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Effect of Hydrogen Bonding on the Viscosity of Alcohols at High Pressures

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Viscosities of several alcohols and vinyl acetate were measured with a rolling-ball viscometer. The viscosity measurements were performed at temperatures from 298 to 413 K and pressures up to 195 MPa with an accuracy of $\pm 2\%$. The viscosities of the alcohols show a stronger dependence on temperature compared with that of substances that do not form hydrogen bonds. In addition, the secondary and tertiary alcohols show a viscosity–temperature dependence not in accordance with an Arrhenius law. An effect of pressure on the association of alcohol molecules resulting from hydrogen bonding was not resolved by means of viscosity data. Separation of the effect of association size upon increasing temperature from the viscosity caused by the change of specific volume was carried out using the Utracki free volume model.

KEY WORDS: alcohols; density; high pressure; hydrogen bond; vinyl acetate; viscosity.

1. INTRODUCTION

Since simulation programs are involved in the design of chemical processes, there is a demand for properties of various substances. One important property is the viscosity. Especially the viscosities of alcohols at high pressure have not been studied extensively. Only a few investigations have been reported [1–8]. Most of them cover only the pressure region up to 50 MPa. Therefore, a viscosity study of primary, secondary, and tertiary alcohols at higher pressures is presented here.

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2. MEASUREMENTS

2.1. Materials

The alcohols employed were supplied by Aldrich–Chemie GmbH & Co. KG, Steinheim. The samples of 1-pentanol and 2-methyl-2-butanol had a purity of better than 99%. 3-Pentanol, 1-heptanol, 3-ethyl-3-pentanol, 1-nonanol, and 5-nonanol had a purity of nominal 98%. Vinyl acetate and *n*-decane supplied by Merck KGaA, Darmstadt, exhibit a purity of 99%. *N*-Decane was used for calibration.

2.2. Procedure

The viscosities were measured with a rolling-ball viscometer, constructed by Stanislawski and Luft, that was described previously [9, 10]. The viscometer consists of a Schott KPG glass tube, closed at one end and a steel ball, whose diameter is a little smaller than the inner diameter of the glass tube. The viscometer is arranged in a high-pressure autoclave. The angle of incline can be varied in six positions to permit measurements over a wide range of viscosities. During the experiment the autoclave is completely filled with the sample. At the beginning of each measurement the steel ball is placed on the upper end of the glass tube, where it is fixed by an electromagnet. When the electromagnet is released, the ball rolls downward. When a constant velocity is reached after a short distance, the velocity of the ball is determined. For this purpose two pairs of measuring coils are arranged at the beginning and the end of the measuring distance, consisting of a high-frequency oscillating and a sensing part. The rolling time between the coils is measured inductively.

The temperature was detected at the middle and the end of the autoclave by two NiCr/Ni thermocouples with an accuracy of ± 0.2 K. The pressure was determined by a calibrated straingauge pressure sensor with an accuracy of 0.25%. Each viscosity value was measured 10 times at different angles of inclination. The deviation of the rolling times is 0.3%.

To calculate the viscosities from the measured velocities, calibration constants are required besides the densities. These parameters had to be determined at all temperatures and pressures where the measurements are performed. The calibration substance was *n*-decane, whose densities [11] and viscosities [12] in the entire temperature and pressure range investigated are well-known.

The determination of the viscosities was carried out with the method of Hubbard and Brown [13]. This method is based on the analysis of the dimensions of all parameters influencing the rolling time. A resistance

Table I. Viscosities (η) and Densities (ρ) of 1-Pentanol

	p (MPa)				
T (K)	50	80	120	160	195
298.15					
η (mPa · s)	5.527	7.001	9.255	11.807	14.209
ρ (g · cm^{-3})	0.845	0.860	0.877	0.891	0.902
323.15					
η (mPa · s)	2.880	3.532	4.590	5.690	7.030
ρ (g · cm^{-3})	0.832	0.848	0.867	0.881	0.893
373.15					
η (mPa · s)	1.048	1.316	1.669	2.088	2.512
ρ (g · cm^{-3})	0.801	0.820	0.840	0.856	0.869

factor was defined from the diameter of the ball and the tube, the ball velocity, the angle of incline, the density of the steel ball, and the density of the substance. At Reynold's numbers below 50 the double logarithmic plot of the resistance factors against the Reynold's numbers shows a slope of -1. The calibration constant depending only on the temperature and on the pressure can be determined from the intersection with the ordinate.

The density of the substances, beside vinyl acetate, was determined from its amount and the autoclave volume as a function of the temperature and pressure measured during calibration with *n*-decane. The estimated error is about 0.4%. The densities of vinyl acetate were taken from the literature [14].

Table II. Viscosities (η) and Densities (ρ) of 3-Pentanol

	p (MPa)				
T (K)	50	80	120	160	195
298.15					
η (mPa · s)	8.297	11.532	16.886	23.828	31.910
ρ (g · cm^{-3})	0.846	0.860	0.877	0.892	0.903
323.15					
η (mPa · s)	2.770	3.625	5.080	6.934	8.948
ρ (g · cm^{-3})	0.826	0.844	0.860	0.874	0.887
373.15					
η (mPa · s)	0.760	0.957	1.261	1.615	1.994
ρ (g · cm^{-3})	0.787	0.807	0.828	0.846	0.859

Table III. Viscosities (η) and Densities (ρ) of 2-Methyl-2-Butanol

T(K)	p (MPa) 50	80	120	160	195
298.15					
η (mPa · s)	8.502	13.730	24.471		
ρ (g · cm^{-3})	0.825	0.841	0.859		
323.15					
η (mPa · s)	2.953	4.253	6.754	10.224	14.623
ρ (g · cm^{-3})	0.806	0.823	0.842	0.857	0.870
373.15					
η (mPa · s)	0.832	1.106	1.549	2.087	2.714
ρ (g · cm^{-3})	0.767	0.788	0.810	0.828	0.841
413.15					
η (mPa · s)	0.455	0.640	0.891	1.158	1.466
ρ (g · cm^{-3})	0.741	0.766	0.791	0.812	0.827
443.15					
η (mPa · s)	0.375	0.487	0.624	0.806	1.012
ρ (g · cm^{-3})	0.715	0.743	0.772	0.793	0.810

3. RESULTS AND DISCUSSION

Tables I to VIII give the viscosities and densities of the alcohols investigated and the viscosities of vinyl acetate for several temperatures and pressures. The measuring error was estimated to be about ±2%, taking into account all individual errors inclusive the accuracy of the literature values used in calibration.

Table IV. Viscosities (η) and Densities (ρ) of 1-Heptanol

T(K)	p (MPa) 50	80	120	160	195
298.15					
η (mPa · s)	10.120	13.449	18.329	24.553	31.054
ρ (g · cm^{-3})	0.847	0.861	0.877	0.892	0.903
323.15					
η (mPa · s)	4.751	6.006	8.006	10.560	13.160
ρ (g · cm^{-3})	0.831	0.845	0.862	0.876	0.888
373.15					
η (mPa · s)	1.534	1.909	2.493	3.160	3.868
ρ (g · cm^{-3})	0.800	0.818	0.837	0.853	0.865

Table V. Viscosities (η) and Densities (ρ) of 3-Ethyl-3-Pentanol

	p (MPa)				
T (K)	50	80	120	160	195
298.15					
η (mPa · s)	14.801	25.694	48.168	93.391	
ρ (g · cm^{-3})	0.870	0.885	0.900	0.913	
323.15					
η (mPa · s)	3.448	5.138	8.307	13.328	20.315
ρ (g · cm^{-3})	0.850	0.865	0.883	0.896	0.907
373.15					
η (mPa · s)	0.840	1.122	1.573	2.129	2.785
ρ (g · cm^{-3})	0.804	0.822	0.843	0.860	0.873
413.15					
η (mPa · s)	0.481	0.616	0.815	1.053	1.322
ρ (g · cm^{-3})	0.768	0.790	0.814	0.833	0.848

3.1. Temperature Dependence of the Viscosities

Figures 1 and 2 show the temperature dependence of the viscosity of the linear and branched alcohols, together with the viscosities of vinyl acetate.

Table VI. Viscosities (η) and Densities (ρ) of 1-Nonanol

	p (MPa)				
T (K)	50	80	120	160	195
298.15					
η (mPa · s)	17.214	23.173	33.690	46.146	
ρ (g · cm^{-3})	0.854	0.867	0.882	0.895	
323.15					
η (mPa · s)	7.151	9.354	13.057	17.538	22.446
ρ (g · cm^{-3})	0.837	0.851	0.867	0.881	0.892
373.15					
η (mPa · s)	2.075	2.662	3.571	4.648	5.908
ρ (g · cm^{-3})	0.800	0.816	0.834	0.850	0.862
413.15					
η (mPa · s)	1.031	1.308	1.708	2.177	2.683
ρ (g · cm^{-3})	0.769	0.788	0.809	0.827	0.840

Table VII. Viscosities (η) and Densities (ρ) of 5-Nonanol

	p (MPa)				
T (K)	50	80	120	160	195
298.15					
η (mPa · s)	20.126	30.244	49.355		
ρ (g · cm^{-3})	0.850	0.864	0.880		
323.15					
η (mPa · s)	6.344	8.973	13.631	19.988	27.354
ρ (g · cm^{-3})	0.831	0.846	0.863	0.878	0.889
373.15					
η (mPa · s)	1.470	1.951	2.719	3.673	4.783
ρ (g · cm^{-3})	0.793	0.810	0.830	0.846	0.859
413.15					
η (mPa · s)	0.742	0.961	1.284	1.673	2.096
ρ (g · cm^{-3})	0.760	0.781	0.803	0.822	0.836

It can be seen that the alcohols exhibit a much higher temperature dependence compared with that of the vinyl acetate. This is due not only to the decreasing viscosity and decreasing density with increasing temperature, but also to a smaller degree of association of the alcohols with increasing temperature. Therefore, the viscosity–temperature dependence of the alcohols is caused by two effects. The slope of the viscosity-versus-temperature curves becomes smaller when the temperature increases. At high temperatures the slopes of the viscosity-versus-temperature curves are as steep as that of nonassociating substances. This can be seen from the temperature dependence of the branched alcohols, which do not follow an Arrhenius law:

$$\eta = A \exp\left(\frac{\Delta H^{\ddagger}_{\mathrm{Vis}}}{RT}\right) \tag{1}$$

Table VIII. Viscosities (η; in mPa · s) of Vinyl Acetate

	p (MPa)				
T (K)	50	80	120	160	195
298.15	0.573	0.679	0.817	0.962	1.078
323.15	0.447	0.517	0.623	0.727	0.832
373.15	0.310	0.367	0.437	0.519	0.598

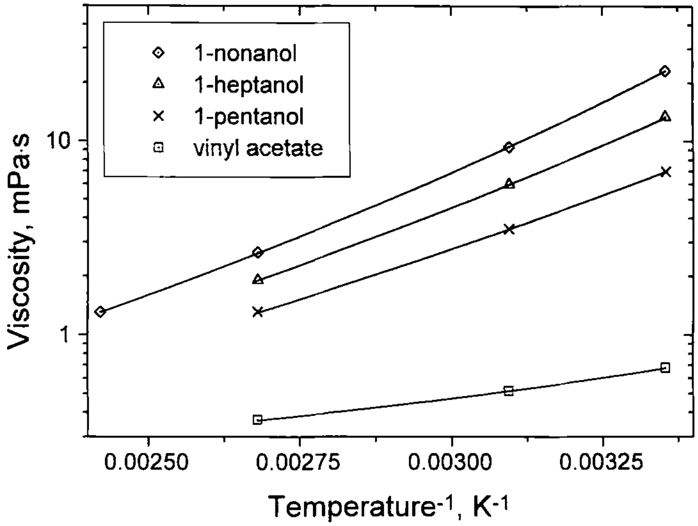

Fig. 1. The viscosities of the investigated linear alcohols and vinyl acetate as a function of temperature at 80 MPa.

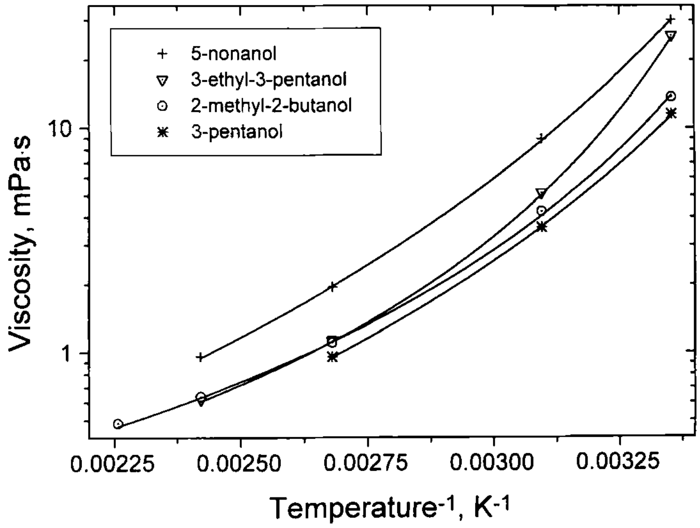

Fig. 2. The viscosities of the investigated branched alcohols as a function of temperature at 80 MPa.

where η is the viscosity, T the temperature, R the molar gas constant, and $\Delta H^{\ddagger}_{\mathrm{Vis}}$ the activation enthalpy of viscous flow. However, in the temperature range investigated this cannot be noticed for the linear alcohols. It is well-known that branched alcohols are less associated than linear ones at the same temperature [15–17]. Branched alcohols become rather noticeably monomolecular at higher temperatures than linear alcohols. Therefore, branched alcohols exhibit a temperature dependence of the viscosity at high temperatures caused by the density change only. This change could be expected for linear alcohols at temperatures higher than those investigated here.

3.2. Pressure Dependence of the Viscosities

The pressure dependence of the viscosity of the investigated liquids can be described by the activation volume $\Delta V^{\ddagger}_{\mathrm{Vis}}$

$$\Delta V^{\ddagger}_{\mathrm{Vis}} = RT\left(\frac{\partial \ln \eta}{\partial P}\right)_T \tag{2}$$

where P is the pressure. In Fig. 3 the viscosity is plotted on a logarithmic scale versus the pressure. The resulting curve shows no difference between the alcohols and vinyl acetate. An effect of pressure on the association

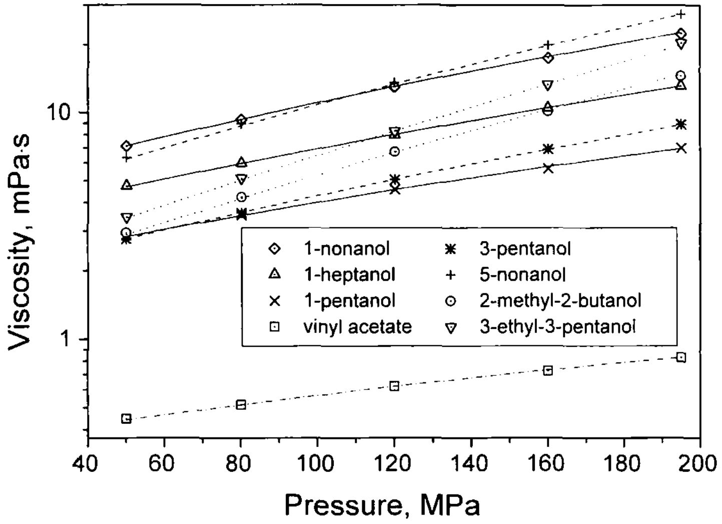

Fig. 3. The dependence of pressure on the viscosity of the alcohols and vinyl acetate at 323.15 K.

of the alcohols is not seen. The viscosities of all substances investigated increase with increasing pressure. The slope of the curves decreases when the pressure increases.

The effect of the pressure on the association is small and does not influence the viscosity. It can be concluded that the decrease in molecular volumes caused by the alcohol association is only small.

3.3. Free-Volume Dependence of the Viscosities

The viscosities of liquids that are not hydrogen bonded can be described by only one parameter, namely, the fraction of the free volume of the total volume. This parameter is calculated from P–V–T data according to the model of Simha and Somcynski [10, 18–20] expressed by the following equation:

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{1}{1-L} + \frac{2y}{\tilde{T}} Q(1.011Q - 1.2045) \tag{3}$$

with

$$Q = \frac{1}{(y\tilde{V})^2} \quad \text{and} \quad L = 2^{-1/6} y (y\tilde{V})^{-1/3}$$

where y is the relative occupied volume, and $\tilde{P}$, $\tilde{V}$, and $\tilde{V}$ are the scaled pressure, volume, and temperature. The relative occupied volume must be determined simultaneously by minimization of the Helmholtz free energy through the following:

$$\begin{gathered}\frac{s}{3c}\left(\frac{s-1}{s} s + y^{-1} \ln(1-y)\right) = \left(\frac{L-\frac{1}{3}}{1-L}\right) + \frac{y}{6\tilde{T}} Q(2.409 - 3.033Q) \\ \tilde{F} = \frac{F}{F^{*}}; \qquad \mathbf{F} = \mathbf{P}, \mathbf{T}, \mathbf{V}; \qquad s = 3c - 3; \qquad c = \frac{\mathbf{P}^{*}\mathbf{V}^{*}\mathbf{M}}{\mathbf{R}T^{*}}\end{gathered} \tag{4}$$

where s is the segment chain length and $3c$ the external degree of freedom. $\mathbf{P}^{*}$, $\mathbf{V}^{*}$, and T^{*} are the determined scaling parameters given in Table IX. Therefore, the viscosities of vinyl acetate can be described by only one curve, although the data points are determined at different temperatures and pressures (Fig. 4). This curve can be described by the model of Utracki [21]:

$$\eta = \exp\left(a + \frac{b}{1 - y + \Delta}\right) \tag{5}$$

Table IX. Scaling Parameters for the Equation of State Model of Simha and Somcynski [18]

	p^* (MPa)	V^* ($cm^3 \cdot g^{-1}$)	T^* (K)	Deviation in volume (%)	
				Average	Max.
1-Pentanol	661.300	1.13652	6649.16	0.10	0.21
3-Pentanol	941.756	1.08376	6030.98	0.17	0.31
2-Methyl-2-butanol	894.448	1.10186	5839.17	0.08	0.18
1-Heptanol	803.639	1.11837	6778.06	0.13	0.31
3-Ethyl-3-pentanol	1202.77	1.03407	6043.18	0.29	0.57
1-Nonanol	1038.94	1.08498	6631.00	0.17	0.24
5-Nonanol	1040.39	1.07778	6370.31	0.11	0.18
Vinyl acetate	722.873	0.92742	5329.38	0.11	0.30

where a and b are adjustable parameters, y is the occupied fraction of the total volume, i.e., the relative occupied volume, and Δ is an excess free volume.

The plot of the alcohol viscosities against the relative occupied volume does not give a single curve. The association is steeply influenced by the temperature; an effect of pressure is not seen in the viscosity data. Therefore, the viscosity points obtained at the same temperature lie on one curve.

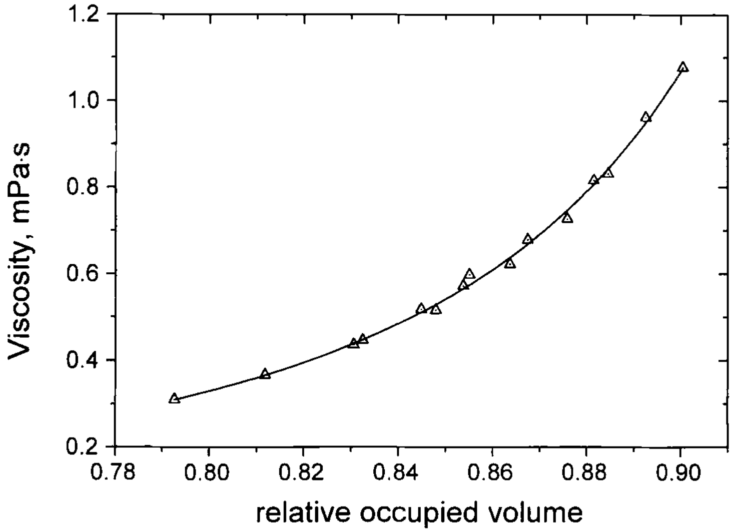

Fig. 4. The viscosity of vinyl acetate as a function of the relative occupied volume.

The viscosity decreases with increasing number of particle movements between equilibrium positions. It can be seen from Fig. 5 that the number of movements is small when the volume of a particle is large and the relative occupied volume is large. For this reason, the relative occupied volume has to be substituted for by an effective relative occupied volume, which must be a function of temperature. The best results were obtained with a Boltzmann-like term leading to the following equation:

$$\eta = \exp\left(a + \frac{b}{1 - y\exp(2E_{\mathrm{U}}/3RT) + \Delta}\right) \tag{6}$$

Through this equation the viscosities of the alcohols can be described in terms of the relative occupied volume and the temperature with a high accuracy (about 2%) (Fig. 6, Table X). With increasing temperature the size of the associates decreases. At high temperatures the alcohols are only monomers. However, a model substance for nonassociated alcohols could be isoelectronic alcane. The model parameters a, b, and Δ determined for the viscosities of 1-nonanol were used to predict the viscosity of *n*-decane with only small errors (9.7%) (Fig. 6). By this modified Utracki model the

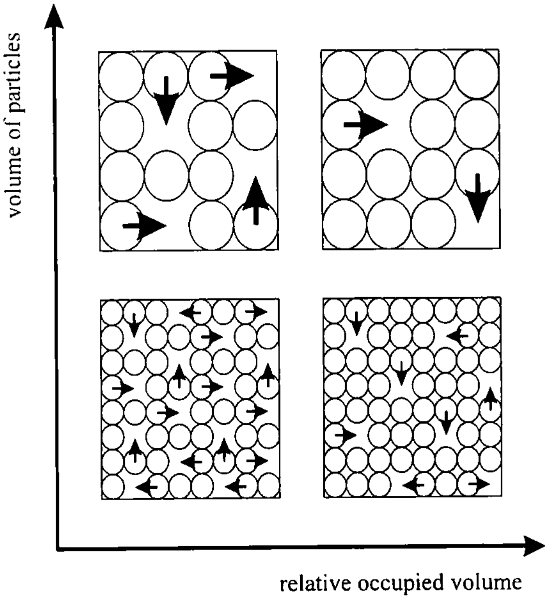

Fig. 5. Influence of the occupied volume and the particle volume on the quantity of place substitutions.

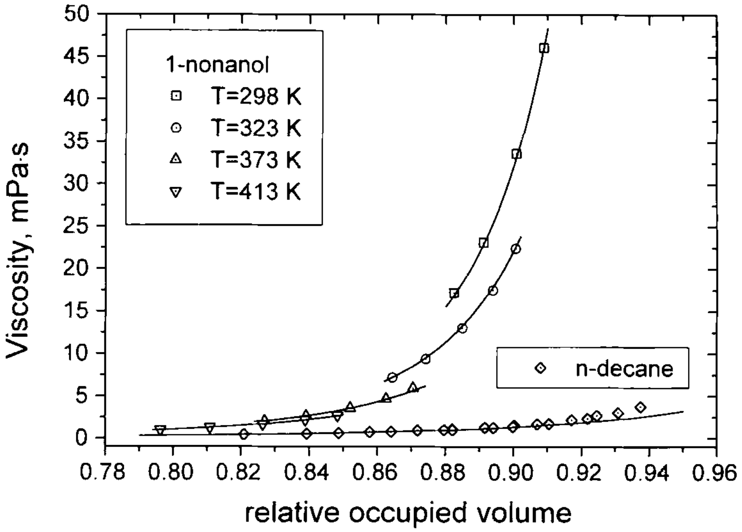

Fig. 6. The viscosities of the alcohols and *n*-decane [11, 12] as a function of the relative occupied volume.

influence of the free volume can be separated from the effect of alcohol association.

4. CONCLUSION

The viscosities and densities of several alcohols and vinyl acetate at high pressures were measured using a rolling-ball viscometer. The viscosity of the alcohols shows a much stronger temperature dependence than that

Table X. Parameter of the Modified Utracki and the Utracki Model [21]

					Deviation (%)	
	a	b	Δ	E_{C} (J · mol^{-1})	Average	Max.
1-Pentanol	−6.68981	3.182595	0.470652	432.548	1.4	3.5
3-Pentanol	−6.36147	2.84482	0.47242	647.775	1.8	5.9
2-Methyl-2-butanol	−4.73845	1.36984	0.220312	403.693	0.8	2.3
1-Heptanol	−8.4043	4.53278	0.48873	415.342	1.6	3.5
3-Ethyl-3-pentanol	−3.57491	0.82701	0.13659	385.152	4.9	10.4
1-Nonanol	−6.48715	2.91436	0.32956	351.142	1.2	4.9
5-Nonanol	−5.27176	1.87476	0.26056	418.204	1.8	4.9
Vinyl acetate	−4.30226	1.18895	0.172111	—	1.4	3.9

of vinyl acetate. This is a result of the alcohol association. A pressure effect on alcohol association cannot be detected. The modified Utracki model proposed allows separation of the free-volume influence from the effect of alcohol association.

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