Excess Volumes of the Binary Mixtures of Substituted Benzenes with Ethyl Acetate and Butyl Acetate

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Volume changes on mixing of binary liquid mixtures of ethyl acetate and butyl acetate with substituted benzenes, namely benzene, toluene, chlorobenzene, bromobenzene, and nitrobenzene, have been measured as a function of composition at 313.15 K, by using a dilatometer. The excess volumes are positive over the entire range of composition for the systems benzene + ethyl acetate and benzene + butyl acetates. The measured excess volumes are negative over the entire composition range in all the remaining systems.

Introduction

The purpose of this paper is to report measurements of the excess volumes of nonelectrolyte solutions of ethyl acetate and butyl acetate with benzene, toluene, chlorobenzene, bromobenzene, and nitrobenzene at 313.15 K.

A literature survey shows that excess volumes for the systems benzene, toluene with ethyl acetate, and benzene, toluene with butyl acetate have been reported previously (*1*) at 298.15 K. Again we made an attempt to measure excess volumes for the above systems to compare with the other substituted benzenes with alkyl acetates at 313.15 K. These measurements were made as part of a continuing project on the thermodynamic properties of nonelectrolyte solutions (*2-5*).

Table I. Boiling Points and Densities of the Pure Components at 303.15 K

compd	bp/K present work	bp/K lit. (*11*)	ρ^a/(g cm^{-3}) present work	ρ^a/(g cm^{-3}) lit. (*11, 12*)
ethyl acetate	350.1	350.26	0.894 51[b]	0.894 55[b]
butyl acetate	399.1	399.26	0.871 34	0.871 29
benzene	353.0	353.25	0.868 19	0.868 25
toluene	383.6	383.77	0.857 59	0.857 66
bromobenzene	428.3	429.05	1.481 45	1.481 50
chlorobenzene	404.6	404.83	1.095 56	1.095 50
nitrobenzene	483.8	483.95	1.193 48	1.193 41

[a] Density. [b] At 298.15 K.

Experimental Section

The excess volumes were measured by using a dilatometer described by Rao and Naidu (*6*). The excess volumes are accurate to ±0.003 cm^3 mol^{-1}. The dilatometer was standardized with a cyclohexane + benzene system at 298.15 K. The measured excess volumes for the standard system are in

Table II. Excess Volumes of Ethyl Acetate with Substituted Benzenes at 313.15 K

x_A[a]	V^E/(cm^3 mol^{-1})	ΔV^E/(cm^3 mol^{-1})	x_A[a]	V^E/(cm^3 mol^{-1})	ΔV^E/(cm^3 mol^{-1})
		Ethyl Acetate + Benzene			
0.1058	0.038	+0.003	0.5626	0.080	+0.004
0.1956	0.055	−0.003	0.6451	0.069	+0.003
0.2506	0.066	−0.002	0.7354	0.050	−0.001
0.3641	0.078	−0.003	0.8146	0.036	+0.000
0.4707	0.085	+0.003	0.8759	0.024	+0.000
		Ethyl Acetate + Toluene			
0.1504	−0.019	−0.001	0.5748	−0.044	+0.000
0.2002	−0.024	+0.001	0.6972	−0.031	+0.003
0.3512	−0.040	+0.001	0.7648	−0.024	+0.002
0.4756	−0.048	−0.002	0.8709	−0.012	+0.004
0.5460	−0.047	−0.002	0.8952	−0.011	−0.001
		Ethyl Acetate + Bromobenzene			
0.1107	−0.106	−0.004	0.5347	−0.334	−0.002
0.1259	−0.151	+0.005	0.6488	−0.321	+0.004
0.2994	−0.243	+0.000	0.7802	−0.271	−0.006
0.3656	−0.275	+0.004	0.8456	−0.206	+0.003
0.4667	−0.321	−0.002	0.8662	−0.188	+0.000
		Ethyl Acetate + Chlorobenzene			
0.1165	−0.152	+0.003	0.6406	−0.435	+0.002
0.2056	−0.285	−0.006	0.7186	−0.357	+0.005
0.2951	−0.385	+0.000	0.7912	−0.275	−0.001
0.3995	−0.467	+0.002	0.8420	−0.211	−0.006
0.5013	−0.496	−0.001	0.8901	−0.136	+0.003
		Ethyl Acetate + Nitrobenzene			
0.1258	−0.141	−0.002	0.5426	−0.728	−0.004
0.2227	−0.292	+0.006	0.6331	−0.733	+0.002
0.2856	−0.412	−0.004	0.7349	−0.664	−0.004
0.3501	−0.508	+0.006	0.8092	−0.543	+0.001
0.4617	−0.665	−0.005	0.8421	−0.474	+0.001

[a] Mole fraction of ethyl acetate.

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Table III. Excess Volumes of Butyl Acetate with Substituted Benzenes at 313.15 K

x_A[a]	V^E/ (cm^3 mol^{-1})	ΔV^E/ (cm^3 mol^{-1})	x_A[a]	V^E/ (cm^3 mol^{-1})	ΔV^E/ (cm^3 mol^{-1})
		Butyl Acetate + Benzene			
0.1036	0.035	+0.000	0.5388	0.032	+0.001
0.1416	0.045	+0.003	0.5809	0.029	+0.002
0.2259	0.047	−0.003	0.6621	0.021	+0.001
0.3506	0.045	−0.003	0.7456	0.015	+0.001
0.4367	0.041	+0.000	0.8902	0.005	−0.001
		Butyl Acetate + Toluene			
0.1196	−0.046	+0.003	0.5961	−0.130	−0.002
0.1654	−0.070	−0.002	0.6360	−0.116	+0.005
0.2527	−0.099	−0.001	0.7589	−0.084	+0.003
0.3901	−0.133	−0.003	0.8463	−0.054	+0.002
0.4847	−0.136	+0.000	0.8771	−0.048	−0.003
		Butyl Acetate + Bromobenzene			
0.1352	−0.125	+0.002	0.5889	−0.340	+0.003
0.2506	−0.230	+0.003	0.6972	−0.288	+0.005
0.3542	−0.306	+0.000	0.7669	−0.241	−0.001
0.4801	−0.357	−0.006	0.8361	−0.174	+0.002
0.4960	−0.358	−0.005	0.9001	−0.111	−0.002
		Butyl Acetate + Chlorobenzene			
0.1253	−0.185	−0.002	0.4567	−0.395	−0.003
0.1930	−0.260	+0.002	0.5368	−0.376	−0.002
0.2719	−0.329	+0.002	0.6859	−0.285	−0.002
0.3156	0.355	+0.004	0.8177	−0.159	+0.003
0.3985	−0.390	−0.002	0.8905	−0.093	−0.001
		Butyl Acetate + Nitrobenzene			
0.1106	−0.240	+0.000	0.5674	−0.701	−0.004
0.1517	−0.322	+0.002	0.6550	−0.630	+0.002
0.2698	−0.535	−0.004	0.7362	−0.533	−0.004
0.3905	−0.666	+0.003	0.8016	−0.420	0.000
0.4689	−0.705	+0.003	0.8473	−0.331	+0.001

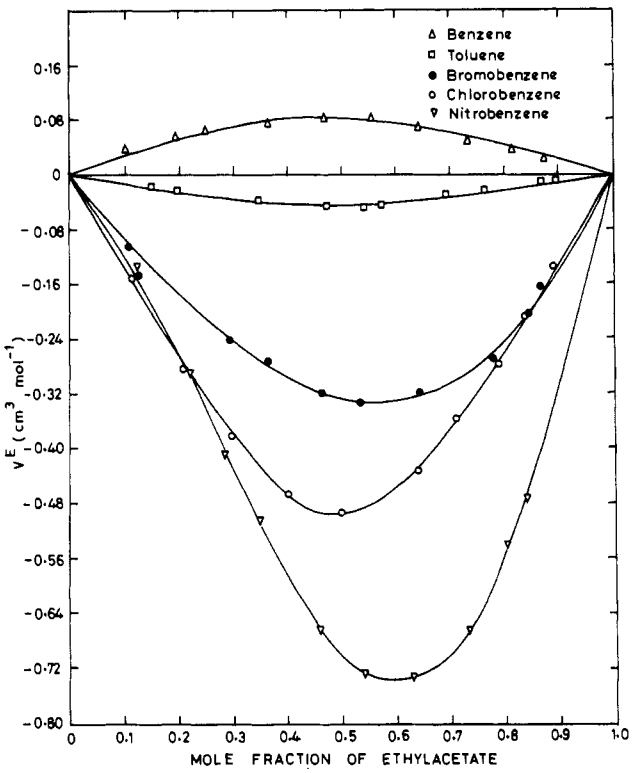

Figure 1. Excess volume–composition curves for substituted benzenes with ethyl acetate at 313.15 K.

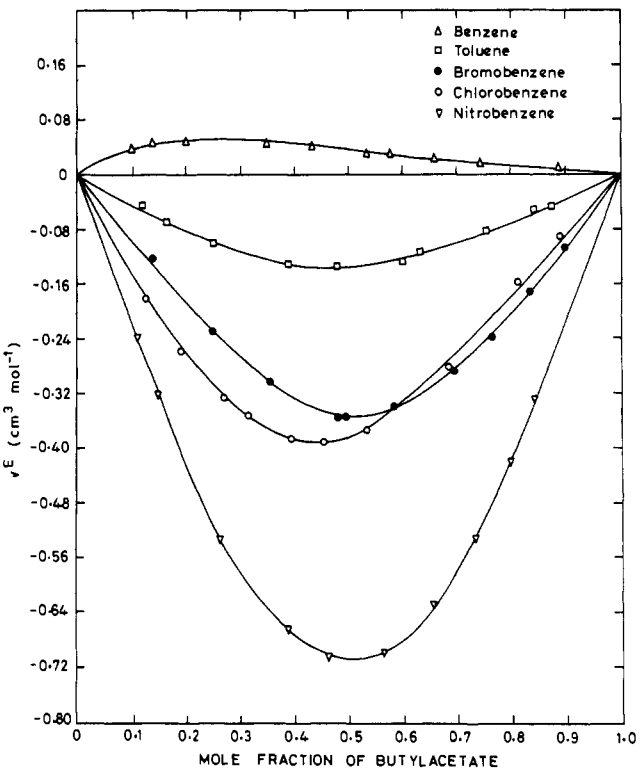

Figure 2. Excess volume–composition curves for substituted benzenes with butyl acetate at 313.15 K.

good agreement with the earlier values reported in the literature (*7*).

Purification of Materials. Ethyl acetate (BDH), and butyl acetate (BDH) were purified by the standard methods described by Vogel (*8*). Benzene (BDH) was purified by the method described by Naidu and Krishnan (*9*).

Toluene was purified by the standard method described previously (*10*).

Chlorobenzene and nitrobenzene were purified by standard methods described previously (*4*).

Bromobenzene (E. Merck, India) was dried with calcium chloride and fractionally distilled under reduced pressure. The

Table IV. Values of the Adjustable Constants in Eq 1 and the Standard Deviation (σ) at 313.15 K for Alkyl Acetate + Substituted Benzenes[a]

system	a_0	a_1	a_2	σ
ethyl acetate + benzene	0.3242	−0.1026	−0.0441	0.003
ethyl acetate + toluene	−0.1848	0.0169	0.1023	0.002
ethyl acetate + bromobenzene	−1.3077	−0.3901	−0.0605	0.004
ethyl acetate + chlorobenzene	−1.9819	0.0438	0.8640	0.004
ethyl acetate + nitrobenzene	−2.7905	−1.5731	0.6225	0.004
butyl acetate + benzene	0.1420	−0.1979	0.1304	0.002
butyl acetate + toluene	−0.5465	0.0365	0.1762	0.003
butyl acetate + bromobenzene	−1.4132	−0.1166	0.4543	0.004
butyl acetate + chlorobenzene	−1.5429	0.4656	0.3834	0.003
butyl acetate + nitrobenzene	−2.8495	−0.0368	0.6273	0.003

[a] All values in $cm^3\ mol^{-1}$.

purities of the chemicals were checked by densities and boiling points.

The densities were measured with a standard bicapillary pycnometer which gave an accuracy of 5 parts in 10^5 parts. The measured densities and boiling points are presented in Table I along with literature values (*11*, *12*).

Results and Discussion

The excess volume–composition data at 313.15 K of all 10 binary liquid mixtures are presented in Tables II and III, and these are graphically represented in Figures 1 and 2. The excess volumes are positive over the entire range of composition in the systems benzene + ethyl acetate and benzene + butyl acetate, whereas in the other systems the V^E values are negative over the entire range of composition. The algebraic values of V^E of all the binary systems with ethyl acetate and with butyl acetate fall in the order

benzene > toluene > bromobenzene > chlorobenzene > nitrobenzene

The graphical representation of the excess volumes–composition data for ethyl acetate with substituted benzenes shows that the curves are symmetrical in all the systems and the maximum is around 0.5, excluding the system ethyl acetate + nitrobenzene, for which the maximum is around 0.6 mole fraction. In the butyl acetate with substituted benzenes the curves are symmetrical in all the systems and the maximum deviation is around 0.5, except in the binary system butyl acetate + benzene, which has a maximum around 0.2 mole fraction.

These results may be represented by an empirical equation of the form

$$V^E = x_A x_B[a_0 + a_1(x_A - x_B) + a_2(x_A - x_B)^2] \quad (1)$$

where x_A and x_B are the mole fractions of the components A and B, respectively, and a_0, a_1, and a_2 are adjustable constants which have been evaluated by the principle of least squares. The values of these constants are included in Table IV along with the standard deviation, σ, which is evaluated from the equation

$$\sigma = +\left[\frac{\sum(\Delta V^E)^2}{n - P}\right]^{1/2} \quad (2)$$

where n is the number of results, P is the number of parameters used in eq 1, and

$$\Delta V^E = V^E_{\text{exptl}} - V^E_{\text{calcd(eq1)}}$$

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Registry No. Ethyl acetate, 141-78-6; butyl acetate, 123-86-4; benzene, 71-43-2; toluene, 108-88-3; chlorobenzene, 108-90-7; bromobenzene, 108-86-1; nitrobenzene, 98-95-3.

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