

PYCNOMETRIC DETERMINATION OF DENSITIES AND EXCESS VOLUMES OF BINARY MIXTURES CONTAINING AT LEAST ONE ASSOCIATING COMPONENT

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Received October 19, 1989

Accepted April 6, 1990

Densities at 20°C and molar excess volumes calculated from them are reported in the work for the mixtures of the substances: propionic acid–n-heptane, propionic acid–benzene, trifluoroacetic acid–benzene, propionic acid–cyclohexane, acetic acid–cyclohexane, acetic acid–trifluoroacetic acid, acetic acid–propionic acid, and propionic acid–trifluoroacetic acid. For the last system mentioned, a strange dependence of excess volume on composition was found which is noted for three local extremes. The dependences of excess volume on composition are correlated by the Redlich–Kister polynomial.

When measuring vapour–liquid equilibrium, the dependence of the mixture density on composition can be employed to analyze the equilibrium sample composition. During the long-term study of behaviour of strongly associating systems, the density data of eight binary systems were gathered in our laboratory. Of these, in five cases there are the systems of the associating component–non-associating component type, viz. the propionic acid–benzene, propionic acid–n-heptane, propionic acid–cyclohexane, acetic acid–cyclohexane, trifluoroacetic acid–benzene systems; the remaining three binary systems, viz. acetic acid–propionic acid, acetic acid–trifluoroacetic acid, and propionic acid–trifluoroacetic acid are systems with both associating components.

EXPERIMENTAL

The density measurements were carried out in an approximately 25 ml pycnometer of the Wood–Brusie type¹. The accurate pycnometer volume was determined by calibrating with redistilled water. The temperature in a U-10 Ultra-Thermostat was maintained, after adjusting the cooling water flow-rate, with accuracy of 0.01°C. With every weighing, the correction for the buoyancy effect was taken. The estimated accuracy of measurement is $s_v \sim 1 \cdot 10^{-4} \text{ g/cm}^3$.

All the chemical substances used were dried and purified by rectification before the measurements. The densities of pure substances used for the respective measurement are given in Tables II–IX. The tabulated values² of densities of the substances used are presented in Table I.

RESULTS

Excess volume was calculated from the measured densities in terms of the relation

$$V_m^E = (x_1 M_1 + x_2 M_2) / \rho - x_1 M_1 / \rho_1^0 - x_2 M_2 / \rho_2^0, \quad (1)$$

where V denotes the volume, ρ density, x mole fraction, M molar mass, superscript 0 refers to pure substance, E to excess quantity and subscript m denotes the molar quantity.

The calculated values of molar excess volume along with the experimental density values are given for single systems in Tables II–IX. Molar excess volume as a function of composition was correlated by the Redlich–Kister polynomial in the form

$$V_m^E = x_1 x_2 \sum_i A_i (x_1 - x_2)^{i-1}, \quad (2)$$

TABLE I

The literature values of densities of substances used: 1 acetic acid, 2 propionic acid, 3 trifluoroacetic acid, 4 benzene, 5 cyclohexane, 6 *n*-heptane

Substance	1	2	3	4	5	6
ρ^{20}	1.04926	0.9934	1.4890	0.87901	0.77855	0.68376

TABLE II

The propionic acid(1)-*n*-heptane(2) system ($M_1 = 74.080$ g/mol, $M_2 = 100.206$ g/mol, $T = 293.15$ K)

x_1	ρ , g/cm ³	V_m^E , cm ³ /mol
0	0.6838	0
0.1820	0.7135	0.336
0.2050	0.7177	0.371
0.2810	0.7326	0.443
0.4050	0.7598	0.567
0.4840	0.7797	0.596
0.7010	0.8475	0.541
0.8410	0.9056	0.380
0.9250	0.9488	0.180
1.0000	0.9935	0

where A_i are coefficients. Standard deviations of weighted correlation given in Table X were calculated from the relation

$$s = \left[\sum_{i=1}^{N_P} w_i (V_{i,\text{exp}}^E - V_{i,\text{calc}}^E)^2 / (N_P - N_C) \right]^{1/2}, \quad (3)$$

TABLE III

The propionic acid(1)-benzene(2) system ($M_1 = 74.080$ g/mol, $M_2 = 78.115$ g/mol, $T = 293.15$ K)

x_1	ρ , g/cm ³	V_m^E , cm ³ /mol
0	0.87890	0
0.0790	0.88525	0.126
0.1800	0.89416	0.247
0.3130	0.90720	0.315
0.4134	0.91734	0.374
0.5145	0.92832	0.396
0.6121	0.93993	0.363
0.7099	0.95218	0.313
0.8200	0.96692	0.224
0.9026	0.97856	0.149
1.0000	0.99350	0

TABLE IV

The trifluoroacetic acid(1)-benzene(2) system ($M_1 = 114.024$ g/mol, $M_2 = 78.115$ g/mol, $T = 293.15$ K)

x_1	ρ , g/cm ³	V_m^E , cm ³ /mol
0	0.87880	0
0.1072	0.92906	0.657
0.1890	0.96773	1.176
0.1910	0.96816	1.235
0.3700	1.06276	1.678
0.4530	1.10995	1.730
0.6835	1.25026	1.650
0.8270	1.34920	1.217
0.9184	1.41904	0.725
1.0000	1.48940	0

where N_p stands for the number of experimental points, N_C number of constants, and w_i is the weight of experimental point, defined as the reciprocal value of variance of molar excess volume at that point. The values of variances of excess volume were obtained by applying the error propagation law with the values of standard deviation in density $s_\rho = 1 \cdot 10^{-4} \text{ g/cm}^3$ and in composition $s_x = 1 \cdot 10^{-4}$. The standard deviations of unweighted correlation are, excepting the trifluoroacetic acid–benzene system, lower than 0.01.

DISCUSSION

In all the systems measured, at least one component was organic acid with high ability to form hydrogen bridges^{3–6} in the liquid and vapour phase. Decreasing the amount of associates present by diluting with a non-associating component results in high positive values of excess volume (as well as of excess enthalpy⁷ and Gibbs energy⁸). The comparison of measured data (Fig. 1) is interesting.

Considering three systems with propionic acid, excess volume decreases in the series propionic acid–cyclohexane, n-heptane, benzene; the value of $Q_{\max}^E = (G^E/RT)_{\max}$ is with first two systems roughly the same ($Q_{\max}^E \sim 0.38$), with the propionic acid–benzene system is lower ($Q_{\max}^E \sim 0.25$). The great difference in excess volumes of first two systems is caused by great difference in molar volumes of cyclohexane and n-heptane. Both these substances behave identically in their relation to acid – they practically do not interact. With the third system (propionic acid–benzene), the decrease in V^E and Q^E can be explained by interaction of the acid with the benzene π -electrons.

If we compare the systems acetic acid–cyclohexane and propionic acid–cyclohexane, then the first one exhibits substantially higher V^E and Q^E ($Q_{\max}^E \sim 0.51$). The statement

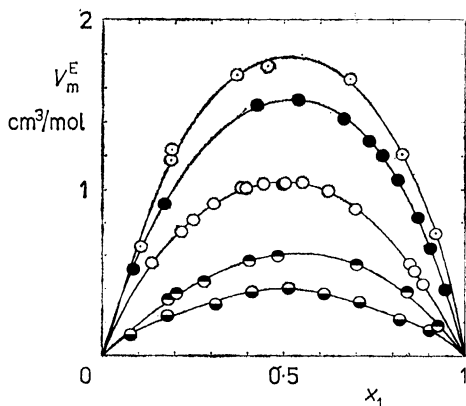


FIG. 1

The dependence of molar excess volume on composition. Circles denote experimental points, solid line results from correlation; \odot trifluoroacetic acid–benzene, \bullet acetic acid–cyclohexane, \circ propionic acid–cyclohexane, \ominus propionic acid–n-heptane, \bullet propionic acid–benzene

TABLE V

The propionic acid(1)-cyclohexane(2) system ($M_1 = 74.080$ g/mol, $M_2 = 84.162$ g/mol, $T = 293.15$ K)

x_1	ρ , g/cm ³	V_m^E , cm ³ /mol
0	0.77840	0
0.1370	0.79535	0.554
0.2180	0.80708	0.747
0.2510	0.81208	0.819
0.3070	0.82099	0.918
0.3820	0.83378	1.012
0.3960	0.83640	1.012
0.4430	0.84513	1.037
0.4970	0.85582	1.035
0.5030	0.85695	1.043
0.5510	0.86680	1.046
0.6220	0.88257	0.996
0.6980	0.90105	0.885
0.8480	0.94249	0.548
0.8610	0.94652	0.504
0.8840	0.95377	0.426
1.0000	0.99330	0

TABLE VI

The acetic acid(1)-cyclohexane(2) system ($M_1 = 60.053$ g/mol, $M_2 = 84.162$ g/mol, $T = 293.15$ K)

x_1	ρ , g/cm ³	V_m^E , cm ³ /mol
0	0.77840	0
0.0850	0.78718	0.516
0.1710	0.79771	0.916
0.4260	0.84022	1.499
0.5400	0.86575	1.532
0.6650	0.89998	1.420
0.7360	0.92302	1.289
0.7720	0.93588	1.204
0.8140	0.95246	1.059
0.8700	0.97690	0.832
0.9050	0.99413	0.643
0.9450	1.01575	0.394
1.0000	1.04925	0

that acetic acid contains more associates in the liquid phase than propionic acid would be therefore in agreement with the measured data. However, the values of dimerization constants in liquid acetic and propionic acids reported by Barton⁵, yield at 20°C 25 times higher value for propionic acid. If we wished to harmonize both the facts, we should have to admit that, if it is possible to model propionic acid in the liquid phase as a mixture of monomeric and dimeric molecules, then this simple model does not comply in the case of acetic acid.

The great difference in the values of V^E and G^E in the systems trifluoroacetic acid–benzene and propionic acid–benzene gives evidence that in trifluoroacetic acid there are, in addition to hydrogen bonds with oxygen atoms, hydrogen bonds with fluorine atoms, too.

The following three systems acetic acid–propionic acid, acetic acid–trifluoroacetic acid, and propionic acid–trifluoroacetic acid (Fig. 2) are very complicated from the molecular point of view. Each of the substances mentioned exists in the liquid phase at least in the form of monomer and dimer. They interact to form a heterodimer. Consequently, each of those “macroscopically” two-component systems is “microscopically” minimally five-component one.

The acetic acid–propionic acid system behaves almost ideally (with small positive deviations in V^E and G^E), on the other hand, both the systems with trifluoroacetic acid exhibit considerable negative deviations from ideal behaviour so giving evidence on a very strong mutual interaction.

TABLE VII

The acetic acid(1)–trifluoroacetic acid(2) system ($M_1 = 60.053$ g/mol, $M_2 = 114.024$ g/mol, $T = 293.15$ K)

x_1	ρ , g/cm ³	V_m^E , cm ³ /mol
0	1.4893	0
0.0830	1.4689	−0.382
0.1250	1.4567	−0.502
0.2080	1.4295	−0.631
0.2290	1.4224	−0.663
0.3760	1.3657	−0.664
0.4760	1.3230	−0.596
0.5350	1.2966	−0.552
0.6830	1.2262	−0.435
0.9120	1.1025	−0.160
0.9660	1.0705	−0.082
1.0000	1.0492	0

TABLE VIII

The acetic acid(1)-propionic acid(2) system ($M_1 = 60.053$ g/mol, $M_2 = 74.080$ g/mol, $T = 293.15$ K. Samples of different purity were used in the measurement. Small amounts of impurities influence V^E very little if the respective values of densities of pure substances are used in calculating.)

x_1	ρ , g/cm ³	V_m^E , cm ³ /mol
0	0.99330	0
0.1100	0.99791	0.017
0.2480	1.00367	0.065
0.2710	1.00474	0.068
0.4110	1.01164	0.078
0.7020	1.02809	0.075
1.0000	1.04925	0
0	0.99360	0
0.1124	0.99827	0.019
0.1441	0.99944	0.038
0.7985	1.03434	0.067
0.8468	1.03776	0.049
0.8979	1.04136	0.040
1.0000	1.04925	0
0	0.99380	0
0.3804	1.01053	0.075
0.3809	1.01058	0.073
0.4868	1.01609	0.077
1.0000	1.04950	0

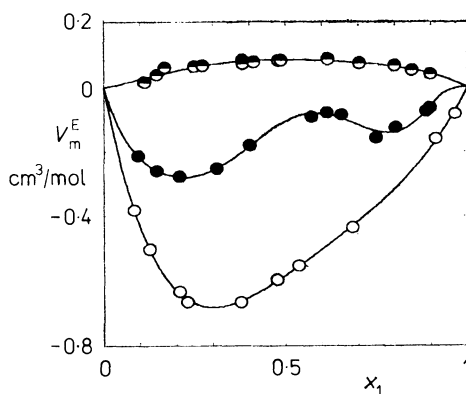


FIG. 2

The dependence of molar excess volume on composition. Circles denote experimental points, solid line results from correlation; ● acetic acid-propionic acid, ● propionic acid-trifluoroacetic acid, ○ acetic acid-trifluoroacetic acid

Curious is the V^E dependence on composition in the propionic acid–trifluoroacetic acid system with two local minima and one maximum. Nothing similar, as far as it is known to us, has hitherto been reported with any binary system. No wonder that this system drew our attention especially because the results of vapour–liquid equilibrium measurements exhibit no anomaly (H^E of this system has not been measured yet). The dependence of excess volume on temperature measured dilatometrically is being prepared for publication⁹.

TABLE IX

The propionic acid(1)–trifluoroacetic acid(2) system ($M_1 = 74.080$ g/mol, $M_2 = 114.024$ g/mol, $T = 293.15$ K)

x_1	ρ , g/cm ³	V_m^E , cm ³ /mol
0	1.48956	0
0.0930	1.44859	−0.214
0.1451	1.42411	−0.262
0.2080	1.39334	−0.261
0.3105	1.34294	−0.257
0.4005	1.29730	−0.186
0.5698	1.21194	−0.106
0.6122	1.19037	−0.079
0.6519	1.17062	−0.085
0.8013	1.09612	−0.122
0.8969	1.04732	−0.091
1.0000	0.99370	0

TABLE X

Results of correlation

System	A_1	A_2	A_3	A_4	A_5	s
Propionic acid–heptane	2.432	−0.4148				1.0
Propionic acid–benzene	1.557		−0.4330		1.062	1.1
Trifluoroacetic acid–benzene	7.053	−0.4791	2.864			2.0
Propionic acid–cyclohexane	4.196		0.4354	0.5685		0.7
Acetic acid–cyclohexane	6.117	−0.4462	1.510			0.9
Acetic acid–trifluoroacetic acid	−2.325	−1.5090	−1.761	−0.3464		1.1
Acetic acid–propionic acid	0.3378	−0.0796				1.0
Propionic acid–trifluoroacetic acid	−0.4994	−0.8936	−1.955			1.6

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Translated by J. Linek.