EXCESS MOLAR VOLUMES OF BINARY MIXTURES OF ACETIC ACID AND PROPIONIC ACID WITH SOME MEMBERS OF HOMOLOGOUS SERIES OF ALKANES

Ondřej DRÁBEK and Ivan CIBULKA

Department of Physical Chemistry,
Prague Institute of Chemical Technology, 166 28 Prague 6

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Excess molar volumes of binary liquid mixtures of (acetic or propionic acid + hexane) at 25 and 35°C, and (acetic or propionic acid + heptane or octane) and (acetic acid + dodecane) at 25°C, measured with a tilting dilution dilatometer, are reported. The excess volumes are positive over the entire concentration range for all mixtures and increase with increasing length of an alkane molecule, decrease with increasing length of the alkyl chain in a molecule of carboxylic acid, and increase with increasing temperature.

Substances associating through the hydrogen bond form a distinguished group of organic compounds. Strength of intermolecular interactions lies between that of physical interactions and that of chemical bonds here and a certain stability may be assumed for associated complexes. The occurrence of the hydrogen bond influences macroscopic properties and manifests itself in some common features of systems containing associating substances.

One of the ways to study the hydrogen bond and its influence on macroscopic properties is the investigation of the mixtures of associating substances with an inert component, i.e. with the substance whose molecules interact with the associated complexes through weak physical interactions only (dispersion and dipole-induced dipole ones). Such an inert component can be represented by a saturated hydrocarbon. On the other hand the most important representatives of the associating substances are alcohols, carboxylic acids (—O··H— bond), and amines (—N··H— bond). In this paper we present the results of study of volumetric properties of liquid mixtures consisting of two carboxylic acids with some members of the homologous series of n-alkanes. While the data on volumetric properties of (1-alkanol + alkane)[1-6], (1-alkanol + cycloalkane)[4,7,8], and (amine + alkane)[9,10] mixtures, and some data for (carboxylic acid + cycloalkane)[11-14] mixtures are available in the literature, this is not the case of (carboxylic acid + alkane) mixtures where, besides values for (isomer of butyric acid + heptane)[15] mixtures, only data for the (acetic acid + heptane)[15], (propionic acid + heptane)[13,15], and (butyric acid + octane)[16] mixtures have been found.

EXPERIMENTAL

Hexane (Reachim, Pure and Lachema, for UV spectroscopy), heptane (Lachema, for UV spectroscopy), octane (Jenapharm Laborchemie, 95%) and dodecane (Reachim, Pure) were shaken with concentrated sulfuric acid and then with an aqueous solution of 0·5 mol dm^{-3} potassium permanganate and 1 mol dm^{-3} sulfuric acid. The samples were then washed with an aqueous solution of sodium carbonate and with water and dried with anhydrous magnesium sulfate. The substances were then fractionated by distillation (except for dodecane) in a column filled with stainless-steel helices. The final step of the dodecane purification was the triple fractional crystallization. The purified hydrocarbons were stored in closed bottles over Nalsit 4A molecular sieves.

Acetic acid (Lachema, Analar Grade) was refluxed with small amounts of potassium permanganate and acetic acid anhydride and then fractionated in a fourty-plate glass column. Propionic acid (Lachema, Pure) was used after twofold rectification on a twenty-plate glass column after the addition of several crystals of potassium permanganate. The acids were stored in closed bottles in a desiccator with phosphorus pentoxide and the samples used for measurements were not older than three weeks.

Densities of pure components determined in either a 10 cm^3 single-stem pyknometer or a 4 cm^3 Ostwald–Sprengel bicapillary pyknometer are summarized in Table I along with some literature values.

TABLE I

Densities of pure components

Compound	t °C	d, g cm^{-3}	
		exp.	lit. (ref.)
Hexane	25	0·65486	0·65487(3); 0·65481(17); 0·65480(18); 0·65489(19); 0·65533(23); 0·65479(24)
	35	0·64584	0·64586(20); 0·64578(21)
Heptane	25	0·67971	0·67957(1); 0·67951(17); 0·67950(18); 0·67957(22); 0·67950(23)
Octane	25	0·69864	0·69867(3); 0·69849(17); 0·69850(18); 0·69876(23); 0·69862(24)
Dodecane	25	0·74526	0·74516(17); 0·74537(24); 0·74539(25); 0·74532(26)
Acetic acid	25	1·04378	1·04366(17); 1·04392(27)
	35	1·03249	1·03263(27)[a]
Propionic acid	25	0·98821	0·98808(27) 0·98823(28)
	35	0·97758	0·97728(27)[b]

[a] Calculated from the equation $d(\text{g cm}^{-3}) = 1{\cdot}075491 - 1{\cdot}1029 \,.\, 10^{-3}t - 0{\cdot}68227/(195{\cdot}15 - t)$ (°C); $s(d) = 0{\cdot}00002$ g cm^{-3}, fitted to the values[27] in the temperature range from 20 to 127°C; [b] calculated from the equation $d(\text{g cm}^{-3}) = 1{\cdot}015128 - 1{\cdot}0783 \,.\, 10^{-3}t - 0{\cdot}00779/(106{\cdot}05 - t)$ (°C); $s(d) = 0{\cdot}00002$ g cm^{-3}, fitted to the values[27] in the temperature range from 15 to 87°C.

Carboxylic acids are rather aggressive substances and their reactivity with mercury could cause problems. The reactivity of acetic acid was examined in the same way as it had been done for propionic and trifluoroacetic acids[28] and similar results, supporting the conclusion that the reactivity is low enough not to influence the excess-volume measurements[28], were obtained.

A tilting dilution dilatometer[29] with a measuring capillary of i.d. 0·8 mm was used to measure excess volumes. Heights of mercury columns were read by a cathetometer with a precision of 0·01 mm. A water-filled thermostat of volume about 40 dm^3 was used for the measurements. Temperature was adjusted with a precision within 0·01 K; the temperature fluctuations were found to be within 1 mK at 25°C and 3 mK at 35°C. Temperature adjustments and the determination of temperature fluctuations were made by means of a calibrated platinum resistance thermometer 25 Ω (Leeds and Northrup) connected to a resistance bridge (Model F26, A.S.L., Ltd.).

Each pure substance had been degassed by boiling under atmospheric pressure (except for dodecane that was boiled under lower pressure) immediately before it was used for measurements and then quickly introduced into the dilatometer.

RESULTS

Measured excess molar volumes and respective mole fractions are recorded in Table II. The equation

$$v^{E}(\mathrm{cm^3\,mol^{-1}}) = x_1(1 - x_1)\sum_{i=0}^{n} a_i(1 - 2x_1)^i \qquad (1)$$

was fitted to each set of experimental values. A statistical F-test[30] was used to determine the number of adjustable parameters, $(n + 1)$. Equation (*1*) was employed for the values obtained for homogeneous mixtures. The straight line

$$v^{E}(\mathrm{cm^3\,mol^{-1}}) = a_0 + a_1 \,.\, x_1 \qquad (2)$$

was fitted to the set of values measured in a region of limited miscibility for the (dodecane + acetic acid) mixture. The parameters a_i obtained by the method of least squares are given in Table III along with the standard deviations, $s(v^E)$.

The measured excess volumes are positive over the entire composition range for all mixtures studied here. The composition dependences are nearly symmetrical (except for the (dodecane + acetic acid) mixture) about equimolar concentration; maxima of the curves are in the interval of x_1 from 0·449 to 0·511.

The {dodecane(1) + acetic acid(2)} mixture exhibits a miscibility gap from $x_1 = 0{\cdot}024$ to $x_1 = 0{\cdot}592$ at 25°C; compositions of the coexisting liquid phases were calculated as the cross points of Eqs (*1*) and (*2*) with parameters obtained for this mixture (see Table III). As can be seen from Table III, the standard deviation of the linear part of the dependence is rather high, most likely due to the insufficient equilibration of the two liquid phases in a mixing bulb of the dilatometer. Stirring of the bulb content is sufficient for homogeneous liquids but more intensive stirring seems to be necessary to improve the measurements in the limited miscibility region.

TABLE II

Measured excess molar volumes v^E (cm^3 mol^{-1}) for the {alkane(1) + carboxylic acid(2)} mixtures

x_1	v^E	x_1	v^E	x_1	v^E
Hexane(1) + acetic acid(2), 25°C					
0·0307	0·1762	0·1890	0·8285	0·4679	1·2313
0·0386	0·2188	0·2253	0·9258	0·5844	1·1888
0·0640	0·3457	0·2702	1·0226	0·6587	1·0974
0·0990	0·5062	0·2823	1·0447	0·7477	0·9323
0·1226	0·6043	0·3084	1·0981	0·8523	0·6331
0·1536	0·7112	0·3689	1·1774	0·9276	0·3429
Hexane(1) + acetic acid(2), 35°C					
0·0640	0·3872	0·3894	1·3027	0·6053	1·2639
0·1490	0·7736	0·4125	1·3119	0·7199	1·0745
0·2728	1·1279	0·4908	1·3483	0·8020	0·8569
0·3340	1·2314	0·5156	1·3318	0·9420	0·3007
Heptane(1) + acetic acid(2), 25°C					
0·0447	0·3281	0·3238	1·2487	0·6680	1·1398
0·1001	0·6433	0·3829	1·3017	0·8012	0·8074
0·1624	0·8943	0·3958	1·3225	0·9120	0·4059
0·2983	1·2050	0·5575	1·2941		
Octane(1) + acetic acid(2), 25°C					
0·0576	0·4630	0·3244	1·2928	0·6225	1·2572
0·1245	0·8170	0·3978	1·3711	0·7408	0·9937
0·2288	1·1230	0·4058	1·3749	0·8535	0·6269
0·2622	1·2022	0·4731	1·3858		
0·3197	1·2936	0·5290	1·3699		
Dodecane(1) + acetic acid(2), 25°C					
0·0042	0·0584	0·0464	0·3728	0·3651	0·9093
0·0097	0·1314	0·1179	0·4996	0·4919	1·1166
0·0098	0·1331	0·1319	0·5139	0·6730	1·1655
0·0134	0·1777	0·2230	0·6722	0·7592	0·9529
0·0193	0·2450	0·2471	0·7209	0·8379	0·6796
0·0227	0·2872	0·2842	0·7748	0·9215	0·3513
0·0340	0·3416	0·3083	0·8292		

TABLE II
(*Continued*)

x_1	v^E	x_1	v^E	x_1	v^E
Hexane(1) + propionic acid(2), 25°C					
0·0536	0·1086	0·4344	0·5204	0·6296	0·4987
0·1432	0·2625	0·4567	0·5200	0·7330	0·4332
0·2533	0·4007	0·4890	0·5312	0·8028	0·3535
0·3352	0·4707	0·5299	0·5242	0·9075	0·1931
Hexane(1) + propionic acid(2), 35°C					
0·0296	0·0650	0·2880	0·4441	0·5722	0·5288
0·0614	0·1292	0·3132	0·4672	0·7174	0·4481
0·1016	0·2009	0·3531	0·5009	0·8600	0·2847
0·1475	0·2708	0·4056	0·5195		
0·2291	0·3830	0·4795	0·5380		
Heptane(1) + propionic acid(2), 25°C					
0·0846	0·2380	0·3058	0·5943	0·5193	0·6684
0·1597	0·3969	0·3697	0·6418	0·7431	0·4769
0·2407	0·5238	0·4560	0·6706	0·8918	0·2508
Octane(1) + propionic acid(2), 25°C					
0·0538	0·1856	0·3540	0·7268	0·5956	0·6933
0·1117	0·3568	0·3819	0·7361	0·7095	0·5753
0·1734	0·4961	0·4136	0·7526	0·8192	0·3969
0·2439	0·6138	0·4503	0·7584	0·9135	0·2115
0·2913	0·6756	0·4503	0·7502		
0·3358	0·7109	0·5262	0·7348		

DISCUSSION

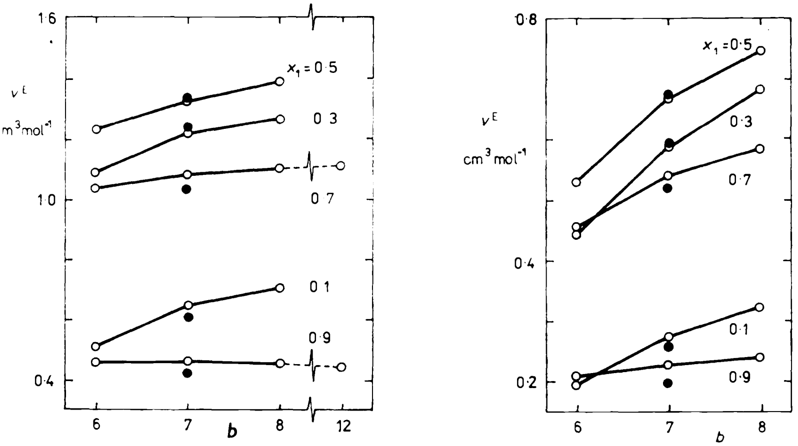
Dependences of the excess molar volume of the measured mixtures, that may be schematically denoted as $\{C_bH_{2b+2} + C_{a-1}H_{2a-1}COOH\}$, on b and a (b and a are the numbers of carbon atoms in alkane and acid molecules, respectively) are shown for five selected compositions in Figs 1 and 2 along with the available literature data. It may be summarized that the inequalities

$$(\delta v^E/\delta a)_{T,x,b=\mathrm{const}} < 0 \tag{3}$$

and (for not very high x_1)

$$(\delta v^E/\delta b)_{T,x,a=\mathrm{const}} > 0 \qquad (4)$$

hold for the measured values. The same inequalities characterize the volumetric behaviour of the mixtures of 1-alkanols[1–6] and primary amines[9,10] (then a is the number of carbon atoms in an 1-alkanol or amine molecule) with alkanes and therefore the relations (3) and (4) may be regarded as characterizing the common feature of the three groups of mixtures.



a *b*

FIG. 1

Dependences of excess molar volume of the $\{C_bH_{2b+2}(1) + C_{a-1}H_{2a-1}COOH(2)\}$ mixtures at 25°C on number of carbon atoms in alkane molecule, *b*, for five selected compositions. *a* Acetic acid ($a = 2$); *b* propionic acid ($a = 3$); ○ this work; ● ref.[15]

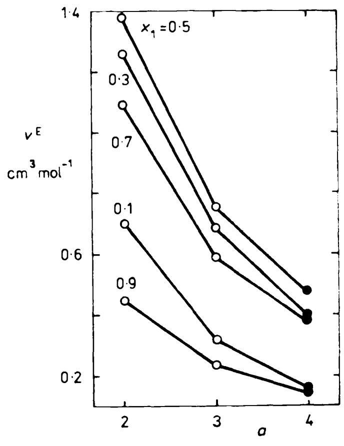


FIG. 2

Dependences of excess molar volume of the $\{C_8H_{18}(1) + C_{a-1}H_{2a-1}COOH(2)\}$ mixtures at 25°C on number of carbon atoms in acid molecule, *a*, for five selected compositions. ○ This work; ● ref.[16]

Table IV presents temperature derivatives of the molar excess volume at equimolar composition calculated from the approximate formula $(\delta v^E/\delta T)_{x=0.5} = \{v^E(x_1 = 0{\cdot}5;\ t = 35°C) - v^E(x_1 = 0{\cdot}5;\ t = 25°C)\}/10$. The results may be generalized in the form of the inequality

$$(\delta v^E/\delta T)_x > 0 \qquad (5)$$

which illustrates another common feature of the three groups of the mixtures mentioned above.

During the measurements no special attention was paid to the dilute composition regions. However, Table V records approximate values of limiting partial molar excess volumes, i.e. the differences between limiting partial molar volumes and molar volumes of pure components, calculated from the smoothing equation (*1*). Limiting partial molar excess volumes of alkanes increase with the size of an alkane molecule for the particular acid. This may be largely attributed to the effect of the differences in size and shape of both the alkane molecules and the associated complexes of acid since no associated complexes of the acid are being broken at a zero concentration of alkane, i.e. only weak physical interactions affect the mixture properties. On the other hand, limiting partial molar excess volumes of a given acid remain nearly constant within the homologous series of alkanes, i.e. they are independent of the size of an alkane molecule. Since all molecules of the acid in an infinitely diluted

TABLE III

Parameters a_i for Eq. (*1*) and standard deviations $s(v^E)$ for $\{C_bH_{2b+2}(1) + C_{a-1}H_{2a-1}COOH.(2)\}$ mixtures

a	b	t °C	a_0	a_1	a_2 cm^3 mol^{-1}	a_3	a_4	$s(v^E)$
2	6	25	4·91878	0·27299	0·69889	0·14771	—	0·0028
2	6	35	5·34658	0·32672	0·82340	0·30067	—	0·0051
2	7	25	5·31665	0·67061	0·71361	0·96644	0·77174	0·0051
2	8	25	5·53574	0·71887	0·25165	1·60805	1·75220	0·0044
2	12[a]	25	4·91923	−1·81375	−0·43789	6·55535	5·22534	0·0018
2	12[b]	25	0·29455	1·69143	—	—	—	0·0080
3	6	25	2·11462	−0·08750	0·18217	—	—	0·0029
3	6	35	2·15512	−0·00917	0·22037	−0·20675	—	0·0032
3	7	25	2·66544	0·31791	0·16172	—	—	0·0061
3	8	25	2·98338	0·58236	0·22168	—	—	0·0029

[a] Eq. (*1*) for $x_1 < 0{\cdot}0236$ and $x_1 > 0{\cdot}5924$ (homogeneous region); [b] Eq. (*2*) for $0{\cdot}0236 < x_1 < 0{\cdot}5924$ (region of limited miscibility).

solution must be present in the form of free non-associated molecules, the constancy of limiting partial molar excess volumes of acids within the series of alkanes may be explained by the dominant role of the dissociation of associated complexes on mixing.

A detailed interpretation of the results is beyond the scope of this paper because it would require a quantitative model describing both the association equilibria and the state behaviour of pure components and their mixtures in a wider context of other properties of the mixtures.

TABLE IV

Temperature derivatives ($cm^3\ mol^{-1}\ K^{-1}$) of excess volume for the $\{C_bH_{2b+2}(1) + C_{a-1}.H_{2a-1}COOH(2)\}$ mixtures at $x_1 = x_2 = 0{\cdot}5$

a	2	2	3	3	4
b	6	7	6	7	8
$(\delta v^E/\delta T) . 10^3$ [a]	10·7 ± 0·6	11·2 ± 0·1[b]	1·0 ± 0·4	3·1 ± 0·2[b] 12·6 ± 2·6[c]	7·8 ± 0·2[d]

[a] Uncertainties estimated from standard deviations of (v^E vs x_1) fits; [b] ref.[15]; [c] calculated from values for 25°C (ref.[15]) and 20°C (ref.[13]); [d] ref.[16].

TABLE V

Limiting partial molar excess volumes for $\{C_bH_{2b+2}(1) + C_{a-1}H_{2a-1}COOH(2)\}$ mixtures evaluated from Eq. (*1*) with parameters recorded in Table III

a	b	t °C	$(v_1^E)_{x_1 \to 0}$	$(v_2^E)_{x_1 \to 1}$
			$cm^3\ mol^{-1}$	
2	6	25	6·04 ± 0·03	5·20 ± 0·04
2	6	35	6·80 ± 0·09	5·54 ± 0·10
2	7	25	8·44 ± 0·12	5·16 ± 0·16
2	8	25	9·87 ± 0·11	5·21 ± 0·18
2	12	25	14·45 ± 0·14	4·97 ± 0·11
3	6	25	2·21 ± 0·03	2·38 ± 0·03
3	6	35	2·16 ± 0·04	2·59 ± 0·07
3	7	25	3·15 ± 0·06	2·51 ± 0·07
3	8	25	3·79 ± 0·02	2·62 ± 0·03
4	8[a]	25	1·77 ± 0·01	1·62 ± 0·01

[a] Ref.[16].

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