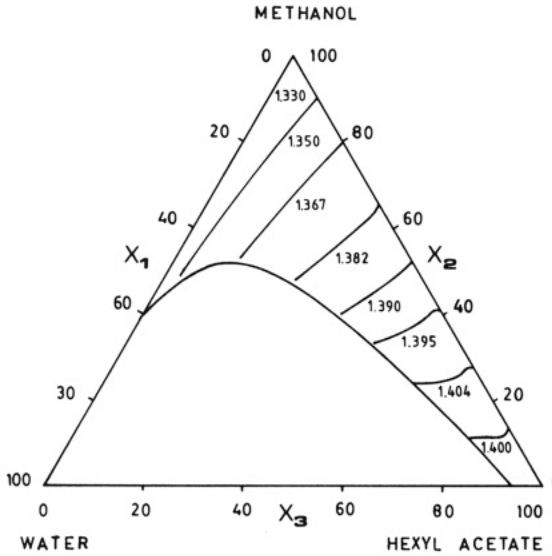

Figure 2. Refractive index isolines for water (1) + methanol (2) + hexyl acetate (3) mixtures at 298.15 K and atmospheric pressure.

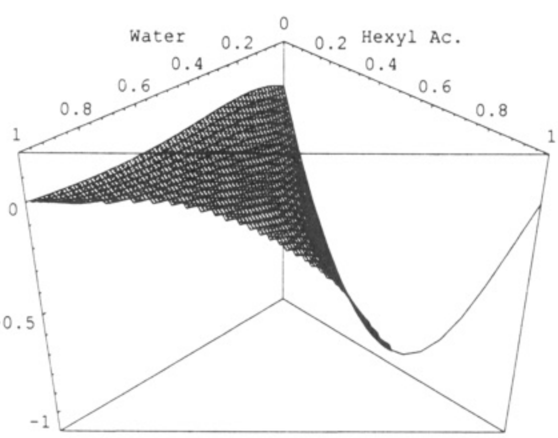

Figure 3. Composition dependence of the excess molar volume of water (1) + methanol (2) + hexyl acetate (3) mixtures at 298.15 K and atmospheric pressure.

each coefficient and Fisher's F test to decide on the inclusion of further terms.

Conclusions

The excess molar volumes of the ternary system water + methanol + hexyl acetate at 298.15 K and atmospheric pressure are negative, except for mixtures with a mole fraction of hexyl acetate of up to about 0.45 at or very near the methanol + hexyl acetate edge of the composition diagram. The total range of V^E is −1.028 to +0.043 $cm^3 \cdot mol^{-1}$. ΔR values range from −0.024 to +0.034; i.e., the refractive index of these mixtures exhibits almost ideal behavior.

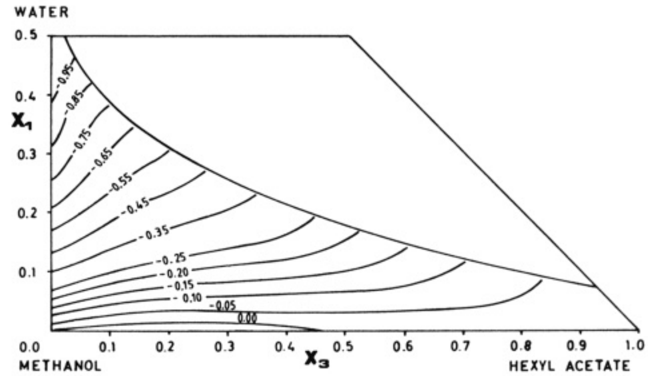

Figure 4. Excess molar volume isolines for the water (1) + methanol (2) + hexyl acetate (3) at 298.15 K and atmospheric pressure.

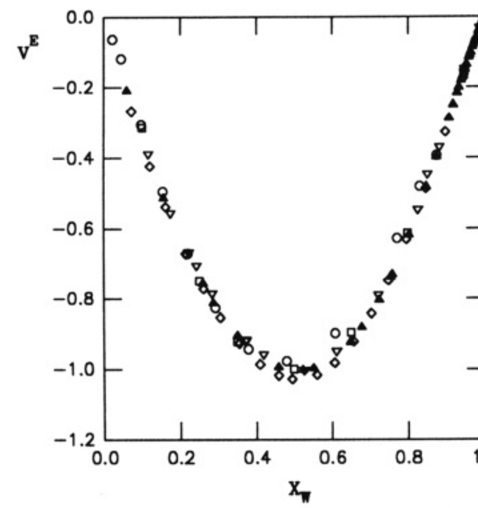

Figure 5. V^E of water + methanol: (◇) this work, (▲) Benson and Kiyohara (*6*), (○) Letellier and Biquard (*7*), (□) Easteal and Woolf (*8*), (▽) Patel and Sandler (*9*).

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